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Supporting Information

Diversity Through a Branched Reaction Pathway: Generation of Multicyclic Scaffolds and Identification of Antimigratory Agents

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General Information

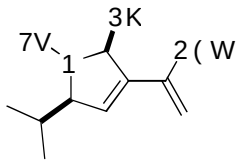
All reactions were performed under Ar atmospheres in oven-dried glassware with dry solvents and anhydrous conditions. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Toluene, dichloromethane (DCM), and MeOH were freshly distilled from CaH_2. THF was distilled from sodium benzophenone ketyl prior to use. Organic solutions were concentrated under reduced pressure on a rotary evaporator or an oil pump. All ethyl allenoates (**1** and **2**), dihydropyrroline esters (**3**), and tetrahydropyridine esters (**4**) were synthesized according to procedures reported previously.[1] Tebbe reagent (*ca*. 1.0 M in toluene) was synthesized according to the procedure reported by Grubbs.[2] Reactions were monitored using thin layer chromatography (TLC) on silica gel–precoated glass plates (0.25 mm thickness, SiliCycle silica gel). Chromatograms were visualized through fluorescence quenching with UV light at 254 nm. Flash column chromatography was performed using SiliCycle Silica-P Flash silica gel (60 Å pore size, 40–63 μm). Infrared spectra were recorded using a Perkin–Elmer Spectrum One FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker Avance 500, ARX-500, or ARX-400 spectrometers, as indicated. Chemical shifts (d, ppm) are provided relative to tetramethylsilane (TMS), with the resonance of the undeuterated solvent or TMS as the internal standard. ^{1}H NMR spectral data are reported as follows: chemical shift, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet), coupling constant(s) (Hz), integration. ^{13}C NMR spectral data are reported in terms of chemical shift. MALDI mass spectra were obtained with an AB/PerSpective DE-STR TOF instrument, with samples dissolved in CH_3CN and using 2,5-dihydroxybenzoic acid or 1,8,9-anthracenetriol as the matrix. X-ray crystallographic data were collected using a Bruker SMART CCD-based diffractometer equipped with a low-temperature apparatus operated at 100 K. Melting points (m.p.) were measured using an electrothermal capillary melting point apparatus; they are uncorrected.

[1] a) Z. Xu and X. Lu, *Tetrahedron Lett.* **1997**, *38*, 3461–3464; b) Z. Xu and X. Lu, *J. Org. Chem.* **1998**, *63*, 5031–5041; c) X.-F. Zhu, J. Lan and O. Kwon, *J. Am. Chem. Soc.* **2003**, *125*, 4716–4717; d) X.-F. Zhu, C. E. Henry and O. Kwon, *Tetrahedron* **2005**, *61*, 6276–6282; e) K. Lu and O. Kwon, *Org. Synth.* **2009**, *86*, 212–224.

[2] L. F. Cannizzo and R. H. Grubbs, *J. Org. Chem.* **1985**, *50*, 2386–2387.

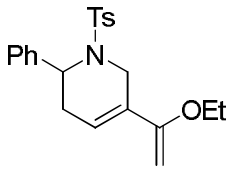
General Procedure for the Synthesis of Dienes 5 and 6

Tebbe reagent (ca. 1.0 M in toluene, 3.0 eq.) was added dropwise over 10 min to a solution of an ester (**3** or **4**, 1.0 mmol) and anhydrous pyridine (0.3 eq.) in dry THF (10 mL) at –78 °C (acetone/dry ice). The reddish mixture was stirred overnight at room temperature, allowing the cooling bath to gradually warm through evaporation of the dry ice. Aqueous NaOH (15%, 0.5 mL) was added dropwise at –78 °C (acetone/dry ice), causing the evolution of CH_4. After 1 h, THF (10 mL) was added to the reaction mixture, which was then stirred for another 4 h at room temperature. The organic solution was filtered through a Celite pad and the filtrate concentrated. The crude residue was purified through flash column chromatography (SiO_2; 10–25% EtOAc and 1% Et_3N in hexanes) to afford the diene.



E

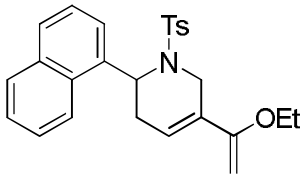
5b: 73% yield; solid; IR (film) ν_{max} 3064, 2963, 2930, 1733, 1597, 1346, 1164, 665 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) d 7.58 (d, *J* = 8.3 Hz, 2H), 7.46–7.44 (m, 2H), 7.31–7.25 (m, 3H), 7.20 (d, *J* = 8.3 Hz, 2H), 6.15 (s, 1H), 5.68 (s, 1H), 4.38–4.37 (m, 1H), 4.00 (d, *J* = 2.6 Hz, 1H), 3.74 (d, *J* = 2.6 Hz, 1H), 3.69–3.59 (m, 2H), 2.37 (s, 3H), 2.04–1.98 (m, 1H), 1.25 (t, *J* = 7.0 Hz, 3H), 1.02 (d, *J* = 6.9 Hz, 3H), 0.86 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 153.9, 143.2, 140.4, 136.7, 135.5, 129.4, 128.8, 128.0, 127.7, 127.5, 125.2, 87.1, 73.2, 69.5, 62.6, 32.9, 21.4, 20.2, 18.0, 14.2; MS (MALDI) calcd. for $C_{24}H_{30}NO_3S$ $[M + H]^+$ 412.19, found 412.24.



6a

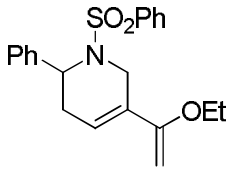
6a: 82% yield; oil; IR (film) ν_{max} 3062, 2978, 2927, 1597, 1340, 1161, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) d 7.68 (d, *J* = 8.3 Hz, 2H), 7.35–7.22 (m, 7H), 6.27–6.26 (m, 1H), 5.28 (d, *J* = 6.7 Hz, 1H), 4.33 (d, *J* = 17.5 Hz, 1H), 3.99 (dd, *J* = 6.9, 2.8 Hz, 2H), 3.73 (qd, *J* = 7.0, 1.5 Hz, 2H), 3.47–3.40 (m, 1H), 2.53 (dd, *J* = 19.6, 5.3 Hz, 1H), 2.44–2.37 (m, 4H), 1.31 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) d 157.2, 143.1, 138.9, 137.7, 129.6, 129.4, 128.4, 127.5, 127.4, 127.0, 120.9, 81.8, 62.8, 52.5, 40.1, 26.2, 21.5, 14.4; MS (MALDI) calcd. for $C_{22}H_{26}NO_3S$ [M + H]$^+$ 384.16, found 384.09.



6c

6c: 80% yield; solid; IR (film) ν_{max} 3051, 2979, 2926, 1597, 1339, 1158, 690 cm^{-1}; ^{1}H NMR (500 MHz, acetone-d_6) d 8.69 (d, *J* = 8.6 Hz, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.85 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.61–7.58 (m, 1H), 7.54–7.51 (m, 1H), 7.40–7.35 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.17 (t, *J* = 2.5 Hz, 1H), 6.07 (d, *J* = 6.7 Hz, 1H), 4.23 (d, *J* = 18.1 Hz, 1H), 4.04 (s, 2H), 3.74 (q, *J* = 7.0 Hz, 2H), 3.23 (ddd, *J* = 18.1, 5.9, 2.8 Hz, 1H), 2.66–2.54 (m, 2H), 2.39 (s, 3H), 1.26 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, acetone-d_6) d 157.5, 143.4, 137.5, 134.3, 134.1, 131.4, 129.3, 129.2, 128.8, 128.6, 127.3, 126.2, 125.6, 124.7, 124.4, 124.2, 121.8, 81.4, 62.4, 49.7, 40.1, 26.2, 20.4, 13.7; MS (MALDI) calcd. for $C_{26}H_{28}NO_3S$ [M + H]$^+$ 434.18, found 434.24.



6e

6e: 80% yield; solid; IR (film) ν_{max} 3062, 2979, 2900, 1666, 1589, 1342, 1162, 691 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6) d 7.85 (d, *J* = 7.8 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.54 (t, *J* = 7.3 Hz, 2H), 7.32–7.23 (m, 5H), 6.23 (d, *J* = 4.4 Hz, 1H), 5.31 (d, *J* = 6.8 Hz, 1H), 4.32 (d, *J* = 17.7 Hz, 1H), 4.04 (d, *J* = 16.2 Hz, 2H), 3.70 (q, *J* = 6.9 Hz, 2H), 3.40 (d, *J* = 17.7 Hz, 1H), 2.61 (dd, *J* = 18.9, 6.8 Hz, 1H), 2.39 (dd, *J* = 18.9, 4.4 Hz, 1H), 1.23 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, acetone-d_6) d 157.2, 141.0, 139.2, 132.6, 129.2, 129.1, 128.4, 127.4, 127.2, 126.8, 121.2, 81.4, 62.5, 52.5, 39.9, 25.9, 13.8; MS (MALDI) calcd. for $C_{21}H_{24}NO_3S$ [M + H]$^+$ 370.15, found 370.18.

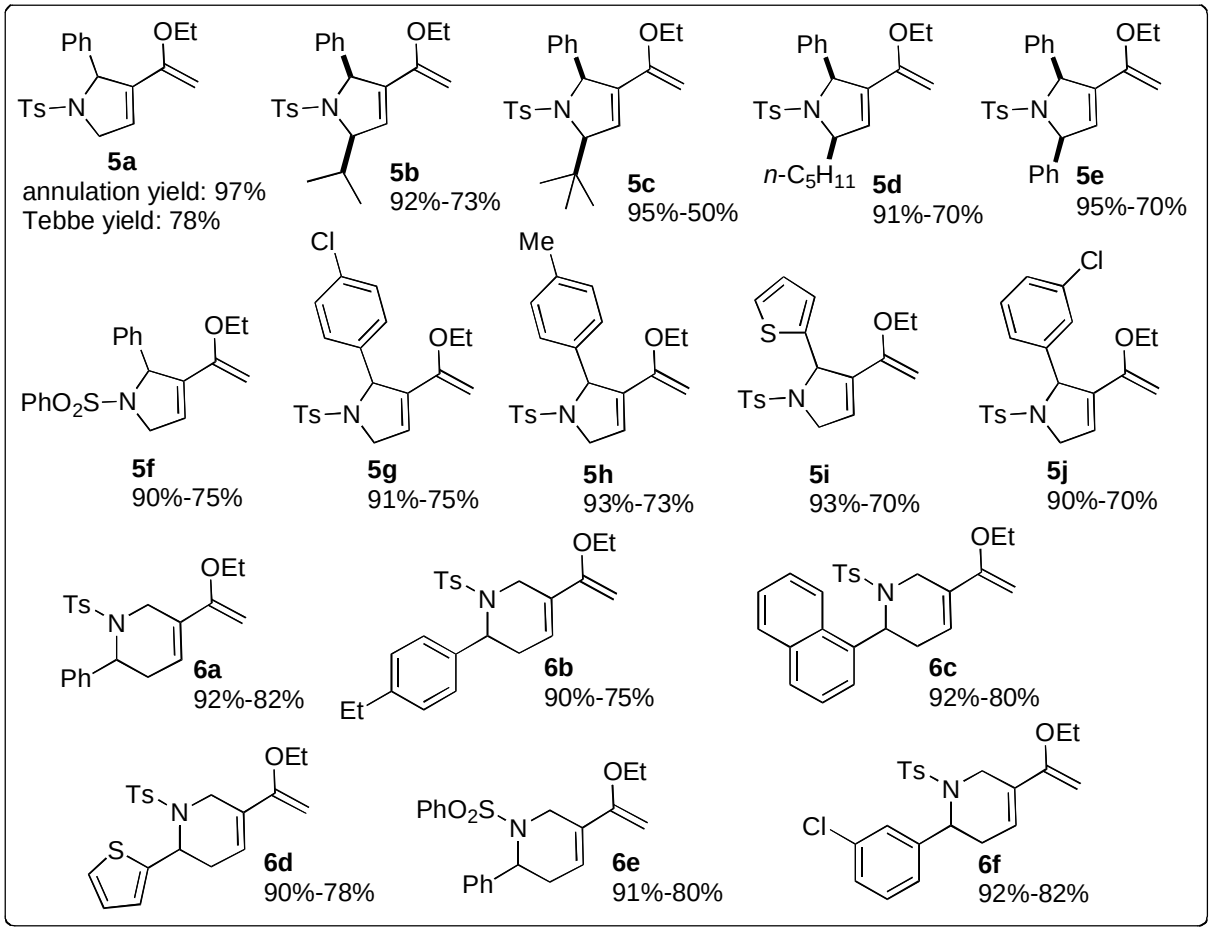


Figure S1. Structures of the Sixteen Dienes and the Yields for Their Formation

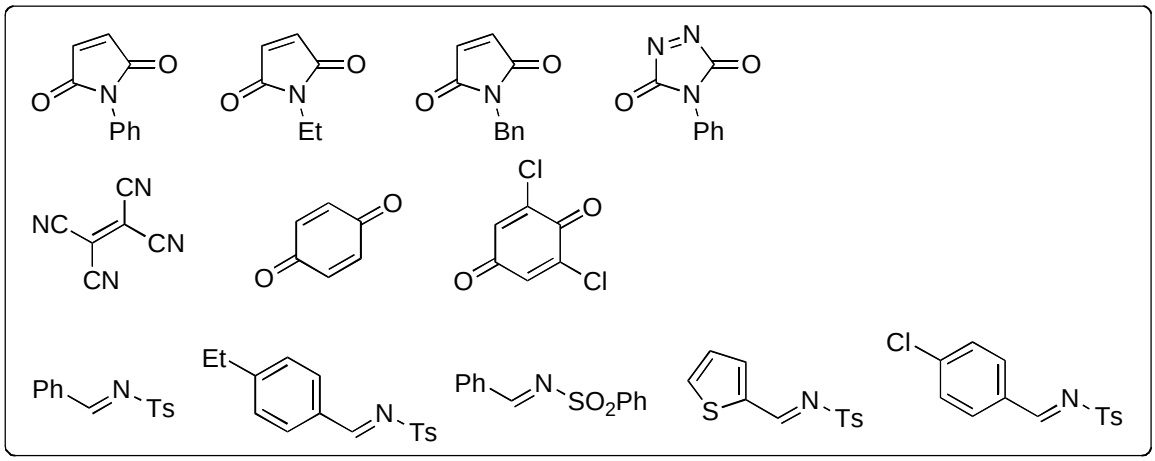


Figure S2. Structures of the Twelve Dienophiles

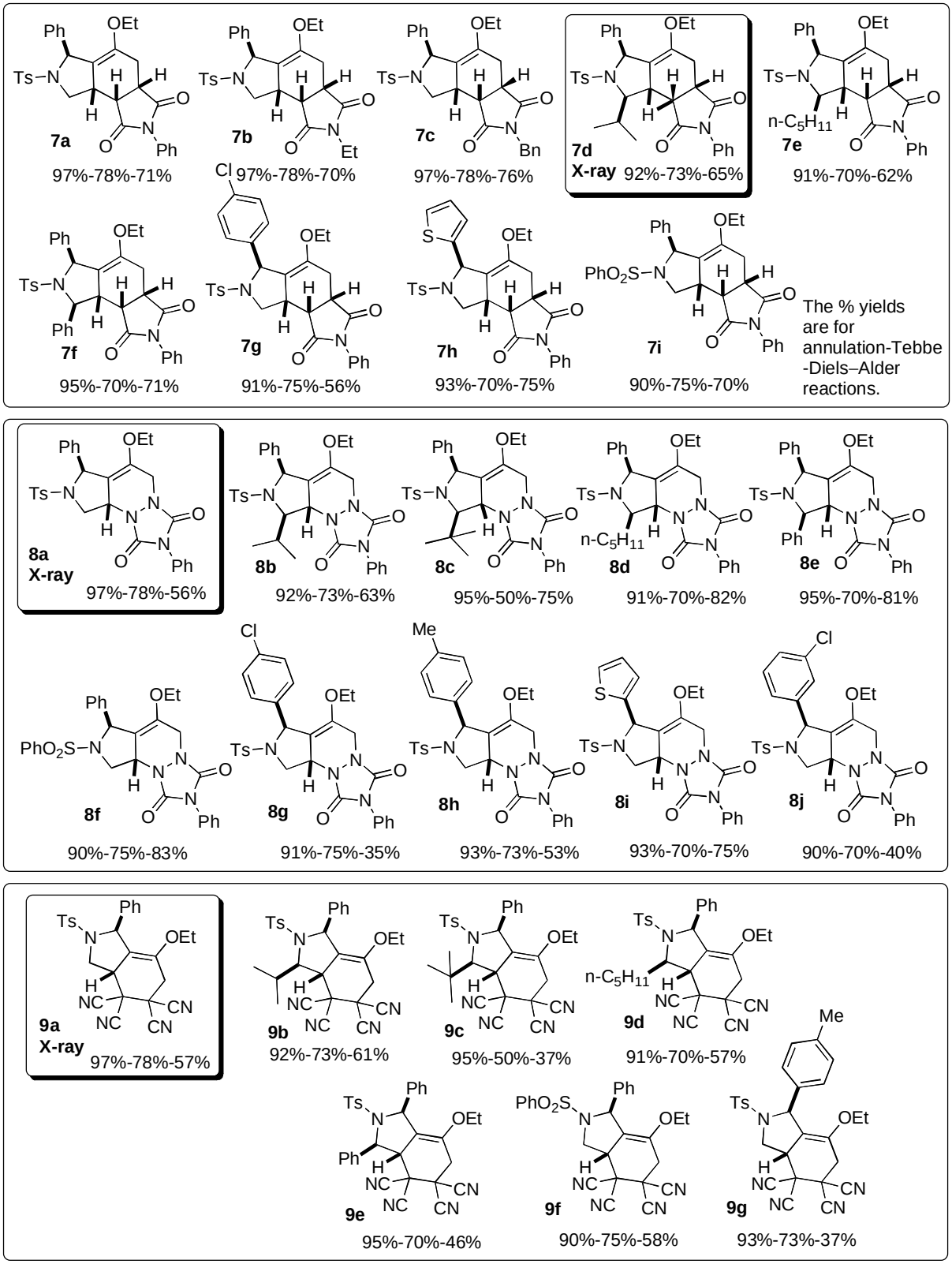
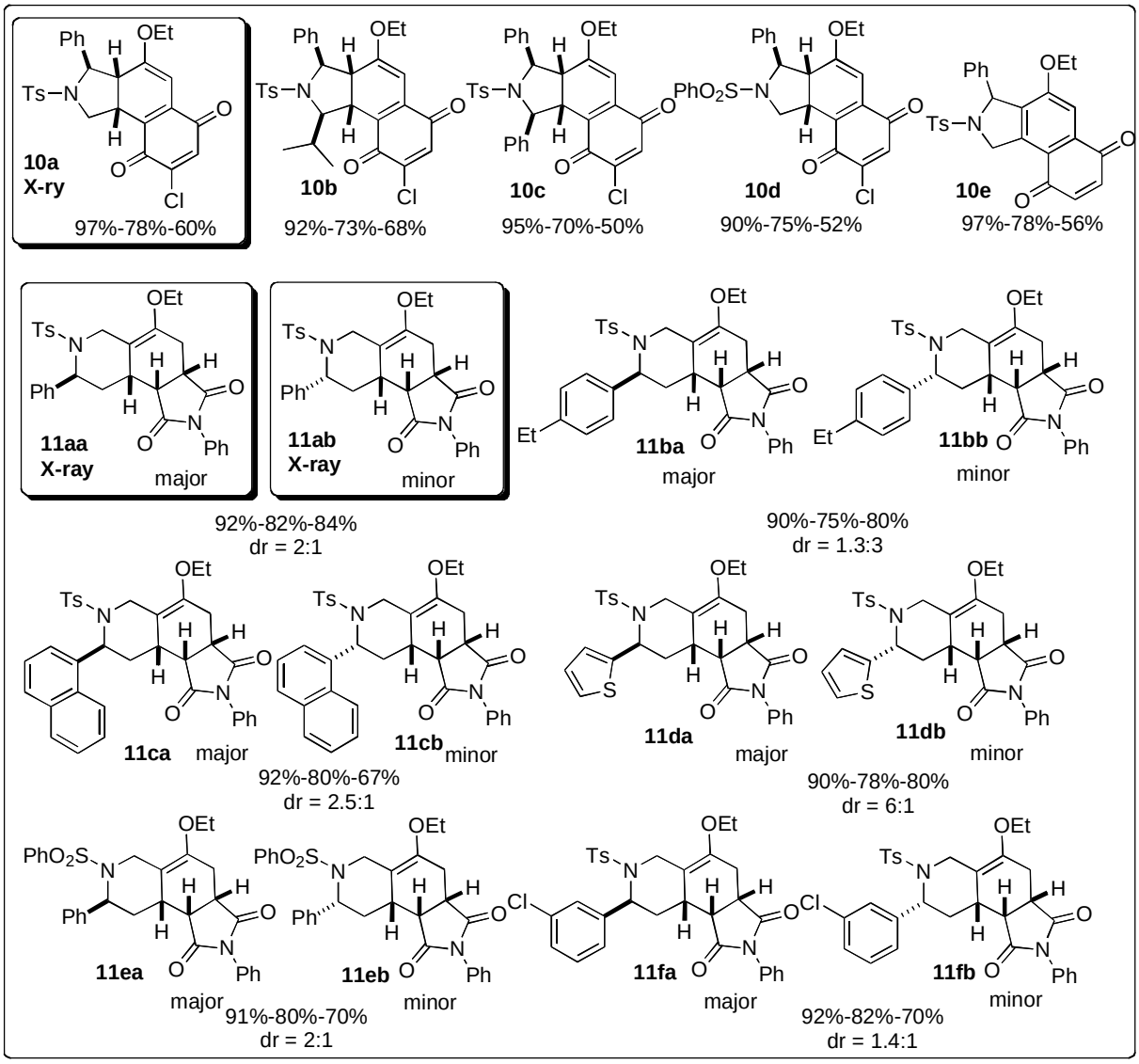


Figure S3. Structures of the Ninety-One Library Compounds and the Yields for Their Formation



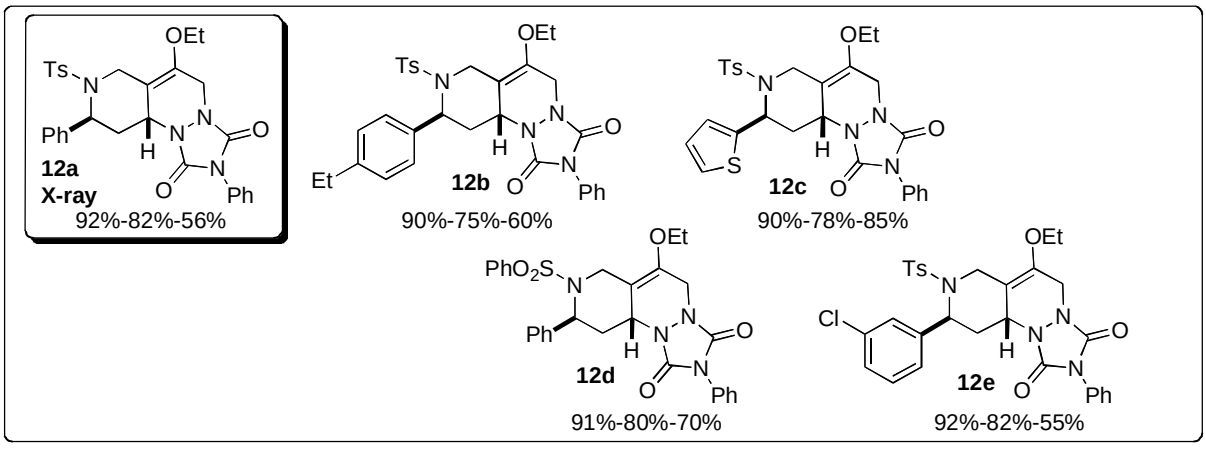


Figure S3. Structures of the Ninety-One Library Compounds and the Yields for Their Formation (Continued)

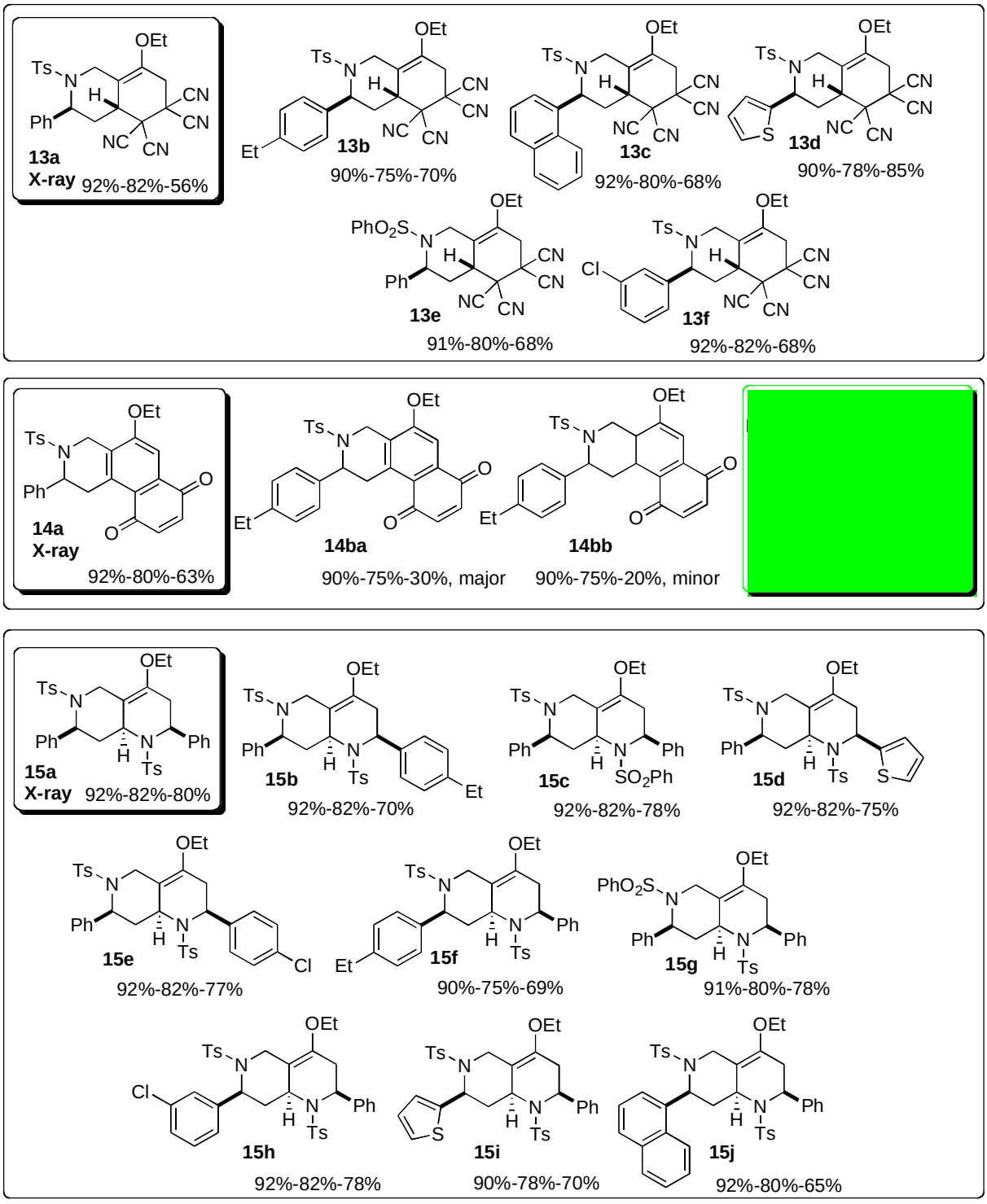


Figure S3. Structures of the Ninety-One Library Compounds and the Yields for Their Formation (Continued)

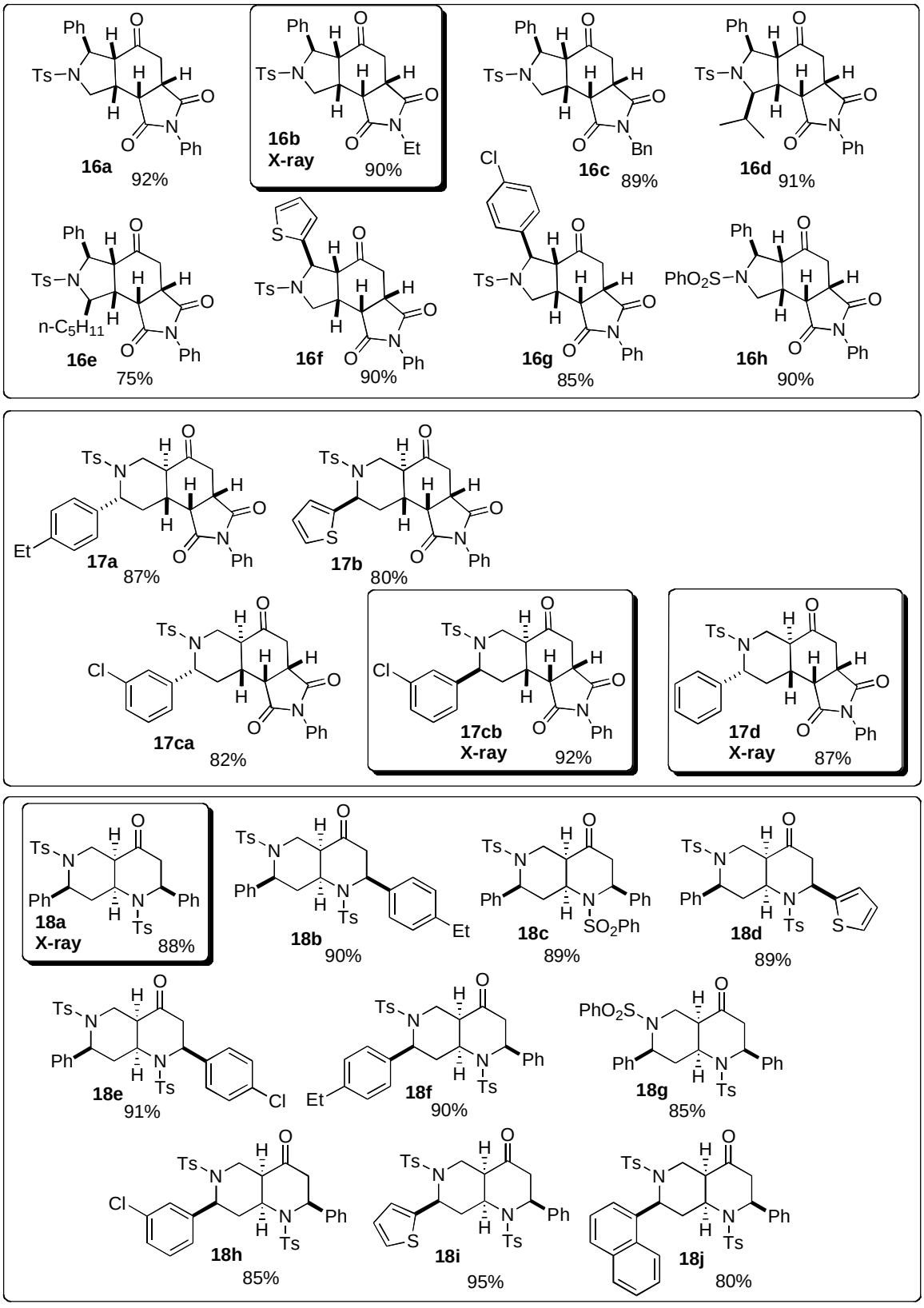
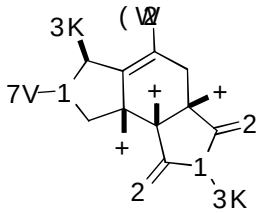


Figure S3. Structures of the Ninety-One Library Compounds and the Yields for Their Formation (Continued)

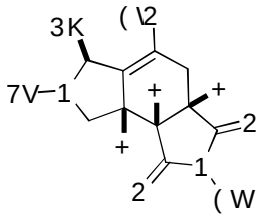
General Procedure for the Synthesis of 7

A solution of 5–15% MeOH in DCM (1.5 mL) was added to a stirred mixture of the diene (**5**, 0.5 mmol) and maleimide (4.0 eq.) under an Ar atmosphere at room temperature. After the reaction had reached completion (16–48 h, TLC), the mixture was concentrated and the crude residue purified through flash column chromatography (SiO_2; 30–50% EtOAc in hexanes) to afford the product.



D

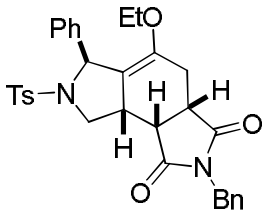
7a: 71% yield; white solid; decomposed at 180 °C; IR (film) ν_{max} 3062, 2978, 2924, 1713, 1381, 1165, 663 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) d 7.55 (d, *J* = 8.3 Hz, 2H), 7.46–7.40 (m, 3H), 7.32–7.21 (m, 5H, overlap with solvent residual peak), 7.16 (d, *J* = 7.9 Hz, 2H), 7.08–7.05 (m, 2H), 5.21 (t, *J* = 2.1 Hz, 1H), 4.04 (dd, *J* = 9.9, 8.1 Hz, 1H), 3.70–3.57 (m, 2H), 3.43–3.31 (m, 4H), 2.95 (dd, *J* = 16.0, 1.6 Hz, 1H), 2.37 (s, 3H), 2.27–2.20 (m, 1H), 0.96 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 177.4, 175.3, 145.0, 143.1, 142.0, 133.8, 131.4, 129.2, 128.9, 128.5, 127.9, 127.7, 127.2, 127.1, 126.1, 118.6, 63.9, 63.5, 50.9, 40.8, 40.1, 36.4, 23.5, 21.4, 14.8; MS (MALDI) calcd. for $C_{31}H_{30}N_2O_5SNa$ $[M + Na]^+$ 565.18, found 565.19; HRMS (ESI) calcd. for $C_{31}H_{31}N_2O_5S$ $[M + H]^+$ 543.1953, found 543.1945.



E

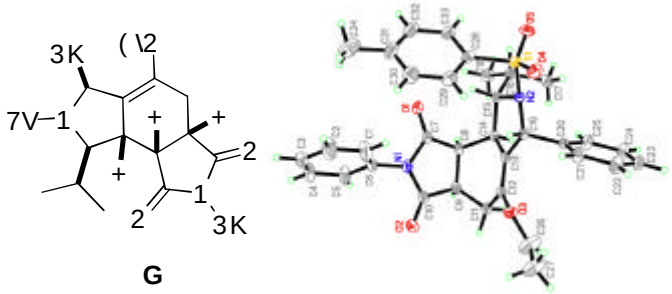
7b: 70% yield; yellow solid; decomposed at 170 °C; IR (film) ν_{max} 3031, 2978, 2938, 1699, 1348, 1162, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) d 7.49 (d, *J* = 8.2 Hz, 2H), 7.22–7.15 (m, 7H), 5.07 (t, *J* = 2.0 Hz, 1H), 3.91 (dd, *J* = 10.0, 8.0 Hz, 1H), 3.70 (dd, *J* = 9.8, 7.7 Hz, 1H), 3.56–3.48 (m, 1H), 3.37 (q, *J* = 7.2 Hz, 2H), 3.30–3.13 (m, 3H), 3.06 (t, *J* = 6.8 Hz, 1H), 2.77

(dd, *J* = 15.7, 1.5 Hz, 1H), 2.35 (s, 3H), 2.13–2.06 (m, 1H), 0.94 (t, *J* = 7.1 Hz, 3H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) d 178.4, 176.3, 145.1, 143.2, 142.1, 134.0, 129.3, 127.9, 127.8, 127.4, 127.2, 119.0, 64.0, 63.6, 50.6, 40.6, 40.1, 36.7, 33.9, 23.9, 21.5, 14.9, 13.0; MS (MALDI) calcd. for $C_{27}H_{30}N_2O_5SNa$ $[M + Na]^+$ 517.18, found 517.17; HRMS (ESI) calcd. for $C_{27}H_{31}N_2O_5S$ $[M + H]^+$ 495.1943, found 495.1961.



7c

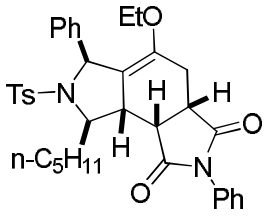
7c: 76% yield; yellow solid; decomposed at 170 °C; IR (film) ν_{max} 3029, 2976, 2917, 1706, 1349, 1166, 667 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) d 7.45 (d, *J* = 8.5 Hz, 2H), 7.32–7.29 (m, 3H), 7.25–7.22 (m, 2H), 7.18–7.12 (m, 7H), 5.09 (t, *J* = 1.9 Hz, 1H), 4.62 (AB d, *J* = 14.3 Hz, 1H), 4.45 (AB d, *J* = 14.3 Hz, 1H), 4.18–4.14 (m, 1H), 3.93–3.88 (m, 1H), 3.26–3.17 (m, 4H), 3.12 (t, *J* = 7.3 Hz, 1H), 2.79 (dd, *J* = 15.6, 1.7 Hz, 1H), 2.35 (s, 3H), 2.16–2.09 (m, 1H), 0.83 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) d 178.3, 176.0, 145.2, 143.0, 141.6, 135.6, 134.8, 129.2, 128.7, 128.4, 128.0, 127.9, 127.7, 127.5, 127.2, 119.1, 64.2, 63.8, 49.6, 42.5, 40.6, 40.5, 37.6, 24.7, 21.5, 14.9; MS (MALDI) calcd. for $C_{32}H_{32}N_2O_5SNa$ $[M + Na]^+$ 579.19, found 579.19; HRMS (ESI) calcd. for $C_{32}H_{33}N_2O_5S$ $[M + H]^+$ 557.2110, found 557.2112.



G

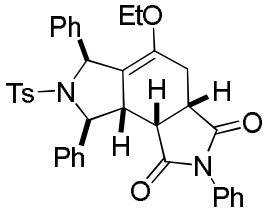
7d: 65% yield; white solid; m.p. 209–210 °C; IR (film) ν_{max} 3061, 2959, 1709, 1334, 1195 cm^{-1}; ^{1}H NMR (500 MHz, acetone-d_6) d 7.68 (d, *J* = 8.3 Hz, 2H), 7.49–7.46 (m, 2H), 7.42–7.39 (m, 1H), 7.33–7.32 (m, 2H), 7.24–7.14 (m, 7H), 5.44 (t, *J* = 2.3 Hz, 1H), 4.97 (t, *J* = 6.5 Hz, 1H), 3.57–3.47 (m, 3H), 3.44–3.38 (m, 1H), 3.19–3.16 (m, 1H), 2.83–2.76 (m, 1H, overlap with H_2O peak), 2.53–2.48 (m, 1H), 2.30 (s, 3H), 2.07–2.03 (m, 1H, overlap with solvent residual peak),

1.02 (d, *J* = 6.9 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H), 0.81 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, acetone-d_6) d 177.8, 176.0, 145.2, 143.2, 142.3, 135.6, 132.7, 129.2, 128.4, 128.3, 127.9, 127.8, 127.5, 126.8, 126.6, 118.5, 66.2, 63.8, 63.1, 42.0, 41.2, 40.7, 33.2, 24.4, 20.5, 19.4, 16.3, 14.3; MS (MALDI) calcd. for $C_{34}H_{36}N_2O_5SNa$ $[M + Na]^+$ 607.22, found 607.16; HRMS (ESI) calcd. for $C_{34}H_{37}N_2O_5S$ $[M + H]^+$ 585.2423, found 585.2393.



7e

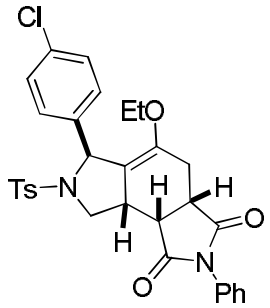
7e: 62% yield; white solid; m.p. 139–140 °C; IR (film) ν_{max} 2955, 2921, 2857, 1708, 1383, 1153, 663 cm^{-1}; ^{1}H NMR (500 MHz, acetone-d_6) d 7.64 (d, *J* = 8.2 Hz, 2H), 7.49–7.45 (m, 2H), 7.43–7.38 (m, 3H), 7.26–7.24 (m, 2H), 7.20–7.16 (m, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.08–7.06 (m, 2H), 5.37 (t, *J* = 2.3 Hz, 1H), 4.91–4.88 (m, 1H), 3.57–3.46 (m, 3H), 3.40–3.34 (m, 1H), 3.14–3.11 (m, 1H), 2.82–2.76 (m, 1H, overlap with H_2O peak), 2.39–2.34 (m, 1H), 2.27 (s, 3H), 2.19–2.13 (m, 1H), 1.81–1.73 (m, 1H), 1.54–1.48 (m, 2H), 1.40–1.29 (m, 4H), 0.88 (t, *J* = 7.1 Hz, 3H), 0.83 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, acetone-d_6) d 177.8, 175.8, 145.0, 143.6, 143.0, 135.5, 132.5, 129.2, 128.4, 128.0, 127.9, 127.6, 127.5, 126.6, 126.5, 118.9, 64.4, 63.1, 61.6, 45.0, 41.5, 40.6, 38.3, 31.5, 25.1, 24.5, 22.3, 20.6, 14.3, 13.3; MS (MALDI) calcd. for $C_{36}H_{40}N_2O_5SNa$ $[M + Na]^+$ 635.26, found 635.11; HRMS (ESI) calcd. for $C_{36}H_{41}N_2O_5S$ $[M + H]^+$ 613.2736, found 613.2703.



7f

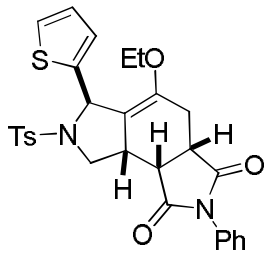
7f: 71% yield; white solid; m.p. 182–183 °C; IR (film) ν_{max} 3061, 3028, 2981, 1708, 1387, 1163, 663 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.59–7.58 (m, 2H), 7.50–7.41 (m, 5H), 7.37–7.25 (m, 8H), 7.14–7.11 (m, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 5.74 (d, *J* = 8.1 Hz, 1H), 5.51 (t, *J* = 2.5 Hz,

1H), 3.56–3.50 (m, 1H), 3.26–3.13 (m, 4H), 2.83 (dd, *J* = 15.5, 1.2 Hz, 1H), 2.29 (s, 3H), 2.25–2.20 (m, 1H), 0.82 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 177.5, 175.5, 145.1, 143.0, 142.9, 141.8, 134.8, 131.5, 129.0, 128.9, 128.6, 128.4, 128.2, 128.0, 127.9, 127.4, 127.2, 127.1, 126.2, 118.3, 65.4, 64.7, 63.8, 49.6, 40.6, 39.7, 25.4, 21.4, 16.7; MS (MALDI) calcd. for $C_{37}H_{34}N_2O_5SNa$ $[M + Na]^+$ 641.21, found 641.23; HRMS (ESI) calcd. for $C_{37}H_{35}N_2O_5S$ $[M + H]^+$ 619.2266, found 619.2261.



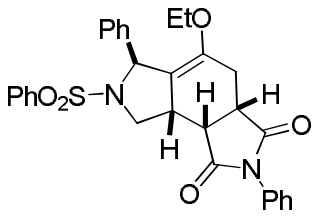
7g

7g: 56% yield; white solid; m.p. 184–185 °C; IR (film) ν_{max} 2979, 2896, 1712, 1385, 1162, 669 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.56 (d, *J* = 8.2 Hz, 2H), 7.45–7.38 (m, 3H), 7.26–7.21 (m, 4H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 7.1 Hz, 2H), 5.12 (s, 1H), 4.03 (t, *J* = 9.0 Hz, 1H), 3.64–3.59 (m, 2H), 3.47–3.36 (m, 2H), 3.33–3.30 (m, 2H), 2.95 (d, *J* = 16.0 Hz, 1H), 2.38 (s, 3H), 2.22–2.18 (m, 1H), 0.97 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 177.4, 175.3, 145.4, 143.5, 140.7, 133.5, 132.8, 131.4, 129.4, 129.0, 128.65, 128.60, 128.1, 127.8, 126.1, 117.7, 63.5, 63.3, 51.1, 40.8, 40.0, 36.2, 23.3, 21.5, 14.9; MS (MALDI) calcd. for $C_{31}H_{29}ClN_2O_5SNa$ $[M + Na]^+$ 599.14, found 599.15; HRMS (ESI) calcd. for $C_{31}H_{30}ClN_2O_5S$ $[M + H]^+$ 577.1564, found 577.1543.



7h

7h: 75% yield; white solid; m.p. 179–180 °C; IR (film) ν_{max} 3066, 2979, 2896, 1706, 1385, 1163, 664 cm^{-1}; ^1H NMR (500 MHz, acetone-d_6) d 7.53 (d, *J* = 8.2 Hz, 2H), 7.48–7.45 (m, 2H), 7.42–7.38 (m, 1H), 7.23–7.21 (m, 3H), 7.11–7.08 (m, 2H), 7.03 (dq, *J* = 3.6, 0.5 Hz, 1H), 6.87 (dd, *J* = 5.1, 3.5 Hz, 1H), 5.65 (t, *J* = 1.8 Hz, 1H), 3.79 (dd, *J* = 7.7, 0.8 Hz, 2H), 3.73–3.58 (m, 2H), 3.54–3.52 (m, 2H), 3.43–3.39 (m, 1H), 2.90–2.78 (m, 1H, overlap with H_2O peak), 2.36–2.30 (m, 1H), 2.33 (s, 3H), 0.98 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, acetone-d_6) d 177.7, 175.5, 145.8, 145.7, 143.1, 134.7, 132.5, 129.2, 128.6, 128.0, 127.5, 126.5, 125.8, 125.4, 124.4, 117.5, 63.2, 59.0, 49.8, 40.7, 40.1, 36.1, 23.3, 20.5, 14.4; MS (MALDI) calcd. for $C_{29}H_{28}N_2O_5S_2Na$ $[M + Na]^+$ 571.13, found 570.90; HRMS (ESI) calcd. for $C_{29}H_{29}N_2O_5S_2$ $[M + H]^+$ 549.1518, found 549.1511.



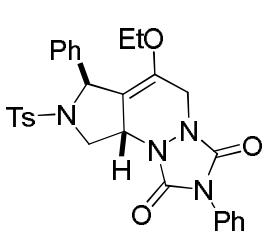
7i

7i: 70% yield; white solid; m.p. 171–172 °C; IR (film) ν_{max} 3059, 2983, 2913, 1704, 1389, 1164, 693 cm^{-1}; ^1H NMR (500 MHz, acetone-d_6) d 7.69–7.67 (m, 2H), 7.62–7.59 (m, 1H), 7.48–7.44 (m, 4H), 7.41–7.37 (m, 1H), 7.34–7.32 (m, 2H), 7.24–7.16 (m, 3H), 7.00–6.98 (m, 2H), 5.21 (t, *J* = 2.3 Hz, 1H), 4.00–3.96 (m, 1H), 3.72–3.69 (m, 1H), 3.61–3.50 (m, 4H), 3.39–3.33 (m, 1H), 2.83–2.79 (m, 1H, overlap with H_2O peak), 2.32–2.27 (m, 1H), 0.86 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, acetone-d_6) d 177.6, 175.7, 145.4, 142.8, 137.0, 132.5, 132.4, 128.8, 128.6, 128.0, 127.58, 127.55, 127.5, 126.7, 126.5, 118.8, 64.0, 63.0, 51.1, 40.8, 40.2, 36.2, 23.3, 14.3; MS (MALDI) calcd. for $C_{30}H_{28}N_2O_5SNa$ $[M + Na]^+$ 551.16, found 551.37; HRMS (ESI) calcd. for $C_{30}H_{29}N_2O_5S$ $[M + H]^+$ 529.1797, found 529.1796.

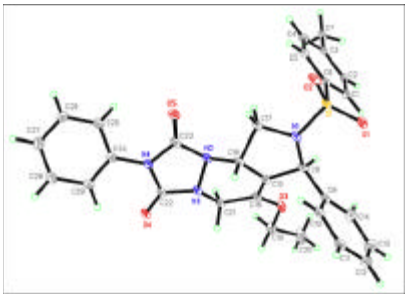
General Procedure for the Synthesis of 8

N-Phenyltriazolinedione (2.0 eq.) was added to a solution of the diene (**5**, 0.5 mmol) in DCM (2.0 mL) at 0 °C. After the reaction had reached completion (10–60 min, TLC), the mixture was

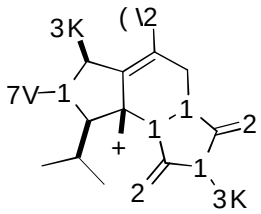
concentrated and the crude residue purified through flash column chromatography (SiO_2; 40–60% EtOAc in hexanes) to afford the product.



8a



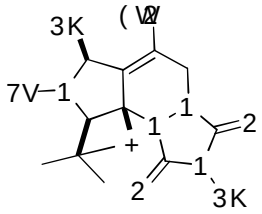
8a: 56% yield; white solid; m.p. 178–179 °C; IR (film) ν_{max} 3062, 2980, 2916, 1719, 1420, 1163, 665 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) d 7.68 (d, *J* = 8.2 Hz, 2H), 7.48–7.44 (m, 4H), 7.41–7.37 (m, 3H), 7.34–7.25 (m, 5H), 5.57 (s, 1H), 4.59 (t, *J* = 8.0 Hz, 1H), 4.40 (d, *J* = 15.3 Hz, 1H), 4.37 (dd, *J* = 9.2, 8.0 Hz, 1H), 3.85 (d, *J* = 15.3 Hz, 1H), 3.78 (qd, *J* = 7.0, 2.3 Hz, 1H), 3.72 (qd, *J* = 7.0, 2.3 Hz, 1H), 3.35 (t, *J* = 9.2 Hz, 1H), 2.43 (s, 3H), 1.23 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 153.6, 151.1, 143.8, 141.1, 140.4, 133.8, 130.6, 129.5, 129.2, 128.38, 128.37, 127.8, 127.6, 126.4, 125.2, 115.2, 64.8, 61.3, 54.4, 52.2, 41.9, 21.5, 15.1; MS (MALDI) calcd. for $C_{29}H_{28}N_4O_5SNa$ $[M + Na]^+$ 567.17, found 567.15; HRMS (ESI) calcd. for $C_{29}H_{29}N_4O_5S$ $[M + H]^+$ 545.1858, found 545.1840.



E

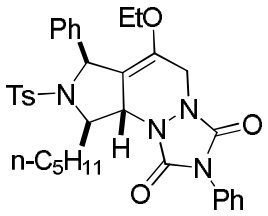
8b: 63% yield; white solid; m.p. 100–101 °C; IR (film) ν_{max} 3061, 2966, 2914, 1719, 1418, 1163, 664 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) d 7.78 (d, *J* = 8.1 Hz, 2H), 7.50–7.47 (m, 6H), 7.41–7.38 (m, 1H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.02 (s, 1H), 4.60 (dd, *J* = 9.1, 2.8 Hz, 1H), 4.33 (d, *J* = 14.6 Hz, 1H), 4.24 (s, 1H), 3.82 (qd, *J* = 7.0, 2.2 Hz, 1H), 3.76 (qd, *J* = 7.0, 2.2 Hz, 1H), 3.21 (dd, *J* = 15.4, 1.8 Hz, 1H), 2.36 (s, 3H), 1.30–1.25 (m, 1H), 1.24 (t, *J* = 7.0 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H), 0.80 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 151.7, 151.5, 143.4, 143.3, 138.4, 135.4, 130.7, 129.2, 128.7,

128.5, 128.3, 128.2, 127.8, 126.9, 125.0, 113.0, 68.3, 65.3, 62.7, 62.2, 43.0, 33.0, 21.4, 20.5, 19.5, 15.4; MS (MALDI) calcd. for $C_{32}H_{34}N_4O_5SNa$ $[M + Na]^+$ 609.21, found 609.20; HRMS (ESI) calcd. for $C_{32}H_{35}N_4O_5S$ $[M + H]^+$ 587.2328, found 587.2346.



F

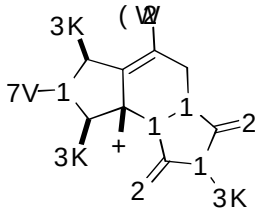
8c: 75% yield; white solid; m.p. 219–220 °C; IR (film) ν_{max} 3059, 2960, 2906, 1719, 1417, 1163, 598cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.83 (d, *J* = 8.2 Hz, 2H), 7.54–7.47 (m, 6H), 7.43–7.40 (m, 1H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.08 (s, 1H), 5.04 (d, *J* = 2.8 Hz, 1H), 4.41–4.36 (m, 2H), 3.84–3.78 (m, 2H), 3.33 (d, *J* = 14.6 Hz, 1H), 2.36 (s, 3H), 1.24 (t, *J* = 7.0 Hz, 3H), 0.71 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) d 152.2, 150.2, 143.8, 143.4, 138.9, 134.9, 130.7, 129.2, 128.8, 128.6, 128.3, 128.2, 127.4, 127.1, 125.0, 114.0, 69.7, 64.6, 63.8, 60.8, 43.7, 35.1, 28.1, 21.4, 15.5; MS (MALDI) calcd. for $C_{33}H_{36}N_4O_5SNa$ $[M + Na]^+$ 623.23, found 623.24; HRMS (ESI) calcd. for $C_{33}H_{37}N_4O_5S$ $[M + H]^+$ 601.2484, found 601.2480.



8d

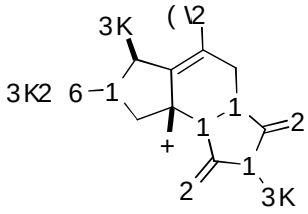
8d: 82% yield; semi-solid; IR (film) ν_{max} 3060, 2920, 2852, 1718, 1420, 1164, 665 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.75 (d, *J* = 8.2 Hz, 2H), 7.49–7.44 (m, 6H), 7.40–7.32 (m, 3H), 7.29–7.24 (m, 3H), 5.90 (s, 1H), 4.51 (dt, *J* = 10.3, 3.7 Hz, 1H), 4.35 (dd, *J* = 15.4, 1.6 Hz, 1H), 4.03 (d, *J* = 2.3 Hz, 1H), 3.79 (qd, *J* = 7.0, 2.1 Hz, 1H), 3.64 (qd, *J* = 7.0, 2.1 Hz, 1H), 3.25 (dd, *J* = 15.4, 2.1 Hz, 1H), 2.39 (s, 3H), 1.83–1.77 (m, 1H), 1.52–1.41 (m, 2H), 1.26–1.03 (m, 5H), 1.22 (t, *J* = 7.0 Hz, 3H), 0.80 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 153.4, 151.0,

143.4, 142.4, 138.5, 135.3, 130.6, 129.2, 129.0, 128.4, 128.3, 128.2, 127.8, 126.6, 125.1, 111.8, 65.0, 64.7, 63.4, 61.8, 41.9, 35.9, 31.3, 25.6, 22.2, 21.4, 15.3, 14.0; MS (MALDI) calcd. for $C_{34}H_{38}N_4O_5SNa$ $[M + Na]^+$ 637.24, found 637.26.



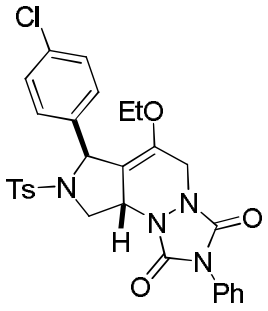
H

8e: 81% yield; yellow solid; m.p. 106–107 °C; IR (film) ν_{max} 3062, 2981, 2914, 1722, 1418, 1163, 663 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) d 7.57 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.42–7.31 (m, 8H), 7.18–7.14 (m, 7H), 6.15 (s, 1H), 5.13 (d, *J* = 6.5 Hz, 1H), 4.80–4.79 (m, 1H), 4.43 (dd, *J* = 15.4, 1.3 Hz, 1H), 3.86 (qd, *J* = 7.0, 2.2 Hz, 1H), 3.79–3.73 (m, 2H), 2.39 (s, 3H), 1.29 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 152.4, 151.8, 143.4, 142.4, 139.3, 138.9, 135.4, 130.6, 129.1, 129.0, 128.9, 128.5, 128.3, 127.9, 127.8, 127.7, 127.6, 127.3, 125.4, 112.7, 68.3, 65.0, 64.2, 61.5, 42.3, 21.5, 15.3; MS (MALDI) calcd. for $C_{35}H_{32}N_4O_5SNa$ $[M + Na]^+$ 643.20, found 643.16; HRMS (ESI) calcd. for $C_{35}H_{33}N_4O_5S$ $[M + H]^+$ 621.2171, found 621.2122.



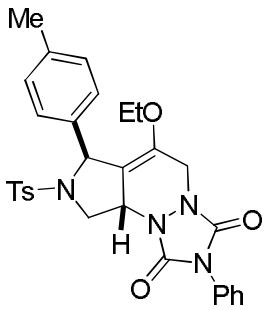
I

8f: 83% yield; white solid; m.p. 89–90 °C; IR (film) ν_{max} 3063, 2980, 2916, 1718, 1420, 1167, 690 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) d 7.79 (d, *J* = 7.5 Hz, 2H), 7.60–7.26 (m, 13H), 5.61 (s, 1H), 4.58 (t, *J* = 7.3 Hz, 1H), 4.41–4.36 (m, 2H), 3.85–3.69 (m, 3H), 3.40 (t, *J* = 9.2 Hz, 1H), 1.23 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 153.6, 151.1, 141.2, 140.2, 136.9, 132.9, 130.6, 129.2, 128.9, 128.4, 128.3, 127.7, 127.6, 126.4, 125.2, 114.2, 64.8, 61.4, 54.4, 52.2, 41.9, 15.1; MS (MALDI) calcd. for $C_{28}H_{26}N_4O_5SNa$ $[M + Na]^+$ 553.15, found 553.16; HRMS (ESI) calcd. for $C_{28}H_{27}N_4O_5S$ $[M + H]^+$ 531.1702, found 531.1713.



8g

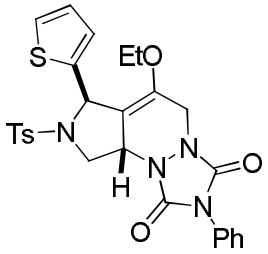
8g: 35% yield; white solid; m.p. 212–213 °C; IR (film) ν_{max} 3064, 2982, 2897, 1719, 1420, 1164, 661 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.68 (d, *J* = 8.2 Hz, 2H), 7.50–7.28 (m, 11H), 5.49 (s, 1H), 4.57–4.54 (m, 1H), 4.41 (dt, *J* = 15.5, 2.0 Hz, 1H), 4.37 (dd, *J* = 9.3, 7.2 Hz, 1H), 3.87 (d, *J* = 15.4 Hz, 1H), 3.79 (qd, *J* = 7.0, 2.2 Hz, 1H), 3.74 (qd, *J* = 7.0, 2.2 Hz, 1H), 3.29 (t, *J* = 9.2 Hz, 1H), 2.44 (s, 3H), 1.23 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 153.6, 151.2, 144.0, 141.5, 139.1, 133.5, 133.4, 130.6, 129.6, 129.2, 128.5, 128.4, 127.9, 127.8, 125.2, 114.6, 64.7, 60.8, 54.2, 52.3, 41.9, 21.5, 15.1; MS (MALDI) calcd. for $C_{29}H_{27}ClN_4O_5SNa$ $[M + Na]^+$ 601.13, found 601.16.



8h

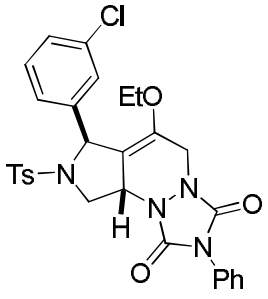
8h: 53% yield; white solid; m.p. 195–196 °C; IR (film) ν_{max} 3055, 2981, 2918, 1718, 1420, 1164, 665 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.69 (d, *J* = 8.2 Hz, 2H), 7.48–7.44 (m, 4H), 7.40–7.36 (m, 1H), 7.30–7.28 (m, 4H), 7.13 (d, *J* = 7.9 Hz, 2H), 5.53 (s, 1H), 4.60–4.57 (m, 1H), 4.38 (dt, *J* = 15.9, 2.0 Hz, 1H), 4.36 (dd, *J* = 9.4, 7.2 Hz, 1H), 3.84 (dq, *J* = 15.4, 1.1 Hz, 1H), 3.77 (qd, *J* = 6.7, 2.1 Hz, 1H), 3.71 (qd, *J* = 6.7, 2.1 Hz, 1H), 3.32 (t, *J* = 9.2 Hz, 1H), 2.43 (s, 3H), 2.34 (s, 3H), 1.23 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 153.6, 151.1, 143.7, 141.0, 137.5, 137.3, 133.8, 130.6, 129.5, 129.2, 129.1, 128.4, 127.8, 126.3, 125.2, 115.4, 64.8,

61.2, 54.4, 52.2, 42.0, 21.5, 21.0, 15.1; MS (MALDI) calcd. for $C_{30}H_{30}N_4O_5SNa$ $[M + Na]^+$ 581.18, found 581.16; HRMS (ESI) calcd. for $C_{30}H_{31}N_4O_5S$ $[M + H]^+$ 559.2015, found 559.2031.



8i

8i: 75% yield; yellow solid; m.p. 104–105 °C; IR (film) ν_{max} 3065, 2981, 1718, 1421, 1164, 663 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) d 7.68 (d, *J* = 8.0 Hz, 2H), 7.45–7.44 (m, 4H), 7.38–7.35 (m, 1H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 4.8 Hz, 1H), 7.07 (d, *J* = 2.9 Hz, 1H), 6.93 (t, *J* = 4.2 Hz, 1H), 5.89 (s, 1H), 4.63 (t, *J* = 7.3 Hz, 1H), 4.42 (d, *J* = 15.4 Hz, 1H), 4.26 (dd, *J* = 9.1, 7.5 Hz, 1H), 3.84 (d, *J* = 15.6 Hz, 1H), 3.81–3.73 (m, 2H), 3.33 (t, *J* = 9.1 Hz, 1H), 2.40 (s, 3H), 1.23 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 153.6, 151.2, 144.6, 143.9, 141.6, 134.0, 130.7, 129.6, 129.2, 128.3, 127.8, 126.7, 125.2, 125.1, 125.0, 114.2, 65.0, 57.0, 54.4, 52.0, 42.0, 21.5, 15.1; MS (MALDI) calcd. for $C_{27}H_{26}N_4O_5S_2Na$ $[M + Na]^+$ 573.12, found 573.16; HRMS (ESI) calcd. for $C_{27}H_{27}N_4O_5S_2$ $[M + H]^+$ 551.1423, found 551.1404.



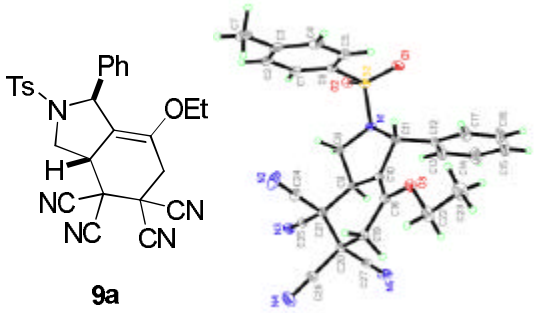
8j

8j: 40% yield; yellow solid; m.p. 143–144 °C; IR (film) ν_{max} 3063, 2981, 1718, 1420, 1164, 661 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) d 7.68 (d, *J* = 8.1 Hz, 2H), 7.47–7.21 (m, 11H), 5.48 (s, 1H), 4.55 (t, *J* = 7.4 Hz, 1H), 4.41–4.36 (m, 2H), 3.85 (d, *J* = 15.4 Hz, 1H), 3.82–3.69 (m, 2H), 3.30 (t, *J* = 9.1 Hz, 1H), 2.42 (s, 3H), 1.24 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 153.6,

151.1, 144.1, 142.6, 141.6, 134.2, 133.5, 130.6, 129.7, 129.6, 129.2, 128.4, 127.8, 127.7, 126.6, 125.2, 124.6, 114.3, 64.6, 60.8, 54.2, 52.4, 41.9, 21.5, 15.1; MS (MALDI) calcd. for $C_{29}H_{27}ClN_4O_5SNa$ $[M + Na]^+$ 601.13, found 601.11.

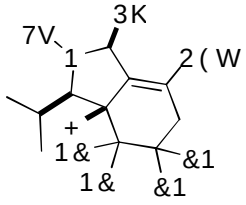
General Procedure for the Synthesis of 9

The diene (**5**, 0.5 mmol) in DCM (0.5 mL) was added dropwise to a solution of tetracyanoethylene (2.0 eq.) in DCM (2.0 mL) at 0 °C under an Ar atmosphere. After the reaction had reached completion (30–60 min, TLC), the resulting mixture was concentrated and the crude residue purified through flash column chromatography (SiO_2; 25–40% EtOAc in hexanes) to afford the product.



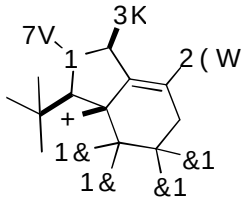
9a

9a: 57% yield; yellow solid; m.p. 156–157 °C; IR (film) ν_{max} 3032, 2984, 2254, 1710, 1354, 1164 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) d 7.57 (d, *J* = 8.2 Hz, 2H), 7.32–7.22 (m, 7H), 5.41 (d, *J* = 1.3 Hz, 1H), 4.21 (dd, *J* = 9.6, 7.7 Hz, 1H), 3.87–3.84 (m, 1H), 3.70–3.59 (m, 2H), 3.48 (t, *J* = 9.6 Hz, 1H), 3.17 (d, *J* = 17.7 Hz, 1H), 3.08 (ddd, *J* = 17.7, 3.1, 1.8 Hz, 1H), 2.40 (s, 3H), 1.11 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 144.4, 140.0, 139.0, 133.6, 129.7, 128.5, 128.1, 127.6, 126.9, 115.5, 110.0, 109.6, 109.4, 107.6, 65.0, 63.2, 50.3, 42.0, 40.6, 39.4, 32.0, 21.5, 14.7; MS (MALDI) calcd. for $C_{27}H_{23}N_5O_3SNa$ $[M + Na]^+$ 520.14, found 520.13.



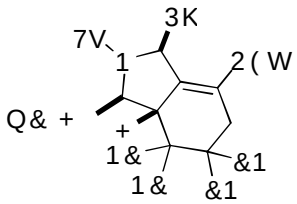
E

9b: 61% yield; white solid; m.p. 171–172 °C; IR (film) ν_{max} 3058, 2968, 2928, 2252, 1713, 1351, 1162 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) d 7.82 (d, *J* = 8.2 Hz, 2H), 7.33–7.28 (m, 7H), 5.82 (s, 1H), 4.03 (dd, *J* = 7.0, 4.0 Hz, 1H), 3.85 (qd, *J* = 7.0, 2.0 Hz, 1H), 3.50 (qd, *J* = 7.0, 2.0 Hz, 1H), 3.37–3.35 (m, 1H), 3.29 (d, *J* = 17.5 Hz, 1H), 3.12 (dd, *J* = 17.5, 3.2 Hz, 1H), 2.42 (s, 3H), 2.02–1.95 (m, 1H), 1.22 (t, *J* = 7.0 Hz, 3H), 1.00 (d, *J* = 6.9 Hz, 3H), 0.84 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 144.5, 140.0, 137.1, 134.4, 129.9, 128.7, 128.4, 128.1, 126.5, 113.1, 110.6, 110.1, 109.9, 108.0, 69.5, 65.0, 61.8, 46.0, 41.5, 40.8, 33.6, 31.7, 21.4, 19.6, 19.0, 15.2; MS (MALDI) calcd. for $C_{30}H_{29}N_5O_3SNa$ $[M + Na]^+$ 562.19, found 562.17; HRMS (ESI) calcd. for $C_{30}H_{30}N_5O_3S$ $[M + H]^+$ 540.2069, found 540.2076.



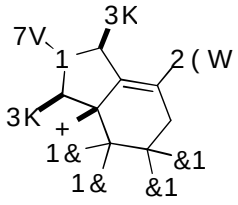
F

9c: 75% yield; white solid; decomposed at 230 °C; IR (film) ν_{max} 3062, 2980, 2251, 1702, 1346, 1160 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) d 7.91 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.25–7.23 (m, 3H), 6.99–6.97 (m, 2H), 5.79 (s, 1H), 4.49 (d, *J* = 5.5 Hz, 1H), 3.86 (qd, *J* = 7.0, 2.2 Hz, 1H), 3.62–3.60 (m, 1H), 3.56 (qd, *J* = 7.0, 2.2 Hz, 1H), 3.35 (d, *J* = 17.5 Hz, 1H), 3.24 (dd, *J* = 17.5, 3.1 Hz, 1H), 2.46 (s, 3H), 1.19 (t, *J* = 7.0 Hz, 3H), 0.82 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) d 144.5, 140.7, 137.2, 135.2, 129.8, 129.1, 128.7, 127.9, 126.6, 113.8, 111.4, 110.3, 110.2, 108.5, 71.8, 64.9, 62.0, 44.6, 42.4, 41.8, 35.4, 31.6, 28.2, 21.5, 15.2; MS (MALDI) calcd. for $C_{31}H_{31}N_5O_3SNa$ $[M + Na]^+$ 576.20, found 576.21; HRMS (ESI) calcd. for $C_{31}H_{32}N_5O_3S$ $[M + H]^+$ 554.2226, found 554.2220.



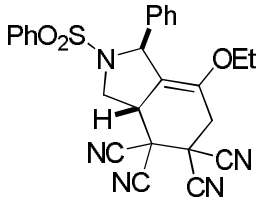
G

9d: 57% yield; white solid; m.p. 110–111 °C; IR (film) ν_{max} 3065, 2930, 2861, 2256, 1714, 1351, 1164 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) d 7.72 (d, *J* = 8.2 Hz, 2H), 7.41–7.28 (m, 7H), 5.74 (s, 1H), 4.07–4.04 (m, 1H), 3.86 (qd, *J* = 7.0, 2.0 Hz, 1H), 3.52 (qd, *J* = 7.0, 2.0 Hz, 1H), 3.38–3.37 (m, 1H), 3.22 (d, *J* = 17.5 Hz, 1H), 3.10 (dd, *J* = 17.5, 2.9 Hz, 1H), 2.40 (s, 3H), 2.11–2.04 (m, 1H), 1.77–1.72 (m, 1H), 1.33–1.18 (m, 6H), 1.20 (t, *J* = 7.0 Hz, 3H), 0.82 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 144.4, 139.5, 138.0, 134.2, 129.8, 128.7, 128.1, 128.0, 126.6, 113.6, 110.0, 109.8, 109.6, 107.8, 65.1, 63.8, 62.0, 46.1, 40.8, 40.2, 34.2, 32.0, 31.3, 23.5, 22.2, 21.4, 15.0, 13.8; MS (MALDI) calcd. for $C_{32}H_{33}N_5O_3SNa$ $[M + Na]^+$ 590.22, found 590.21.



