Supporting Information for

A catalyst-free 1,3-dipolar cycloaddition of C,N-cyclic azomethine imines and 3-nitroindoles: an easy access to five-ring-fused tetrahydroisoquinolines

Xihong Liu[a], Dongxu Yang[a], Kezhou Wang[a], Jinlong Zhang[a], and Rui Wang*[,a,b]

[a]*School of Life Sciences, Institute of Biochemistry and Molecular Biology, Lanzhou University, Lanzhou 730000, P. R. China*
[b]*State Key Laboratory of Chiroscience, Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Kowloon, Hong Kong, P. R. China*

E-mail: wangrui@lzu.edu.cn

Table of contents

A) General Information

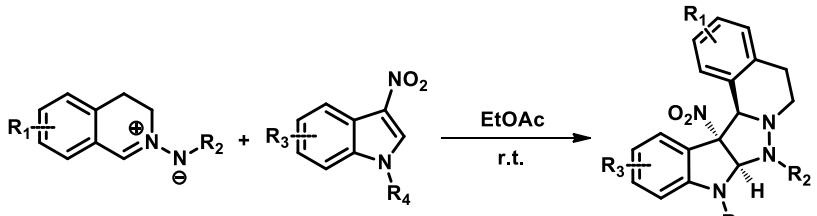
Unless stated otherwise, all reactions were carried out in flame dried glassware. All solvents were purified and dried according to standard methods prior to use. Reactions were monitored by thin layer chromatography (TLC), column chromatography purifications were carried out using silica gel. Proton nuclear resonance (^{1}H NMR) spectra were recorded on 300 MHz spectrometer in $CDCl_3$ and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on 75 MHz spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as internal standard. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet or unresolved, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). High resolution mass spectra (HRMS) were obtained by the ESI ionization sources. Substrates C,N-cyclic azomethine imines **1**[1] and 3-nitroindoles **2**[2] were synthesized according to the previously reported procedures.

---

[1] (a) T. Hashimoto, Y. Maeda, M. Omote, H. Nakatsu and K. Maruoka, *J. Am. Chem. Soc.*, 2010, **132**, 4076; (b) L. Zhang, H. Liu, G. Qiao, Z. Hou, Y. Liu, Y. Xiao and H. Guo, *J. Am. Chem. Soc.*, 2015, **137**, 4316.

[2] (a) G. W. Gribble, E. T. Pelkey, W. M. Simon and H. A. Trujillo, *Tetrahedron*, 2000, **56**, 10133; (b) E. T. Pelkey, G. W. Gribble, *Synthesis*, 1999, 1117.

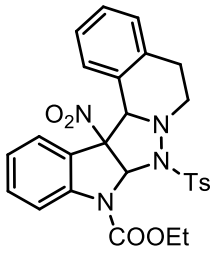
B) General procedure for the catalyst-free 1,3-dipolar cycloaddition of C,N-cyclic azomethine imines and 3-nitroindoles



1 2 3

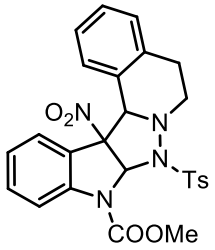
A mixture of C,N-cyclic azomethine imines **1** (0.12 mmol, 1.2 equiv) and 3-nitroindoles **2** (0.1 mmol, 1.0 equiv) in dry ethyl acetate (0.4 mL) was stirred at room temperature for appropriate time, the process of which was monitored by TLC analysis. Then the solvent was removed under vacuum. And the residue was purified by silica gel chromatography (PE : EA = 15:1 to 5:1 as eluent) to afford the desired products **3**.

C) Characterization of products



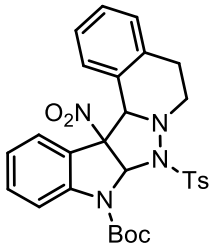
3aa

ethyl 13b-nitro-8-tosyl-8,8a,13b,13c-tetrahydro-5*H*-indolo[2',3':3,4]pyrazolo[5,1-*a*]isoquinoline-9(6*H*)-carboxylate: White solid, m.p. 153 – 154 ^{o}C; 94% yield; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.30 – 7.13 (m, 5H), 7.1 (s, 1H), 7.05 – 6.94 (m, 1H), 6.94 – 6.87 (m, 1H), 6.59 (t, *J* = 7.6 Hz, 3H), 6.28 (d, *J* = 7.6 Hz, 1H), 4.78 (s, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 2.80 – 2.58 (m, 2H), 2.33 (s, 3H), 2.31 – 2.11 (m, 2H), 1.41 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 152.1, 144.6, 142.6, 134.0, 132.1, 129.3, 129.0, 128.7, 128.3, 127.5, 127.3, 126.2, 122.8, 121.1, 115.5, 104.5, 84.9, 70.7, 62.8, 48.5, 29.1, 21. 6, 14.3 ppm; **HRMS** (ESI): $C_{27}H_{26}N_4NaO_6S$ $[M + Na]^+$ calcd: 557.1465, found: 557.1476.



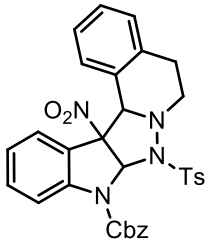
3ab

methyl 13b-nitro-8-tosyl-8,8a,13b,13c-tetrahydro-5*H*-indolo[2',3':3,4]pyrazolo[5,1-*a*]isoquinoline-9(6*H*)-carboxylate: White solid, m.p. 141 – 142 °C; 92% yield; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.91 – 7.81 (m, 1H), 7.32 (d, *J* = 8.1 Hz, 3H), 7.31 – 7.20 (m, 2H), 7.18 (s, 1H), 7.14 – 7.05 (m, 1H), 7.05 – 6.96 (m, 1H), 6.77 – 6.65 (m, 1H), 6.37 (d, *J* = 7.3 Hz, 1H), 4.85 (s, 1H), 4.02 (s, 3H), 2.87 – 2.68 (m, 2H), 2.44 (s, 3H), 2.38 – 2.22 (m, 1H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 152.6, 144.7, 142.6, 134.1, 132.2, 129.5, 129.1, 128.8, 128.4, 127.6, 127.5, 126.3, 123.0, 121.2, 115.5, 104.6, 85.1, 70.7, 53.2, 48.6, 29.2, 21.6 ppm; **HRMS** (ESI): $C_{26}H_{24}N_4NaO_6S$ $[M + Na]^+$ calcd: 543.1309, found: 543.1316.



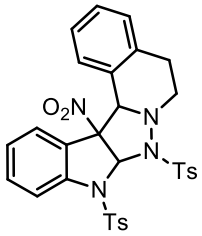
3ac

***tert*-butyl 13b-nitro-8-tosyl-8,8a,13b,13c-tetrahydro-5*H*-indolo[2',3':3,4]pyrazolo[5,1-*a*]isoquinoline-9(6*H*)-carboxylate**: White solid, m.p. 145 – 146 °C; 81% yield; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.32 (d, *J* = 8.7 Hz, 3H), 7.29 – 7.21 (m, 2H), 7.12 (s, 1H), 7.02 (t, *J* = 6.9 Hz, 2H), 6.78 – 6.57 (m, 1H), 6.30 (d, *J* = 7.1 Hz, 1H), 4.83 (s, 1H), 2.88 – 2.69 (m, 2H), 2.44 (s, 3H), 2.38 – 2.18 (m, 2H), 1.69 (s, 9H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 151.21, 144.60, 143.23, 134.09, 132.05, 129.45, 129.07, 128.79, 128.75, 128.57, 127.59, 127.26, 126.29, 122.69, 121.27, 116.09, 104.09, 85.09, 83.93, 70.41, 48.52, 29.13, 28.31, 27.96, 21.67 ppm; **HRMS** (ESI): $C_{29}H_{30}N_4NaO_6S$ $[M + Na]^+$ calcd: 585.1778, found: 585.1785.



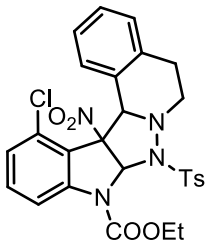
3ad

benzyl 13b-nitro-8-tosyl-8,8a,13b,13c-tetrahydro-5*H*-indolo[2',3':3,4]pyrazolo[5,1-*a*]isoquinoline-9(6*H*)-carboxylate: White solid, m.p. 88 – 89 °C; 87% yield; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.90 – 7.78 (m, 3H), 7.60 (d, *J* = 6.4 Hz, 2H), 7.45 – 7.32 (m, 3H), 7.33 – 7.17 (m, 5H), 7.13 – 7.06 (m, 1H), 7.03 – 6.93 (m, 1H), 6.68 (t, *J* = 7.7 Hz, 1H), 6.37 (d, *J* = 7.8 Hz, 1H), 5.45 (s, 2H), 4.96 (s, 1H), 2.80 – 2.60 (m, 2H), 2.41 (s, 3H), 2.37 – 2.18 (m, 2H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 152.0, 144.5, 142.6, 135.6, 134.1, 132.1, 129.4, 129.2, 129.1, 128.8, 128.5, 128.5, 127.6, 127.5, 126.3, 123.0, 121.3, 115.7, 104.6, 84.9, 70.8, 68.2, 48.5, 29.1, 21.6 ppm; **HRMS** (ESI): $C_{32}H_{28}N_4NaO_6S$ [M + Na]$^+$ calcd: 619.1622, found: 619.1627.



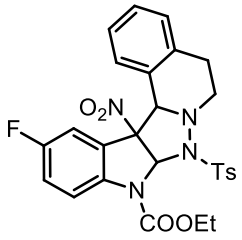
3ae

13b-nitro-8,9-ditosyl-6,8,8a,9,13b,13c-hexahydro-5*H*-indolo[2',3':3,4]pyrazolo[5,1-*a*]isoquinoline: White solid, m.p. 169 – 170 °C; 75% yield; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.2 Hz, 2H), 7.80 – 7.70 (m, 3H), 7.40 – 7.29 (m, 3H), 7.30 – 7.17 (m, 4H), 7.14 – 7.03 (m, 2H), 7.03 – 6.90 (m, 1H), 6.74 (t, *J* = 7.6 Hz, 1H), 6.33 (d, *J* = 7.7 Hz, 1H), 4.99 (s, 1H), 2.79 – 2.55 (m, 2H), 2.44 (s, 3H), 2.39 (s, 3H), 2.32 – 2.12 (m, 2H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 145.2, 144.7, 142.6, 134.1, 134.1, 133.8, 132.3, 130.0, 129.5, 129.1, 128.8, 128.3, 127.7, 127.4, 127.4, 126.3, 124.2, 122.6, 116.3, 104.8, 86.3, 71.0, 48.4, 29.0, 21.7, 21.6 ppm; **HRMS** (ESI): $C_{31}H_{28}N_4NaO_6S_2$ [M + Na]$^+$ calcd: 639.1342, found: 639.1350.



3ag

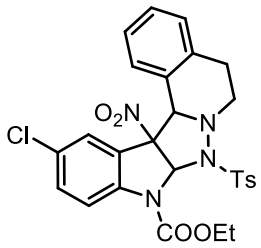
ethyl 13-chloro-13b-nitro-8-tosyl-8,8a,13b,13c-tetrahydro-5*H*-indolo[2',3':3,4]pyrazolo[5,1-*a*]isoquinoline-9(6*H*)-carboxylate: White solid, m.p. 147 – 148 °C; 86% yield; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.93 – 7.81 (m, 3H), 7.49 – 7.16 (m, 5H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 6.0 Hz, 2H), 6.75 (d, *J* = 8.0 Hz, 1H), 5.42 (s, 1H), 4.47 (q, *J* = 7.1 Hz, 2H), 2.93 – 2.83 (m, 1H), 2.84 – 2.73 (m, 1H), 2.68 – 2.53 (m, 1H), 2.47 (s, 3H), 2.23 (dt, *J* = 16.3, 4.9 Hz, 1H), 1.51 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 151.9, 145.4, 144.9, 134.4, 133.6, 133.1, 132.2, 131.5, 129.6, 128.9, 127.9, 127.8, 125.6, 125.1, 121.0, 113.9, 106.0, 86.3, 68.9, 63.2, 49.8, 28.8, 21.7, 14.4 ppm; **HRMS** (ESI): $C_{27}H_{25}ClN_4NaO_6S$ $[M + Na]^+$ calcd: 591.1076, found: 591.1092.



3ah

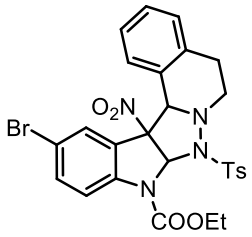
ethyl 12-fluoro-13b-nitro-8-tosyl-8,8a,13b,13c-tetrahydro-5*H*-indolo[2',3':3,4]pyrazolo[5,1-*a*]isoquinoline-9(6*H*)-carboxylate: Pale yellow solid, m.p. 150 – 151 °C; 95% yield; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.24 (m, 4H), 7.20 (s, 1H), 7.09 – 6.97 (m, 3H), 6.06 (dd, *J* = 8.5, 2.6 Hz, 1H), 4.84 (s, 1H), 4.46 (q, *J* = 7.1 Hz, 2H), 2.89 – 2.70 (m, 2H), 2.44 (s, 3H), 2.41 – 2.21 (m, 2H), 1.51 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 158.0 (J_{C-F} = 242.6 Hz), 152.2, 144.8, 138.9, 134.0, 133.9, 129.4, 129.1, 129.0, 128.0, 127.6, 127.1, 126.5, 122.4 (J_{C-F} = 9.2 Hz), 119.1 (J_{C-F} = 23.4 Hz), 116.5 (J_{C-F} = 7.9 Hz), 114.7 (J_{C-F} = 26.2 Hz), 104.0, 85.4, 71.0, 63.1, 48.6, 29.1, 21.7, 14.4 ppm; **HRMS** (ESI): $C_{27}H_{25}FN_4NaO_6S$

$[M + Na]^+$ calcd: 575.1371, found: 575.1364.



3ai

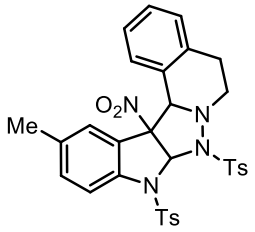
ethyl 12-chloro-13b-nitro-8-tosyl-8,8a,13b,13c-tetrahydro-5*H*-indolo[2',3':3,4]pyrazolo[5,1-*a*]isoquinoline-9(6*H*)-carboxylate: White solid, m.p. 125 – 126 °C; 92% yield; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.89 – 7.75 (m, 1H), 7.42 – 7.23 (m, 5H), 7.20 (s, 1H), 7.11 – 6.94 (m, 2H), 6.30 (d, *J* = 2.1 Hz, 1H), 4.83 (s, 1H), 4.47 (q, *J* = 7.1 Hz, 2H), 2.90 – 2.68 (m, 2H), 2.44 (s, 3H), 2.41 – 2.24 (m, 2H), 1.51 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 152.0, 144.8, 141.3, 133.9, 133.9, 132.1, 129.4, 129.1, 129.0, 128.0, 127.7, 127.1, 126.5, 122.5, 116.5, 104.1, 85.3, 71.0, 63.2, 48.6, 29.1, 21.7, 14.4 ppm; **HRMS** (ESI): $C_{27}H_{25}ClN_4NaO_6S$ $[M + Na]^+$ calcd: 591.1076, found: 591.1090.



3aj

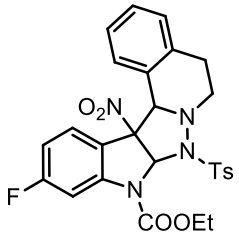
ethyl 12-bromo-13b-nitro-8-tosyl-8,8a,13b,13c-tetrahydro-5*H*-indolo[2',3':3,4]pyrazolo[5,1-*a*]isoquinoline-9(6*H*)-carboxylate: White solid, m.p. 118 – 119 °C; 83% yield; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.41 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.37 – 7.23 (m, 4H), 7.18 (s, 1H), 7.14 – 6.97 (m, 2H), 6.43 (d, *J* = 1.9 Hz, 1H), 4.82 (s, 1H), 4.47 (q, *J* = 7.1 Hz, 2H), 2.91 – 2.66 (m, 2H), 2.44 (s, 3H), 2.41 – 2.18 (m, 2H), 1.51 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 152.0, 144.8, 141.7, 135.0, 133.9, 133.9, 130.7, 129.5, 129.1, 128.9, 128.0, 127.1, 126.5, 122.8, 116.9, 115.2, 104.1, 85.2, 71.1, 63.2, 48.7, 29.7, 29.6, 29.1, 21.7, 14.4

ppm; **HRMS** (ESI): $C_{27}H_{25}BrN_4NaO_6S$ [M + Na]$^+$ calcd: 635.0572, found: 635.0570.



3ak

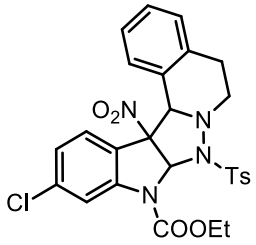
12-methyl-13b-nitro-8,9-ditosyl-6,8,8a,9,13b,13c-hexahydro-5*H*-indolo[2',3':3,4]pyrazolo[5,1-*a*]isoquinoline: White solid, m.p. 164 – 165 ^{o}C; 87% yield; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.3 Hz, 2H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.27 – 7.18 (m, 4H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.12 – 7.02 (m, 2H), 7.02 – 6.91 (m, 1H), 6.04 (s, 1H), 4.99 (s, 1H), 2.81 – 2.54 (m, 2H), 2.44 (s, 3H), 2.38 (s, 3H), 2.31 – 2.13 (m, 2H), 1.94 (s, 3H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 145.0, 144.7, 140.4, 134.3, 134.1, 133.8, 133.0, 129.9, 129.5, 129.1, 128.6, 128.4, 128.1, 127.5, 127.4, 126.2, 122.8, 116.2, 104.8, 86.5, 70.9, 48.4, 29.0, 21.7, 21.6, 20.6 ppm; **HRMS** (ESI): $C_{32}H_{30}N_4NaO_6S_2$ [M + Na]$^+$ calcd: 653.1499, found: 653.1511.



3al

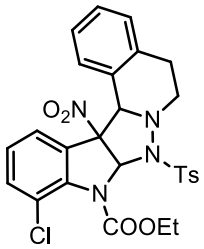
ethyl 11-fluoro-13b-nitro-8-tosyl-8,8a,13b,13c-tetrahydro-5*H*-indolo[2',3':3,4]pyrazolo[5,1-*a*]isoquinoline-9(6*H*)-carboxylate: White solid, m.p. 151 – 152 ^{o}C; 83% yield; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 9.4 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.24 (m, 2H), 7.21 (s, 1H), 7.03 (dd, *J* = 5.0, 2.1 Hz, 2H), 6.49 – 6.22 (m, 2H), 4.82 (s, 1H), 4.48 (q, *J* = 7.1 Hz, 2H), 2.89 – 2.71 (m, 2H), 2.44 (s, 3H), 2.42 – 2.27 (m, 2H), 1.52 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δδ 165.3 ($J_{C\text{-}F}$ = 250.2 Hz), 151.9, 144.8, 144.3 ($J_{C\text{-}F}$ = 13.1 Hz), 134.0, 133.9, 129.4, 129.1, 128.9, 128.3, 127.3, 126.4, 116.7, 110.2 ($J_{C\text{-}F}$ = 23.3 Hz), 104.0 ($J_{C\text{-}F}$ = 14.6 Hz), 103.5,

85.7, 70.9, 63.2, 48.6, 29.1, 21.7, 14.4 ppm; **HRMS** (ESI): $C_{27}H_{26}FN_4O_6S$ $[M + H]^+$ calcd: 553.1552, found: 553.1562.



3am

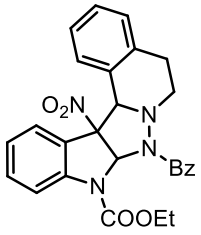
ethyl 11-chloro-13b-nitro-8-tosyl-8,8a,13b,13c-tetrahydro-5*H*-indolo[2',3':3,4]pyrazolo[5,1-*a*]isoquinoline-9(6*H*)-carboxylate: Pale yellow solid, m.p. 167 – 168 °C; 79% yield; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.02 – 7.89 (m, 3H), 7.42 – 7.21 (m, 4H), 7.20 (s, 1H), 7.10 – 7.97 (m, 2H), 6.67 (dd, *J* = 8.4, 1.7 Hz, 1H), 6.29 (d, *J* = 8.4 Hz, 1H), 4.84 (s, 1H), 4.48 (q, *J* = 7.1 Hz, 2H), 2.88 – 2.69 (m, 2H), 2.43 (s, 3H), 2.41 – 2.25 (m, 2H), 1.52 (t, *J* = 7.1 Hz, 3H) ppm;**^{13}C NMR** (75 MHz, $CDCl_3$) δ 151.9, 144.8, 143.6, 138.5, 134.0, 133.9, 129.4, 129.1, 128.9, 128.4, 128.2, 127.3, 126.4, 123.2, 119.6, 116.0, 104.2, 85.5, 70.9, 63.2, 48.6, 29.1, 21.6, 14.4 ppm; **HRMS** (ESI): $C_{27}H_{25}ClN_4NaO_6S$ $[M + Na]^+$ calcd: 591.1076, found: 591.1091.



3an

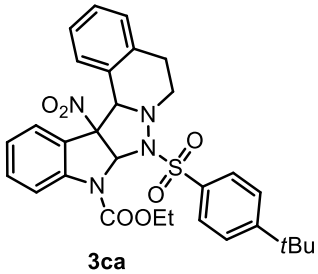
ethyl 10-chloro-13b-nitro-8-tosyl-8,8a,13b,13c-tetrahydro-5*H*-indolo[2',3':3,4]pyrazolo[5,1-*a*]isoquinoline-9(6*H*)-carboxylate: White solid, m.p. 156 – 157 °C; 94% yield; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 2H), 7.41 – 7.31 (m, 3H), 7.30 – 7.14 (m, 2H), 7.11 – 6.99 (m, 2H), 6.89 (d, *J* = 7.5 Hz, 1H), 6.75 (t, *J* = 7.9 Hz, 1H), 6.08 (d, *J* = 7.3 Hz, 1H), 4.70 (s, 1H), 4.49 – 4.27 (m, 2H), 2.99 – 2.77 (m, 2H), 2.45 (s, 3H), 2.40 – 2.28 (m, 1H), 1.89 – 1.72 (m, 1H), 1.52 – 1.38 (m, 3H) ppm; **^{13}C NMR** (75

MHz, $CDCl_3$) δ 152.5, 144.9, 140.7, 134.1, 133.8, 133.3, 129.7, 129.0, 129.0, 128.9, 128.1, 126.8, 126.7, 126.5, 125.9, 125.7, 125.2, 102.9, 87.1, 69.1, 63.7, 49.0, 28.9, 21.7, 14.2 ppm; **HRMS** (ESI): $C_{27}H_{26}ClN_4O_6S$ $[M + H]^+$ calcd: 569.1256, found: 569.1270.



3ba

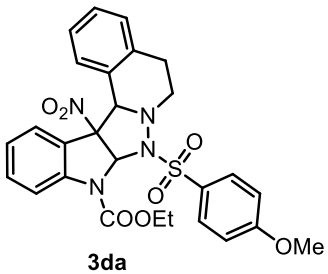
ethyl 8-benzoyl-13b-nitro-8,8a,13b,13c-tetrahydro-5*H*-indolo[2',3':3,4]pyrazolo[5,1-*a*]isoquinoline-9(6*H*)-carboxylate: White solid, m.p. 139 – 140 °C; 67% yield; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 1H), 7.83 (s, 1H), 7.78 – 7.65 (m, 2H), 7.56 – 7.31 (m, 5H), 7.31 – 7.17 (m, 2H), 7.07 – 6.93 (m, 1H), 6.83 – 6.67 (m, 1H), 6.56 (d, *J* = 7.1 Hz, 1H), 5.02 (s, 1H), 4.48 – 4.24 (m, 2H), 3.39 – 3.16 (m, 1H), 2.87 – 2.62 (m, 2H), 2.54 – 2.29 (m, 1H), 1.36 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 173.2, 152.3, 143.3, 134.3, 133.9, 132.1, 131.2, 128.8, 128.2, 127.8, 127.4, 126.4, 122.8, 121.9, 115.3, 104.3, 82.2, 73.0, 62.6, 47.8, 29.0, 14.4 ppm; **HRMS** (ESI): $C_{27}H_{24}N_4NaO_5$ $[M + Na]^+$ calcd: 507.1639, found: 507.1637.



3ca

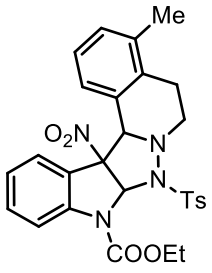
ethyl 8-((4-(tert-butyl)phenyl)sulfonyl)-13b-nitro-8,8a,13b,13c-tetrahydro-5*H*-indolo[2',3':3,4]pyrazolo[5,1-*a*]isoquinoline-9(6*H*)-carboxylate: White solid, m.p. 161 – 162 °C; 84% yield; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.6 Hz, 2H), 7.87 (d, *J* = 7.4 Hz, 1H), 7.54 (d, *J* = 8.6 Hz, 2H), 7.36 – 7.22 (m, 3H), 7.19 (s, 1H), 7.13 – 6.95 (m, 2H), 6.77 – 6.63 (m, 1H), 6.34 (d, *J* = 7.3 Hz, 1H), 4.77 (s, 1H), 4.47 (q, *J* = 7.1 Hz, 2H), 2.88 – 2.69 (m, 2H), 2.45 – 2.18 (m, 2H), 1.52 (t, *J* = 7.1 Hz, 3H), 1.34 (s, 9H) ppm; **^{13}C NMR**

(75 MHz, $CDCl_3$) δ 157.7, 152.2, 142.7, 134.1, 133.8, 132.1, 128.9, 128.8, 128.4, 127.4, 127.3, 126.3, 125.8, 122.9, 121.2, 115.6, 104.6, 85.1, 70.5, 62.9, 48.6, 35.2, 31.0, 29.1, 14.4 ppm; **HRMS** (ESI): $C_{30}H_{32}N_4NaO_6S$ $[M + Na]^+$ calcd: 599.1935, found: 599.1922.



3da

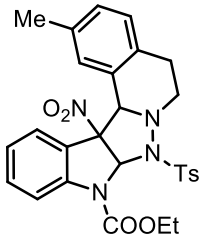
ethyl 8-((4-methoxyphenyl)sulfonyl)-13b-nitro-8,8a,13b,13c-tetrahydro-5*H*-indolo[2',3':3,4]pyrazolo[5,1-*a*]isoquinoline-9(6*H*)-carboxylate: White solid, m.p. 76 – 77 °C; 92% yield; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.9 Hz, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.38 – 7.21 (m, 3H), 7.17 (s, 1H), 7.12 – 7.04 (m, 1H), 7.02 – 6.90 (m, 3H), 6.70 (t, *J* = 7.6 Hz, 1H), 6.37 (d, *J* = 7.6 Hz, 1H), 4.84 (s, 1H), 4.47 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 2.92 – 2.65 (m, 2H), 2.40 – 2.23 (m, 2H), 1.51 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 163.6, 152.2, 142.7, 134.0, 132.1, 131.3, 128.8, 128.4, 128.3, 127.6, 127.4, 126.3, 122.9, 121.1, 115.6, 113.9, 104.6, 85.1, 70.7, 62.9, 55.6, 48.6, 29.1, 14.4 ppm; **HRMS** (ESI): $C_{27}H_{26}N_4NaO_7S$ $[M + Na]^+$ calcd: 573.1414, found: 573.1421.



3ea

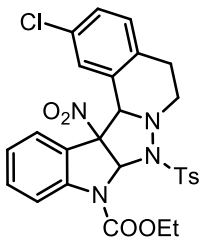
ethyl 4-methyl-13b-nitro-8-tosyl-8,8a,13b,13c-tetrahydro-5*H*-indolo[2',3':3,4]pyrazolo[5,1-*a*]isoquinoline-9(6*H*)-carboxylate: White solid, m.p. 144 – 145 °C; 78% yield; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.86 (t, *J* = 7.6 Hz, 1H), 7.40 – 7.28 (m, 3H), 7.22 – 7.09 (m, 3H), 6.92 –6.81 (m, 1H), 6.71 (t, *J* = 7.6 Hz, 1H), 6.43 (d, *J* = 7.5 Hz, 1H), 4.83 (s, 1H), 4.47 (q, *J* = 7.1 Hz, 2H), 2.87 –2.77 (m, 2H), 2.61 – 2.45 (m, 1H), 2.43 (s, 3H), 2.40 – 2.21 (m, 2H), 2.10 (s, 3H), 1.51 (t, *J* = 7.1 Hz,

3H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 152.2, 144.6, 142.7, 136.5, 134.1, 132.6, 132.1, 130.1, 129.4, 129.1, 128.3, 127.8, 126.1, 125.1, 122.9, 121.3, 115.6, 104.6, 85.1, 71.1, 62.9, 48.4, 26.5, 21.7, 19.4, 14.4 ppm; **HRMS** (ESI): $C_{28}H_{29}N_4O_6S$ $[M + H]^+$ calcd: 549.1802, found: 549.1807.