H

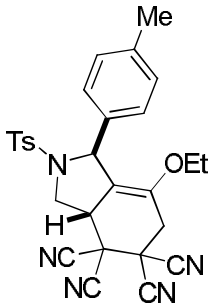
9e: 46% yield; white solid; m.p. 234–235 °C; IR (film) ν_{max} 3033, 2984, 2895, 2251, 1712, 1356, 1164 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) d 7.52 (d, *J* = 7.4 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.39–7.34 (m, 2H), 7.29–7.28 (m, 4H), 7.05 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 5.94 (d, *J* = 1.1 Hz, 1H), 4.78 (d, *J* = 9.8 Hz, 1H), 3.80–3.74 (m, 2H), 3.69 (ddd, *J* = 9.8, 4.1, 2.4 Hz, 1H), 3.20 (s, 2H), 2.32 (s, 3H), 1.23 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 143.7, 139.7, 139.6, 135.5, 134.8, 129.7, 129.1, 129.0, 128.8, 128.2, 128.0, 127.4, 127.3, 113.9, 109.8, 109.4, 108.2, 108.0, 68.1, 65.1, 62.8, 51.6, 40.0, 32.2, 21.4, 14.9; MS (MALDI) calcd. for $C_{33}H_{27}N_5O_3SNa$ $[M + Na]^+$ 596.17, found 596.23.



9f

9f: 58% yield; green solid; m.p. 176–177 °C; IR (film) ν_{max} 3064, 2984, 2894, 2254, 1710, 1355, 1168 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) d 7.68–7.66 (m, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.28–7.25 (m, 5H), 5.46 (d, *J* = 1.5 Hz, 1H), 4.23 (dd, *J* = 9.4, 7.7 Hz, 1H), 3.89–

3.84 (m, 1H), 3.72–3.62 (m, 2H), 3.57–3.50 (m, 1H), 3.17 (dt, *J* = 17.7, 1.7 Hz, 1H), 3.10 (ddd, *J* = 17.7, 3.4, 1.8 Hz, 1H), 1.13 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 140.0, 138.8, 136.8, 133.3, 129.1, 128.6, 128.2, 127.4, 126.9, 115.5, 110.0, 109.6, 109.4, 107.6, 65.0, 63.3, 50.3, 42.1, 40.6, 39.3, 32.1, 14.8; MS (MALDI) calcd. for $C_{26}H_{21}N_5O_3SNa$ $[M + Na]^+$ 506.12, found 506.10; HRMS (ESI) calcd. for $C_{26}H_{25}N_6O_3S$ $[M + NH_4]^+$ 501.1709, found 501.1715.

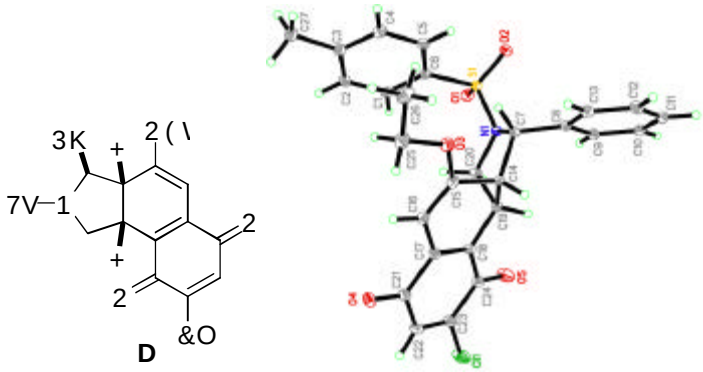


9g

9g: 37% yield; yellow solid; m.p. 114–115 °C; IR (film) ν_{max} 3027, 2984, 2921, 2255, 1710, 1353, 1165 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.58 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 5.37 (s, 1H), 4.21 (dd, *J* = 9.2, 7.7 Hz, 1H), 3.89–3.86 (m, 1H), 3.70–3.60 (m, 2H), 3.46 (t, *J* = 9.2 Hz, 1H), 3.17 (d, *J* = 17.8 Hz, 1H), 3.07 (d, *J* = 17.8 Hz, 1H), 2.40 (s, 3H), 2.31 (s, 3H), 1.11 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 144.4, 139.9, 137.8, 136.2, 133.5, 129.7, 129.2, 127.6, 126.8, 115.6, 110.1, 109.8, 109.4, 107.7, 65.0, 63.1, 50.4, 42.0, 40.7, 39.4, 31.9, 21.5, 21.0, 14.8; MS (MALDI) calcd. for $C_{28}H_{25}N_5O_3SNa$ $[M + Na]^+$ 534.16, found 534.20.

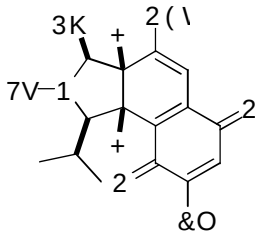
General Procedure for the Synthesis of 10a - d

Toluene (2.0 mL) was added to a mixture of the diene (**5**, 0.5 mmol) and 2,6-dichlorobenzoquinone or benzoquinone (4.0 eq.) under an Ar atmosphere. The mixture was then stirred at 80 °C. After the reaction had reached completion (2–5 h, TLC), the mixture was concentrated and the crude residue purified through flash column chromatography (SiO_2; 25% EtOAc in hexanes) to afford the product.



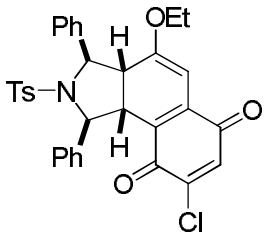
D

10a: 60% yield; deep-blue solid; m.p. 152–153 °C; IR (film) ν_{max} 3070, 2985, 2939, 1659, 1551, 1165 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.64 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 7.4 Hz, 2H), 7.35 (d, *J* = 7.4 Hz, 2H), 7.28–7.23 (m, 3H), 6.86 (s, 1H), 5.45 (d, *J* = 1.3 Hz, 1H), 5.41 (s, 1H), 4.00 (dd, *J* = 9.3, 8.3 Hz, 1H), 3.90 (qd, *J* = 7.0, 2.4 Hz, 1H), 3.77 (td, *J* = 9.8, 8.3 Hz, 1H), 3.59 (qd, *J* = 7.0, 2.4 Hz, 1H), 3.18 (t, *J* = 9.8 Hz, 1H), 3.08 (d, *J* = 9.3 Hz, 1H), 2.41 (s, 3H), 1.39 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 183.4, 177.4, 163.8, 144.9, 143.6, 141.9, 137.9, 134.4, 132.1, 129.4, 128.5, 127.6, 127.4, 126.6, 125.9, 89.1, 65.9, 65.1, 53.1, 51.6, 34.4, 21.5, 14.0; MS (MALDI) calcd. for $C_{27}H_{24}ClNO_5SNa$ $[M + Na]^+$ 532.10, found 532.08; HRMS (ESI) calcd. for $C_{27}H_{25}ClNO_5S$ $[M + H]^+$ 510.1142, found 510.1153.



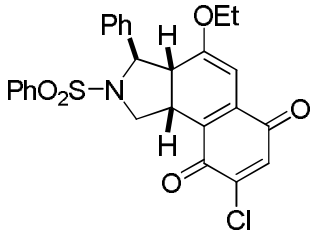
E

10b: 68% yield; deep-blue solid; m.p. 224–225 °C; IR (film) ν_{max} 3060, 2980, 2929, 1658, 1538, 1165 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.57 (d, *J* = 8.2 Hz, 2H), 7.40–7.34 (m, 4H), 7.31–7.28 (m, 1H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.70 (s, 1H), 5.48 (s, 1H), 4.45 (d, *J* = 9.6 Hz, 1H), 4.29 (d, *J* = 8.4 Hz, 1H), 3.87 (q, *J* = 7.0 Hz, 2H), 3.46 (d, *J* = 9.3 Hz, 1H), 3.01 (t, *J* = 9.4 Hz, 1H), 2.34 (s, 3H), 2.11–2.04 (m, 1H), 1.36 (d, *J* = 6.9 Hz, 3H), 1.25 (d, *J* = 6.6 Hz, 3H), 1.12 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 183.0, 177.9, 167.1, 145.5, 143.6, 141.4, 139.1, 133.8, 130.9, 129.4, 128.3, 127.6, 126.6, 126.1, 87.9, 73.6, 72.0, 64.8, 50.0, 43.8, 35.0, 21.2, 20.9, 20.0, 13.7; MS (MALDI) calcd. for $C_{30}H_{30}ClNO_5SNa$ $[M + Na]^+$ 574.14, found 574.10.



10c

10c: 50% yield; deep-blue solid; m.p. 102–103 °C; IR (film) ν_{max} 3063, 3027, 2983, 1659, 1542, 1166 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.59 (d, *J* = 7.5 Hz, 2H), 7.52–7.48 (m, 4H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.35–7.29 (m, 4H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.80 (s, 1H), 5.57 (s, 1H), 5.31 (d, *J* = 4.0 Hz, 1H), 4.84 (d, *J* = 7.4 Hz, 1H), 3.92 (qd, *J* = 7.0, 2.4 Hz, 1H), 3.80 (t, *J* = 8.0 Hz, 1H), 3.73 (qd, *J* = 7.0, 2.4 Hz, 1H), 3.17 (dd, *J* = 8.5, 4.3 Hz, 1H), 2.39 (s, 3H), 1.30 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 183.2, 176.7, 165.3, 145.0, 143.6, 141.3, 139.6, 138.6, 133.8, 131.6, 129.2, 128.5, 128.2, 128.1, 128.0, 127.6, 127.2, 126.7, 125.6, 88.9, 68.9, 68.7, 65.2, 50.1, 45.6, 21.5, 14.0; MS (MALDI) calcd. for $C_{33}H_{28}ClNO_5SNa$ $[M + Na]^+$ 608.13, found 608.17.

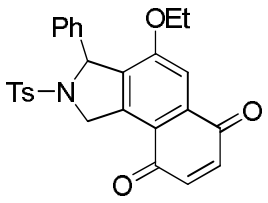


10d

10d: 52% yield; deep-blue solid; m.p. 128–129 °C; IR (film) ν_{max} 3060, 2983, 2936, 1658, 1549, 1348, 1166 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.77–7.75 (m, 2H), 7.59–7.55 (m, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.40 (d, *J* = 7.3 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.27 (t, *J* = 7.3 Hz, 1H), 6.86 (s, 1H), 5.47 (s, 1H), 5.45 (d, *J* = 1.5 Hz, 1H), 4.02 (dd, *J* = 9.1, 8.4 Hz, 1H), 3.89 (qd, *J* = 7.0, 2.4 Hz, 1H), 3.79 (td, *J* = 9.8, 7.4 Hz, 1H), 3.59 (qd, *J* = 7.0, 2.4 Hz, 1H), 3.16 (t, *J* = 9.8 Hz, 1H), 3.09 (d, *J* = 9.2 Hz, 1H), 1.04 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 183.2, 177.4, 163.6, 144.8, 141.7, 137.9, 137.2, 132.7, 132.2, 128.7, 128.5, 127.5, 127.4, 126.5, 125.8, 89.1, 65.8, 65.1, 53.0, 51.6, 34.1, 14.1; MS (MALDI) calcd. for $C_{26}H_{22}ClNO_5SNa$ $[M + Na]^+$ 518.08, found 518.04.

Compound 10e

A solution of the diene **5a** (0.5 mmol) and benzoquinone (4.0 eq.) in toluene (2.0 mL) was stirred at 80 °C under Ar. After the reaction had reached completion (TLC), the mixture was concentrated and the crude product dissolved in a minimal amount of $CHCl_3$. Silica gel (2 g) purged in triethylamine was added and the mixture stirred at room temperature overnight.[1] After evaporating the solvent, the crude residue was purified through flash column chromatography (SiO_2; 20% EtOAc in hexanes) to afford the product.



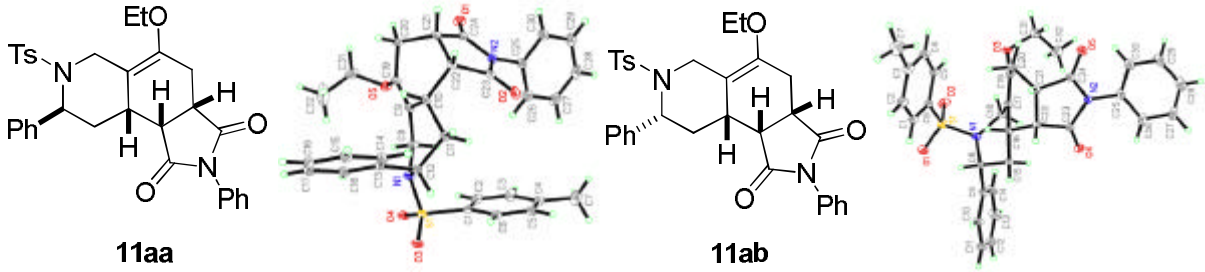
10e

10e: 56% yield; yellow solid; decomposed at 180 °C; IR (film) ν_{max} 3062, 2985, 2931, 1666, 1589, 1335, 1088 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) d 7.45 (d, *J* = 8.2 Hz, 2H), 7.34 (s, 1H), 7.21–7.10 (m, 7H), 6.90 (t, *J* = 2.5 Hz, 2H), 6.11 (d, *J* = 2.9 Hz, 1H), 5.28 (d, *J* = 16.8 Hz, 1H), 5.11 (dd, *J* = 16.8, 3.1 Hz, 1H), 4.09 (qd, *J* = 7.0, 2.3 Hz, 1H), 3.93 (qd, *J* = 7.0, 2.3 Hz, 1H), 2.33 (s, 3H), 1.19 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 184.55, 184.54, 157.8, 143.0, 139.8, 139.5, 138.8, 137.8, 135.9, 135.5, 134.7, 129.3, 128.0, 127.8, 127.7, 127.0, 120.2, 108.6, 66.6, 64.6, 54.9, 21.3, 14.0; MS (MALDI) calcd. for $C_{27}H_{24}NO_5S$ $[M + H]^+$ 474.14, found 474.12; HRMS (ESI) calcd. for $C_{27}H_{25}NO_5S$ $[M + H]^+$ 474.1375, found 474.1368.

General Procedure for the Synthesis of 11

A solution of 5–15% MeOH in DCM (1.5 mL) was added to a mixture of the diene (**6**, 0.5 mmol) and maleimide (4.0 eq.) under an Ar atmosphere and then the mixture was stirred at room temperature. After the reaction had reached completion (16–48 h, TLC), the mixture was concentrated and the crude residue purified through flash column chromatography (SiO_2; 30–50% EtOAc in hexanes) to afford the product.

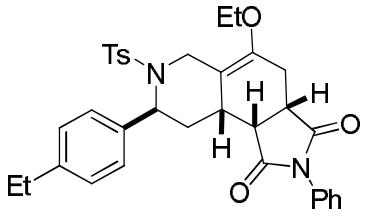
[1] Kaliappan, K. P.; Ravikumar, V. *Org. Biomol. Chem*. **2005**, *3*, 848.



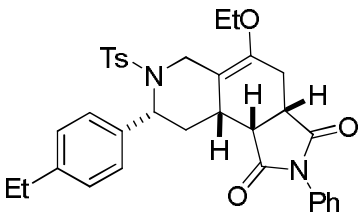
84% yield; dr = 2:1 (**11aa**:**11ab**)

11aa: white solid; m.p. 196–197 °C; IR (film) ν_{max} 3062, 2977, 1709, 1384, 1161, 693 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.66 (d, *J* = 8.2 Hz, 2H), 7.46-7.42 (m, 2H), 7.40-7.37 (m, 1H), 7.31-7.30 (m, 4H), 7.26-7.22 (m, 3H), 7.11-7.08 (m, 2H), 5.15 (dd, *J* = 4.7, 2.8 Hz, 1H), 4.69 (d, *J* = 13.6 Hz, 1H), 3.84 (qd, *J* = 7.0, 2.6 Hz, 1H), 3.77 (qd, *J* = 7.0, 2.6 Hz, 1H), 3.46 (d, *J* = 13.6 Hz, 1H), 3.20 (t, *J* = 7.1 Hz, 1H), 2.98-2.74 (m, 2H), 2.51 (td, *J* = 13.6, 4.9 Hz, 1H), 2.39 (s, 3H), 2.26-2.17 (m, 2H), 2.12-2.08 (m, 1H), 1.26 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 177.8, 176.3, 147.3, 143.4, 141.8, 134.9, 131.5, 129.6, 129.1, 128.7, 128.2, 127.3, 126.8, 126.2, 126.1, 111.3, 64.6, 56.6, 42.5, 40.4, 39.6, 30.7, 29.7, 24.9, 21.4, 15.2; MS (MALDI) calcd. for $C_{32}H_{32}N_2O_5SNa$ $[M + Na]^+$ 579.19, found 579.05; HRMS (ESI) calcd. for $C_{32}H_{33}N_2O_5S$ $[M + H]^+$ 557.2110, found 557.2102.

11ab: white solid; m.p. 139–140 °C; IR (film) ν_{max} 3062, 2978, 1713, 1381, 1165, 694 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.71 (d, *J* = 8.2 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.38–7.31 (m, 5H), 7.25–7.21 (m, 3H), 7.18–7.16 (m, 2H), 5.05 (d, *J* = 16.1 Hz, 1H), 4.61 (dd, *J* = 11.8, 6.1 Hz, 1H), 3.91 (qd, *J* = 7.0, 2.6 Hz, 1H), 3.76 (d, *J* = 16.1 Hz, 1H), 3.70 (qd, *J* = 7.0, 2.6 Hz, 1H), 3.20–3.16 (m, 1H), 3.06 (dd, *J* = 8.9, 6.8 Hz, 1H), 2.89 (d, *J* = 15.5 Hz, 1H), 2.46 (s, 3H), 2.33–2.26 (m, 2H), 1.80–1.70 (m, 2H), 1.30 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 178.0, 175.8, 146.6, 143.4, 142.8, 136.1, 131.5, 129.0, 128.9, 128.6, 128.4, 127.6, 127.1, 126.1, 125.6, 112.2, 64.5, 59.1, 42.3, 39.8, 39.4, 33.7, 33.2, 24.2, 21.5, 15.3; MS (MALDI) calcd. for $C_{32}H_{32}N_2O_5SNa$ $[M + Na]^+$ 579.19, found 579.23; HRMS (ESI) calcd. for $C_{32}H_{33}N_2O_5S$ $[M + H]^+$ 557.2110, found 557.2112.



11ba

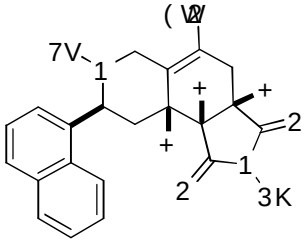


11bb

80% yield; dr = 1.3:1 (**11ba**:**11bb**)

11ba: yellow solid; m.p. 110–111 °C; IR (film) ν_{max} 2965, 2927, 1712, 1383, 1157, 664 cm^{-1}; ^1H NMR (500 MHz, acetone-d_6) d 7.75 (d, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.42–7.38 (m, 3H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 5.26 (s, 1H), 4.65 (d, *J* = 13.6 Hz, 1H), 3.90 (qd, *J* = 7.0, 3.0 Hz, 1H), 3.81 (qd, *J* = 7.0, 3.0 Hz, 1H), 3.59 (d, *J* = 13.6 Hz, 1H), 3.36 (t, *J* = 7.3 Hz, 1H), 3.10 (dd, *J* = 8.5, 6.5 Hz, 1H), 2.88 (d, *J* = 15.5 Hz, 1H), 2.66 (q, *J* = 7.6 Hz, 2H), 2.48–2.42 (m, 1H), 2.40 (s, 3H), 2.30–2.22 (m, 2H), 2.17–2.12 (m, 1H), 1.26 (t, *J* = 7.6 Hz, 3H), 1.25 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, acetone-d_6) d 177.9, 176.4, 147.6, 143.3, 142.3, 139.6, 135.5, 132.6, 129.6, 128.6, 128.0, 127.4, 127.3, 126.6, 126.3, 111.3, 64.1, 56.4, 42.5, 40.6, 39.8, 30.3, 29.5, 28.0, 24.6, 20.5, 15.1, 14.8; MS (MALDI) calcd. for $C_{34}H_{36}N_2O_5SNa$ $[M + Na]^+$ 607.22, found 607.23; HRMS (ESI) calcd. for $C_{34}H_{37}N_2O_5S$ $[M + H]^+$ 585.2423, found 585.2413.

11bb: white solid; m.p. 103–104 °C; IR (film) ν_{max} 2966, 2924, 1709, 1384, 1159, 692 cm^{-1}; ^1H NMR (500 MHz, acetone-d_6) d 7.77 (d, *J* = 8.1 Hz, 2H), 7.45–7.36 (m, 7H), 7.22–7.19 (m, 4H), 4.99 (d, *J* = 16.2 Hz, 1H), 4.67 (t, *J* = 9.0 Hz, 1H), 3.94–3.88 (m, 2H), 3.72 (qd, *J* = 7.0, 3.0 Hz, 1H), 3.30 (t, *J* = 7.2 Hz, 1H), 3.16 (dd, *J* = 8.8, 7.1 Hz, 1H), 2.80 (d, *J* = 15.4 Hz, 1H), 2.65 (q, *J* = 7.6 Hz, 2H), 2.47 (s, 3H), 2.30–2.27 (m, 2H), 2.09–2.07 (m, 2H), 1.26 (t, *J* = 7.0 Hz, 3H), 1.24 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, acetone-d_6) d 178.1, 175.9, 146.7, 143.0, 142.5, 142.1, 136.4, 132.6, 128.9, 128.6, 128.0, 127.53, 127.50, 126.6, 125.7, 112.0, 63.9, 59.0, 42.32, 40.0, 39.3, 33.5, 33.4, 28.1, 23.9, 20.5, 15.2, 14.8; MS (MALDI) calcd. for $C_{34}H_{36}N_2O_5SNa$ $[M + Na]^+$ 607.22, found 607.17; HRMS (ESI) calcd. for $C_{34}H_{37}N_2O_5S$ $[M + H]^+$ 585.2423, found 585.2408.



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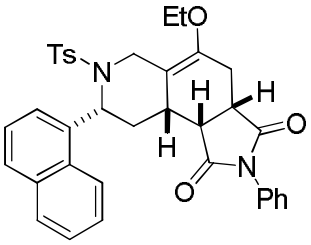
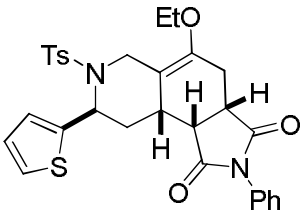


11cb

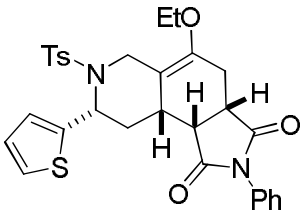
67% yield; dr = 2.5:1 (**11ca**:**11cb**)

11ca: yellow solid; m.p. 154–155 °C; IR (film) ν_{max} 3060, 2974, 1709, 1386, 1161, 654 cm^{-1}; ^1H NMR (500 MHz, acetone-d_6) d 8.22 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.76–7.71 (m, 3H), 7.57 (t, *J* = 7.9 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.41–7.30 (m, 6H), 7.08 (d, *J* = 8.7 Hz, 2H), 6.04 (s, 1H), 4.89 (d, *J* = 13.2 Hz, 1H), 3.88 (qd, *J* = 7.0, 3.0 Hz, 1H), 3.77 (qd, *J* = 7.0, 3.0 Hz, 1H), 3.43 (d, *J* = 13.2 Hz, 1H), 3.14–3.10 (m, 1H), 2.82–2.77 (m, 2H), 2.67 (td, *J* = 13.9, 5.0 Hz, 1H), 2.38 (s, 3H), 2.20–2.10 (m, 2H), 2.03–2.01 (m, 1H), 1.23 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, acetone-d_6) d 178.0, 176.5, 148.1, 143.5, 138.0, 135.0, 133.9, 132.6, 129.8, 129.6, 128.9, 128.6, 128.1, 127.4, 127.3, 126.7, 126.2, 125.4, 124.9, 124.6, 122.6, 111.4, 64.3, 53.8, 42.7, 40.7, 39.9, 30.2, 29.0, 25.1, 20.5, 14.8; MS (MALDI) calcd. for $C_{36}H_{34}N_2O_5SNa$ $[M + Na]^+$ 629.21, found 629.19; HRMS (ESI) calcd. for $C_{36}H_{38}N_3O_5S$ $[M + NH_4]^+$ 624.2532, found 624.2496.

11cb: white solid; decomposed at 230 °C; IR (film) ν_{max} 3060, 2977, 1708, 1385, 1159, 692 cm^{-1}; ^1H NMR (500 MHz, acetone-d_6) d 8.24 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.78–7.77 (m, 4H), 7.56–7.48 (m, 3H), 7.40–7.28 (m, 5H), 7.10 (d, *J* = 7.5 Hz, 2H), 5.46 (dd, *J* = 12.4, 5.1 Hz, 1H), 5.07 (d, *J* = 16.2 Hz, 1H), 4.05 (d, *J* = 16.2 Hz, 1H), 3.88 (qd, *J* = 7.0, 2.8 Hz, 1H), 3.69 (qd, *J* = 7.0, 2.8 Hz, 1H), 3.31–3.27 (m, 1H), 3.17 (dd, *J* = 8.7, 7.1 Hz, 1H), 2.78 (d, *J* = 17.0 Hz, 1H, overlap with H_2O/HDO peak), 2.54 (dt, *J* = 14.3, 4.1 Hz, 1H), 2.45 (s, 3H), 2.22 (dd, *J* = 26.9, 13.6 Hz, 1H), 1.97–1.94 (m, 1H), 1.75–1.70 (m, 1H), 1.24 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, acetone-d_6) d 178.1, 175.8, 146.8, 143.1, 140.8, 136.2, 133.8, 132.6, 129.7, 129.0, 128.7, 128.5, 128.0, 127.6, 127.1, 126.6, 126.0, 125.6, 125.2, 123.0, 122.4, 112.2, 63.9, 56.0, 42.3, 40.0, 39.7, 33.8, 32.9, 23.9, 20.5, 14.8; MS (MALDI) calcd. for $C_{36}H_{34}N_2O_5SNa$ $[M + Na]^+$ 629.21, found 629.24; HRMS (ESI) calcd. for $C_{36}H_{35}N_2O_5S$ $[M + H]^+$ 607.2266, found 607.2220.



11da

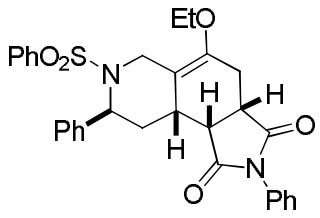


11db

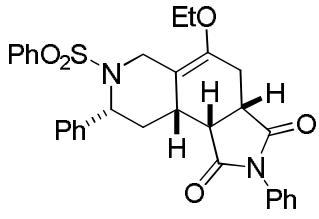
80% yield; dr = 6:1 (**11da**:**11db**)

11da: white solid; m.p. 189–190 °C; IR (film) ν_{max} 2974, 1709, 1383, 1161, 667 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.66 (d, *J* = 6.7 Hz, 2H), 7.46–7.43 (m, 2H), 7.40–7.37 (m, 1H), 7.22 (d, *J* = 7.6 Hz, 2H), 7.18–7.17 (m, 1H), 7.10 (d, *J* = 7.6 Hz, 2H), 6.94–6.93 (m, 2H), 5.44 (s, 1H), 4.41 (d, *J* = 14.2 Hz, 1H), 3.85–3.72 (m, 3H), 3.26–3.22 (m, 1H), 3.09–3.05 (m, 1H), 2.94 (dd, *J* = 15.8, 3.8 Hz, 1H), 2.56–2.52 (m, 1H), 2.40–2.33 (m, 4H), 2.25–2.16 (m, 2H), 1.23 (td, *J* = 7.0, 1.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 177.6, 176.3, 147.1, 145.7, 143.6, 135.1, 131.5, 129.6, 129.0, 128.6, 127.3, 126.9, 126.2, 124.3, 124.2, 110.4, 64.5, 53.1, 42.2, 40.3, 39.6, 31.2, 30.0, 24.3, 21.4, 15.2; MS (MALDI) calcd. for $C_{30}H_{30}N_2O_5S_2Na$ $[M + Na]^+$ 585.15, found 585.18; HRMS (ESI) calcd. for $C_{30}H_{31}N_2O_5S_2$ $[M + H]^+$ 563.1674, found 563.1896.

11db: semi-solid; IR (film) ν_{max} 2977, 1709, 1384, 1158, 658 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) d 7.67 (d, *J* = 8.2 Hz, 2H), 7.44–7.33 (m, 3H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.18–7.12 (m, 3H), 7.06 (d, *J* = 3.4 Hz, 1H), 6.93 (dd, *J* = 5.0, 3.4 Hz, 1H), 4.96 (dd, *J* = 10.4, 7.6 Hz, 1H), 4.85 (d, *J* = 16.2 Hz, 1H), 3.85 (qd, *J* = 7.0, 2.7 Hz, 1H), 3.67–3.59 (m, 2H), 3.16–3.11 (m, 1H), 3.03 (dd, *J* = 9.0, 6.8 Hz, 1H), 2.82 (d, *J* = 15.3 Hz, 1H), 2.41 (s, 3H), 2.41–2.38 (m, 2H), 1.71–1.60 (m, 2H), 1.23 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) d 178.1, 176.0, 147.3, 147.3, 143.1, 136.3, 131.6, 129.15, 129.13, 128.8, 127.7, 126.7, 126.2, 124.1, 123.9, 112.0, 64.6, 54.7, 42.3, 39.8, 38.7, 33.1, 33.0, 24.3, 21.6, 15.4; MS (MALDI) calcd. for $C_{30}H_{30}N_2O_5S_2Na$ $[M + Na]^+$ 585.15, found 585.13; HRMS (ESI) calcd. for $C_{30}H_{31}N_2O_5S_2$ $[M + H]^+$ 563.1674, found 563.1671.



11ea

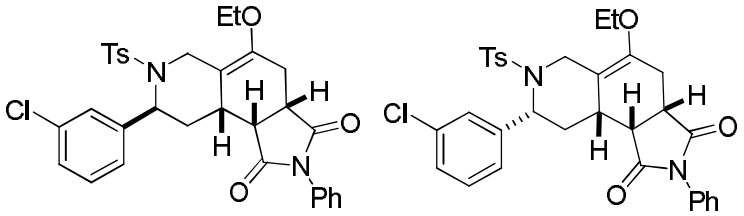


11eb

70% yield; dr = 2:1 (**11ea**:**11eb**)

11ea: semi-solid; IR (film) ν_{max} 3061, 2919, 1712, 1384, 1159, 691 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) d 7.80 (d, *J* = 7.2 Hz, 2H), 7.60–7.39 (m, 6H), 7.34–7.22 (m, 5H), 7.13 (d, *J* = 7.5 Hz, 2H), 5.24 (dd, *J* = 4.4, 2.8 Hz, 1H), 4.76 (d, *J* = 13.6 Hz, 1H), 3.91–3.77 (m, 2H), 3.55 (d, *J* = 13.6 Hz, 1H), 3.21 (t, *J* = 7.3 Hz, 1H), 2.98–2.94 (m, 2H), 2.59 (td, *J* = 13.6, 4.7 Hz, 1H), 2.25–2.13 (m, 3H), 1.29 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 177.8, 176.3, 147.5, 141.6, 138.0, 132.6, 131.6, 129.0, 128.9, 128.6, 128.2, 127.2, 126.9, 126.2, 126.1, 111.0, 64.6, 56.7, 42.5, 40.4, 39.7, 30.8, 29.7, 24.9, 15.2; MS (MALDI) calcd. for $C_{31}H_{30}N_2O_5SNa$ $[M + Na]^+$ 565.18, found 565.14.

11eb: semi-solid; IR (film) ν_{max} 3064, 2936, 1711, 1384, 1158, 692 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) d 7.78 (d, *J* = 7.4 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.43–7.30 (m, 10H), 7.12 (d, *J* = 7.7 Hz, 2H), 5.02 (d, *J* = 16.2 Hz, 1H), 4.58 (dd, *J* = 11.4, 6.5 Hz, 1H), 3.86 (qd, *J* = 7.0, 2.6 Hz, 1H), 3.73 (d, *J* = 16.2 Hz, 1H), 3.65 (qd, *J* = 7.0, 2.6 Hz, 1H), 3.11 (t, *J* = 7.4 Hz, 1H), 3.00 (dd, *J* = 8.8, 6.9 Hz, 1H), 2.82 (d, *J* = 15.4 Hz, 1H), 2.30–2.24 (m, 2H), 1.71–1.63 (m, 2H), 1.25 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 178.0, 175.8, 146.7, 143.2, 139.0, 132.2, 131.5, 129.0, 128.6, 128.4, 128.3, 127.5, 127.2, 126.1, 125.6, 111.8, 64.5, 59.2, 42.2, 39.7, 39.5, 33.7, 33.2, 24.2, 15.3; MS (MALDI) calcd. for $C_{31}H_{30}N_2O_5SNa$ $[M + Na]^+$ 565.18, found 565.11; HRMS (ESI) calcd. for $C_{31}H_{34}N_3O_5S$ $[M + NH_4]^+$ 560.2219, found 560.2226.



11fa **11fb**

70% yield; dr = 1.4:1 (**11fa**:**11fb**)

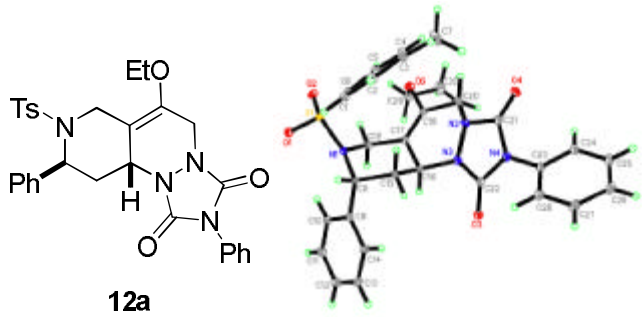
11fa: semi-solid; IR (film) ν_{max} 3064, 2978, 2925, 1713, 1382, 1158, 666 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) d 7.63 (d, *J* = 8.2 Hz, 2H), 7.44–7.35 (m, 3H), 7.26–7.18 (m, 6H), 7.10–7.08 (m, 2H), 5.10 (dd, *J* = 4.3, 2.9 Hz, 1H), 4.69 (d, *J* = 13.6 Hz, 1H), 3.85 (qd, *J* = 7.0, 2.9 Hz, 1H), 3.78 (qd, *J* = 7.0, 2.9 Hz, 1H), 3.42 (d, *J* = 13.6 Hz, 1H), 3.22–3.18 (m, 1H), 2.95 (dd, *J* = 8.8, 6.3 Hz, 2H), 2.53 (td, *J* = 13.6, 4.8 Hz, 1H), 2.39 (s, 3H), 2.18–2.16 (m, 2H), 2.08–2.03 (m, 1H), 1.25 (t,

J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 177.7, 176.2, 147.6, 144.2, 143.6, 134.7, 134.2, 131.5, 129.7, 129.6, 129.0, 128.6, 127.2, 127.1, 126.4, 126.2, 124.5, 110.8, 64.6, 56.2, 42.5, 40.4, 39.6, 30.6, 29.8, 25.0, 21.5, 15.2; MS (MALDI) calcd. for $C_{32}H_{31}ClN_2O_5SNa$ $[M + Na]^+$ 613.15, found 613.17; HRMS (ESI) calcd. for $C_{32}H_{32}ClN_2O_5S$ $[M + H]^+$ 591.1720, found 591.1721.

11fb: semi-solid; IR (film) ν_{max} 3061, 2921, 1712, 1384, 1158, 657 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.65 (d, *J* = 8.1 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.31 (s, 1H), 7.24–7.18 (m, 5H), 7.12 (d, *J* = 7.4 Hz, 2H), 5.01 (d, *J* = 16.2 Hz, 1H), 4.51 (dd, *J* = 11.5, 6.4 Hz, 1H), 3.86 (qd, *J* = 7.0, 2.7 Hz, 1H), 3.71–3.62 (m, 2H), 3.15 (t, *J* = 7.4 Hz, 1H), 3.03 (dd, *J* = 8.8, 6.8 Hz, 1H), 2.85 (d, *J* = 15.4 Hz, 1H), 2.41 (s, 3H), 2.30–2.16 (m, 2H), 1.74–1.65 (m, 2H), 1.25 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 177.9, 175.8, 146.8, 145.4, 143.1, 135.9, 134.3, 131.4, 129.8, 129.03, 129.00, 128.6, 127.5, 127.3, 126.1, 125.9, 123.9, 111.8, 64.6, 58.7, 42.2, 39.7, 39.4, 33.7, 33.1, 24.2, 21.5, 15.3; MS (MALDI) calcd. for $C_{32}H_{31}ClN_2O_5SNa$ $[M + Na]^+$ 613.15, found 613.10; HRMS (ESI) calcd. for $C_{32}H_{32}ClN_2O_5S$ $[M + H]^+$ 591.1720, found 591.1708.

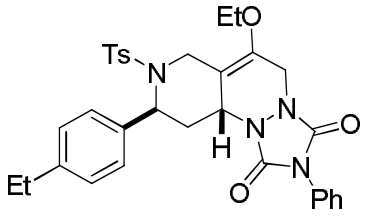
General Procedure for the Synthesis of 12

A solution of the diene (**6**, 0.5 mmol) in DCM (0.5 mL) was added dropwise to a solution of *N*-phenyltriazolinedione (2.0 eq.) in DCM (2.0 mL) at –78 °C under an Ar atmosphere. After the reaction had reached completion (3–5 h, TLC), the mixture was concentrated and the crude residue purified through flash column chromatography (SiO_2; 30–50% EtOAc in hexanes) to afford the product.



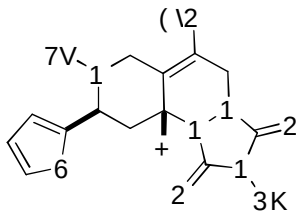
12a

12a: 56% yield; white solid; m.p. 170–171 °C; IR (film) ν_{max} 3055, 2978, 2900, 1713, 1419, 1157, 656 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) d 7.82 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.49–7.45 (m, 4H), 7.40–7.33 (m, 3H), 7.30–7.28 (m, 3H), 5.40 (d, *J* = 3.7 Hz, 1H), 5.15 (d, *J* = 15.5 Hz, 1H), 4.39 (d, *J* = 10.3 Hz, 1H), 4.16 (td, *J* = 15.5, 2.2 Hz, 1H), 3.92–3.78 (m, 3H), 3.36–3.29 (m, 2H), 2.44 (s, 3H), 1.51 (td, *J* = 12.6, 4.8 Hz, 1H), 1.34 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 152.1, 151.5, 143.5, 141.1, 137.6, 136.5, 130.8, 129.5, 129.1, 129.0, 128.2, 127.5, 127.2, 126.7, 125.1, 109.6, 65.9, 54.5, 50.8, 42.0, 38.8, 30.3, 21.5, 15.2; MS (MALDI) calcd. for $C_{30}H_{30}N_4O_5SNa$ $[M + Na]^+$ 581.18, found 581.23; HRMS (ESI) calcd. for $C_{30}H_{31}N_4O_5S$ $[M + H]^+$ 559.2015, found 559.2015.



12b

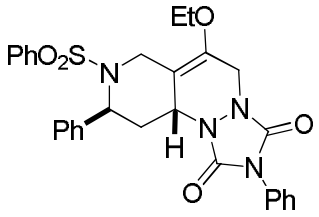
12b: 60% yield; yellow solid; m.p. 110–111 °C; IR (film) ν_{max} 2966, 2923, 1716, 1418, 1158, 663 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) d 7.81 (d, *J* = 8.2 Hz, 2H), 7.48–7.43 (m, 6H), 7.35 (t, *J* = 7.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 5.37 (d, *J* = 2.7 Hz, 1H), 5.14 (d, *J* = 15.5 Hz, 1H), 4.40 (d, *J* = 10.5 Hz, 1H), 4.15 (d, *J* = 15.5 Hz, 1H), 3.91–3.78 (m, 3H), 3.35 (d, *J* = 15.5 Hz, 1H), 3.28 (d, *J* = 12.6 Hz, 1H), 2.62 (q, *J* = 7.6 Hz, 2H), 2.42 (s, 3H), 1.49 (td, *J* = 12.6, 4.9 Hz, 1H), 1.33 (t, *J* = 7.0 Hz, 3H), 1.21 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 152.1, 151.5, 143.6, 143.4, 141.0, 137.7, 133.6, 130.8, 129.4, 129.0, 128.5, 128.1, 127.2, 126.6, 125.1, 109.7, 65.9, 54.4, 50.8, 42.0, 38.8, 30.4, 28.2, 21.5, 15.4, 15.2; MS (MALDI) calcd. for $C_{32}H_{34}N_4O_5SNa$ $[M + Na]^+$ 609.21, found 609.16.



F

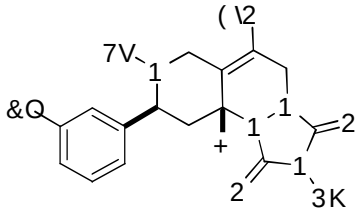
12c: 85% yield; yellow solid; m.p. 117–118 °C; IR (film) ν_{max} 2980, 2930, 1716, 1420, 1160, 664 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) d 7.79 (d, *J* = 8.3 Hz, 2H), 7.48–7.42 (m, 4H), 7.36–7.33

(m, 1H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 5.0 Hz, 1H), 7.09–7.08 (m, 1H), 6.95–6.94 (m, 1H), 5.52 (d, *J* = 4.1 Hz, 1H), 5.13 (d, *J* = 15.4 Hz, 1H), 4.56 (d, *J* = 9.8 Hz, 1H), 4.14 (td, *J* = 15.3, 2.1 Hz, 1H), 3.98 (d, *J* = 15.4 Hz, 1H), 3.90–3.80 (m, 2H), 3.53 (d, *J* = 5.5 Hz, 1H), 3.15 (ddd, *J* = 12.9, 3.9, 1.9 Hz, 1H), 2.42 (s, 3H), 1.66 (td, *J* = 12.5, 5.1 Hz, 1H), 1.33 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 152.0, 151.6, 143.7, 142.1, 141.4, 137.1, 130.8, 129.5, 129.1, 128.2, 127.4, 127.3, 125.8, 125.6, 125.1, 109.3, 65.9, 52.5, 50.8, 42.1, 38.8, 32.4, 21.5, 15.3; MS (MALDI) calcd. for $C_{28}H_{28}N_4O_5S_2Na$ $[M + Na]^+$ 587.14, found 587.12; HRMS (ESI) calcd. for $C_{28}H_{32}N_5O_5S_2$ $[M + NH_4]^+$ 582.1845, found 582.1837.



12d

12d: 70% yield; white solid; m.p. 168–169 °C; IR (film) ν_{max} 3059, 2980, 2896, 1716, 1420, 1161, 639 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.95 (d, *J* = 7.5 Hz, 2H), 7.59–7.37 (m, 12H), 7.28 (t, *J* = 7.3 Hz, 1H), 5.43 (d, *J* = 3.2 Hz, 1H), 5.16 (d, *J* = 15.6 Hz, 1H), 4.39 (d, *J* = 10.3 Hz, 1H), 4.16 (d, *J* = 15.6 Hz, 1H), 3.89–3.79 (m, 3H), 3.37–3.29 (m, 2H), 1.47 (td, *J* = 12.6, 9.0 Hz, 1H), 1.34 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 152.1, 151.5, 141.1, 140.6, 136.4, 132.7, 130.7, 129.1, 129.0, 128.9, 128.2, 127.6, 127.1, 126.6, 125.1, 109.4, 65.8, 54.6, 50.7, 42.0, 38.9, 30.3, 15.3; MS (MALDI) calcd. for $C_{29}H_{28}N_4O_5SNa$ $[M + Na]^+$ 567.17, found 567.15; HRMS (ESI) calcd. for $C_{29}H_{32}N_5O_5S$ $[M + NH_4]^+$ 562.2125, found 562.2115.



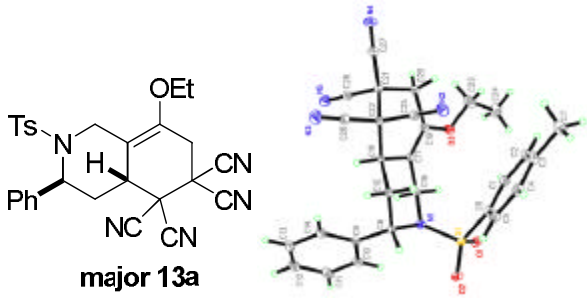
H

12e: 55% yield; white solid; m.p. 193–194 °C; IR (film) ν_{max} 3056, 2980, 2854, 1716, 1420, 1159, 665 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.81 (d, *J* = 8.2 Hz, 2H), 7.51–7.25 (m, 11H), 5.36 (s, 1H), 5.19 (d, *J* = 15.6 Hz, 1H), 4.36 (d, *J* = 11.1 Hz, 1H), 4.18 (d, *J* = 15.6 Hz, 1H), 3.94–3.81 (m, 3H), 3.33 (d, *J* = 15.6 Hz, 1H), 3.25 (ddd, *J* = 11.9, 3.5, 2.1 Hz, 1H), 2.45 (s, 3H),

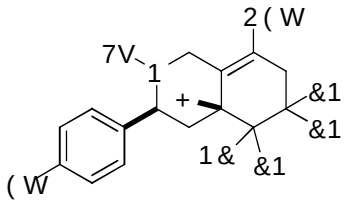
1.51 (td, *J* = 12.7, 4.7 Hz, 1H), 1.36 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 152.1, 151.5, 143.7, 141.3, 138.9, 137.4, 135.2, 130.7, 130.2, 129.5, 129.1, 128.2, 127.8, 127.2, 127.0, 125.1, 124.7, 109.2, 65.9, 54.2, 50.6, 42.0, 38.9, 30.4, 21.5, 15.3; MS (MALDI) calcd. for $C_{30}H_{29}ClN_4O_5SNa$ $[M + Na]^+$ 615.14, found 615.19.

General Procedure for the Synthesis of 13

A solution of the diene (**5**, 0.5 mmol) in DCM (0.5 mL) was added dropwise to a solution of tetracyanoethylene (2.0 eq.) in DCM (2.0 mL) at –78 °C under an Ar atmosphere. After the reaction had reached completion (3–5 h, TLC), the mixture was concentrated and the dr ratio determined using ^{1}H NMR spectroscopy. The crude residue was purified through flash column chromatography (SiO_2; 25% EtOAc in hexanes) to afford the product.

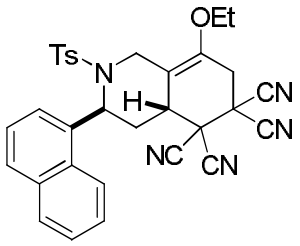


13a: 56% yield; dr > 10:1; white solid; IR (film) ν_{max} 3055, 2985, 2931, 1682, 1342, 1157, 663 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.75 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.39–7.33 (m, 3H), 7.30 (d, *J* = 8.2 Hz, 2H), 5.52 (d, *J* = 4.2 Hz, 1H), 5.14 (d, *J* = 16.6 Hz, 1H), 3.89–3.78 (m, 2H), 3.34 (dd, *J* = 16.6, 1.7 Hz, 1H), 3.17 (d, *J* = 12.5 Hz, 1H), 3.11–3.02 (m, 2H), 2.72 (ddd, *J* = 13.4, 4.0, 2.2 Hz, 1H), 2.39 (s, 3H), 1.78 (td, *J* = 13.1, 1.8 Hz, 1H), 1.36 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 144.4, 139.8, 137.0, 135.0, 130.0, 129.6, 128.1, 126.7, 126.0, 110.3, 110.1, 109.6, 109.4, 108.0, 65.5, 53.5, 43.7, 37.9, 37.7, 36.8, 31.7, 28.1, 21.4, 15.1; MS (MALDI) calcd. for $C_{28}H_{25}N_5O_3SNa$ $[M + Na]^+$ 534.16, found 534.14.



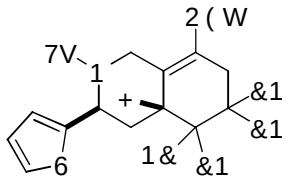
major 13b

13b: 70% yield; dr = 10:1 (^{1}H NMR); semi-solid; IR (film) ν_{max} 2967, 2929, 2252, 1683, 1352, 1161, 663 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.75 (d, *J* = 8.2 Hz, 2H), 7.58 (minor, d, *J* = 8.2 Hz, 0.2H), 7.30–7.25 (m, 6H), 5.48 (d, *J* = 3.5 Hz, 1H), 5.13 (d, *J* = 16.6 Hz, 1H), 5.03 (minor, dd, *J* = 11.2, 7.1 Hz, 0.1H), 4.94 (minor, d, *J* = 18.3 Hz, 0.1H), 3.85–3.77 (m, 2H), 3.34 (d, *J* = 17.8 Hz, 1H), 3.19–3.11 (m, 2H), 3.05–3.01 (m, 1H), 2.71–2.65 (m, 3H), 2.38 (s, 3H), 1.74 (td, *J* = 13.0, 5.1 Hz, 1H), 1.34 (t, *J* = 7.0 Hz, 3H), 1.25 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 144.5, 144.3, 139.9, 137.0, 132.1, 130.0, 129.1, 126.7, 126.1, 110.4, 110.3, 109.5, 109.4, 108.2, 65.4, 53.4, 43.8, 37.8, 37.7, 36.7, 31.5, 28.2, 28.1, 21.4, 15.3, 15.1; MS (MALDI) calcd. for $C_{30}H_{29}N_5O_3SNa$ $[M + Na]^+$ 562.19, found 562.16.



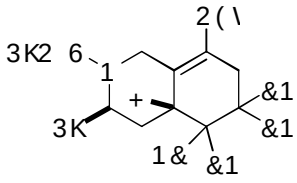
major 13c

13c: 68% yield; dr = 9.1:1 (^{1}H NMR); white solid; IR (film) ν_{max} 3053, 2978, 2919, 2255, 1684, 1341, 1160, 666 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 8.22 (d, *J* = 8.5 Hz, 1H), 7.96 (minor, d, *J* = 8.5 Hz, 0.14H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.67–7.51 (m, 4H), 7.34–7.28 (m, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.12 (minor, d, *J* = 8.0 Hz, 0.28H), 6.33 (d, *J* = 5.5 Hz, 1H), 5.72 (minor, dd, *J* = 11.6, 6.0 Hz, 0.11H), 4.93 (d, *J* = 16.5 Hz, 1H), 3.86–3.78 (m, 3H), 3.35 (d, *J* = 11.6 Hz, 1H), 3.16 (s, 2H), 2.75–2.71 (m, 1H), 2.37 (s, 3H), 2.35–2.29 (m, 1H), 1.30 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 144.3, 140.2, 135.6, 134.3, 133.0, 130.2, 129.7, 129.3, 129.2, 127.3, 126.8, 126.1, 124.7, 124.6, 122.8, 110.3, 110.1, 109.6, 108.9, 108.2, 65.4, 51.7, 43.8, 39.8, 38.1, 36.7, 31.8, 31.5, 21.5, 15.1; MS (MALDI) calcd. for $C_{32}H_{27}N_5O_3SNa$ $[M + Na]^+$ 584.17, found 584.16.



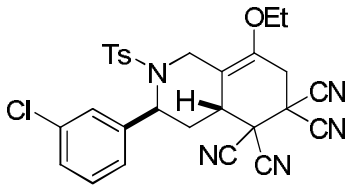
P DIWRU G

13d: 85% yield; dr = 3.3:1 (^{1}H NMR); yellow solid; IR (film) ν_{max} 2979, 2927, 2250, 1684, 1377, 1163, 664 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.69 (d, *J* = 8.2 Hz, 2H), 7.61 (minor, d, *J* = 8.2 Hz, 0.6H), 7.31–7.22 (m, 3H), 7.02–7.01 (m, 1H), 6.96–6.94 (m, 1H), 5.66 (d, *J* = 4.1 Hz, 1H), 5.46 (minor, dd, *J* = 10.5, 7.8 Hz, 0.3H), 5.12 (d, *J* = 16.5 Hz, 1H), 4.78 (minor, d, *J* = 18.2 Hz, 0.3H), 3.91–3.79 (m, 2H), 3.52 (dd, *J* = 16.5, 1.5 Hz, 1H), 3.36 (d, *J* = 12.5 Hz, 1H), 3.18–3.05 (m, 2H), 2.56 (ddd, *J* = 13.2, 4.1, 1.9 Hz, 1H), 2.38 (s, 3H), 1.89 (td, *J* = 13.0, 5.2 Hz, 1H), 1.34 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 144.6, 140.2, 136.4, 130.1, 130.0, 127.8, 126.9, 126.4, 125.6, 110.2, 109.5, 109.4, 109.0, 108.1, 65.5, 51.6, 43.8, 37.8, 37.7, 36.9, 31.6, 30.4, 21.5, 15.1; MS (MALDI) calcd. for $C_{26}H_{23}N_5O_3S_2Na$ $[M + Na]^+$ 540.11, found 540.02.



P DIWRU H

13e: 68% yield; dr > 10:1; white solid; IR (film) ν_{max} 3063, 2983, 2254, 1683, 1352, 1164, 640 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.88 (d, *J* = 8.2 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.37–7.34 (m, 3H), 5.56 (d, *J* = 4.2 Hz, 1H), 5.13 (d, *J* = 16.8 Hz, 1H), 3.85 (qd, *J* = 7.0, 2.4 Hz, 1H), 3.78 (qd, *J* = 7.0, 2.4 Hz, 1H), 3.35 (dd, *J* = 16.6, 1.7 Hz, 1H), 3.17 (d, *J* = 12.4 Hz, 1H), 3.12–3.02 (m, 2H), 2.77 (ddd, *J* = 13.4, 4.0, 2.2 Hz, 1H), 1.85 (td, *J* = 13.1, 5.1 Hz, 1H), 1.34 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 140.0, 139.9, 134.9, 133.3, 129.6, 129.4, 128.2, 126.7, 126.0, 110.3, 110.1, 109.4, 109.3, 108.0, 65.5, 53.6, 43.7, 37.9, 37.7, 36.7, 31.6, 28.6, 15.1; MS (MALDI) calcd. for $C_{27}H_{23}N_5O_3SNa$ $[M + Na]^+$ 520.14, found 520.10.

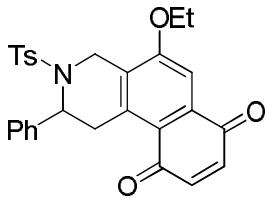


major 13f

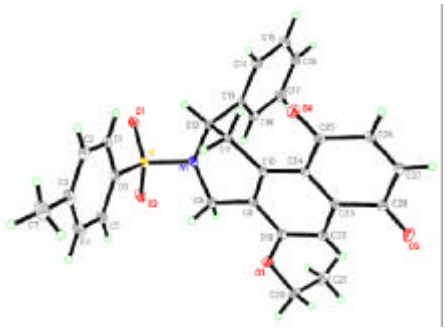
13f: 68% yield; dr = 5.7:1 (^{1}H NMR); white solid; IR (film) ν_{max} 2983, 2910, 2252, 1684, 1352, 1162, 663 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.74 (d, *J* = 8.2 Hz, 2H), 7.59 (minor, d, *J* = 8.2 Hz, 0.34H), 7.38–7.18 (m, 6H), 5.48 (d, *J* = 3.6 Hz, 1H), 5.17 (d, *J* = 16.7 Hz, 1H), 3.89–3.80 (m, 2H), 3.32 (d, *J* = 16.7 Hz, 1H), 3.13–3.02 (m, 3H), 2.66–2.65 (m, 1H), 2.39 (s, 3H), 1.76 (td, *J* = 13.0, 5.1 Hz, 1H), 1.36 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 144.8, 140.1, 137.4, 136.7, 135.9, 130.8, 130.0, 128.5, 126.8, 126.7, 123.8, 110.2, 110.1, 109.3, 109.0, 108.0, 65.5, 53.2, 43.6, 38.0, 37.7, 36.7, 31.6, 28.3, 21.4, 15.1; MS (MALDI) calcd. for $C_{28}H_{24}ClN_5O_3SNa$ $[M + Na]^+$ 568.12, found 568.15.

General Procedure for the Synthesis of 14

A solution of the diene (**6**, 0.5 mmol) and benzoquinone (4.0 eq.) in toluene (2.0 mL) was stirred at 80 °C under Ar. After the reaction had reached completion (5–10 h, TLC), the mixture was concentrated and the crude residue purified through flash column chromatography (SiO_2; 25% EtOAc in hexanes) to afford the product.

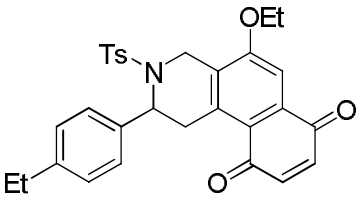


14a

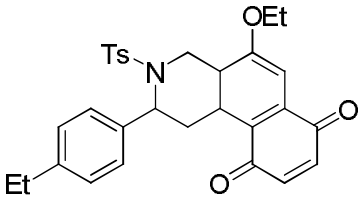


14a: 63% yield; yellow solid; m.p. 204–205 °C; IR (film) ν_{max} 3055, 2985, 2931, 1659, 1581, 1319, 1103, 694 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.69 (d, *J* = 8.2 Hz, 2H), 7.38 (s, 1H), 7.21–7.15 (m, 7H), 6.84 (d, *J* = 10.1 Hz, 1H), 6.80 (d, *J* = 10.1 Hz, 1H), 5.48 (d, *J* = 6.2 Hz, 1H), 4.90 (d, *J* = 18.8 Hz, 1H), 4.20–4.11 (m, 3H), 3.95 (d, *J* = 18.8 Hz, 1H), 3.26 (dd, *J* = 18.6, 6.2

Hz, 1H), 2.34 (s, 3H), 1.44 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 186.1, 185.1, 158.4, 143.3, 140.7, 138.5, 137.8, 137.2, 136.0, 133.9, 129.5, 128.4, 127.8, 127.4, 127.1, 126.9, 122.2, 106.1, 64.5, 52.8, 39.2, 28.8, 21.4, 14.4; MS (MALDI) calcd. for $C_{28}H_{26}NO_5S$ $[M + H]^+$ 488.15, found 488.13.



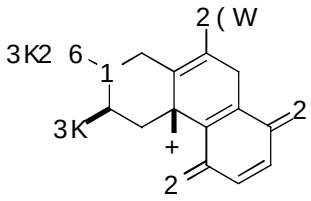
14ba



14bb

14ba: 30% yield; yellow solid; decomposed at 190 °C; IR (film) ν_{max} 2966, 2932, 1654, 1578, 1314, 1159, 683 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.68 (d, *J* = 8.3 Hz, 2H), 7.38 (s, 1H), 7.17 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 2H), 6.84 (d, *J* = 10.1 Hz, 1H), 6.80 (d, *J* = 10.1 Hz, 1H), 5.45 (d, *J* = 6.3 Hz, 1H), 4.90 (d, *J* = 18.8 Hz, 1H), 4.19–4.14 (m, 2H), 4.10 (d, *J* = 18.6 Hz, 1H), 3.94 (d, *J* = 18.8Hz, 1H), 3.26 (dd, *J* = 18.6, 6.3 Hz, 1H), 2.55 (q, *J* = 7.6 Hz, 2H), 2.33 (s, 3H), 1.44 (t, *J* = 7.0 Hz, 3H), 1.16 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 186.0, 185.1, 158.4, 143.4, 143.2, 140.7, 137.9, 137.3, 135.9, 135.6, 133.8, 129.5, 127.9, 127.0, 126.9, 122.2, 106.1, 64.5, 52.6, 39.2, 29.0, 28.2, 21.3, 15.2, 14.4; MS (MALDI) calcd. for $C_{30}H_{30}NO_5S$ $[M + H]^+$ 516.18, found 516.12; HRMS (ESI) calcd. for $C_{30}H_{31}NO_5S$ $[M + H]^+$ 516.1844, found 516.1858.

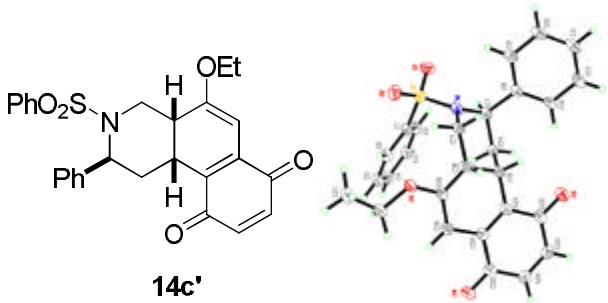
14bb: 20% yield; deep-blue solid; m.p. 175–176 °C; IR (film) ν_{max} 2964, 2931, 1645, 1549, 1321, 1157, 663 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.71 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.25–7.22 (m, 4H), 6.65 (d, *J* = 1.0 Hz, 2H), 5.61 (d, *J* = 1.6 Hz, 1H), 5.13 (s, 1H), 4.66 (d, *J* = 14.4 Hz, 1H), 3.93 (qd, *J* = 7.0, 2.6 Hz, 1H), 3.76 (qd, *J* = 7.0, 2.6 Hz, 1H), 3.35–3.29 (m, 1H), 3.20 (dd, *J* = 14.4, 4.0 Hz, 1H), 2.65 (q, *J* = 7.6 Hz, 2H), 2.62–2.58 (m, 1H), 2.40 (s, 3H), 2.08 (dt, *J* = 13.0, 3.0 Hz, 1H), 1.96 (td, *J* = 13.0, 4.8 Hz, 1H), 1.34 (t, *J* = 7.0 Hz, 3H), 1.25 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 186.2, 185.2, 164.2, 143.3, 143.0, 138.3, 138.0, 137.2, 135.2, 133.9, 130.1, 129.4, 128.4, 127.2, 127.1, 89.6, 65.0, 54.7, 37.0, 36.9, 28.4, 27.3, 26.3, 21.5, 15.5, 14.0; MS (MALDI) calcd. for $C_{30}H_{32}NO_5S$ $[M + H]^+$ 518.20, found 518.17.



F

14c: 40% yield; deep-blue solid; m.p. 159–160 °C; IR (film) ν_{max} 3062, 2980, 1655, 1550, 1302, 1159, 691 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.94 (d, *J* = 7.3 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.46–7.43 (m, 3H), 7.31 (t, *J* = 7.2 Hz, 1H), 6.71 (d, *J* = 10.1 Hz, 1H), 6.68 (d, *J* = 10.1 Hz, 1H), 5.31 (s, 1H), 5.16 (d, *J* = 15.1 Hz, 1H), 3.86 (qd, *J* = 7.0, 2.3 Hz, 1H), 3.77 (qd, *J* = 7.0, 2.3 Hz, 1H), 3.16 (ddd, *J* = 23.4, 6.5, 2.3 Hz, 1H), 2.87 (dd, *J* = 23.4, 7.4 Hz, 2H), 2.77 (dt, *J* = 13.2, 2.3 Hz, 1H), 1.30 (t, *J* = 7.0 Hz, 3H), 1.18 (td, *J* = 12.8, 4.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) d 186.4, 186.1, 142.3, 141.0, 140.6, 138.4, 137.2, 136.7, 135.9, 132.3, 128.8, 128.6, 127.24, 127.20, 127.1, 109.8, 64.0, 55.5, 39.5, 33.0, 32.6, 23.7, 15.3; MS (MALDI) calcd. for $C_{27}H_{26}NO_5S$ $[M + H]^+$ 476.15, found 476.08.

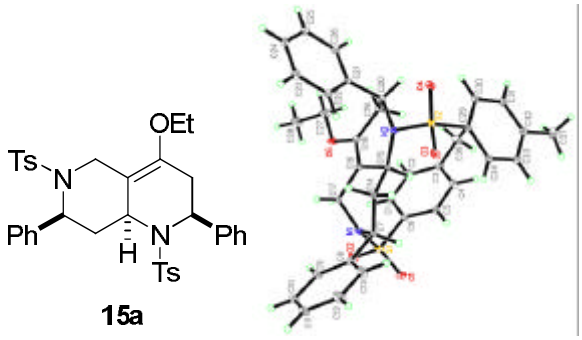
The neat sample of **14c**, upon sitting at room temperature over an extended period of time (6 months), isomerized into compound **14c´**, with the enol ether double bond in conjugation with the benzoquinone motif (cf. compound **14bb**). This new compound **14c´** was crystallized from dichloromethane/pentane solution. Because **14c´** was obtained in a small quantity and was not readily separable from **14c**, its physical and spectroscopic data are not available at this point.



14c'

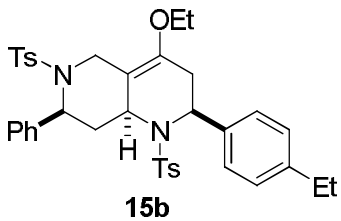
General Procedure for the Synthesis of 15

A solution of the diene (**6**, 0.5 mmol) and imine (4.0 eq.) in toluene (2.0 mL) was stirred at 65 °C under Ar. After the reaction had reached completion (16–24 h, TLC), the mixture was concentrated and the crude residue purified through flash column chromatography (SiO_2; 30–50% EtOAc in hexanes) to afford the product.



15a

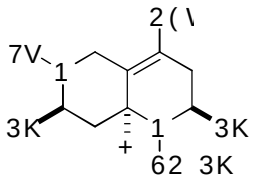
15a: 80% yield; white solid; m.p. 192–193 °C; IR (film) ν_{max} 3055, 2978, 2931, 1697, 1342, 1157, 656 cm^{-1}; ^1H NMR (500 MHz, acetone-d_6) d 7.62 (d, J = 8.3 Hz, 2H), 7.56 (d, J = 8.2 Hz, 2H), 7.44–7.35 (m, 6H), 7.25 (t, J = 7.7 Hz, 2H), 7.19–7.12 (m, 4H), 7.05–7.04 (m, 2H), 5.21 (d, J = 5.7 Hz, 1H), 4.83 (dd, J = 10.1, 7.5 Hz, 1H), 4.31 (d, J = 16.9 Hz, 1H), 4.05 (d, J = 16.9 Hz, 1H), 3.95 (d, J = 12.4 Hz, 1H), 3.80 (qd, J = 7.0, 3.0 Hz, 1H), 3.66 (qd, J = 7.0, 3.0 Hz, 1H), 2.65 (d, J = 16.7 Hz, 1H), 2.45 (s, 3H), 2.40 (s, 3H), 2.27 (ddd, J = 13.0, 7.4, 4.1 Hz, 1H), 1.82 (ddt, J = 16.7, 5.8, 2.9 Hz, 1H), 1.22 (td, J = 12.7, 10.3 Hz, 1H), 1.08 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, acetone-d_6) d 143.6, 143.2, 143.1, 142.0, 140.5, 137.5, 136.9, 129.8, 129.6, 128.0, 127.9, 127.3, 127.1, 127.0, 126.8, 126.7, 126.2, 109.8, 62.8, 58.2, 52.9, 51.8, 42.2, 39.1, 25.3, 20.5, 20.4, 14.5; MS (MALDI) calcd. for $C_{36}H_{38}N_2O_5S_2Na$ $[M + Na]^+$ 665.21, found 665.28; HRMS (ESI) calcd. for $C_{36}H_{39}N_2O_5S_2$ $[M + H]^+$ 643.2300, found 643.2275.



15b

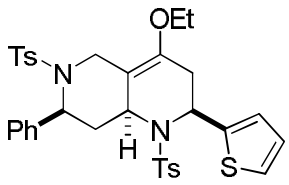
15b: 70% yield; white solid; m.p. 178–179 °C; IR (film) ν_{max} 3027, 2968, 2925, 1701, 1346, 1161, 656 cm^{-1}; ^1H NMR (500 MHz, acetone-d_6) d 7.61 (d, J = 8.3 Hz, 2H), 7.56 (d, J = 8.3 Hz, 2H), 7.42–7.38 (m, 4H), 7.26 (d, J = 8.0 Hz, 2H), 7.16–7.10 (m, 5H), 7.02–6.99 (m, 2H), 5.19 (d,

J = 5.7 Hz, 1H), 4.76 (dd, *J* = 9.9, 7.4 Hz, 1H), 4.20 (d, *J* = 16.5 Hz, 1H), 4.11 (d, *J* = 16.5 Hz, 1H), 3.98 (d, *J* = 12.2 Hz, 1H), 3.81 (qd, *J* = 7.0, 3.0 Hz, 1H), 3.66 (qd, *J* = 7.0, 3.0 Hz, 1H), 2.62 (d, *J* = 16.7 Hz, 1H), 2.53 (q, *J* = 7.6 Hz, 2H), 2.44 (s, 3H), 2.40 (s, 3H), 2.19 (ddd, *J* = 13.0, 7.3, 4.2 Hz, 1H), 1.83 (ddt, *J* = 16.6, 6.0, 3.0 Hz, 1H), 1.20 (td, *J* = 12.7, 10.2 Hz, 1H), 1.11 (t, *J* = 7.6 Hz, 3H), 1.08 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, acetone-d_6) d 143.5, 143.24, 143.22, 143.1, 141.9, 137.7, 137.6, 136.8, 129.8, 129.6, 127.9, 127.5, 127.4, 127.2, 126.9, 126.7, 126.4, 109.7, 62.9, 58.3, 52.7, 51.7, 42.5, 39.2, 27.9, 25.3, 20.5, 20.4, 15.1, 14.6; MS (MALDI) calcd. for $C_{38}H_{42}N_2O_5S_2Na$ $[M + Na]^+$ 693.24, found 693.20; HRMS (ESI) calcd. for $C_{38}H_{46}N_3O_5S_2$ $[M + H]^+$ 688.2879, found 688.2873.



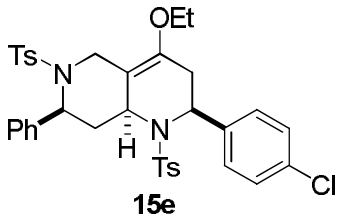
F

15c: 77% yield; white solid; m.p. 151–152 °C; IR (film) ν_{max} 3062, 3031, 2979, 1701, 1346, 1163, 664 cm^{-1}; ^{1}H NMR (500 MHz, acetone-d_6) d 7.73–7.60 (m, 7H), 7.40–7.36 (m, 4H), 7.26 (t, *J* = 7.7 Hz, 2H), 7.19–7.12 (m, 4H), 7.05–7.03 (m, 2H), 5.23 (d, *J* = 5.6 Hz, 1H), 4.84 (dd, *J* = 10.1, 7.5 Hz, 1H), 4.32 (d, *J* = 17.0 Hz, 1H), 4.07 (d, *J* = 17.0 Hz, 1H), 3.98 (d, *J* = 12.3 Hz, 1H), 3.80 (qd, *J* = 7.0, 3.0 Hz, 1H), 3.65 (qd, *J* = 7.0, 3.0 Hz, 1H), 2.65 (d, *J* = 16.7 Hz, 1H), 2.40 (s, 3H), 2.27 (ddd, *J* = 12.9, 7.4, 4.1 Hz, 1H), 1.80 (ddt, *J* = 16.7, 6.0, 3.0 Hz, 1H), 1.22 (td, *J* = 12.7, 10.3 Hz, 1H), 1.07 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, acetone-d_6) d 143.2, 143.1, 142.0, 140.4, 140.3, 136.9, 132.8, 129.6, 129.4, 128.1, 128.0, 127.3, 127.1, 126.9, 126.7, 126.2, 109.8, 62.8, 58.1, 52.9, 51.8, 42.3, 39.1, 25.3, 20.6, 14.6; MS (MALDI) calcd. for $C_{35}H_{36}N_2O_5S_2Na$ $[M + Na]^+$ 651.20, found 651.14; HRMS (ESI) calcd. for $C_{35}H_{37}N_2O_5S_2$ $[M + H]^+$ 629.2144, found 629.2131.



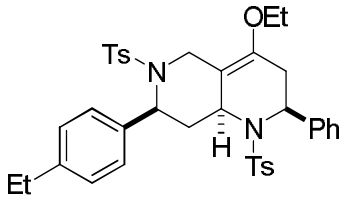
15d

15d: 75% yield; white solid; m.p. 186–187 °C; IR (film) ν_{max} 3063, 2978, 2918, 1699, 1346, 1161, 667 cm^{-1}; ^1H NMR (500 MHz, acetone-d_6) d 7.70 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 7.9 Hz, 2H), 7.31–7.21 (m, 6H), 6.96–6.90 (m, 2H), 5.46 (d, *J* = 5.7 Hz, 1H), 4.95 (dd, *J* = 10.6, 7.2 Hz, 1H), 4.54 (d, *J* = 17.3 Hz, 1H), 4.13 (d, *J* = 17.3 Hz, 1H), 3.94 (d, *J* = 11.8 Hz, 1H), 3.86 (qd, *J* = 7.0, 3.0 Hz, 1H), 3.74 (qd, *J* = 7.0, 3.0 Hz, 1H), 2.65 (d, *J* = 16.6 Hz, 1H), 2.51 (s, 3H), 2.46 (s, 3H), 2.49–2.45 (m, 1H), 2.02–1.97 (m, 1H), 1.62 (td, *J* = 12.7, 10.7 Hz, 1H), 1.18 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, acetone-d_6) d 145.2, 143.7, 143.2, 143.0, 142.3, 137.2, 137.0, 129.8, 129.5, 128.1, 127.1, 126.9, 126.3, 126.0, 125.1, 125.2, 109.4, 62.9, 58.2, 51.6, 50.5, 42.2, 39.4, 28.1, 20.5, 20.4, 14.7; MS (MALDI) calcd. for $C_{34}H_{36}N_2O_5S_3Na$ $[M + Na]^+$ 671.17, found 671.13; HRMS (ESI) calcd. for $C_{34}H_{40}N_3O_5S_3$ $[M + NH_4]^+$ 666.2130, found 666.2122.



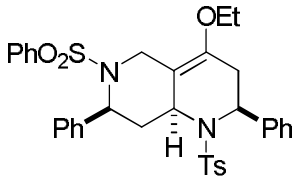
15e

15e: 77% yield; white solid; m.p. 181–182 °C; IR (film) ν_{max} 3060, 2978, 2913, 1700, 1346, 1162, 660 cm^{-1}; ^1H NMR (500 MHz, acetone-d_6) d 7.62 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.40–7.35 (m, 4H), 7.30–7.28 (m, 2H), 7.21–7.14 (m, 3H), 7.08–7.06 (m, 2H), 5.20 (d, *J* = 5.4 Hz, 1H), 4.84 (dd, *J* = 10.2, 7.3 Hz, 1H), 4.32 (d, *J* = 16.9 Hz, 1H), 4.08 (d, *J* = 16.9 Hz, 1H), 3.93 (d, *J* = 12.0 Hz, 1H), 3.80 (qd, *J* = 7.0, 3.0 Hz, 1H), 3.65 (qd, *J* = 7.0, 3.0 Hz, 1H), 2.64 (d, *J* = 16.7 Hz, 1H), 2.45 (s, 3H), 2.40 (s, 3H), 2.32 (ddd, *J* = 12.9, 7.3, 4.1 Hz, 1H), 1.81 (ddt, *J* = 16.7, 5.8, 2.9 Hz, 1H), 1.25 (td, *J* = 12.7, 10.3 Hz, 1H), 1.08 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, acetone-d_6) d 143.8, 143.2, 143.0, 142.0, 139.6, 137.3, 136.9, 132.4, 129.9, 129.6, 129.2, 128.1, 128.0, 127.1, 126.9, 126.8, 126.2, 109.9, 62.9, 58.1, 52.6, 51.8, 42.1, 39.3, 25.5, 20.5, 20.4, 14.5; MS (MALDI) calcd. for $C_{36}H_{37}ClN_2O_5S_2Na$ $[M + Na]^+$ 699.17, found 699.14; HRMS (ESI) calcd. for $C_{36}H_{38}ClN_2O_5S_2$ $[M + H]^+$ 677.1910, found 677.1895.



15f

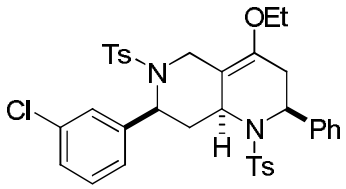
15f: 69% yield; white solid; m.p. 149–150 °C; IR (film) ν_{max} 3029, 2967, 2930, 1701, 1345, 1162, 655 cm^{-1}; ^1H NMR (500 MHz, acetone-d_6) d 7.60–7.56 (m, 4H), 7.42 (d, J = 7.9 Hz, 2H), 7.38–7.35 (m, 4H), 7.26 (t, J = 7.7 Hz, 2H), 7.17 (t, J = 7.3 Hz, 1H), 6.99 (d, J = 8.2 Hz, 2H), 6.92 (d, J = 8.2 Hz, 2H), 5.22 (d, J = 5.7 Hz, 1H), 4.81 (dd, J = 10.1, 7.4 Hz, 1H), 4.31 (d, J = 17.0 Hz, 1H), 4.06 (d, J = 17.0 Hz, 1H), 3.98 (d, J = 12.2 Hz, 1H), 3.80 (qd, J = 7.0, 3.0 Hz, 1H), 3.66 (qd, J = 7.0, 3.0 Hz, 1H), 2.64 (d, J = 16.7 Hz, 1H), 2.53 (q, J = 7.6 Hz, 2H), 2.44 (s, 3H), 2.39 (s, 3H), 2.24 (ddd, J = 13.0, 7.4, 4.1 Hz, 1H), 1.81 (ddt, J = 16.6, 5.9, 3.0 Hz, 1H), 1.23 (td, J = 12.7, 10.3 Hz, 1H), 1.14 (t, J = 7.6 Hz, 3H), 1.08 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, acetone-d_6) d 143.6, 143.1, 143.0, 142.8, 140.5, 139.1, 137.6, 137.2, 129.8, 129.5, 128.0, 127.4, 127.1, 127.0, 126.8, 126.4, 110.0, 62.8, 58.0, 52.9, 51.8, 42.2, 39.0, 28.0, 25.3, 20.6, 20.5, 15.0, 14.5; MS (MALDI) calcd. for $C_{38}H_{42}N_2O_5S_2Na$ $[M + Na]^+$ 693.24, found 693.30; HRMS (ESI) calcd. for $C_{38}H_{46}N_3O_5S_2$ $[M + NH_4]^+$ 688.2879, found 688.2827.



15g

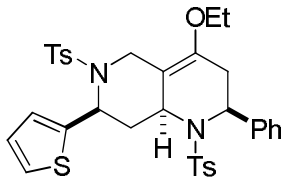
15g: 78% yield; white solid; m.p. 176–177 °C; IR (film) ν_{max} 3062, 2978, 1700, 1346, 1164, 698 cm^{-1}; ^1H NMR (500 MHz, acetone-d_6) d 7.81–7.75 (m, 3H), 7.65 (t, J = 7.6 Hz, 2H), 7.58 (t, J = 8.2 Hz, 2H), 7.49 (d, J = 8.2 Hz, 2H), 7.42 (d, J = 7.6 Hz, 2H), 7.31 (t, J = 7.6 Hz, 2H), 7.25–7.18 (m, 4H), 7.13 (d, J = 6.7 Hz, 2H), 5.26 (d, J = 5.5 Hz, 1H), 4.90 (dd, J = 10.3, 7.3 Hz, 1H), 4.47 (d, J = 17.2 Hz, 1H), 4.11 (d, J = 17.2 Hz, 1H), 3.94 (d, J = 12.0 Hz, 1H), 3.87 (qd, J = 7.0, 3.0 Hz, 1H), 3.74 (qd, J = 7.0, 3.0 Hz, 1H), 2.72 (d, J = 16.7 Hz, 1H), 2.51 (s, 3H), 2.36 (ddd, J = 12.9, 7.2, 3.9 Hz, 1H), 1.88–1.84 (m, 1H), 1.30 (td, J = 12.7, 10.5 Hz, 1H), 1.15 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, acetone-d_6) d 143.6, 143.3, 142.0, 140.5, 139.8, 137.4, 132.6, 129.9, 129.0, 128.0, 127.9, 127.2, 127.05, 126.99, 126.89, 126.80, 126.1, 109.7, 62.9, 58.3, 53.0, 51.8,

42.2, 39.3, 25.5, 20.4, 14.6; MS (MALDI) calcd. for $C_{35}H_{36}N_2O_5S_2Na$ $[M + Na]^+$ 651.20, found 651.15; HRMS (ESI) calcd. for $C_{35}H_{40}N_3O_5S_2$ $[M + NH_4]^+$ 646.2410, found 646.2392.



15h

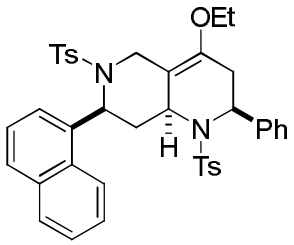
15h: 78% yield; white solid; m.p. 168–169 °C; IR (film) ν_{max} 3062, 2978, 2917, 1701, 1346, 1162, 665 cm^{-1}; ^1H NMR (500 MHz, acetone-d_6) d 7.61 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.44–7.35 (m, 6H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.22–7.16 (m, 3H), 7.02–7.01 (m, 2H), 5.23 (d, *J* = 5.7 Hz, 1H), 4.77 (dd, *J* = 10.4, 7.1 Hz, 1H), 4.40 (d, *J* = 16.7 Hz, 1H), 4.16 (d, *J* = 16.7 Hz, 1H), 3.95 (d, *J* = 12.2 Hz, 1H), 3.81 (qd, *J* = 7.0, 3.0 Hz, 1H), 3.67 (qd, *J* = 7.0, 3.0 Hz, 1H), 2.65 (d, *J* = 16.7 Hz, 1H), 2.45 (s, 3H), 2.41 (s, 3H), 2.23 (ddd, *J* = 12.9, 7.0, 4.0 Hz, 1H), 1.84 (ddt, *J* = 16.7, 5.9, 2.9 Hz, 1H), 1.16 (td, *J* = 12.7, 10.5 Hz, 1H), 1.08 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, acetone-d_6) d 144.4, 143.7, 143.5, 143.4, 140.5, 137.5, 136.5, 133.3, 129.8, 129.7, 129.6, 128.0, 127.3, 127.2, 127.1, 126.9, 126.8, 126.4, 124.9, 109.5, 62.9, 58.0, 53.0, 51.8, 42.4, 39.2, 25.4, 20.5, 20.4, 14.5; MS (MALDI) calcd. for $C_{36}H_{37}ClN_2O_5S_2Na$ $[M + Na]^+$ 699.17, found 699.11; HRMS (ESI) calcd. for $C_{36}H_{41}ClN_3O_5S_2$ $[M + NH_4]^+$ 694.2176, found 694.2164.



15i

15i: 70% yield; white solid; m.p. 183–184 °C; IR (film) ν_{max} 3063, 2978, 1701, 1344, 1162, 655 cm^{-1}; ^1H NMR (500 MHz, acetone-d_6) d 7.68 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.43–7.36 (m, 6H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.23–7.20 (m, 2H), 6.80 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.58 (d, *J* = 3.5 Hz, 1H), 5.34 (t, *J* = 8.7 Hz, 1H), 5.22 (d, *J* = 5.8 Hz, 1H), 4.34 (d, *J* = 17.7 Hz, 1H), 4.00 (d, *J* = 12.2 Hz, 1H), 3.84 (d, *J* = 17.7 Hz, 1H), 3.79 (qd, *J* = 7.0, 3.0 Hz, 1H), 3.64 (qd, *J* = 7.0, 3.0 Hz, 1H), 2.65 (d, *J* = 16.8 Hz, 1H), 2.44 (s, 3H), 2.39 (s, 3H), 2.42–2.36 (m, 1H), 1.82 (ddt, *J* = 16.7, 6.1, 3.1 Hz, 1H), 1.32 (td, *J* = 12.7, 8.8 Hz, 1H), 1.05 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, acetone-d_6) d 145.4, 143.6, 143.3, 143.0, 140.4, 137.6, 137.4, 129.8, 129.7, 128.1, 127.4,

127.2, 127.0, 126.7, 126.2, 124.8, 124.7, 109.4, 62.7, 52.7, 52.6, 50.9, 41.1, 38.2, 25.0, 20.5, 20.4, 14.4; MS (MALDI) calcd. for $C_{34}H_{36}N_2O_5S_3Na$ $[M + Na]^+$ 671.17, found 671.08.

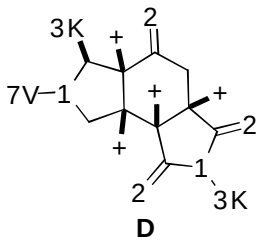


15j

15j: 65% yield; white solid; m.p. 195–196 °C; IR (film) ν_{max} 3029, 2979, 1699, 1341, 1162, 656 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) d 7.82–7.79 (m, 1H), 7.71–7.66 (m, 3H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.38–7.36 (m, 4H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.27–7.20 (m, 5H), 7.12 (t, *J* = 7.3 Hz, 2H), 6.93 (d, *J* = 7.9 Hz, 1H), 5.31–5.24 (m, 2H), 4.63 (d, *J* = 16.2 Hz, 1H), 4.35 (d, *J* = 12.3 Hz, 1H), 4.22 (d, *J* = 16.2 Hz, 1H), 3.89 (qd, *J* = 7.0, 2.8 Hz, 1H), 3.75 (qd, *J* = 7.0, 2.8 Hz, 1H), 2.62 (d, *J* = 16.5 Hz, 1H), 2.46 (s, 3H), 2.36 (ddd, *J* = 13.0, 5.4, 4.0 Hz, 1H), 2.26 (s, 3H), 2.04 (ddt, *J* = 16.6, 6.1, 2.7 Hz, 1H), 1.59–1.50 (m, 1H), 1.24 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) d 143.6, 143.1, 142.6, 139.7, 137.5, 136.4, 136.0, 133.5, 130.5, 130.0, 128.8, 128.5, 128.4, 128.1, 127.6, 127.5, 127.2, 127.0, 126.1, 125.2, 125.0, 124.6, 123.2, 111.6, 63.8, 57.4, 53.2, 53.0, 44.3, 38.9, 25.9, 21.6, 21.4, 15.3; MS (MALDI) calcd. for $C_{40}H_{40}N_2O_5S_2Na$ $[M + Na]^+$ 715.23, found 715.22; HRMS (ESI) calcd. for $C_{40}H_{44}N_3O_5S_2$ $[M + NH_4]^+$ 710.2723, found 710.2686.

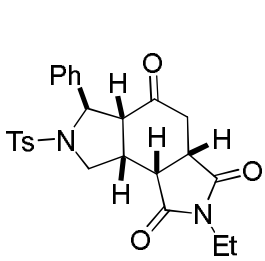
General Procedure for the Synthesis of 16–18

Concentrated HCl (12.1 M, 0.10 mL) was added dropwise to a solution of the enol ether (**7**, **11**, or **15**, 0.17 mmol) in acetone (13 mL). The mixture was stirred overnight at room temperature. The resulting mixture was concentrated and dissolved in DCM (15 mL). The solution was washed with saturated $NaHCO_3$ (2 × 10 mL) and brine (2 × 10 mL) and then dried ($NaSO_4$). The organic phase was concentrated and the crude residue purified through flash column chromatography (SiO_2; 30–50% EtOAc in hexanes) to afford the product.

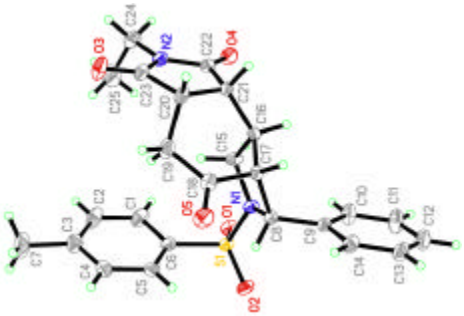


D

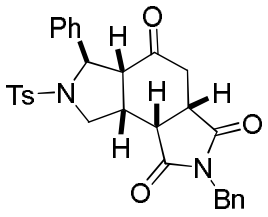
16a: 92% yield; white solid; m.p. 118–119 °C; IR (film) ν_{max} 3065, 2919, 2871, 1715, 1382, 1165, 670 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) d 7.59–7.51 (m, 4H), 7.48–7.44 (m, 1H), 7.36–7.25 (m, 9H), 5.37 (s 1H), 3.98 (dd, *J* = 9.4, 8.6 Hz, 1H), 3.47–3.39 (m, 1H), 3.33–3.28 (m, 2H), 2.96 (dd, *J* = 11.1, 10.0 Hz, 1H), 2.64–2.58 (m, 2H), 2.44 (s, 3H), 1.94–1.84 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) d 205.0, 176.2, 175.1, 144.3, 140.9, 133.7, 131.1, 129.8, 129.5, 129.2, 128.7, 127.8, 127.4, 126.2, 125.7, 66.2, 57.5, 48.9, 37.6, 37.5, 35.8, 35.6, 21.6; MS (MALDI) calcd. for $C_{29}H_{26}N_2O_5SNa$ $[M + Na]^+$ 537.14, found 537.16; HRMS (ESI) calcd. for $C_{29}H_{27}N_2O_5S$ $[M + H]^+$ 515.1640, found 515.1639.



16b

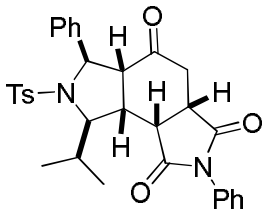


16b: 90% yield; white solid; decomposed at 200 °C; IR (film) ν_{max} 3062, 2979, 2939, 1702, 1348, 1161, 671 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) d 7.54 (d, *J* = 8.2 Hz, 2H), 7.31–7.23 (m, 7H), 5.29 (s 1H), 3.86 (t, *J* = 9.1 Hz, 1H), 3.59 (q, *J* = 7.2 Hz, 2H), 3.35–3.29 (m, 1H), 3.13–3.06 (m, 2H), 2.75 (t, *J* = 10.6 Hz, 1H), 2.57–2.49 (m, 2H), 2.44 (s, 3H), 1.71–1.64 (m, 1H), 1.20 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) d 205.4, 177.0, 175.8, 144.3, 140.9, 133.7, 129.8, 128.7, 127.7, 127.4, 125.7, 66.3, 57.3, 48.9, 37.3, 37.2, 35.6, 35.4, 34.2, 21.6, 13.0; MS (MALDI) calcd. for $C_{25}H_{26}N_2O_5SNa$ $[M + Na]^+$ 489.14, found 489.16; HRMS (ESI) calcd. for $C_{25}H_{30}N_3O_5SNa$ $[M + NH_4]^+$ 484.1906, found 484.1904.



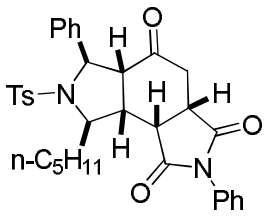
16c

16c: 89% yield; white solid; m.p. 129–130 °C; IR (film) ν_{max} 3030, 2921, 2870, 1706, 1348, 1164, 670 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) d 7.46–7.40 (m, 5H), 7.34–7.25 (m, 7H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.20 (s, 1H), 4.73 (AB d, *J* = 13.8 Hz, 1H), 4.61 (AB d, *J* = 13.8 Hz, 1H), 3.66 (dd, *J* = 9.9, 8.7 Hz, 1H), 3.34–3.25 (m, 1H), 3.11–3.06 (m, 2H), 2.52 (d, *J* = 6.7 Hz, 1H), 2.48–2.37 (m, 5H), 1.39–1.30 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) d 205.5, 176.8, 175.7, 144.2, 141.0, 135.5, 133.2, 129.7, 129.1, 129.0, 128.69, 128.67, 127.7, 127.3, 125.6, 66.5, 57.3, 48.7, 42.8, 37.2, 37.1, 35.7, 35.2, 21.6; MS (MALDI) calcd. for $C_{30}H_{28}N_2O_5SNa$ $[M + Na]^+$ 551.16, found 551.09; HRMS (ESI) calcd. for $C_{30}H_{29}N_2O_5S$ $[M + H]^+$ 529.1797, found 529.1797.



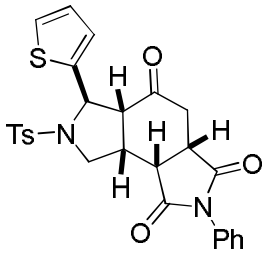
16d

16d: 91% yield; white solid; decomposed at 265 °C; IR (film) ν_{max} 3035, 2959, 2914, 1717, 1389, 1150, 671 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.46–7.37 (m, 3H), 7.21–7.06 (m, 9H), 6.90 (d, *J* = 8.0 Hz, 2H), 5.11 (s, 1H), 4.67 (d, *J* = 8.6 Hz, 1H), 3.60 (t, *J* = 8.3 Hz, 1H), 3.21–3.18 (m, 3H), 2.91 (dd, *J* = 12.1, 9.9 Hz, 1H), 2.68–2.65 (m, 1H), 2.54 (d, *J* = 12.6 Hz, 1H), 2.56 (s, 3H), 1.07 (d, *J* = 6.3 Hz, 3H), 1.06 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 205.9, 176.2, 175.1, 142.2, 139.0, 137.7, 131.3, 129.1, 128.8, 128.55, 128.52, 127.9, 127.6, 127.2, 126.4, 67.5, 65.2, 59.8, 41.4, 41.1, 39.6, 38.2, 31.8, 21.2, 19.7, 15.0; MS (MALDI) calcd. for $C_{32}H_{32}N_2O_5SNa$ $[M + Na]^+$ 579.19, found 579.10; HRMS (MALDI) calcd. for $C_{32}H_{36}N_3O_5S$ $[M + NH_4]^+$ 574.2376, found 574.2372.



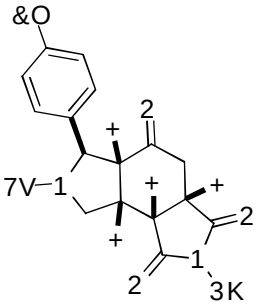
16e

16e: 75% yield; white solid; m.p. 105–106 °C; IR (film) ν_{max} 3030, 2924, 2853, 1716, 1388, 1155, 677 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) d 7.51–7.47 (m, 2H), 7.44–7.38 (m, 3H), 7.32–7.20 (m, 7H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.01 (d, *J* = 4.9 Hz, 1H), 4.22 (td, *J* = 6.5, 3.2 Hz, 1H), 3.43 (td, *J* = 9.4, 6.4 Hz, 1H), 3.28 (dd, *J* = 9.5, 5.9 Hz, 1H), 3.16–3.11 (m, 1H), 3.04 (dd, *J* = 7.9, 5.0 Hz, 1H), 2.63 (dd, *J* = 15.4, 9.4 Hz, 1H), 2.37 (s, 3H), 2.01–1.92 (m, 2H), 1.83–1.75 (m, 1H), 1.42–1.38 (m, 2H), 1.29–1.26 (m, 4H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) d 206.7, 176.4, 174.6, 143.6, 140.0, 135.7, 131.4, 129.4, 129.3, 129.0, 128.3, 127.6, 127.5, 127.2, 126.2, 66.0, 62.6, 58.0, 42.1, 39.4, 38.9, 36.7, 35.7, 31.8, 24.9, 22.6, 21.5, 14.0; MS (MALDI) calcd. for $C_{34}H_{36}N_2O_5SNa$ $[M + Na]^+$ 607.22, found 607.21; HRMS (ESI) calcd. for $C_{34}H_{40}N_3O_5S$ $[M + NH_4]^+$ 602.2689, found 602.2664.



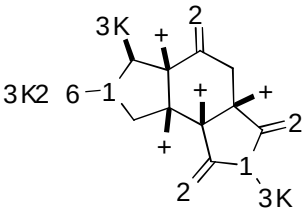
16f

16f: 90% yield; white solid; m.p. 108–109 °C; IR (film) ν_{max} 3063, 2914, 2845, 1711, 1385, 1163, 671 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) d 7.58–7.49 (m, 5H), 7.31–7.19 (m, 5H), 7.04 (d, *J* = 2.8 Hz, 1H), 6.93 (t, *J* = 4.2 Hz, 1H), 5.65 (s, 1H), 3.90 (t, *J* = 9.0 Hz, 1H), 3.70–3.64 (m, 1H), 3.48–3.38 (m, 2H), 2.98 (t, *J* = 10.4 Hz, 1H), 2.82 (d, *J* = 6.5 Hz, 1H), 2.74–2.67 (m, 1H), 2.46 (s, 3H), 2.10 (dd, *J* = 17.1, 9.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) d 204.3, 176.0, 175.0, 144.5, 144.2, 133.7, 131.0, 129.6, 129.3, 129.0, 127.3, 127.0, 126.1, 125.1, 125.0, 62.2, 57.2, 48.2, 37.6, 37.5, 36.5, 35.6, 21.4; MS (MALDI) calcd. for $C_{27}H_{24}N_2O_5S_2Na$ $[M + Na]^+$ 543.10, found 543.00; HRMS (ESI) calcd. for $C_{27}H_{25}N_2O_5S_2$ $[M + H]^+$ 521.1205, found 521.1199.



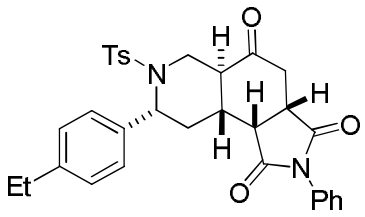
J

16g: 85% yield; white solid; m.p. 158–159 °C; IR (film) ν_{max} 3061, 2911, 2845, 1715, 1385, 1165, 670 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.60–7.46 (m, 5H), 7.34–7.28 (m, 8H), 5.33 (s 1H), 3.98 (t, *J* = 8.7 Hz, 1H), 3.42–3.32 (m, 3H), 2.94 (t, *J* = 10.4 Hz, 1H), 2.66–2.61 (m, 2H), 2.48 (s, 3H), 1.97–1.92 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) d 204.5, 176.0, 174.9, 144.4, 139.4, 133.5, 133.3, 131.0, 129.7, 129.3, 129.0, 128.7, 127.3, 127.1, 126.0, 65.1, 57.2, 48.9, 37.5, 37.2, 35.7, 35.3, 21.5; MS (MALDI) calcd. for $C_{29}H_{25}ClN_2O_5SNa$ $[M + Na]^+$ 571.11, found 571.07; HRMS (ESI) calcd. for $C_{29}H_{26}ClN_2O_5S$ $[M + H]^+$ 549.1251, found 549.1240.



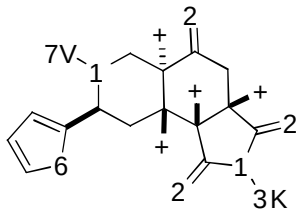
K

16h: 90% yield; white solid; m.p. 209–210 °C; IR (film) ν_{max} 3061, 2914, 2846, 1713, 1385, 1165, 695 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.67 (d, *J* = 7.5 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.52–7.42 (m, 5H), 7.32–7.23 (m, 7H), 5.36 (s, 1H), 3.96 (t, *J* = 9.0 Hz, 1H), 3.39–3.34 (m, 1H), 3.30–3.24 (m, 2H), 2.92 (t, *J* = 10.6 Hz, 1H), 2.60–2.54 (m, 2H), 1.92–1.85 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) d 204.7, 176.1, 175.0, 140.6, 136.4, 133.3, 131.1, 129.3, 129.1, 129.0, 128.6, 127.7, 127.2, 126.1, 125.6, 65.8, 57.3, 48.8, 37.5, 37.3, 35.6, 35.4; MS (MALDI) calcd. for $C_{28}H_{24}N_2O_5SNa$ $[M + Na]^+$ 523.13, found 523.10; HRMS (ESI) calcd. for $C_{28}H_{25}N_2O_5S$ $[M + H]^+$ 501.1484, found 501.1485.



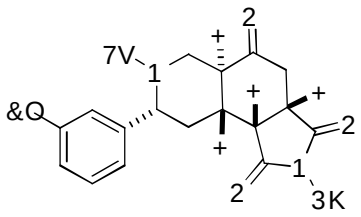
17a

17a: 87% yield; white solid; m.p. 116–117 °C; IR (film) ν_{max} 3059, 2964, 2927, 1712, 1383, 1155, 657 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.54 (d, *J* = 8.2 Hz, 2H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.23–7.21 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 5.05 (dd, *J* = 10.4, 7.5 Hz, 1H), 3.96 (dd, *J* = 15.0, 2.8 Hz, 1H), 3.49 (t, *J* = 8.0 Hz, 1H), 3.42 (dd, *J* = 9.6, 6.1 Hz, 1H), 3.35 (dd, *J* = 15.0, 8.0 Hz, 1H), 3.10 (dd, *J* = 17.6, 1.1 Hz, 1H), 2.71 (dd, *J* = 17.6, 7.5 Hz, 1H), 2.64–2.58 (m, 3H), 2.40 (s, 3H), 2.40–2.32 (m, 1H), 2.04–1.97 (m, 1H), 1.92–1.87 (m, 1H), 1.21 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 205.1, 176.8, 175.3, 143.5, 143.4, 137.7, 135.9, 131.2, 129.4, 129.1, 128.8, 127.83, 127.79, 126.2, 126.1, 57.6, 47.6, 41.6, 39.6, 37.4, 36.0, 33.4, 32.9, 28.3, 21.5, 15.5; MS (MALDI) calcd. for $C_{32}H_{32}N_2O_5SNa$ $[M + Na]^+$ 579.19, found 579.23; HRMS (ESI) calcd. for $C_{32}H_{33}N_2O_5S$ $[M + H]^+$ 557.2110, found 557.2088.



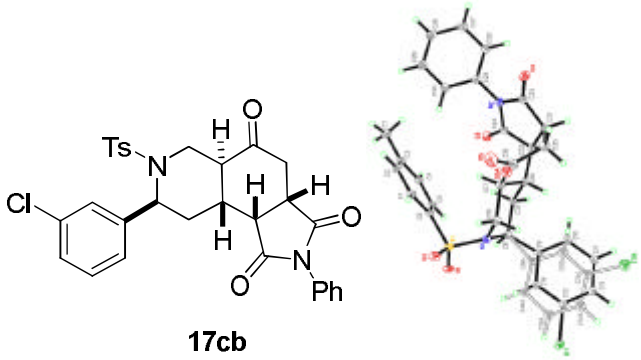
E

17b: 80% yield; white solid; m.p. 222–223 °C; IR (film) ν_{max} 3062, 2919, 2866, 1712, 1385, 1159, 664 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.70 (d, *J* = 8.2 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.24–7.18 (m, 5H), 6.96–6.93 (m, 1H), 6.87–6.86 (m, 1H), 5.64 (s, 1H), 4.22 (dd, *J* = 15.0, 5.1 Hz, 1H), 3.46–3.42 (m, 1H), 3.26 (dd, *J* = 9.6, 6.1 Hz, 1H), 3.01–2.95 (m, 2H), 2.60 (dd, *J* = 17.5, 7.9 Hz, 1H), 2.52–2.45 (m, 1H), 2.42–2.34 (m, 2H), 2.25 (s, 3H), 1.96–1.91 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) d 205.8, 176.4, 174.6, 143.8, 142.1, 136.8, 131.2, 129.8, 129.2, 128.9, 127.3, 127.0, 126.2, 125.42, 125.40, 52.1, 45.3, 41.5, 40.8, 37.4, 36.3, 31.5, 31.2, 21.3; MS (MALDI) calcd. for $C_{28}H_{26}N_2O_5S_2Na$ $[M + Na]^+$ 557.12, found 557.08; HRMS (ESI) calcd. for $C_{28}H_{30}N_3O_5S_2$ $[M + NH_4]^+$ 552.1627, found 552.1647.



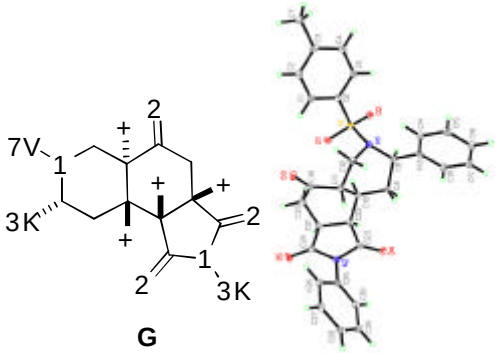
FD

17ca: 82% yield; white solid; m.p. 223–224 °C; IR (film) ν_{max} 3064, 2924, 1712, 1393, 1156, 693 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) d 7.53 (d, *J* = 8.3 Hz, 2H), 7.45–7.35 (m, 3H), 7.25–7.17 (m, 6H), 7.14–7.10 (m, 2H), 4.96 (dd, *J* = 10.7, 7.2 Hz, 1H), 3.99 (dd, *J* = 14.9, 2.9 Hz, 1H), 3.47 (td, *J* = 8.6, 1.4 Hz, 1H), 3.42–3.31 (m, 2H), 3.07 (dd, *J* = 17.7, 1.4 Hz, 1H), 2.67 (dd, *J* = 17.7, 7.7 Hz, 1H), 2.62–2.56 (m, 1H), 2.41 (s, 3H), 2.35–2.25 (m, 1H), 1.95–1.88 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) d 205.1, 177.0, 175.5, 144.0, 142.8, 135.7, 134.4, 131.3, 129.9, 129.7, 129.2, 129.0, 127.8, 127.7, 126.5, 126.2, 124.6, 57.7, 47.5, 41.7, 39.9, 37.5, 36.1, 33.4, 33.0, 21.6; MS (MALDI) calcd. for $C_{30}H_{27}ClN_2O_5SNa$ $[M + Na]^+$ 585.12, found 585.11; HRMS (ESI) calcd. for $C_{30}H_{31}ClN_3O_5S$ $[M + NH_4]^+$ 580.1673, found 580.1647.



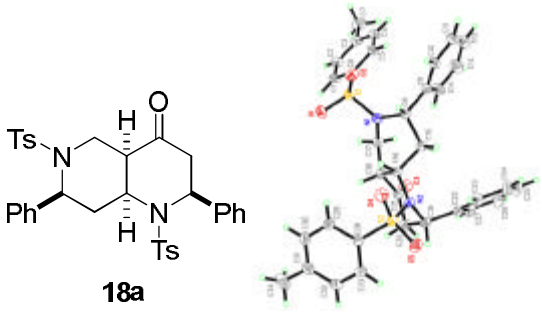
17cb

17cb: 92% yield; white solid; m.p. 200–201 °C; IR (film) ν_{max} 3063, 2922, 1712, 1385, 1158, 665 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.72 (d, *J* = 8.2 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.32–7.15 (m, 8H), 5.44 (s, 1H), 4.29 (dd, *J* = 15.2, 4.9 Hz, 1H), 3.40 (t, *J* = 8.0 Hz, 1H), 3.23 (dd, *J* = 9.5, 5.1 Hz, 1H), 2.95 (d, *J* = 16.6 Hz, 1H), 2.79 (dd, *J* = 15.3, 11.0 Hz, 1H), 2.56–2.49 (m, 2H), 2.21 (s, 3H), 2.21–2.19 (m, 2H), 1.86–1.82 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) d 205.7, 176.4, 174.4, 144.0, 139.3, 137.2, 135.1, 131.2, 130.4, 130.0, 129.2, 128.8, 127.6, 126.7, 126.6, 126.1, 124.7, 53.8, 45.1, 41.4, 40.9, 37.3, 36.3, 31.3, 28.9, 21.2; MS (MALDI) calcd. for $C_{30}H_{27}ClN_2O_5SNa$ $[M + Na]^+$ 585.12, found 585.08; HRMS (ESI) calcd. for $C_{30}H_{31}ClN_3O_5S$ $[M + NH_4]^+$ 580.1673, found 580.1653.



G

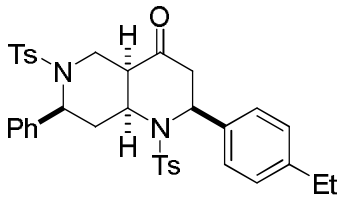
17d: 87% yield; yellow solid; decomposed at 200 °C; IR (film) ν_{max} 3063, 2919, 1710, 1383, 1156, 656 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.55 (d, *J* = 8.3 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.38–7.35 (m, 1H), 7.26–7.21 (m, 9H), 5.03 (dd, *J* = 10.6, 7.4 Hz, 1H), 3.98 (dd, *J* = 15.0, 2.8 Hz, 1H), 3.47–3.43 (m, 1H), 3.40–3.32 (m, 2H), 3.05 (dd, *J* = 17.7, 1.5 Hz, 1H), 2.67–2.59 (m, 2H), 2.40 (s, 3H), 2.33–2.26 (m, 1H), 2.01–1.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) d 205.3, 177.0, 175.5, 143.7, 140.9, 135.9, 131.4, 129.6, 129.2, 128.9, 128.5, 127.9, 127.5, 126.3, 126.2, 58.0, 47.6, 41.7, 39.7, 37.5, 36.1, 33.4, 33.1, 21.6; MS (MALDI) calcd. for $C_{30}H_{28}N_2O_5SNa$ $[M + Na]^+$ 551.16, found 551.15; HRMS (ESI) calcd. for $C_{30}H_{29}N_2O_5S$ $[M + H]^+$ 529.1797, found 529.1805.



18a

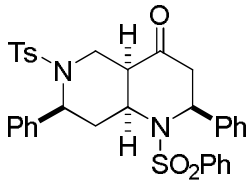
18a: 88% yield; white solid; m.p. 205–206 °C; IR (film) ν_{max} 3062, 2921, 1714, 1347, 1161, 659 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.78 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.40–7.37 (m, 4H), 7.23 (t, *J* = 7.5 Hz, 2H), 7.18–7.16 (m, 3H), 7.12–7.07 (m, 3H), 6.84–6.83 (m, 2H), 5.72 (d, *J* = 6.7 Hz, 1H), 4.92 (dd, *J* = 11.2, 7.1 Hz, 1H), 4.63–4.58 (m, 1H), 3.81 (dd, *J* = 15.3, 8.0 Hz, 1H), 3.43 (dd, *J* = 15.3, 9.2 Hz, 1H), 2.95 (dd, *J* = 14.8, 2.0 Hz, 1H), 2.68 (dd, *J* = 17.5, 8.9 Hz, 1H), 2.49 (s, 3H), 2.38 (s, 3H), 2.23 (dd, *J* = 14.1, 7.2 Hz, 1H), 1.76 (ddd, *J* = 13.6, 7.0, 2.0 Hz, 1H), 0.95 (td, *J* = 13.5, 11.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) d 206.6, 144.2, 143.2, 140.2, 139.4, 137.4, 137.0, 130.3, 129.4, 128.5, 128.2, 128.0, 127.3, 127.0, 126.7, 125.8,

58.5, 55.1, 53.3, 45.4, 41.4, 40.5, 36.3, 21.6, 21.4; MS (MALDI) calcd. for $C_{34}H_{34}N_2O_5S_2Na$ [M + Na]$^+$ 637.18, found 637.08; HRMS (ESI) calcd. for $C_{34}H_{35}N_2O_5S_2$ [M + H]$^+$ 615.1987, found 615.1975.



18b

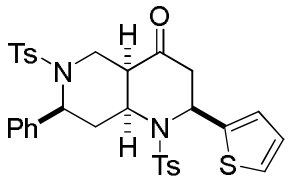
18b: 90% yield; white solid; m.p. 210–211 °C; IR (film) ν_{max} 3024, 2964, 2923, 1716, 1347, 1093, 659 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.75 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.12–7.03 (m, 5H), 6.83 (d, *J* = 6.7 Hz, 2H), 5.69 (d, *J* = 6.5 Hz, 1H), 4.90 (dd, *J* = 11.3, 7.1 Hz, 1H), 4.59–4.54 (m, 1H), 3.81 (dd, *J* = 15.3, 8.0 Hz, 1H), 3.40 (dd, *J* = 15.3, 9.3 Hz, 1H), 2.93 (dd, *J* = 14.9, 1.9 Hz, 1H), 2.66 (dd, *J* = 17.5, 8.9 Hz, 1H), 2.51 (q, *J* = 7.6 Hz, 2H), 2.48 (s, 3H), 2.38 (s, 3H), 2.22 (dd, *J* = 14.5, 7.3 Hz, 1H), 1.75 (ddd, *J* = 13.5, 7.1, 2.1 Hz, 1H), 1.06 (t, *J* = 7.6 Hz, 3H), 0.92 (td, *J* = 13.5, 11.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) d 206.7, 144.4, 144.1, 143.2, 140.2, 137.5, 137.1, 136.6, 130.3, 129.4, 128.1, 128.0, 127.4, 127.3, 127.0, 126.6, 125.8, 58.3, 54.9, 53.1, 45.4, 41.5, 40.5, 36.6, 28.3, 21.6, 21.4, 15.6; MS (MALDI) calcd. for $C_{36}H_{38}N_2O_5S_2Na$ [M + Na]$^+$ 665.21, found 665.20; HRMS (ESI) calcd. for $C_{36}H_{39}N_2O_5S_2$ [M + H]$^+$ 643.2300, found 643.2287.



18c

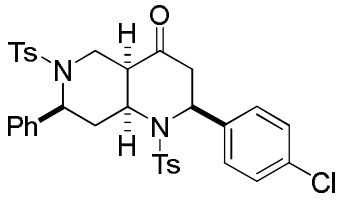
18c: 89% yield; white solid; m.p. 173–174 °C; IR (film) ν_{max} 3062, 3027, 2917, 1715, 1347, 1163, 660 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.89 (d, *J* = 7.4 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 7.6 Hz, 2H), 7.24–7.08 (m, 8H), 6.84 (d, *J* = 6.7 Hz, 2H), 5.73 (d, *J* = 6.5 Hz, 1H), 4.93 (dd, *J* = 11.1, 7.1 Hz, 1H), 4.61 (t, *J* = 10.5 Hz, 1H), 3.80 (dd, *J* = 15.4, 8.0 Hz, 1H), 3.44 (dd, *J* = 15.3, 9.2 Hz, 1H), 2.96 (dd, *J* = 14.8, 1.5 Hz, 1H), 2.67 (dd, *J* = 17.4, 8.7 Hz, 1H), 2.37 (s, 3H), 2.22 (dd, *J* = 14.7, 7.1 Hz, 1H), 1.78

(ddd, *J* = 13.3, 7.0, 1.8 Hz, 1H), 0.97 (td, *J* = 12.5, 11.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) d 206.4, 143.3, 140.3, 140.1, 139.2, 137.0, 133.2, 129.7, 129.5, 128.5, 128.2, 128.0, 127.34, 127.31, 127.0, 126.6, 125.8, 58.4, 55.2, 53.4, 45.4, 41.4, 40.4, 36.3, 21.4; MS (MALDI) calcd. for $C_{33}H_{32}N_2O_5S_2Na$ $[M + Na]^+$ 623.16, found 623.09; HRMS (ESI) calcd. for $C_{33}H_{33}N_2O_5S_2$ $[M + H]^+$ 601.1831, found 601.1792.



18d

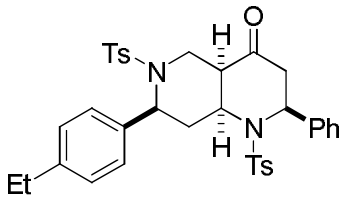
18d: 89% yield; white solid; m.p. 192–193 °C; IR (film) ν_{max} 3062, 3030, 2915, 1716, 1346, 1160, 660 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.77 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.18–7.11 (m, 6H), 6.93–6.91 (m, 2H), 6.80–6.75 (m, 2H), 5.84 (d, *J* = 6.7 Hz, 1H), 4.93 (dd, *J* = 11.3, 7.1 Hz, 1H), 4.57 (t, *J* = 12.4 Hz, 1H), 3.88 (dd, *J* = 15.3, 7.9 Hz, 1H), 3.50 (dd, *J* = 15.4, 9.4 Hz, 1H), 2.96 (dd, *J* = 14.6, 1.6 Hz, 1H), 2.78 (dd, *J* = 17.4, 9.0 Hz, 1H), 2.48 (s, 3H), 2.44–2.39 (m, 1H), 2.37 (s, 3H), 1.98 (ddd, *J* = 13.6, 7.0, 2.4 Hz, 1H), 1.16 (td, *J* = 13.4, 11.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) d 205.8, 144.2, 144.1, 143.2, 140.3, 137.2, 137.0, 130.2, 129.5, 128.3, 127.4, 127.0, 126.8, 126.5, 126.4, 125.8, 58.5, 53.3, 52.4, 45.6, 43.1, 40.5, 35.8, 21.5, 21.4; MS (MALDI) calcd. for $C_{32}H_{32}N_2O_5S_3Na$ $[M + Na]^+$ 643.14, found 643.15; HRMS (ESI) calcd. for $C_{32}H_{33}N_2O_5S_3$ $[M + H]^+$ 621.1551, found 621.1517.



18e

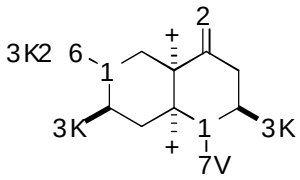
18e: 91% yield; white solid; m.p. 217–218 °C; IR (film) ν_{max} 3063, 3027, 2917, 1715, 1347, 1162, 659 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.78 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.22–7.10 (m, 7H), 6.86 (d, *J* = 6.3 Hz, 2H), 5.67 (d, *J* = 6.5 Hz, 1H), 4.95 (dd, *J* = 11.1, 7.0 Hz, 1H), 4.64 (t, *J* = 10.3 Hz, 1H), 3.77 (dd, *J* = 15.4, 8.0 Hz, 1H), 3.46 (dd, *J* = 15.4, 9.4 Hz, 1H), 2.90 (dd, *J* = 14.7, 1.9 Hz, 1H), 2.69 (dd, *J* = 17.4, 8.8 Hz, 1H), 2.49 (s, 3H), 2.38 (s, 3H), 2.24 (dd, *J* = 14.7, 7.1 Hz, 1H), 1.81 (ddd, *J* = 13.4,

6.9, 2.1 Hz, 1H), 0.99 (td, *J* = 13.5, 11.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) d 206.2, 144.3, 143.3, 140.0, 138.0, 137.1, 137.0, 134.0, 130.4, 129.4, 128.8, 128.7, 128.3, 127.4, 127.1, 126.6, 125.8, 58.4, 54.9, 53.5, 45.5, 41.3, 40.3, 36.5, 21.5, 21.4; MS (MALDI) calcd. for $C_{34}H_{33}ClN_2O_5S_2Na$ $[M + Na]^+$ 671.14, found 671.13; HRMS (MALDI) calcd. for $C_{34}H_{34}ClN_2O_5S_2$ $[M + H]^+$ 649.1597, found 649.1586.



18f

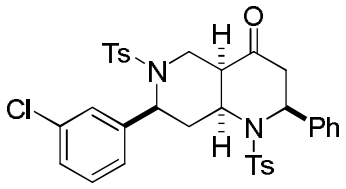
18f: 90% yield; white solid; m.p. 186–187 °C; IR (film) ν_{max} 3057, 2964, 2921, 1716, 1347, 1162, 660 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.77 (d, *J* = 8.1 Hz, 2H), 7.42–7.36 (m, 6H), 7.23 (d, *J* = 7.5 Hz, 2H), 7.18–7.14 (m, 3H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.75 (d, *J* = 8.0 Hz, 2H), 5.71 (d, *J* = 6.4 Hz, 1H), 4.87 (dd, *J* = 11.1, 7.0 Hz, 1H), 4.60 (t, *J* = 10.5 Hz, 1H), 3.78 (dd, *J* = 15.3, 8.0 Hz, 1H), 3.47 (dd, *J* = 15.3, 9.1 Hz, 1H), 2.95 (dd, *J* = 15.0, 1.5 Hz, 1H), 2.68 (dd, *J* = 17.3, 8.7 Hz, 1H), 2.52 (q, *J* = 7.6 Hz, 2H), 2.47 (s, 3H), 2.36 (s, 3H), 2.24 (dd, *J* = 14.7, 7.1 Hz, 1H), 1.76–1.73 (m, 1H), 1.16 (t, *J* = 7.6 Hz, 3H), 1.01 (td, *J* = 12.5, 11.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) d 206.6, 144.2, 143.4, 143.0, 139.5, 137.4, 137.22, 137.21, 130.3, 129.4, 128.5, 128.0, 127.6, 127.3, 127.0, 126.6, 126.0, 58.4, 55.2, 53.4, 45.6, 41.1, 40.4, 36.3, 28.3, 21.5, 21.4, 15.4; MS (MALDI) calcd. for $C_{36}H_{38}N_2O_5S_2Na$ $[M + Na]^+$ 665.21, found 665.18; HRMS (ESI) calcd. for $C_{36}H_{39}N_2O_5S_2$ $[M + H]^+$ 643.2300, found 643.2286.



J

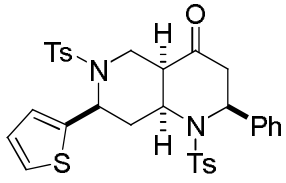
18g: 89% yield; white solid; m.p. 202–203 °C; IR (film) ν_{max} 3063, 3027, 2917, 1714, 1348, 1162, 660 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.78 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.39–7.34 (m, 6H), 7.22 (t, *J* = 7.5 Hz, 2H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.12–7.05 (m, 3H), 6.81 (d, *J* = 7.2 Hz, 2H), 5.74 (d, *J* = 6.5 Hz, 1H), 4.93 (dd, *J* = 11.2, 7.0 Hz, 1H), 4.62 (t, *J* = 10.5 Hz, 1H), 3.83 (dd, *J* = 15.3, 7.9 Hz, 1H), 3.48 (dd, *J* = 15.3, 9.2 Hz, 1H),

2.97 (dd, *J* = 14.8, 1.3 Hz, 1H), 2.69 (dd, *J* = 17.3, 8.7 Hz, 1H), 2.48 (s, 3H), 2.27 (dd, *J* = 14.7, 7.1 Hz, 1H), 1.76 (ddd, *J* = 13.5, 6.8, 2.0 Hz, 1H), 0.98 (td, *J* = 12.5, 11.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) d 206.5, 144.2, 140.0, 139.9, 139.4, 137.3, 132.3, 130.4, 128.8, 128.5, 128.2, 128.0, 127.4, 127.3, 126.9, 126.7, 125.9, 58.7, 55.1, 53.3, 45.6, 41.4, 40.6, 36.4, 21.5; MS (MALDI) calcd. for $C_{33}H_{32}N_2O_5S_2Na$ $[M + Na]^+$ 623.16, found 623.10; HRMS (ESI) calcd. for $C_{33}H_{33}N_2O_5S_2$ $[M + H]^+$ 601.1831, found 601.1801.



18h

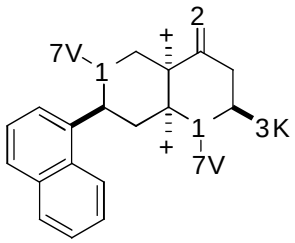
18h: 85% yield; white solid; m.p. 183–184 °C; IR (film) ν_{max} 3063, 2920, 1714, 1348, 1162, 660 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.76 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.39–7.37 (m, 4H), 7.25–7.16 (m, 5H), 7.07–7.01 (m, 2H), 6.75 (d, *J* = 7.4 Hz, 1H), 6.63 (s, 1H), 5.72 (d, *J* = 6.7 Hz, 1H), 4.80 (dd, *J* = 11.3, 6.8 Hz, 1H), 4.59–4.54 (m, 1H), 3.79 (dd, *J* = 15.2, 7.8 Hz, 1H), 3.46 (dd, *J* = 15.3, 8.9 Hz, 1H), 2.96 (dd, *J* = 14.8, 1.9 Hz, 1H), 2.66 (dd, *J* = 17.1, 8.6 Hz, 1H), 2.47 (s, 3H), 2.38 (s, 3H), 2.24 (dd, *J* = 14.7, 7.1 Hz, 1H), 1.71 (ddd, *J* = 13.6, 6.8, 2.3 Hz, 1H), 0.87 (td, *J* = 13.4, 11.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) d 206.3, 144.2, 143.6, 142.0, 139.4, 137.3, 136.9, 134.0, 130.3, 129.6, 129.5, 128.6, 128.1, 127.5, 127.3, 127.0, 126.6, 126.0, 124.3, 58.0, 55.1, 53.2, 45.4, 41.4, 40.7, 36.4, 21.6, 21.4; MS (MALDI) calcd. for $C_{34}H_{33}ClN_2O_5S_2Na$ $[M + Na]^+$ 671.14, found 671.14; HRMS (MALDI) calcd. for $C_{34}H_{34}ClN_2O_5S_2Na$ $[M + H]^+$ 649.1597, found 649.1590.



18i

18i: 95% yield; white solid; decomposed at 210 °C; IR (film) ν_{max} 3063, 2921, 1713, 1347, 1161, 660 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) d 7.81 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.42–7.38 (m, 4H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.25–7.20 (m, 3H), 7.02 (dd, *J* = 5.0, 1.1 Hz, 1H), 6.75 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.55 (d, *J* = 3.5 Hz, 1H), 5.77 (d, *J* = 6.7 Hz, 1H), 5.28 (dd, *J* = 10.8,

7.7 Hz, 1H), 4.62 (t, *J* = 10.5 Hz, 1H), 3.66 (dd, *J* = 15.4, 8.1 Hz, 1H), 3.29 (dd, *J* = 15.4, 9.5 Hz, 1H), 2.97 (dd, *J* = 14.8, 1.7 Hz, 1H), 2.69 (dd, *J* = 17.9, 9.0 Hz, 1H), 2.48 (s, 3H), 2.38 (s, 3H), 2.25 (dd, *J* = 14.4, 7.2 Hz, 1H), 1.83 (ddd, *J* = 13.6, 7.6, 2.1 Hz, 1H), 1.03 (td, *J* = 13.5, 11.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) d 206.8, 144.2, 143.7, 143.4, 139.5, 137.4, 136.8, 130.3, 129.5, 128.6, 128.1, 127.5, 127.1, 126.7, 126.3, 125.0, 124.6, 55.0, 53.5, 52.8, 45.3, 41.4, 39.2, 36.1, 21.6, 21.4; MS (MALDI) calcd. for $C_{32}H_{32}N_2O_5S_3Na$ $[M + Na]^+$ 643.14, found 643.10; HRMS (ESI) calcd. for $C_{32}H_{33}N_2O_5S_3$ $[M + H]^+$ 621.1551, found 621.1550.

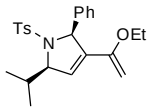


M

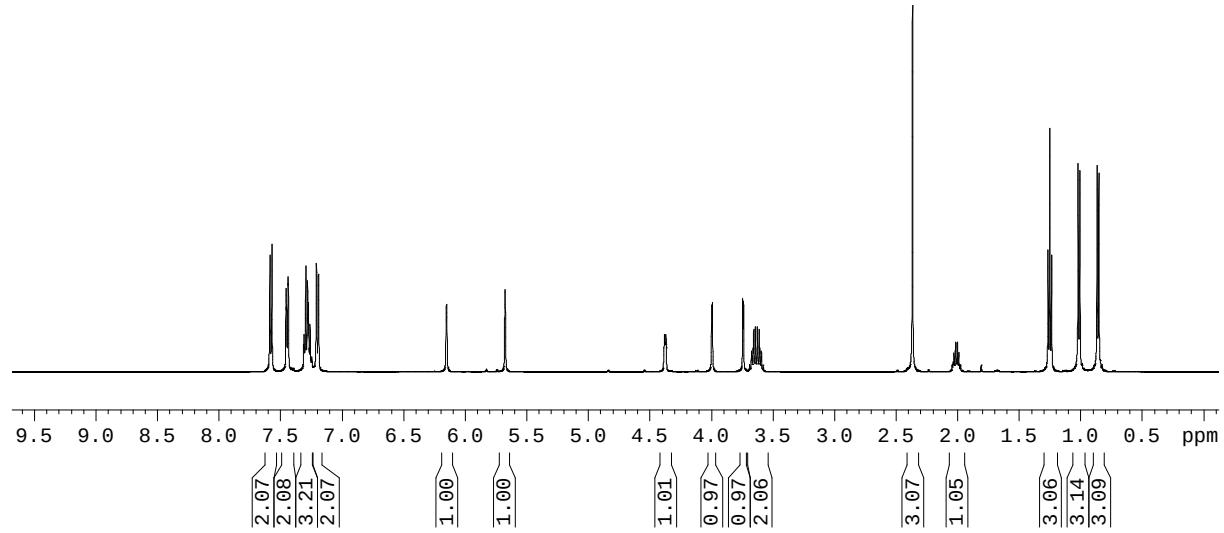
18j: 80% yield; white solid; decomposed at 218 °C; IR (film) ν_{max} 3062, 2914, 1715, 1348, 1162, 660 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) d 7.83 (d, *J* = 8.2 Hz, 3H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.52–7.37 (m, 6H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.16–7.06 (m, 5H), 7.00 (t, *J* = 7.8 Hz, 2H), 5.71 (d, *J* = 5.9 Hz, 1H), 5.63 (dd, *J* = 11.6, 6.3 Hz, 1H), 4.77–4.71 (m, 1H), 4.02 (dd, *J* = 15.4, 7.8 Hz, 1H), 3.67 (dd, *J* = 15.4, 9.2 Hz, 1H), 2.97 (dd, *J* = 14.8, 2.3 Hz, 1H), 2.81 (dd, *J* = 17.3, 8.8 Hz, 1H), 2.51 (s, 3H), 2.32 (s, 3H), 2.32–2.27 (m, 1H), 1.98 (ddd, *J* = 13.8, 6.2, 2.3 Hz, 1H), 1.03 (td, *J* = 13.5, 11.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) d 206.7, 144.3, 143.3, 139.2, 137.5, 136.8, 136.3, 133.6, 130.4, 129.8, 129.3, 128.7, 128.6, 128.1, 128.0, 127.3, 127.2, 126.8, 126.4, 125.6, 125.1, 122.8, 122.5, 56.0, 55.3, 53.9, 46.0, 41.7, 41.6, 37.1, 21.7, 21.5; MS (MALDI) calcd. for $C_{38}H_{36}N_2O_5S_2Na$ $[M + Na]^+$ 687.20, found 687.23; HRMS (ESI) calcd. for $C_{38}H_{37}N_2O_5S_2$ $[M + H]^+$ 665.2143, found 665.2134.

Crystallographic Data for 7d, 8a, 9a, 10a, 11aa, 11ab, 12a, 13a, 14a, 14c´, 15a, 16b, 17cb, 17d, and 18a

Crystallographic data for **7d**, **8a**, **9a**, **10a**, **11aa**, **11ab**, **12a**, **13a**, **14a**, **15a**, **16b**, **17cb**, **17d**, **18a**, and **14c´** have been deposited with the Cambridge Crystallographic Data Centre as supplementary numbers CCDC 767099–767112 and CCDC 782217. These data can be obtained online free of charge [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk].


Ph
Ts
N
OEt

5b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2.08
3.21
2.07
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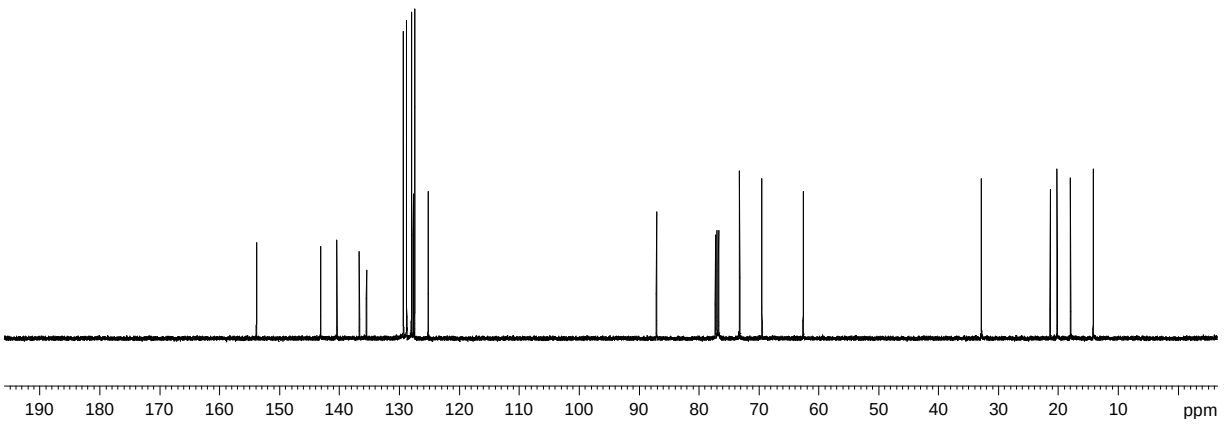
1.00
1.01
0.97
0.97
2.06
3.07
1.05
3.06
3.14
3.09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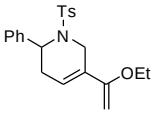
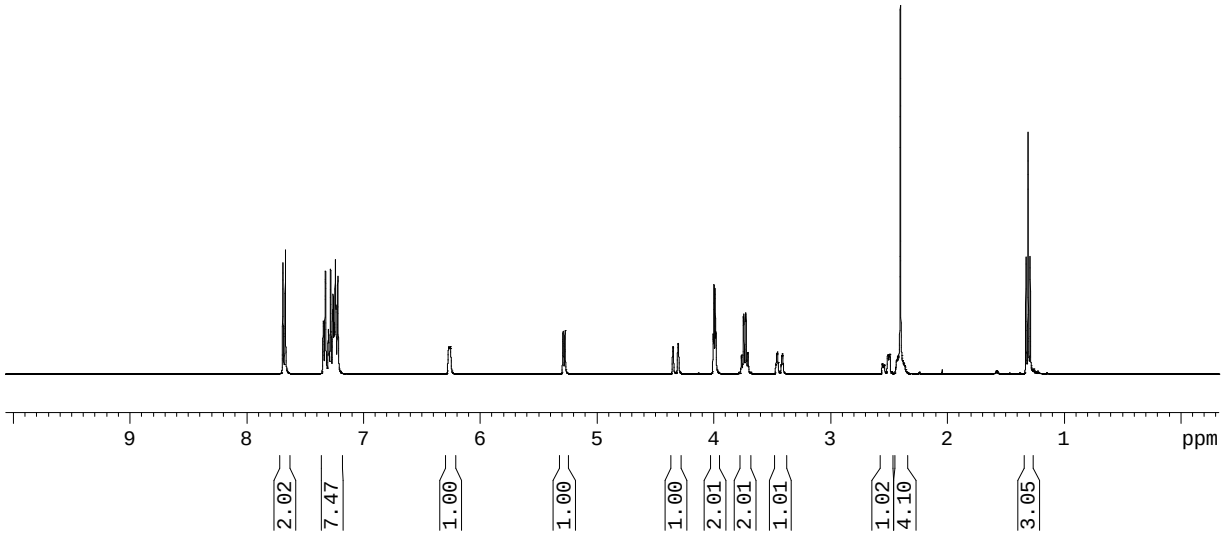

Ts
Ph
N
OEt

6a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1.02
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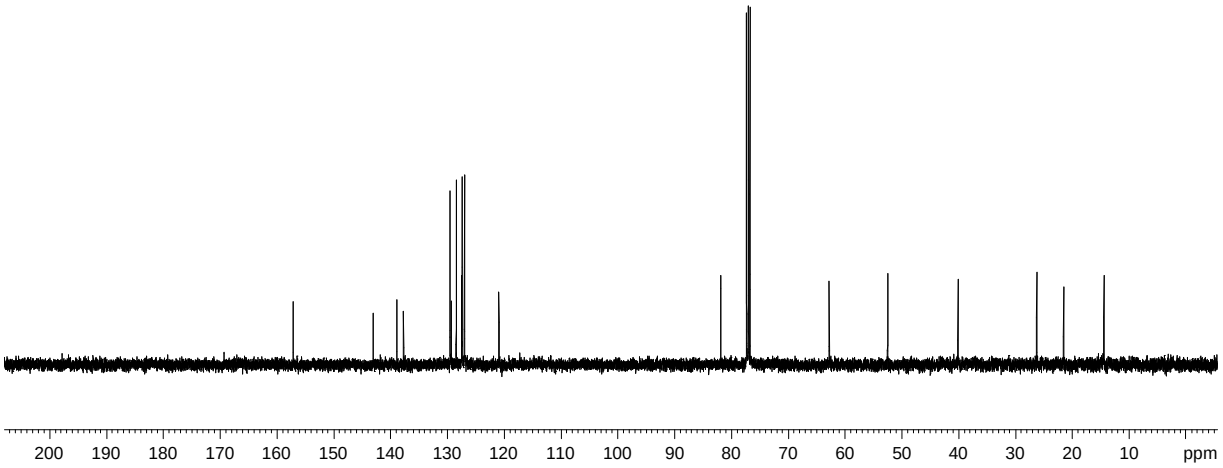
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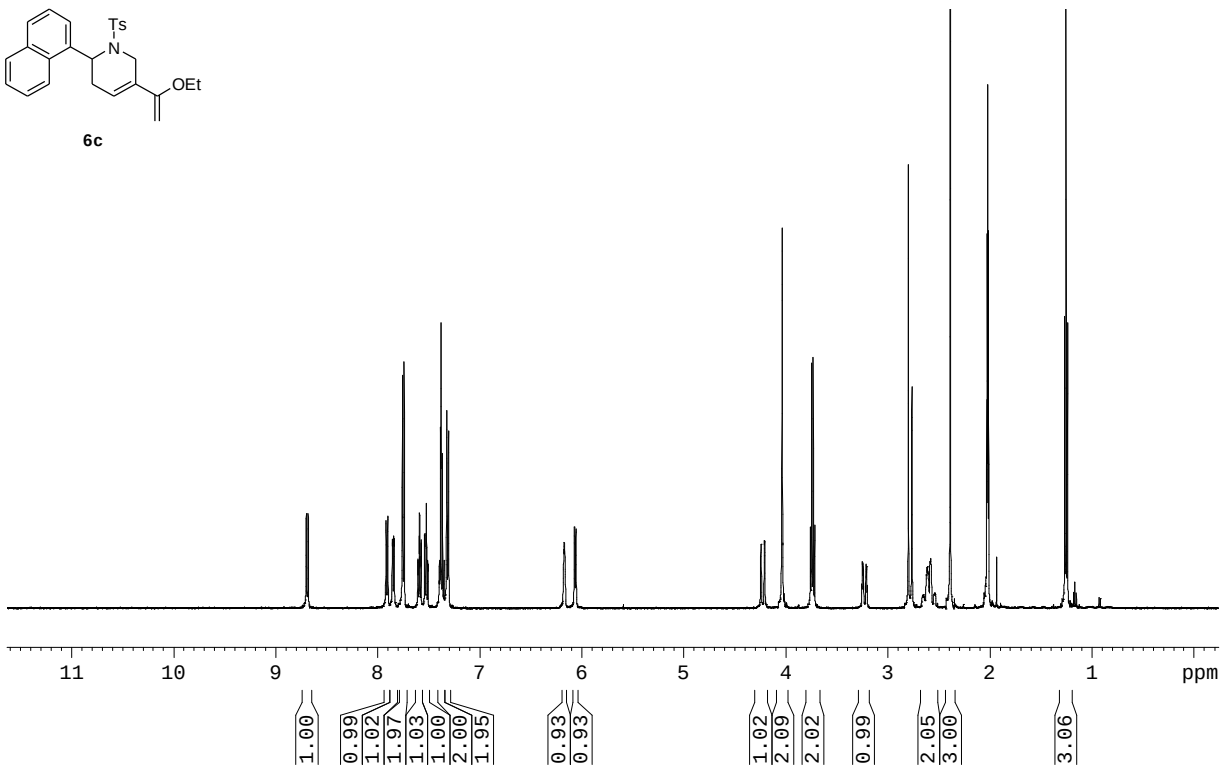
40
30
20
10
ppm


Ts
N
OEt
6c
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6
5
4
3
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1
ppm
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1.97
1.03
1.00
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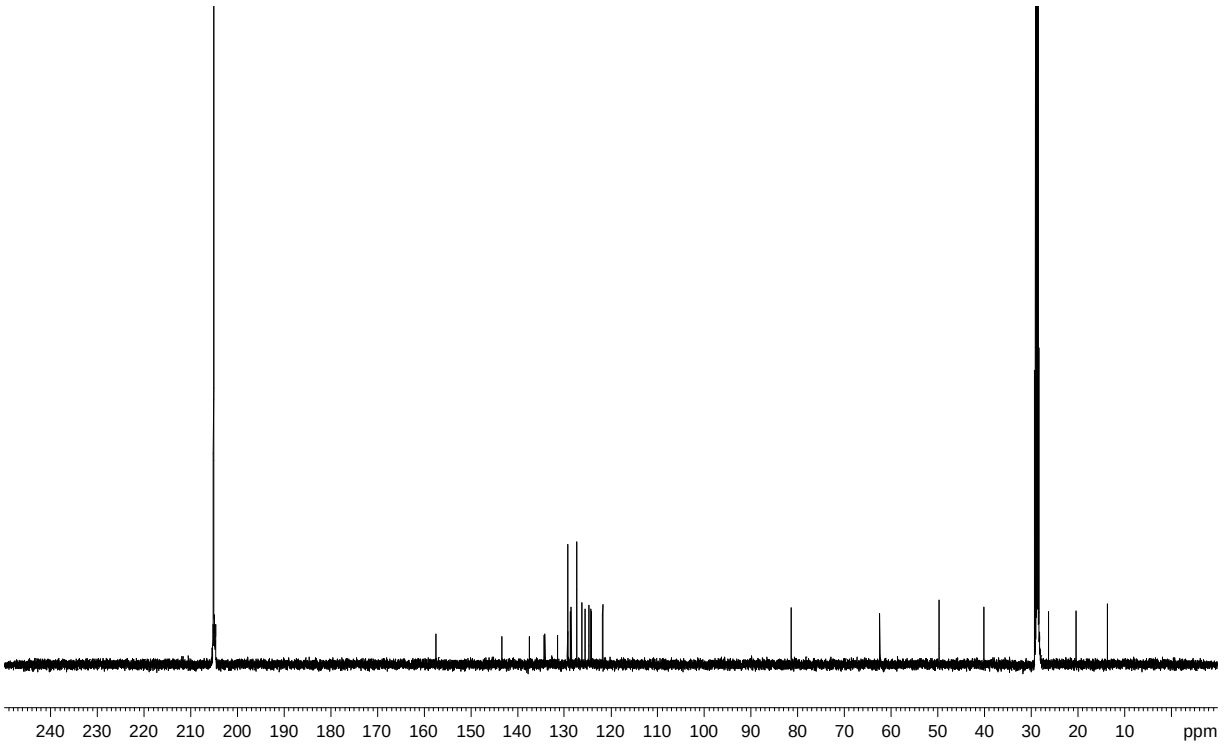
3.06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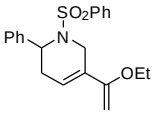
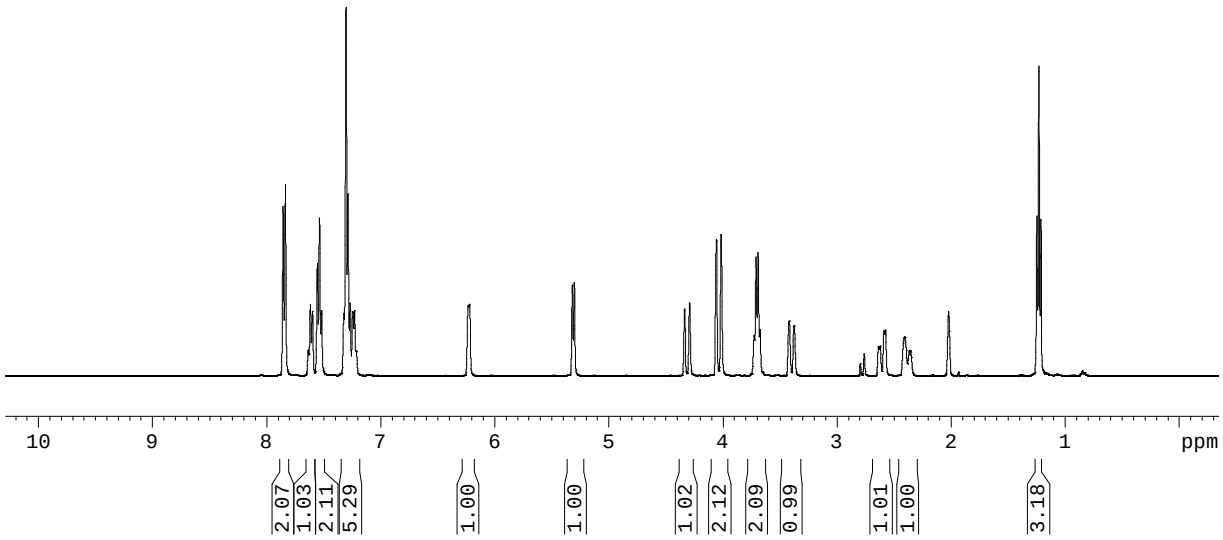
30
20
10
ppm