3fa

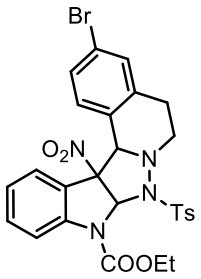
ethyl 2-methyl-13b-nitro-8-tosyl-8,8a,13b,13c-tetrahydro-5*H*-indolo[2',3':3,4]pyrazolo[5,1-*a*]isoquinoline-9(6*H*)-carboxylate: White solid, m.p. 87 – 88 °C; 82% yield; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.91 – 7.79 (m, 1H), 7.40 – 7.28 (m, 1H), 7.16 (s, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 6.98 – 6.79 (m, 2H), 6.71 (t, *J* = 7.6 Hz, 1H), 6.35 (d, *J* = 7.7 Hz, 1H), 4.80 (s, 1H), 4.47 (q, *J* = 7.1 Hz, 2H), 2.84 – 2.60 (m, 2H), 2.44 (s, 3H), 2.39 – 2.19 (m, 5H), 1.51 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 152.2, 144.6, 142.7, 136.0, 134.0, 132.1, 131.0, 129.7, 129.4, 129.1, 128.6, 128.3, 127.7, 127.6, 122.9, 121.2, 115.6, 104.5, 85.1, 70.7, 62.9, 48.7, 28.7, 21.7, 21.0, 14.4 ppm; **HRMS** (ESI): $C_{28}H_{29}N_4O_6S$ $[M + H]^+$ calcd: 549.1802, found: 549.1810.



3ga

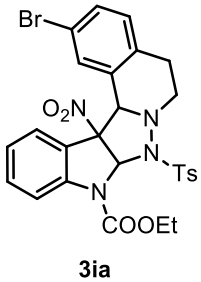
ethyl 2-chloro-13b-nitro-8-tosyl-8,8a,13b,13c-tetrahydro-5*H*-indolo[2',3':3,4]pyrazolo[5,1-*a*]isoquinoline-9(6*H*)-carboxylate: White solid, m.p. 86 – 87 °C; 64% yield; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.01 – 7.80 (m, 1H), 7.50 – 7.29 (m, 3H), 7.28 – 7.22 (m, 1H), 7.20 (s, 1H), 7.17 (d, *J* = 1.8 Hz, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.76 (m, 1H), 6.47 (d, *J* = 7.8 Hz, 1H), 4.79 (s, 1H), 4.47 (q, *J* = 7.1 Hz, 2H), 2.84 – 2.62

(m, 2H), 2.46 (s, 3H), 2.41 – 2.22 (m, 2H), 1.51 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 152.2, 144.9, 142.8, 133.9, 132.7, 132.4, 132.1, 130.2, 130.2, 129.5, 129.0, 129.0, 127.4, 127.2, 123.1, 121.2, 121.1, 115.7, 104.5, 85.0, 69.8, 63.0, 48.5, 28.7, 21.7, 14.4 ppm; **HRMS** (ESI): $C_{27}H_{25}ClN_4NaO_6S$ [M + Na]$^+$ calcd: 591.1076, found: 591.1081.



3ha

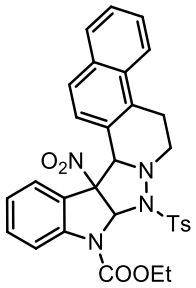
ethyl 3-bromo-13b-nitro-8-tosyl-8,8a,13b,13c-tetrahydro-5*H*-indolo[2',3':3,4]pyrazolo[5,1-*a*]isoquinoline-9(6*H*)-carboxylate: White solid, m.p. 157 – 158 °C; 55% yield; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.99 – 7.81 (m, 3H), 7.45 – 7.28 (m, 4H), 7.21 (s, 1H), 7.17 (d, *J* = 1.6 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.76 (dd, *J* = 11.1, 4.2 Hz, 1H), 6.46 (d, *J* = 7.3 Hz, 1H), 4.78 (s, 1H), 4.48 (q, *J* = 7.1 Hz, 2H), 2.86 – 2.65 (m, 2H), 2.44 (s, 3H), 2.38 – 2.20 (m, 2H), 1.51 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 152.2, 144.8, 142.8, 136.4, 133.9, 132.4, 131.8, 129.6, 129.5, 129.2, 129.1, 127.5, 127.3, 123.1, 122.8, 121.0, 115.7, 104.5, 84.9, 70.1, 63.0, 48.2, 29.0, 21.7, 14.4 ppm; **HRMS** (ESI): $C_{27}H_{25}BrN_4NaO_6S$ [M + Na]$^+$ calcd: 635.0570, found: 635.0579.



3ia

ethyl 2-bromo-13b-nitro-8-tosyl-8,8a,13b,13c-tetrahydro-5*H*-indolo[2',3':3,4]pyrazolo[5,1-*a*]isoquinoline-9(6*H*)-carboxylate: White solid, m.p. 160 – 161 °C; 60% yield; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.04 – 7.77 (m, 3H), 7.45 – 7.29 (m, 5H), 7.20 (s, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 6.76 (t, *J* = 7.6 Hz, 1H), 6.47 (d, *J* = 7.5 Hz, 1H),

4.79 (s, 1H), 4.47 (q, *J* = 7.1 Hz, 2H), 2.83 –2.72 (m, 1H), 2.73 – 2.60 (m, 1H), 2.46 (s, 3H), 2.42 – 2.18 (m, 2H), 1.51 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 152.2, 144.9, 142.8, 133.9, 133.2, 132.4, 131.9, 130.7, 130.4, 130.3, 129.5, 129.0, 127.2, 123.1, 121.1, 119.9, 115.8, 104.6, 85.0, 69.7, 63.0, 48.4, 28.8, 21.7, 14.4 ppm; **HRMS** (ESI): $C_{27}H_{26}BrN_4O_6S$ $[M + H]^+$ calcd: 613.0751, found: 613.0756.

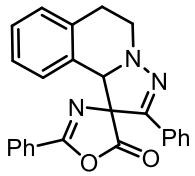


3ja

ethyl 13b-nitro-8-tosyl-8,8a,13b,13c-tetrahydro-5*H*-benzo[f]indolo[2',3':3,4]pyrazolo[5,1-*a*]isoquinoline-9(6*H*)-carboxylate: White solid, m.p. 83 – 84 °C; 84% yield; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.92 – 7.80 (m, 2H), 7.81 – 7.70 (m, 2H), 7.60 – 7.43 (m, 2H), 7.39 – 7.18 (m, 4H), 7.11 (d, *J* = 8.6 Hz, 1H), 6.59 (t, *J* = 7.5 Hz, 1H), 6.50 (d, *J* = 7.4 Hz, 1H), 4.95 (s, 1H), 4.49 (q, *J* = 7.1 Hz, 2H), 3.09 – 2.83 (m, 3H), 2.56 – 2.29 (m, 4H), 1.53 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 152.2, 144.7, 142.6, 134.0, 133.0, 132.1, 131.2, 130.6, 129.4, 129.2, 128.6, 127.7, 127.2, 126.8, 126.6, 125.6, 124.5, 123.2, 123.0, 121.2, 115.6, 104.6, 85.5, 71.3, 63.0, 53.4, 48.2, 25.8, 21.6, 14.4 ppm; **HRMS** (ESI): $C_{31}H_{28}N_4NaO_6S$ $[M + Na]^+$ calcd: 607.1622, found: 607.1632.

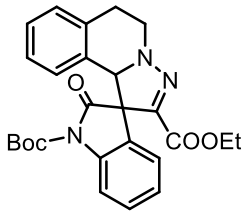
D) Synthesis of compounds 6a and 7a

A mixture of C,N-cyclic azomethine imines **1a** (0.12 mmol, 1.2 equiv) and alkylidene azlactone **4** or methyleneindolinone **5** (0.1 mmol, 1.0 equiv) in dry ethyl acetate (0.4 mL) was stirred at room temperature for appropriate time, the process of which was monitored by TLC analysis. Then the solvent was removed under vacuum. And the residue was purified by silica gel chromatography (PE : EA = 15:1 to 5:1 as eluent) to afford the desired product **6a** or **7a**.



6a

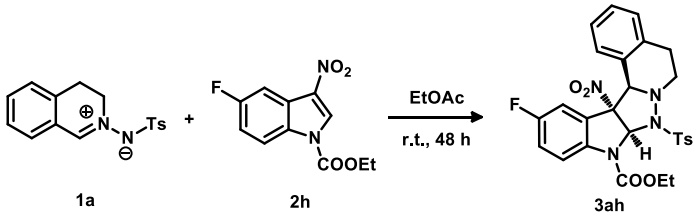
2,2'-diphenyl-6',10b'-dihydro-5*H*,5'*H*-spiro[oxazole-4,1'-pyrazolo[5,1-*a*]isoquinolin]-5-one: Yellow solid, m.p. 147 – 148 ^{o}C; 77% yield; **^{1}H NMR** (300 MHz, CDCl3) δ 7.93 – 7.80 (m, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.51 – 7.35 (m, 4H), 7.35 – 7.21 (m, 3H), 7.20 – 7.11 (m, 2H), 7.11 – 7.01 (m, 1H), 6.78 (d, J = 7.6 Hz, 1H), 5.45 (s, 1H), 4.12 (ddd, J = 12.9, 4.5, 3.1 Hz, 1H), 3.55 – 3.40 (m, 1H), 3.16 (ddd, J = 15.9, 11.3, 4.8 Hz, 1H), 2.78 (dt, J = 15.7, 2.9 Hz, 1H) ppm; **^{13}C NMR** (75 MHz, CDCl3) δ 177.1, 160.9, 146.3, 136.8, 133.4, 130.7, 129.9, 129.2, 128.9, 128.8, 128.8, 128.3, 127.6, 126.9, 126.3, 125.7, 125.4, 124.9, 82.8, 73.2, 49.1, 28.2 ppm; HRMS (ESI): $C_{25}H_{20}N_3O_2$ $[M + H]^+$ calcd: 394.1550, found: 394.1562.



7a

1-tert-butyl 2'-ethyl 2-oxo-6', 10b'-dihydro-5'*H*-spiro[indoline-3,1'-pyrazolo[5,1-*a*]isoquinoline]-1,2'-dicarboxylate: Yellow solid, m.p. 53 – 54 ^{o}C; 92% yield; **^{1}H NMR** (300 MHz, CDCl3) δ 7.82 (d, J = 8.2 Hz, 1H), 7.22 – 7.13 (m, 1H), 7.12 – 7.01 (m, 2H), 6.84 (t, J = 7.3 Hz, 1H), 6.76 (t, J = 7.5 Hz, 1H), 6.36 (d, J = 7.4 Hz, 1H), 6.26 (d, J = 7.7 Hz, 1H), 5.71 (s, 1H), 4.36 (dd, J = 13.1, 4.5 Hz, 1H), 4.05 (q, J = 7.1 Hz, 2H), 3.60 (td, J = 12.6, 3.5 Hz, 1H), 3.29 – 3.09 (m, 1H), 2.86 (d, J = 14.4 Hz, 1H), 1.70 (s, 9H), 1.08 (t, J = 7.1 Hz, 3H) ppm; **^{13}C NMR** (75 MHz, CDCl3) δ 175.0, 160.3, 149.0, 139.1, 137.7, 134.8, 130.6, 129.1, 128.9, 127.3, 126.8, 126.4, 125.4, 124.6, 124.2, 114.6, 84.7, 72.8, 64.8, 60.9, 47.7, 29.2, 28.0, 13.7 ppm; HRMS (ESI): $C_{26}H_{27}N_3NaO_5$ $[M + Na]^+$ calcd: 484.1843, found: 484.1863.

E) Large-scale preparation of 3ah



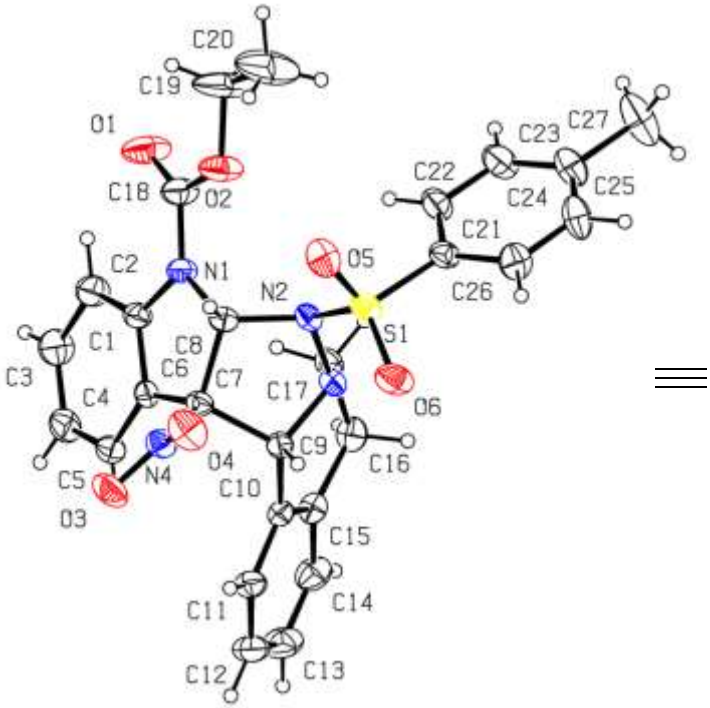
A mixture of C,N-cyclic azomethine imine **1a** (2.4 mmol, 720 mg, 1.2 equiv) and 3-nitroindole **2h** (2.0 mmol, 504 mg, 1.0 equiv) in dry ethyl acetate (4.0 mL) was stirred at room temperature for 48 h. After the complete consumption of **2h** (the process of which was monitored by TLC analysis), the solvent was removed under vacuum. And the residue was purified by silica gel chromatography (PE : EA = 15:1 to 5:1 as eluent) to afford the desired products **3ah**, which was then further purified by recrystallization. (*Note: An obvious decomposition of **3ah** in the purification process of silica gel chromatography was observed.*)

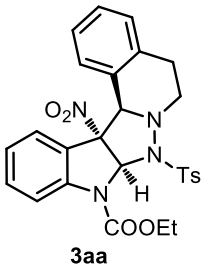
F) Synthesis of compound 8

To a solution of cycloadduct **3aa** (0.15 mmol, 80.1 mg) and TMSCl (0.6 mL) in methanol (1.5 mL) was added Zn nanopowder (3.0 mmol, 196.1 mg). The mixture was then stirred at room temperature for 30 min. After the complete consumption of the start material, the reaction mixture was filtrated and washed with CH_2Cl_2 (5 mL x 2). Then $NaHCO_3$ aq. solution (20 mL) was added to the obtained solution and the resulting mixture was extracted with CH_2Cl_2. The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel (eluting with PE/EA = 1:1) to afford the corresponding product **8** in 71% yield. White solid, m.p. 147 – 148 ^oC; **^{1}H NMR** (300

MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.2 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.38 (s, 1H), 7.36 – 7.25 (m, 1H), 7.22 – 7.10 (m, 3H), 7.11 – 7.00 (m, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 5.40 (s, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 3.32 – 3.18 (m, 1H), 3.18 – 2.95 (m, 2H), 2.95 – 2.80 (m, 1H), 2.03 (s, 1H), 1.43 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 151.0, 137.0, 136.0, 135.2, 129.3, 129.1, 127.5, 126.4, 125.7, 124.6, 124.5, 122.8, 120.1, 115.3, 63.1, 53.7, 41.8, 29.6, 14.4 ppm; **HRMS** (ESI): $C_{20}H_{21}N_2O_2$ $[M + H]^+$ calcd: 321.1598, found: 321.1606.

G) X-ray structure and data of 3aa





3aa

Displacement ellipsoids are drawn at the 50% probability level.

Bond precision:	C-C = 0.0047 A		Wavelength = 0.71073
Cell:	a = 17.4184(11)	b = 8.2542(5)	c = 18.8202(12)
	alpha = 90	beta = 104.911(7)	gamma = 90

Temperature: 293 K

	Calculated	Reported
Volume	2614.8(3)	2614.7(3)

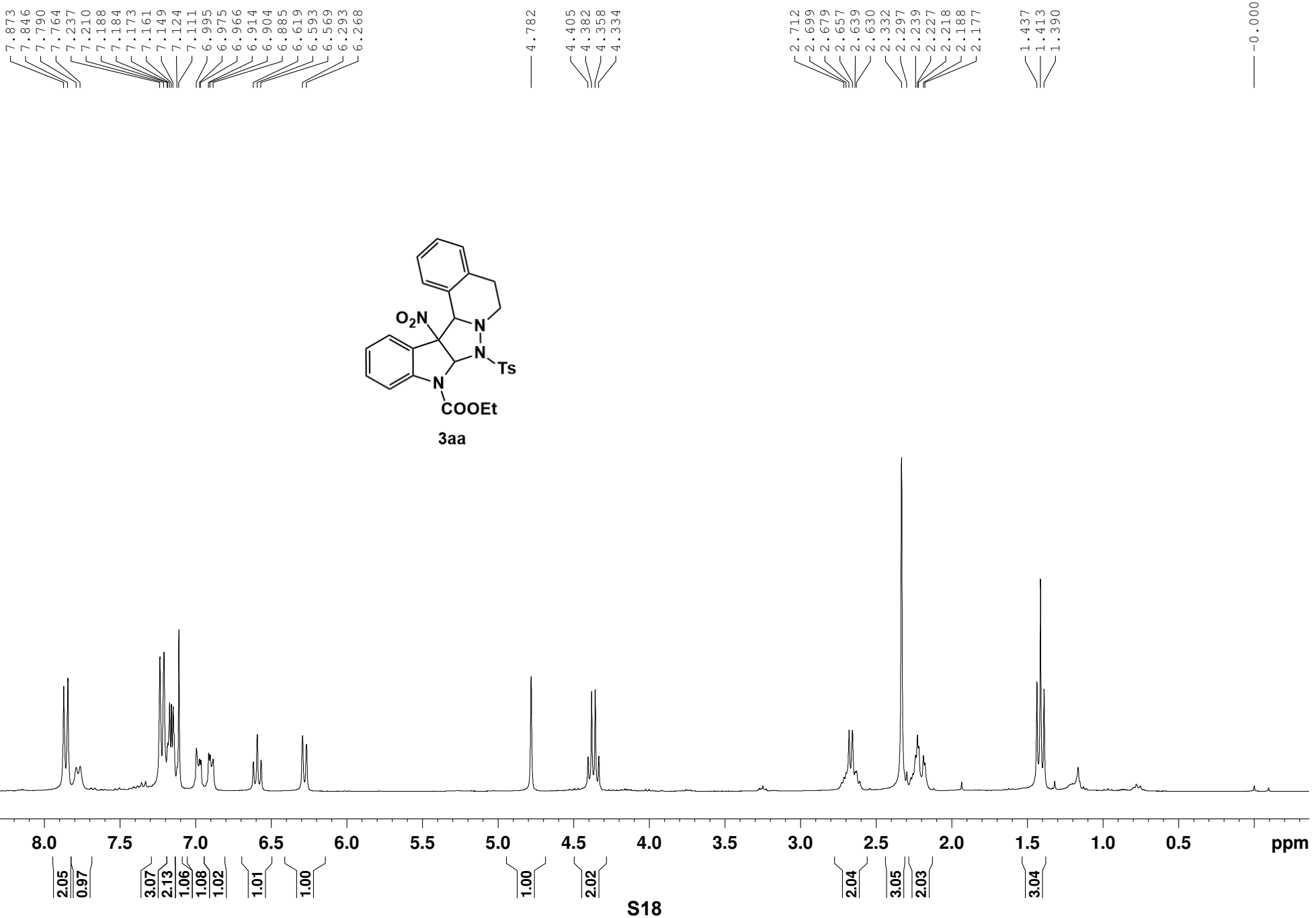
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C27 H26 N4 O6 S	C27 H26 N4 O6 S
Sum formula	C27 H26 N4 O6 S	C27 H26 N4 O6 S
Mr	534.58	534.58
Dx, g cm-3	1.358	1.358
Z	4	4
Mu (mm-1)	0.173	0.173
F000	1120.0	1120.0
F000'	1121.01	
h, k, lmax	21,10,23	21,10,23
Nref	5149	5140
Tmin, Tmax	0.969,0.976	0.884,1.000
Tmin'	0.964	

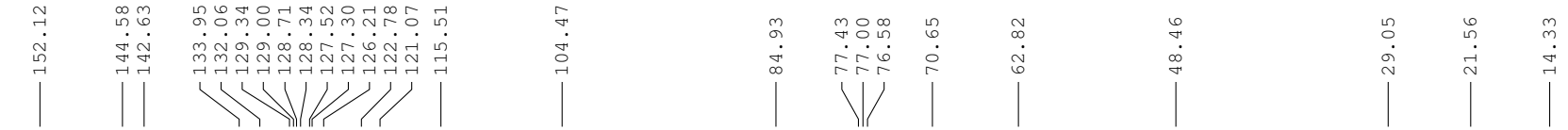
Correction method = # Reported T Limits: Tmin=0.884 Tmax=1.000 AbsCorr = MULTI-SCAN

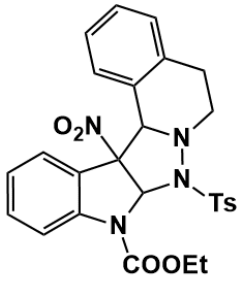
Data completeness= 0.998 Theta(max)= 26.020

R(reflections)= 0.0573(3225) wR2(reflections)= 0.1517(5140)

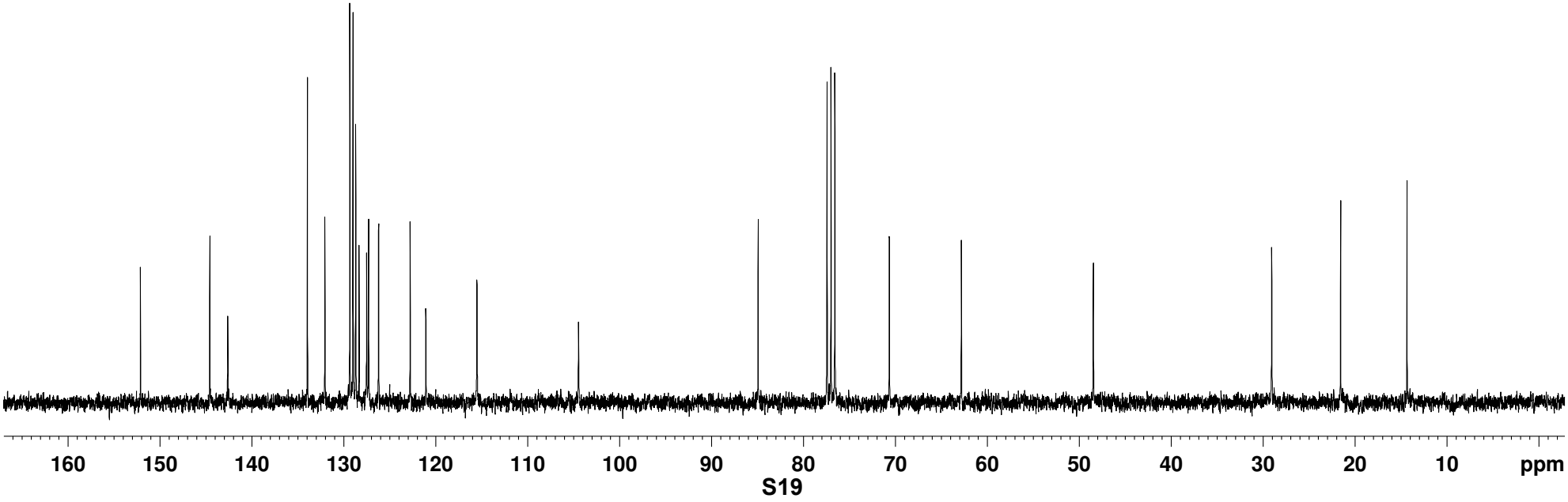
S = 1.035 Npar= 345

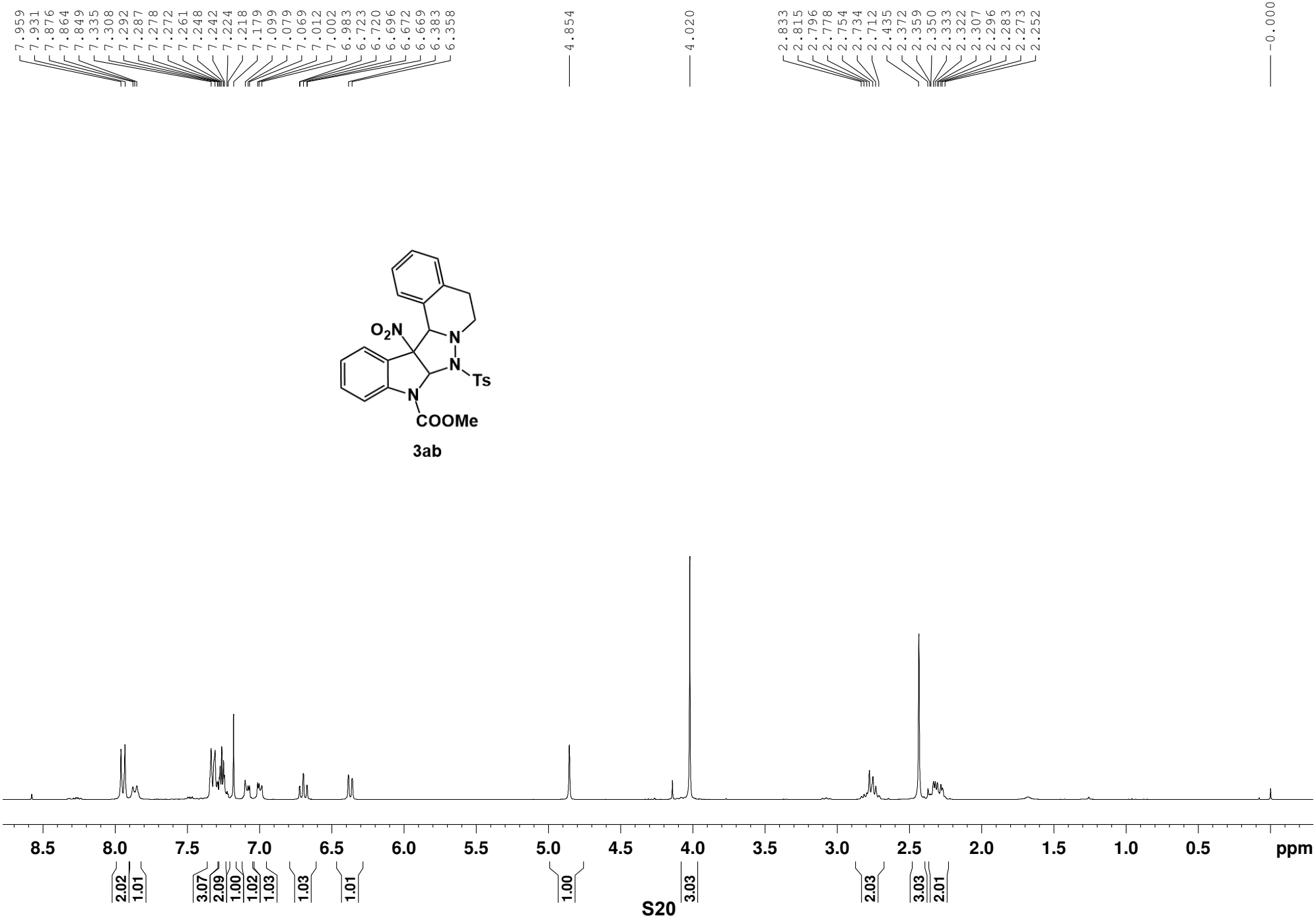

7.873
7.846
7.790
7.764
7.237
7.210
7.188
7.184
7.173
7.161
7.149
7.124
7.111
6.995
6.975
6.966
6.914
6.904
6.885
6.619
6.593
6.569
6.293
6.268
4.782
4.405
4.382
4.358
4.334
2.712
2.699
2.679
2.657
2.639
2.630
2.332
2.297
2.239
2.227
2.218
2.188
2.177
1.437
1.413
1.390
0.000
O2N
N
N
Ts
N
COOEt
3aa
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.05
0.97
3.07
2.13
1.06
1.08
1.02
1.01
1.00
1.00
2.02
2.04
3.05
2.03
3.04

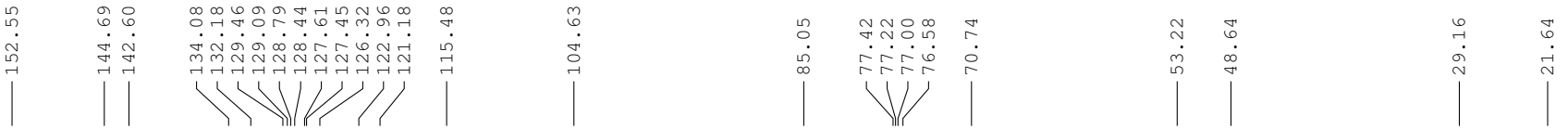

152.12
144.58
142.63
133.95
132.06
129.34
129.00
128.71
128.34
127.52
127.30
126.21
122.78
121.07
115.51
104.47
84.93
77.43
77.00
76.58
70.65
62.82
48.46
29.05
21.56
14.33