SO2Ph
Ph
N
OEt

6e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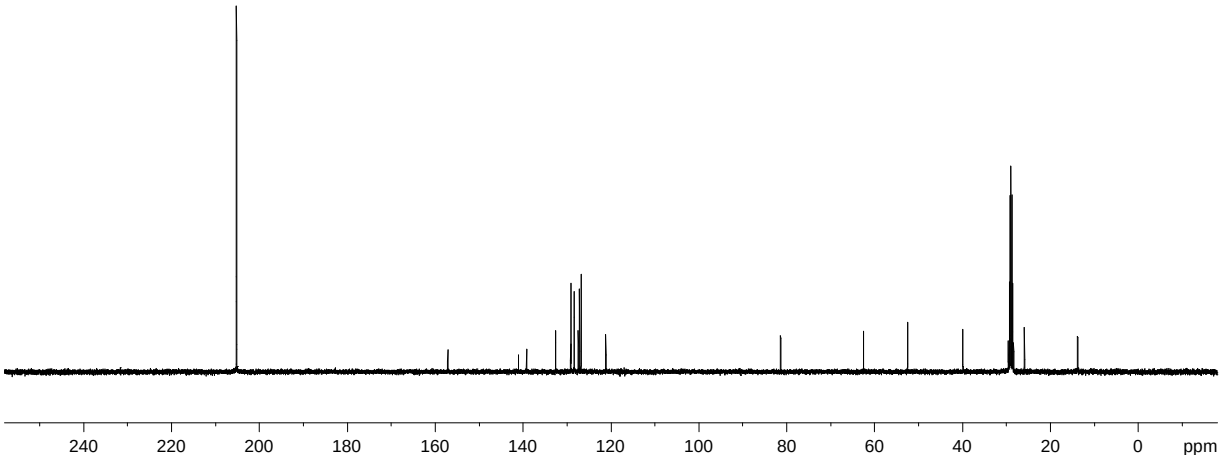
1.01
1.00
3.18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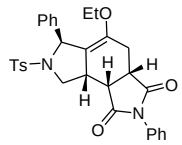
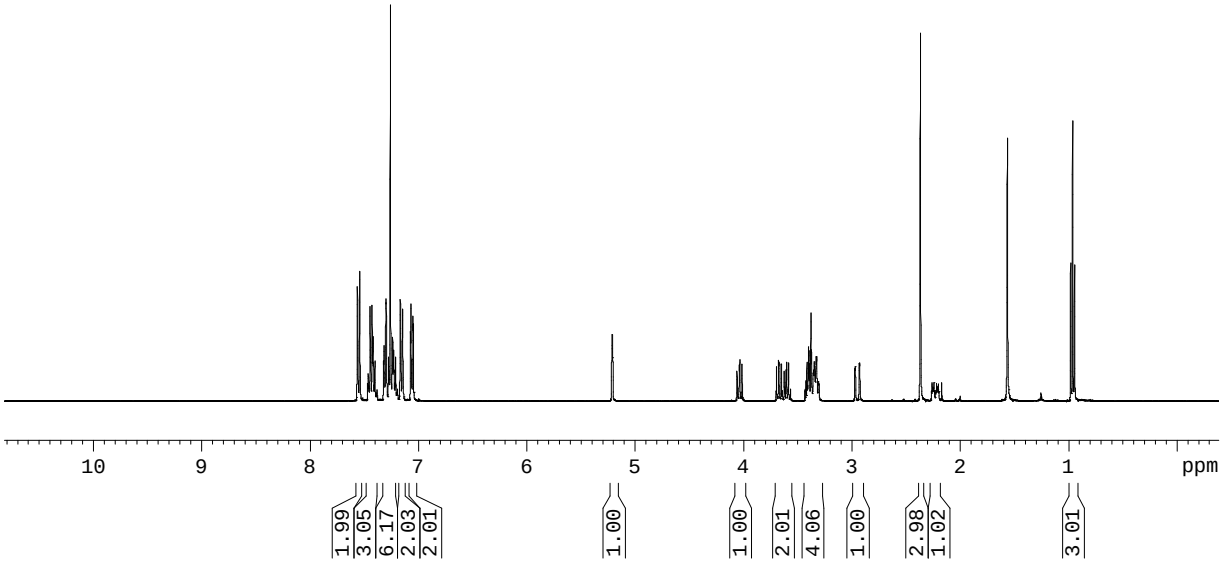
140
120
100
80
60
40
20
0
ppm


Ph
EtO
Ts–N
H
H
H
O
O
N
Ph

7a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6
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4
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ppm
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2.01
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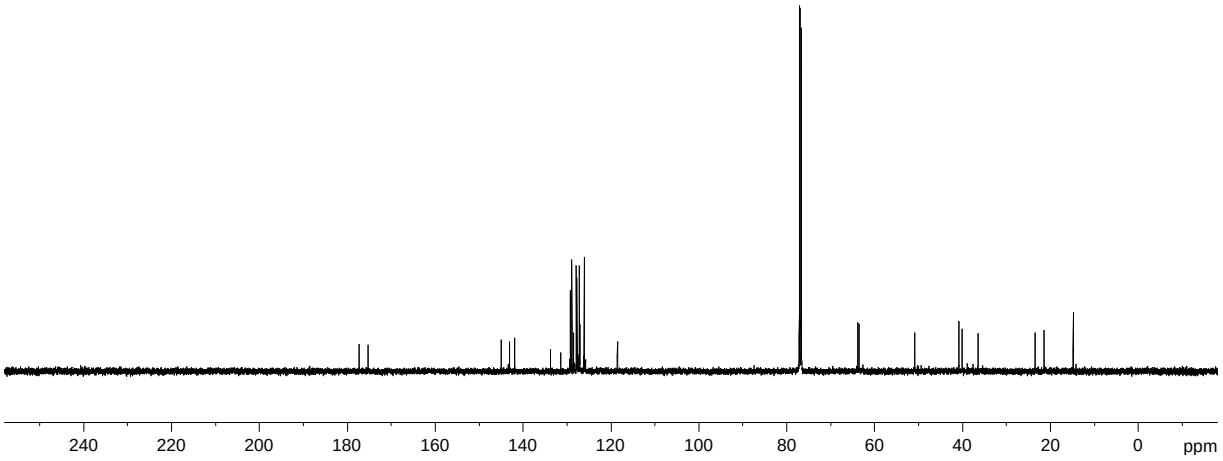
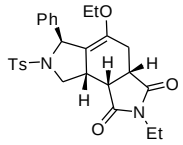
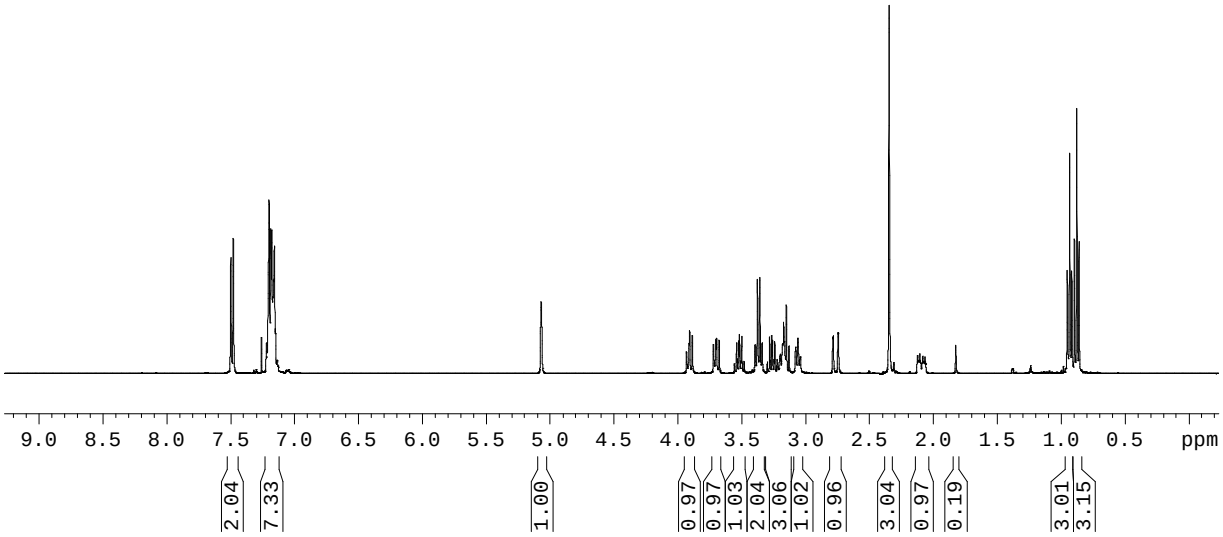
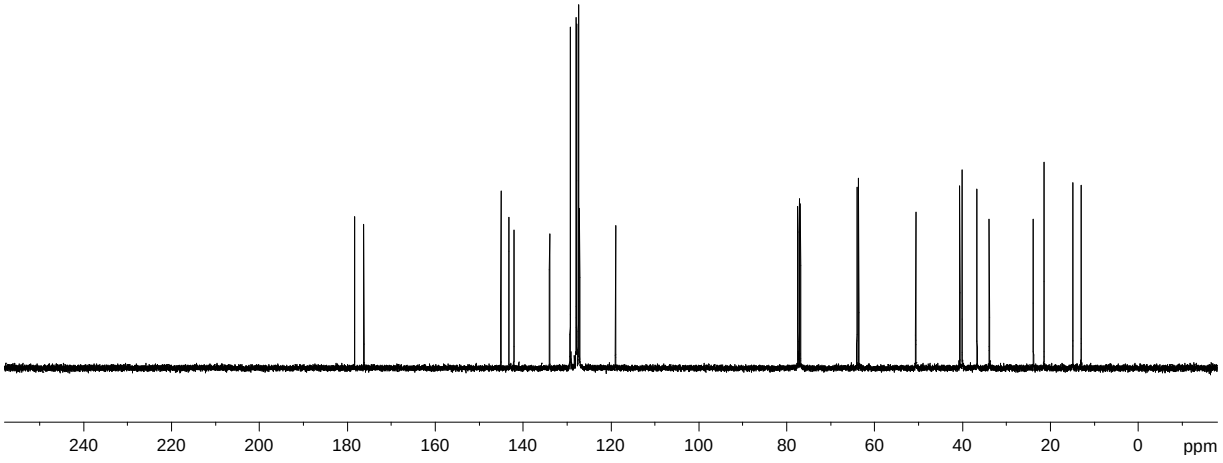
1.00
2.01
4.06
1.00
2.98
1.02
3.01

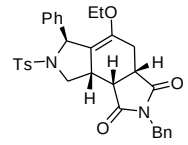

240
220
200
180
160
140
120
100
80
60
40
20
0
ppm


Ph
EtO
Ts–N
H
H
H
O
N
Et
O

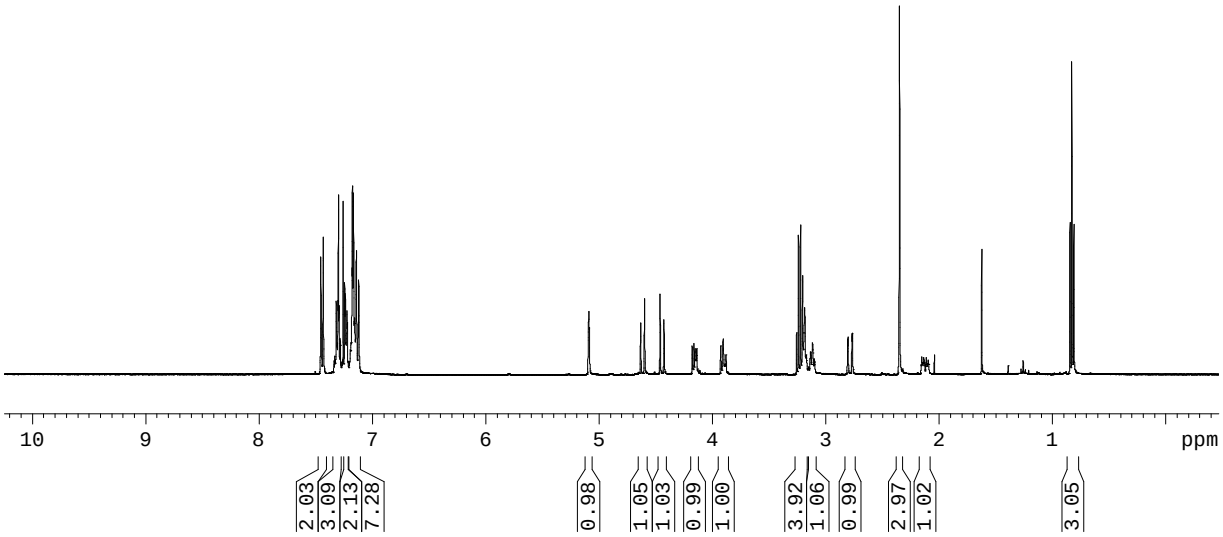
7b

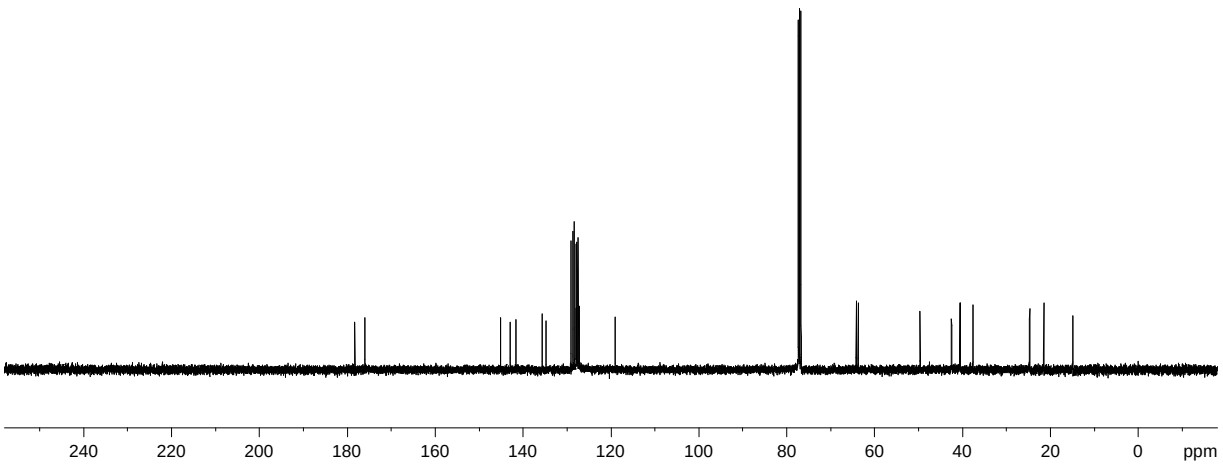

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.04
7.33
1.00
0.97
0.97
1.03
2.04
3.06
1.02
0.96
3.04
0.97
0.19
3.01
3.15

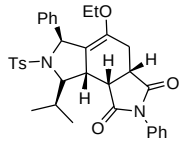

240 220 200 180 160 140 120 100 80 60 40 20 0 ppm


Ph
EtO
Ts–N
H
H
H
O
O
N
Bn

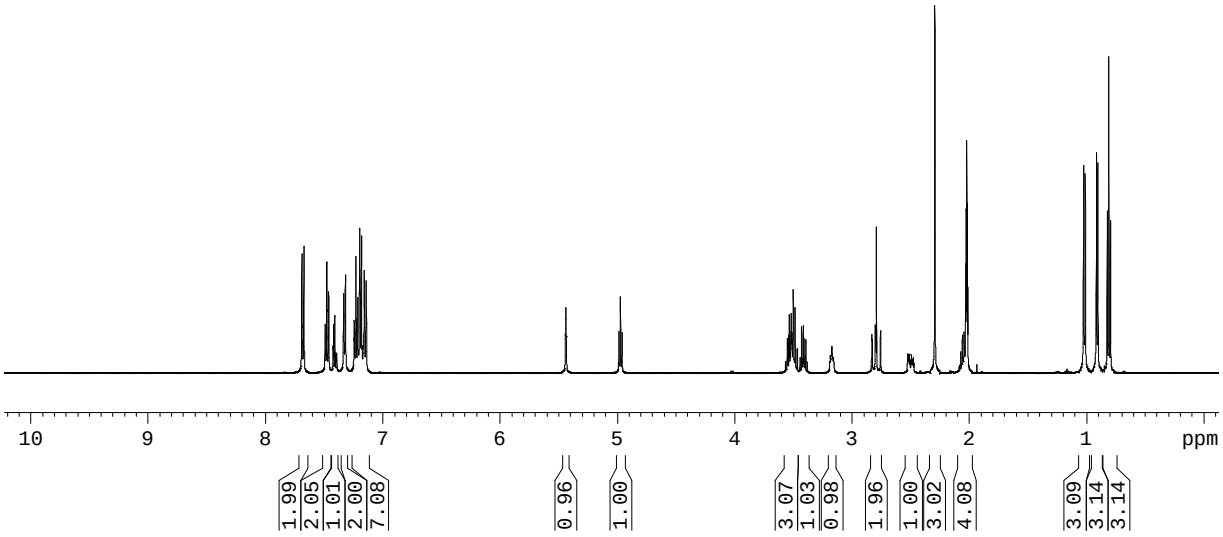
7c

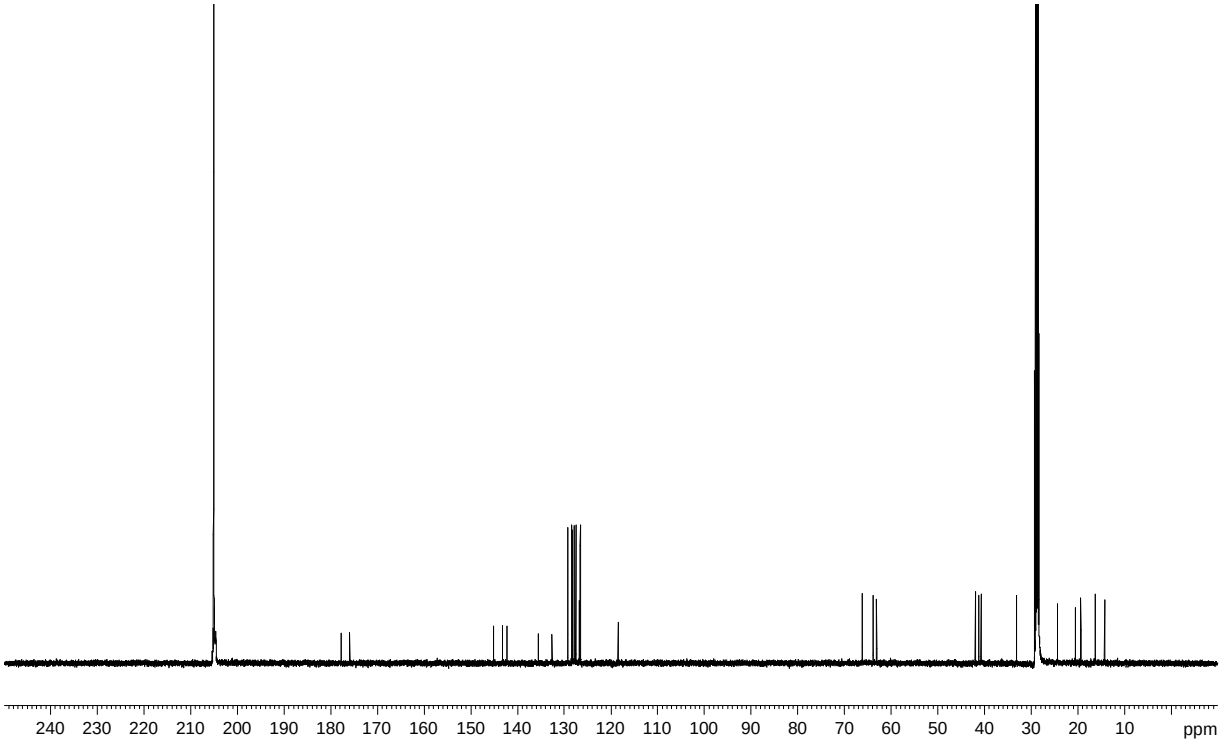

10
9
8
7
6
5
4
3
2
1
ppm
2.03
3.09
2.13
7.28
0.98
1.05
1.03
0.99
1.00
3.92
1.06
0.99
2.97
1.02
3.05


240
220
200
180
160
140
120
100
80
60
40
20
0
ppm


Ph
EtO
Ts–N
H
H
H
O
O
N
Ph

7d


10
9
8
7
6
5
4
3
2
1
ppm
1.99
2.05
1.01
2.00
7.08
0.96
1.00
3.07
1.03
0.98
1.96
1.00
3.02
4.08
3.09
3.14
3.14


240
230
220
210
200
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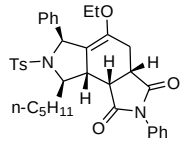
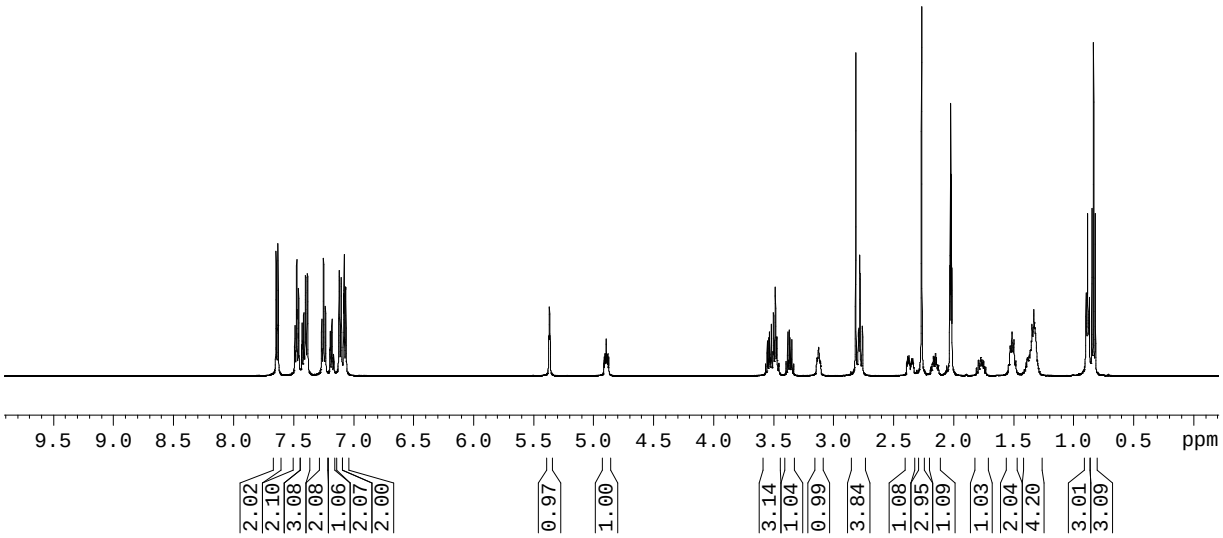
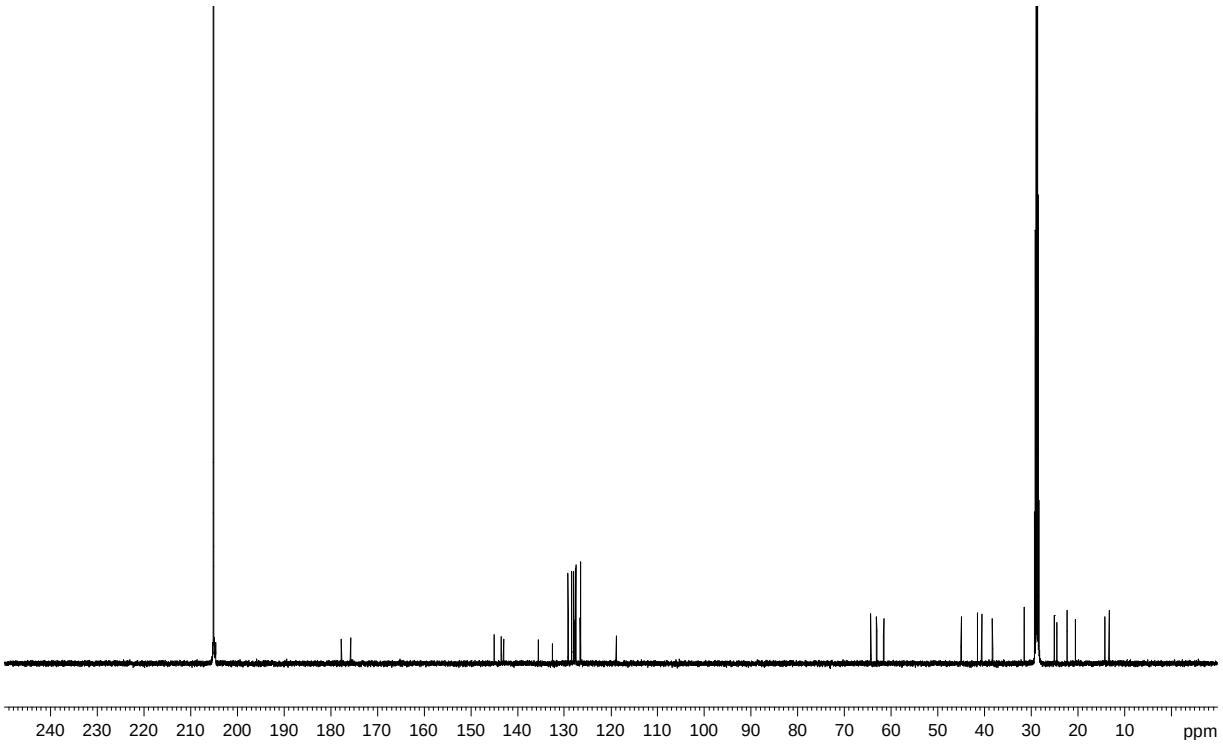
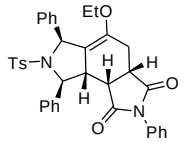
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ph
EtO
Ts–N
H
H
O
n-C5H11
H
O
N
Ph

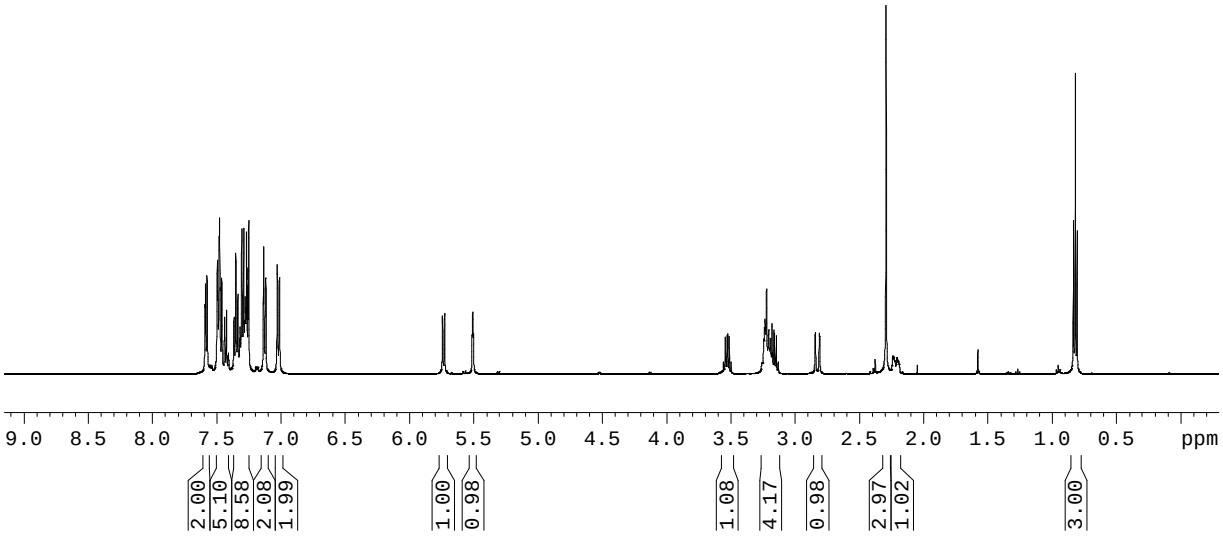
7e

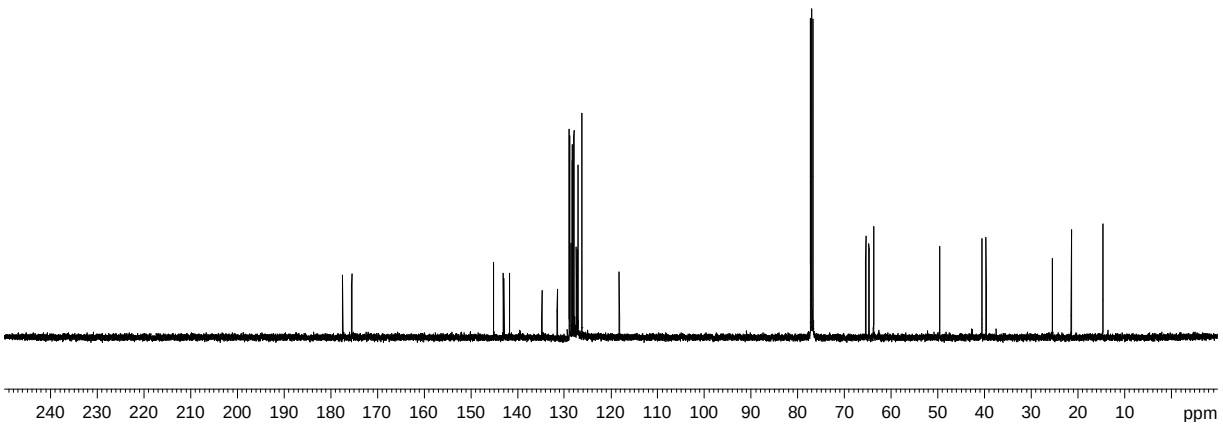

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.02 2.10 3.08 2.08 1.06 2.07 2.00 0.97 1.00 3.14 1.04 0.99 3.84 1.08 2.95 1.09 1.03 2.04 4.20 3.01 3.09

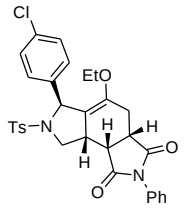

240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Ph
EtO
Ts–N
H
H
O
Ph
H
O
N
Ph

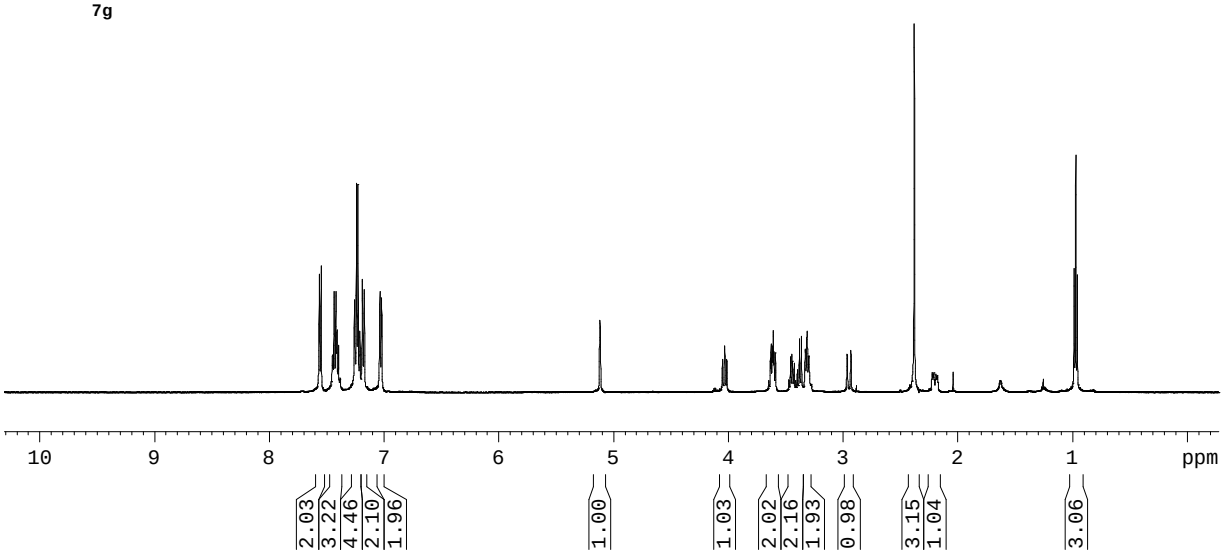
7f

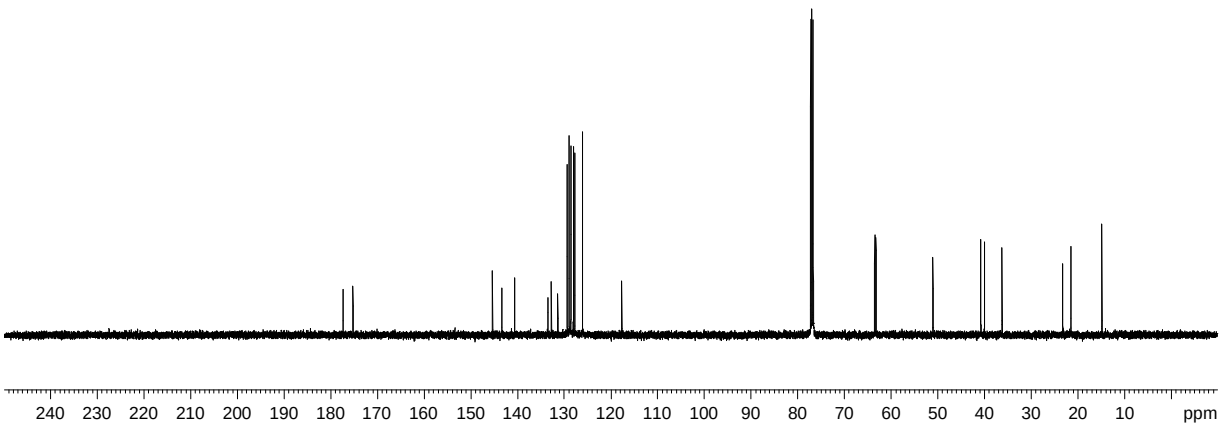

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
5.10
8.58
2.08
1.99
1.00
0.98
1.08
4.17
0.98
2.97
1.02
3.00


240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Cl
EtO
Ts–N
H
H
H
O
O
N
Ph

7g


10
9
8
7
6
5
4
3
2
1
ppm
2.03
3.22
4.46
2.10
1.96
1.00
1.03
2.02
2.16
1.93
0.98
3.15
1.04
3.06


240
230
220
210
200
190
180
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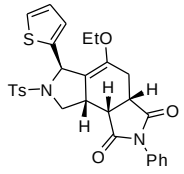
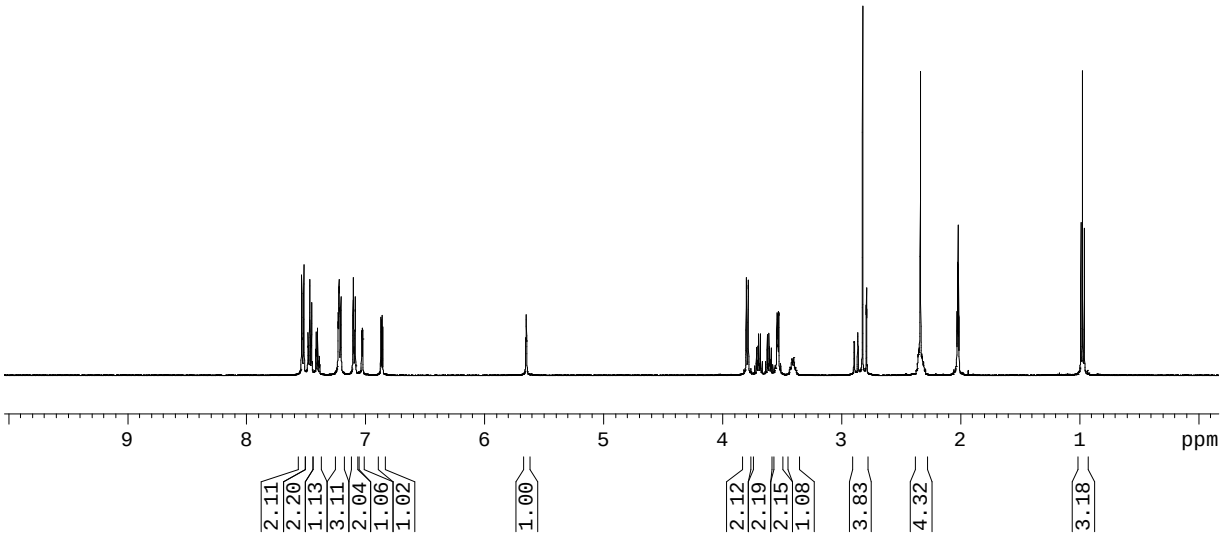
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


S
EtO
Ts–N
H
H
H
O
O
N
Ph

7h


9
8
7
6
5
4
3
2
1
ppm
2.11
2.20
1.13
3.11
2.04
1.06
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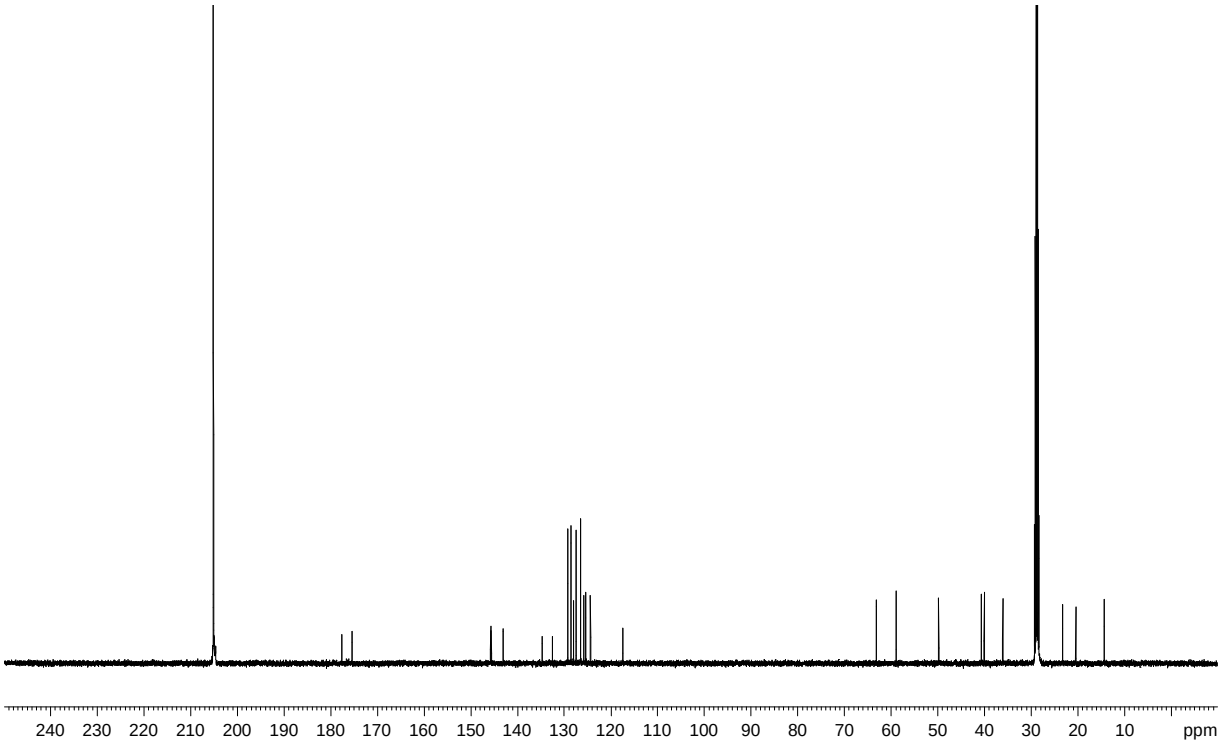
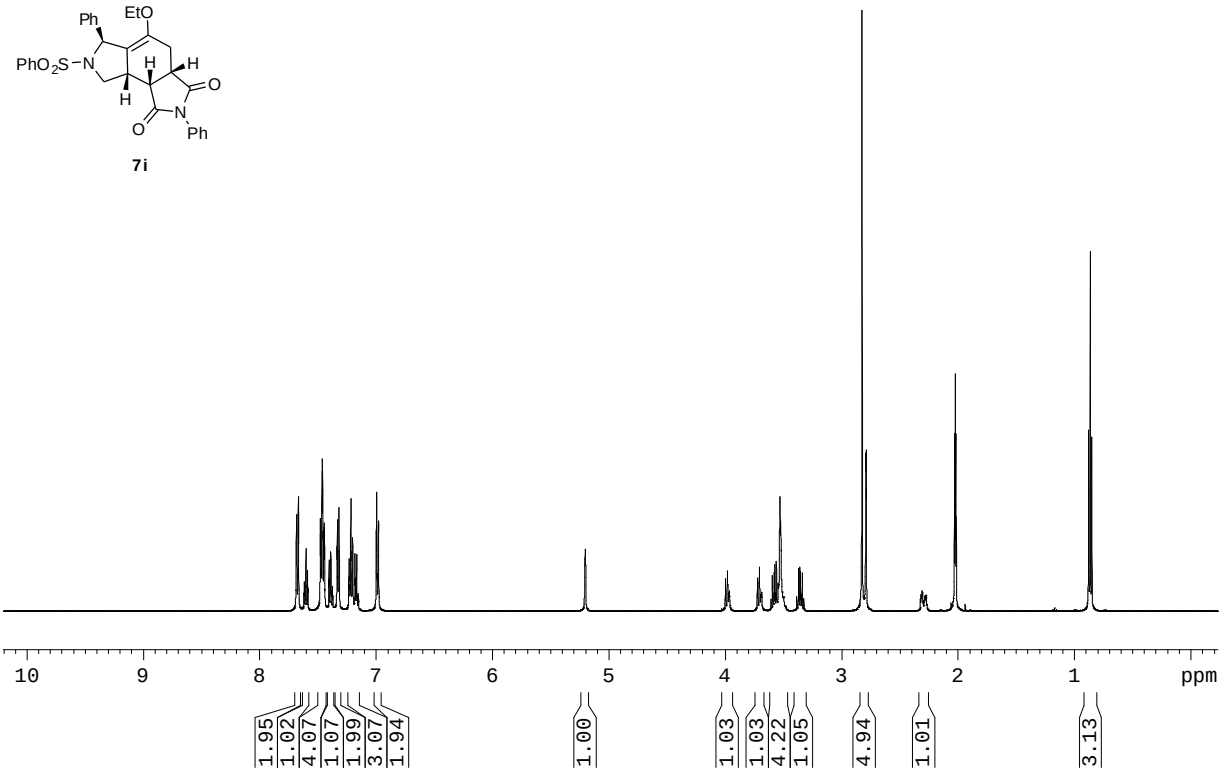
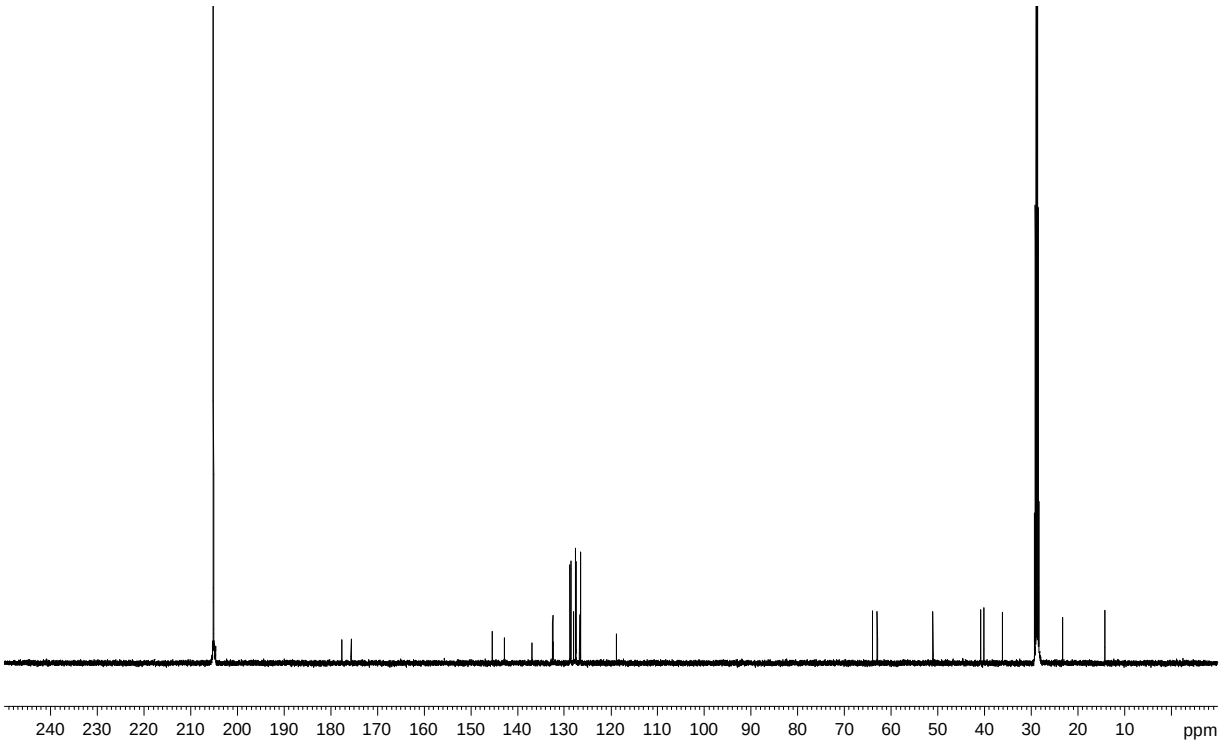
2.19
2.15
1.08
3.83
4.32
3.18


240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ph
EtO
PhO2S
N
H
H
H
O
O
N
Ph
7i
10
9
8
7
6
5
4
3
2
1
ppm
1.95
1.02
4.07
1.07
1.99
3.07
1.94
1.00
1.03
1.03
4.22
1.05
4.94
1.01
3.13


240
230
220
210
200
190
180
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150
140
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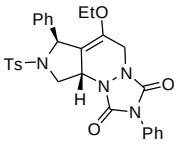
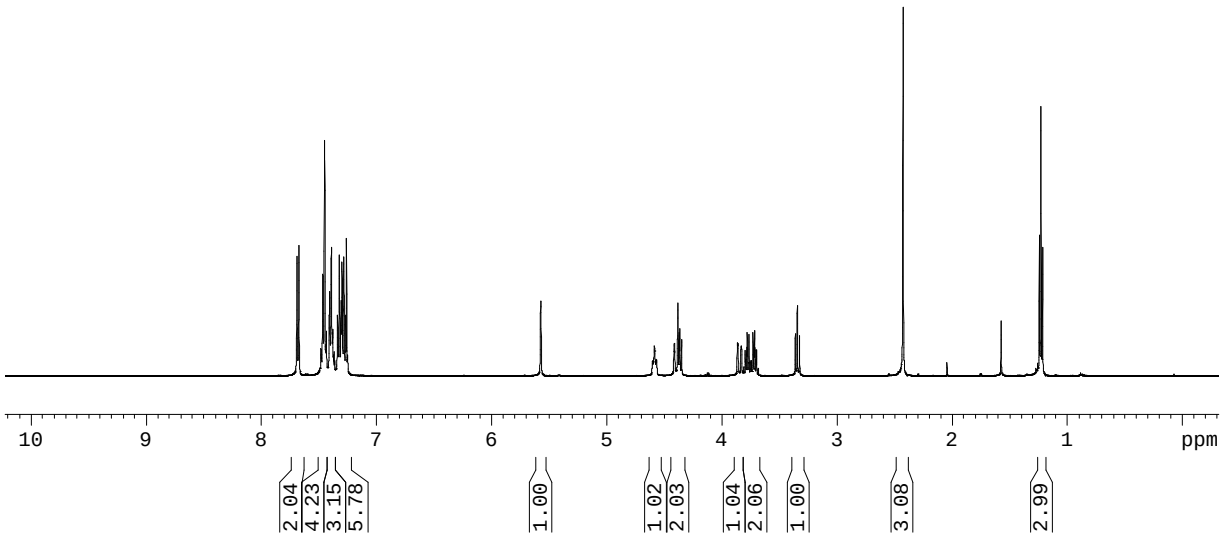
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ph
EtO
Ts
N
H
N
N
O
O
N
Ph

8a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9
8
7
6
5
4
3
2
1
ppm
2.04
4.23
3.15
5.78
1.00
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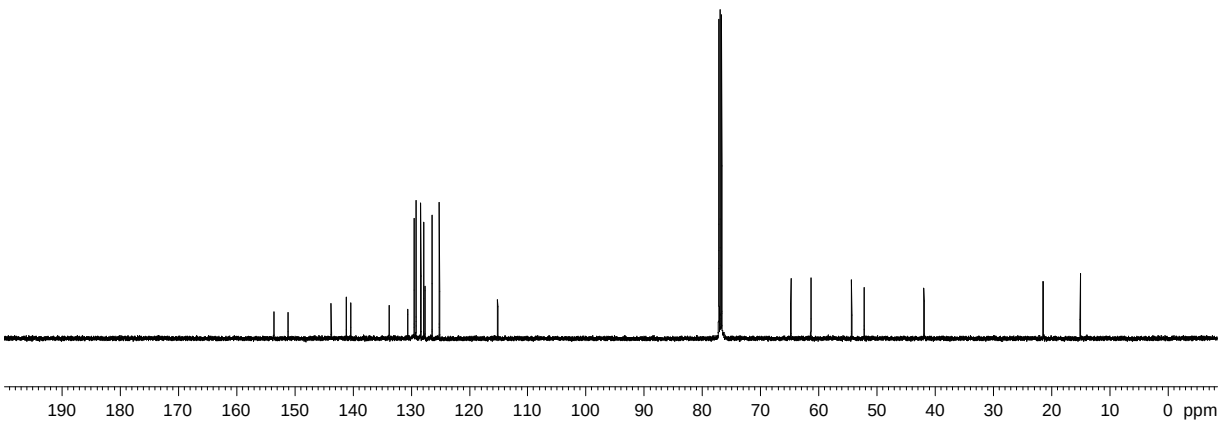
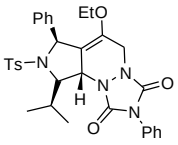
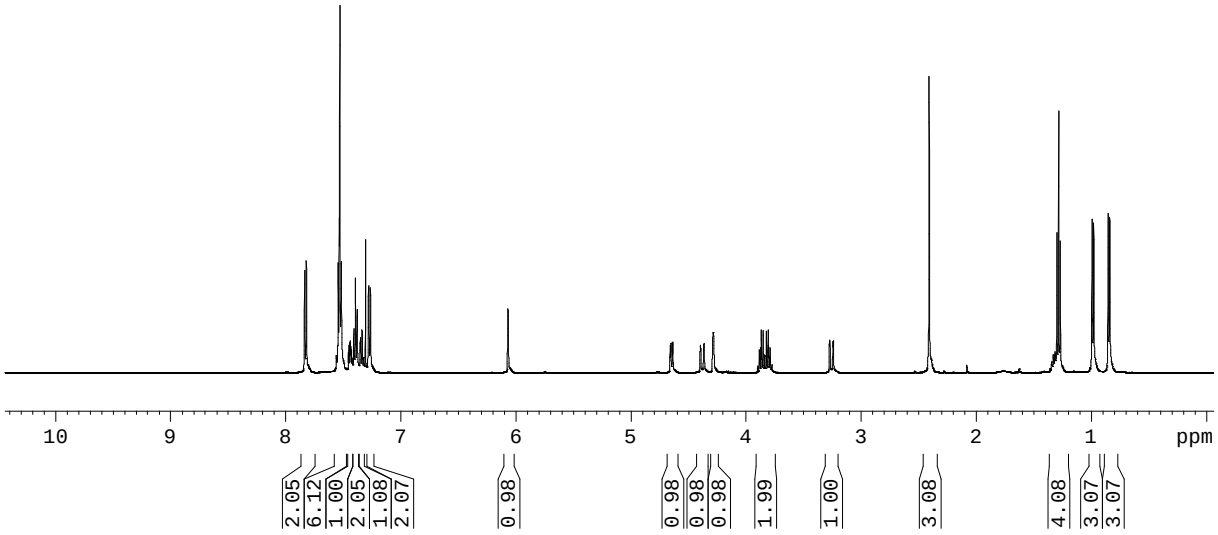
2.03
1.04
2.06
1.00
3.08
2.99


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm


Ph
EtO
Ts
N
N
N
O
H
O
N
Ph

8b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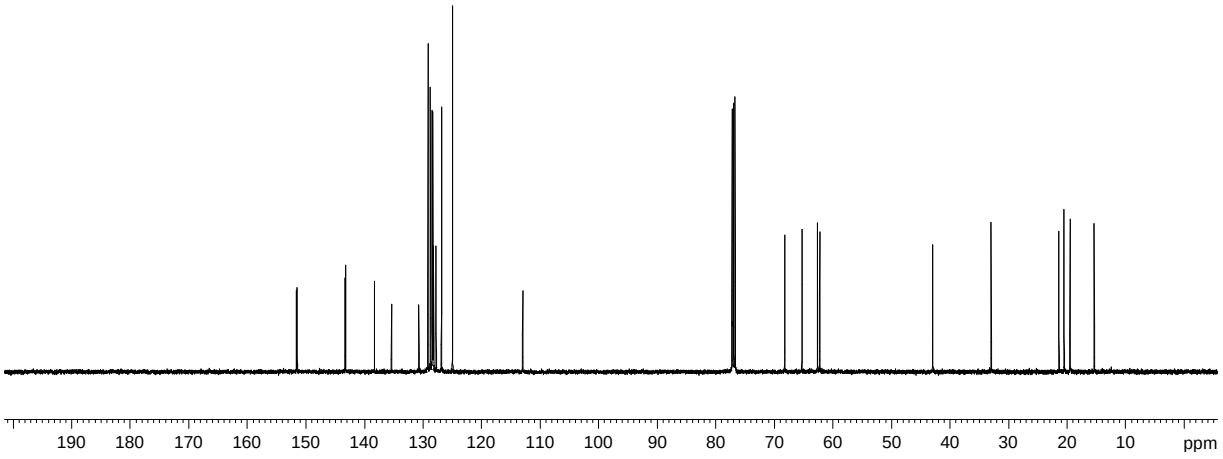
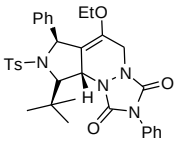
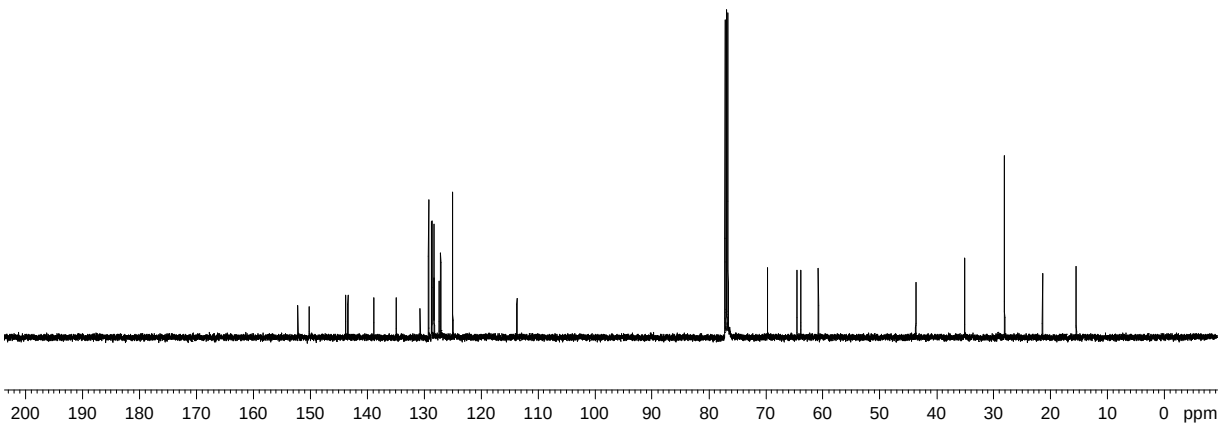
9
8
7
6
5
4
3
2
1
ppm
2.05
6.12
1.00
2.05
1.08
2.07
0.98
0.98
0.98
0.98
1.99
1.00
3.08
4.08
3.07
3.07

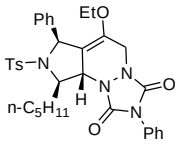

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ph
EtO
Ts
N
N
N
H
O
O
N
Ph

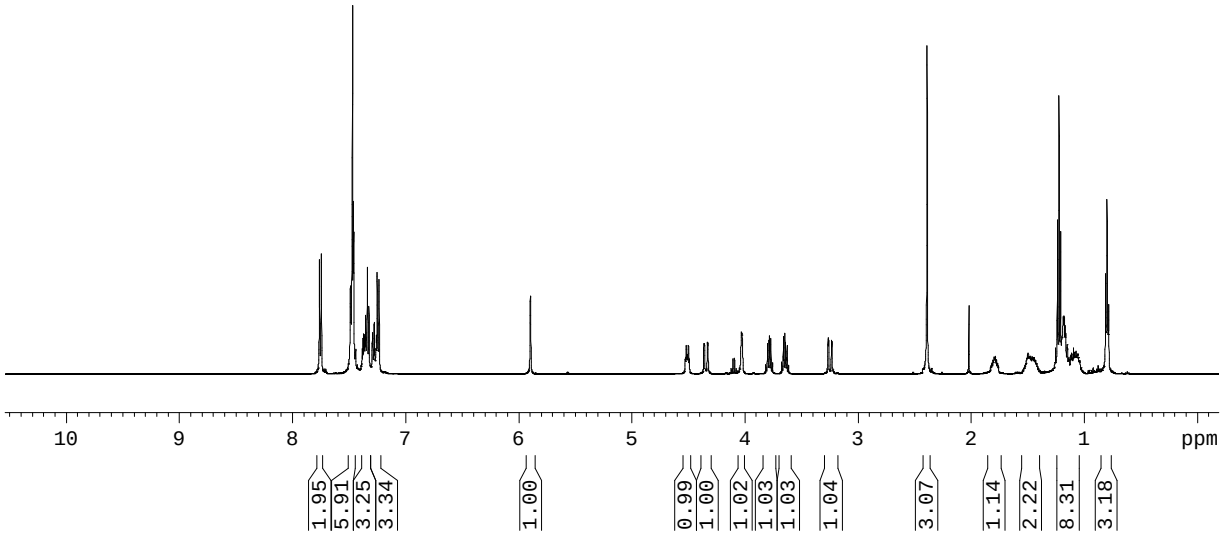
8c

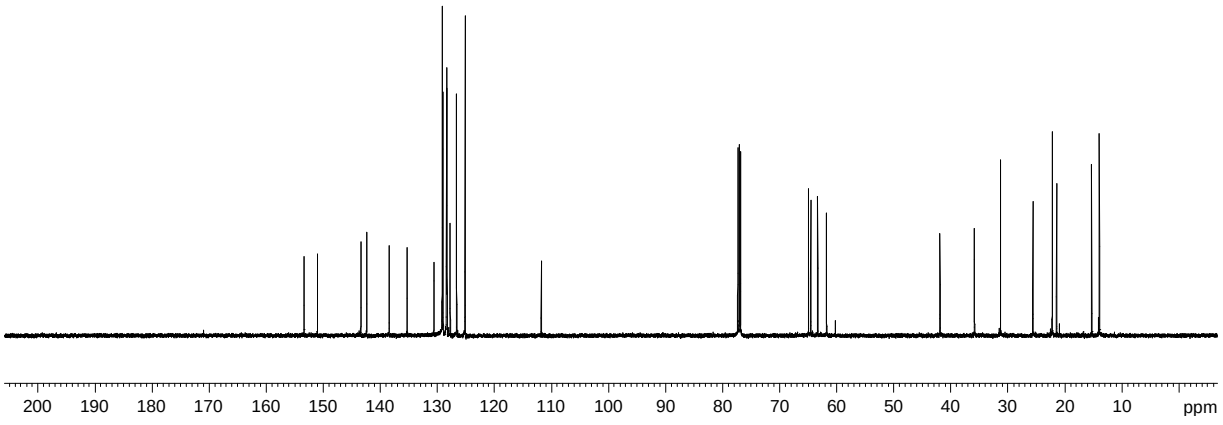
10
9
8
7
6
5
4
3
2
1
ppm
2.03
6.23
1.17
2.09
1.13
2.00
1.00
1.00
2.05
2.01
0.99
3.05
3.08
9.16

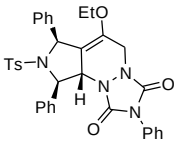

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


Ph
EtO
Ts
N
N
N
O
H
n-C5H11
O
N
Ph

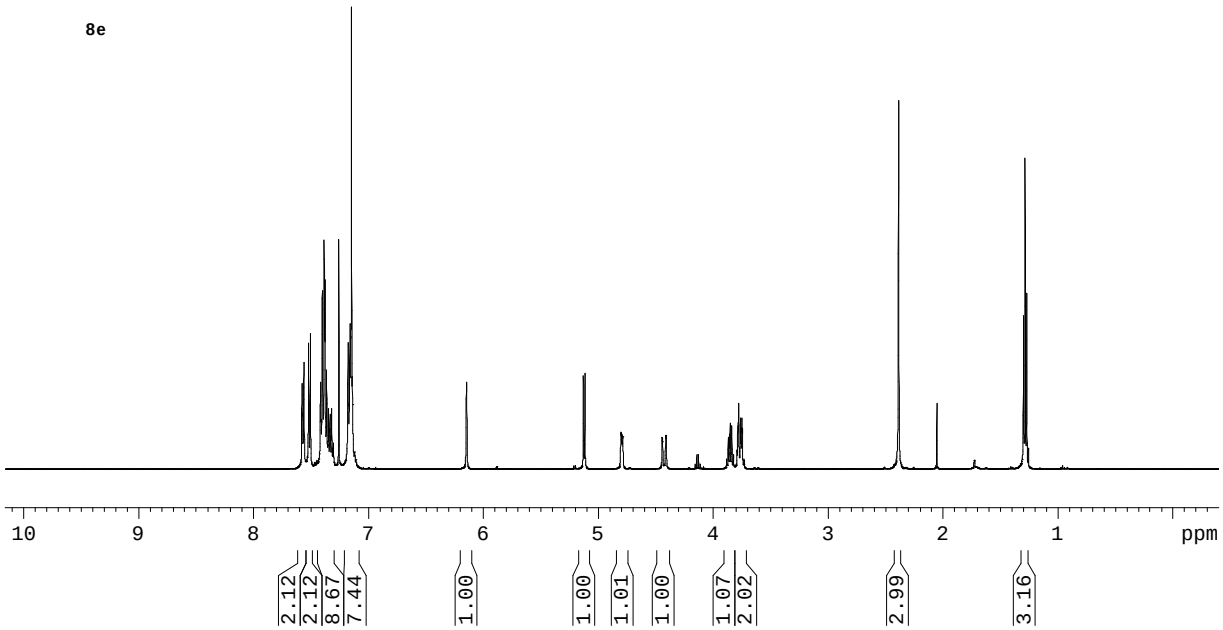
8d

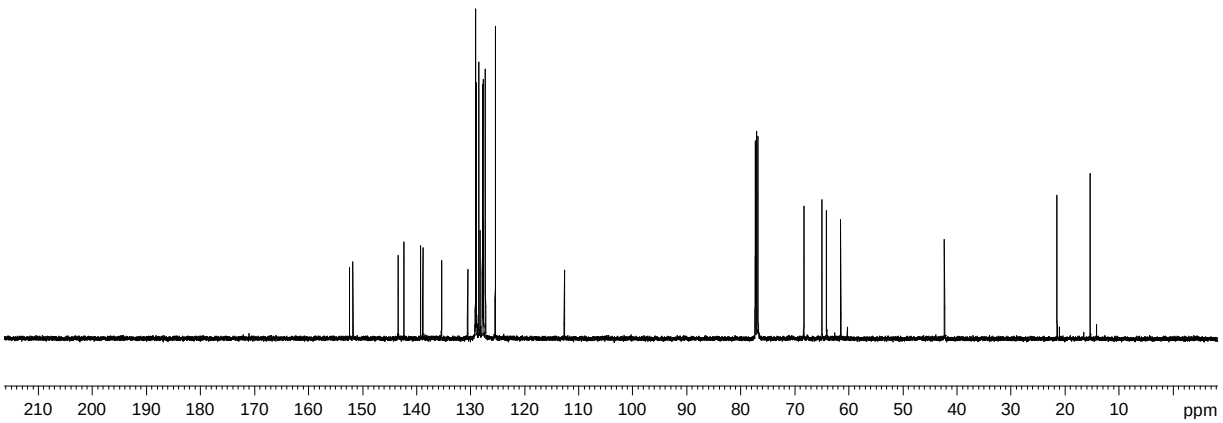

10
9
8
7
6
5
4
3
2
1
ppm
1.95
5.91
3.25
3.34
1.00
0.99
1.00
1.02
1.03
1.03
1.04
3.07
1.14
2.22
8.31
3.18

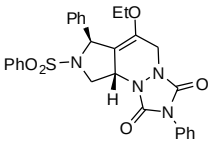

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ph
EtO
Ts
N
N
N
O
H
Ph
O
N
Ph

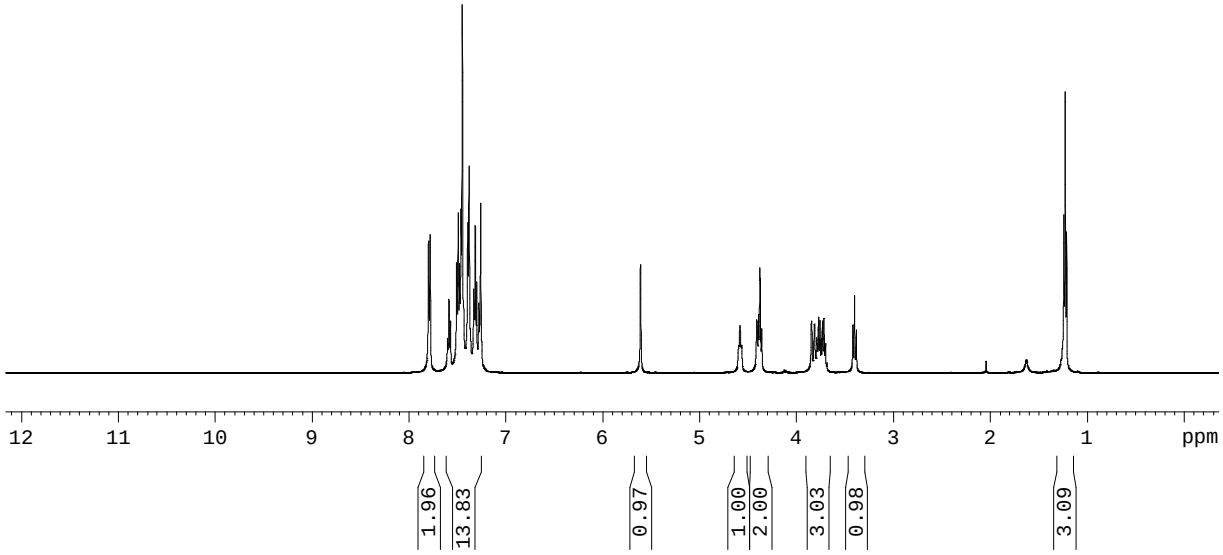
8e

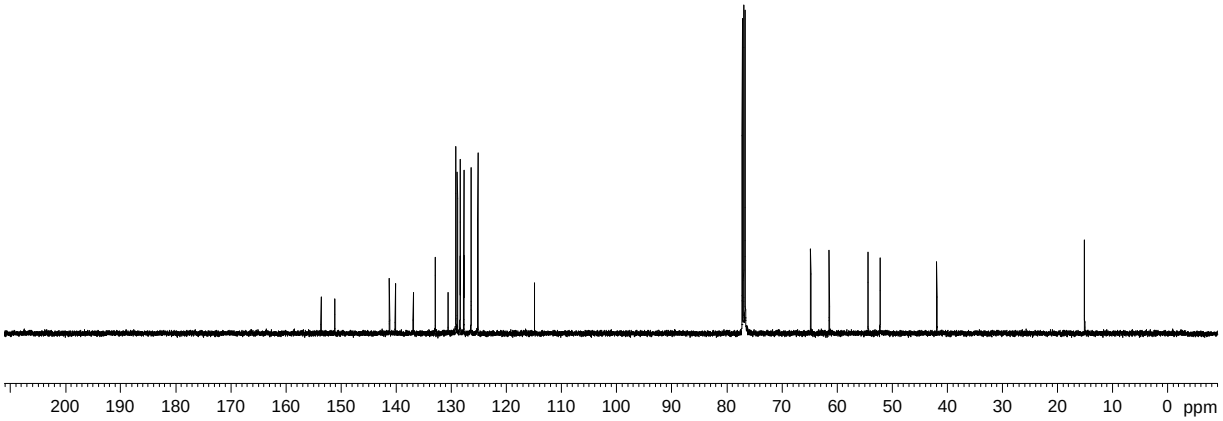

10
9
8
7
6
5
4
3
2
1
ppm
2.12
2.12
8.67
7.44
1.00
1.00
1.01
1.00
1.07
2.02
2.99
3.16

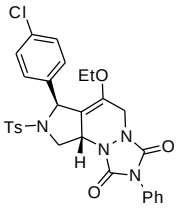

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ph
EtO
PhO2S
N
N
N
H
O
O
N
Ph

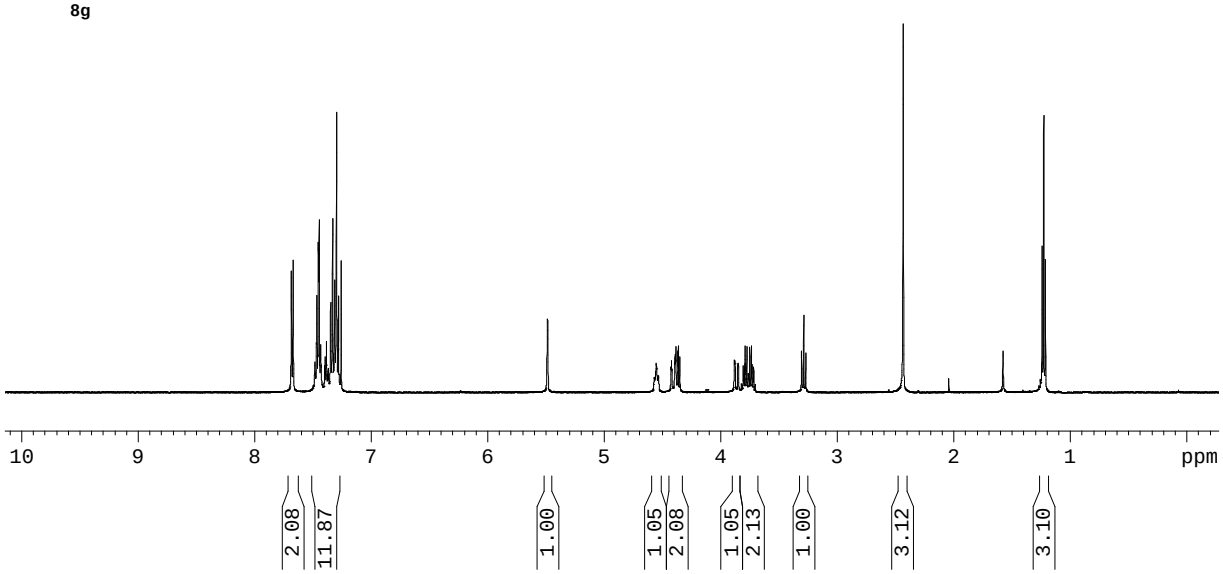
8f

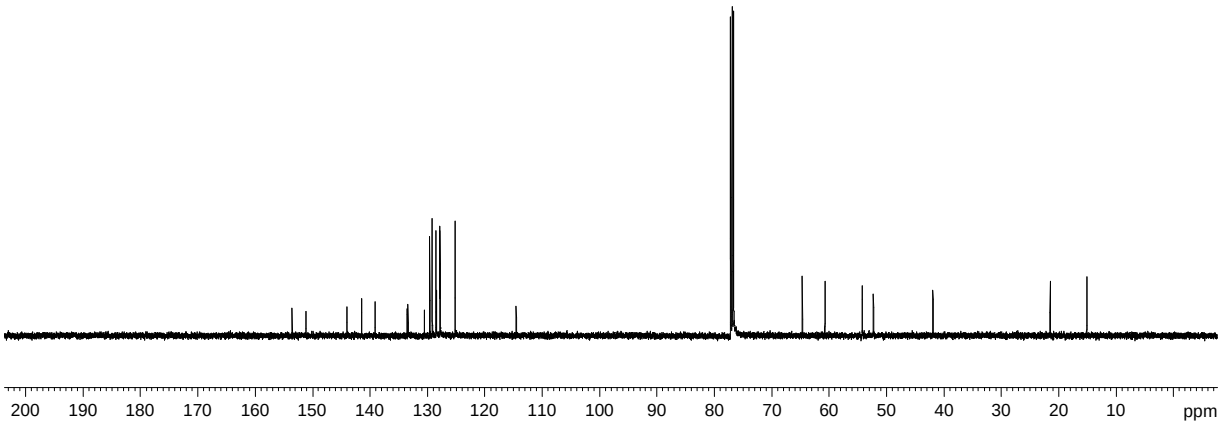

12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.96
13.83
0.97
1.00
2.00
3.03
0.98
3.09


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


Cl
EtO
Ts
N
H
N
N
O
O
N
Ph

8g


10
9
8
7
6
5
4
3
2
1
ppm
2.08
11.87
1.00
1.05
2.08
1.05
2.13
1.00
3.12
3.10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100
90
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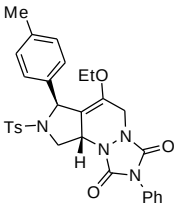
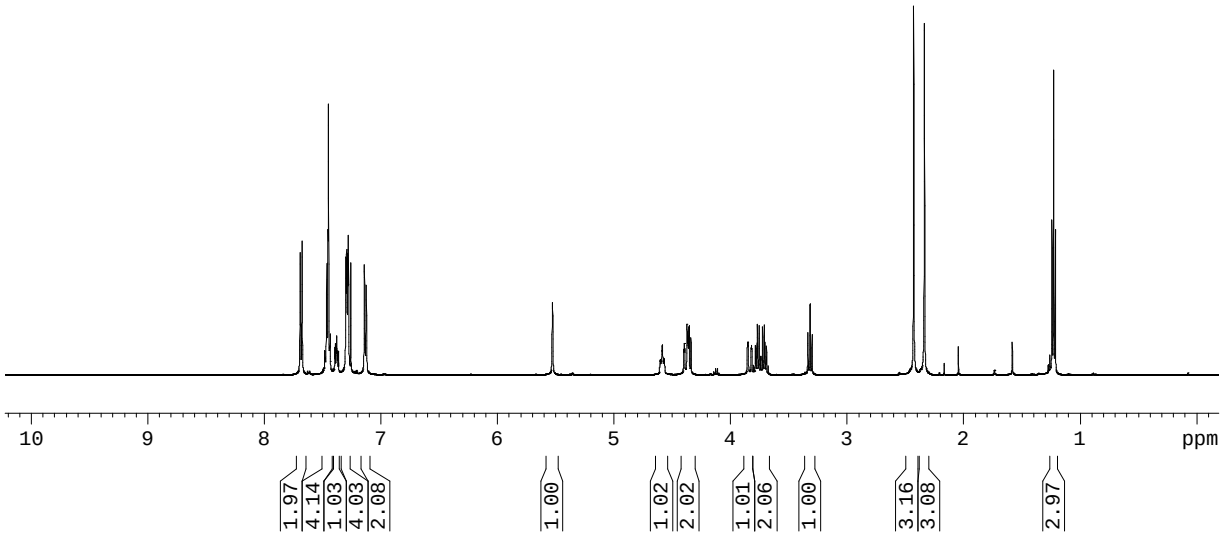
30
20
10
ppm


Me
EtO
Ts
N
H
N
N
O
O
N
Ph

8h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9
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6
5
4
3
2
1
ppm
1.97
4.14
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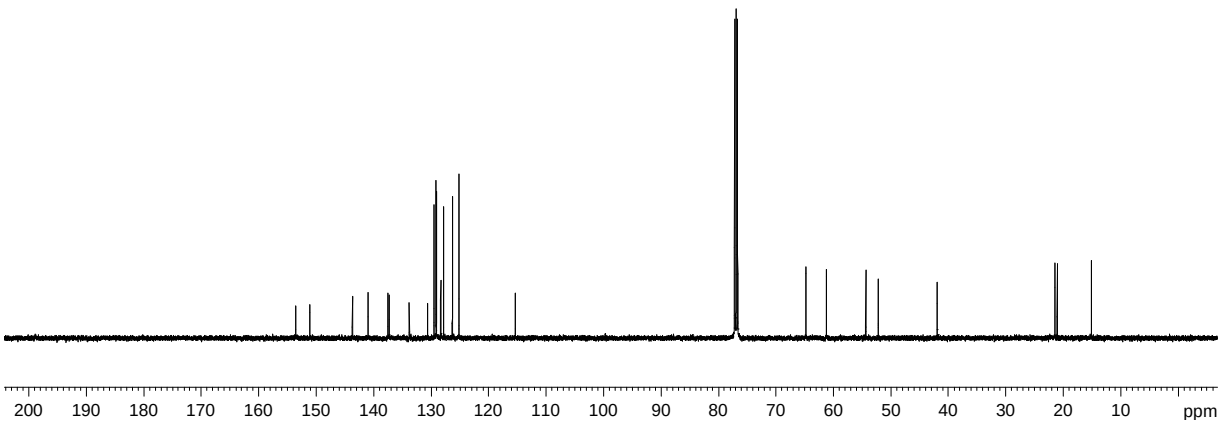
4.03
2.08
1.00
1.02
2.02
1.01
2.06
1.00
3.16
3.08
2.97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150
140
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70
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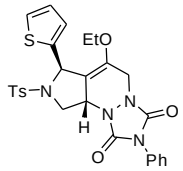
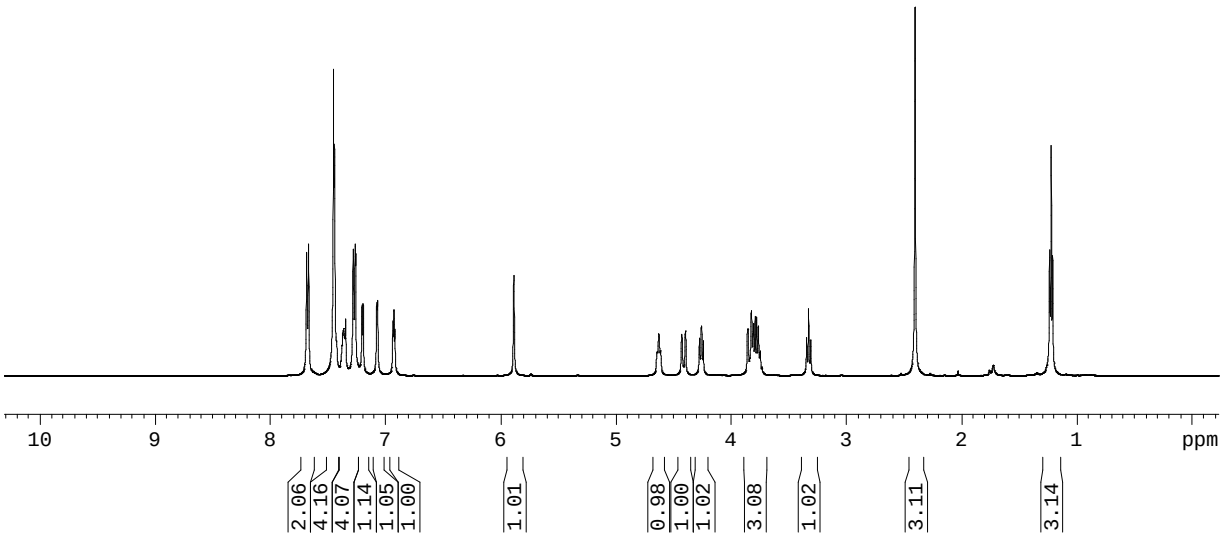
30
20
10
ppm


S
EtO
Ts–N
H
N
N
O
O
N
Ph

8i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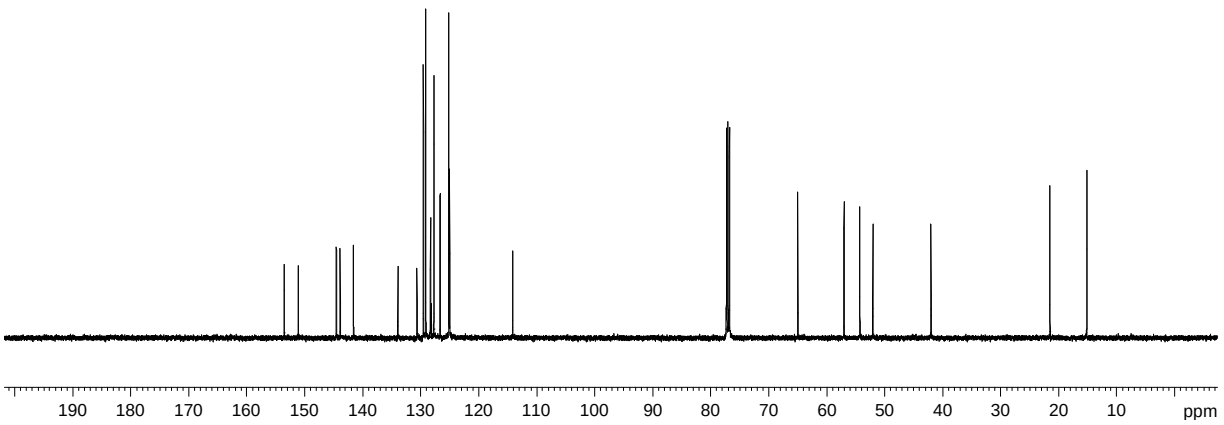
9
8
7
6
5
4
3
2
1
ppm
2.06
4.16
4.07
1.14
1.05
1.00
1.01
0.98
1.00
1.02
3.08
1.02
3.11
3.14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180
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160
150
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100
90
80
70
60
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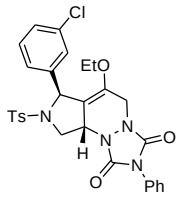
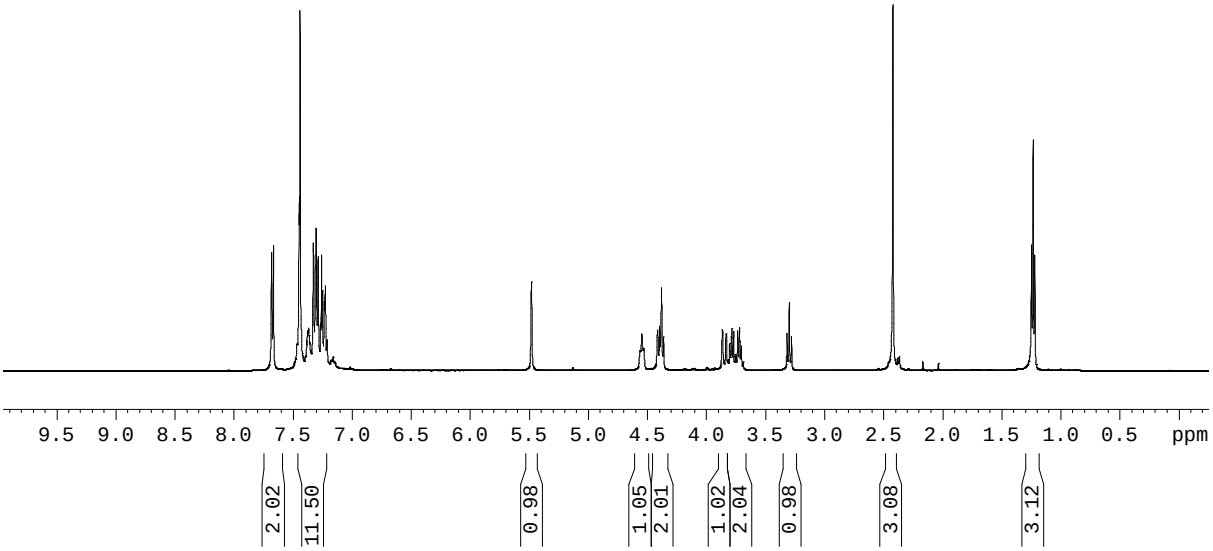
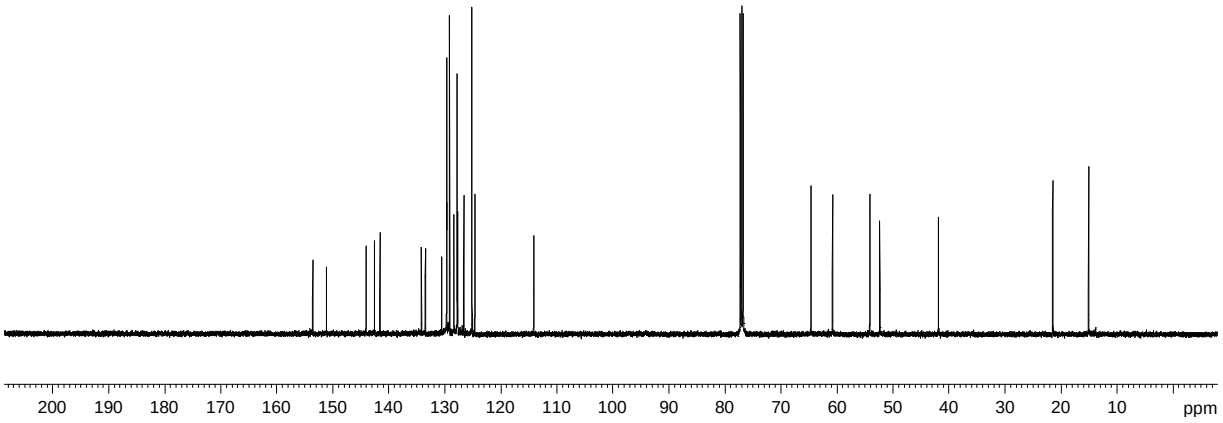
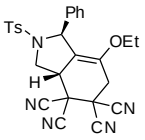
40
30
20
10
ppm


Cl
EtO
Ts–N
H
N
N
O
O
N
Ph

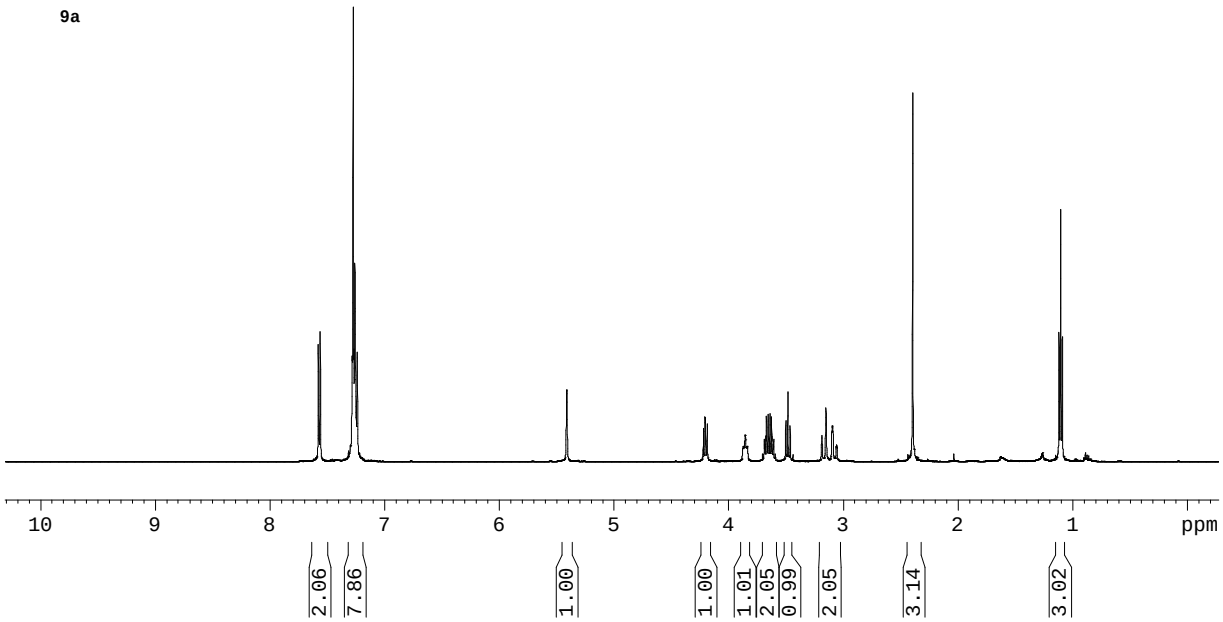
8j


9.5 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
2.02
11.50
0.98
1.05
2.01
1.02
2.04
0.98
3.08
3.12


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Ts
N
Ph
OEt
H
NC
NC
CN
CN

9a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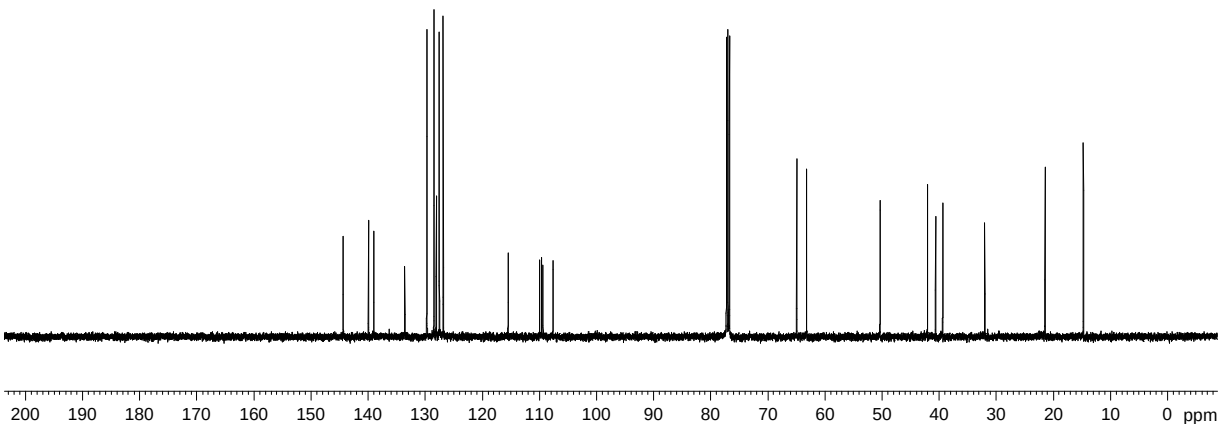
9
8
7
6
5
4
3
2
1
ppm
2.06
7.86
1.00
1.00
1.01
2.05
0.99
2.05
3.14
3.02


200
190
180
170
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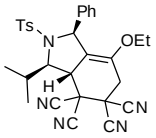
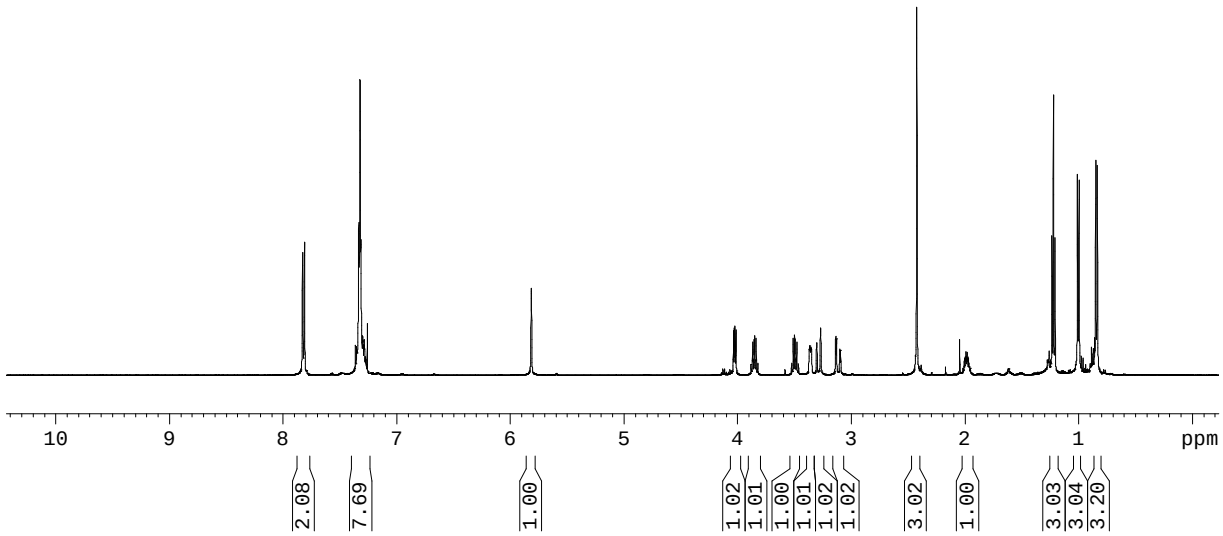
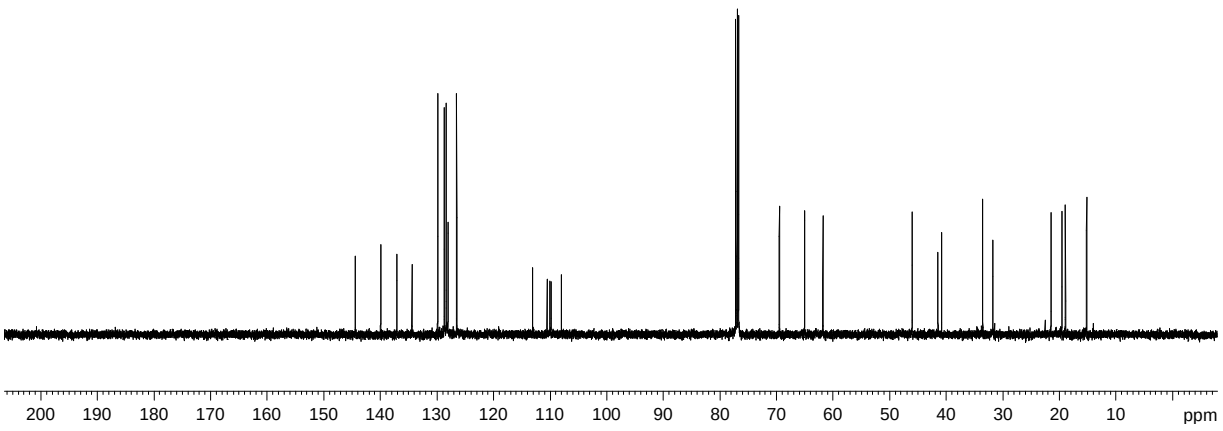
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


Ts
N
Ph
OEt
H
NC
NC
CN
CN

9b


10
9
8
7
6
5
4
3
2
1
ppm
2.08
7.69
1.00
1.02
1.01
1.00
1.01
1.02
1.02
3.02
1.00
3.03
3.04
3.20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190
180
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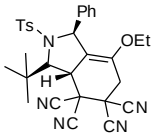
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ts
N
Ph
OEt
H
NC
NC
CN
CN

9c

10
9
8
7
6
5
4
3
2
1
ppm
2.08
2.12
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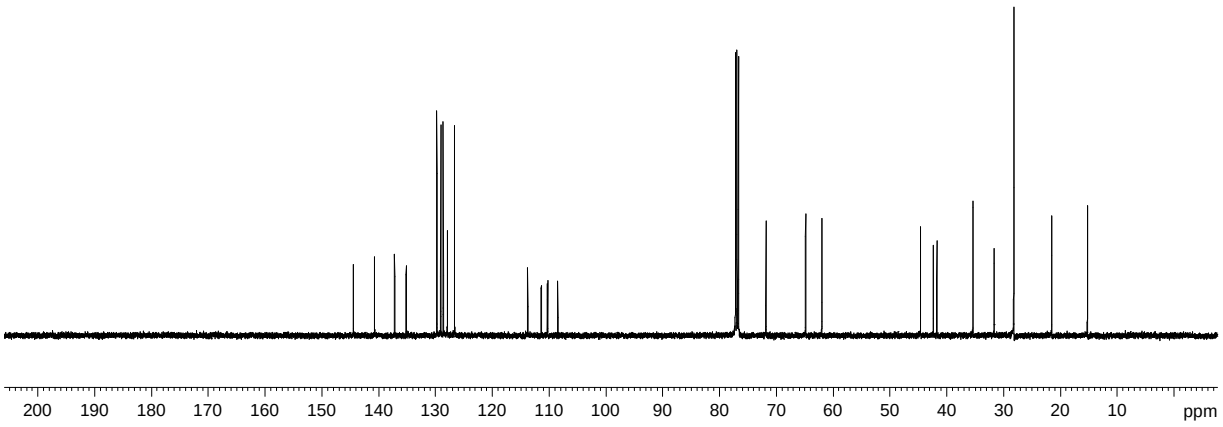
1.00
0.99
1.03
1.07
1.01
1.00
0.98
3.05
3.03
9.41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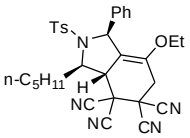
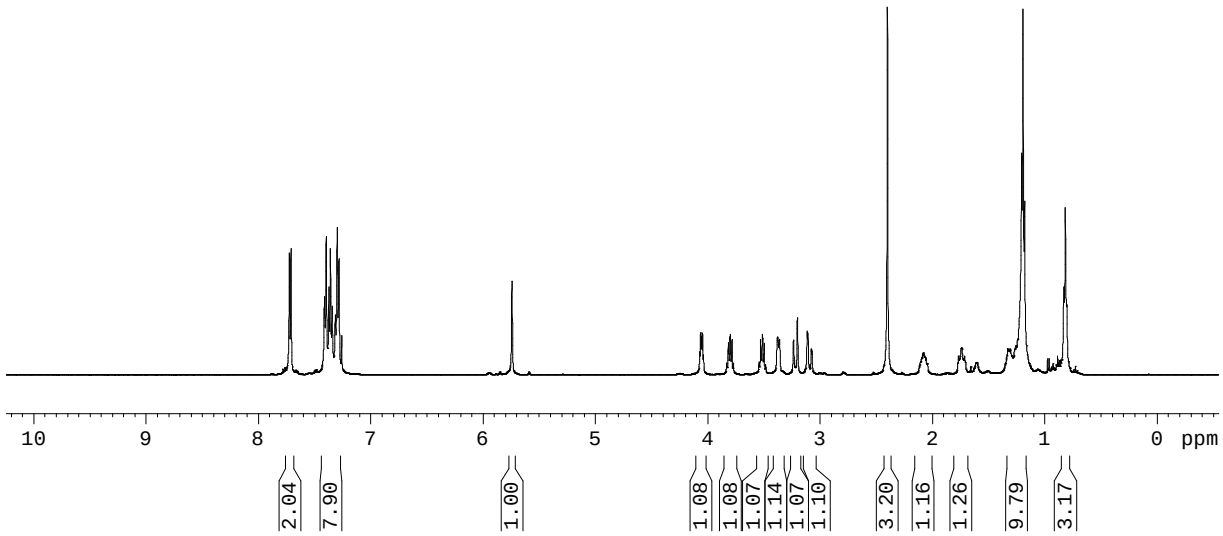
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ts
N
Ph
OEt
n-C5H11
H
NC
NC
CN
CN

9d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9
8
7
6
5
4
3
2
1
0
ppm
2.04
7.90
1.00
1.08
1.08
1.07
1.14
1.07
1.10
3.20
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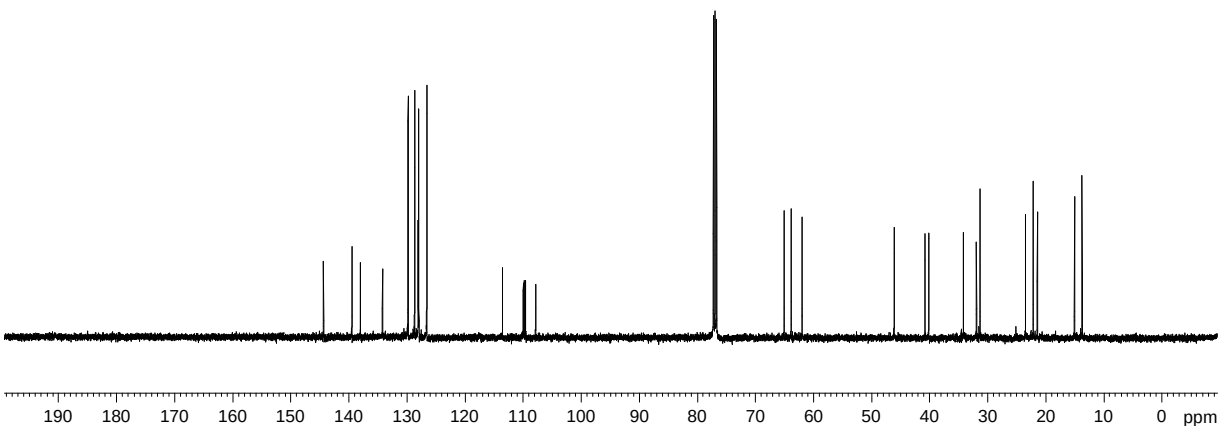
1.26
9.79
3.17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140
130
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110
100
90
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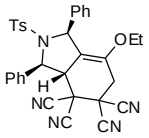
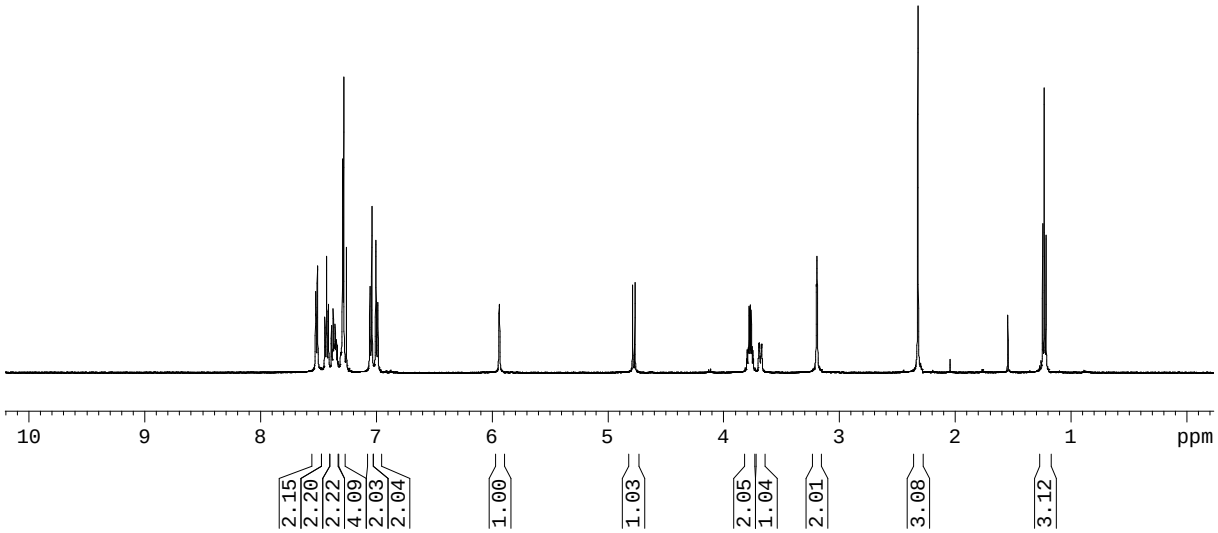
70
60
50
40
30
20
10
0
ppm


Ts
N
Ph
OEt
Ph
H
NC
NC
CN
CN

9e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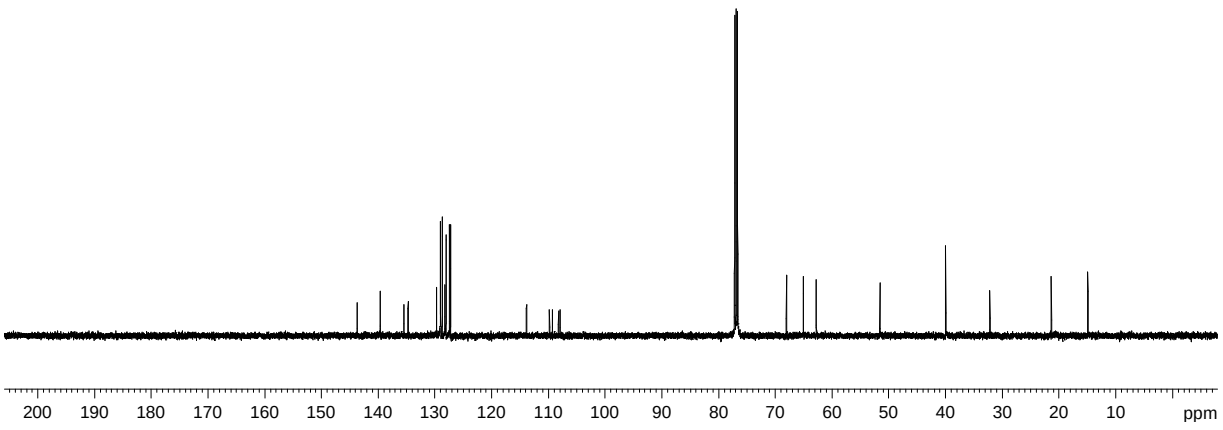
9
8
7
6
5
4
3
2
1
ppm
2.15
2.20
2.22
4.09
2.03
2.04
1.00
1.03
2.05
1.04
2.01
3.08
3.12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150
140
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120
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100
90
80
70
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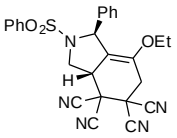
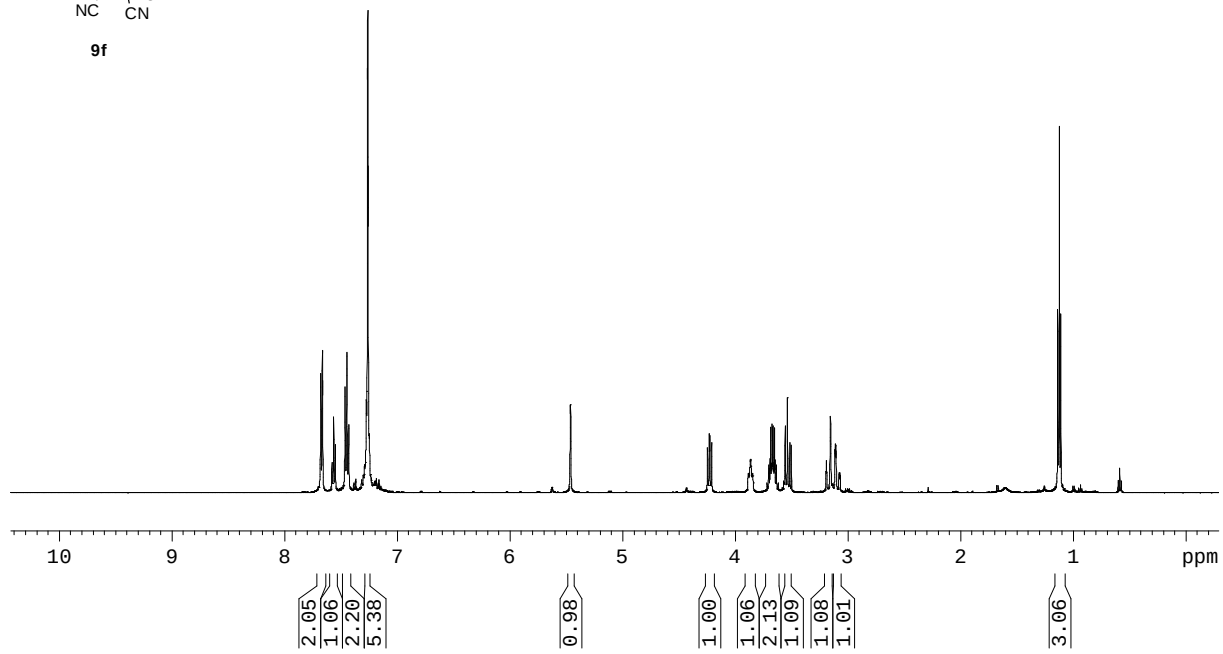
30
20
10
ppm


PhO2S
N
Ph
OEt
H
NC
NC
CN
CN

9f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8
7
6
5
4
3
2
1
ppm
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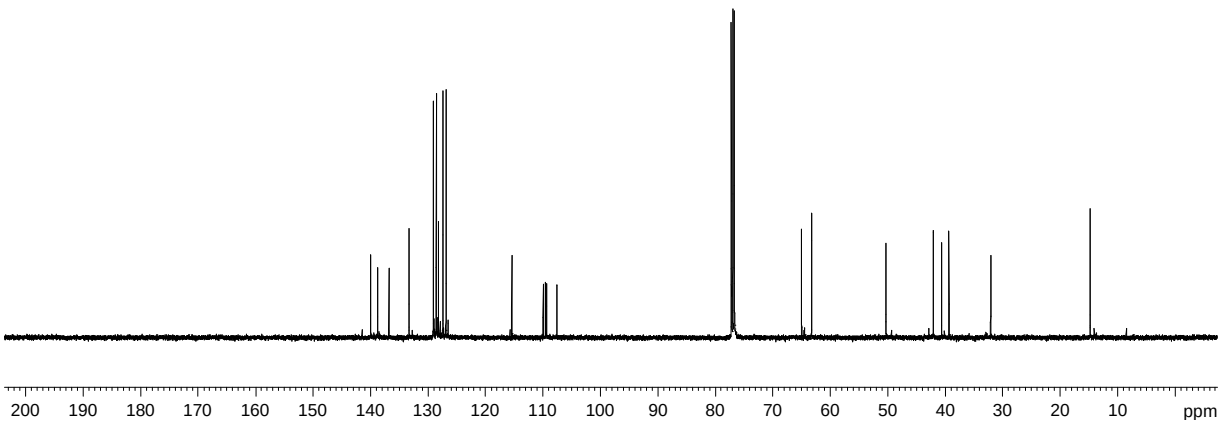
1.06
2.20
5.38
0.98
1.00
1.06
2.13
1.09
1.08
1.01
3.06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180
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150
140
130
120
110
100
90
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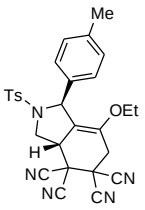
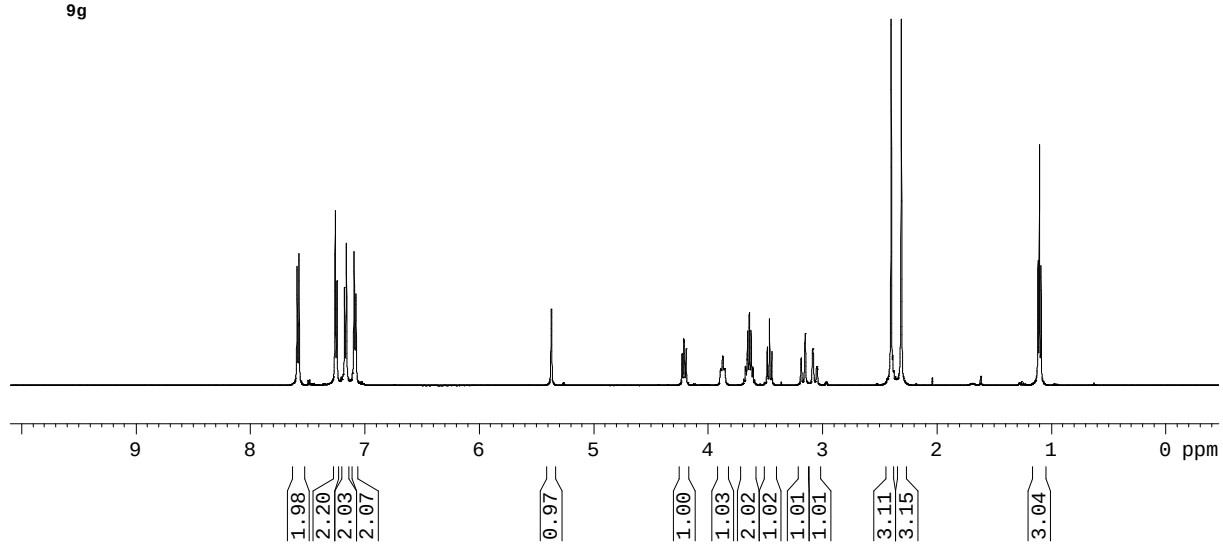
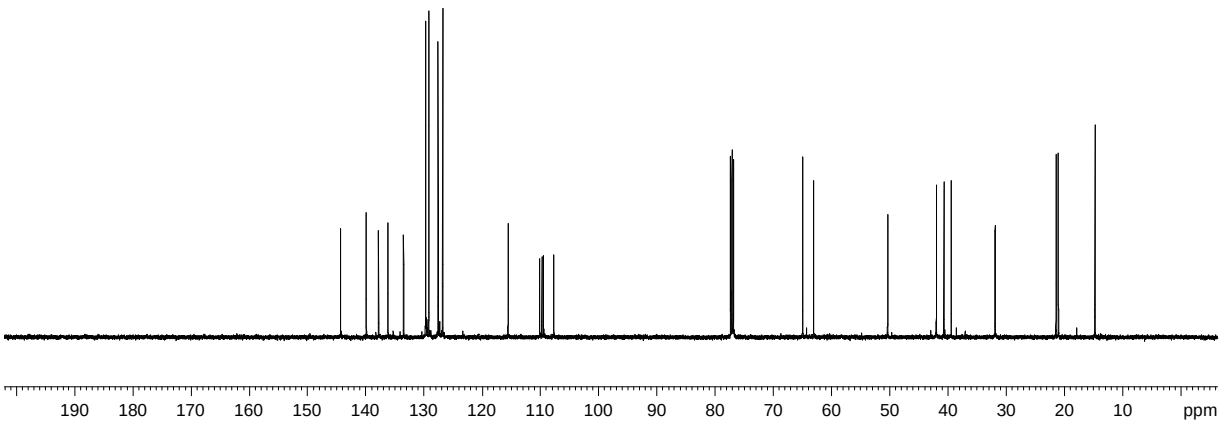
70
60
50
40
30
20
10
ppm


Me
Ts
N
OEt
H
NC
NC
CN
CN

9g


9
8
7
6
5
4
3
2
1
0 ppm
1.98
2.20
2.03
2.07
0.97
1.00
1.03
2.02
1.02
1.01
1.01
3.11
3.15
3.04


190
180
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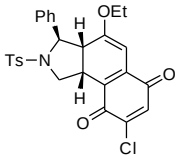
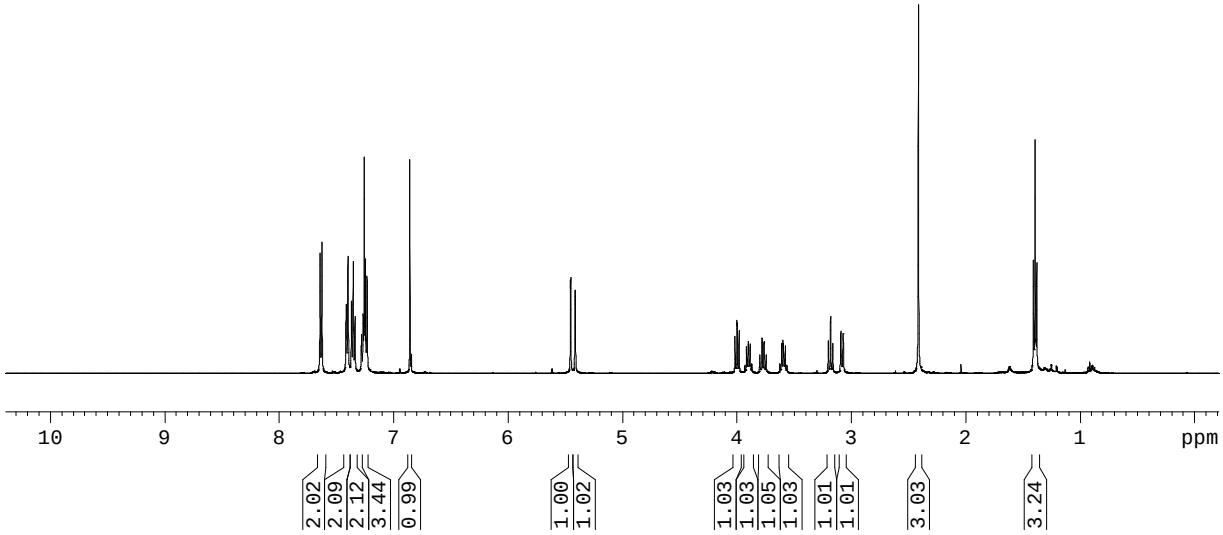
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ph
H
OEt
Ts–N
O
H
O
Cl

10a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9
8
7
6
5
4
3
2
1
ppm
2.02
2.09
2.12
3.44
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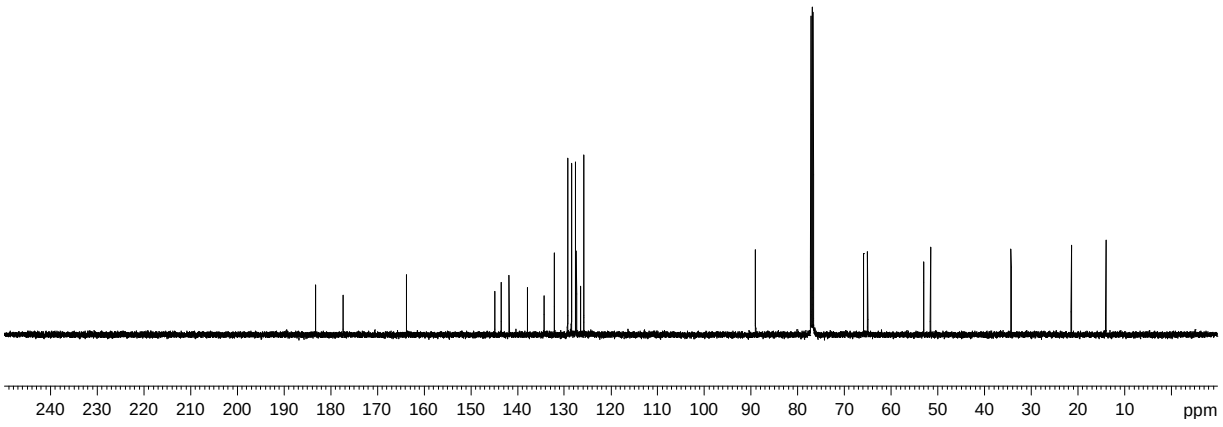
1.00
1.02
1.03
1.03
1.05
1.03
1.01
1.01
3.03
3.24


240
230
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210
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180
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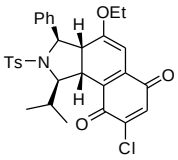
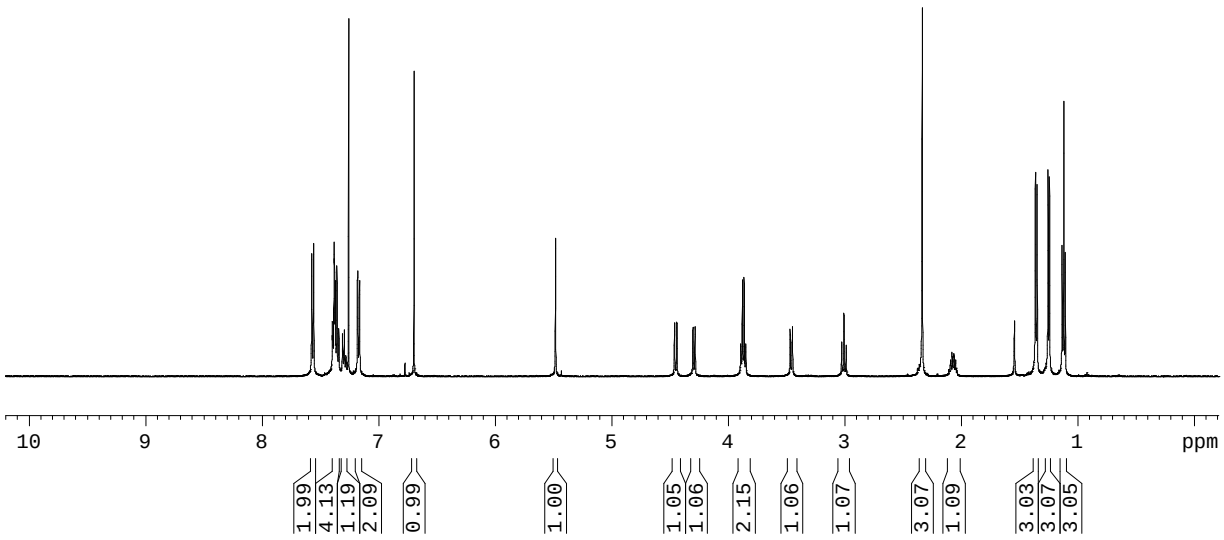
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ph
H
OEt
Ts
N
H
O
O
Cl

10b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9
8
7
6
5
4
3
2
1
ppm
1.99
4.13
1.19
2.09
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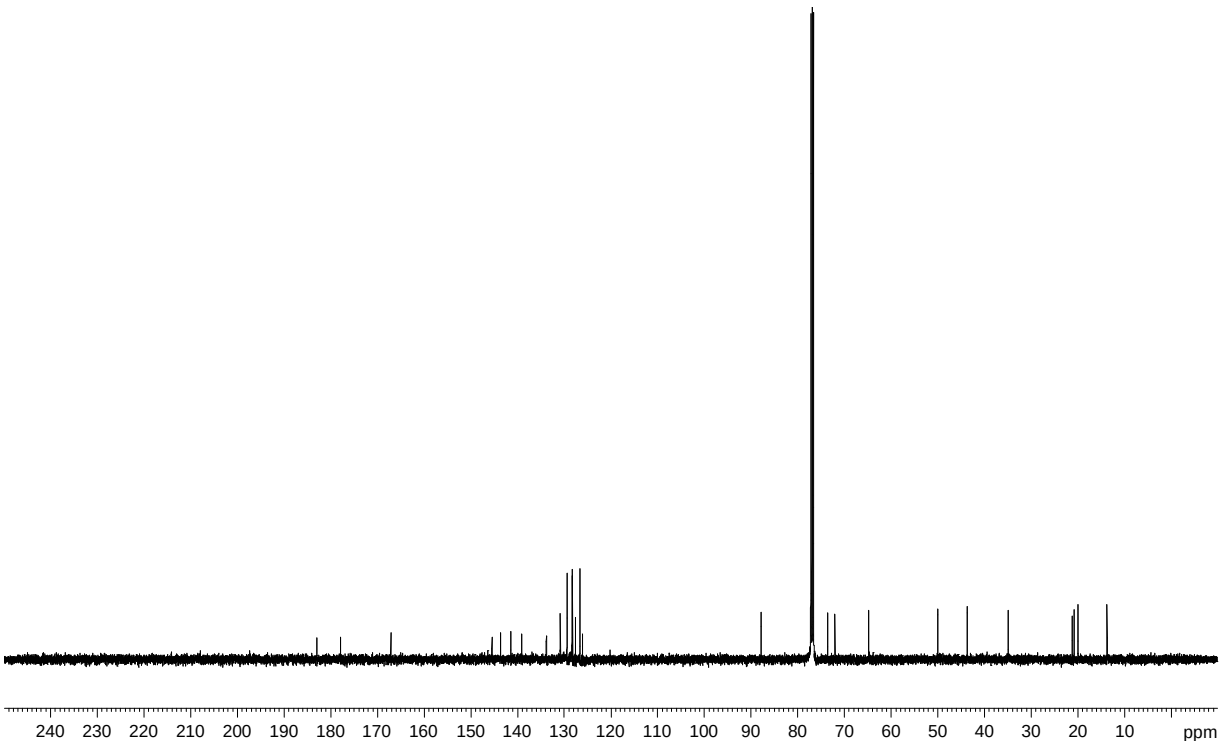
1.05
1.06
2.15
1.06
1.07
3.07
1.09
3.03
3.07
3.05


240
230
220
210
200
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180
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150
140
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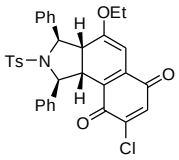
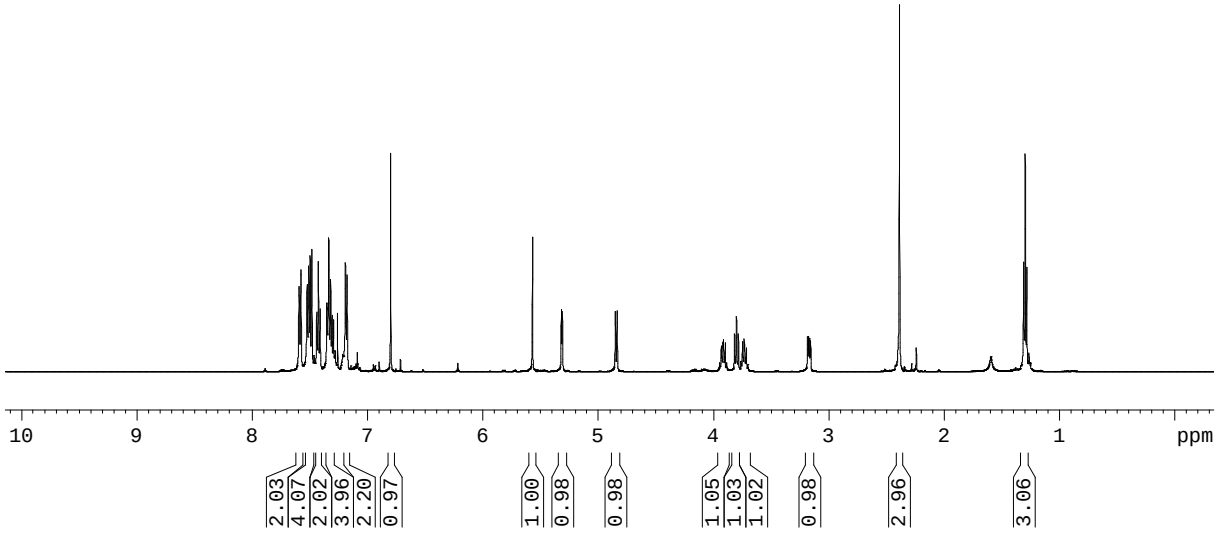
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ph
H
OEt
Ts–N
O
Ph
H
O
Cl

10c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9
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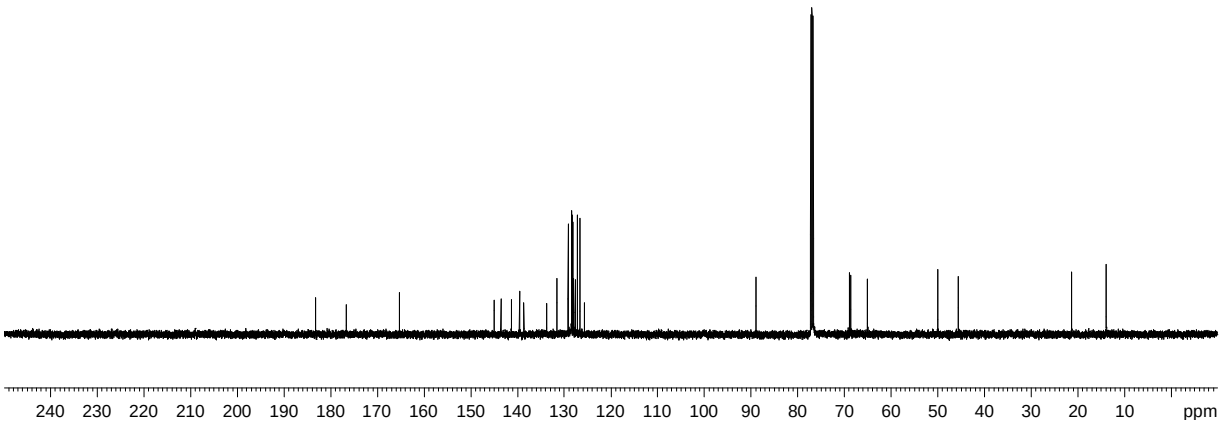
7
6
5
4
3
2
1
ppm
2.03
4.07
2.02
3.96
2.20
0.97
1.00
0.98
0.98
1.05
1.03
1.02
0.98
2.96
3.06


240
230
220
210
200
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140
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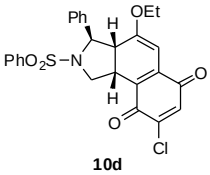
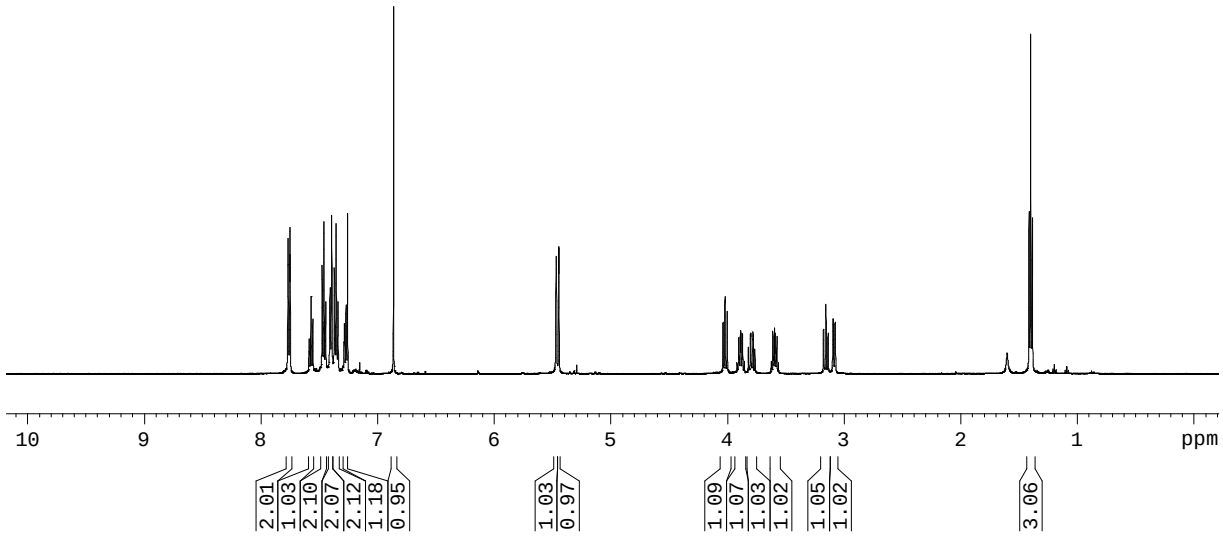
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ph
H
OEt
PhO2S–N
H
O
O
Cl

10d


10
9
8
7
6
5
4
3
2
1
ppm
2.01
1.03
2.10
2.07
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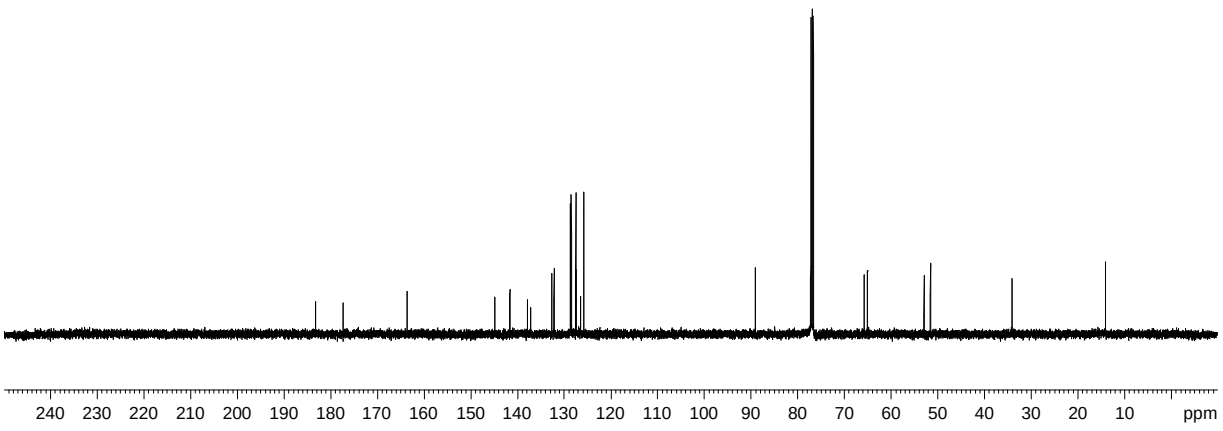
0.95
1.03
0.97
1.09
1.07
1.03
1.02
1.05
1.02
3.06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70
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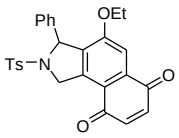
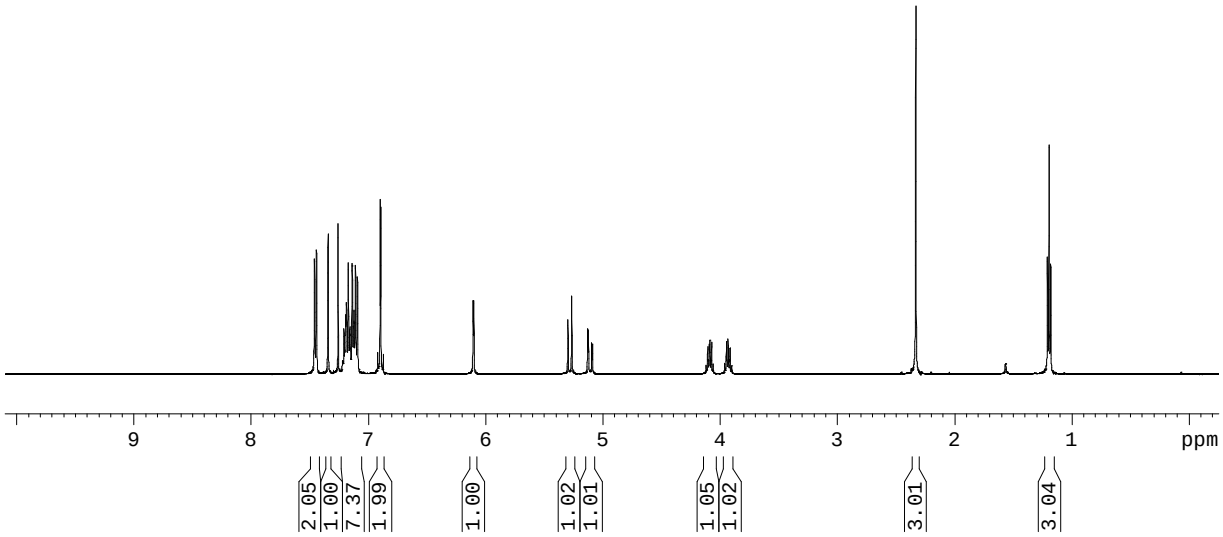
40
30
20
10
ppm


Ph
OEt
Ts
N
O
O

10e


9
8
7
6
5
4
3
2
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ppm
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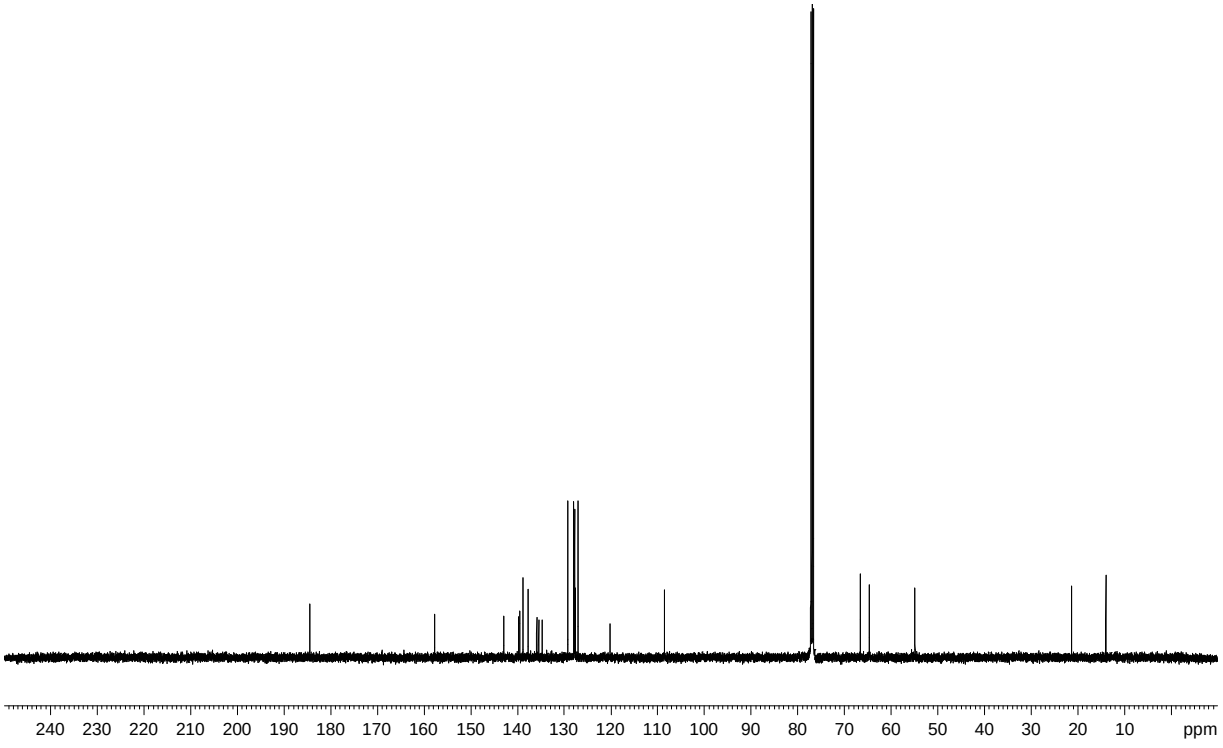
1.00
1.02
1.01
1.05
1.02
3.01
3.04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100
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70
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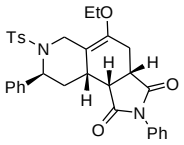
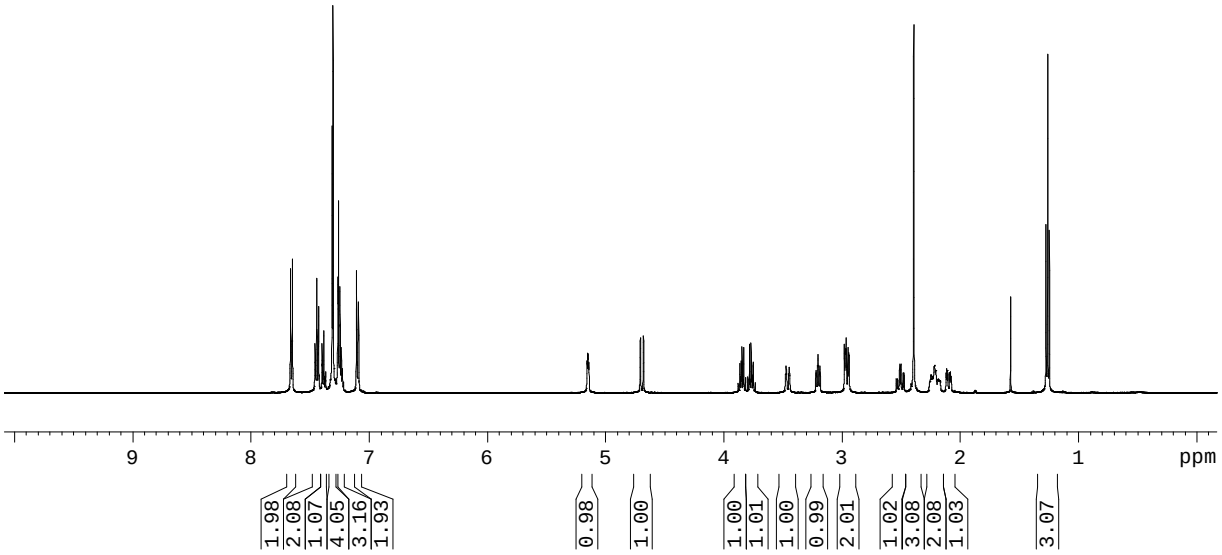
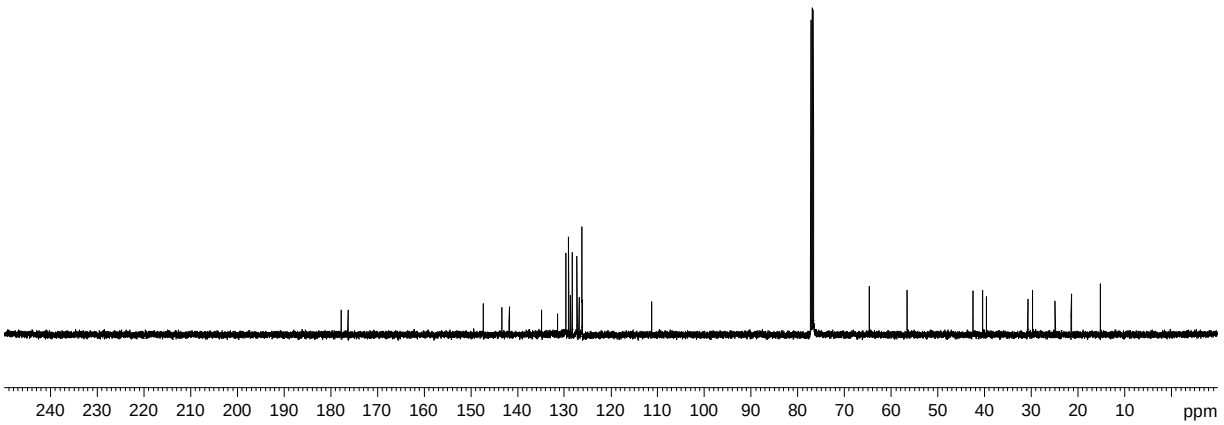
40
30
20
10
ppm