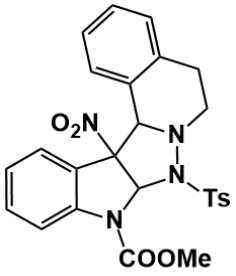

O2N
N
N
Ts
N
COOEt

3aa

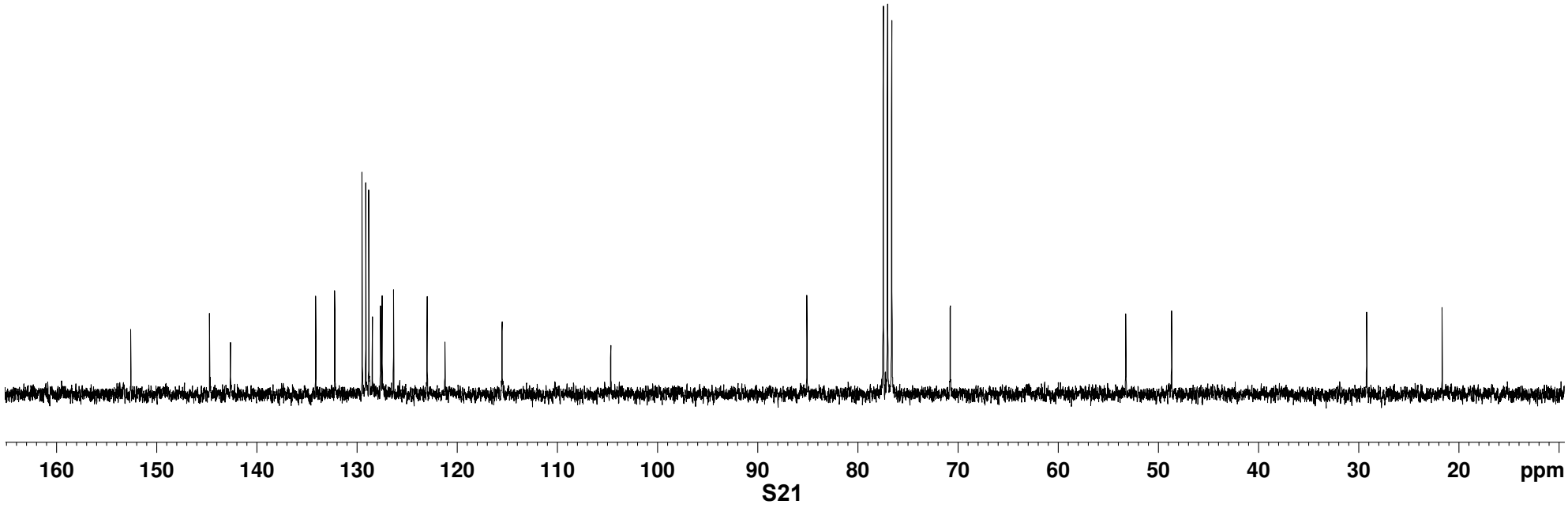

160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

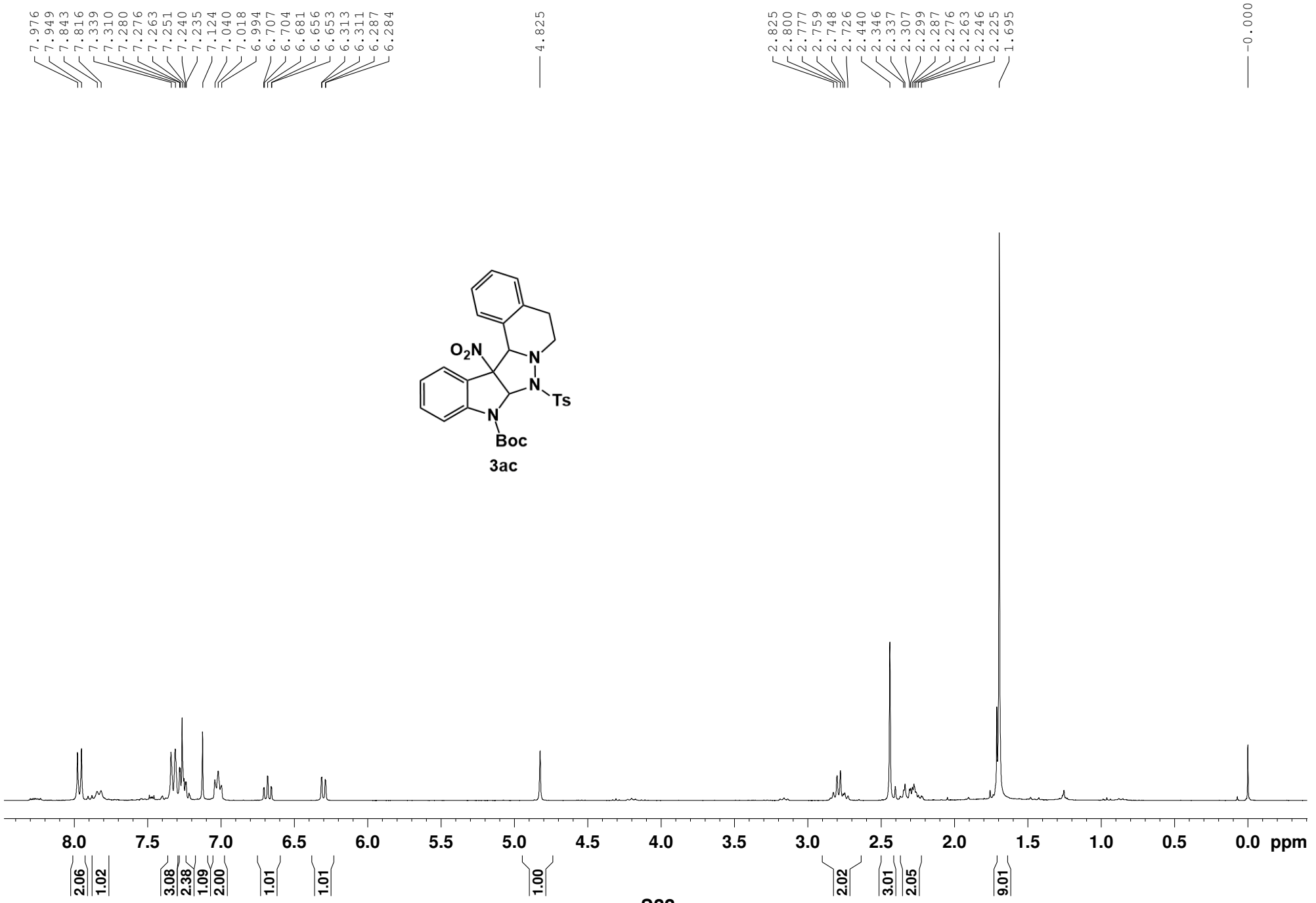

7.959
7.931
7.876
7.864
7.849
7.335
7.308
7.292
7.287
7.278
7.272
7.261
7.248
7.242
7.224
7.218
7.179
7.099
7.079
7.069
7.012
7.002
6.983
6.723
6.720
6.696
6.672
6.669
6.383
6.358
4.854
4.020
2.833
2.815
2.796
2.778
2.754
2.734
2.712
2.435
2.372
2.359
2.350
2.333
2.322
2.307
2.296
2.283
2.273
2.252
0.000
O2N
N
N
Ts
N
COOMe
3ab
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.02
1.01
3.07
2.09
1.00
1.02
1.03
1.03
1.01
1.00
3.03
2.03
3.03
2.01


152.55
144.69
142.60
134.08
132.18
129.46
129.09
128.79
128.44
127.61
127.45
126.32
122.96
121.18
115.48
104.63
85.05
77.42
77.22
77.00
76.58
70.74
53.22
48.64
29.16
21.64

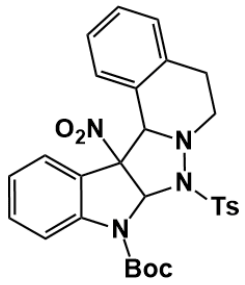

O2N
N
N
Ts
N
COOMe

3ab

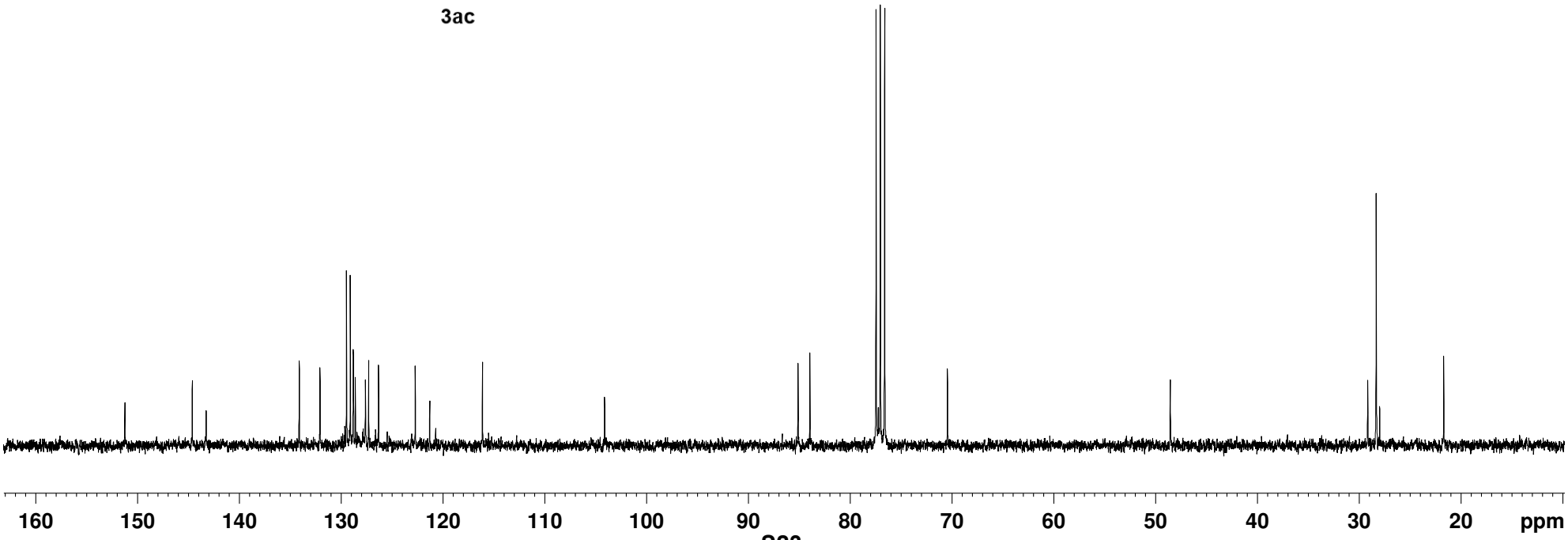

160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

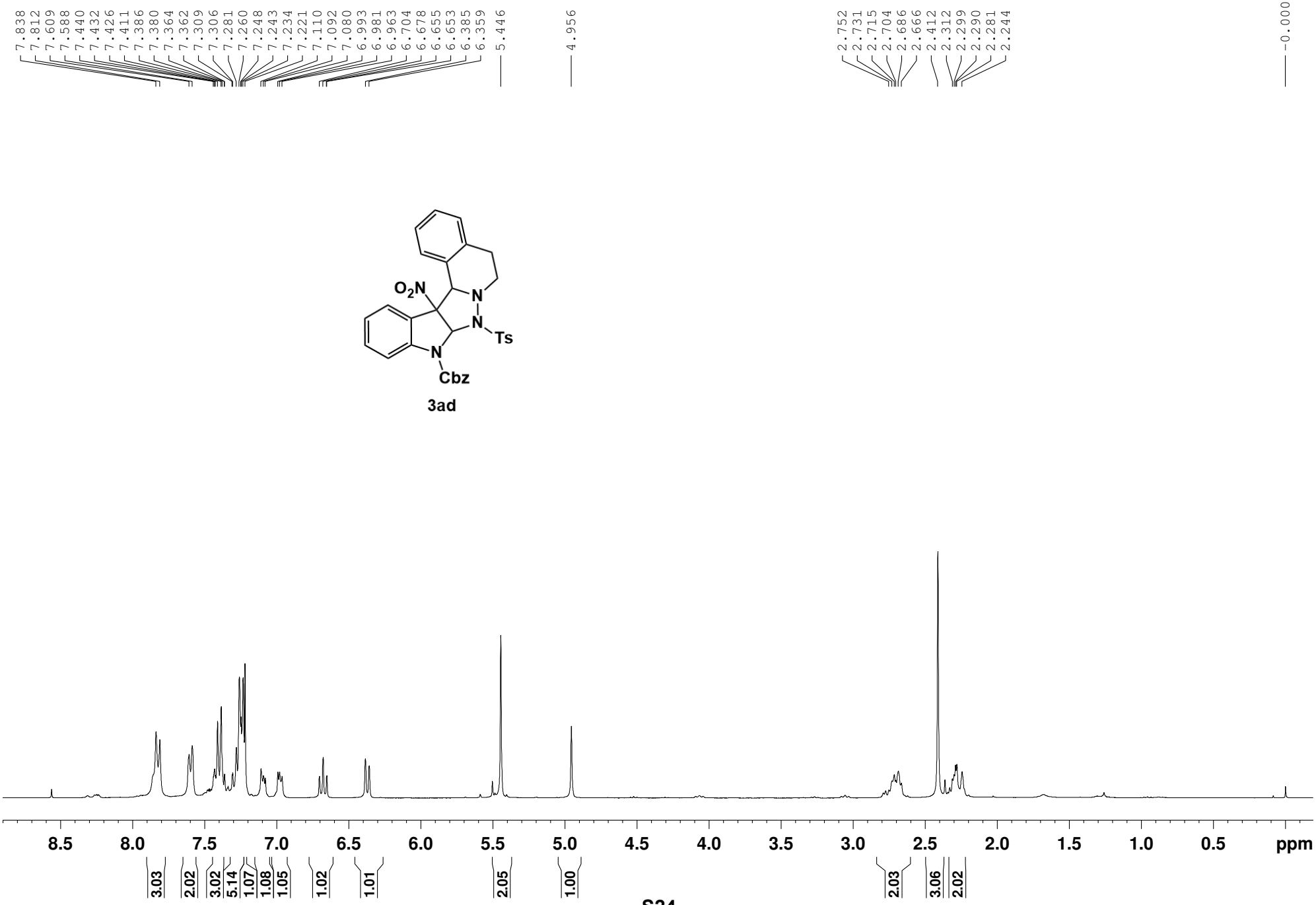

7.976
7.949
7.843
7.816
7.339
7.310
7.280
7.276
7.263
7.251
7.240
7.235
7.124
7.040
7.018
6.994
6.707
6.704
6.681
6.656
6.653
6.313
6.311
6.287
6.284
4.825
2.825
2.800
2.777
2.759
2.748
2.726
2.440
2.346
2.337
2.307
2.299
2.287
2.276
2.263
2.246
2.225
1.695
0.000
O2N
N
N
Ts
N
Boc
3ac
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.06
1.02
3.08
2.38
1.09
2.00
1.01
1.01
1.00
2.02
3.01
2.05
9.01

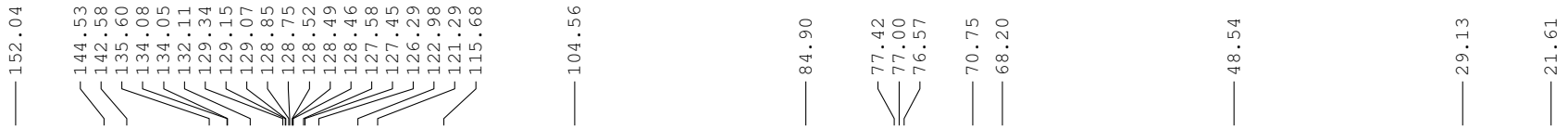
151.21
144.59
143.22
134.09
134.07
132.04
129.44
129.07
128.79
128.75
128.57
127.59
127.26
126.29
122.69
121.26
116.08
104.09
85.09
83.92
77.42
77.00
76.58
70.41
48.52
29.13
28.30
27.95
21.66

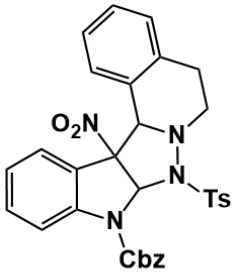


3ac

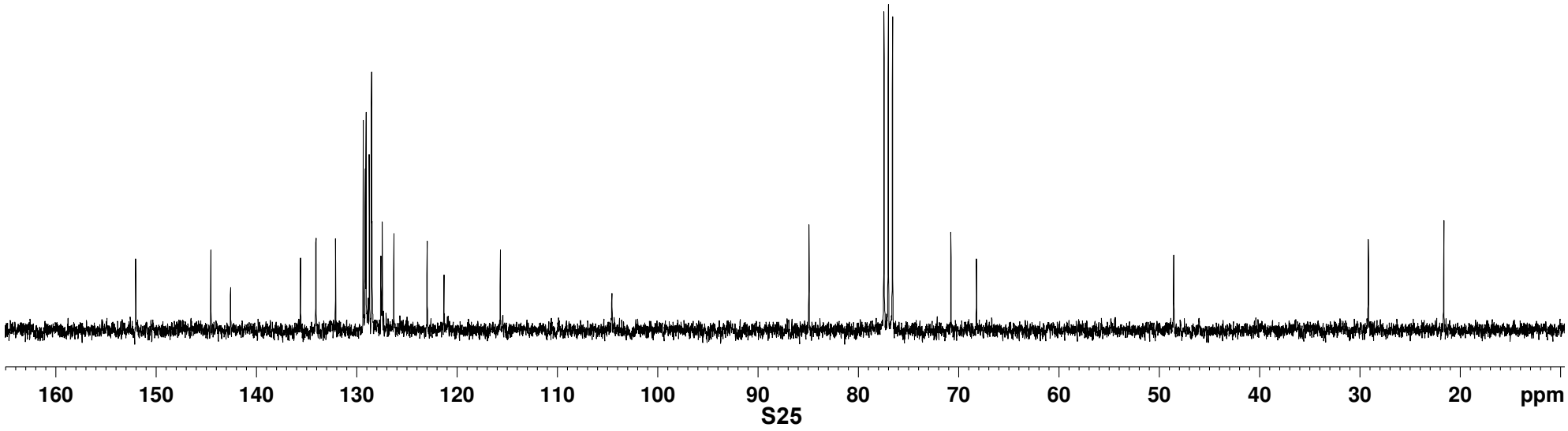



7.838
7.812
7.609
7.588
7.440
7.432
7.426
7.411
7.386
7.380
7.364
7.362
7.309
7.306
7.281
7.260
7.248
7.243
7.234
7.221
7.110
7.092
7.080
6.993
6.981
6.963
6.704
6.678
6.655
6.653
6.385
6.359
5.446
4.956
2.752
2.731
2.715
2.704
2.686
2.666
2.412
2.312
2.299
2.290
2.281
2.244
0.000
O2N
N
N
Ts
N
Cbz
3ad
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
3.03
2.02
3.02
5.14
1.07
1.08
1.05
1.02
1.01
2.05
1.00
2.03
3.06
2.02


152.04
144.53
142.58
135.60
134.08
134.05
132.11
129.34
129.15
129.07
128.85
128.75
128.52
128.49
128.46
127.58
127.45
126.29
122.98
121.29
115.68
104.56
84.90
77.42
77.00
76.57
70.75
68.20
48.54
29.13
21.61


O2N
N
N
Ts
N
Cbz

3ad

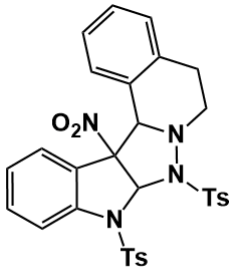

160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

8.043
8.016
7.786
7.758
7.748
7.720
7.372
7.351
7.324
7.294
7.264
7.238
7.221
7.213
7.194
7.092
7.065
7.057
6.978
6.970
6.950
6.768
6.743
6.718
6.339
6.313

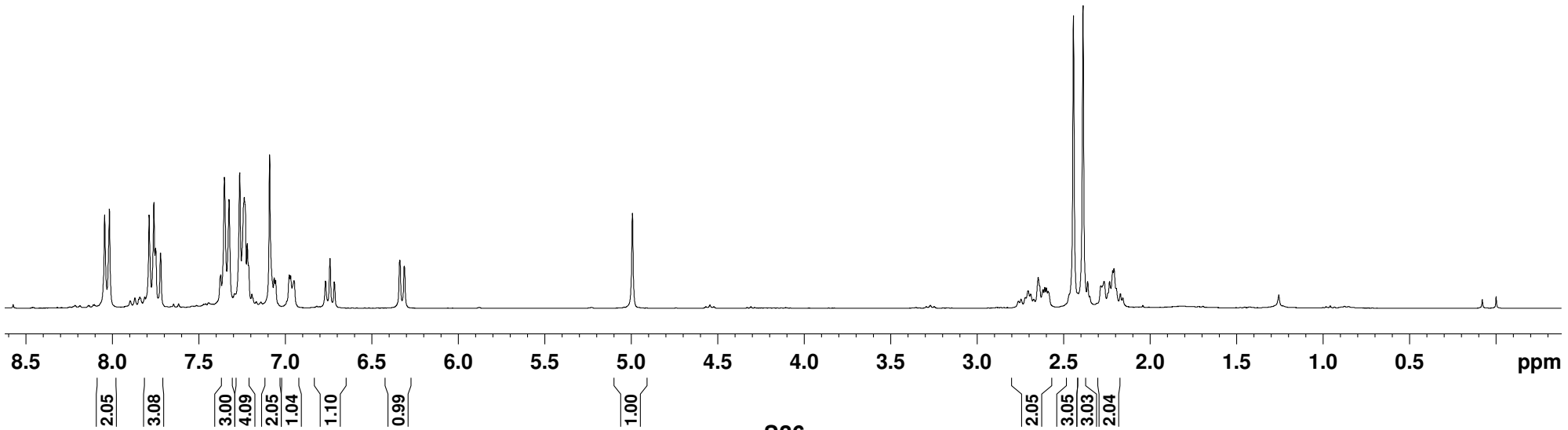
4.994

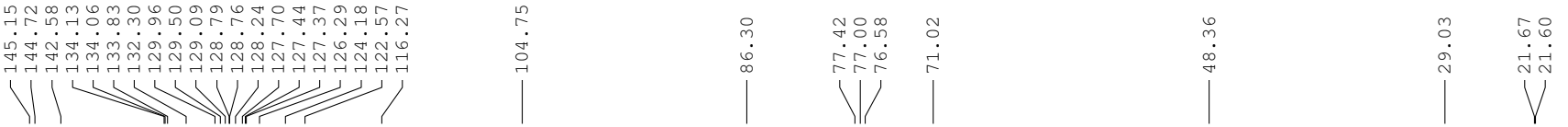
2.762
2.747
2.722
2.706
2.691
2.674
2.647
2.620
2.610
2.600
2.591
2.444
2.388
2.361
2.349
2.286
2.267
2.235
2.217
2.209
2.197
2.172
2.158

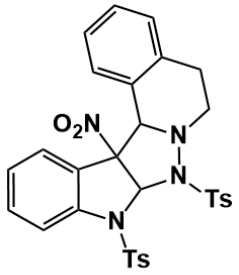
-0.000



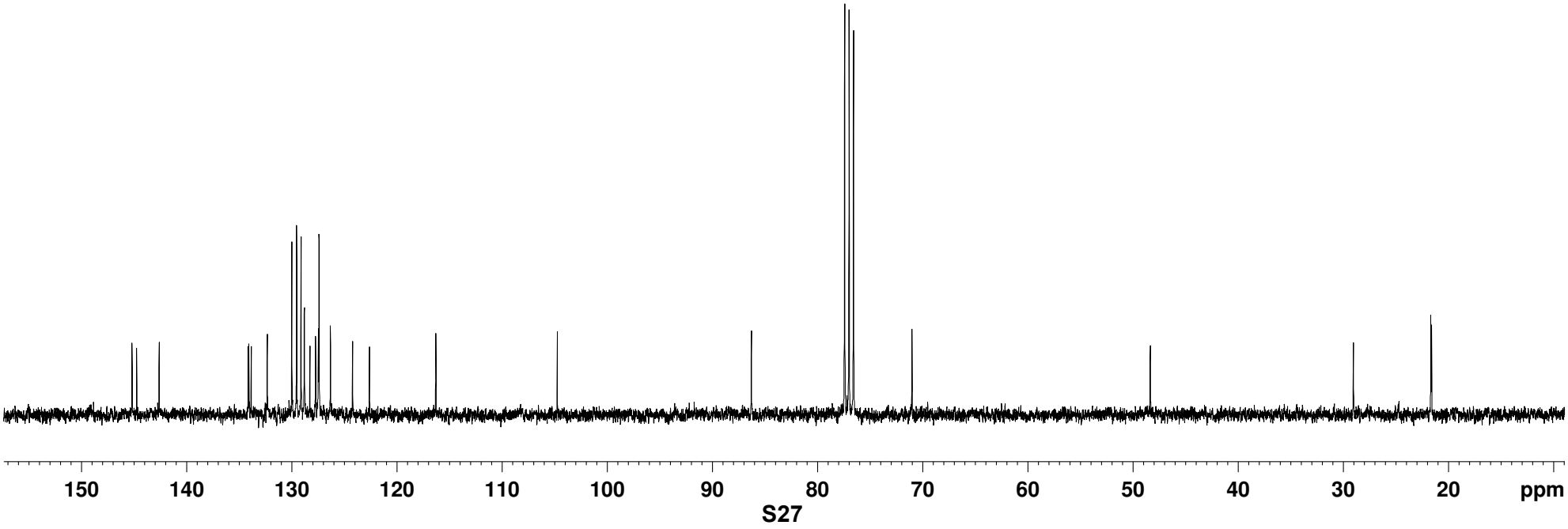
3ae




145.15
144.72
142.58
134.13
134.06
133.83
132.30
129.96
129.50
129.09
128.79
128.76
128.24
127.70
127.44
127.37
126.29
124.18
122.57
116.27
104.75
86.30
77.42
77.00
76.58
71.02
48.36
29.03
21.67
21.60


O2N
N
N
Ts
N
Ts

3ae


150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

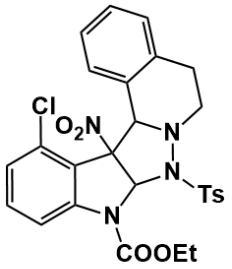
7.898
7.875
7.848
7.415
7.390
7.344
7.317
7.289
7.262
7.234
7.210
7.206
7.185
7.127
7.103
7.079
6.922
6.902
6.758
6.731

5.418

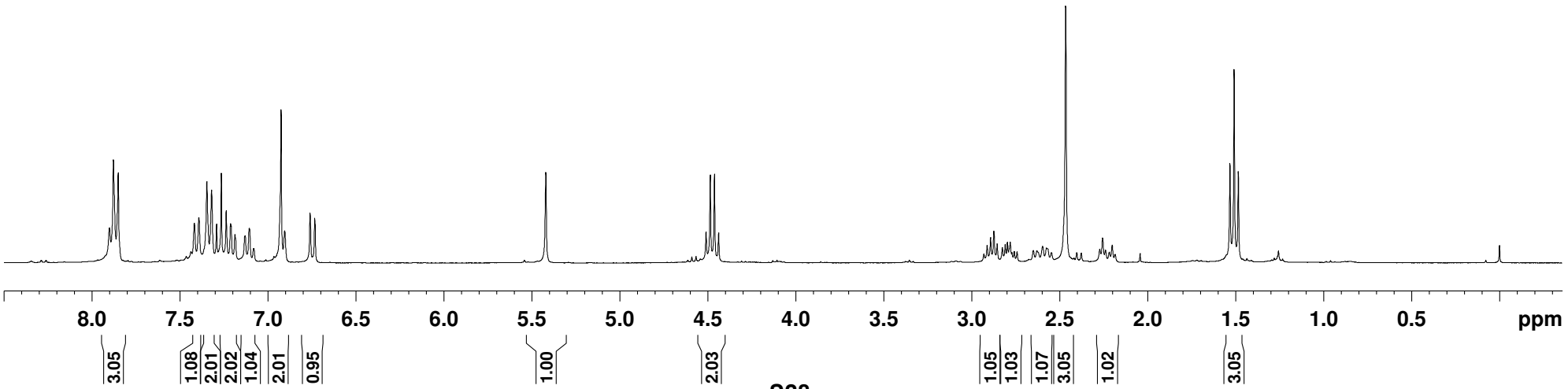
4.509
4.486
4.462
4.438

2.930
2.912
2.892
2.873
2.855
2.825
2.809
2.797
2.781
2.771
2.758
2.742
2.675
2.649
2.629
2.596
2.574
2.567
2.547
2.465
2.272
2.256
2.239
2.218
2.201
2.185
1.532
1.508
1.484