EtO
Ts
N
H
H
Ph
H
O
O
N
Ph

11aa


9
8
7
6
5
4
3
2
1
ppm
1.98
2.08
1.07
4.05
3.16
1.93
0.98
1.00
1.00
1.01
1.00
0.99
2.01
1.02
3.08
2.08
1.03
3.07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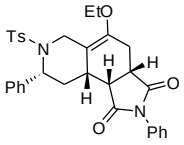
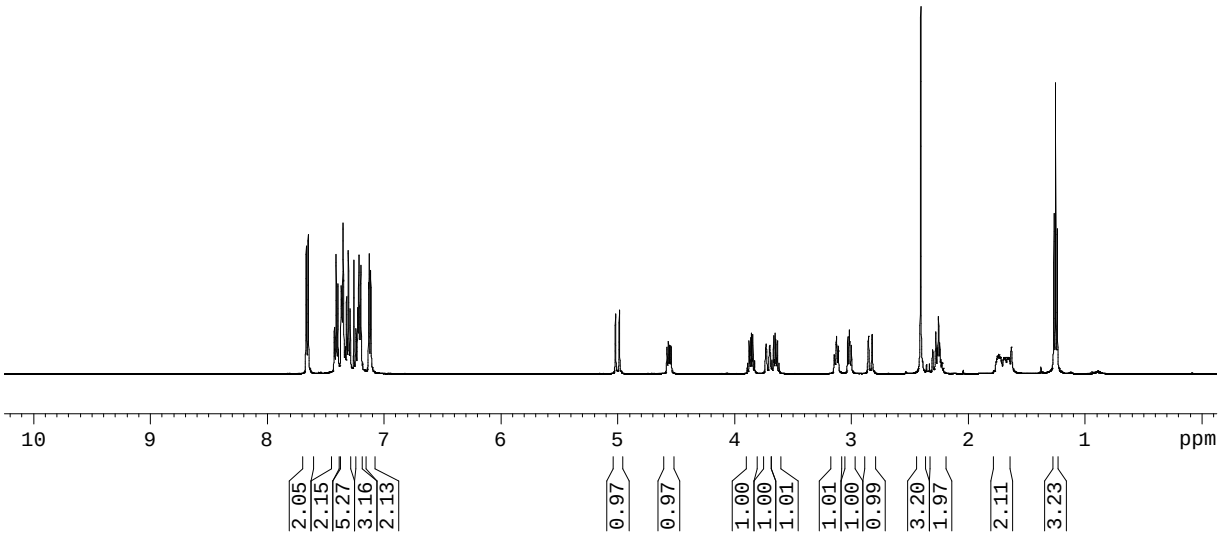
ppm


EtO
Ts
N
H
H
Ph
H
O
O
N
Ph

11ab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9
8
7
6
5
4
3
2
1
ppm
2.05
2.15
5.27
3.16
2.13
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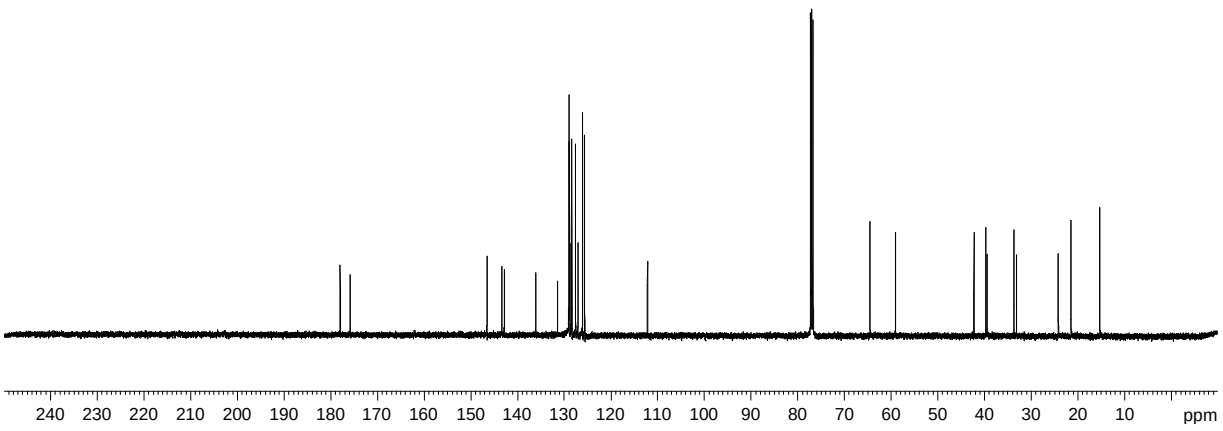
0.97
1.00
1.00
1.01
1.01
1.00
0.99
3.20
1.97
2.11
3.23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230
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120
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100
90
80
70
60
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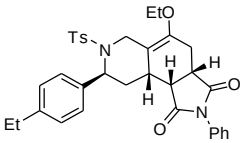
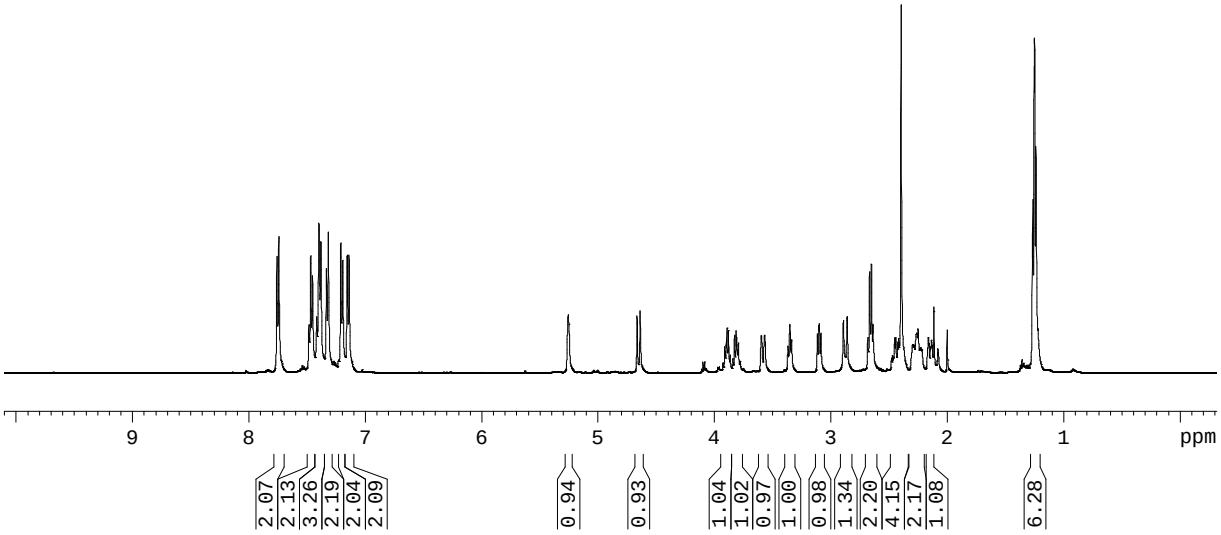
40
30
20
10
ppm


EtO
Ts
N
H
H
H
O
N
O
Ph
Et

11ba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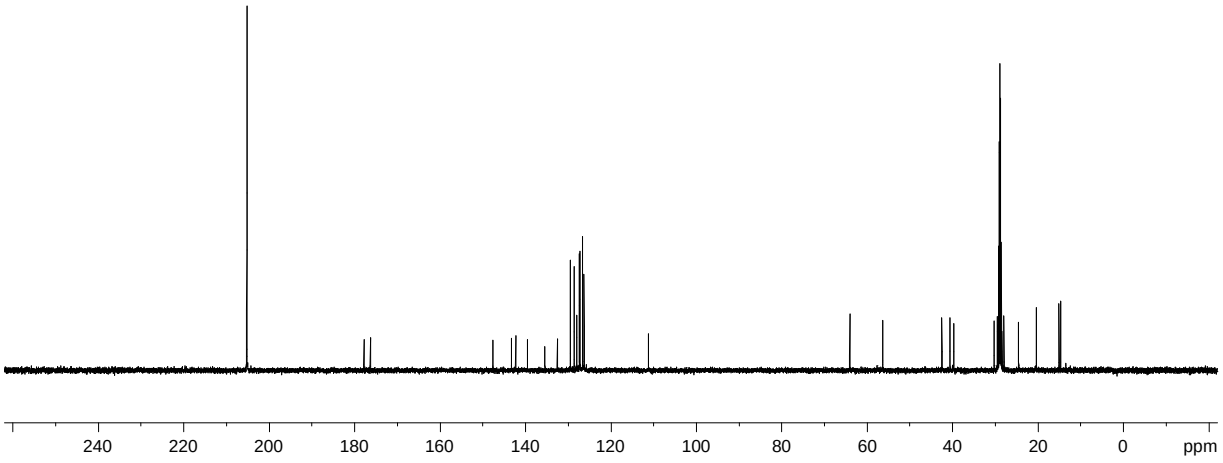
8
7
6
5
4
3
2
1
ppm
2.07
2.13
3.26
2.19
2.04
2.09
0.94
0.93
1.04
1.02
0.97
1.00
0.98
1.34
2.20
4.15
2.17
1.08
6.28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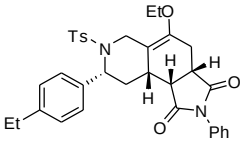
180
160
140
120
100
80
60
40
20
0
ppm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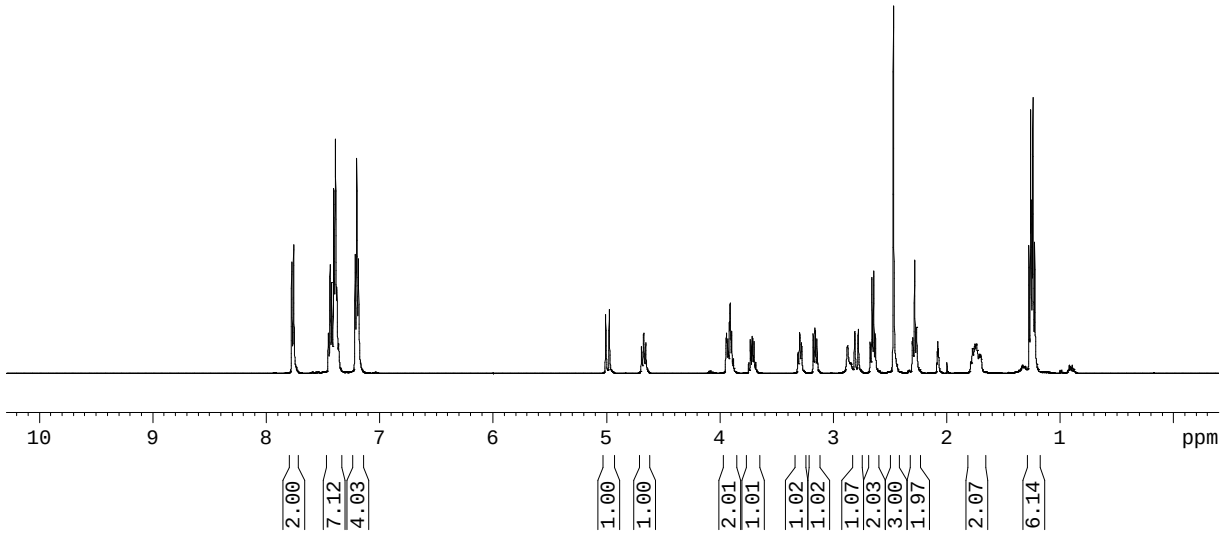
Ts
N
H
H
H
O
N
O
Ph
Et

11bb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9
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7
6
5
4
3
2
1
ppm
2.00
7.12
4.03
1.00
1.00
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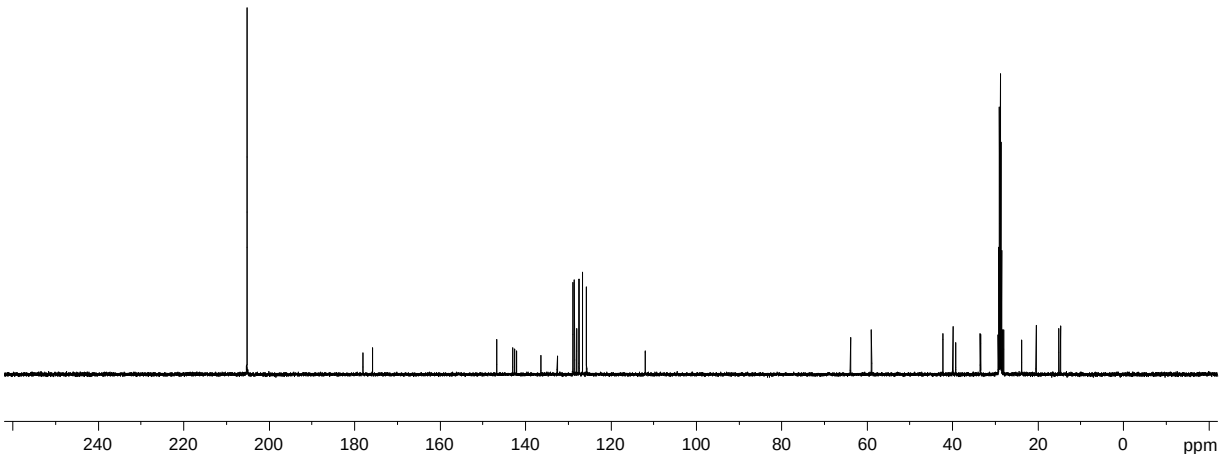
1.07
2.03
3.00
1.97
2.07
6.14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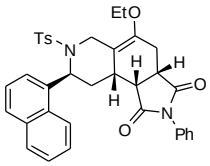
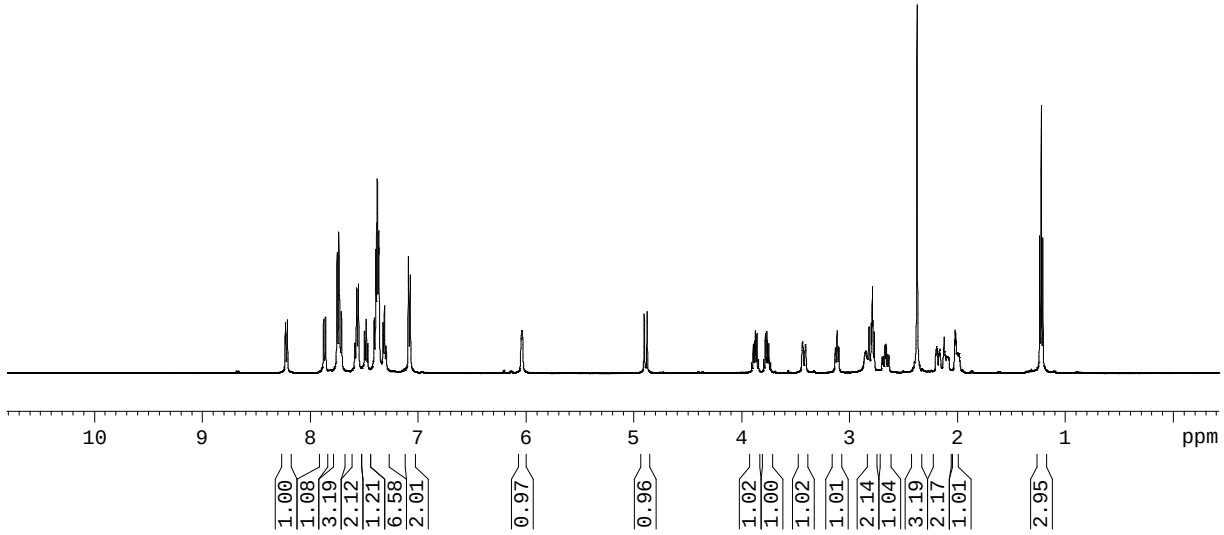
100
80
60
40
20
0
ppm


EtO
Ts
N
H
H
H
O
O
N
Ph

11ca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6
5
4
3
2
1
ppm
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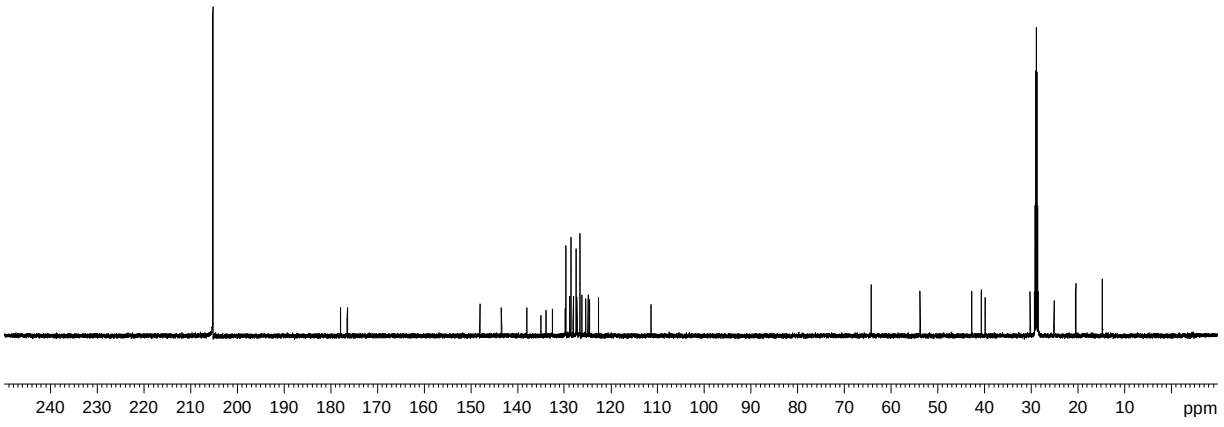
1.08
3.19
2.12
1.21
6.58
2.01
0.97
0.96
1.02
1.00
1.02
1.01
2.14
1.04
3.19
2.17
1.01
2.95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230
220
210
200
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180
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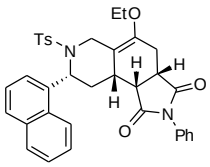
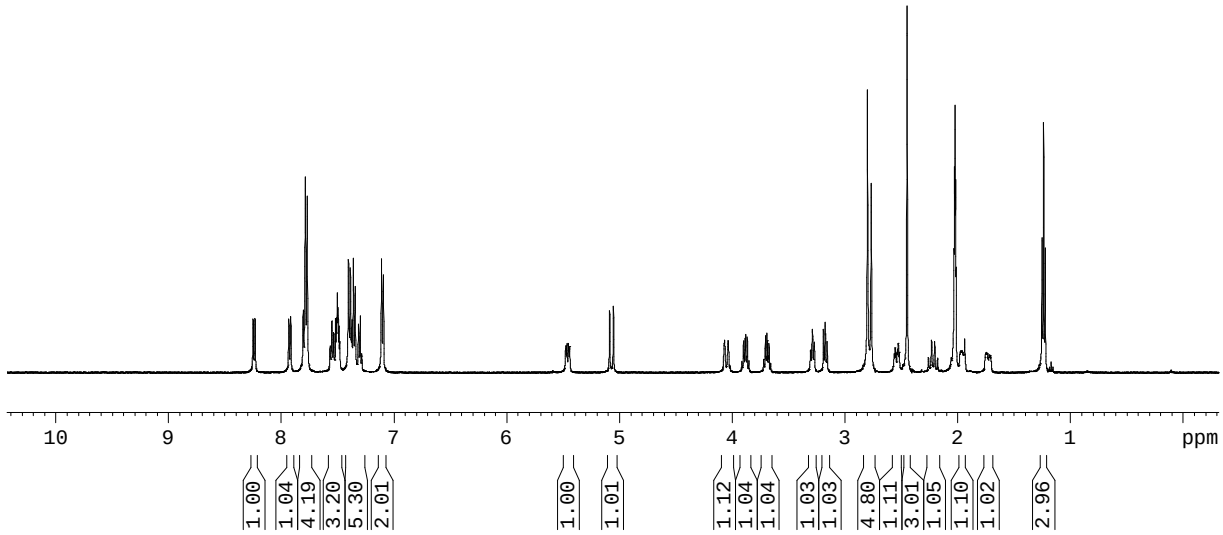
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


EtO
Ts
N
H
H
H
O
O
N
Ph

11cb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9
8
7
6
5
4
3
2
1
ppm
1.00
1.04
4.19
3.20
5.30
2.01
1.00
1.01
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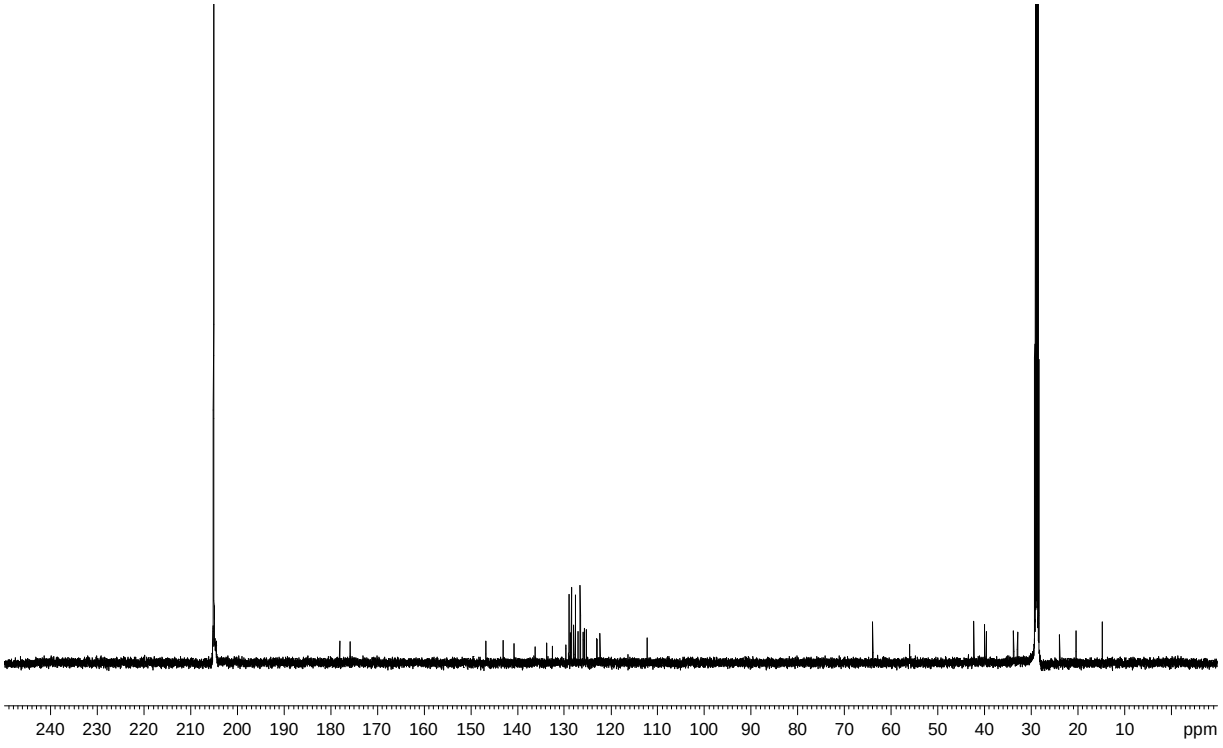
1.11
3.01
1.05
1.10
1.02
2.96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230
220
210
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110
100
90
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70
60
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40
30
20
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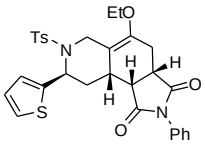
ppm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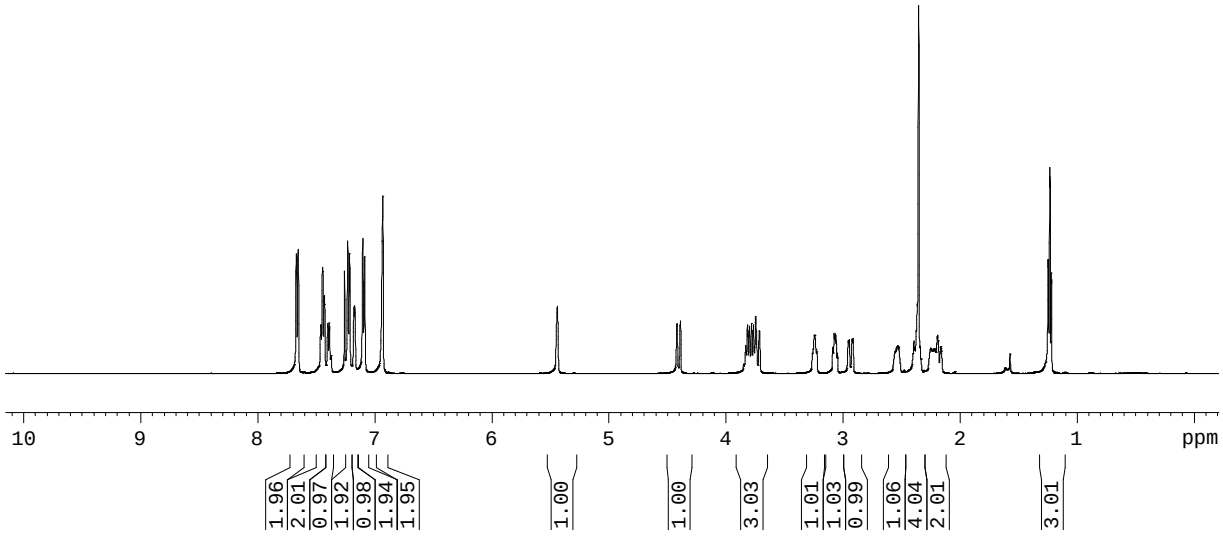
Ts
N
H
H
H
O
S
O
N
Ph

11da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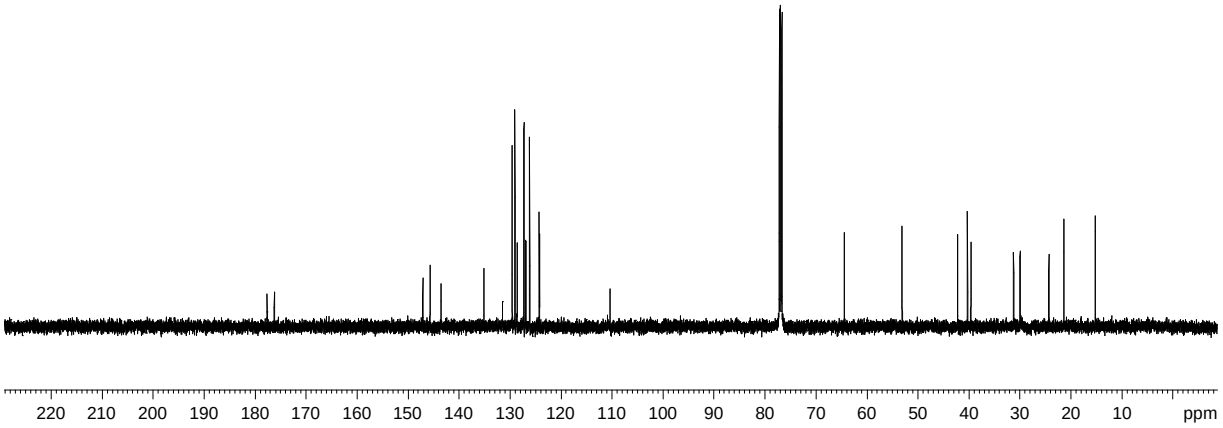
9
8
7
6
5
4
3
2
1
ppm
1.96
2.01
0.97
1.92
0.98
1.94
1.95
1.00
1.00
3.03
1.01
1.03
0.99
1.06
4.04
2.01
3.01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210
200
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180
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150
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100
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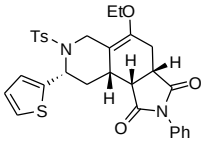
70
60
50
40
30
20
10
ppm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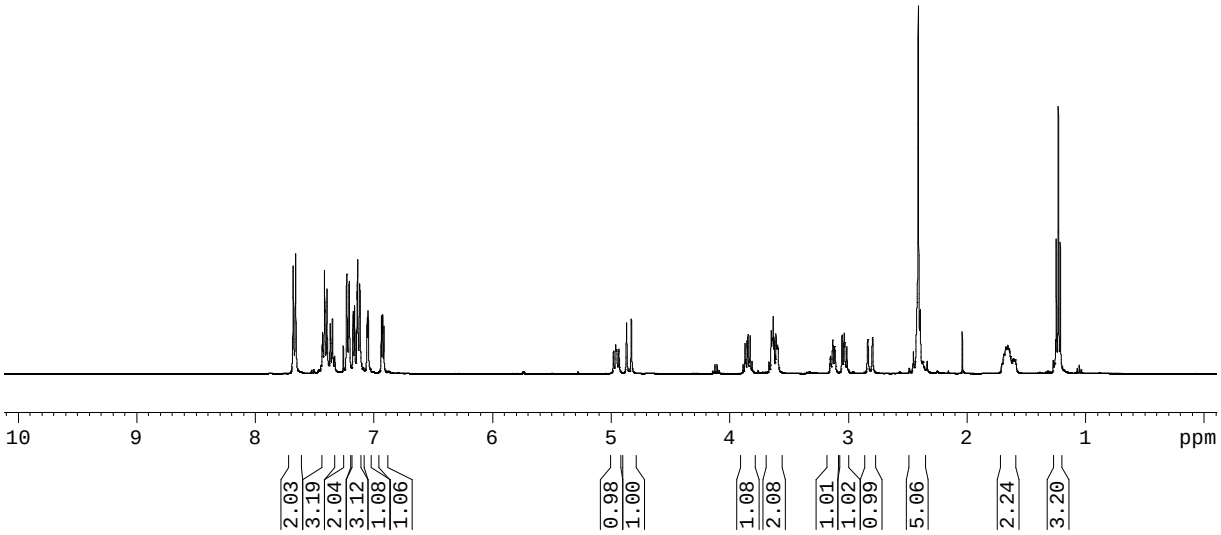
Ts
N
H
H
H
O
S
O
N
Ph

11db


10
9
8
7
6
5
4
3
2
1
ppm
2.03
3.19
2.04
3.12
1.08
1.06
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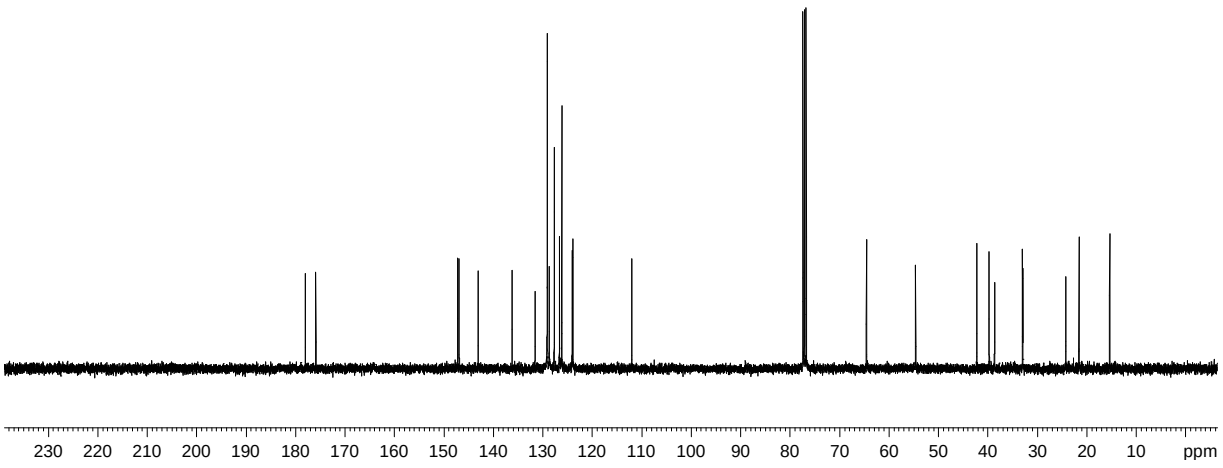
1.00
1.08
2.08
1.01
1.02
0.99
5.06
2.24
3.20


230
220
210
200
190
180
170
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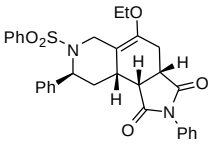
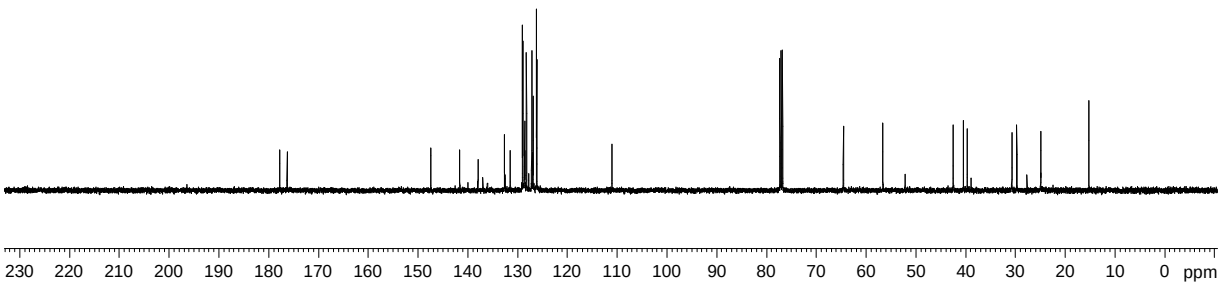
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


EtO
PhO2S
N
H
H
Ph
H
O
N
O
Ph

11ea

10
9
8
7
6
5
4
3
2
1
ppm
2.24
6.52
5.25
2.02
1.00
0.99
2.00
0.97
1.01
1.94
1.03
3.07
3.05


230
220
210
200
190
180
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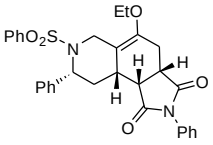
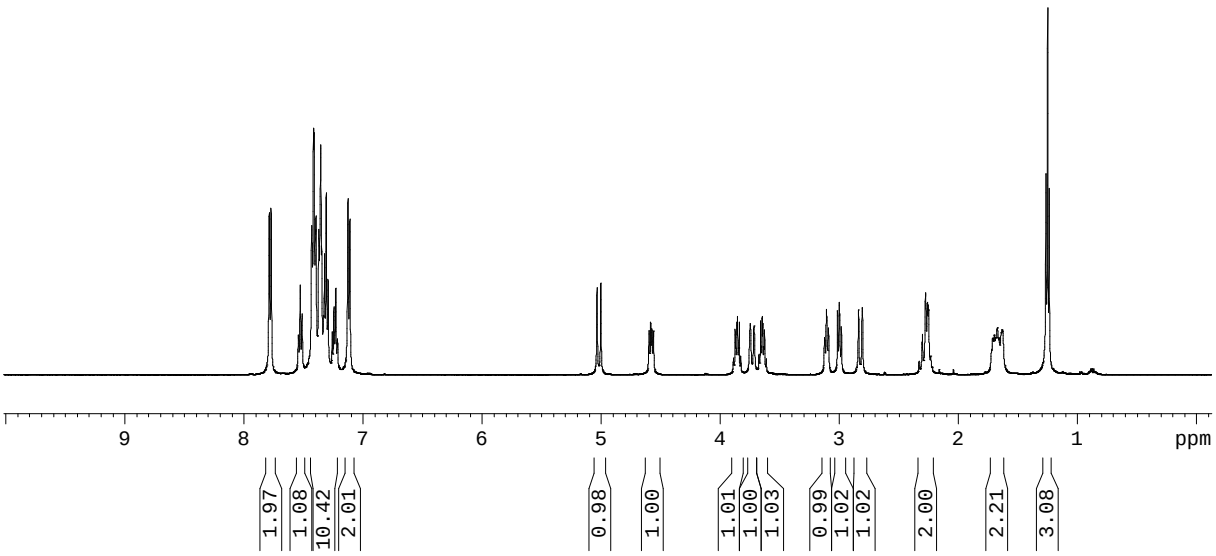
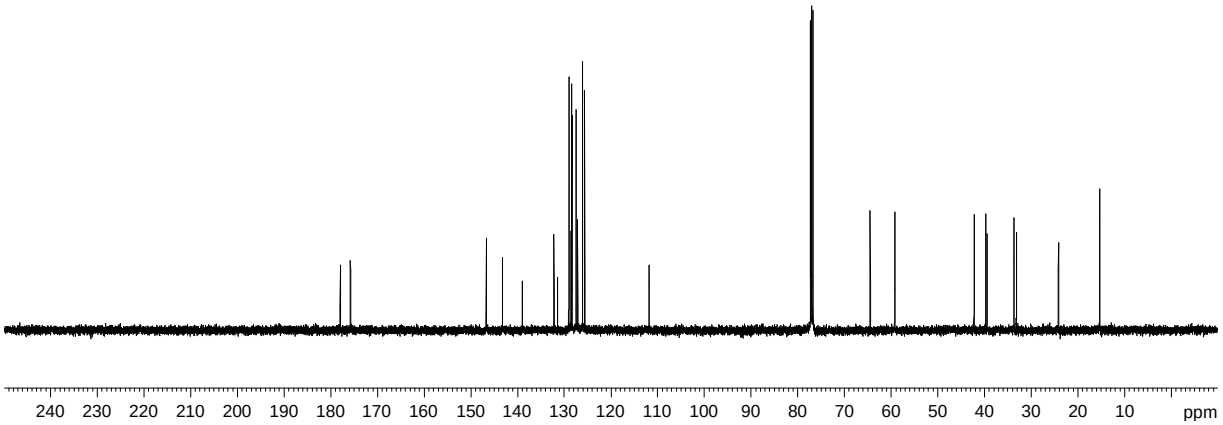
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


EtO
PhO2S
N
Ph
H
H
H
O
N
O
Ph

11eb


9
8
7
6
5
4
3
2
1
ppm
1.97
1.08
10.42
2.01
0.98
1.00
1.01
1.00
1.03
0.99
1.02
1.02
2.00
2.21
3.08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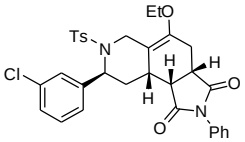
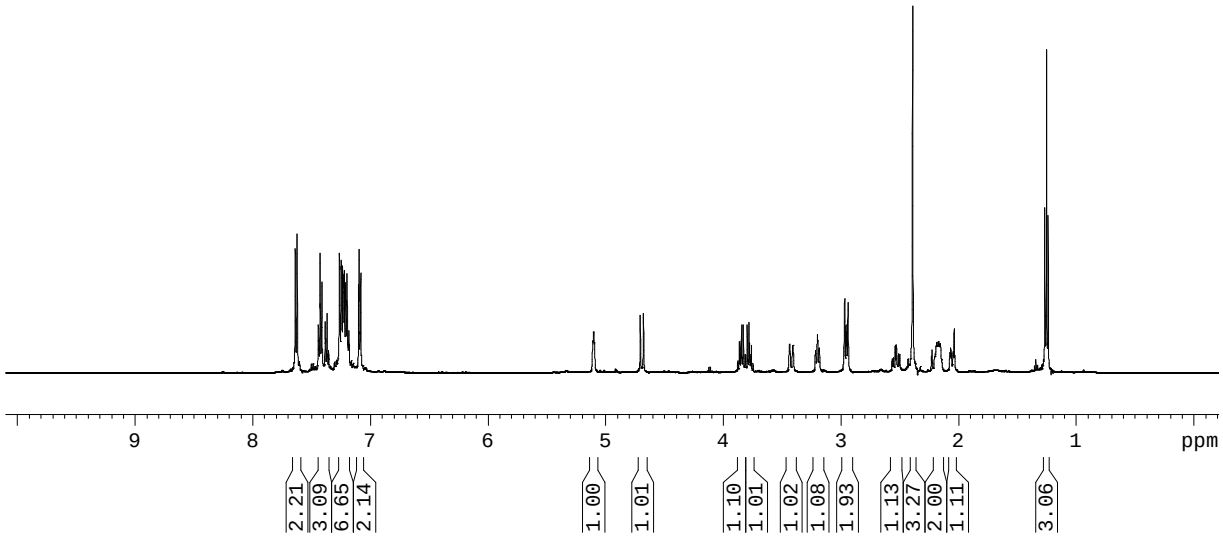
ppm


EtO
Ts
N
H
H
H
Cl
O
N
O
Ph

11fa


9
8
7
6
5
4
3
2
1
ppm
2.21
3.09
6.65
2.14
1.00
1.01
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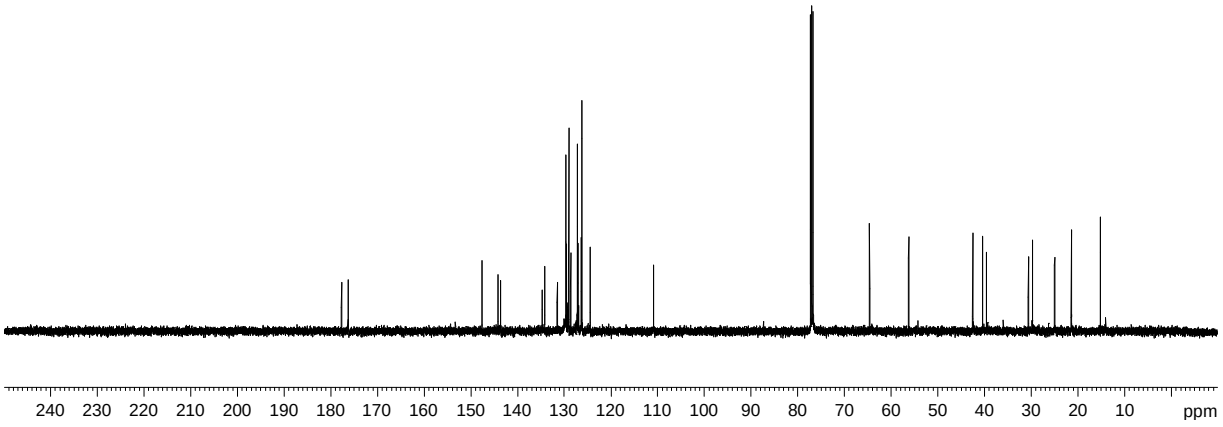
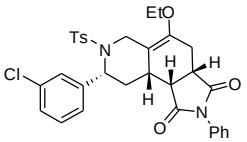
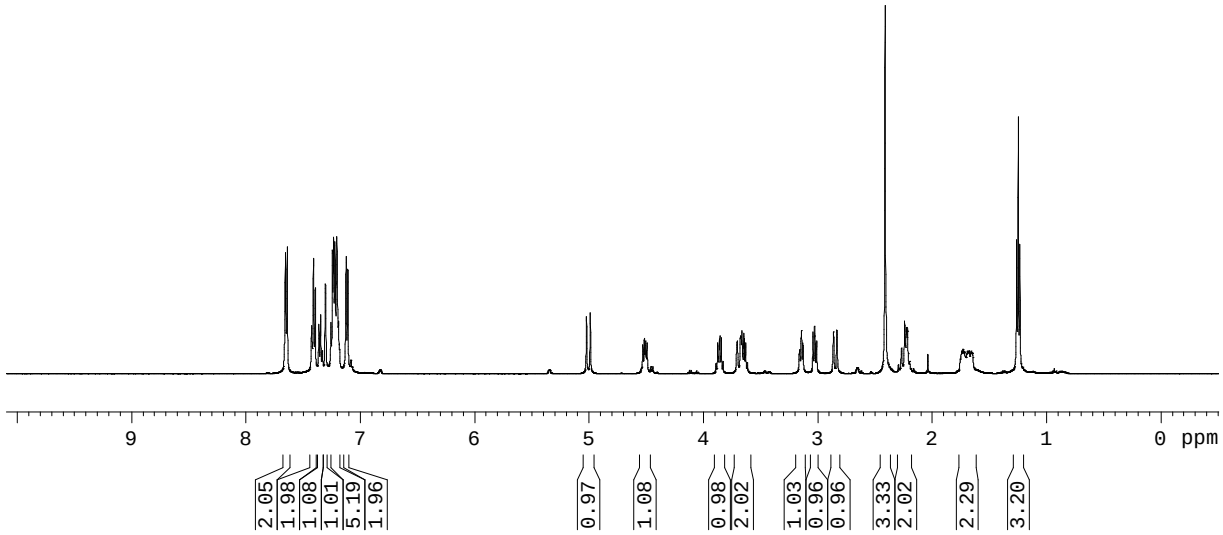
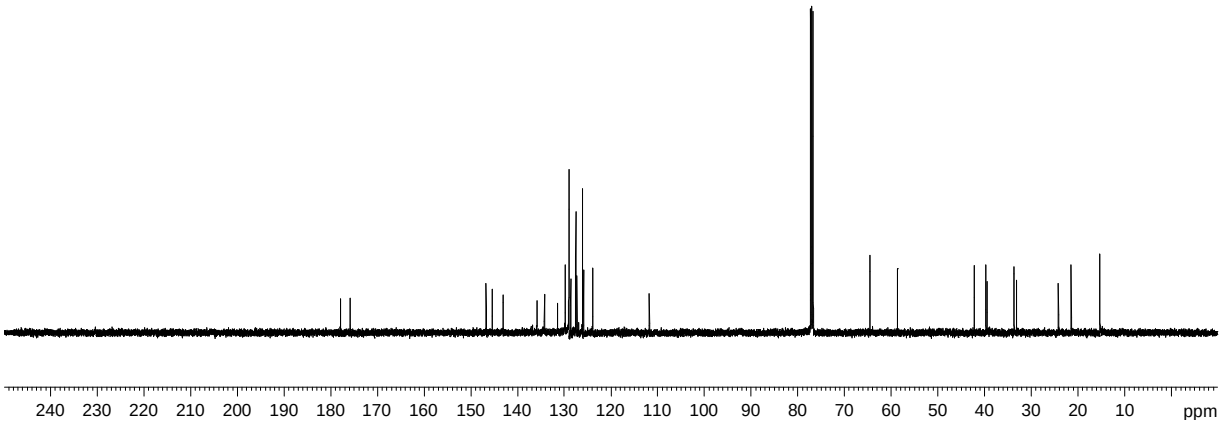
1.01
1.02
1.08
1.93
1.13
3.27
2.00
1.11
3.06

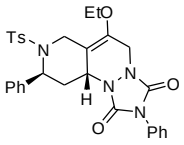

240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


EtO
Ts
N
H
H
H
Cl
O
N
O
Ph

11fb


9
8
7
6
5
4
3
2
1
0 ppm
2.05
1.98
1.08
1.01
5.19
1.96
0.97
1.08
0.98
2.02
1.03
0.96
0.96
3.33
2.02
2.29
3.20


240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


EtO
Ts
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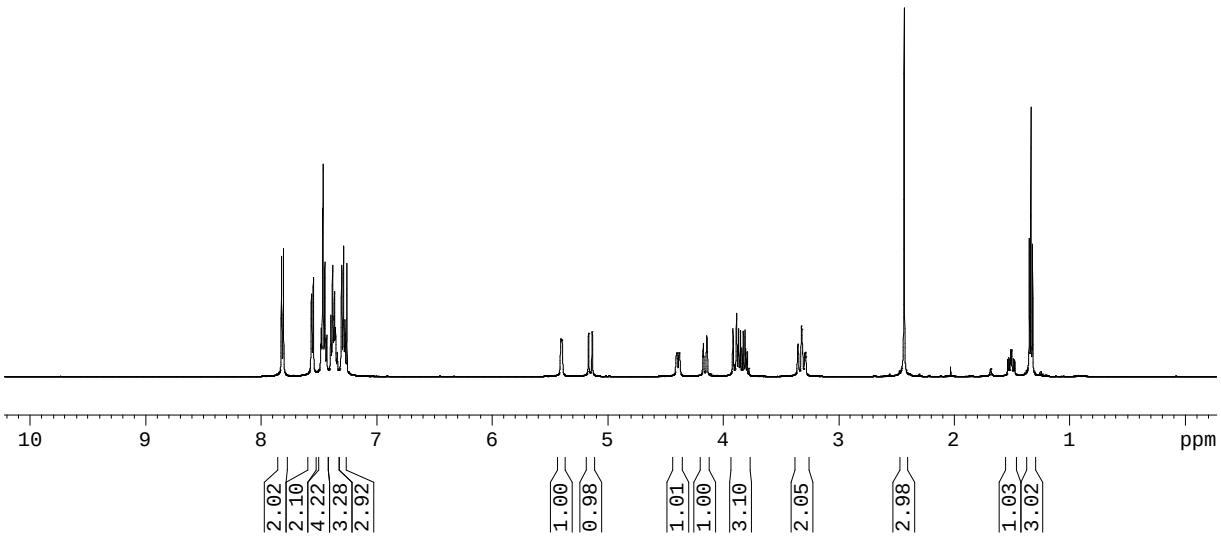
Ph
H
N
N
O
O
N
Ph

12a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9
8
7
6
5
4
3
2
1
ppm
2.02
2.10
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3.28
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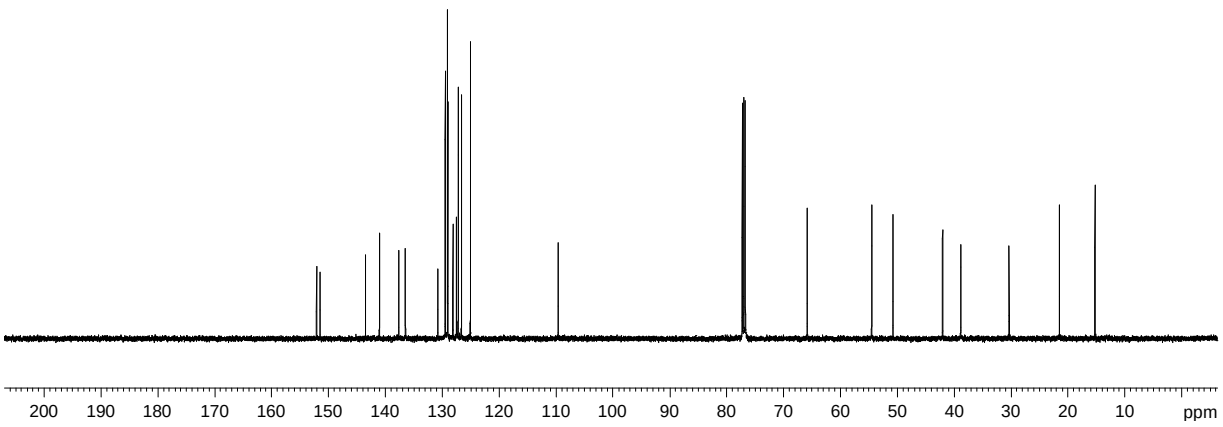
1.00
0.98
1.01
1.00
3.10
2.05
2.98
1.03
3.02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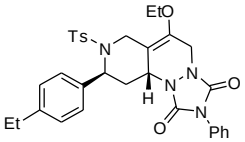
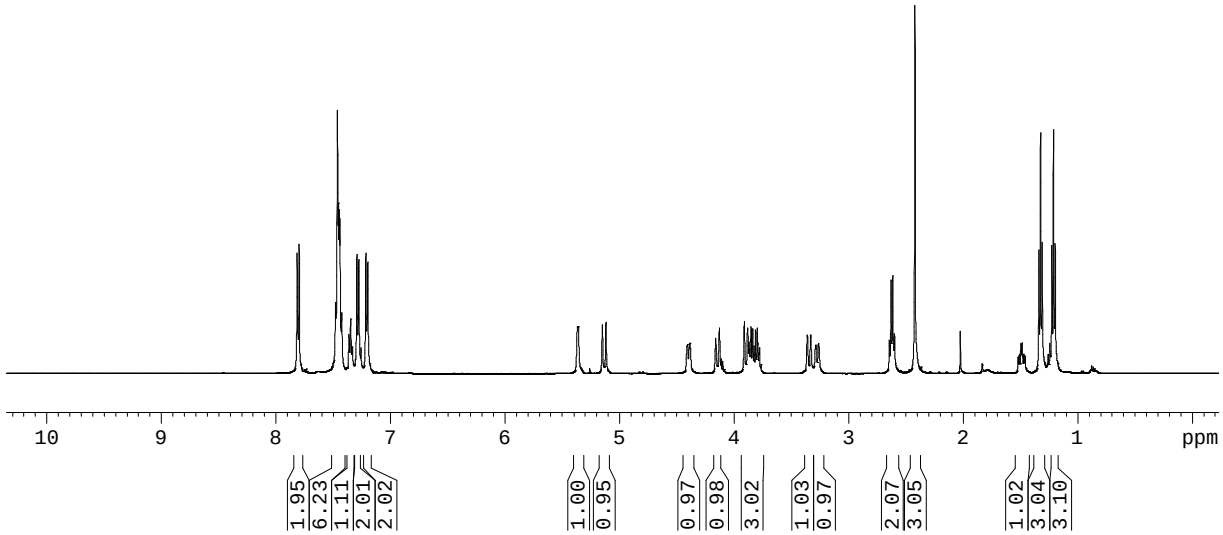
30
20
10
ppm


EtO
Ts
N
N
N
O
H
O
N
Ph
Et

12b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9
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6
5
4
3
2
1
ppm
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6.23
1.11
2.01
2.02
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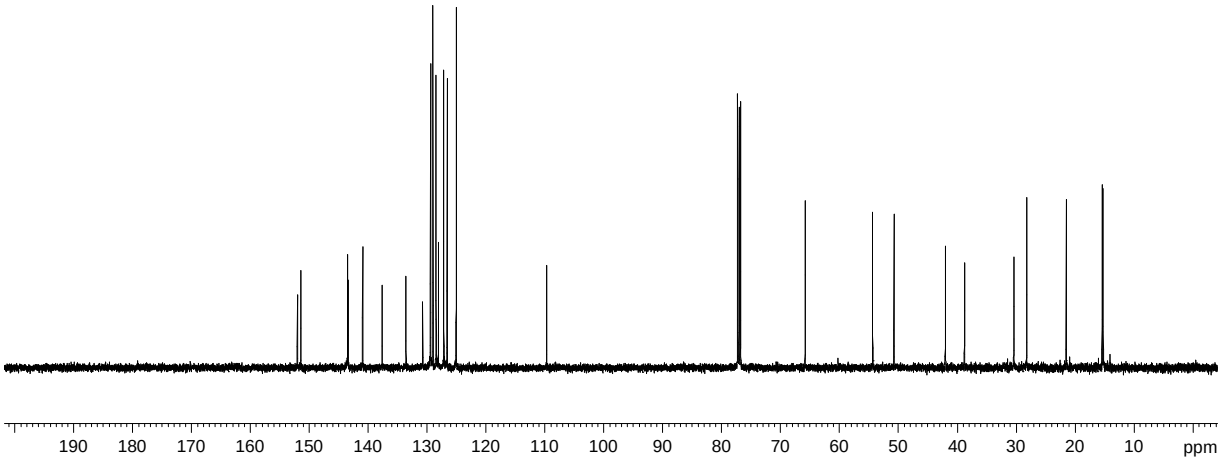
0.98
3.02
1.03
0.97
2.07
3.05
1.02
3.04
3.10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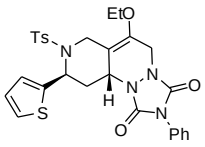
30
20
10
ppm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Ts
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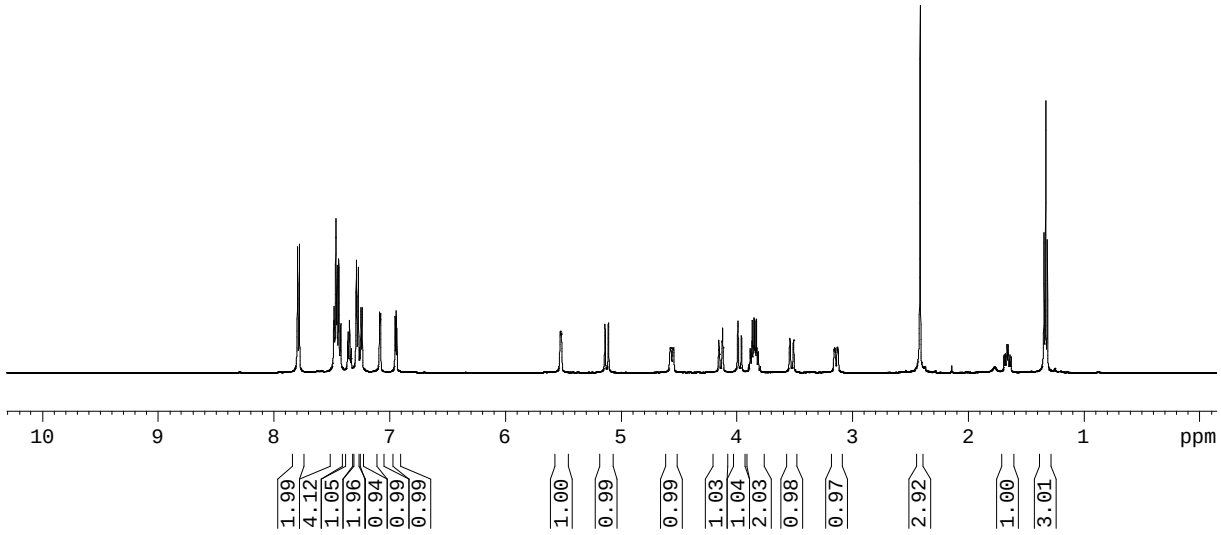
H
N
N
O
S
O
N
Ph

12c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5
4
3
2
1
ppm
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4.12
1.05
1.96
0.94
0.99
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0.99
0.99
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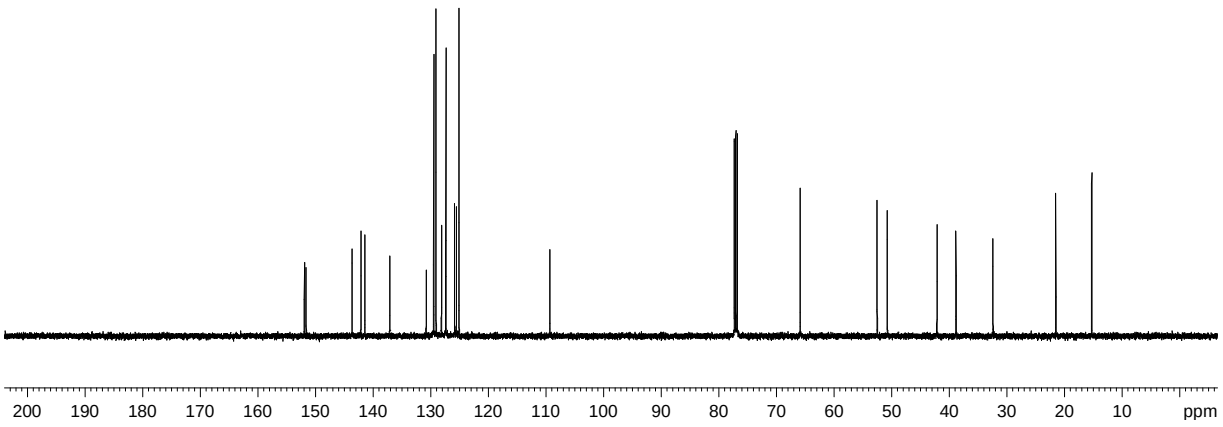
1.04
2.03
0.98
0.97
2.92
1.00
3.01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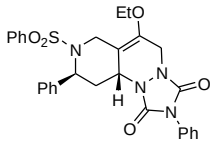
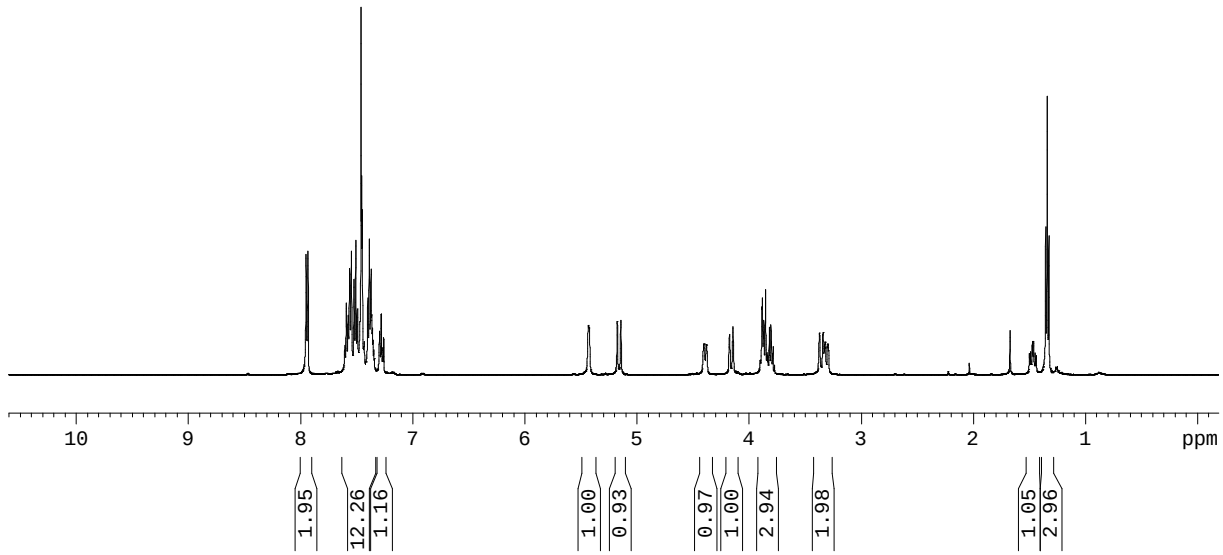
ppm


EtO
PhO2S
N
Ph
H
N
N
O
O
N
Ph

12d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6
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4
3
2
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ppm
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1.00
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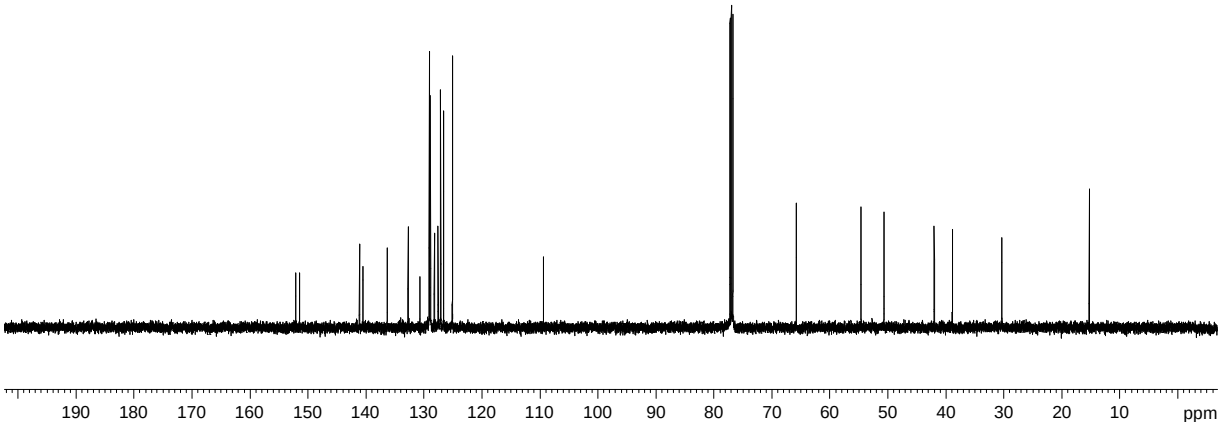
1.98
1.05
2.96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30
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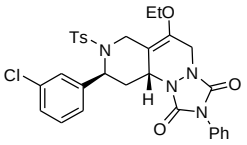
10
ppm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Ts
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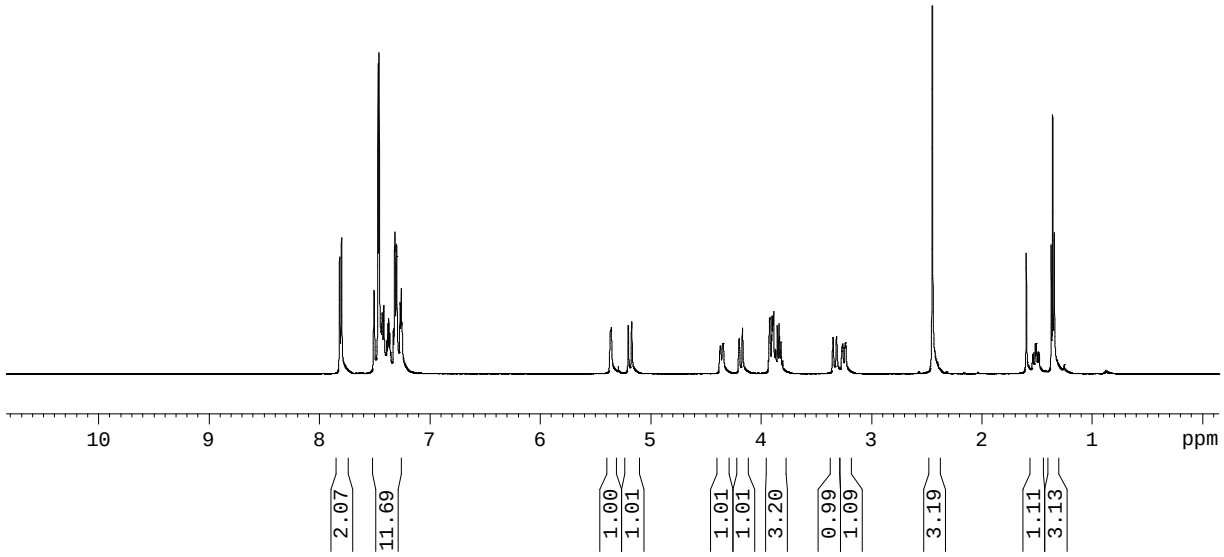
Cl
H
N
N
O
O
N
Ph

12e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6
5
4
3
2
1
ppm
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1.01
1.01
1.01
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0.99
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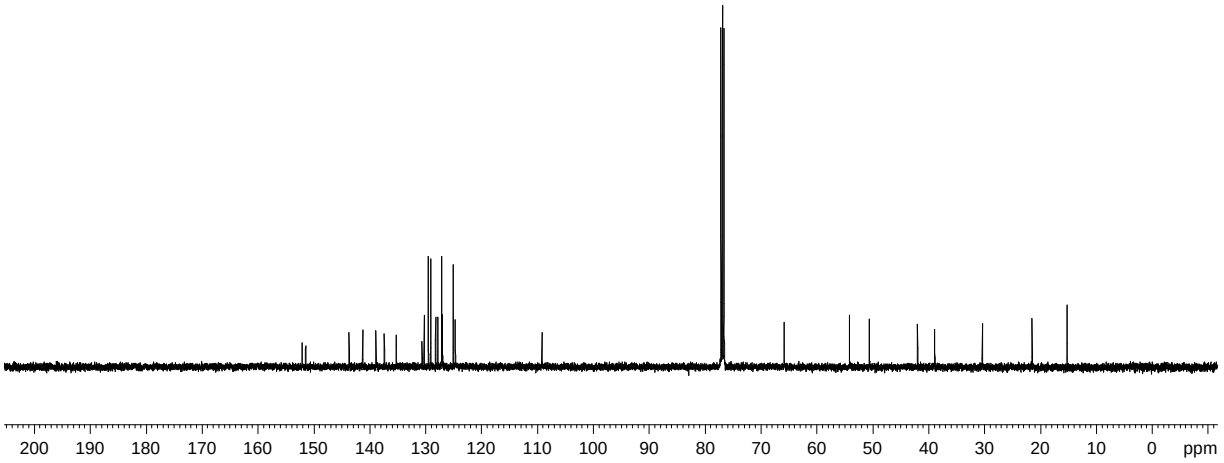
3.19
1.11
3.13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20
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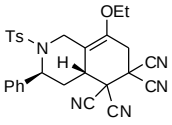
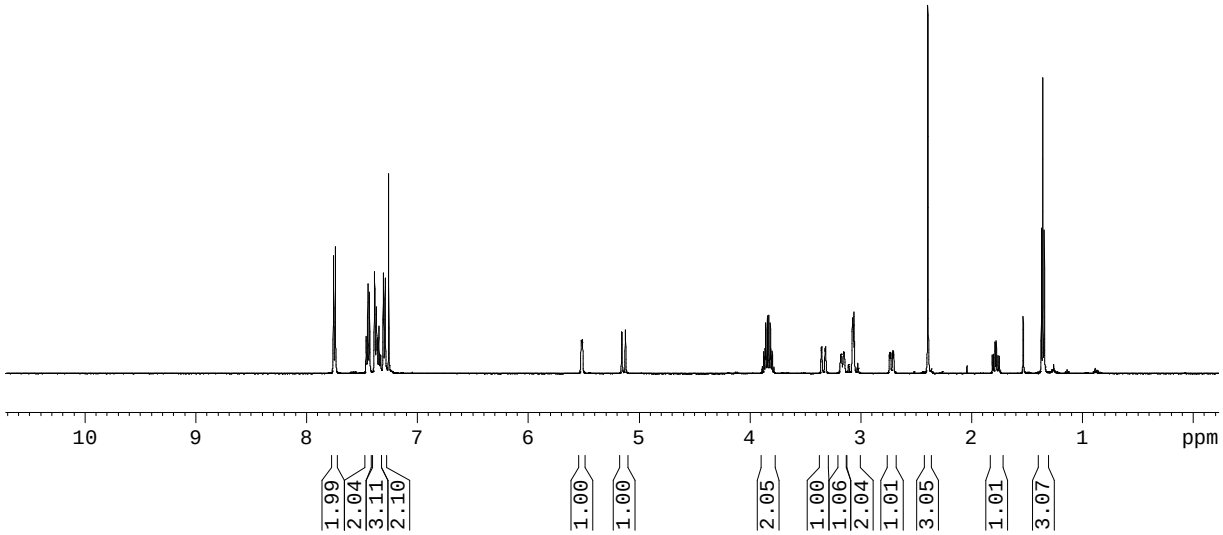
0
ppm