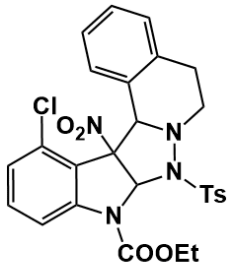
0.000



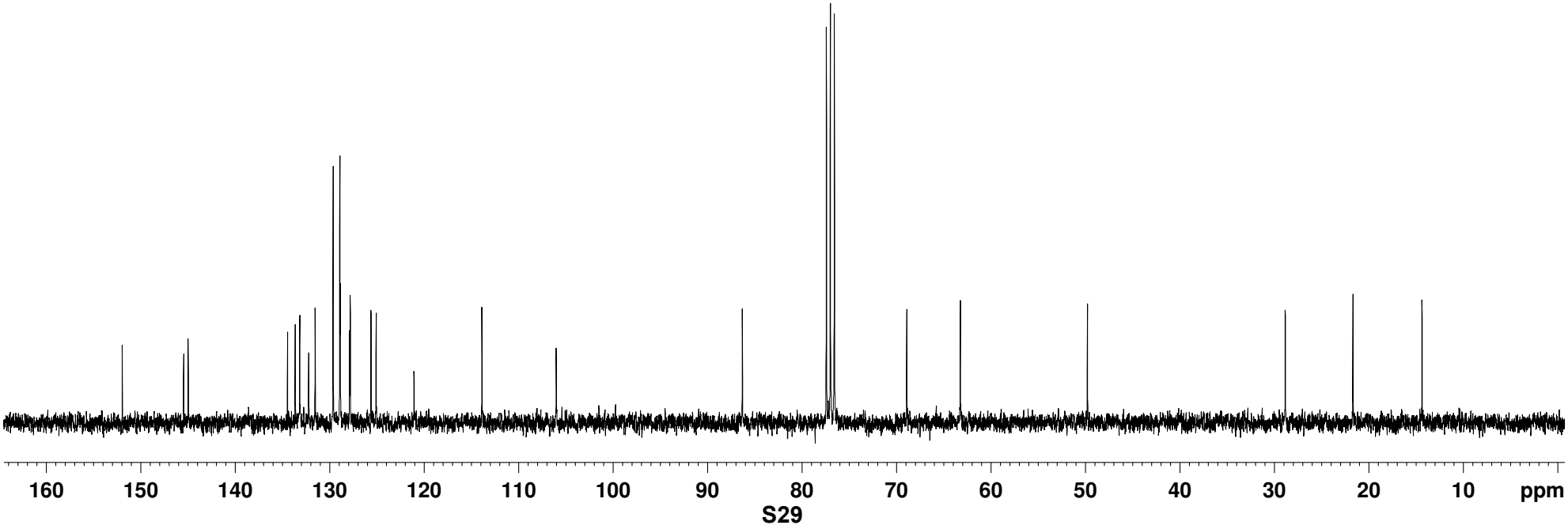
3ag



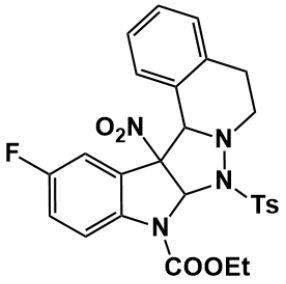
151.92
145.42
144.94
134.43
133.61
133.13
132.18
131.50
129.60
128.89
128.85
127.85
127.78
125.58
125.04
121.03
113.84
106.03
86.32
77.42
77.00
76.58
68.91
63.23
49.78
28.84
21.67
14.36



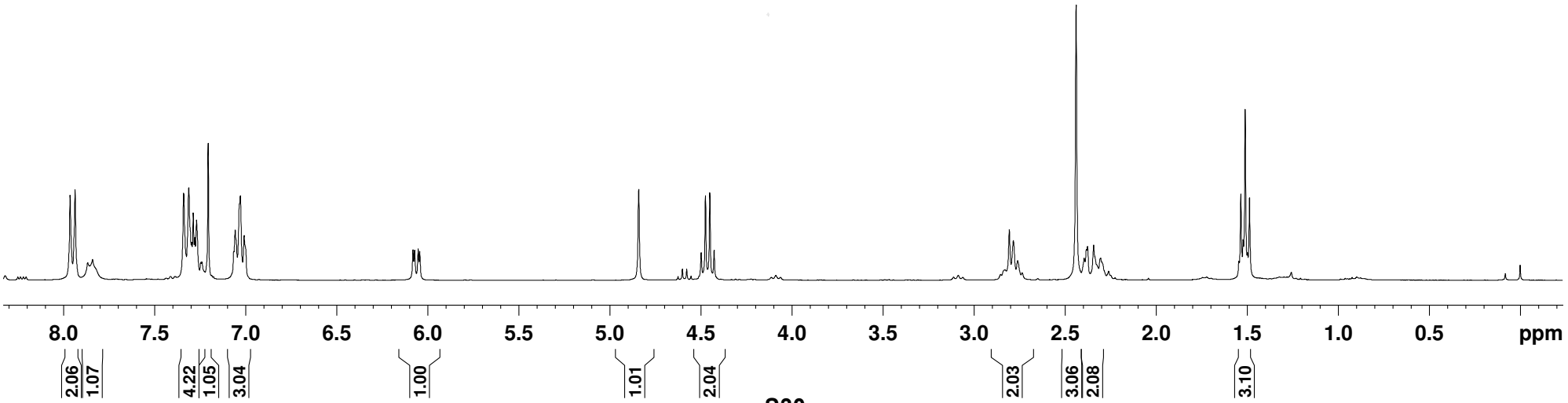
3ag

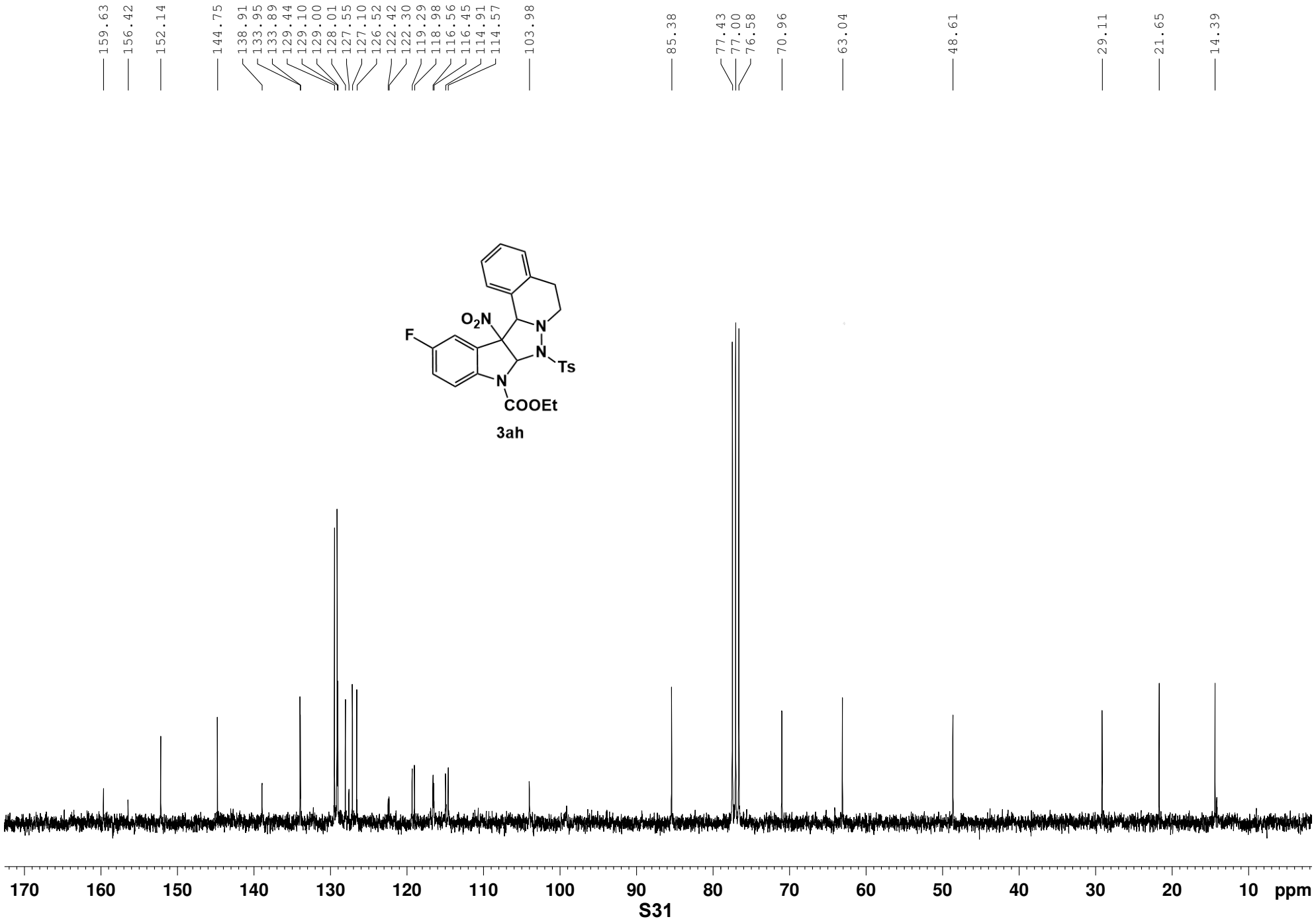


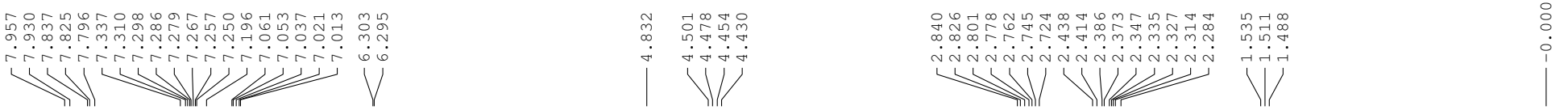

7.963
7.935
7.866
7.839
7.339
7.311
7.295
7.286
7.278
7.268
7.245
7.239
7.204
7.064
7.056
7.027
7.007
6.080
6.071
6.051
6.042
4.840
4.497
4.473
4.450
4.426
2.853
2.828
2.805
2.782
2.759
2.734
2.438
2.394
2.382
2.375
2.342
2.304
2.259
1.533
1.510
1.486
0.000

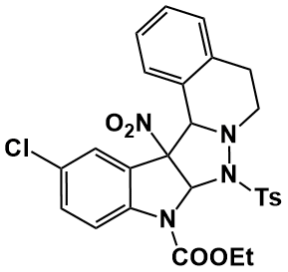

O2N
F
N
N
Ts
N
COOEt

3ah

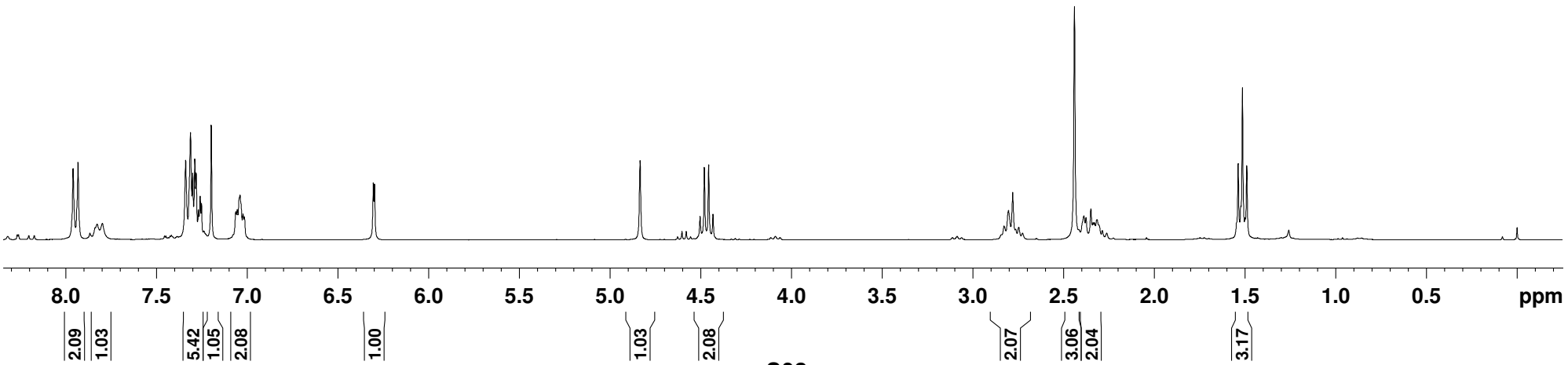

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.06
1.07
4.22
1.05
3.04
1.00
1.01
2.04
2.03
3.06
2.08
3.10


159.63
156.42
152.14
144.75
138.91
133.95
133.89
129.44
129.10
129.00
128.01
127.55
127.10
126.52
122.42
122.30
119.29
118.98
116.56
116.45
114.91
114.57
103.98
85.38
77.43
77.00
76.58
70.96
63.04
48.61
29.11
21.65
14.39
O2N
F
N
N
Ts
N
COOEt
3ah
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

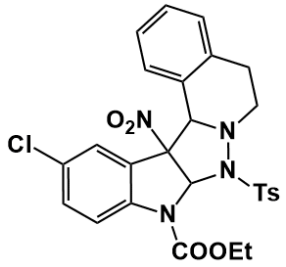

7.957
7.930
7.837
7.825
7.796
7.337
7.310
7.298
7.286
7.279
7.267
7.257
7.250
7.196
7.061
7.053
7.037
7.021
7.013
6.303
6.295
4.832
4.501
4.478
4.454
4.430
2.840
2.826
2.801
2.778
2.762
2.745
2.724
2.438
2.414
2.386
2.373
2.347
2.335
2.327
2.314
2.284
1.535
1.511
1.488
0.000


Cl
O2N
N
N
Ts
N
COOEt

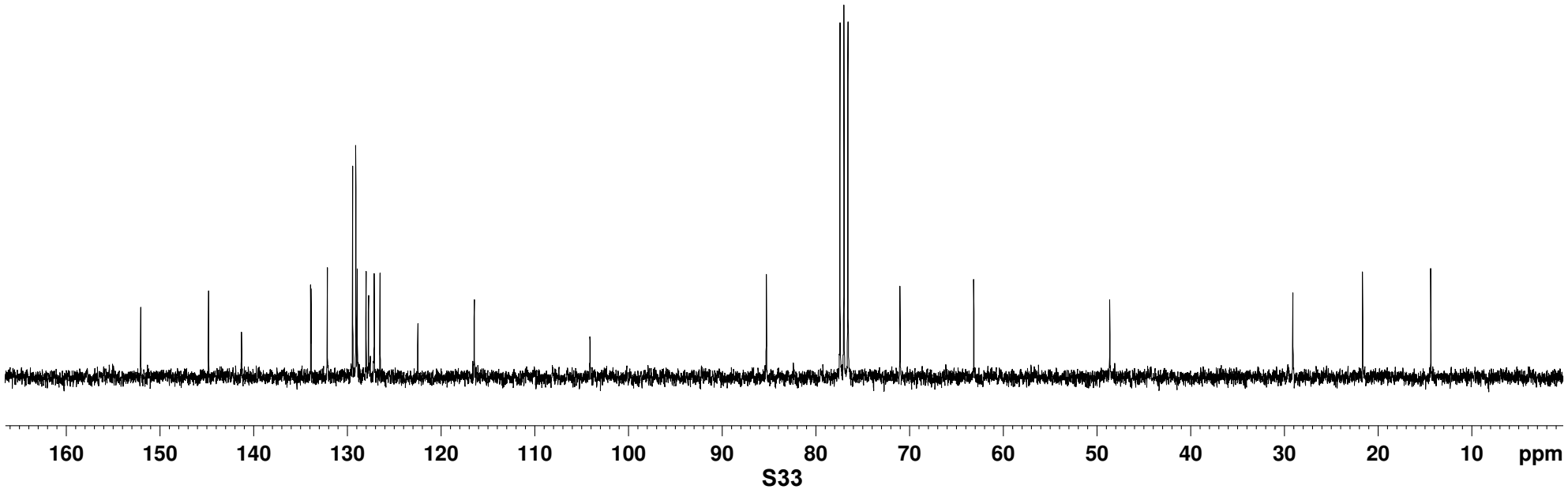
3ai

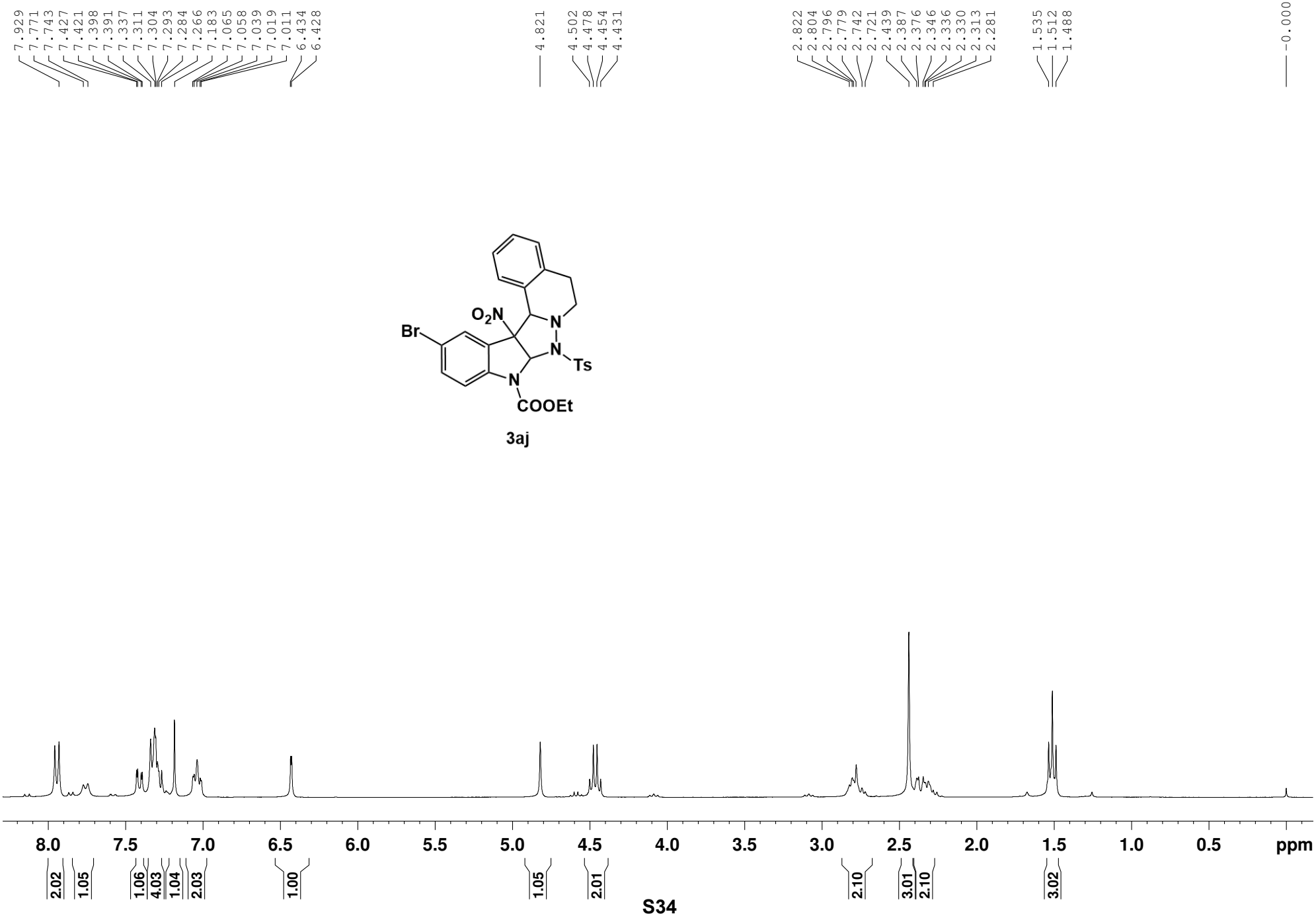

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.09
1.03
5.42
1.05
2.08
1.00
1.03
2.08
2.07
3.06
2.04
3.17

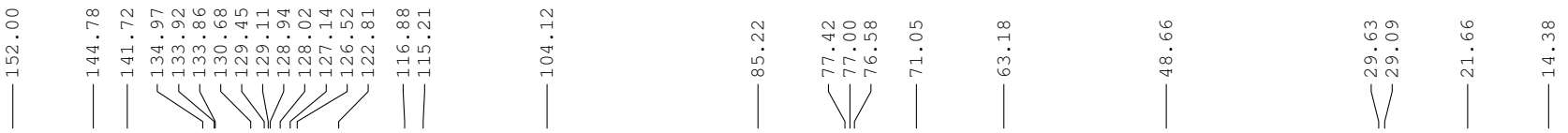
152.01
144.76
141.26
133.91
133.87
132.14
129.44
129.10
128.94
128.01
127.99
127.74
127.14
126.52
122.48
116.45
104.10
85.28
77.42
77.00
76.58
71.02
63.14
48.63
29.09
21.65
14.37

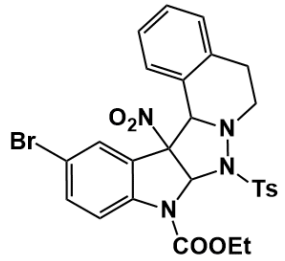


3ai

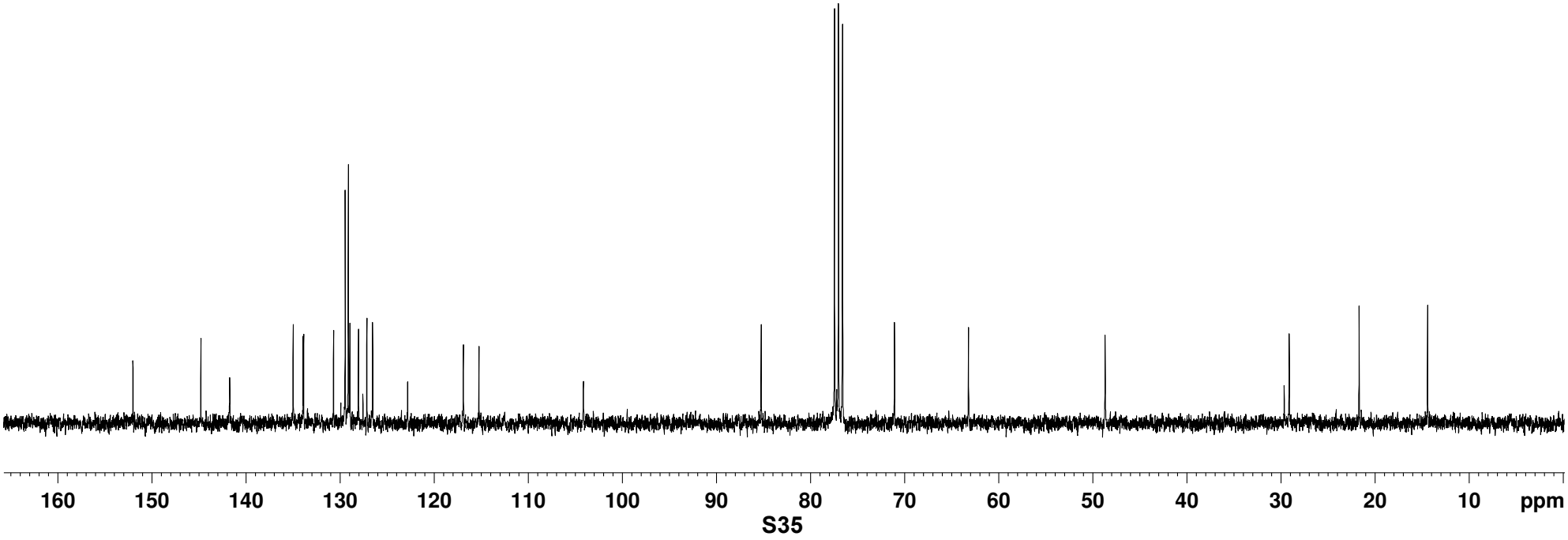


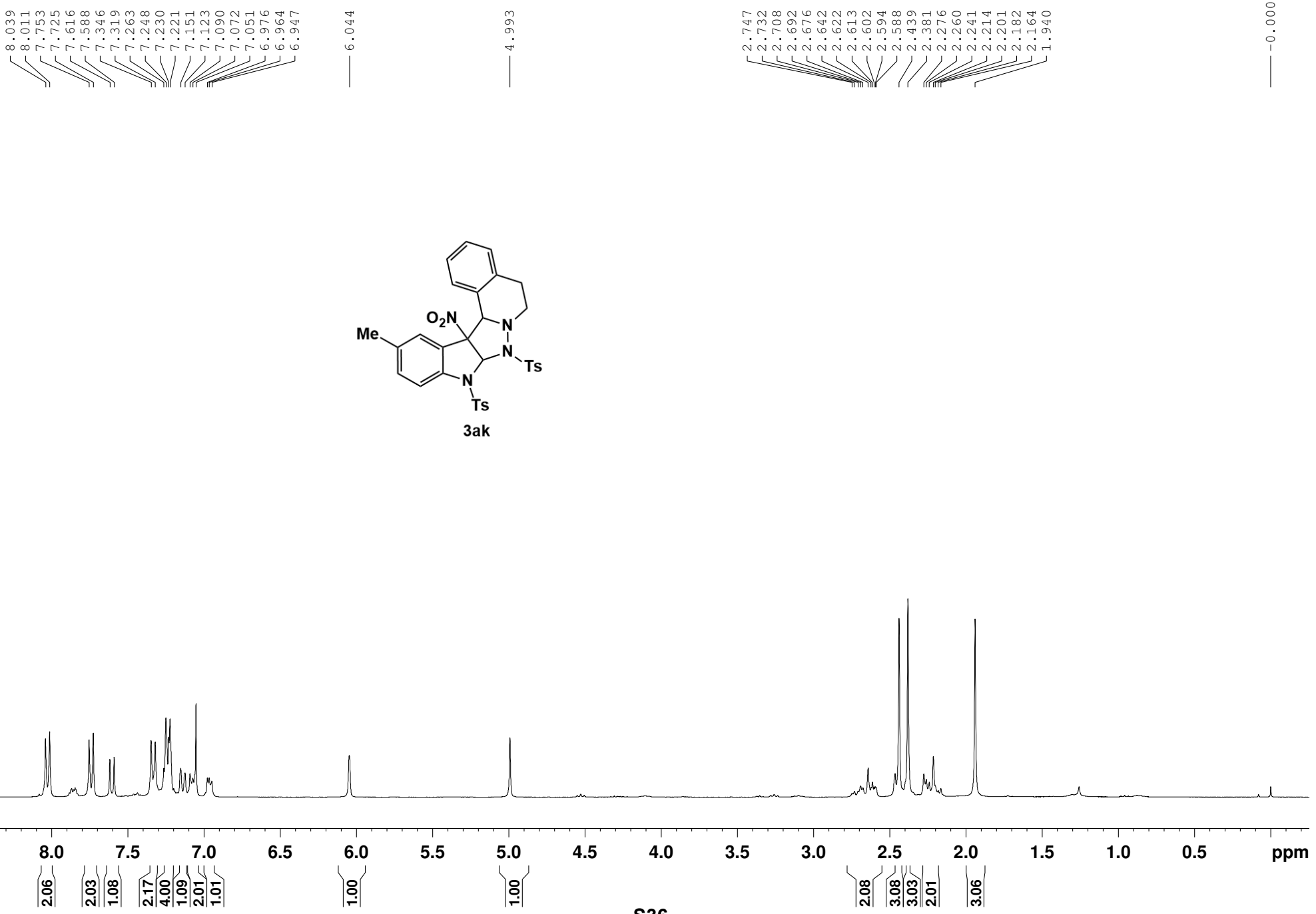

7.929
7.771
7.743
7.427
7.421
7.398
7.391
7.337
7.311
7.304
7.293
7.284
7.266
7.183
7.065
7.058
7.039
7.019
7.011
6.434
6.428
4.821
4.502
4.478
4.454
4.431
2.822
2.804
2.796
2.779
2.742
2.721
2.439
2.387
2.376
2.346
2.336
2.330
2.313
2.281
1.535
1.512
1.488
0.000
Br
O2N
N
N
Ts
N
COOEt
3aj
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.02
1.05
1.06
4.03
1.04
2.03
1.00
1.05
2.01
2.10
3.01
2.10
3.02

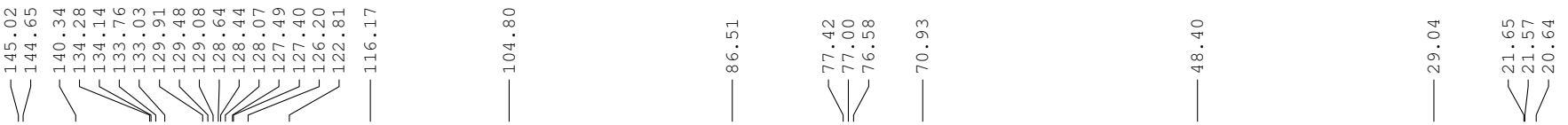

152.00
144.78
141.72
134.97
133.92
133.86
130.68
129.45
129.11
128.94
128.02
127.14
126.52
122.81
116.88
115.21
104.12
85.22
77.42
77.00
76.58
71.05
63.18
48.66
29.63
29.09
21.66
14.38

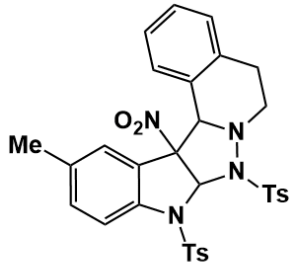

O2N
Br
N
N
Ts
N
COOEt

3aj

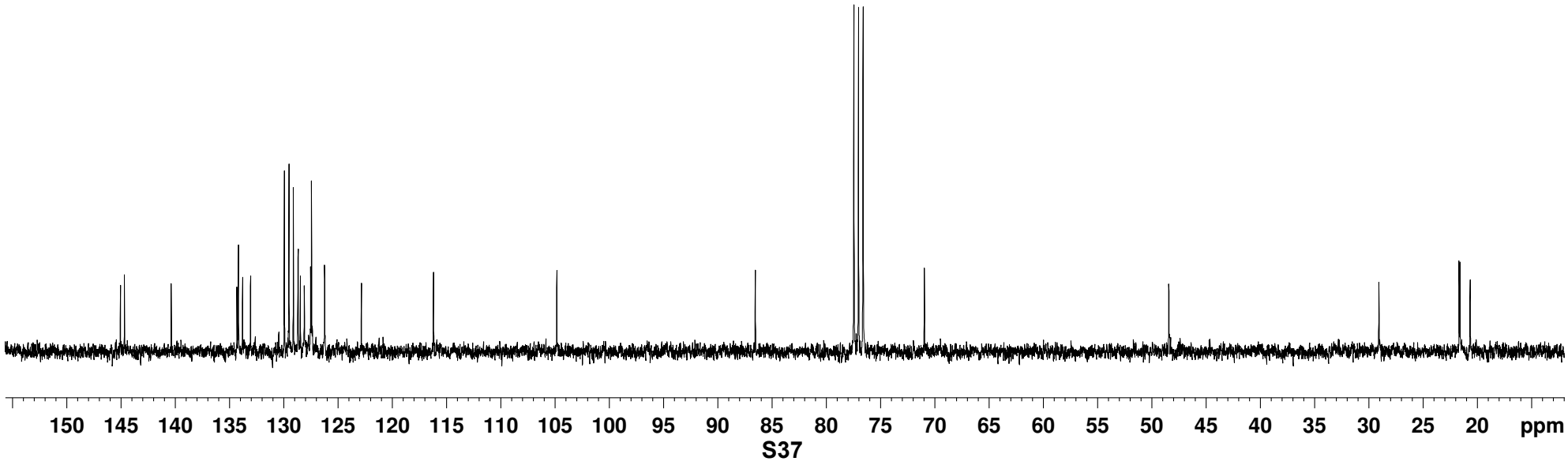

160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

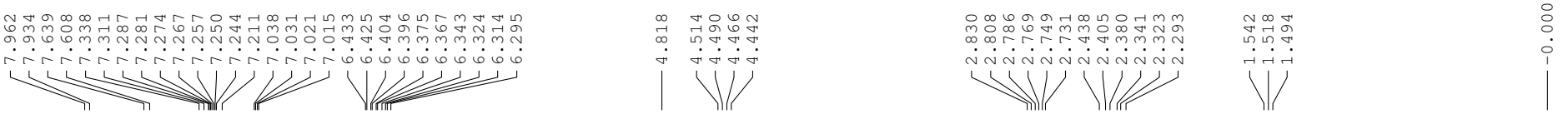

8.039
8.011
7.753
7.725
7.616
7.588
7.346
7.319
7.263
7.248
7.230
7.221
7.151
7.123
7.090
7.072
7.051
6.976
6.964
6.947
6.044
4.993
2.747
2.732
2.708
2.692
2.676
2.642
2.622
2.613
2.602
2.594
2.588
2.439
2.381
2.276
2.260
2.241
2.214
2.201
2.182
2.164
1.940
0.000
Me
O2N
N
N
Ts
N
Ts
3ak
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.06
2.03
1.08
2.17
4.00
1.09
2.01
1.01
1.00
1.00
2.08
3.08
3.03
2.01
3.06

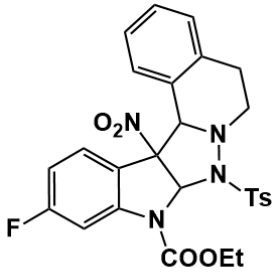

145.02
144.65
140.34
134.28
134.14
133.76
133.03
129.91
129.48
129.08
128.64
128.44
128.07
127.49
127.40
126.20
122.81
116.17
104.80
86.51
77.42
77.00
76.58
70.93
48.40
29.04
21.65
21.57
20.64


O2N
Me
N
N
Ts
N
Ts

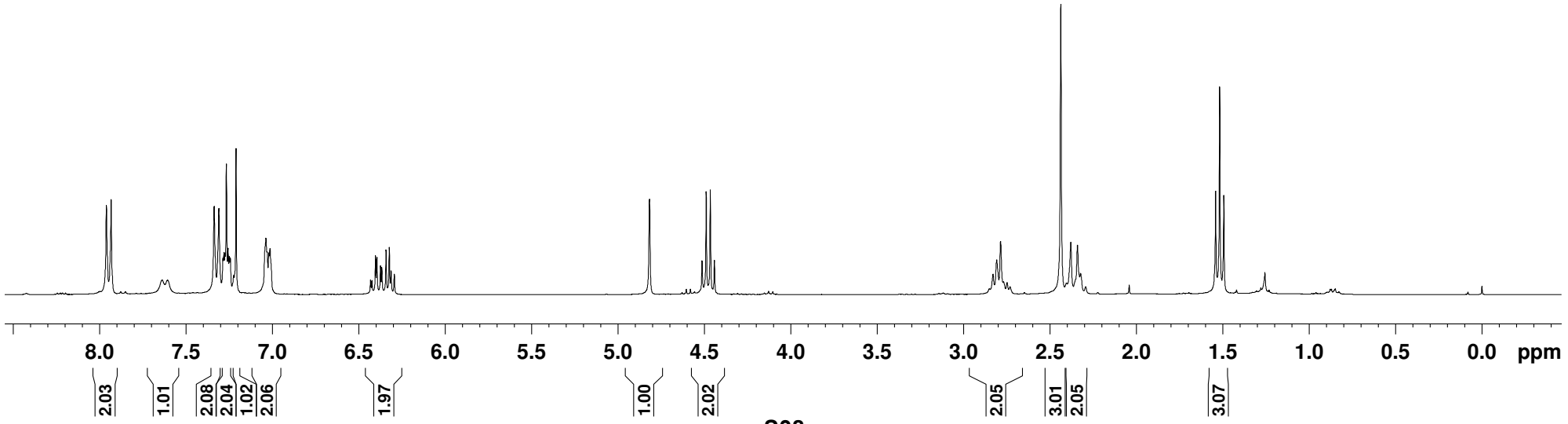
3ak

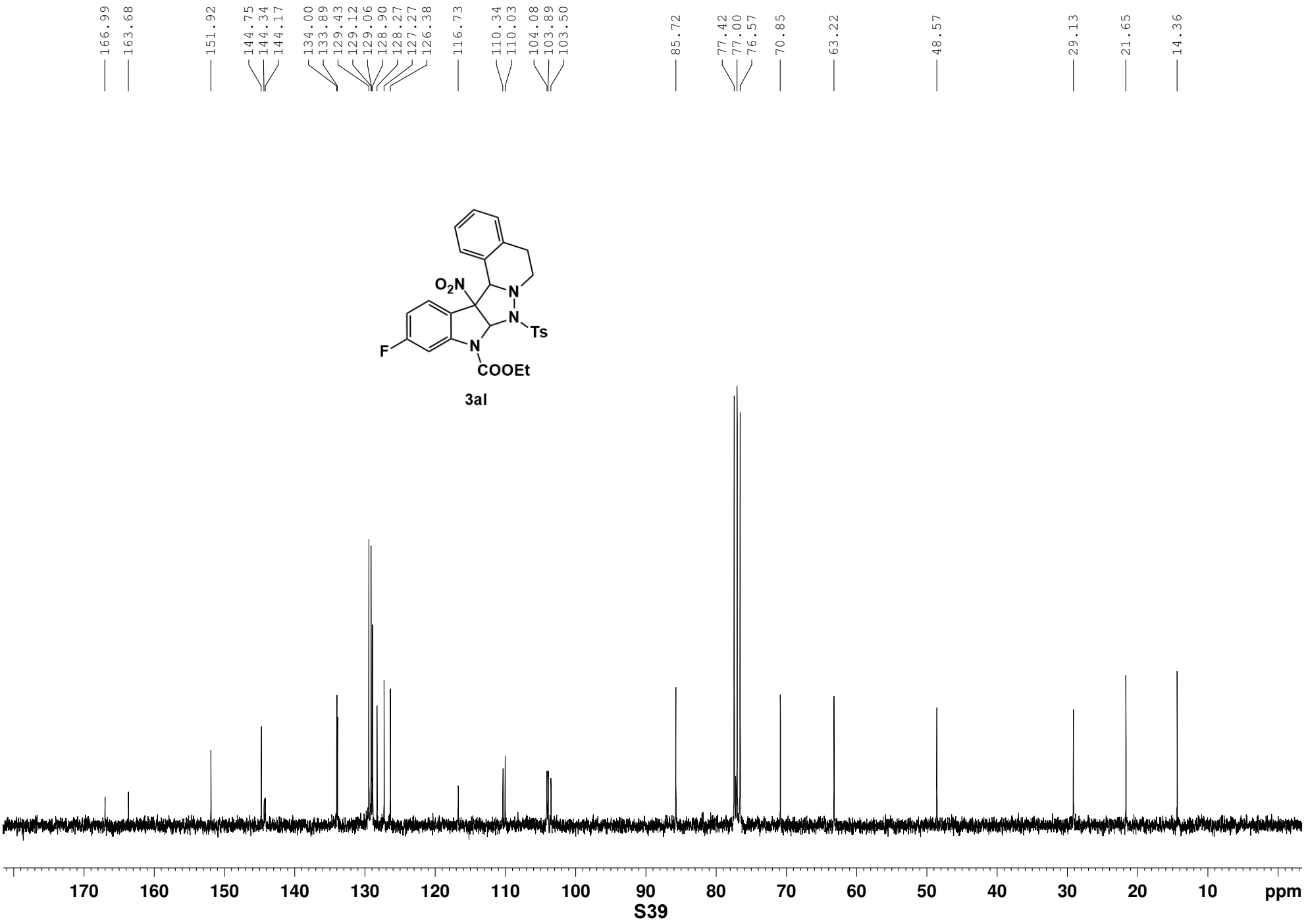

150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 ppm

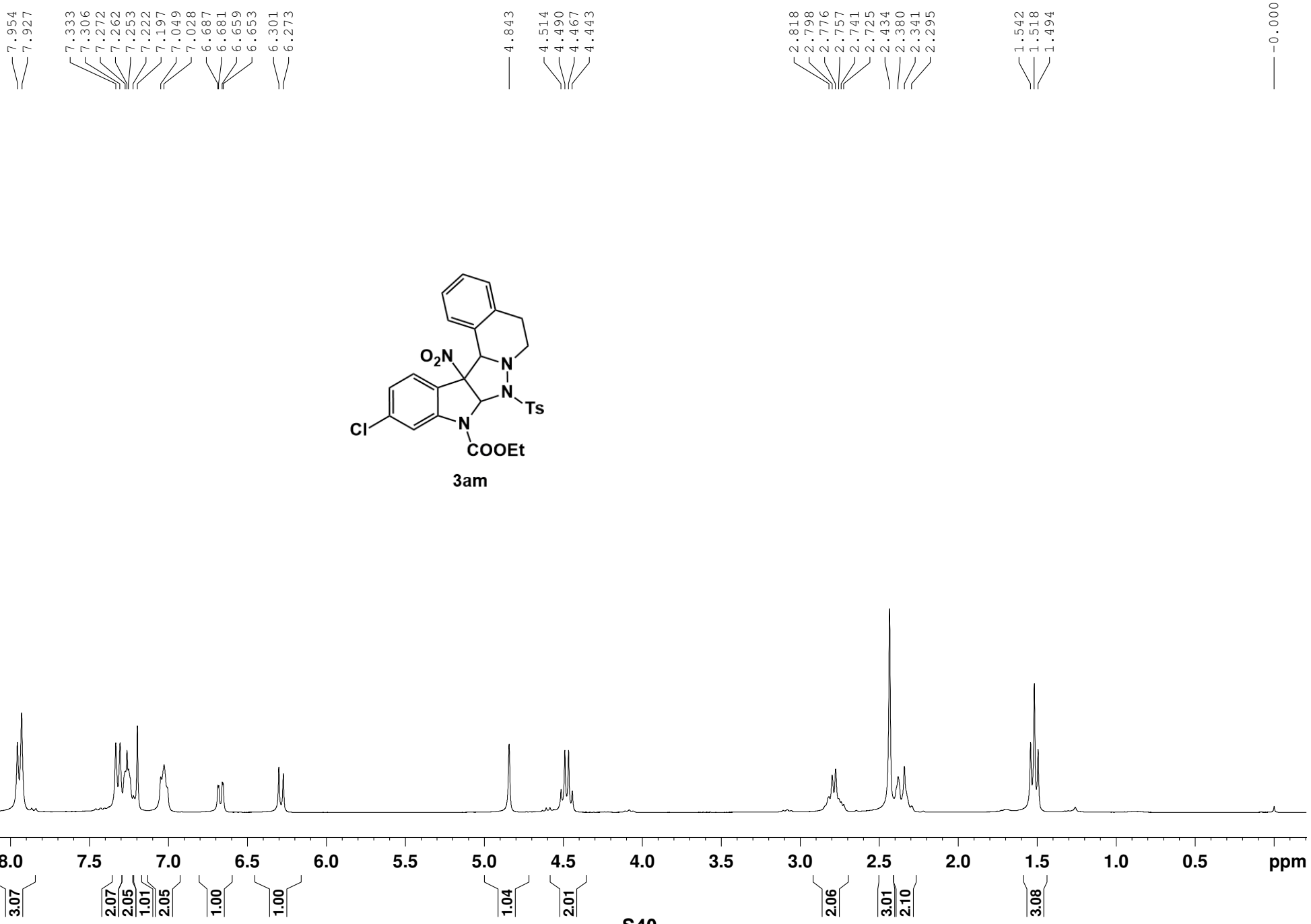

7.962
7.934
7.639
7.608
7.338
7.311
7.287
7.281
7.274
7.267
7.257
7.250
7.244
7.211
7.038
7.031
7.021
7.015
6.433
6.425
6.404
6.396
6.375
6.367
6.343
6.324
6.314
6.295
4.818
4.514
4.490
4.466
4.442
2.830
2.808
2.786
2.769
2.749
2.731
2.438
2.405
2.380
2.341
2.323
2.293
1.542
1.518
1.494
-0.000

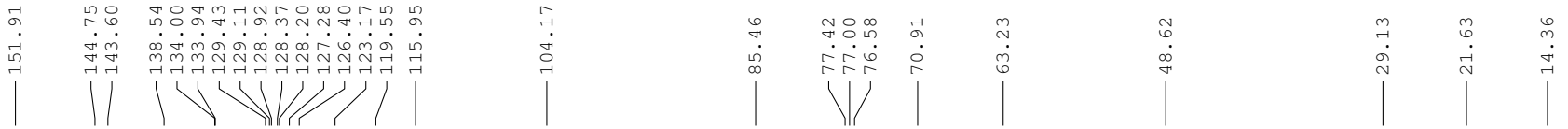

O2N
N
N
Ts
F
N
COOEt

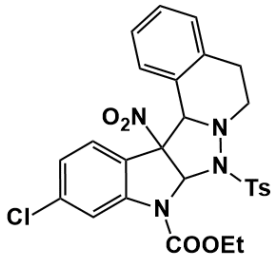
3al


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.03
1.01
2.08
2.04
1.02
2.06
1.97
1.00
2.02
2.05
3.01
2.05
3.07

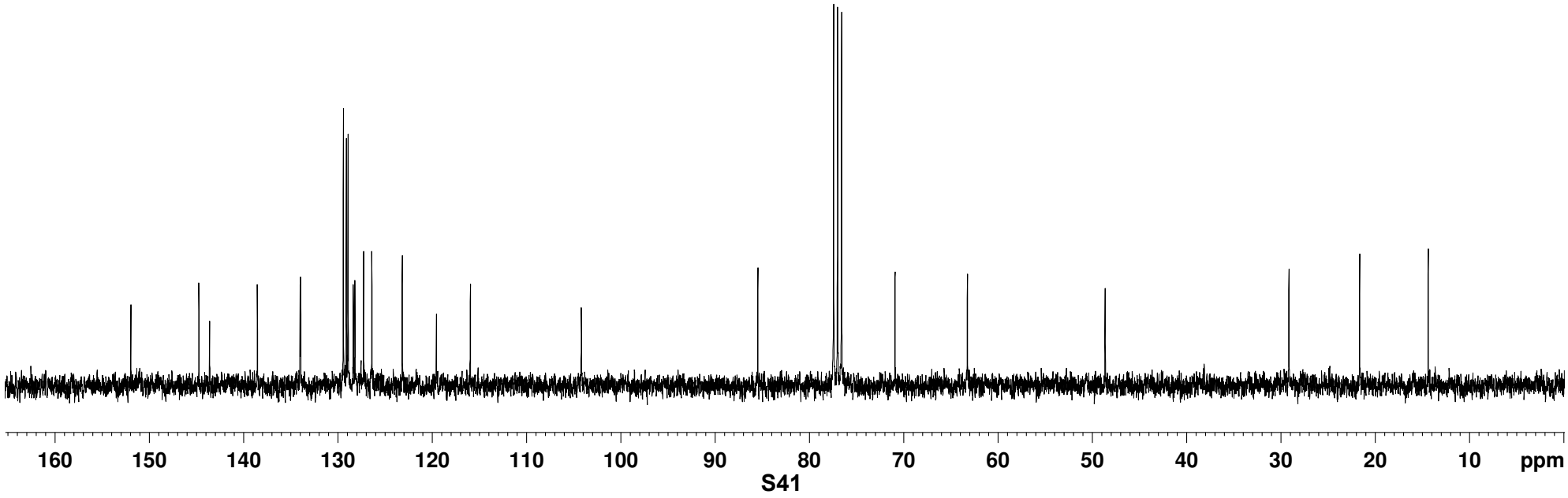

166.99
163.68
151.92
144.75
144.34
144.17
134.00
133.89
129.43
129.12
129.06
128.90
128.27
127.27
126.38
116.73
110.34
110.03
104.08
103.89
103.50
85.72
77.42
77.00
76.57
70.85
63.22
48.57
29.13
21.65
14.36
O2N
N
N
Ts
F
N
COOEt
3al
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.954
7.927
7.333
7.306
7.272
7.262
7.253
7.222
7.197
7.049
7.028
6.687
6.681
6.659
6.653
6.301
6.273
4.843
4.514
4.490
4.467
4.443
2.818
2.798
2.776
2.757
2.741
2.725
2.434
2.380
2.341
2.295
1.542
1.518
1.494
0.000
O2N
N
N
Ts
Cl
N
COOEt
3am
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
3.07
2.07
2.05
1.01
2.05
1.00
1.00
1.04
2.01
2.06
3.01
2.10
3.08


151.91
144.75
143.60
138.54
134.00
133.94
129.43
129.11
128.92
128.37
128.20
127.28
126.40
123.17
119.55
115.95
104.17
85.46
77.42
77.00
76.58
70.91
63.23
48.62
29.13
21.63
14.36


O2N
N
N
Ts
Cl
N
COOEt

3am


160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

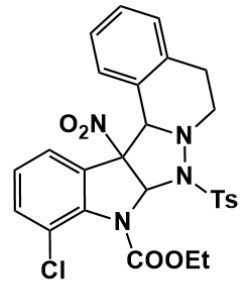
8.008
7.981
7.398
7.372
7.345
7.319
7.295
7.265
7.243
7.218
7.193
7.183
7.150
7.130
7.070
7.058
7.044
6.898
6.872
6.774
6.748
6.721
6.092
6.067

4.700
4.423
4.413
4.400
4.390
4.376
4.366
4.353
4.343

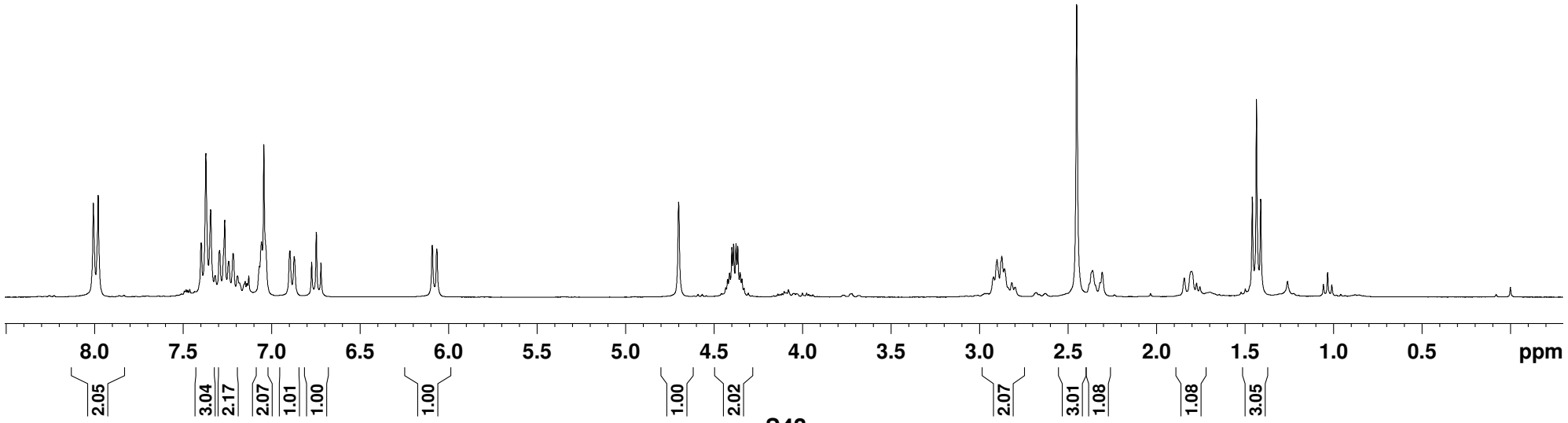
2.921
2.901
2.873
2.859
2.817
2.799
2.451
2.362
2.319
2.307

1.843
1.806
1.801
1.774
1.754
1.458
1.435
1.411

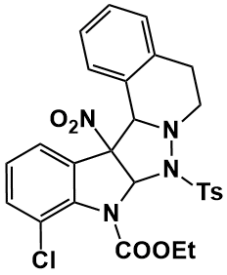
0.000



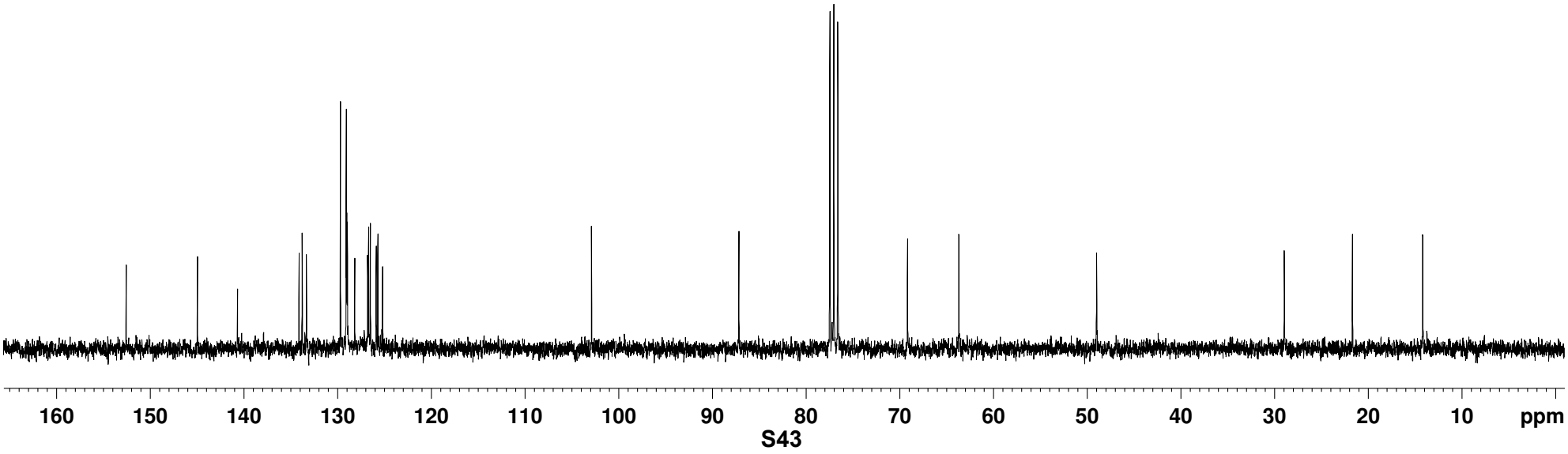
3an

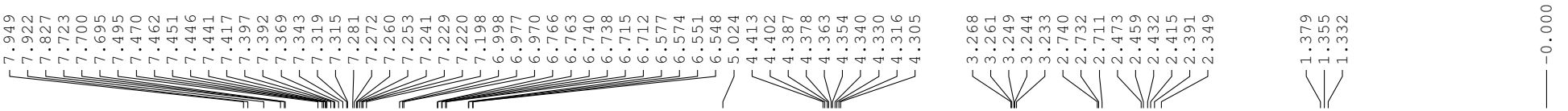


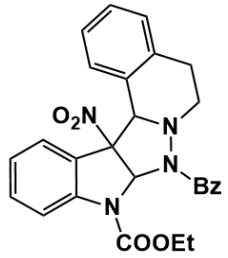
152.52
144.92
140.64
134.08
133.74
133.29
129.65
129.04
128.98
128.92
128.14
126.75
126.66
126.46
125.84
125.66
125.16
102.86
87.13
77.42
77.00
76.57
69.14
63.66
48.95
28.92
21.65
14.15