OEt
Ts
N
H
Ph
CN
CN
NC
CN

major 13a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6
5
4
3
2
1
ppm
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2.04
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2.10
1.00
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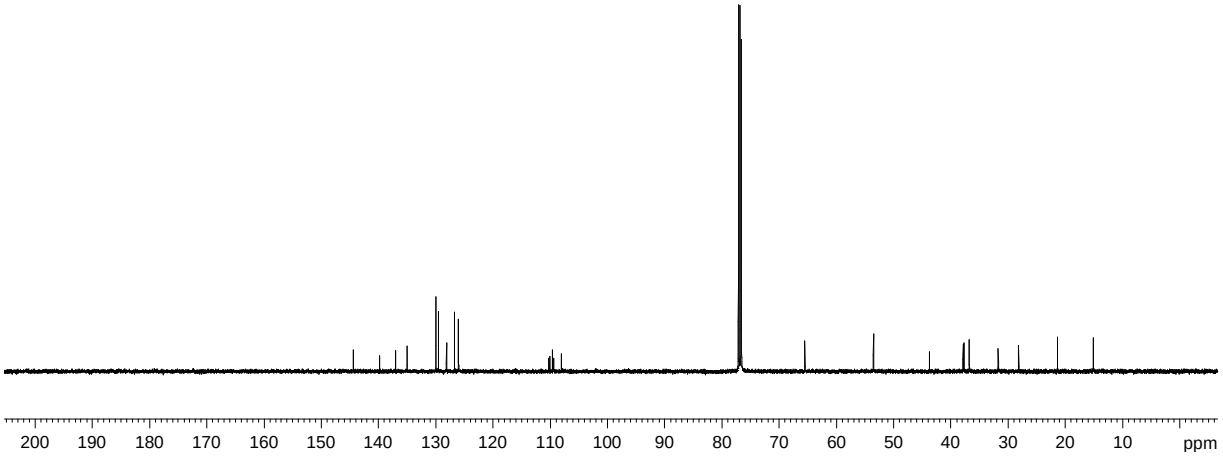
1.06
2.04
1.01
3.05
1.01
3.07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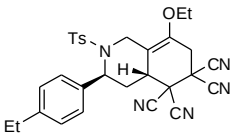
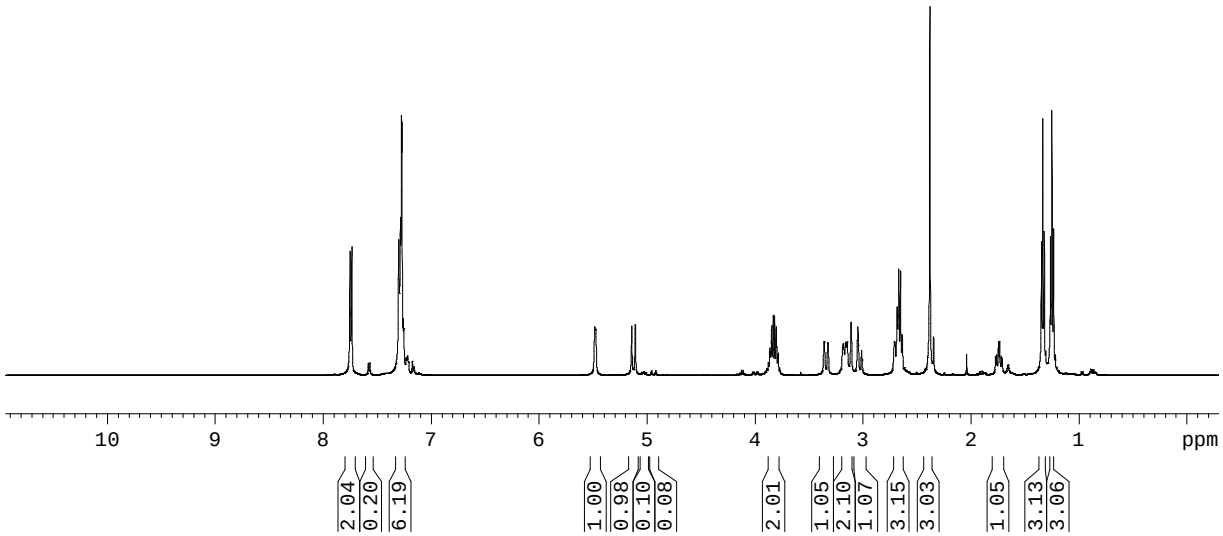
10
ppm


OEt
Ts
N
H
CN
CN
NC
CN
Et

major 13b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5
4
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2
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ppm
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0.20
6.19
1.00
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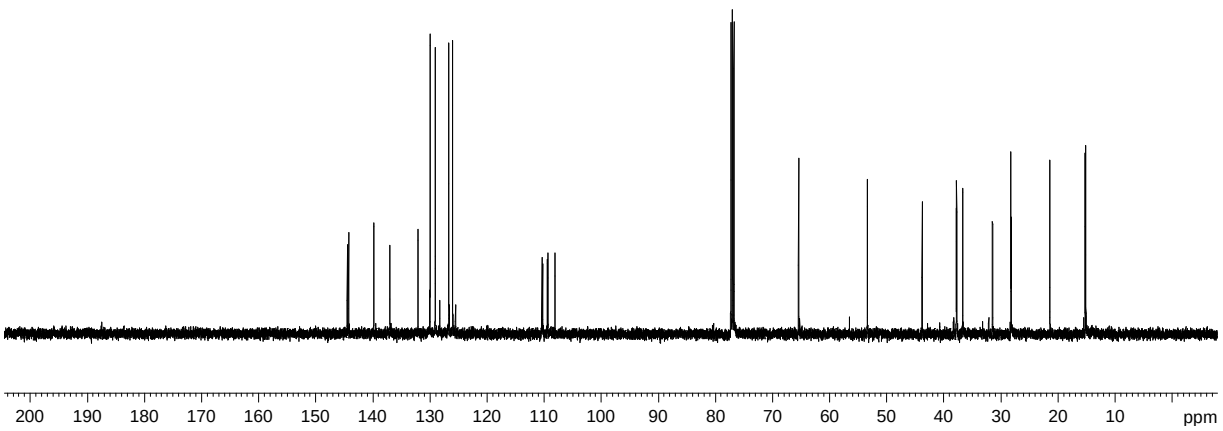
0.08
2.01
1.05
2.10
1.07
3.15
3.03
1.05
3.13
3.06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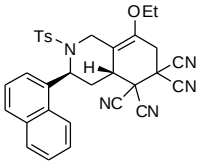
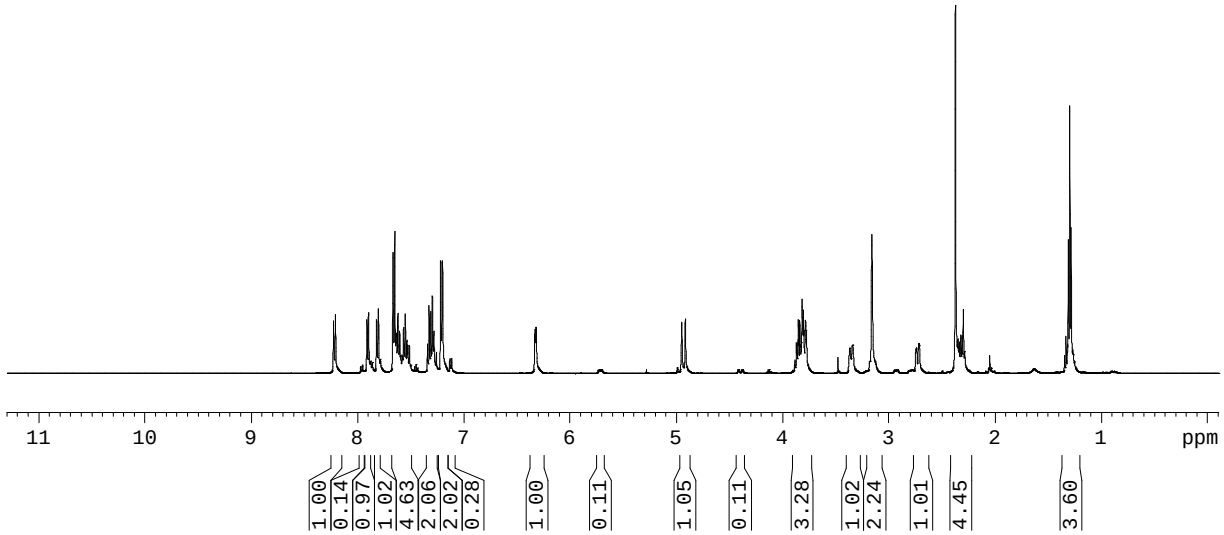
30
20
10
ppm


OEt
Ts
N
H
CN
CN
NC
CN

major 13c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6
5
4
3
2
1
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0.97
1.02
4.63
2.06
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0.11
1.05
0.11
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1.02
2.24
1.01
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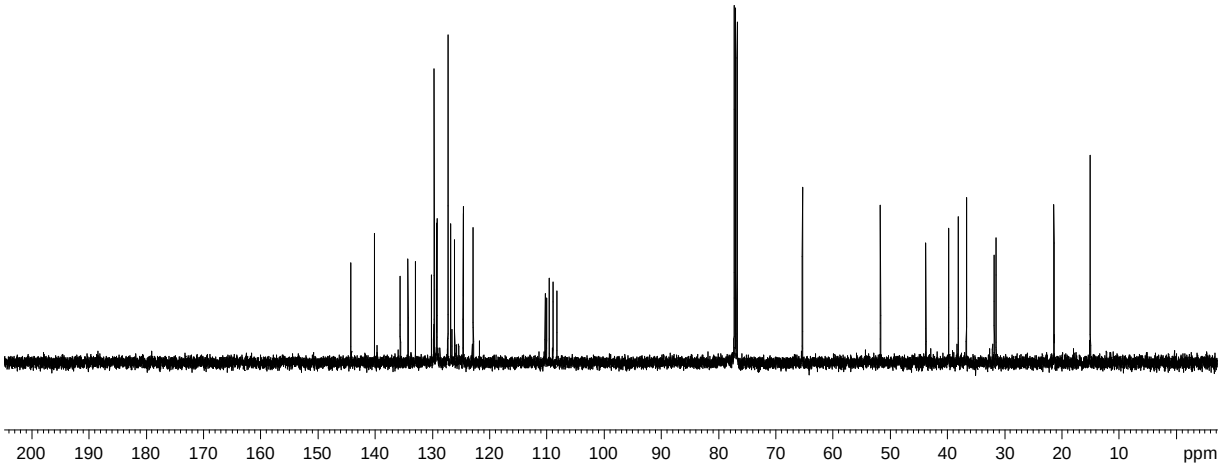
3.60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150
140
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60
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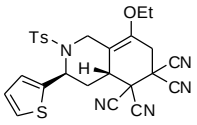
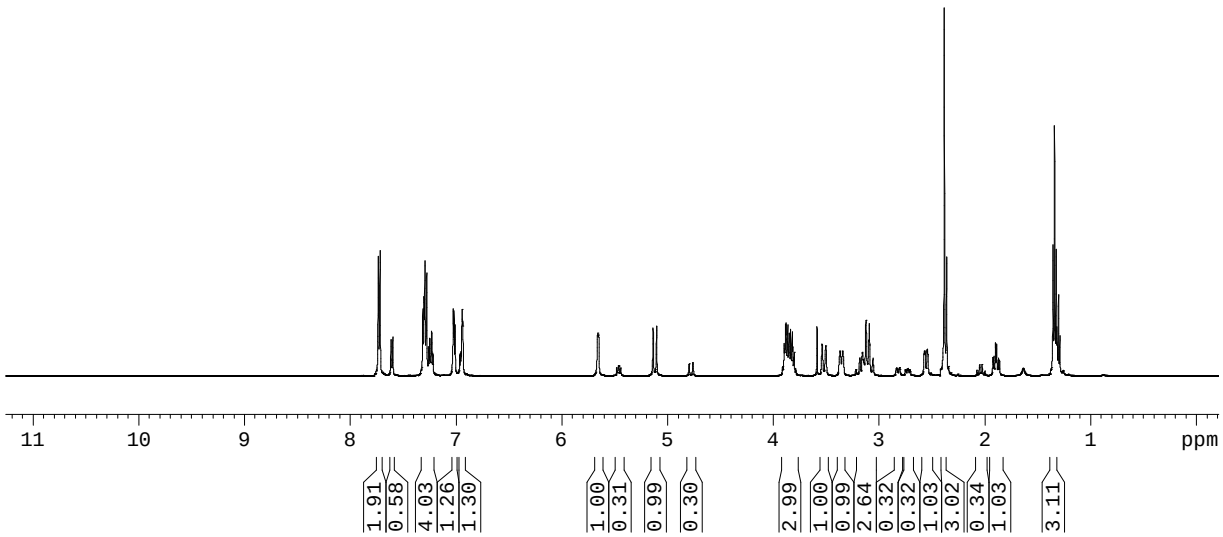
30
20
10
ppm


OEt
Ts
N
H
CN
CN
NC
CN
S

major 13d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7
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5
4
3
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1
ppm
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0.99
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0.99
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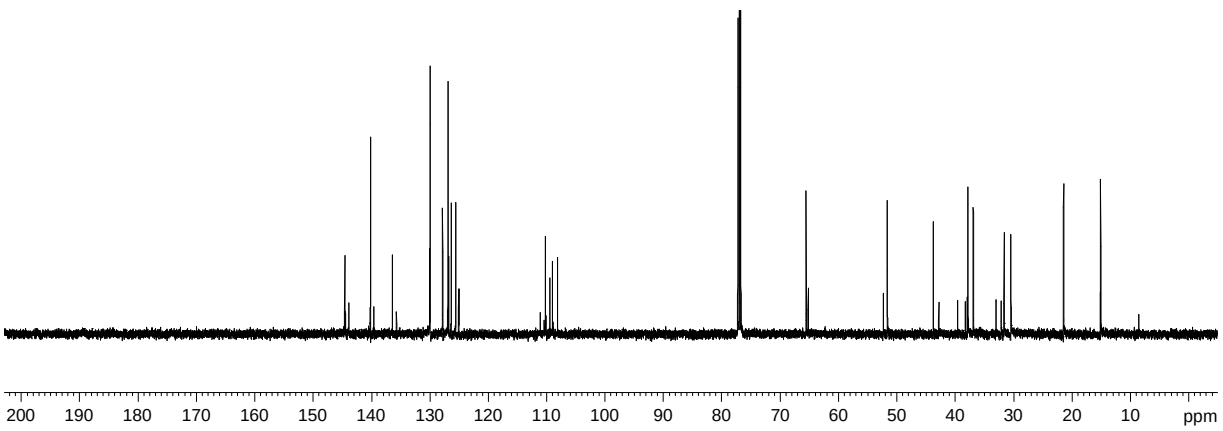
1.03
3.11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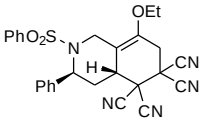
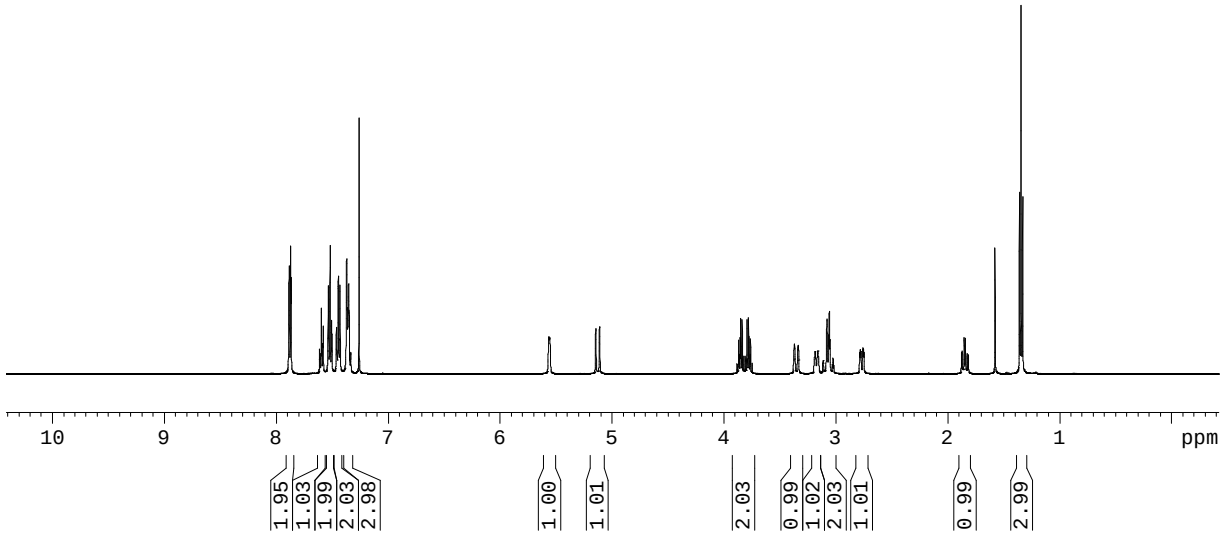
30
20
10
ppm


OEt
PhO2S
N
H
Ph
CN
CN
NC
CN

major 13e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6
5
4
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ppm
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2.03
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1.02
2.03
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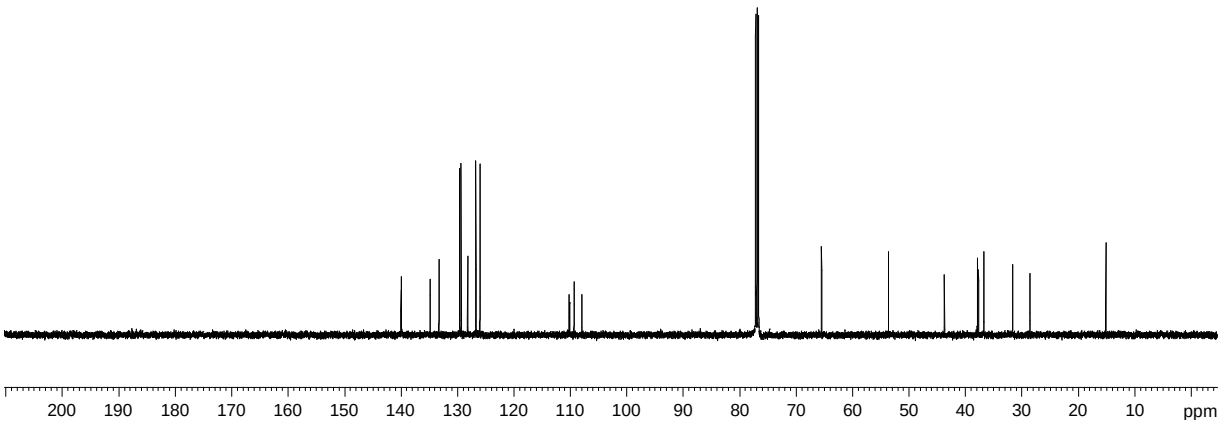
0.99
2.99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150
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50
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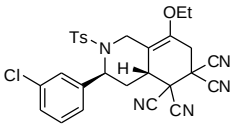
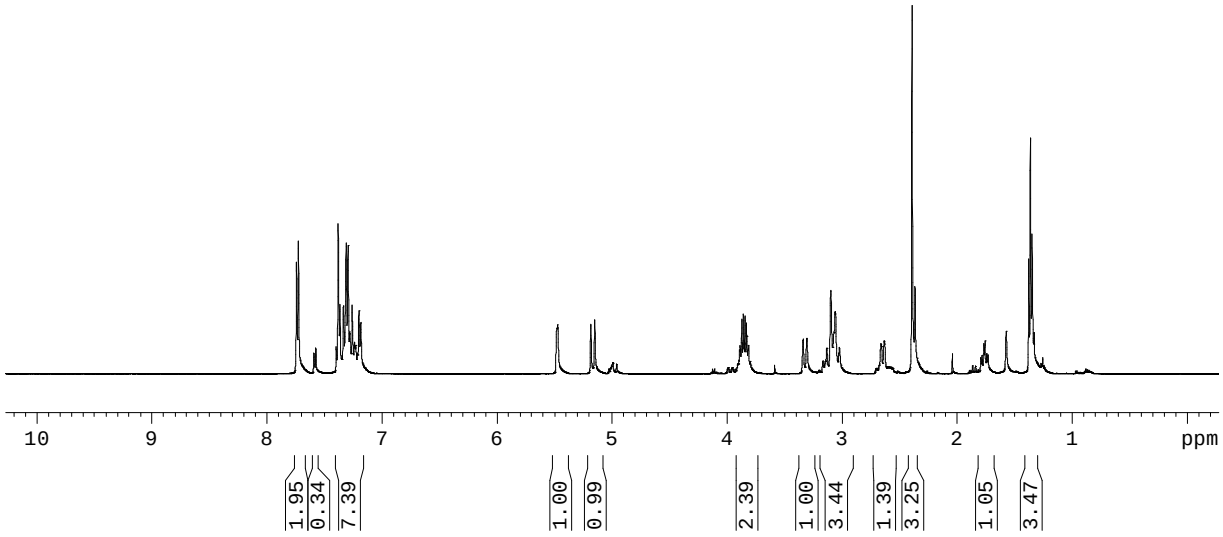
30
20
10
ppm


OEt
Ts
N
H
Cl
CN
CN
NC
CN

major 13f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7
6
5
4
3
2
1
ppm
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0.99
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1.00
3.44
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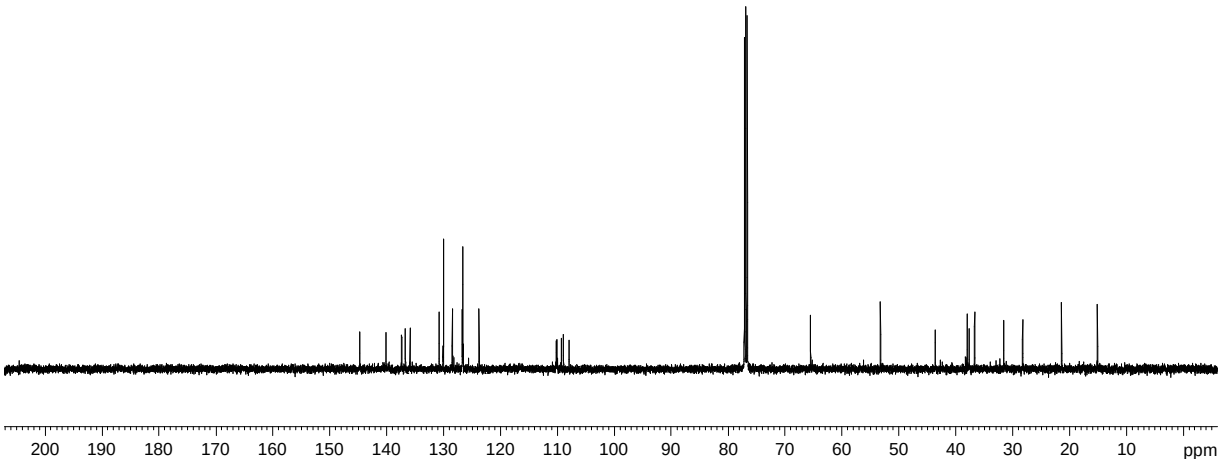
3.25
1.05
3.47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150
140
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120
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100
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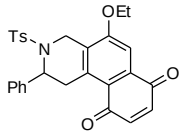
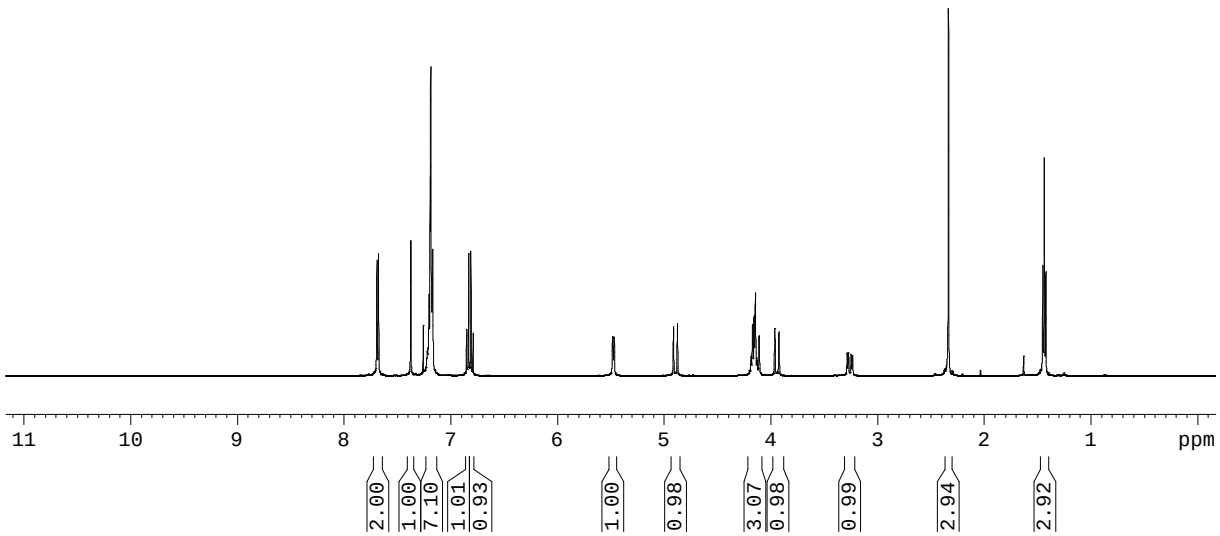
30
20
10
ppm


OEt
Ts
N
Ph
O
O

14a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9
8
7
6
5
4
3
2
1
ppm
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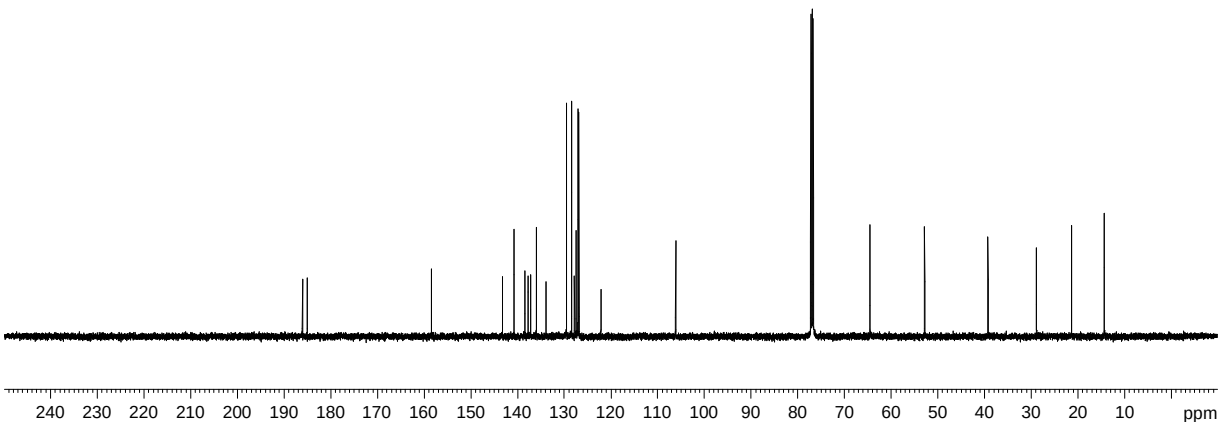
1.00
7.10
1.01
0.93
1.00
0.98
3.07
0.98
0.99
2.94
2.92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30
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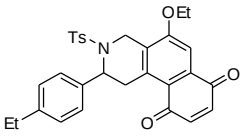
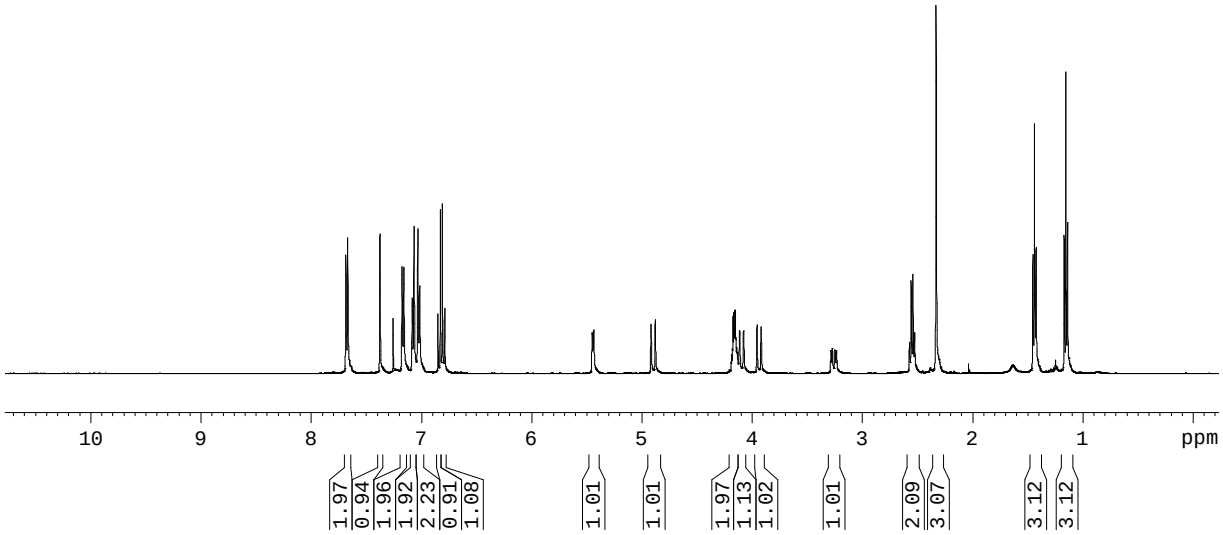
10
ppm


OEt
Ts
N
O
O
Et

14ba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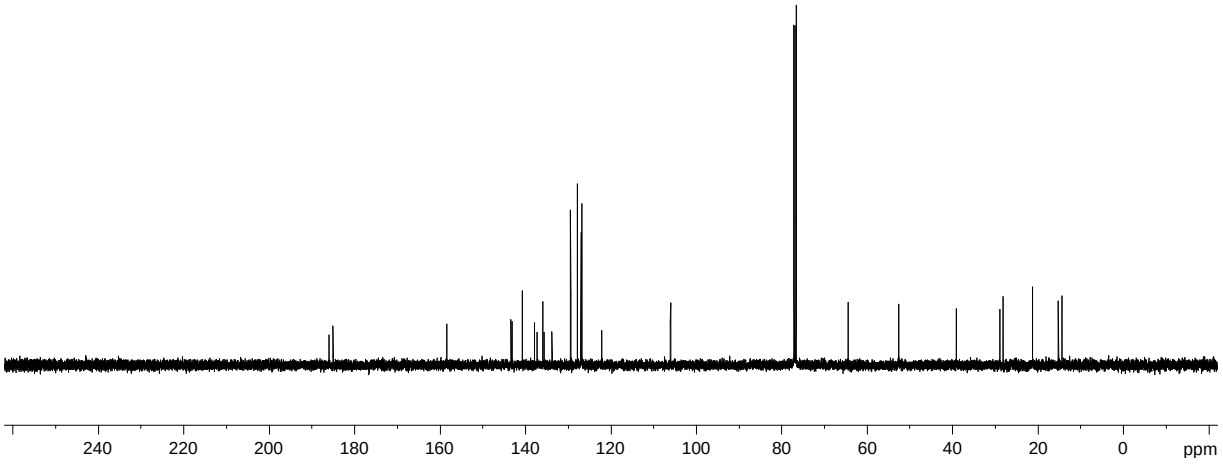
7
6
5
4
3
2
1
ppm
1.97
0.94
1.96
1.92
2.23
0.91
1.08
1.01
1.01
1.97
1.13
1.02
1.01
2.09
3.07
3.12
3.12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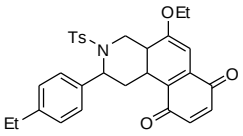
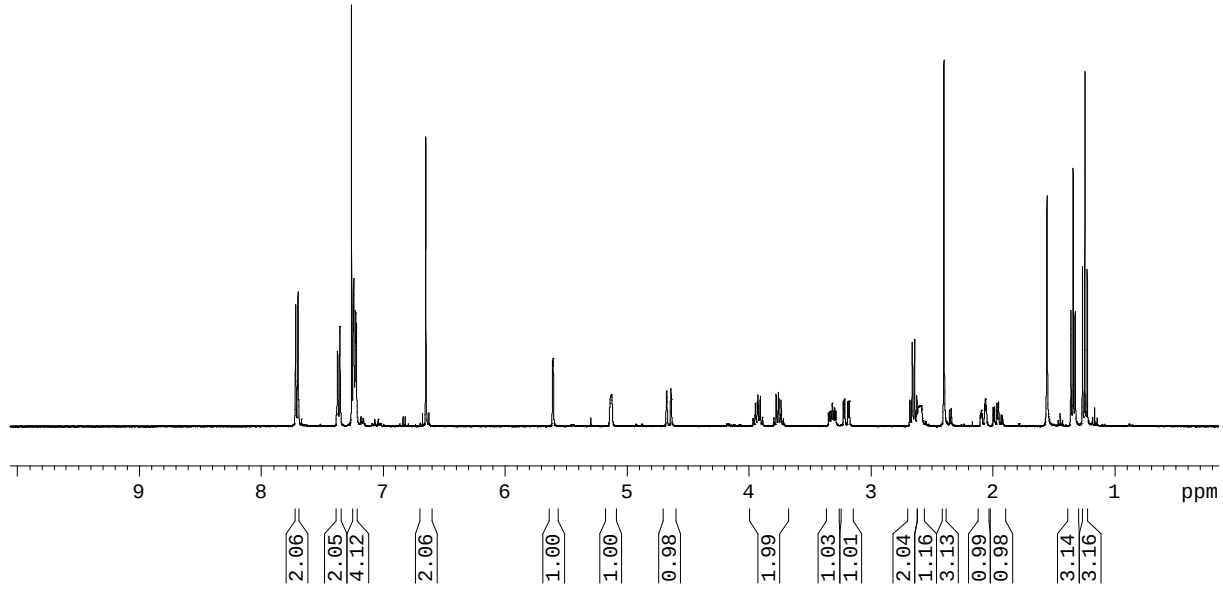
200
180
160
140
120
100
80
60
40
20
0
ppm


OEt
Ts
N
O
O
Et

14bb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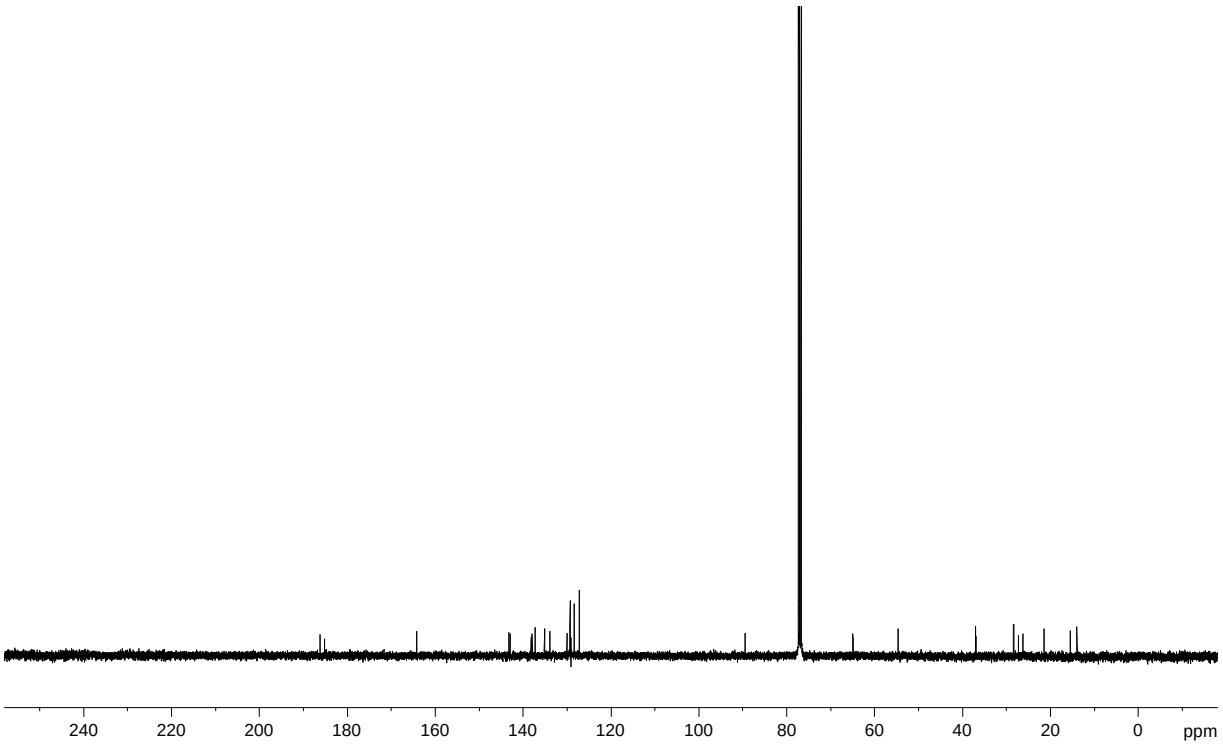
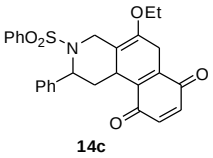
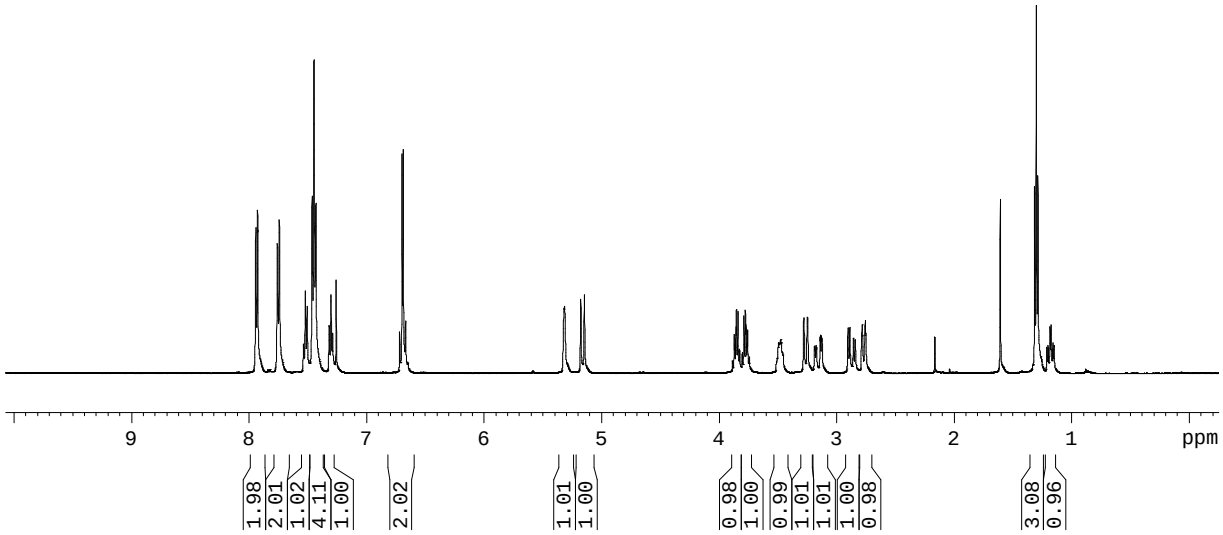
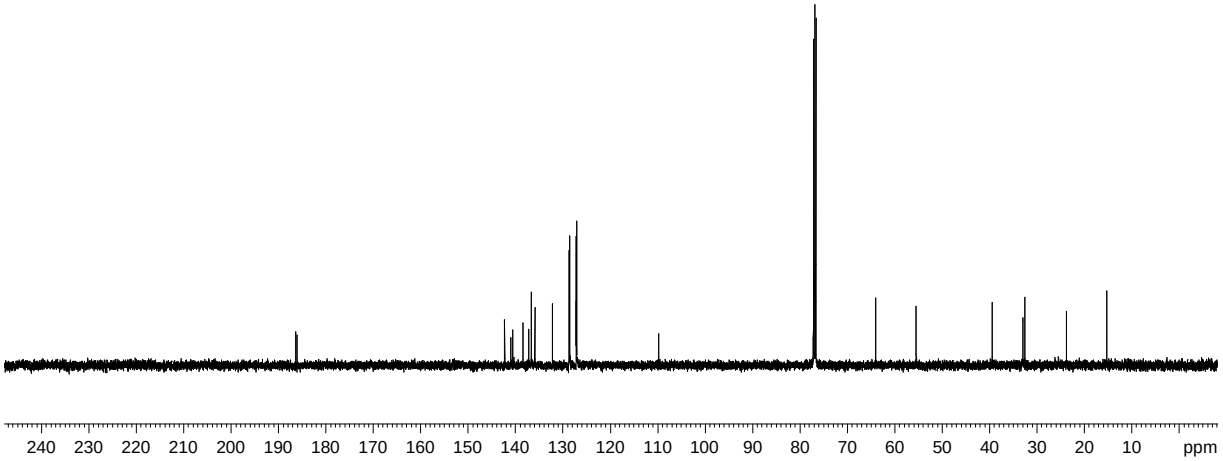
6
5
4
3
2
1
ppm
2.06
2.05
4.12
2.06
1.00
1.00
0.98
1.99
1.03
1.01
2.04
1.16
3.13
0.99
0.98
3.14
3.16

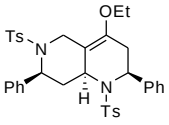

240
220
200
180
160
140
120
100
80
60
40
20
0
ppm


OEt
PhO2S
N
Ph
O
O

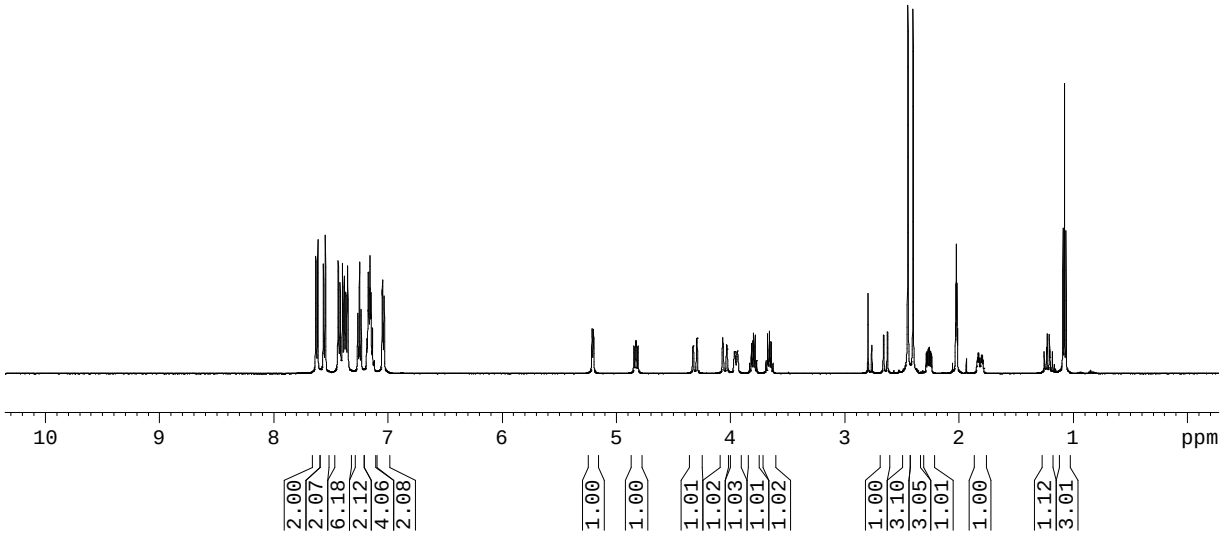
14c

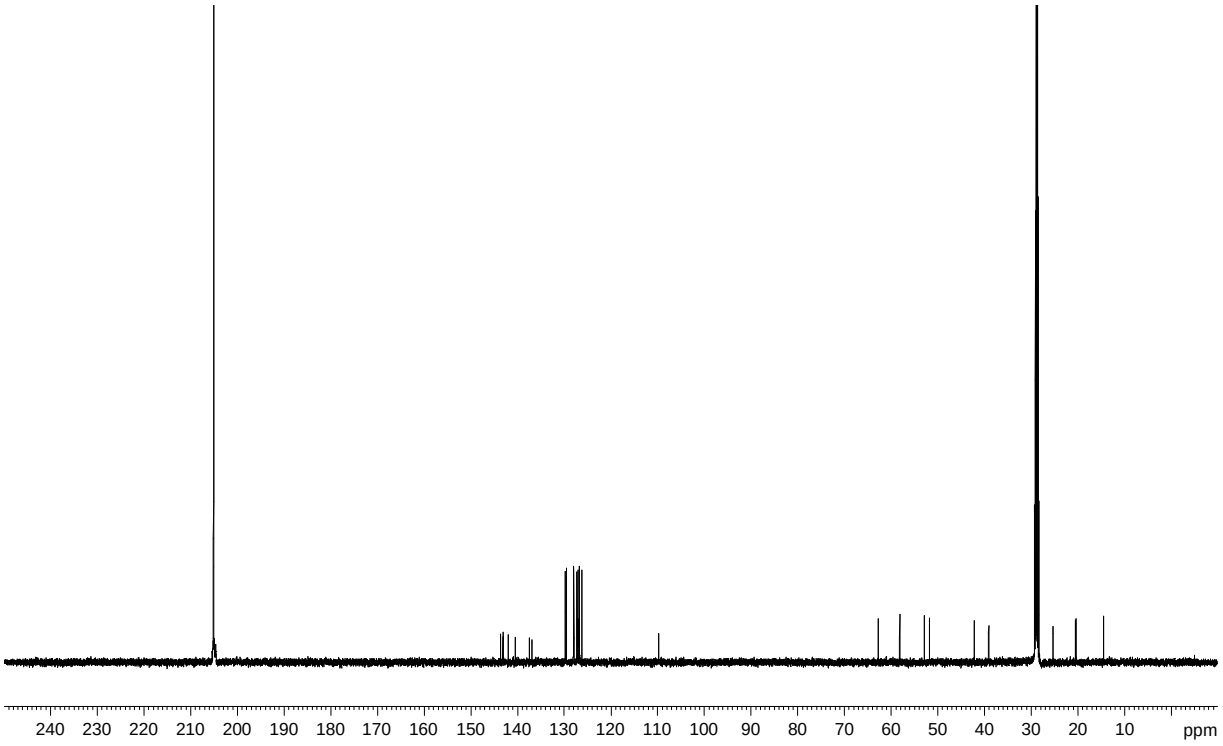

9
8
7
6
5
4
3
2
1
ppm
1.98
2.01
1.02
4.11
1.00
2.02
1.01
1.00
0.98
1.00
0.99
1.01
1.01
1.00
0.98
3.08
0.96

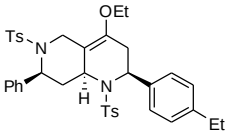

240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


OEt
Ts
N
Ph
H
N
Ts
Ph

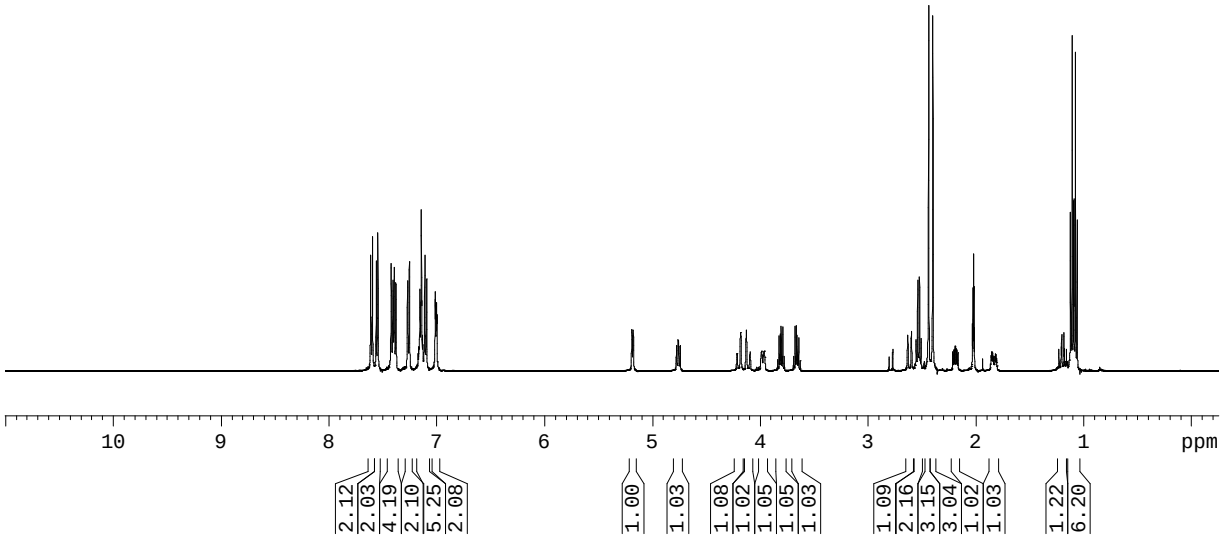
15a

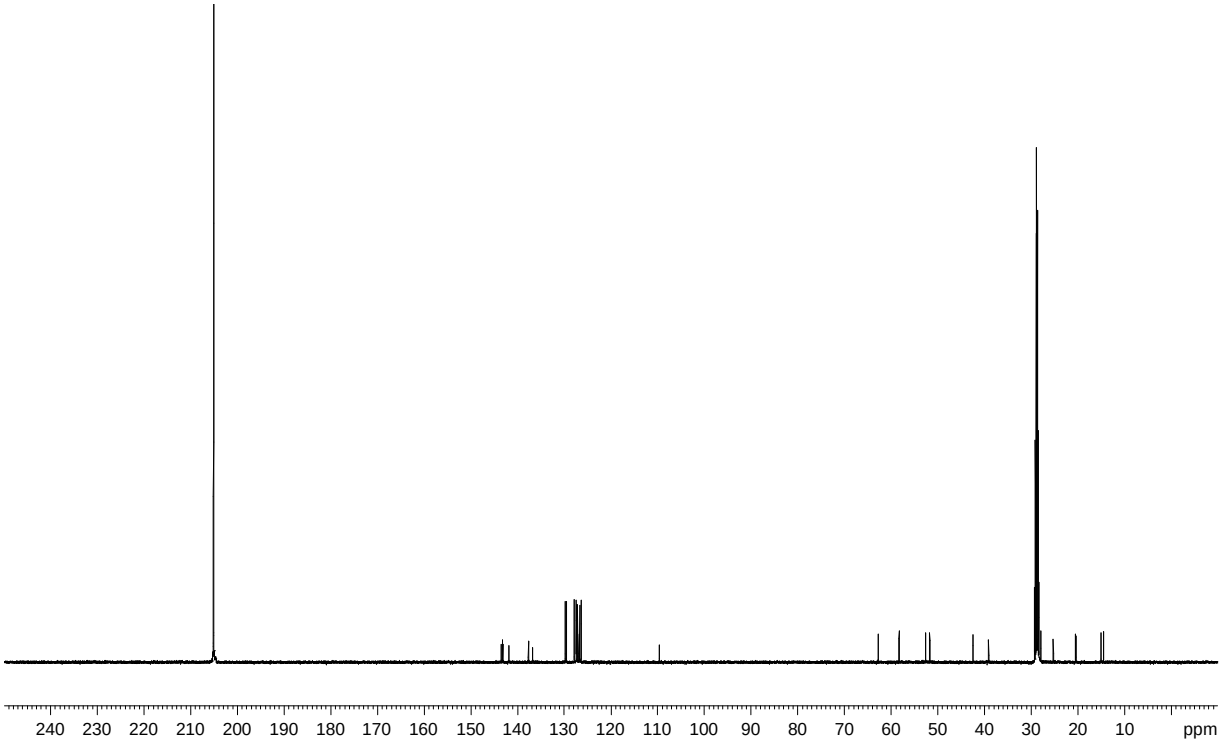

10
9
8
7
6
5
4
3
2
1
ppm
2.00
2.07
6.18
2.12
4.06
2.08
1.00
1.00
1.01
1.02
1.03
1.01
1.02
1.00
3.10
3.05
1.01
1.00
1.12
3.01

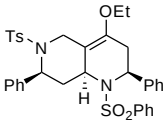

240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


OEt
Ts
N
Ph
H
N
Ts
Et

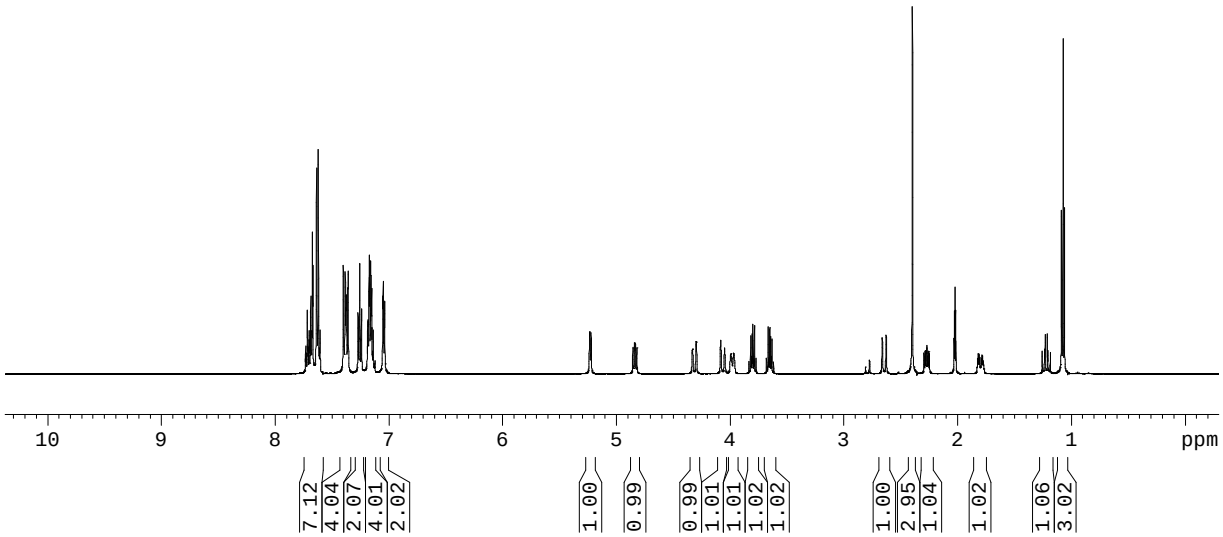
15b

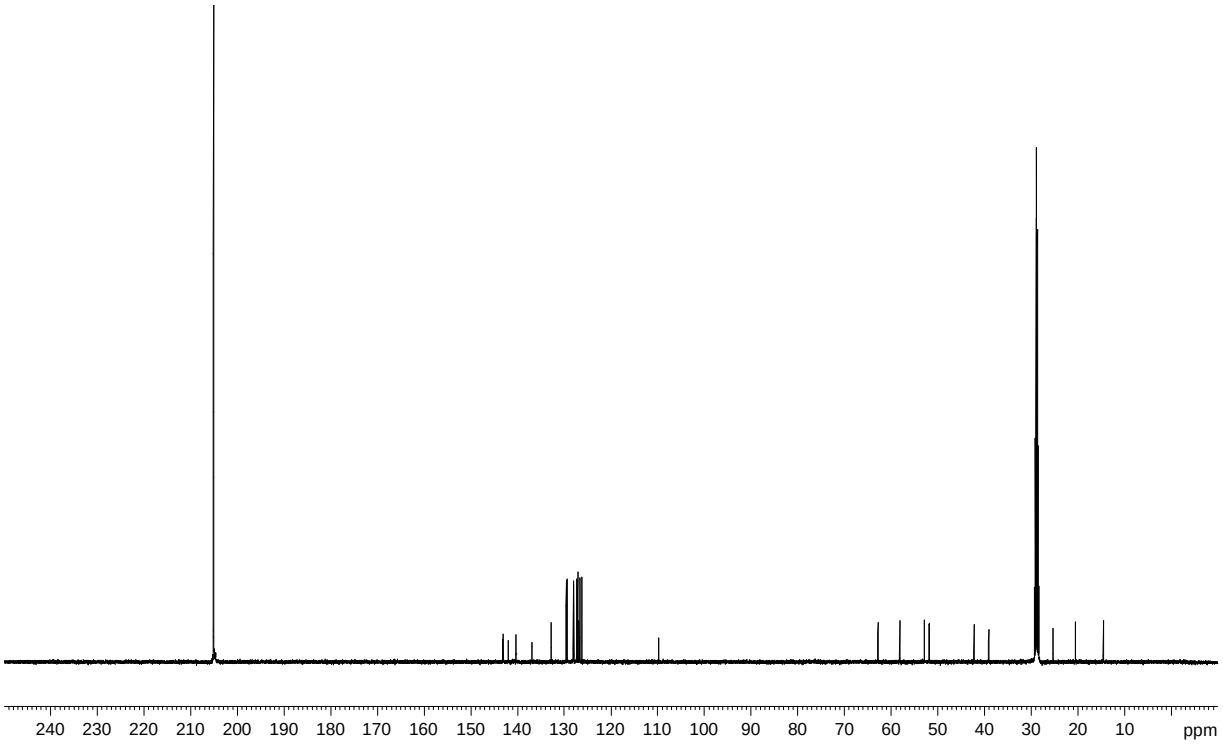

10 9 8 7 6 5 4 3 2 1 ppm
2.12 2.03 4.19 2.10 5.25 2.08 1.00 1.03 1.08 1.02 1.05 1.05 1.03 1.09 2.16 3.15 3.04 1.02 1.03 1.22 6.20

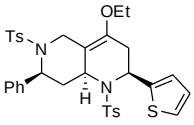

240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


OEt
Ts
N
Ph
H
N
Ph
SO2Ph

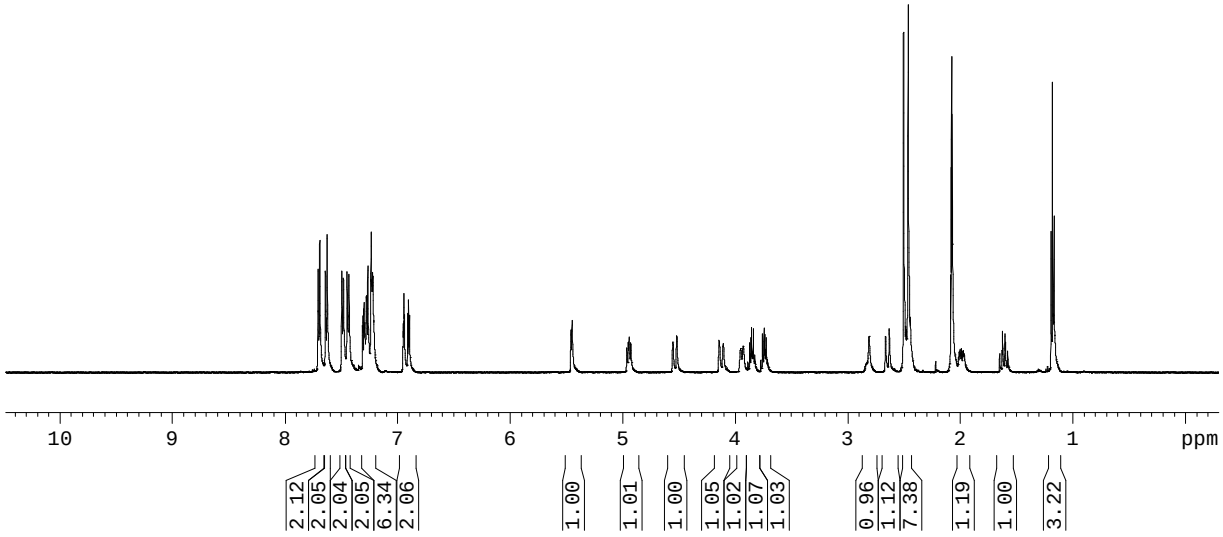
15c

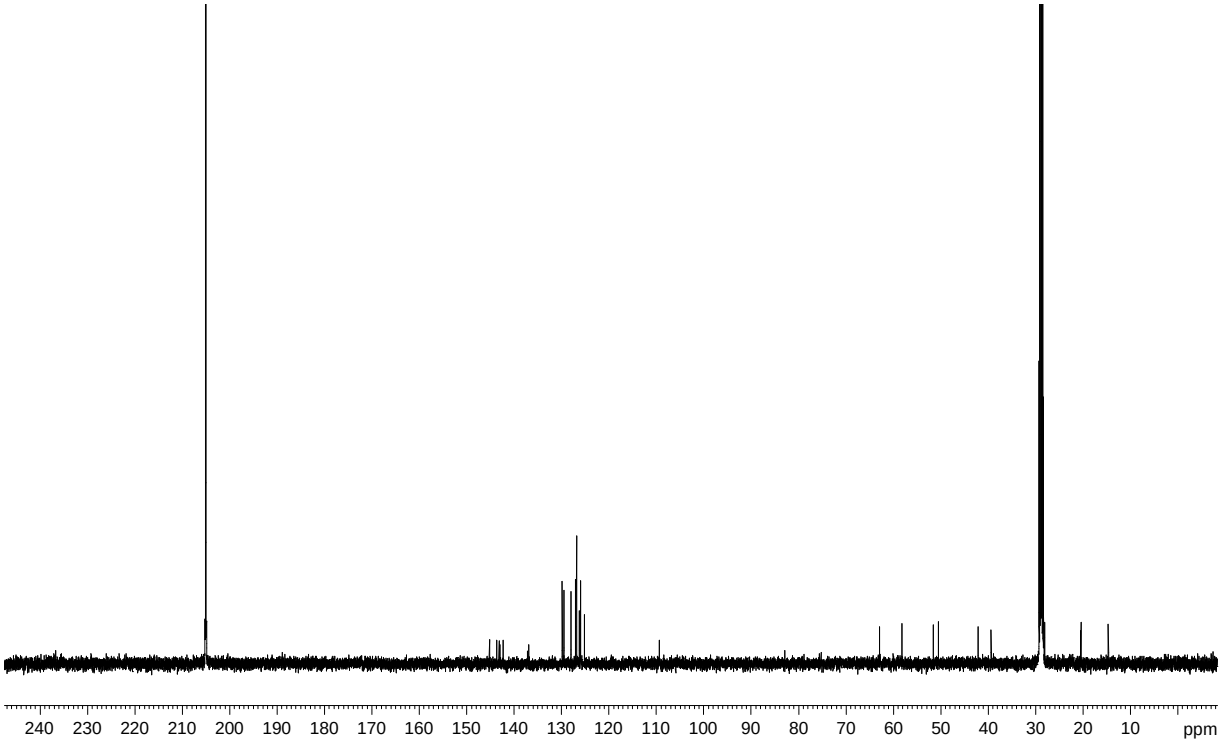

10
9
8
7
6
5
4
3
2
1
ppm
7.12
4.04
2.07
4.01
2.02
1.00
0.99
0.99
1.01
1.01
1.02
1.02
1.00
2.95
1.04
1.02
1.06
3.02

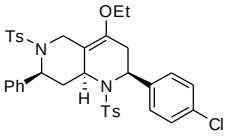

240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


OEt
Ts
N
Ph
H
N
Ts
S

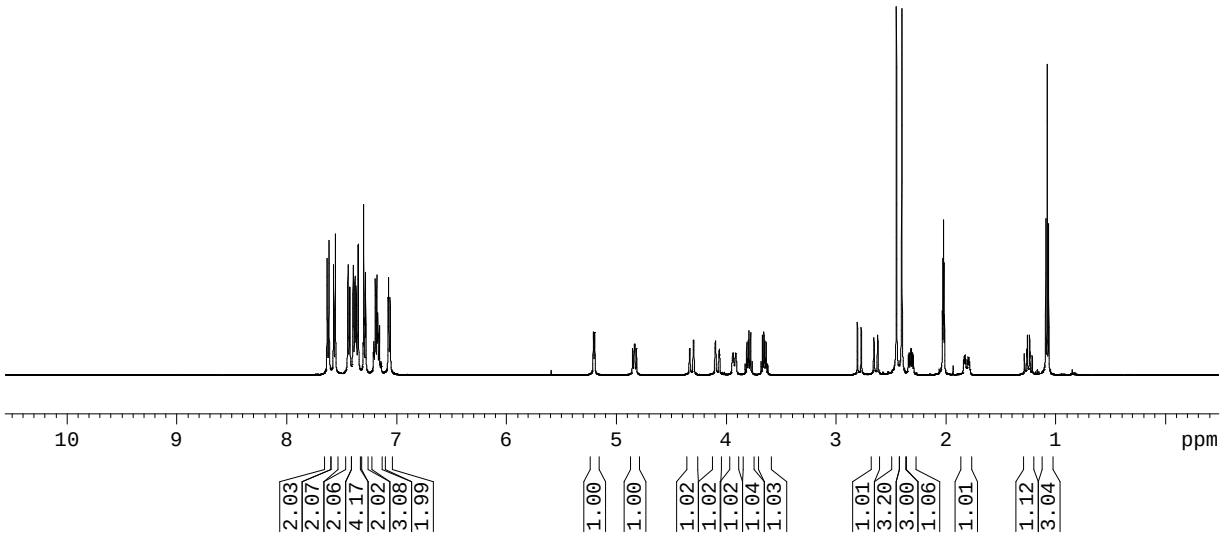
15d

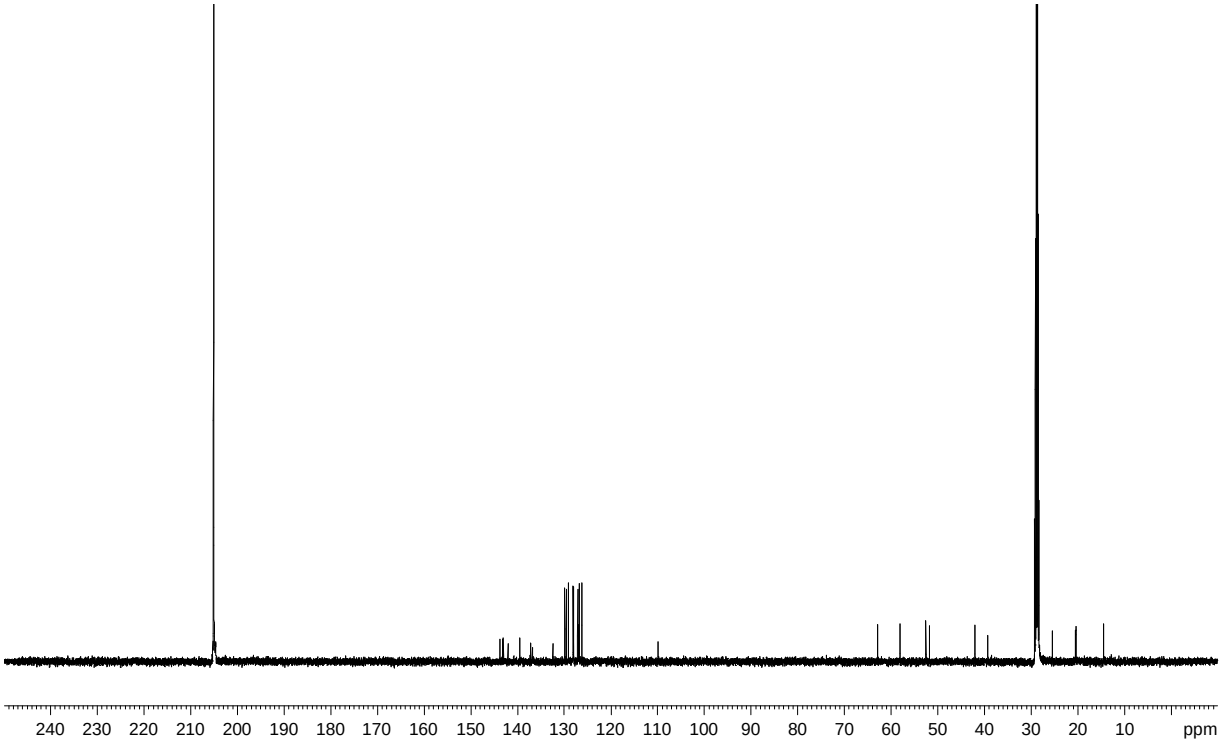

10
9
8
7
6
5
4
3
2
1
ppm
2.12
2.05
2.04
2.05
6.34
2.06
1.00
1.01
1.00
1.05
1.02
1.07
1.03
0.96
1.12
7.38
1.19
1.00
3.22

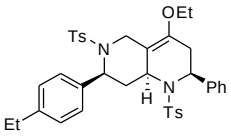

240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


OEt
Ts
N
Ph
H
N
Ts
Cl

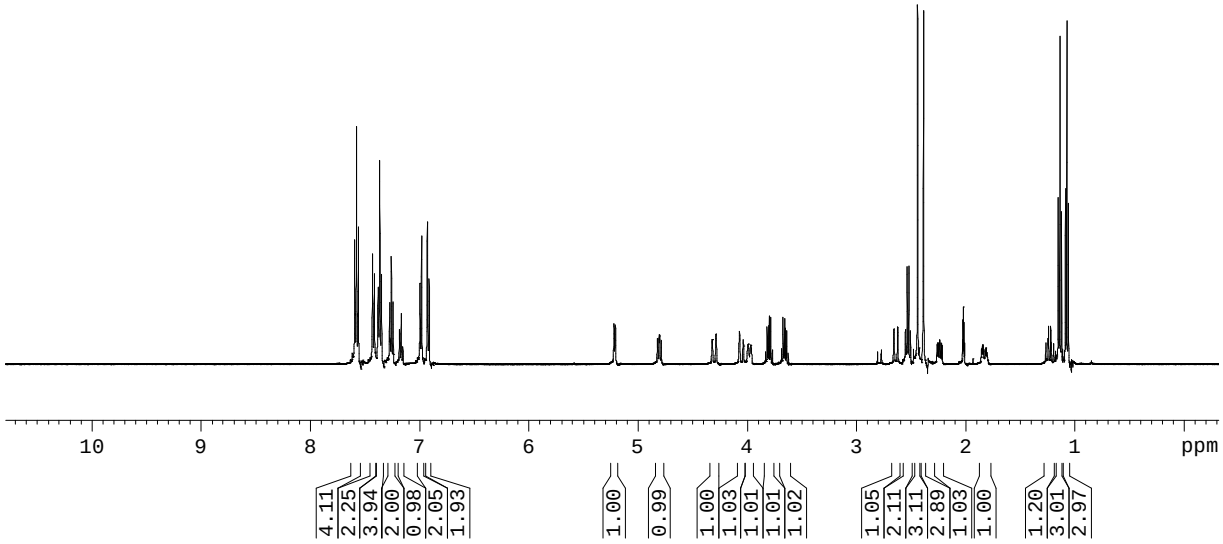
15e

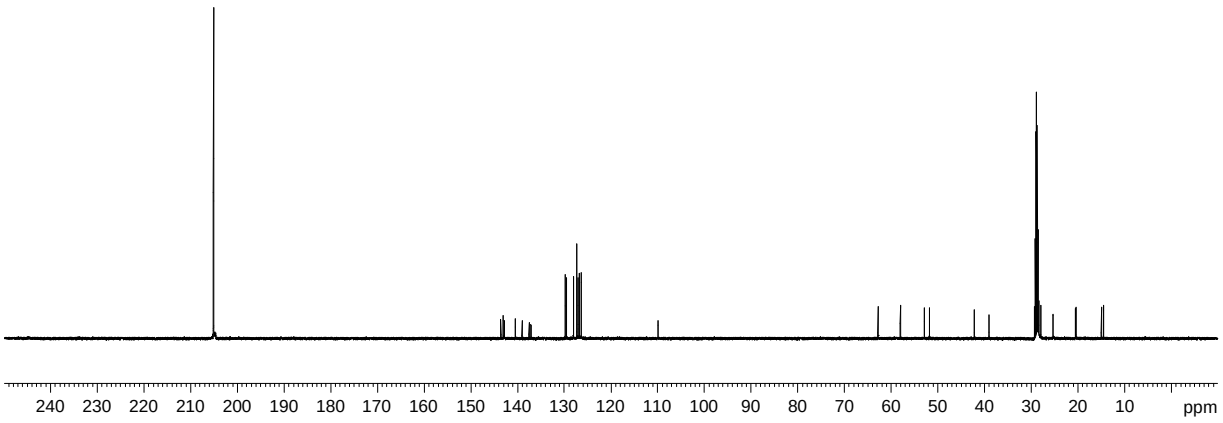

10
9
8
7
6
5
4
3
2
1
ppm
2.03
2.07
2.06
4.17
2.02
3.08
1.99
1.00
1.00
1.02
1.02
1.02
1.04
1.03
1.01
3.20
3.00
1.06
1.01
1.12
3.04