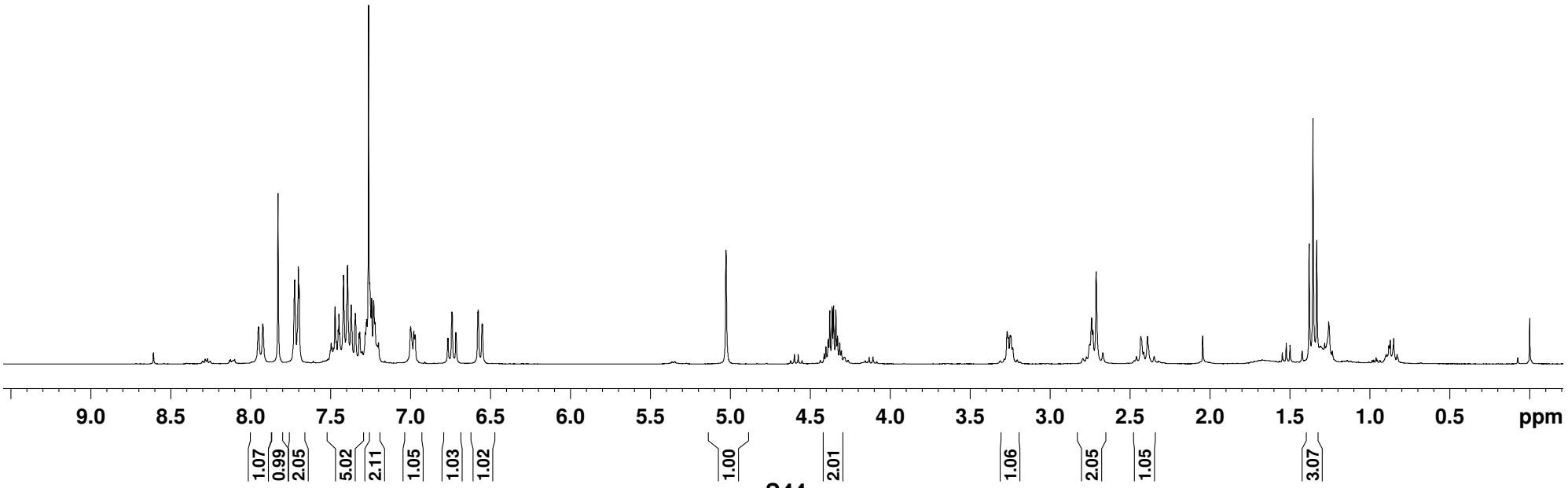
3an

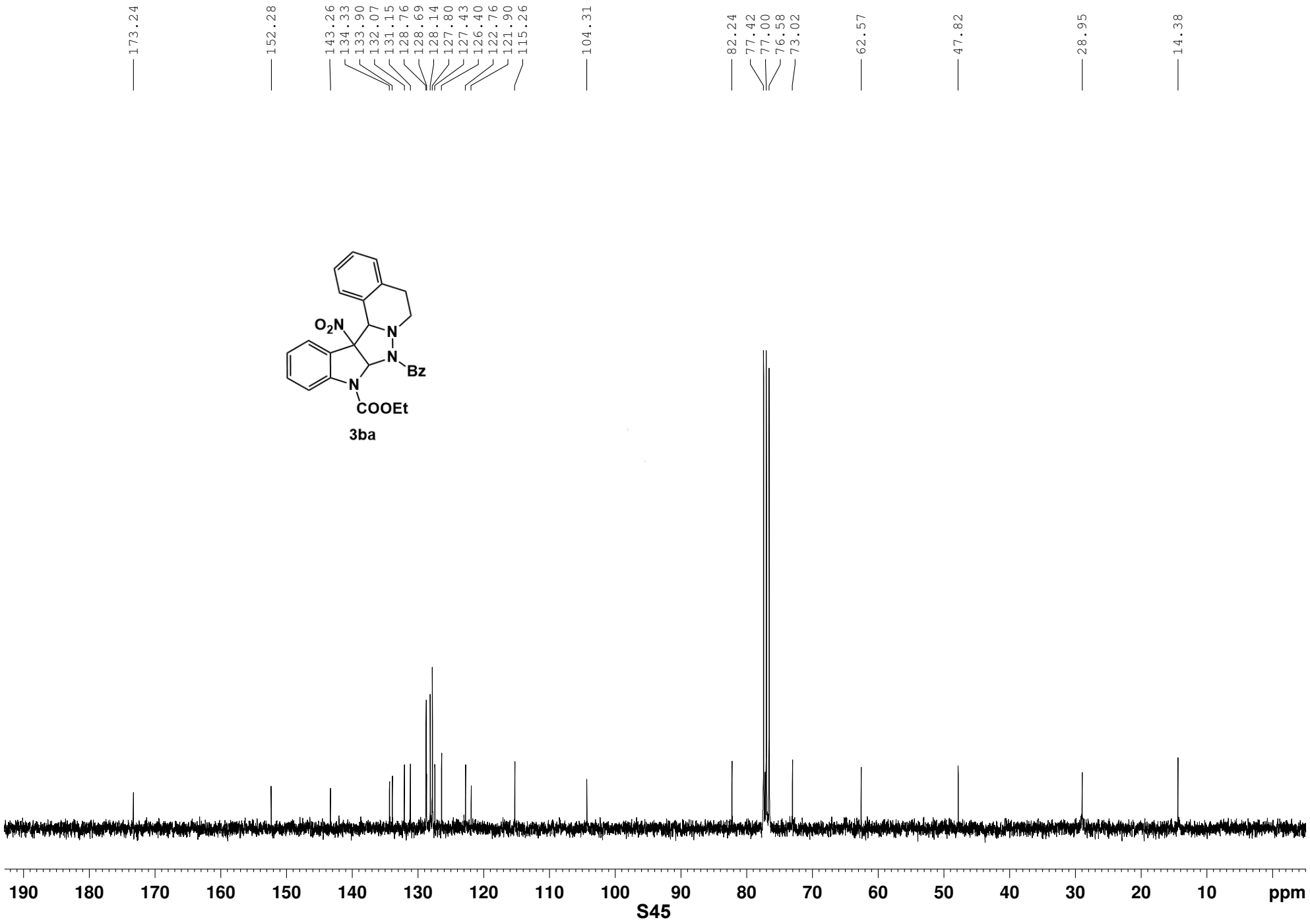


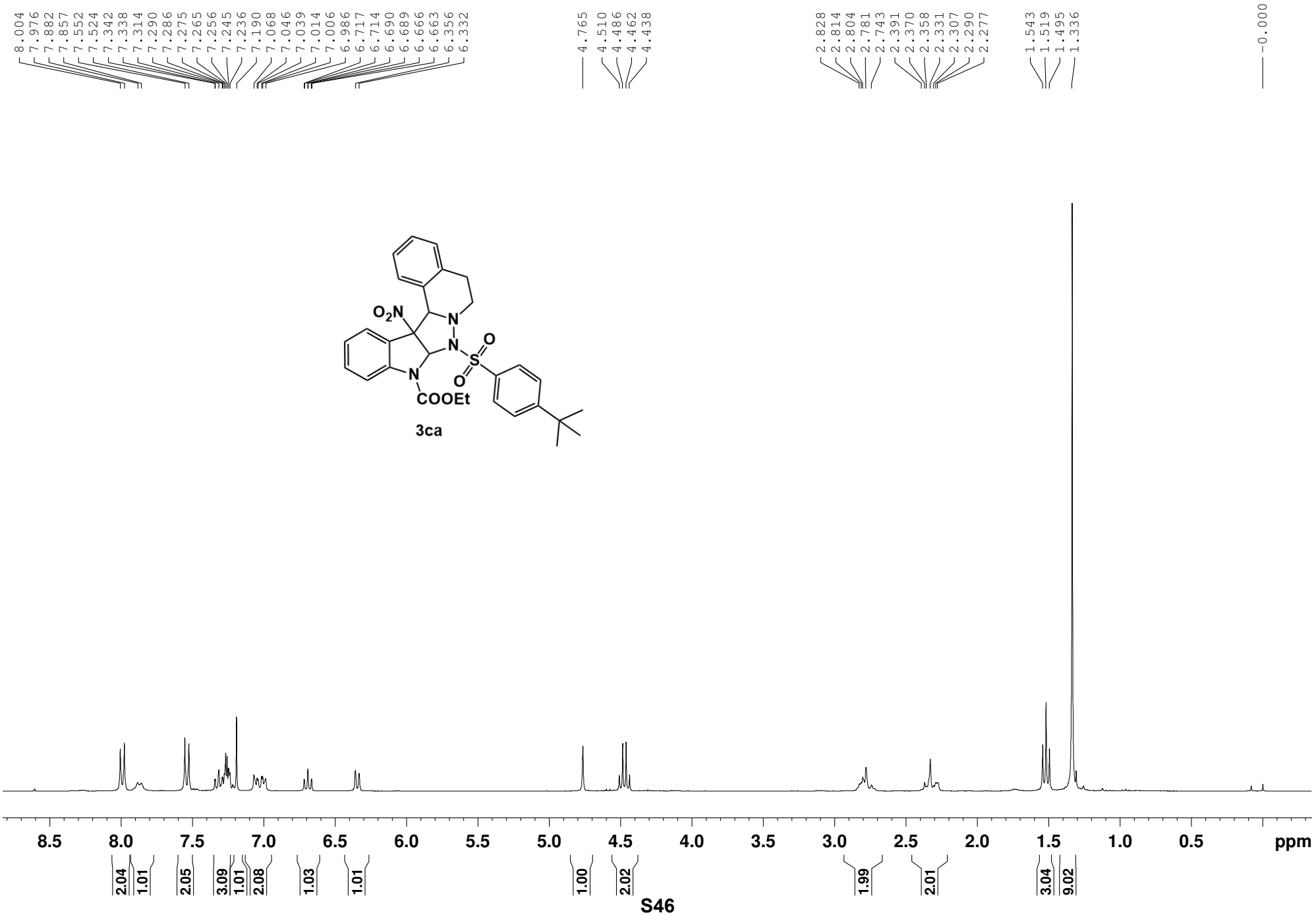

7.949
7.922
7.827
7.723
7.700
7.695
7.495
7.470
7.462
7.451
7.446
7.441
7.417
7.397
7.392
7.369
7.343
7.319
7.315
7.281
7.272
7.260
7.253
7.241
7.229
7.220
7.198
6.998
6.977
6.970
6.766
6.763
6.740
6.738
6.715
6.712
6.577
6.574
6.551
6.548
5.024
4.413
4.402
4.387
4.378
4.363
4.354
4.340
4.330
4.316
4.305
3.268
3.261
3.249
3.244
3.233
2.740
2.732
2.711
2.473
2.459
2.432
2.415
2.391
2.349
1.379
1.355
1.332
0.000


O2N
N
N
Bz
N
COOEt

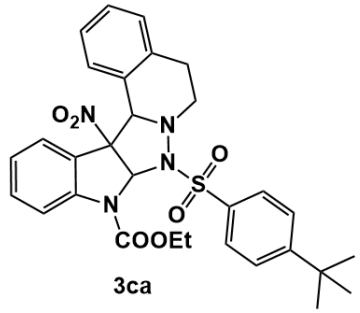
3ba


9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.07
0.99
2.05
5.02
2.11
1.05
1.03
1.02
1.00
2.01
1.06
2.05
1.05
3.07

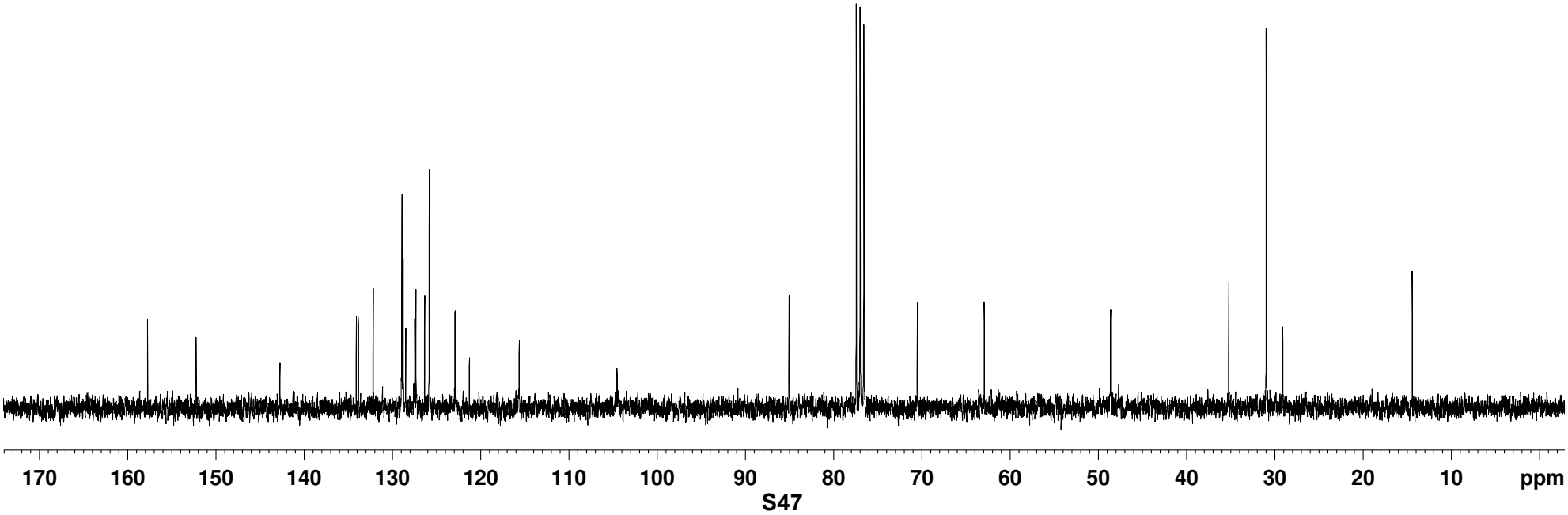

173.24
152.28
143.26
134.33
133.90
132.07
131.15
128.76
128.69
128.14
127.80
127.43
126.40
122.76
121.90
115.26
104.31
82.24
77.42
77.00
76.58
73.02
62.57
47.82
28.95
14.38
O2N
N
N
Bz
N
COOEt
3ba
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

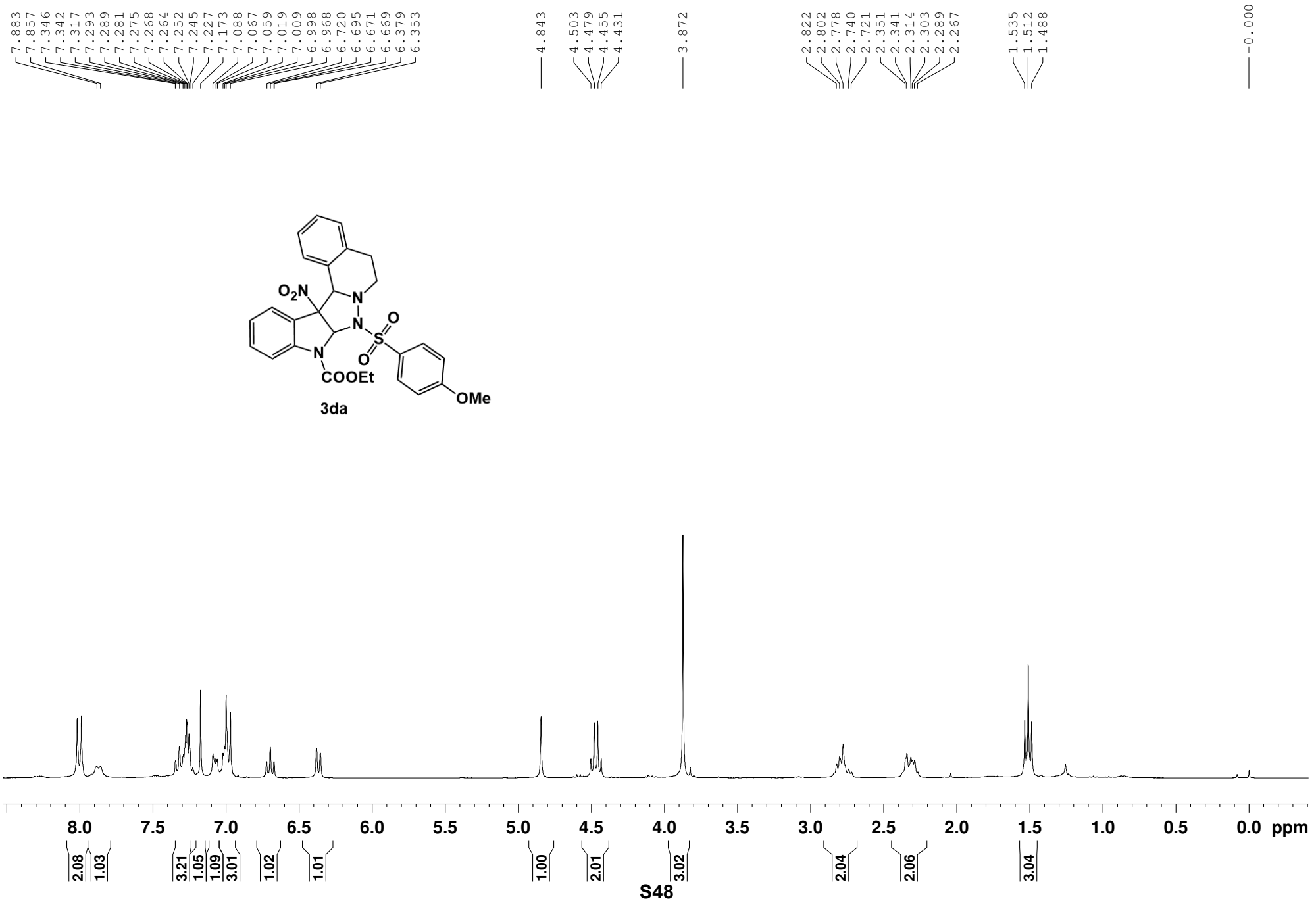

8.004
7.976
7.882
7.857
7.552
7.524
7.342
7.338
7.314
7.290
7.286
7.275
7.265
7.256
7.245
7.236
7.190
7.068
7.046
7.039
7.014
7.006
6.986
6.717
6.714
6.690
6.689
6.666
6.663
6.356
6.332
4.765
4.510
4.486
4.462
4.438
2.828
2.814
2.804
2.781
2.743
2.391
2.370
2.358
2.331
2.307
2.290
2.277
1.543
1.519
1.495
1.336
0.000
O2N
N
N
S
O
O
N
COOEt
3ca
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.04
1.01
2.05
3.09
1.01
2.08
1.03
1.01
1.00
2.02
1.99
2.01
3.04
9.02

157.70
152.21
142.70
134.05
133.82
132.13
128.87
128.75
128.44
127.43
127.29
126.30
125.77
122.86
121.23
115.59
104.55
85.05
77.42
77.00
76.57
70.51
62.92
48.61
35.21
30.97
29.10
14.42

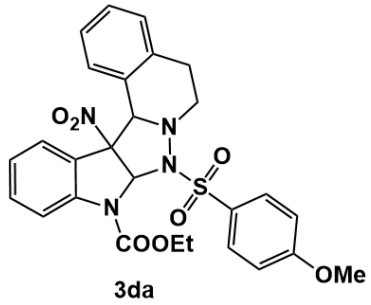


3ca

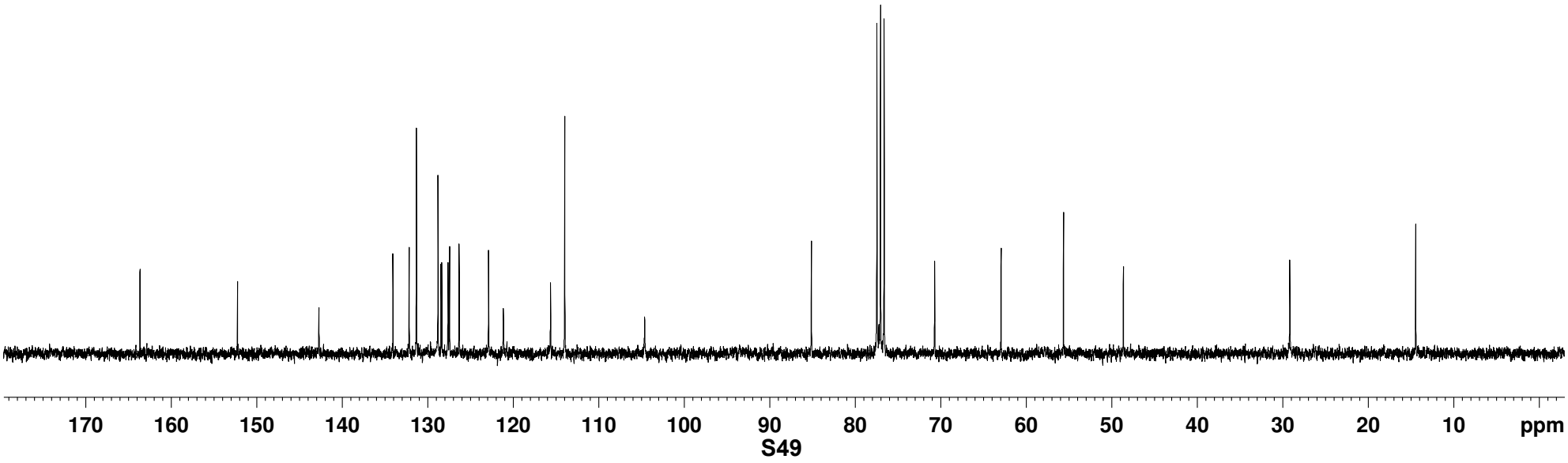


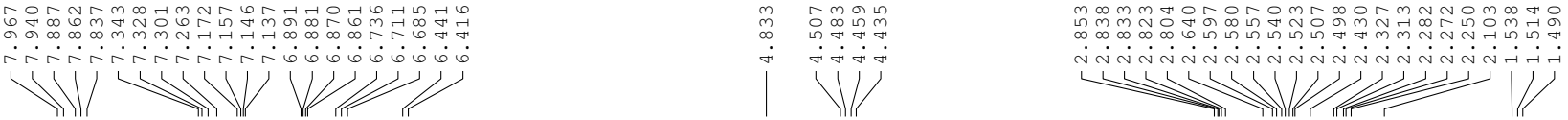

7.883
7.857
7.346
7.342
7.317
7.293
7.289
7.281
7.275
7.268
7.264
7.252
7.245
7.227
7.173
7.088
7.067
7.059
7.019
7.009
6.998
6.968
6.720
6.695
6.671
6.669
6.379
6.353
4.843
4.503
4.479
4.455
4.431
3.872
2.822
2.802
2.778
2.740
2.721
2.351
2.341
2.314
2.303
2.289
2.267
1.535
1.512
1.488
0.000
O2N
N
N
O
S
O
N
COOEt
OMe
3da
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.08
1.03
3.21
1.05
1.09
3.01
1.02
1.01
1.00
2.01
3.02
2.04
2.06
3.04

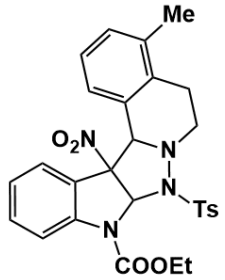

163.61
152.20
142.68
134.03
132.13
131.28
128.76
128.41
128.31
127.58
127.40
126.28
122.85
121.11
115.59
113.93
104.59
85.08
77.43
77.00
76.58
70.67
62.90
55.60
48.60
29.13
14.40


O2N
N
N
O
S
O
N
COOEt
OMe

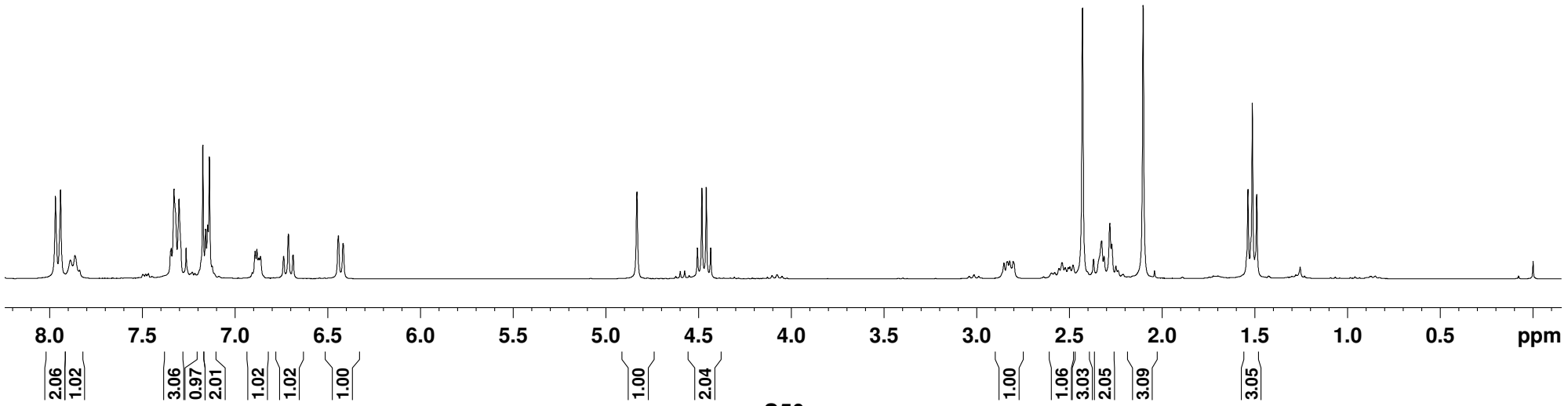
3da

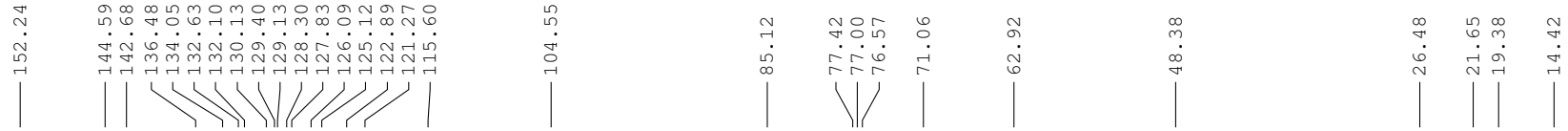

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

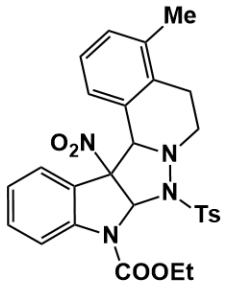

7.967
7.940
7.887
7.862
7.837
7.343
7.328
7.301
7.263
7.172
7.157
7.146
7.137
6.891
6.881
6.870
6.861
6.736
6.711
6.685
6.441
6.416
4.833
4.507
4.483
4.459
4.435
2.853
2.838
2.833
2.823
2.804
2.640
2.597
2.580
2.557
2.540
2.523
2.507
2.498
2.430
2.327
2.313
2.282
2.272
2.250
2.103
1.538
1.514
1.490


Me
O_2N
N
N
Ts
N
COOEt

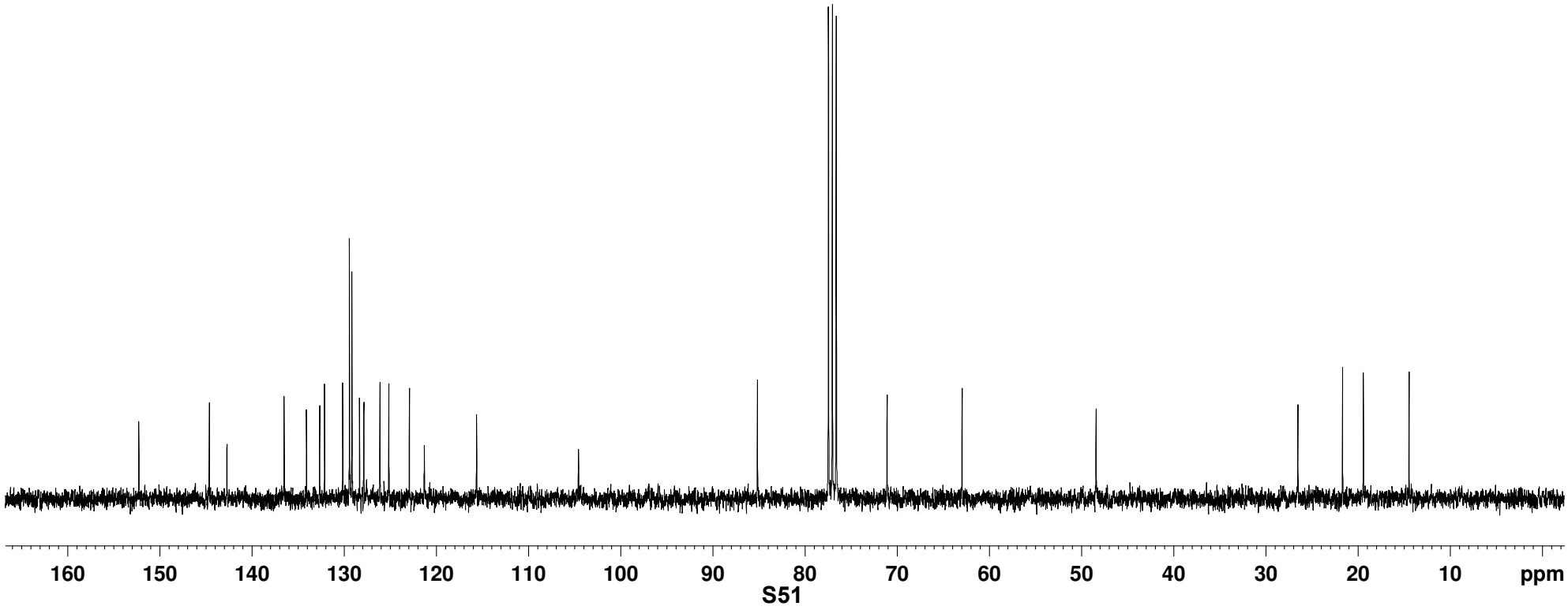
3ea

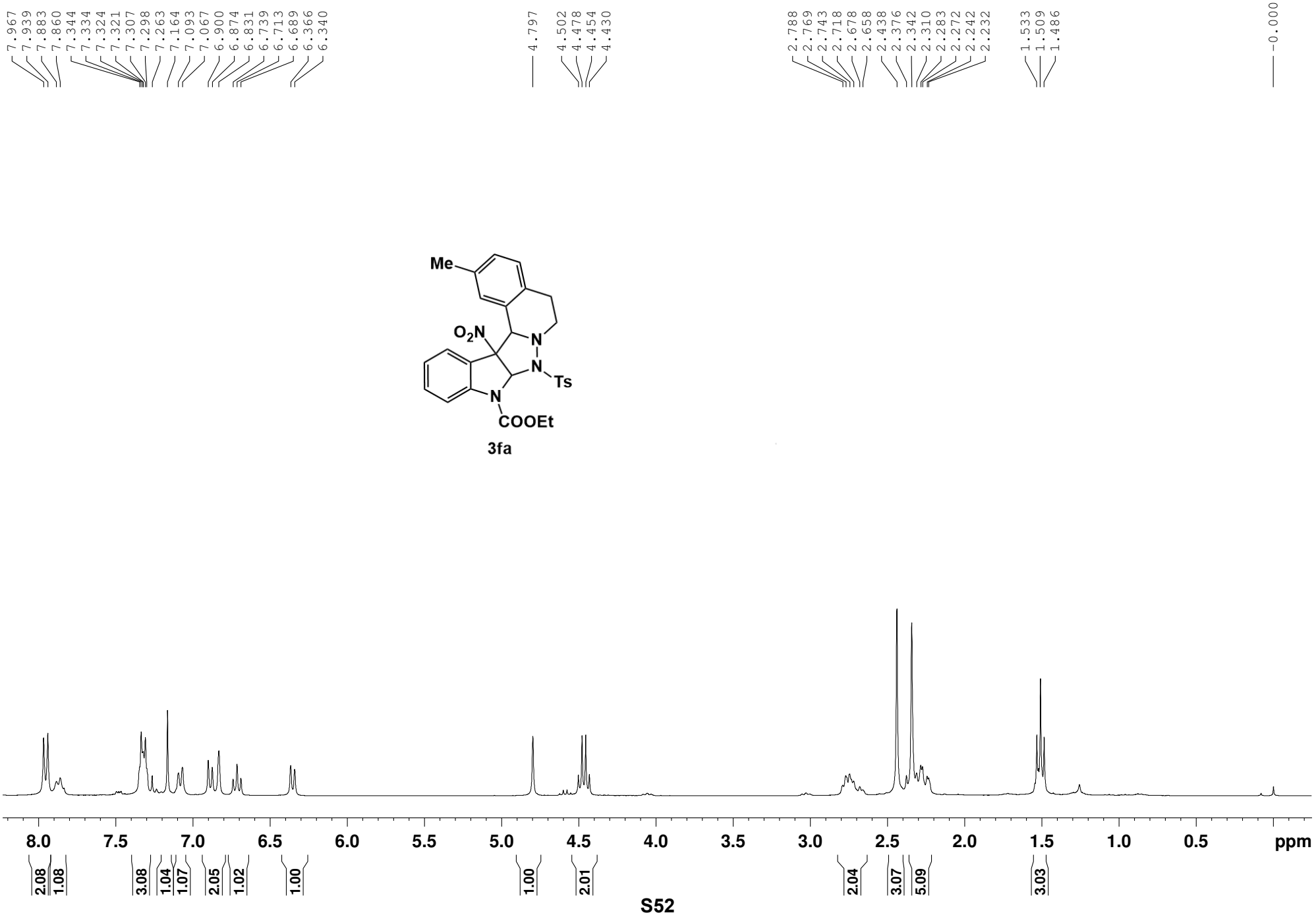

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.06
1.02
3.06
0.97
2.01
1.02
1.02
1.00
1.00
2.04
1.00
1.06
3.03
2.05
3.09
3.05


152.24
144.59
142.68
136.48
134.05
132.63
132.10
130.13
129.40
129.13
128.30
127.83
126.09
125.12
122.89
121.27
115.60
104.55
85.12
77.42
77.00
76.57
71.06
62.92
48.38
26.48
21.65
19.38
14.42

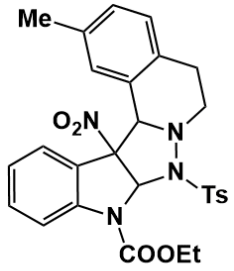

Me
O2N
N
N
Ts
N
COOEt

3ea

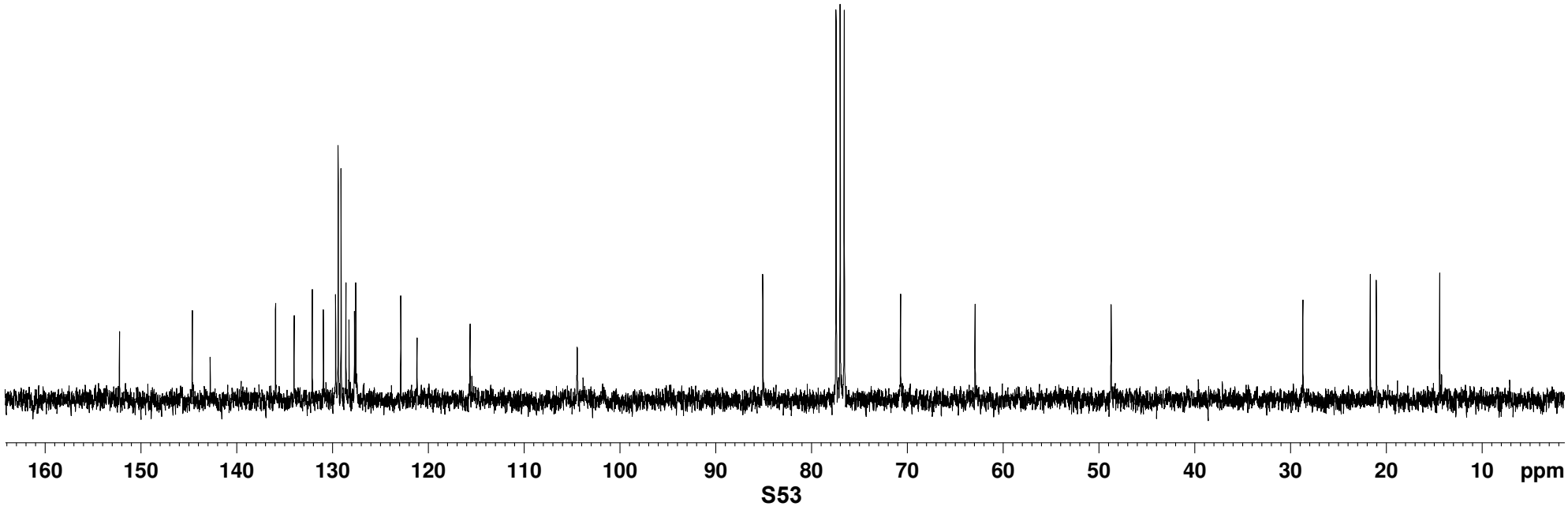

160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

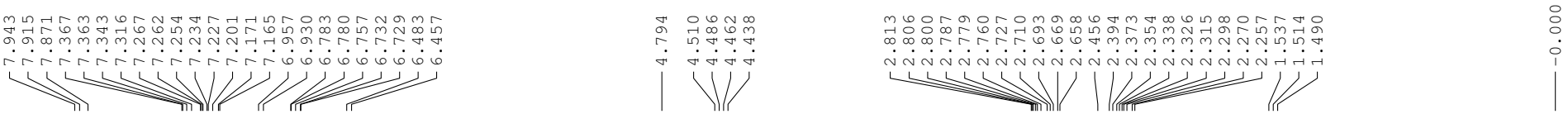

7.967
7.939
7.883
7.860
7.344
7.334
7.324
7.321
7.307
7.298
7.263
7.164
7.093
7.067
6.900
6.874
6.831
6.739
6.713
6.689
6.366
6.340
4.797
4.502
4.478
4.454
4.430
2.788
2.769
2.743
2.718
2.678
2.658
2.438
2.376
2.342
2.310
2.283
2.272
2.242
2.232
1.533
1.509
1.486
-0.000
Me
O2N
N
N
Ts
N
COOEt
3fa
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.08
1.08
3.08
1.04
1.07
2.05
1.02
1.00
1.00
2.01
2.04
3.07
5.09
3.03

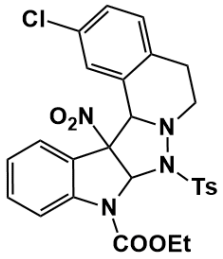
152.20
144.59
142.73
135.95
134.01
132.11
130.95
129.67
129.41
129.11
128.60
128.28
127.71
127.58
122.88
121.17
115.64
104.45
85.07
77.42
77.00
76.58
70.69
62.91
48.71
28.70
21.65
21.01
14.40



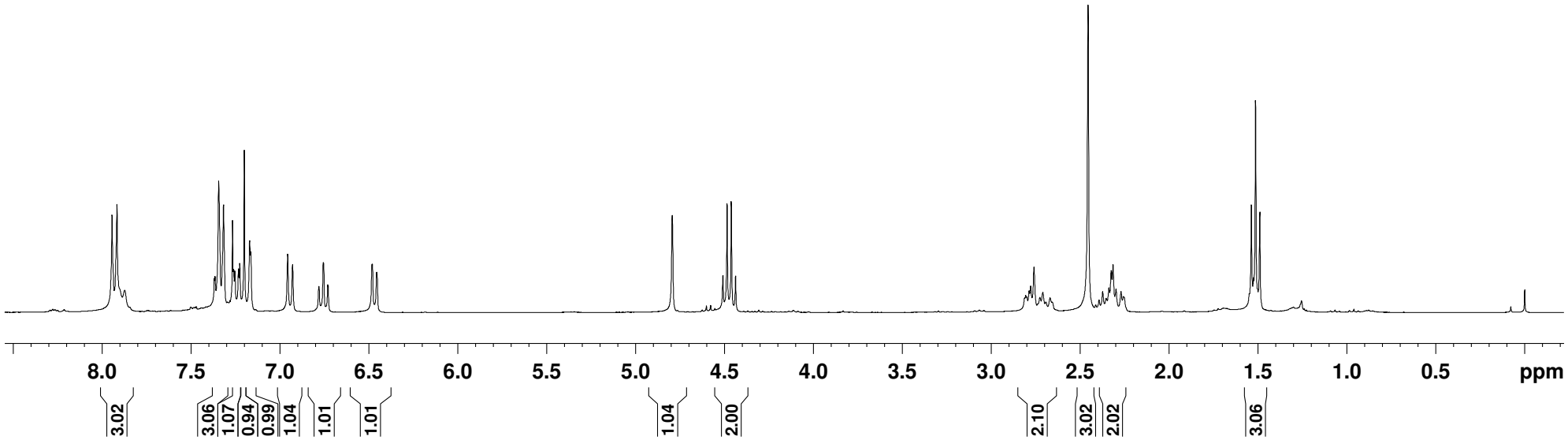
3fa

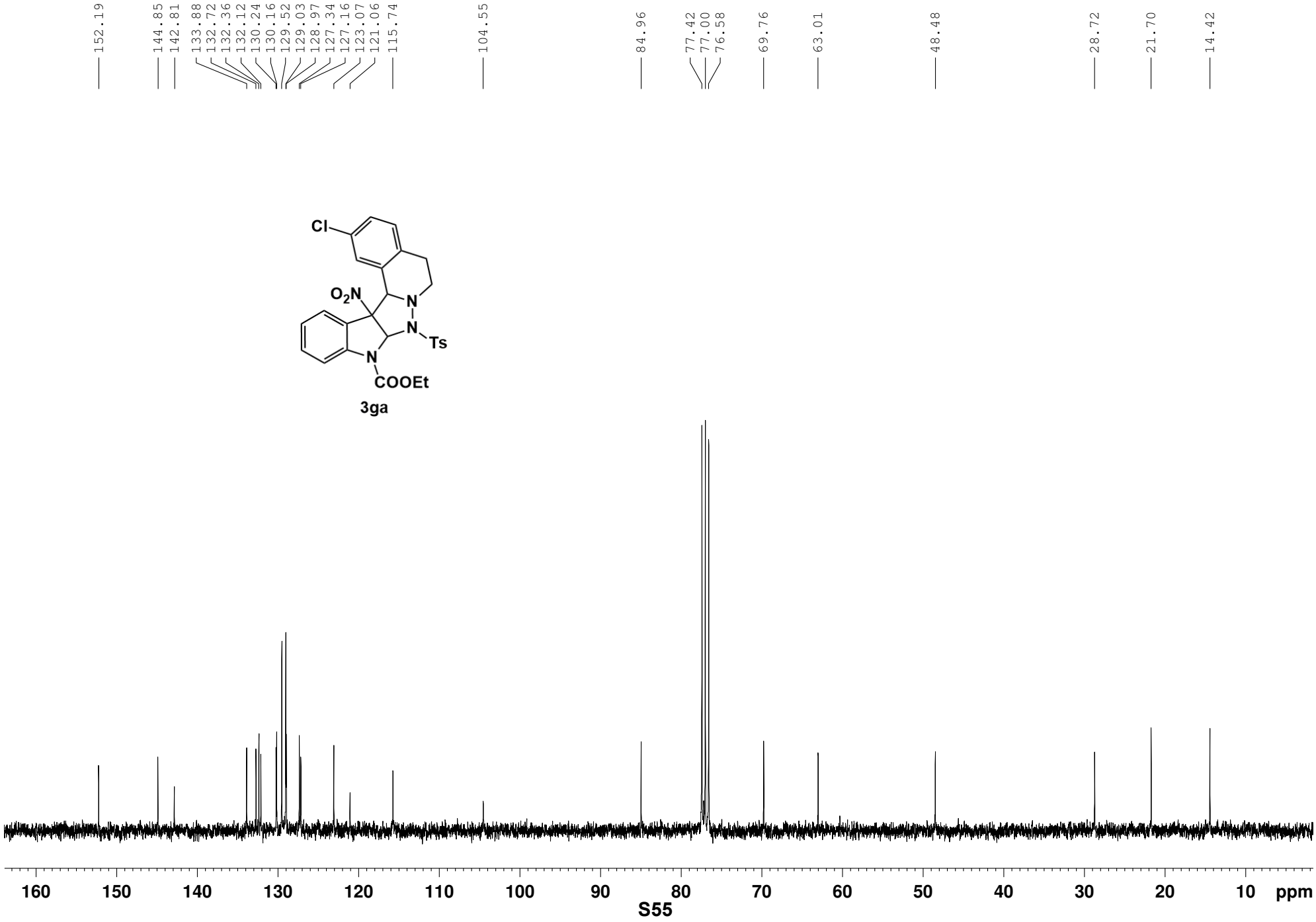


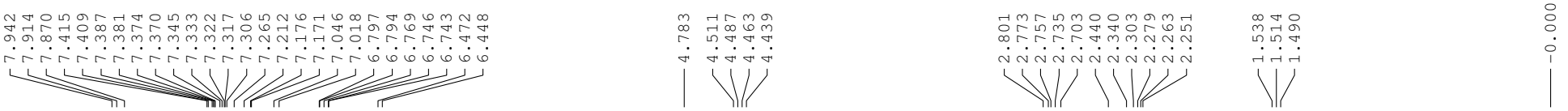

7.943
7.915
7.871
7.367
7.363
7.343
7.316
7.267
7.262
7.254
7.234
7.227
7.201
7.171
7.165
6.957
6.930
6.783
6.780
6.757
6.732
6.729
6.483
6.457
4.794
4.510
4.486
4.462
4.438
2.813
2.806
2.800
2.787
2.779
2.760
2.727
2.710
2.693
2.669
2.658
2.456
2.394
2.373
2.354
2.338
2.326
2.315
2.298
2.270
2.257
1.537
1.514
1.490
0.000

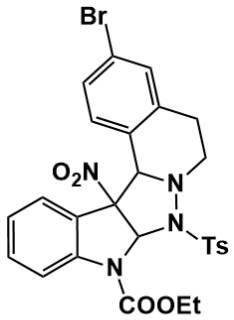

Cl
O2N
N
N
Ts
N
COOEt

3ga

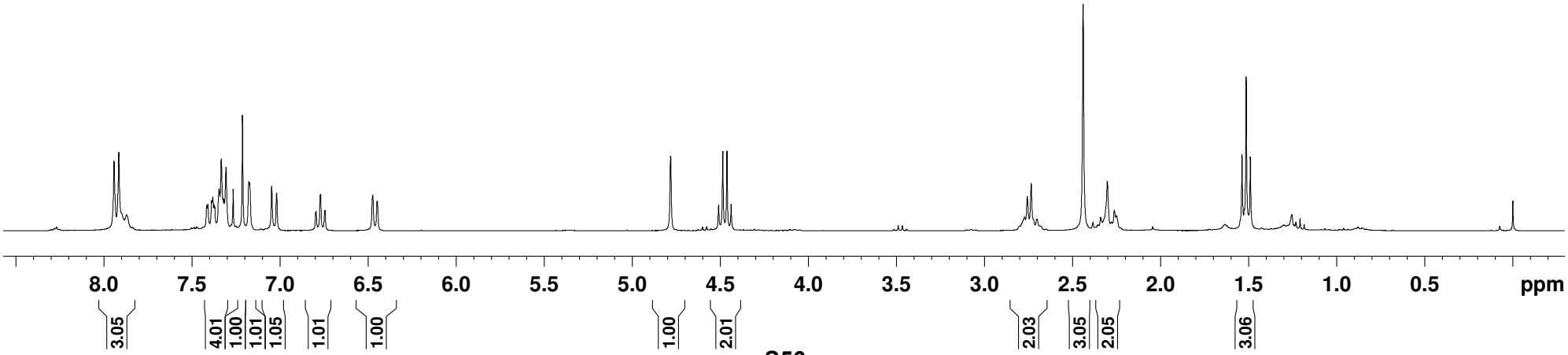

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
3.02
3.06
1.07
0.94
0.99
1.04
1.01
1.01
1.04
2.00
2.10
3.02
2.02
3.06

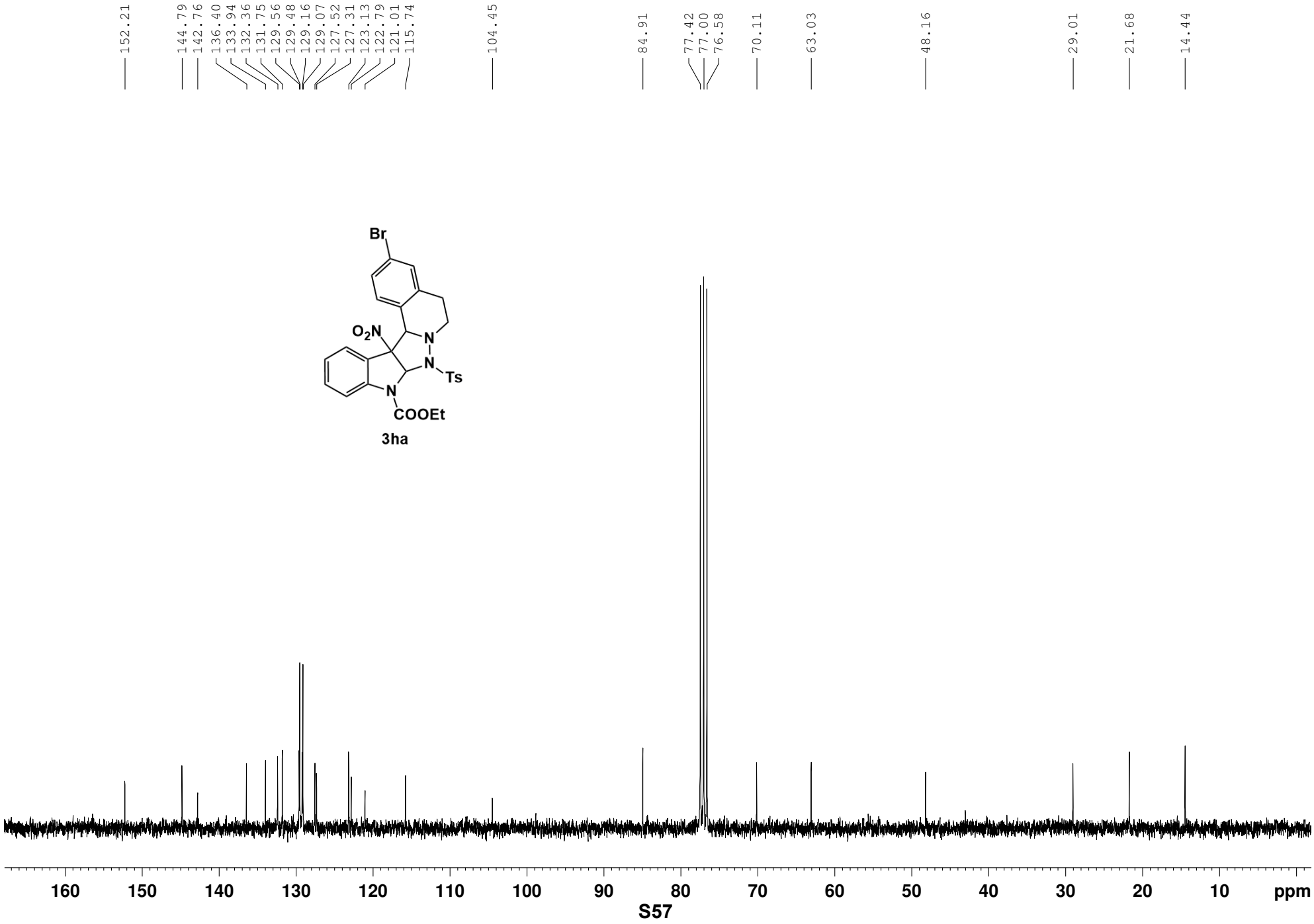

152.19
144.85
142.81
133.88
132.72
132.36
132.12
130.24
130.16
129.52
129.03
128.97
127.34
127.16
123.07
121.06
115.74
104.55
84.96
77.42
77.00
76.58
69.76
63.01
48.48
28.72
21.70
14.42
Cl
O2N
N
N
Ts
N
COOEt
3ga
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

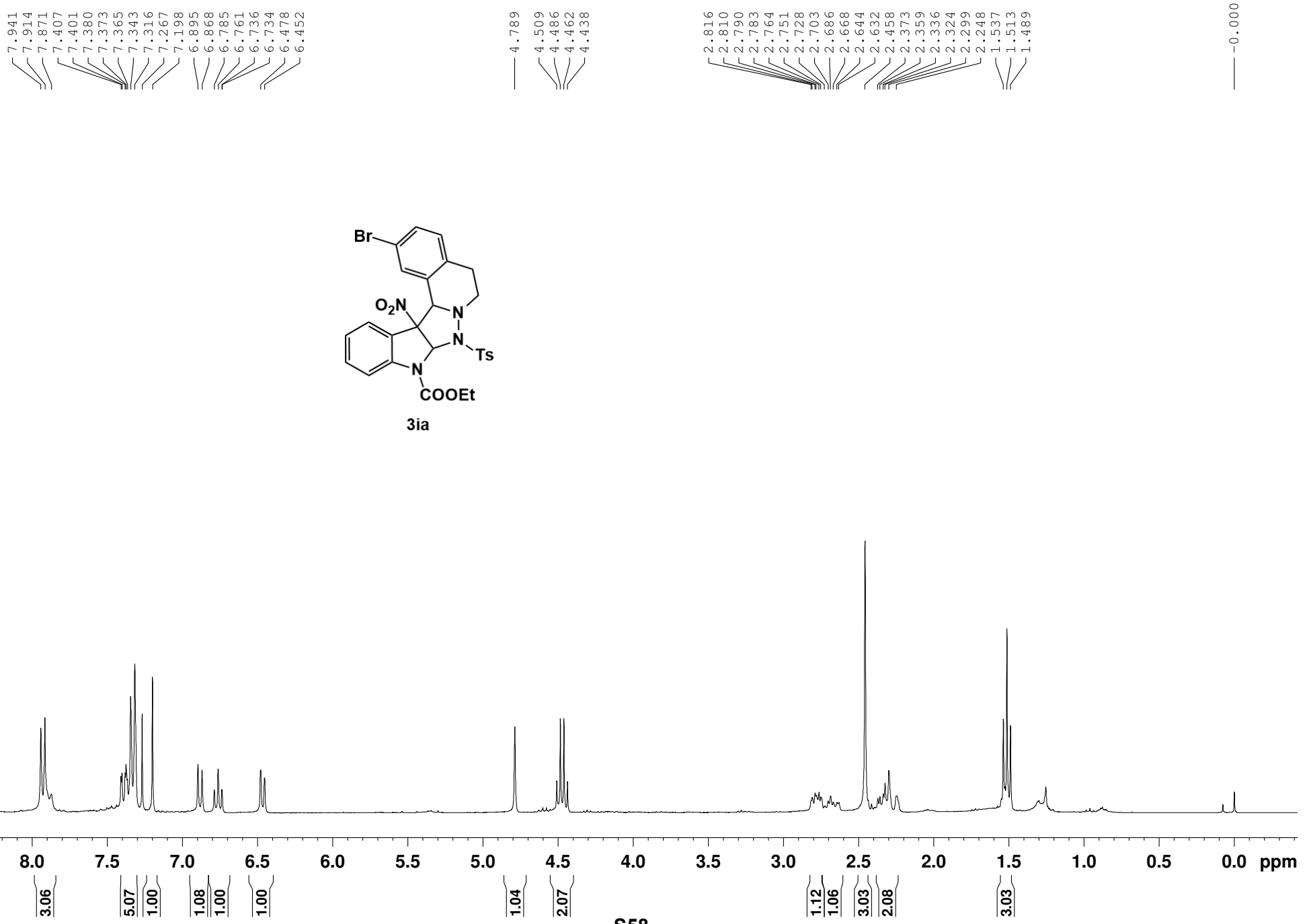

7.942
7.914
7.870
7.415
7.409
7.387
7.381
7.374
7.370
7.345
7.333
7.322
7.317
7.306
7.265
7.212
7.176
7.171
7.046
7.018
6.797
6.794
6.769
6.746
6.743
6.472
6.448
4.783
4.511
4.487
4.463
4.439
2.801
2.773
2.757
2.735
2.703
2.440
2.340
2.303
2.279
2.263
2.251
1.538
1.514
1.490
0.000

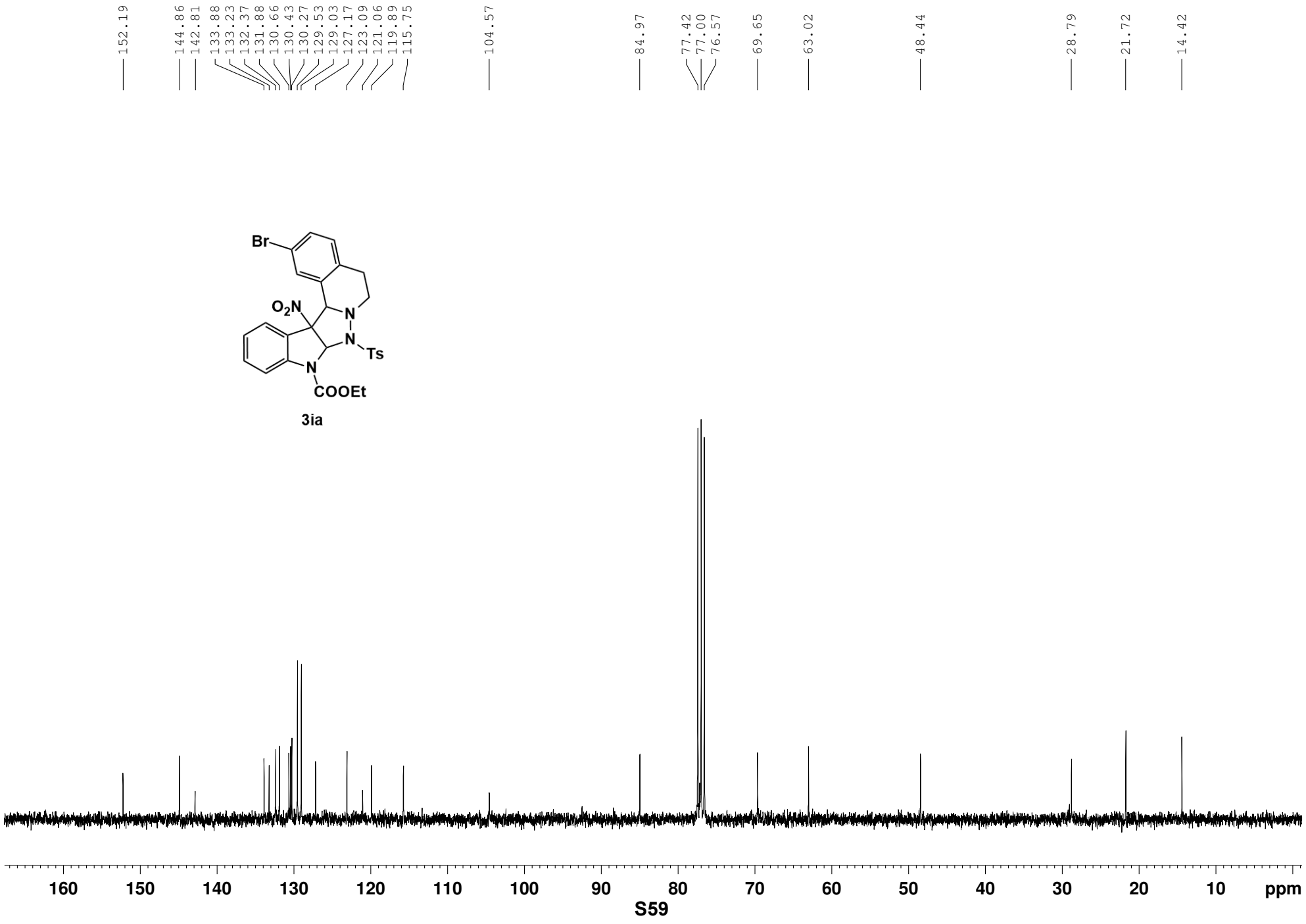

Br
O2N
N
N
Ts
N
COOEt

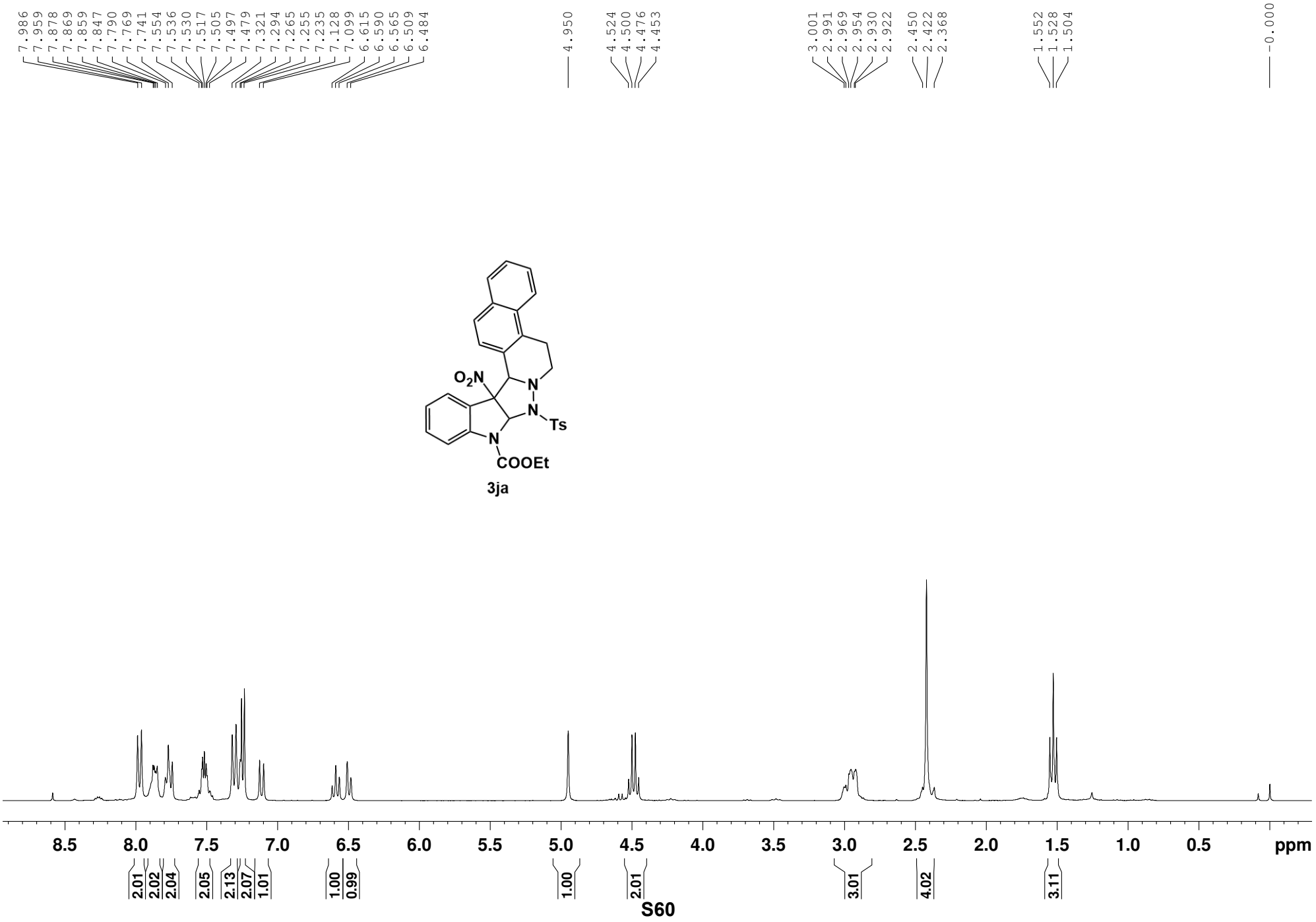
3ha

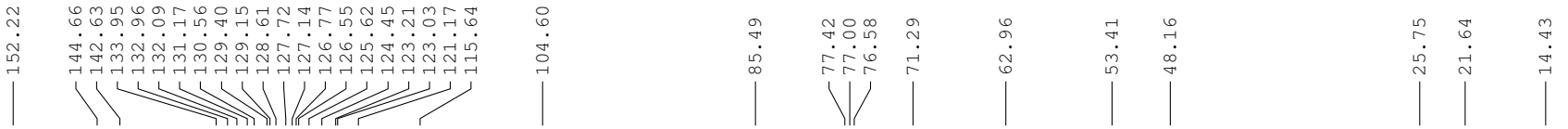

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
3.05
4.01
1.00
1.01
1.05
1.01
1.00
1.00
2.01
2.03
3.05
2.05
3.06

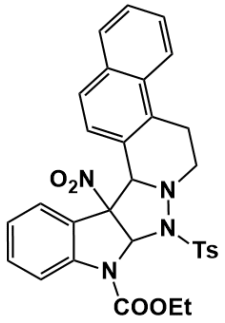

152.21
144.79
142.76
136.40
133.94
132.36
131.75
129.56
129.48
129.16
129.07
127.52
127.31
123.13
122.79
121.01
115.74
104.45
84.91
77.42
77.00
76.58
70.11
63.03
48.16
29.01
21.68
14.44
Br
O2N
N
N
Ts
N
COOEt
3ha
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.941
7.914
7.871
7.407
7.401
7.380
7.373
7.365
7.343
7.316
7.267
7.198
6.895
6.868
6.785
6.761
6.736
6.734
6.478
6.452
4.789
4.509
4.486
4.462
4.438
2.816
2.810
2.790
2.783
2.764
2.751
2.728
2.703
2.686
2.668
2.644
2.632
2.458
2.373
2.359
2.336
2.324
2.299
2.248
1.537
1.513
1.489
0.000
Br
O2N
N
N
Ts
N
COOEt
3ia
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
3.06
5.07
1.00
1.08
1.00
1.00
1.04
2.07
1.12
1.06
3.03
2.08
3.03

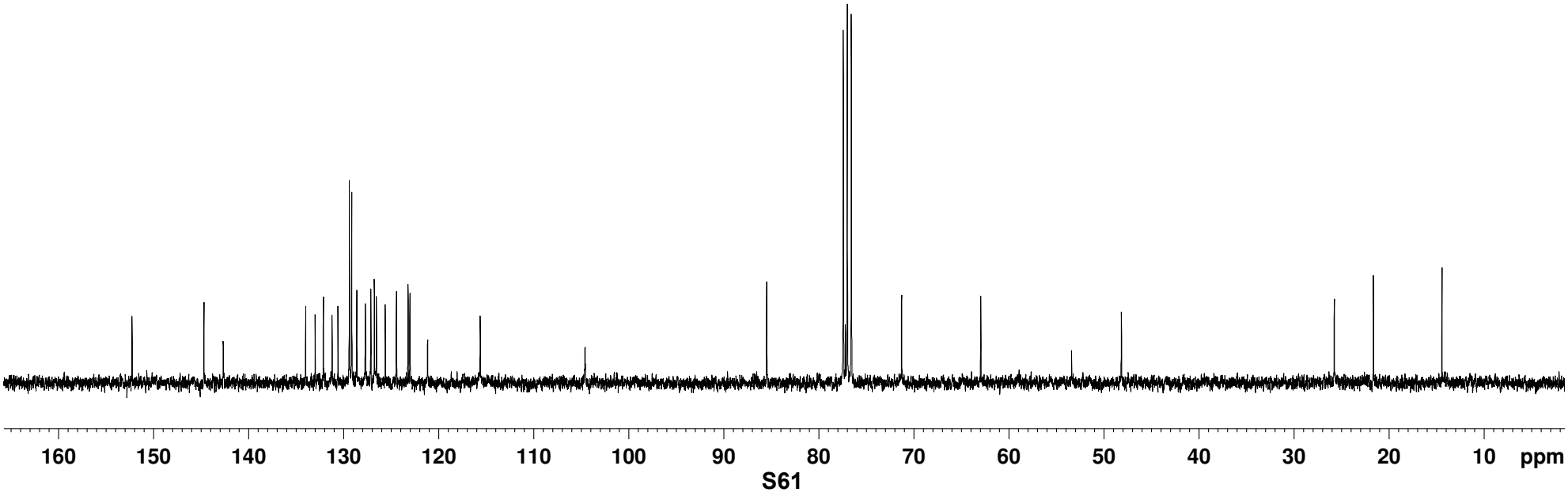

152.19
144.86
142.81
133.88
133.23
132.37
131.88
130.66
130.43
130.27
129.53
129.03
127.17
123.09
121.06
119.89
115.75
104.57
84.97
77.42
77.00
76.57
69.65
63.02
48.44
28.79
21.72
14.42
Br
O2N
N
N
Ts
N
COOEt
3ia
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

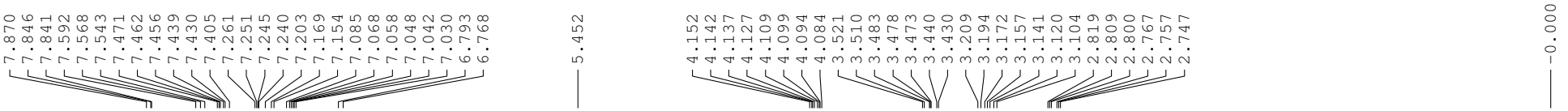

7.986
7.959
7.878
7.869
7.859
7.847
7.790
7.769
7.741
7.554
7.536
7.530
7.517
7.505
7.497
7.479
7.321
7.294
7.265
7.255
7.235
7.128
7.099
6.615
6.590
6.565
6.509
6.484
4.950
4.524
4.500
4.476
4.453
3.001
2.991
2.969
2.954
2.930
2.922
2.450
2.422
2.368
1.552
1.528
1.504
0.000
O2N
N
N
Ts
N
COOEt
3ja
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.01
2.02
2.04
2.05
2.13
2.07
1.01
1.00
0.99
1.00
2.01
3.01
4.02
3.11

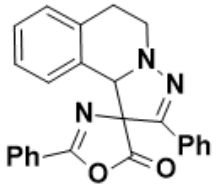

152.22
144.66
142.63
133.95
132.96
132.09
131.17
130.56
129.40
129.15
128.61
127.72
127.14
126.77
126.55
125.62
124.45
123.21
123.03
121.17
115.64
104.60
85.49
77.42
77.00
76.58
71.29
62.96
53.41
48.16
25.75
21.64
14.43


O2N
N
N
Ts
N
COOEt

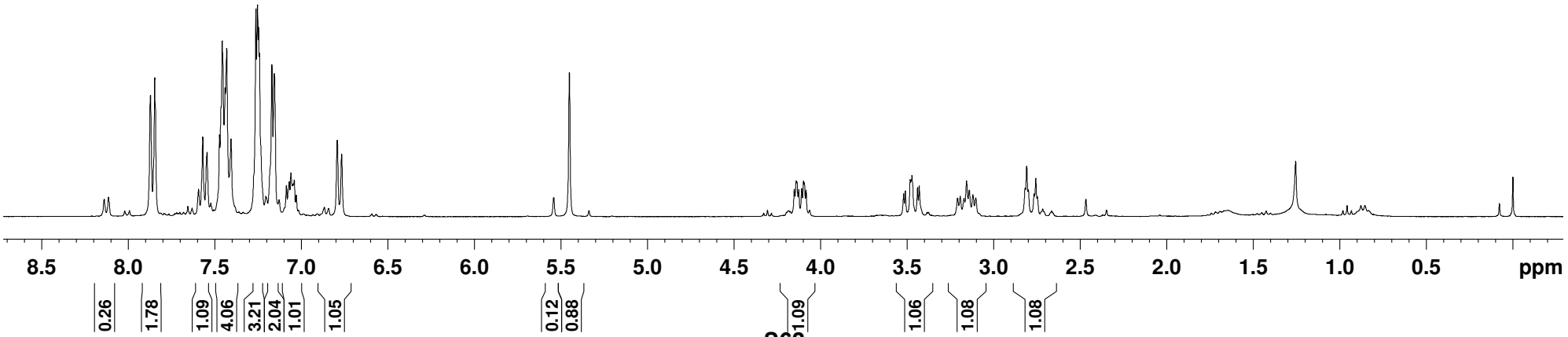
3ja


160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

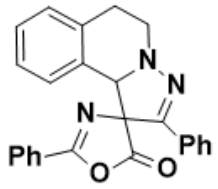

7.870
7.846
7.841
7.592
7.568
7.543
7.471
7.462
7.456
7.439
7.430
7.405
7.261
7.251
7.245
7.240
7.203
7.169
7.154
7.085
7.068
7.058
7.048
7.042
7.030
6.793
6.768
5.452
4.152
4.142
4.137
4.127
4.109
4.099
4.094
4.084
3.521
3.510
3.483
3.478
3.473
3.440
3.430
3.209
3.194
3.172
3.157
3.141
3.120
3.104
2.819
2.809
2.800
2.767
2.757
2.747
0.000


N
N
N
Ph
Ph
O
O

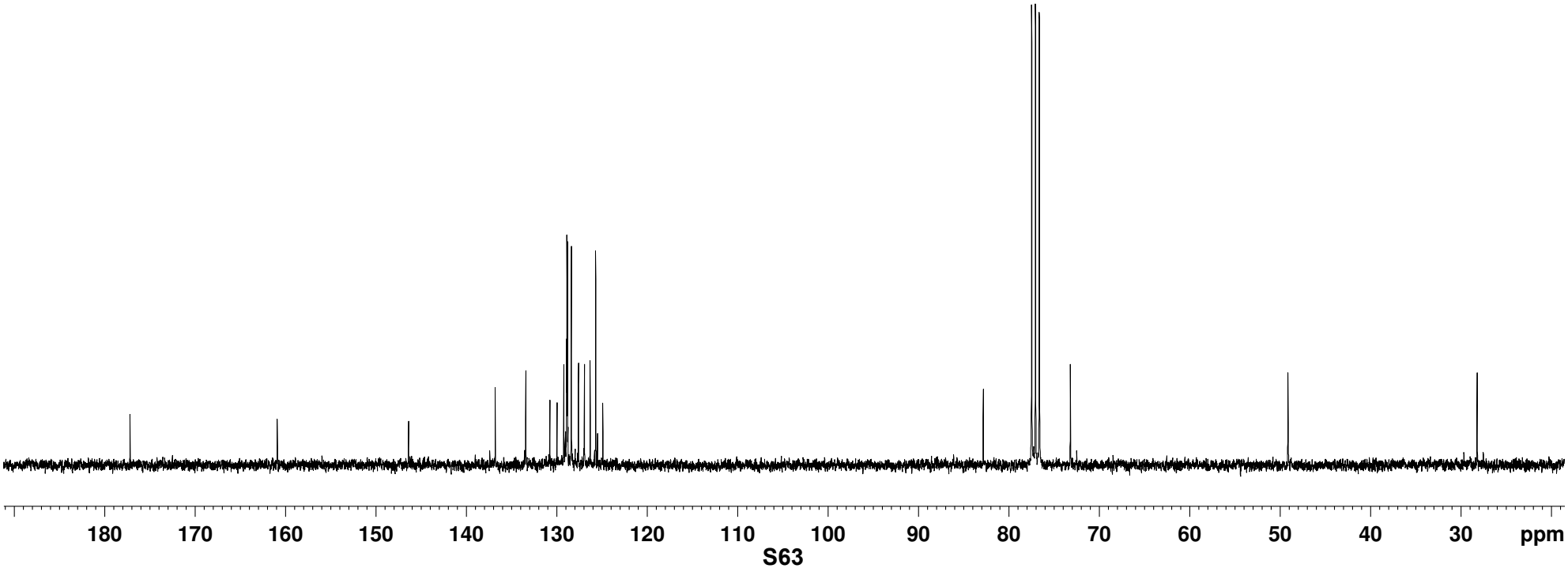
6a

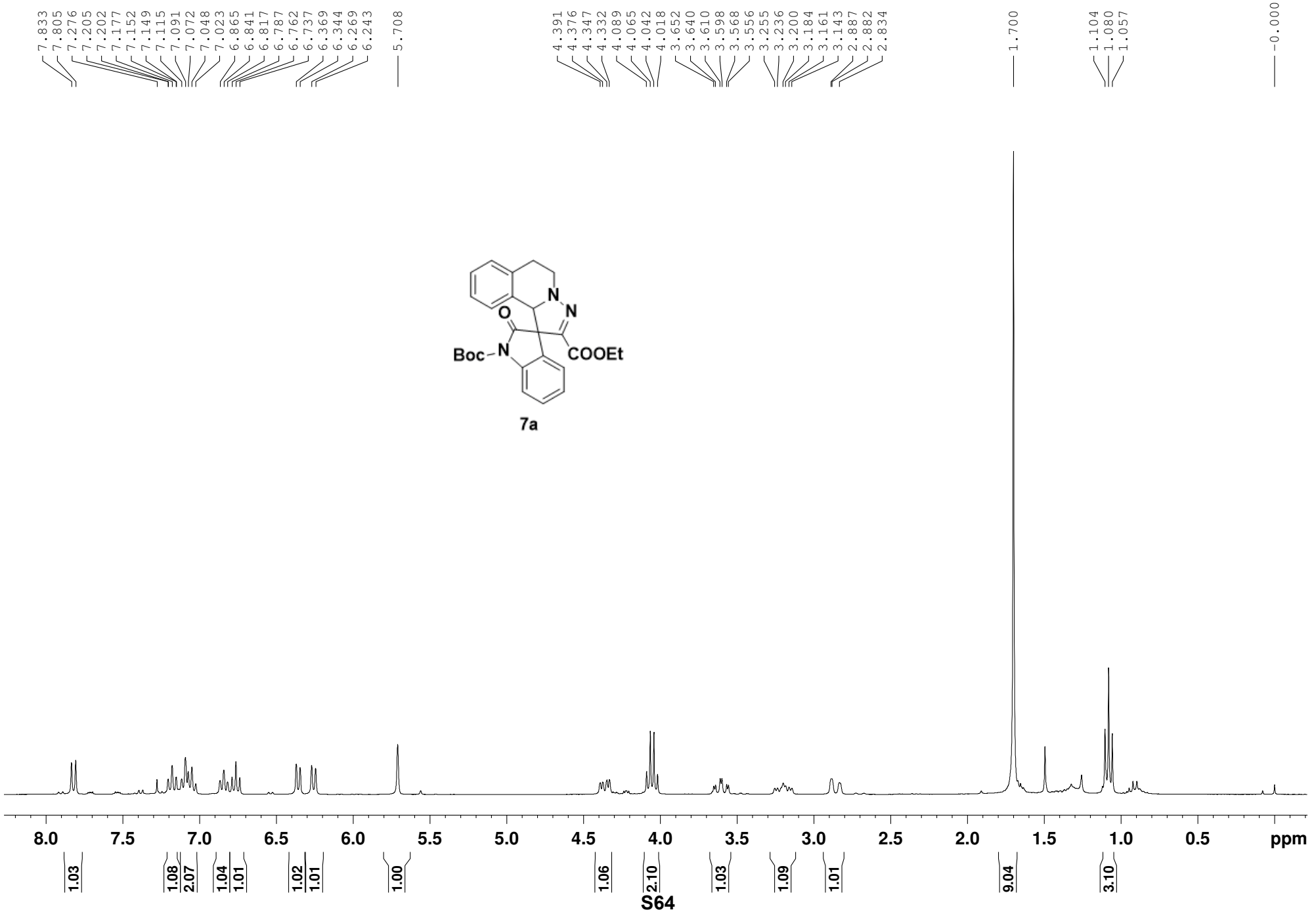

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.26
1.78
1.09
4.06
3.21
2.04
1.01
1.05
0.12
0.88
1.09
1.06
1.08
1.08

177.14
160.86
146.33
136.76
133.38
130.70
129.91
129.17
128.86
128.82
128.76
128.34
127.55
126.89
126.26
125.64
125.44
124.85
82.78
77.42
77.00
76.58
73.15
49.08
28.20

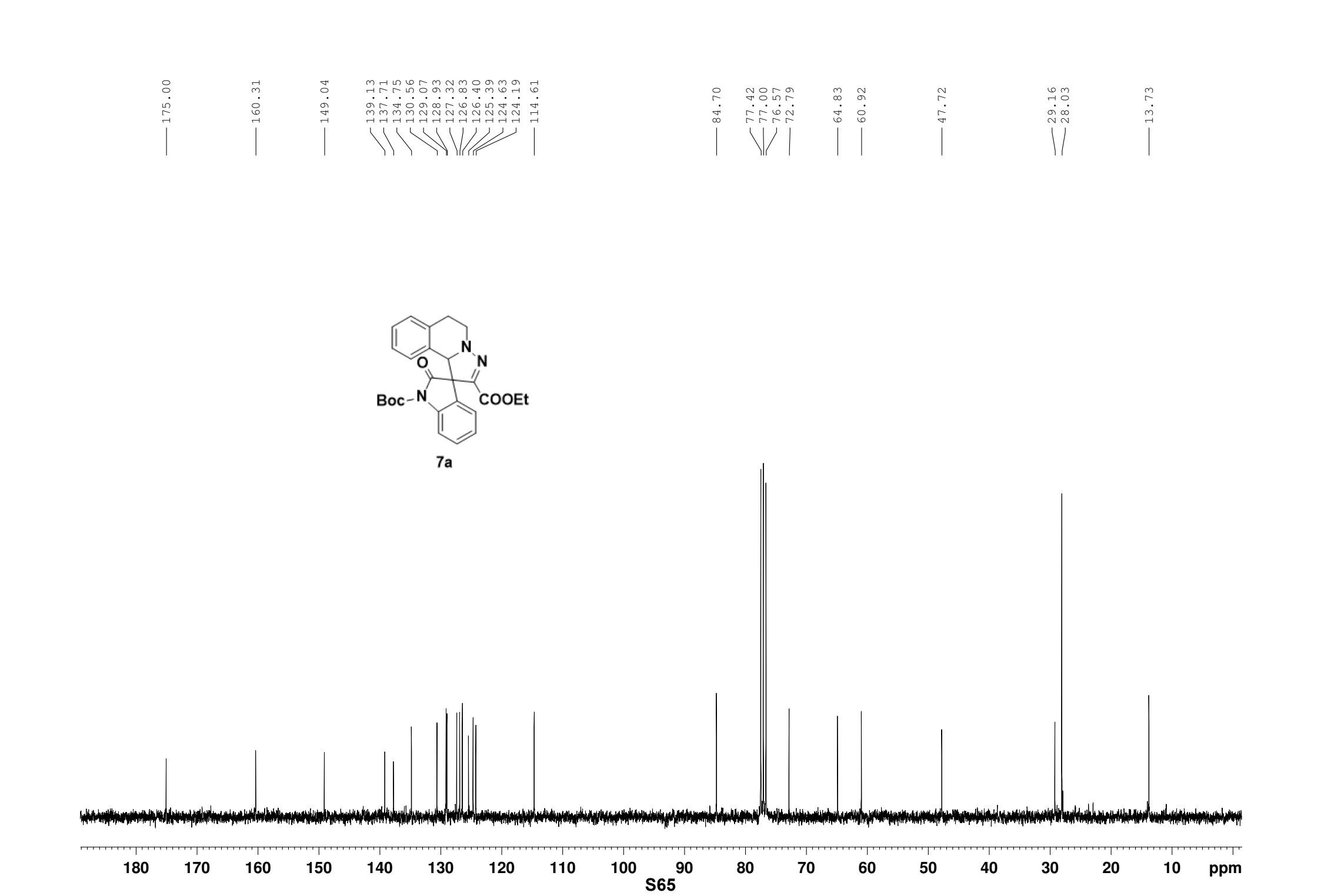


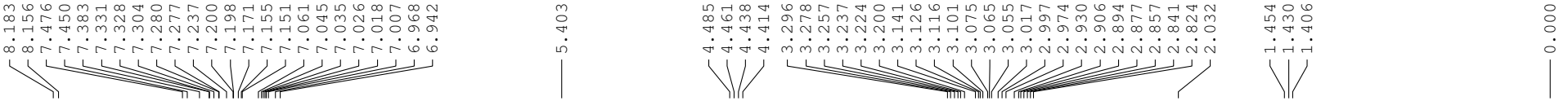
6a

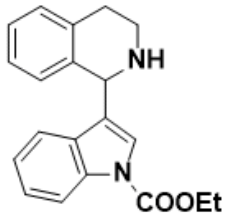



7.833
7.805
7.276
7.205
7.202
7.177
7.152
7.149
7.115
7.091
7.072
7.048
7.023
6.865
6.841
6.817
6.787
6.762
6.737
6.369
6.344
6.269
6.243
5.708
4.391
4.376
4.347
4.332
4.089
4.065
4.042
4.018
3.652
3.640
3.610
3.598
3.568
3.556
3.255
3.236
3.200
3.184
3.161
3.143
2.887
2.882
2.834
1.700
1.104
1.080
1.057
0.000
O
N
N
Boc
N
COOEt
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.03
1.08
2.07
1.04
1.01
1.02
1.01
1.00
1.06
2.10
1.03
1.09
1.01
9.04
3.10

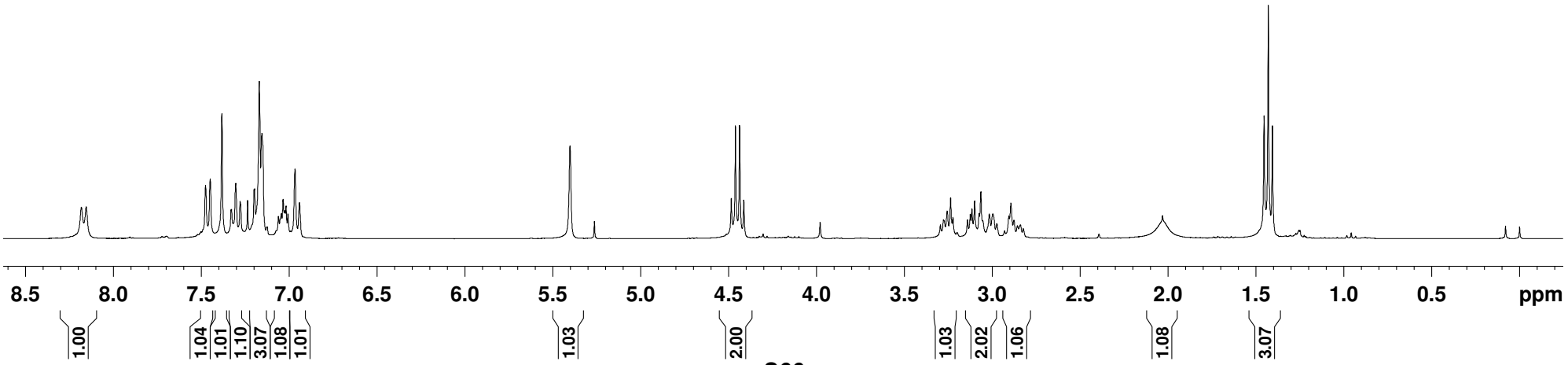
7a

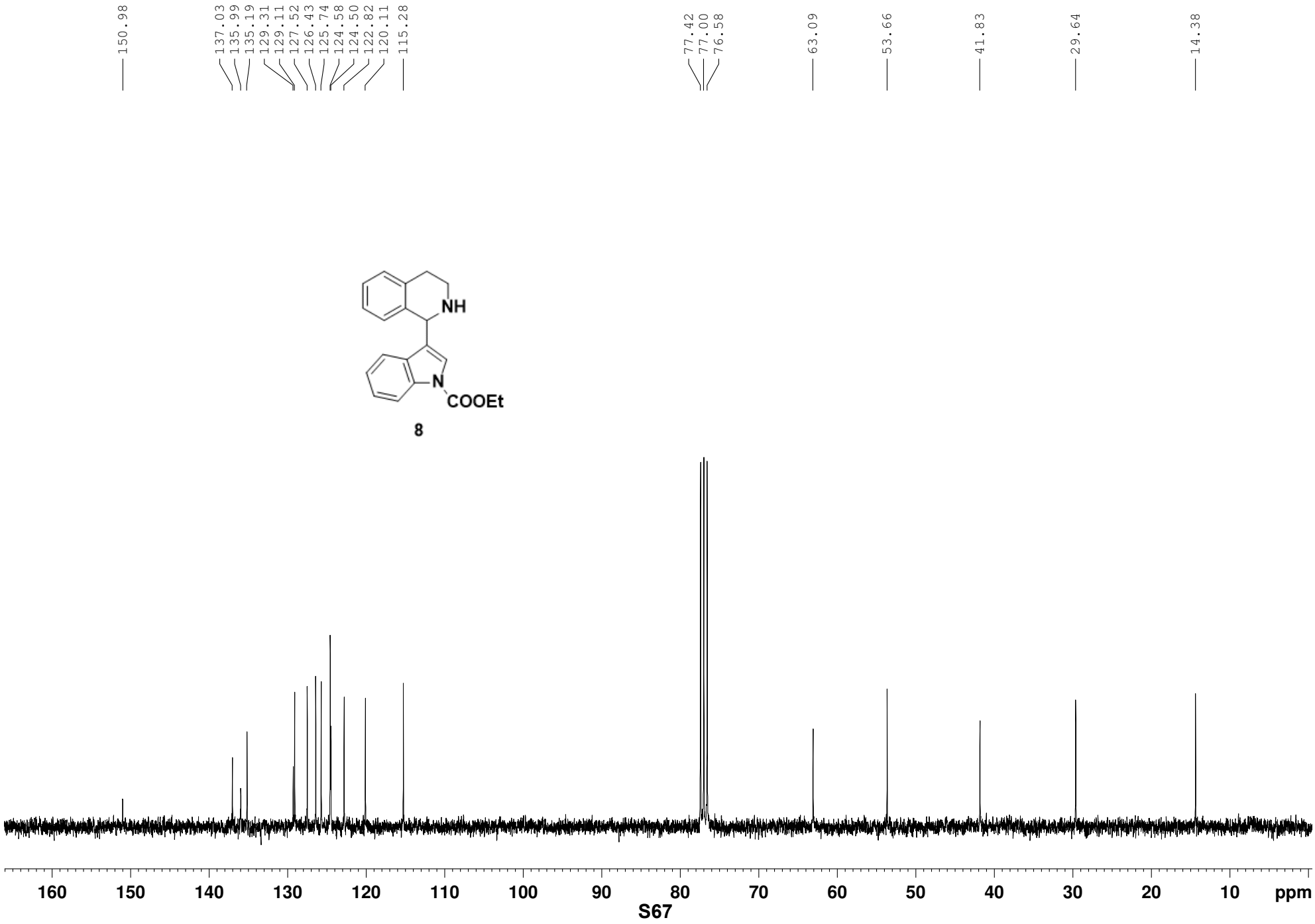

175.00
160.31
149.04
139.13
137.71
134.75
130.56
129.07
128.93
127.32
126.83
126.40
125.39
124.63
124.19
114.61
84.70
77.42
77.00
76.57
72.79
64.83
60.92
47.72
29.16
28.03
13.73
O
N
N
Boc–N
COOEt
7a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.183
8.156
7.476
7.450
7.383
7.331
7.328
7.304
7.280
7.277
7.237
7.200
7.198
7.171
7.155
7.151
7.061
7.045
7.035
7.026
7.018
7.007
6.968
6.942
5.403
4.485
4.461
4.438
4.414
3.296
3.278
3.257
3.237
3.224
3.200
3.141
3.126
3.116
3.101
3.075
3.065
3.055
3.017
2.997
2.974
2.930
2.906
2.894
2.877
2.857
2.841
2.824
2.032
1.454
1.430
1.406
0.000


NH
N
COOEt

8


8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.04
1.01
1.10
3.07
1.08
1.01
1.03
2.00
1.03
2.02
1.06
1.08
3.07


150.98
137.03
135.99
135.19
129.31
129.11
127.52
126.43
125.74
124.58
124.50
122.82
120.11
115.28
77.42
77.00
76.58
63.09
53.66
41.83
29.64
14.38
NH
N
COOEt
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

8