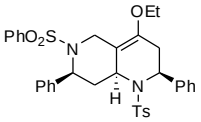

240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


OEt
Ts
N
H
N
Ts
Ph
Et

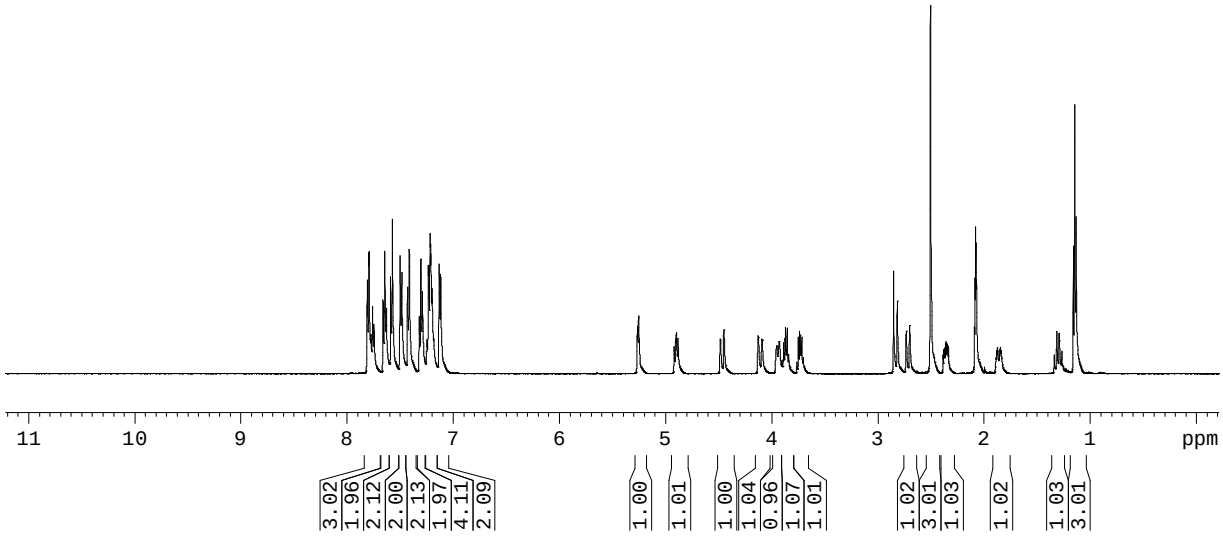
15f

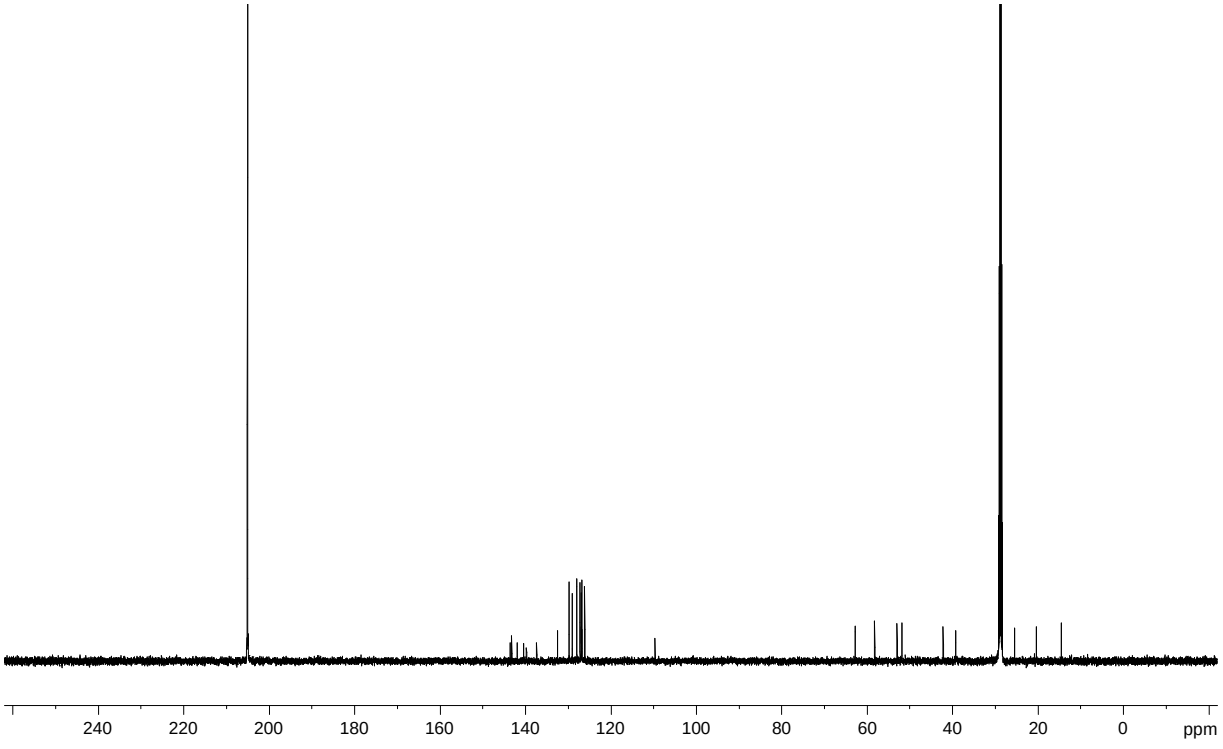

10
9
8
7
6
5
4
3
2
1
ppm
4.11
2.25
3.94
2.00
0.98
2.05
1.93
1.00
0.99
1.00
1.03
1.01
1.01
1.02
1.05
2.11
3.11
2.89
1.03
1.00
1.20
3.01
2.97

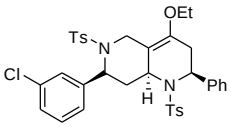

240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


OEt
PhO2S
N
Ph
H
N
Ts
Ph

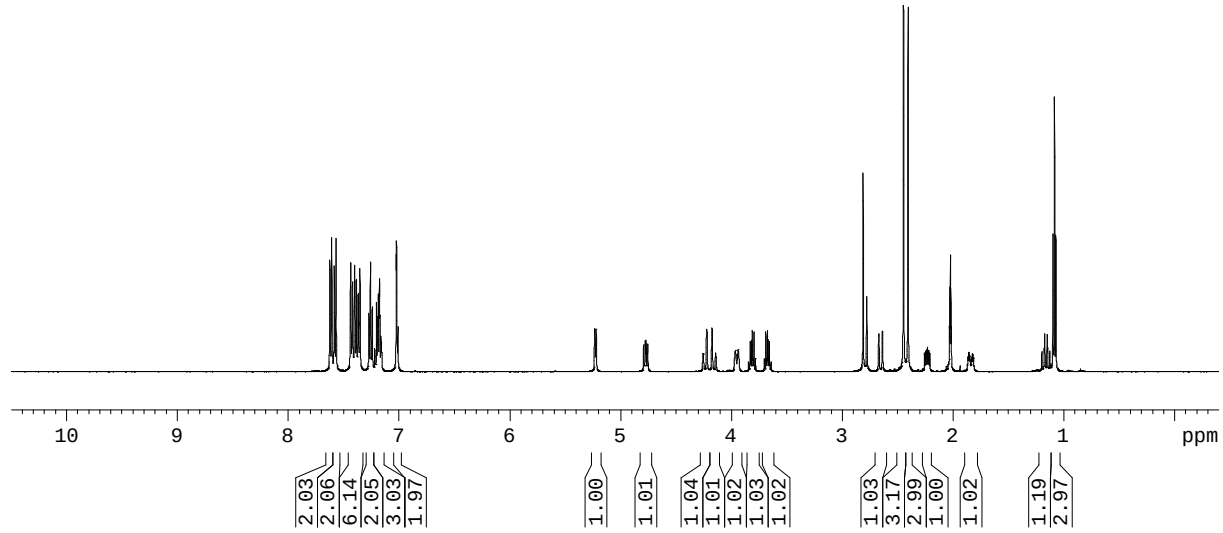
15g

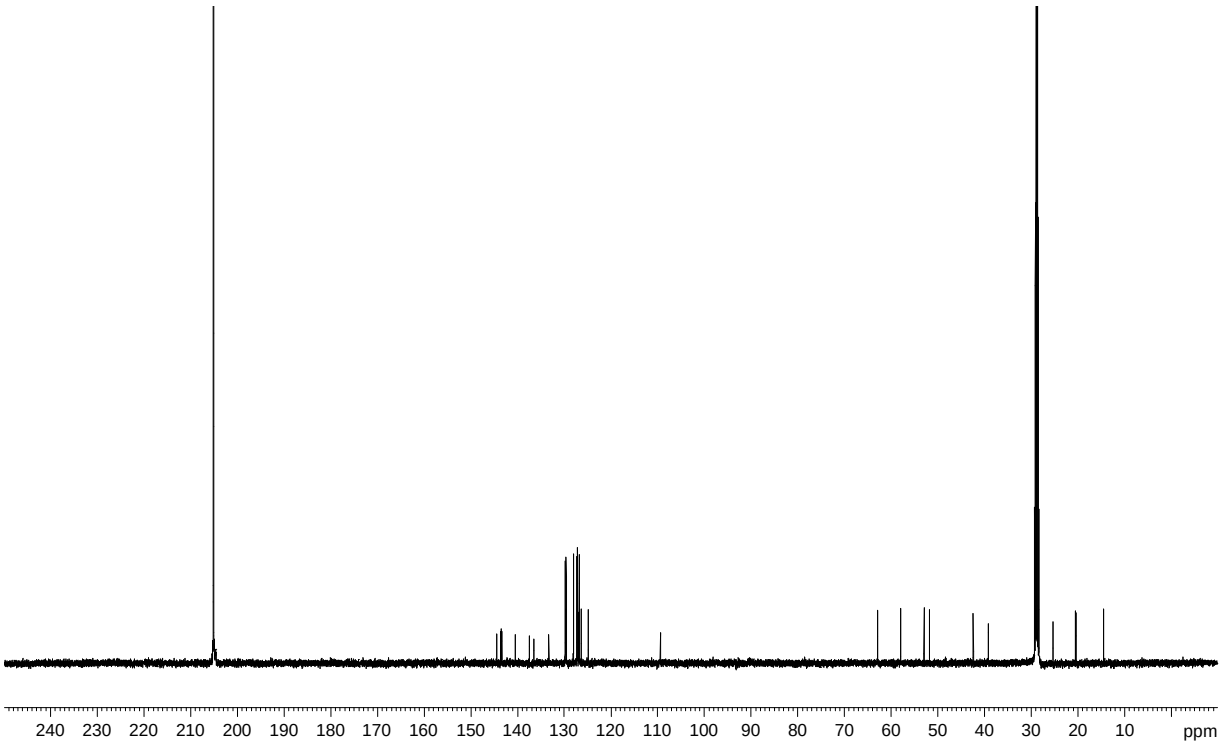

11
10
9
8
7
6
5
4
3
2
1
ppm
3.02
1.96
2.12
2.00
2.13
1.97
4.11
2.09
1.00
1.01
1.00
1.04
0.96
1.07
1.01
1.02
3.01
1.03
1.02
1.03
3.01

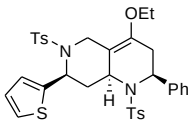

240
220
200
180
160
140
120
100
80
60
40
20
0
ppm


OEt
Ts
N
Cl
Ph
H
N
Ts

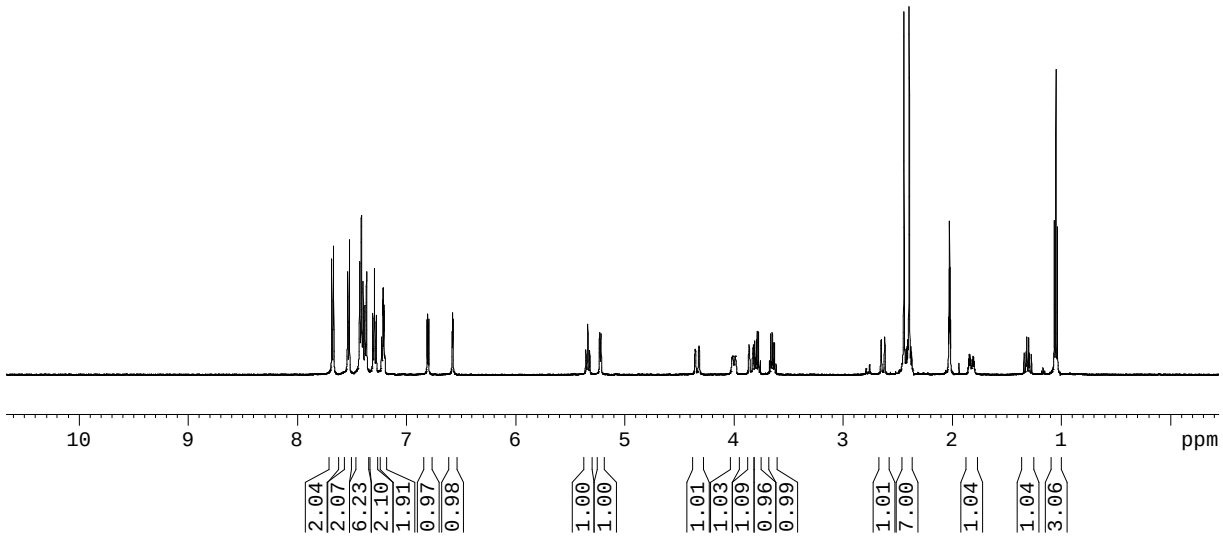
15h

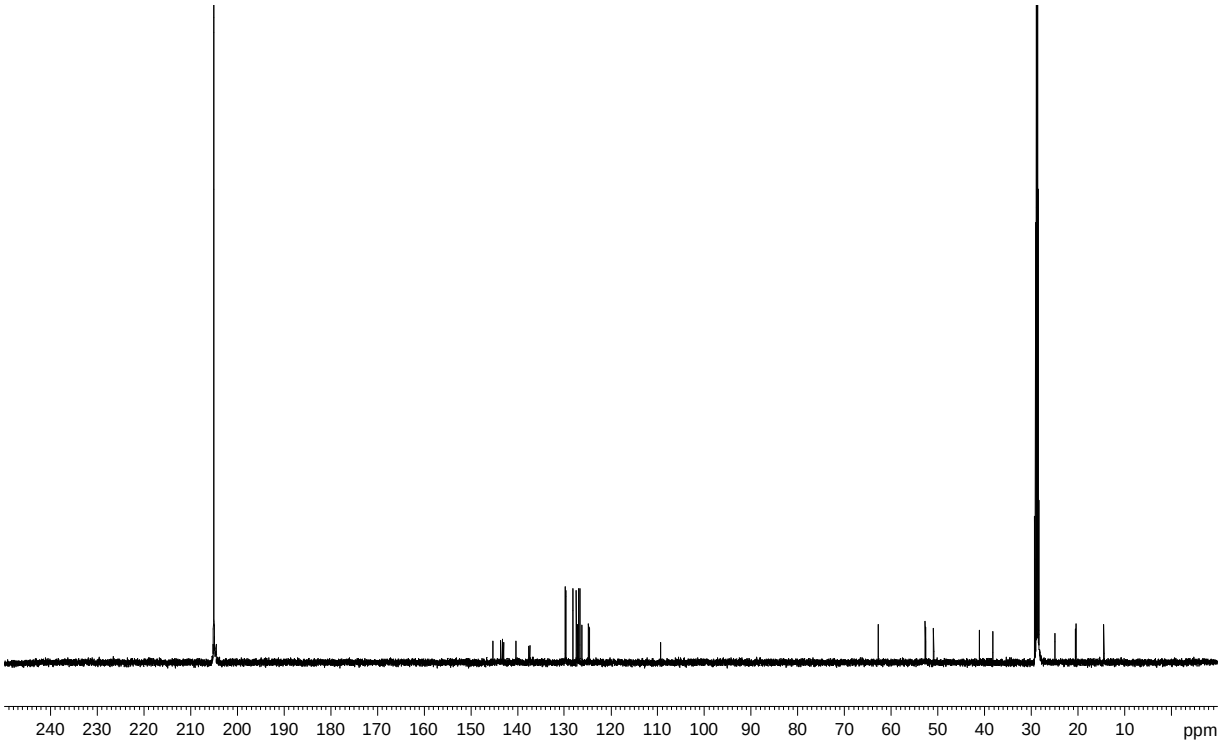

10
9
8
7
6
5
4
3
2
1
ppm
2.03
2.06
6.14
2.05
3.03
1.97
1.00
1.01
1.04
1.01
1.02
1.03
1.02
1.03
3.17
2.99
1.00
1.02
1.19
2.97

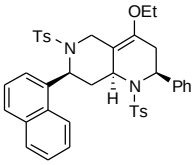

240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


OEt
Ts
N
H
N
Ts
Ph
S

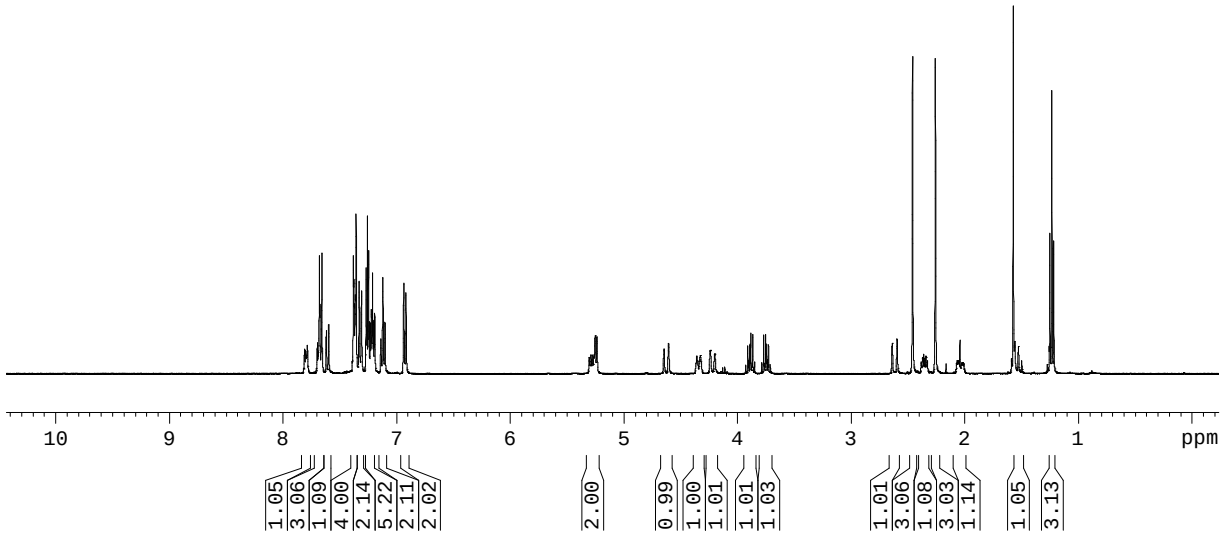
15i

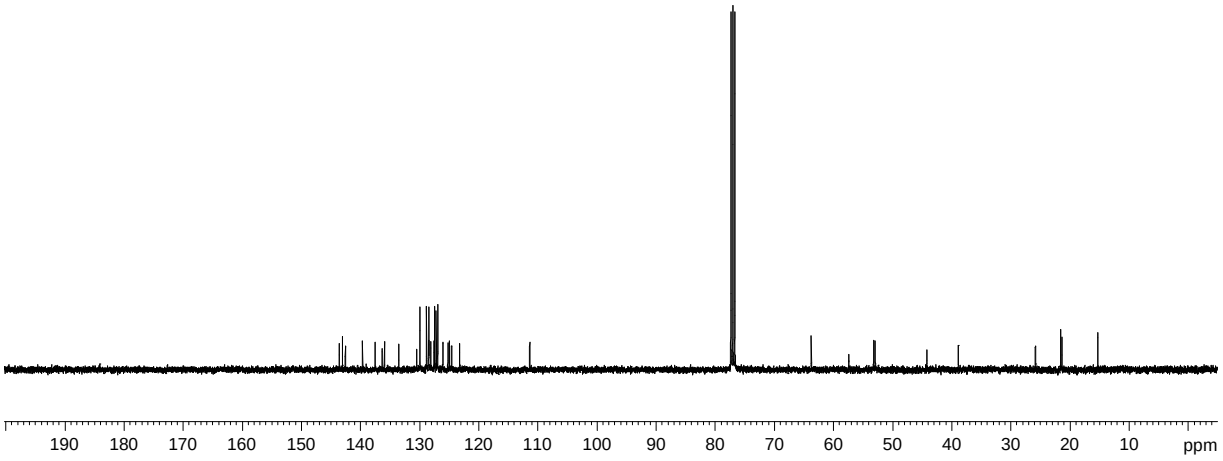

10 9 8 7 6 5 4 3 2 1 ppm
2.04 2.07 6.23 2.10 1.91 0.97 0.98
1.00 1.00
1.01 1.03 1.09 0.96 0.99
1.01 7.00
1.04
1.04 3.06

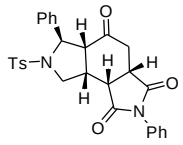

240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


OEt
Ts
N
H
N
Ts
Ph

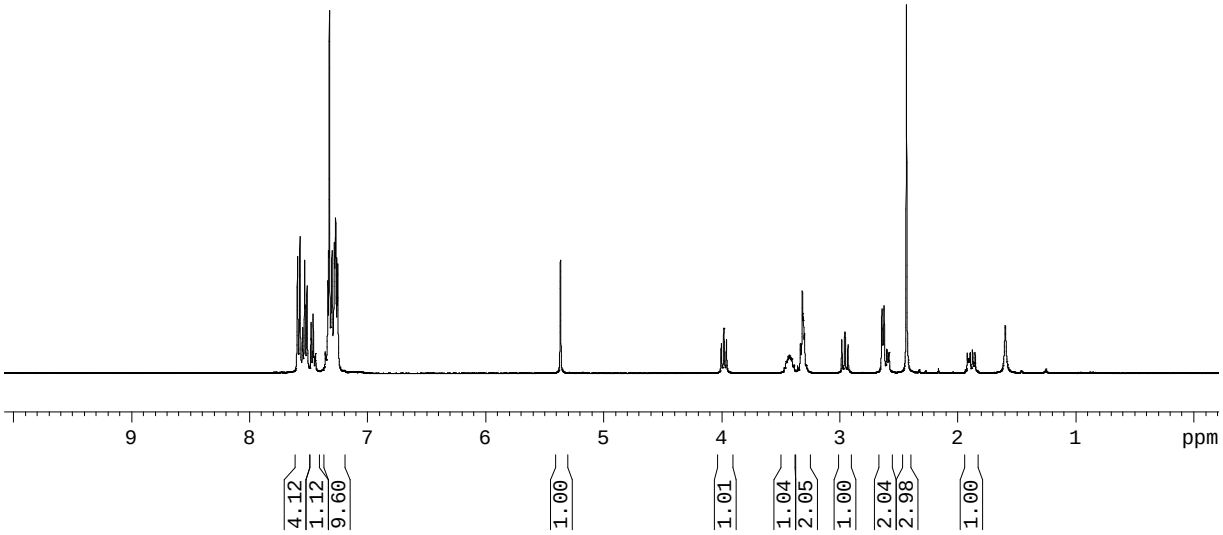
15j

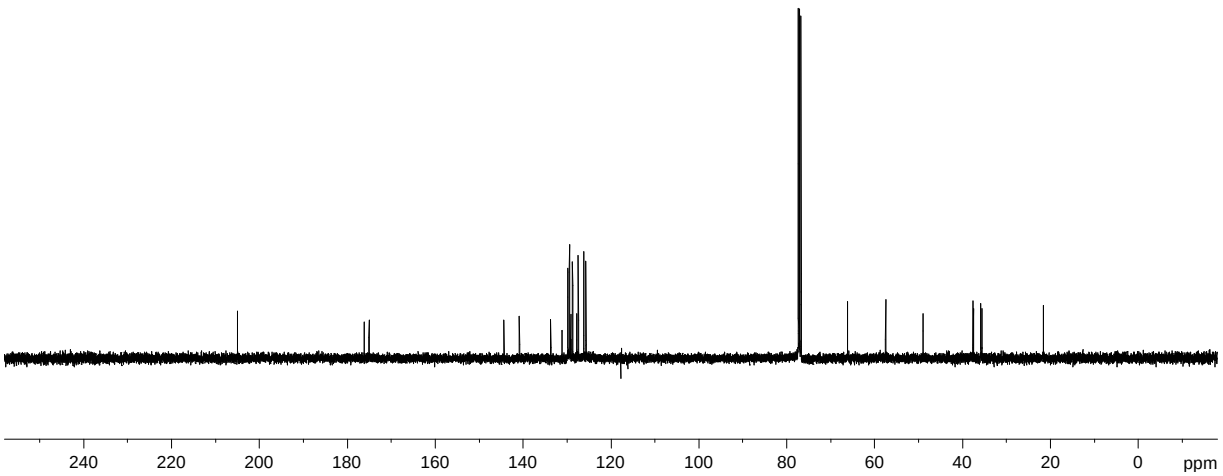

10
9
8
7
6
5
4
3
2
1
ppm
1.05
3.06
1.09
4.00
2.14
5.22
2.11
2.02
2.00
0.99
1.00
1.01
1.01
1.03
1.01
3.06
1.08
3.03
1.14
1.05
3.13

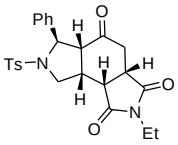

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ph
H
O
Ts–N
H
H
H
O
N
Ph
O

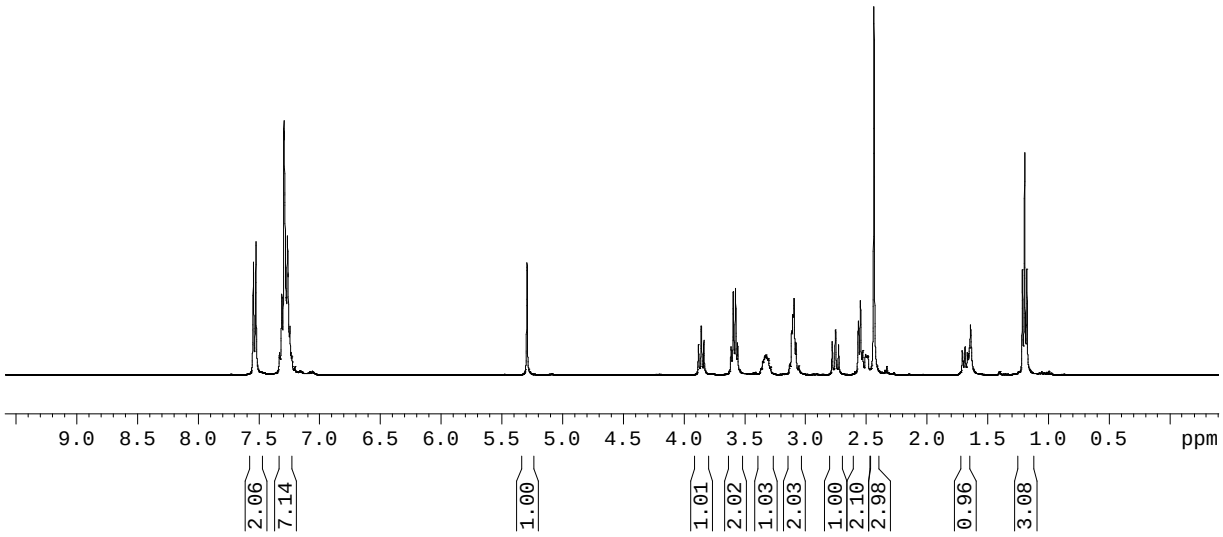
16a

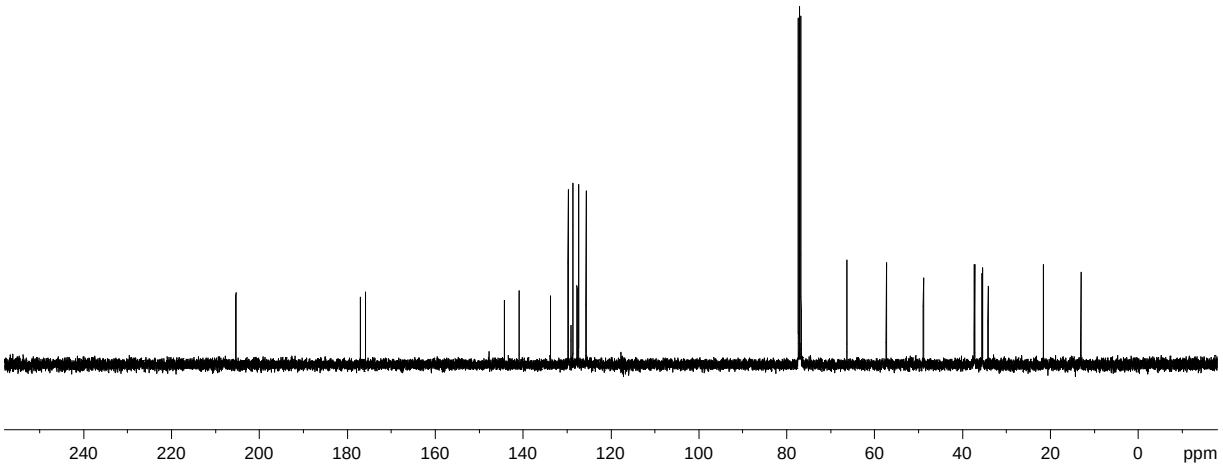

9
8
7
6
5
4
3
2
1
ppm
4.12
1.12
9.60
1.00
1.01
1.04
2.05
1.00
2.04
2.98
1.00

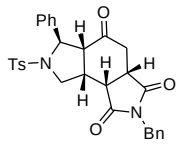

240
220
200
180
160
140
120
100
80
60
40
20
0
ppm


Ph
H
O
Ts–N
H
H
H
O
N
Et
O

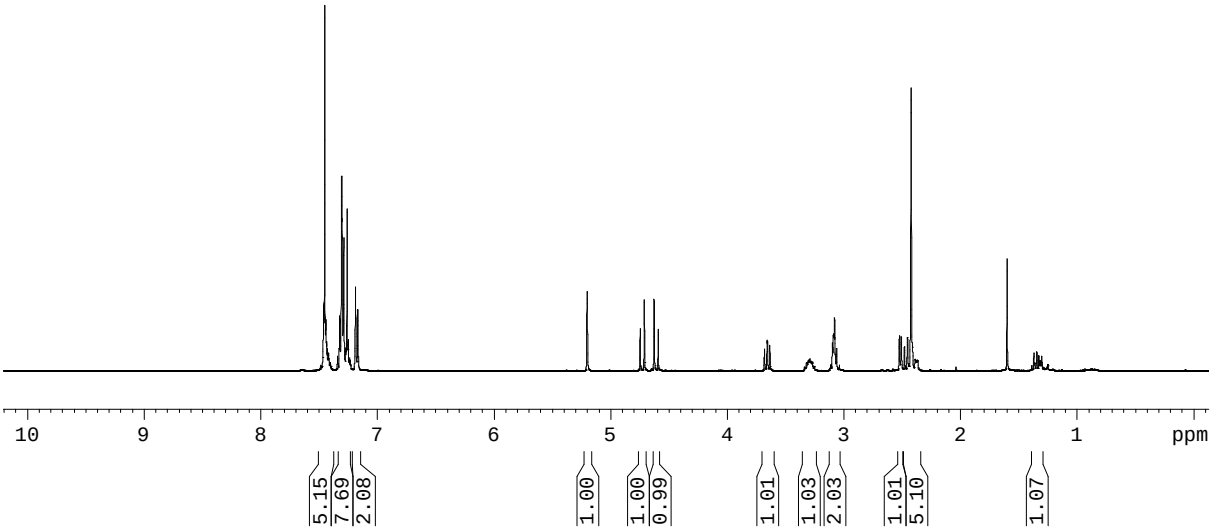
16b


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
2.06
7.14
1.00
1.01
2.02
1.03
2.03
1.00
2.10
2.98
0.96
3.08


240 220 200 180 160 140 120 100 80 60 40 20 0 ppm


Ph
H
O
Ts–N
H
H
H
O
N
Bn
O

16c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9
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2
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1.00
1.00
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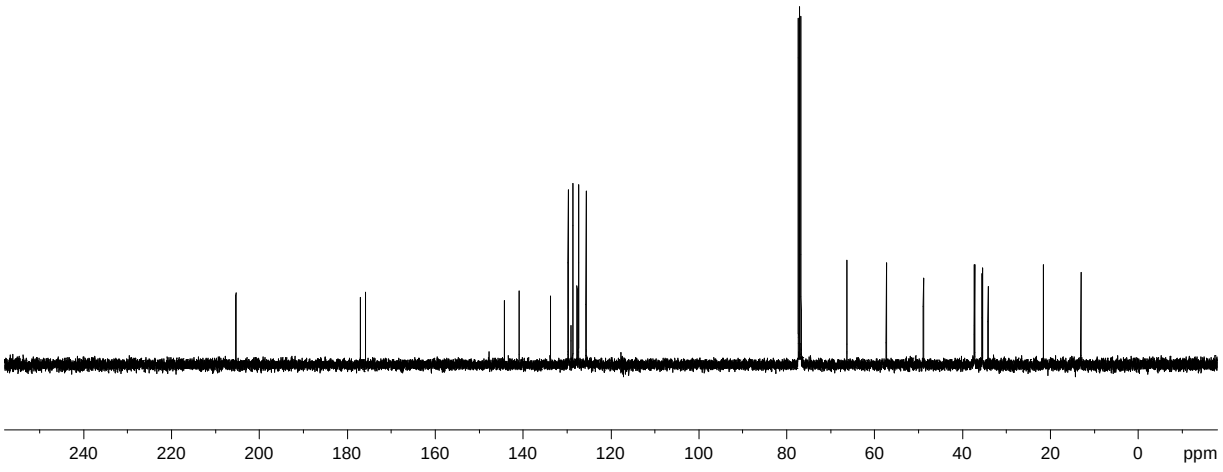
1.01
1.03
2.03
1.01
5.10
1.07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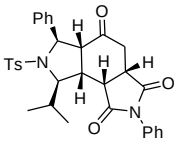
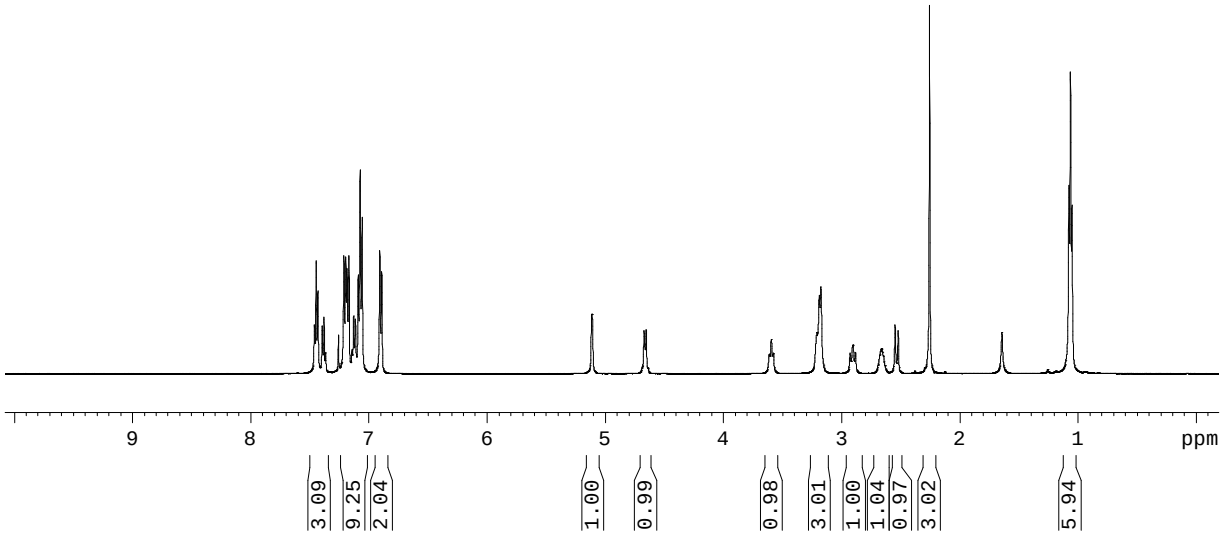
ppm


Ph
H
O
Ts–N
H
H
H
O
O
N
Ph

16d


9
8
7
6
5
4
3
2
1
ppm
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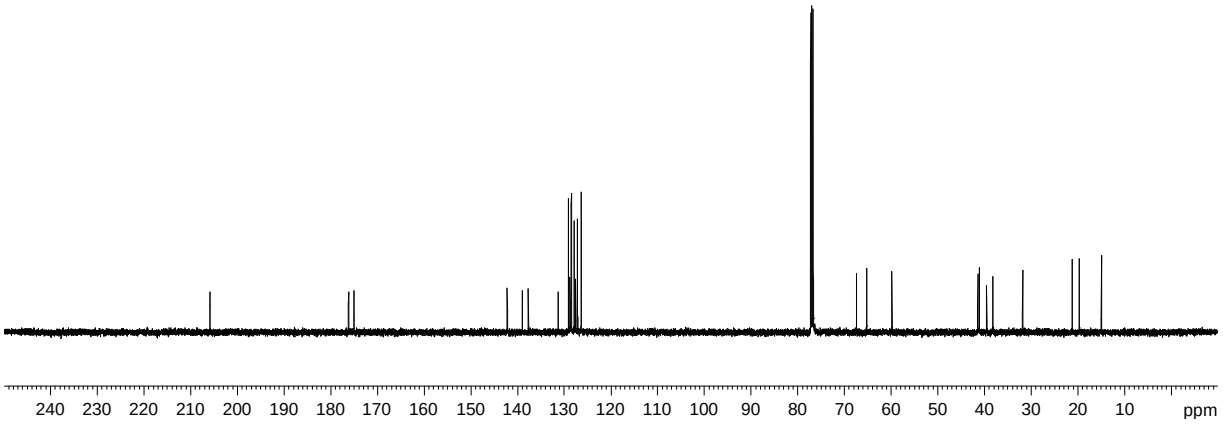
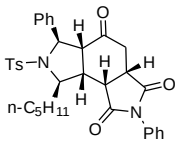
2.04
1.00
0.99
0.98
3.01
1.00
1.04
0.97
3.02
5.94


240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm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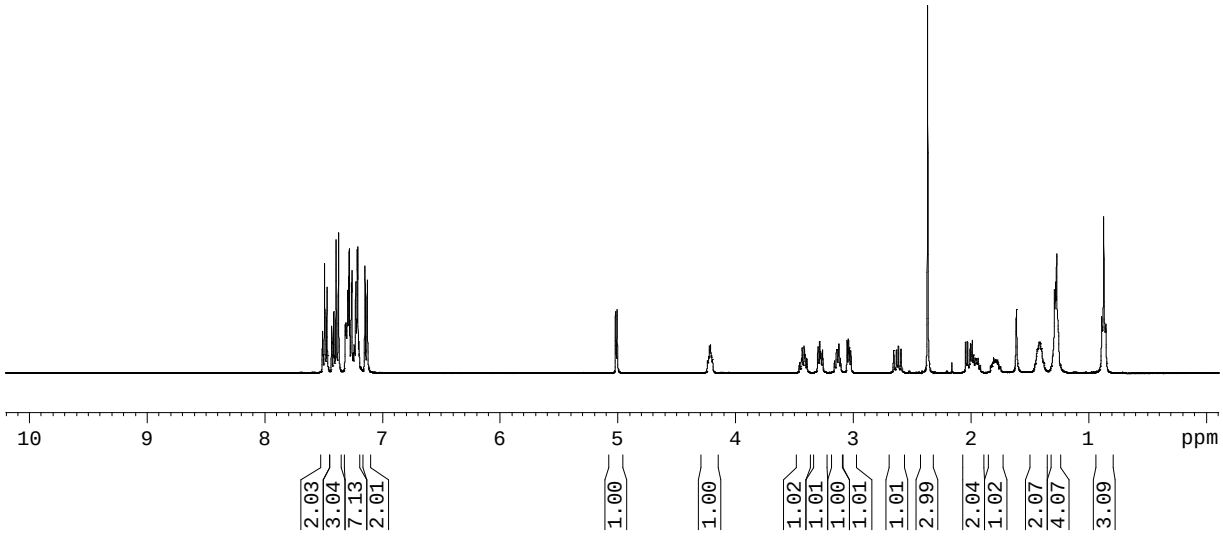
O
Ts–N
H
H
O
n-C5H11
H
O
N
Ph

16e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6
5
4
3
2
1
ppm
2.03
3.04
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2.01
1.00
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1.00
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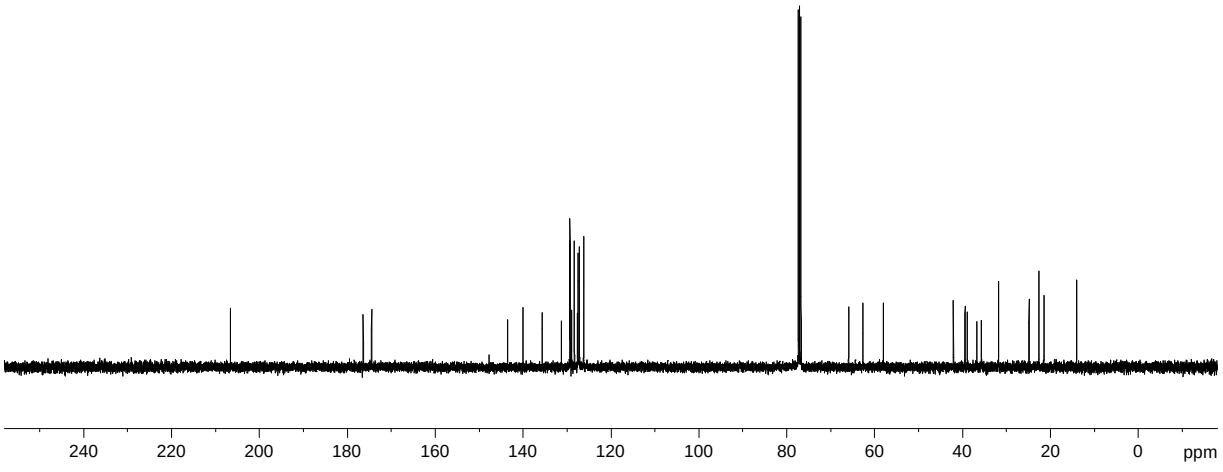
1.01
2.99
2.04
1.02
2.07
4.07
3.09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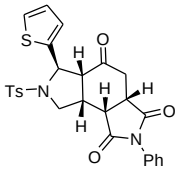
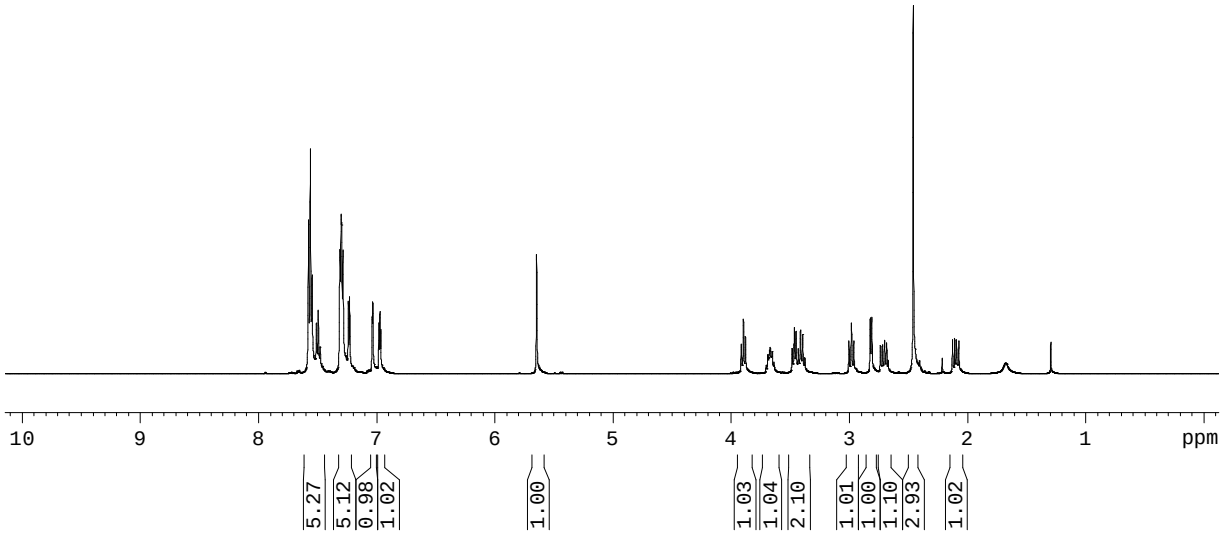
ppm


S
H
O
Ts–N
H
H
H
O
O
N
Ph

16f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9
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7
6
5
4
3
2
1
ppm
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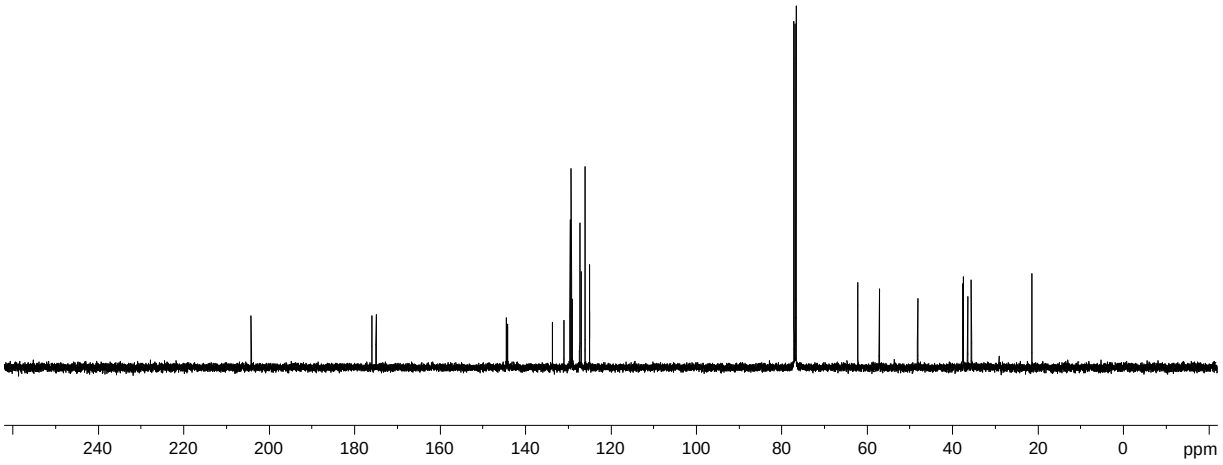
1.02
1.00
1.03
1.04
2.10
1.01
1.00
1.10
2.93
1.02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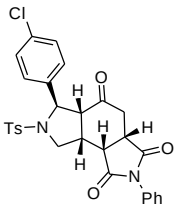
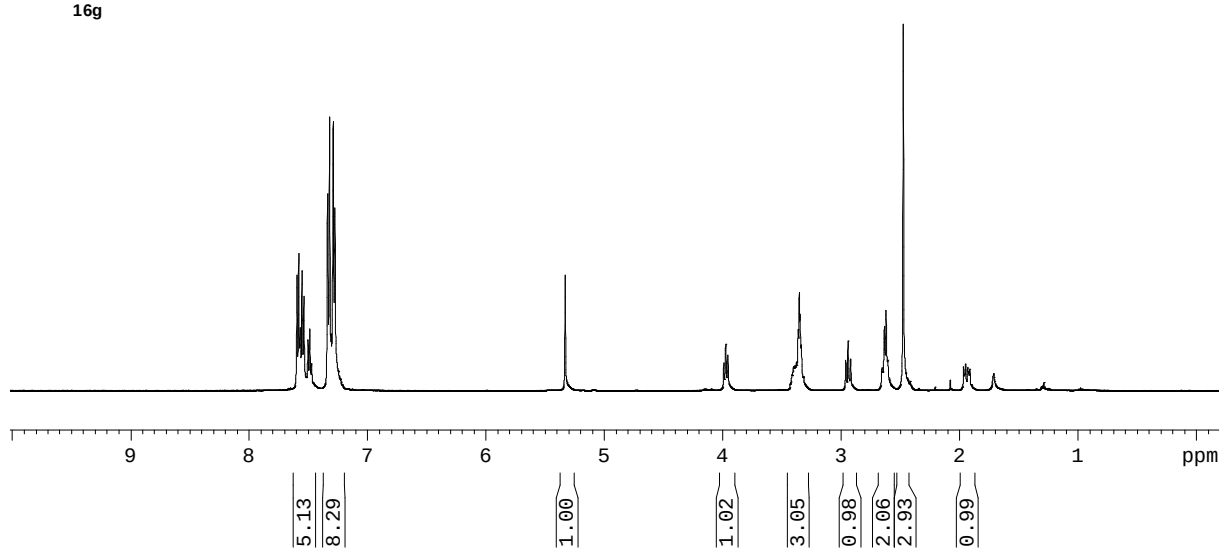
ppm


Cl
O
H
Ts–N
H
H
H
O
N
O
Ph

16g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8
7
6
5
4
3
2
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ppm
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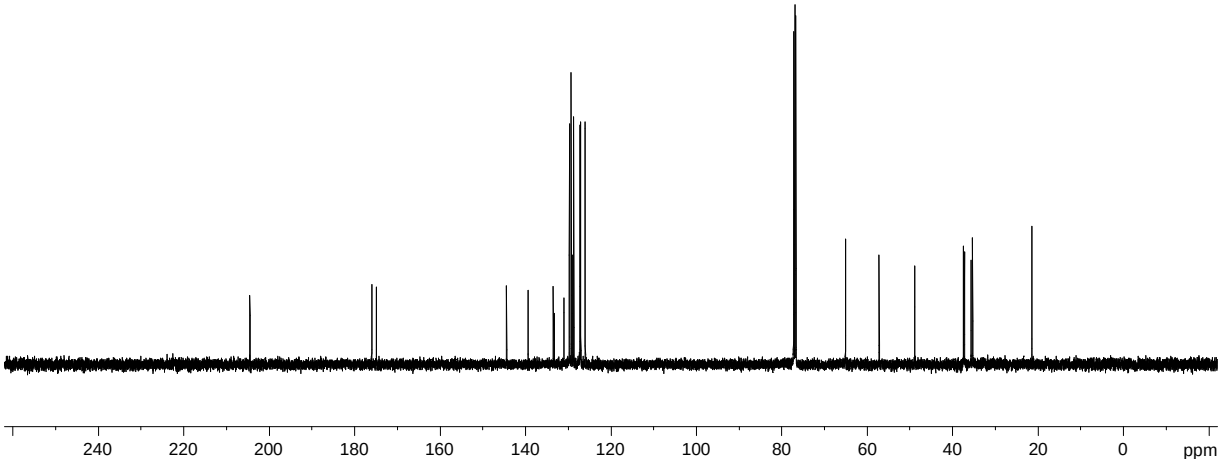
1.00
1.02
3.05
0.98
2.06
2.93
0.99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40
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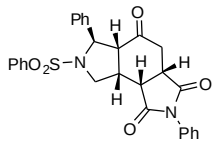
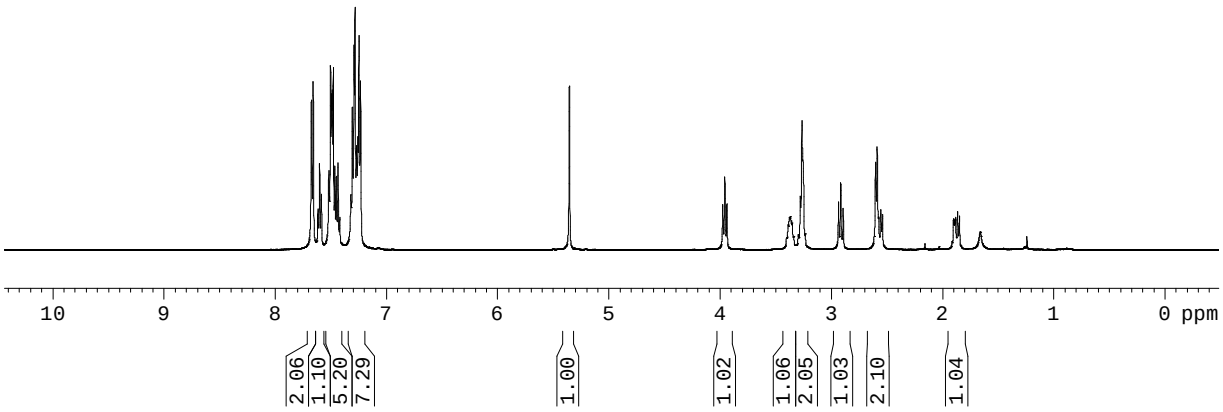
ppm


Ph
H
O
PhO2S–N
H
H
H
O
N
Ph
O

16h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6
5
4
3
2
1
0 ppm
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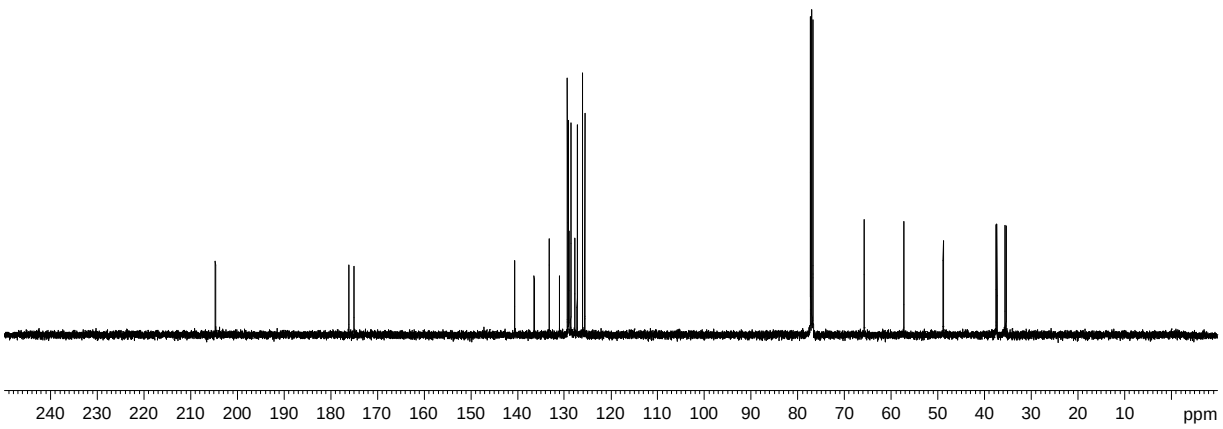
1.10
5.20
7.29
1.00
1.02
1.06
2.05
1.03
2.10
1.04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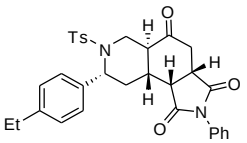
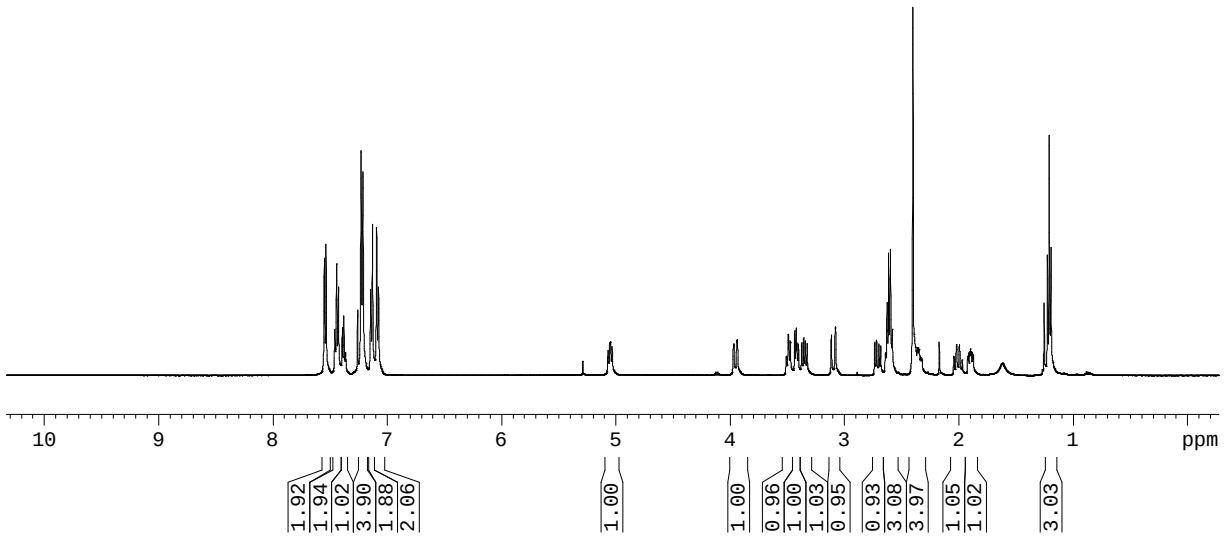
30
20
10
ppm


Ts
N
H
O
H
H
H
O
Et
O
N
Ph

17a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6
5
4
3
2
1
ppm
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1.94
1.02
3.90
1.88
2.06
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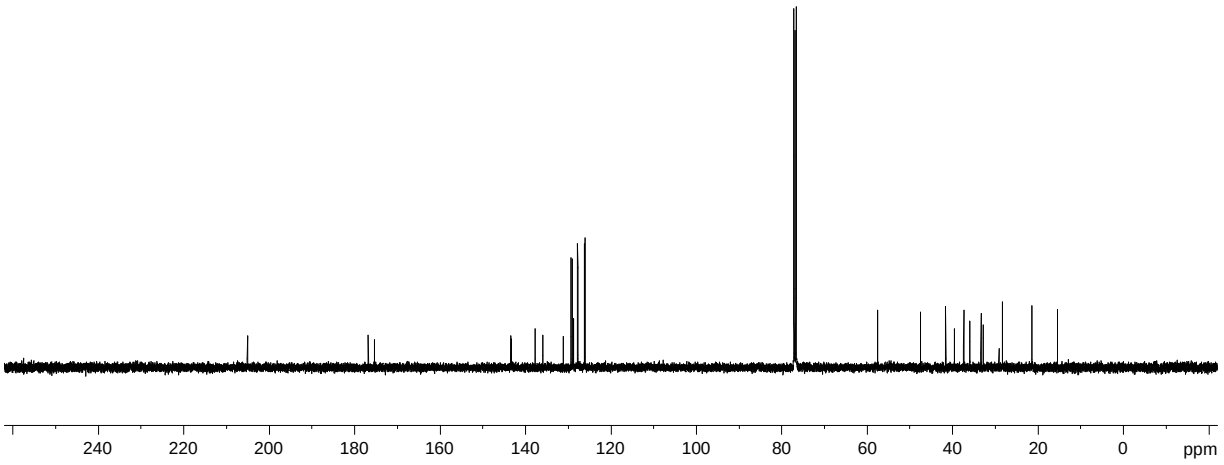
0.96
1.00
1.03
0.95
0.93
3.08
3.97
1.05
1.02
3.03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40
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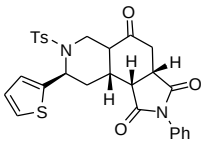
ppm


Ts
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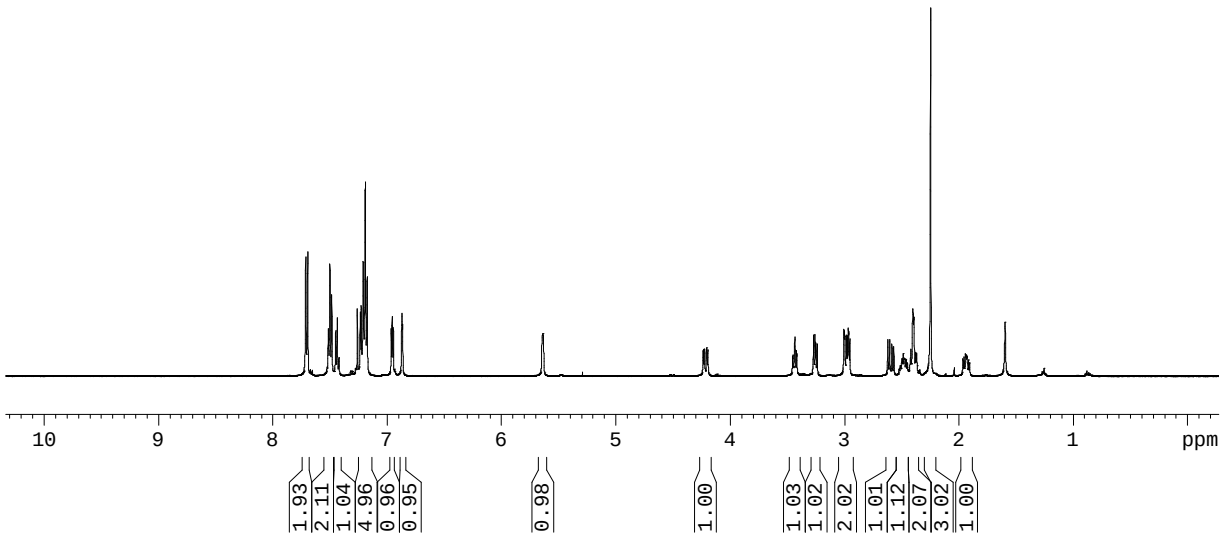
O
H
H
H
O
S
O
N
Ph

17b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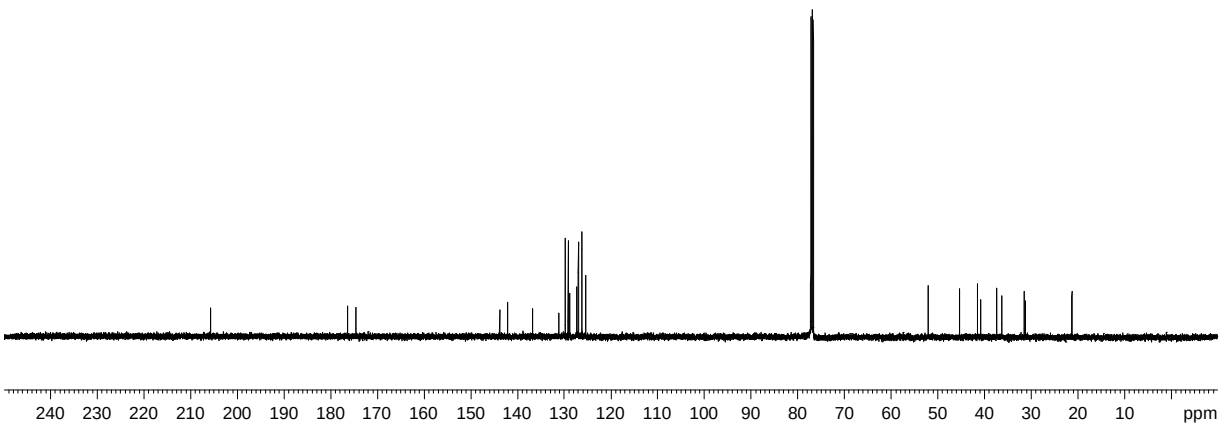
8
7
6
5
4
3
2
1
ppm
1.93
2.11
1.04
4.96
0.96
0.95
0.98
1.00
1.03
1.02
2.02
1.01
1.12
2.07
3.02
1.00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230
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210
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180
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140
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110
100
90
80
70
60
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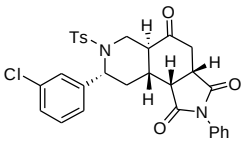
30
20
10
ppm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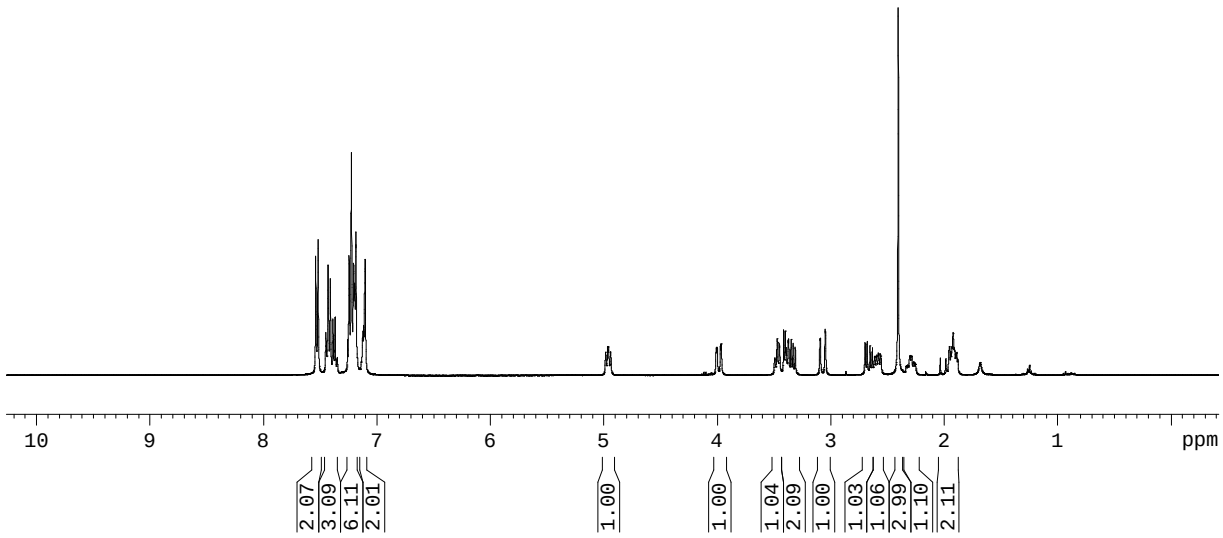
O
Cl
H
H
H
O
O
N
Ph

17ca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7
6
5
4
3
2
1
ppm
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3.09
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1.00
1.00
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2.09
1.00
1.03
1.06
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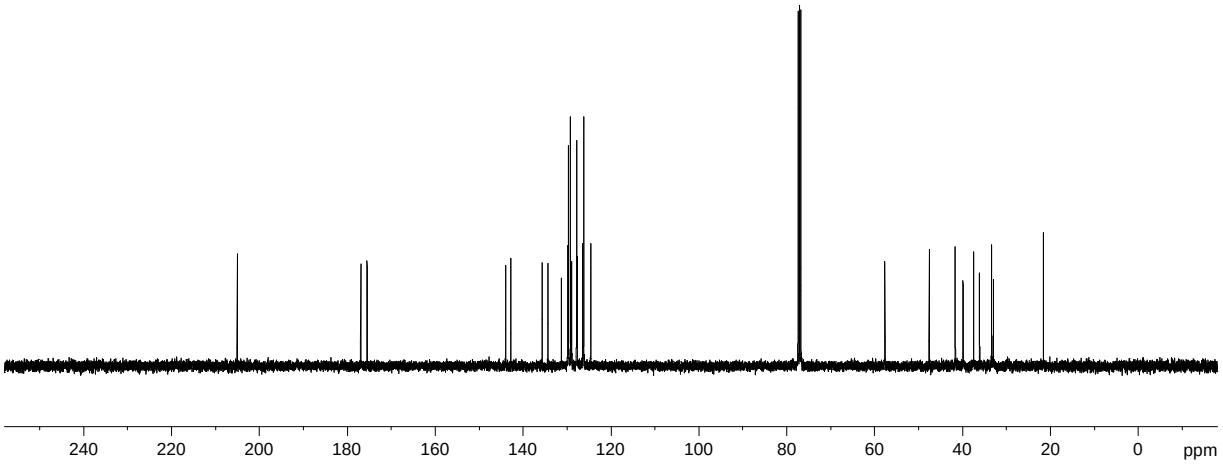
1.10
2.11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60
40
20
0
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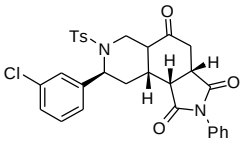
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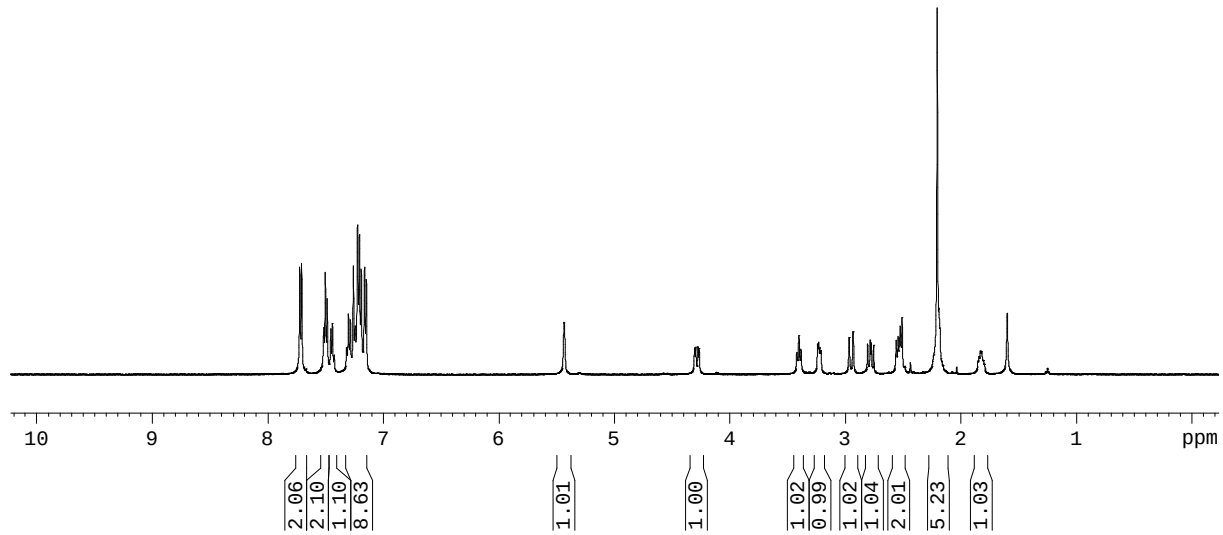
H
H
O
N
Ph
O

17cb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ppm
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1.02
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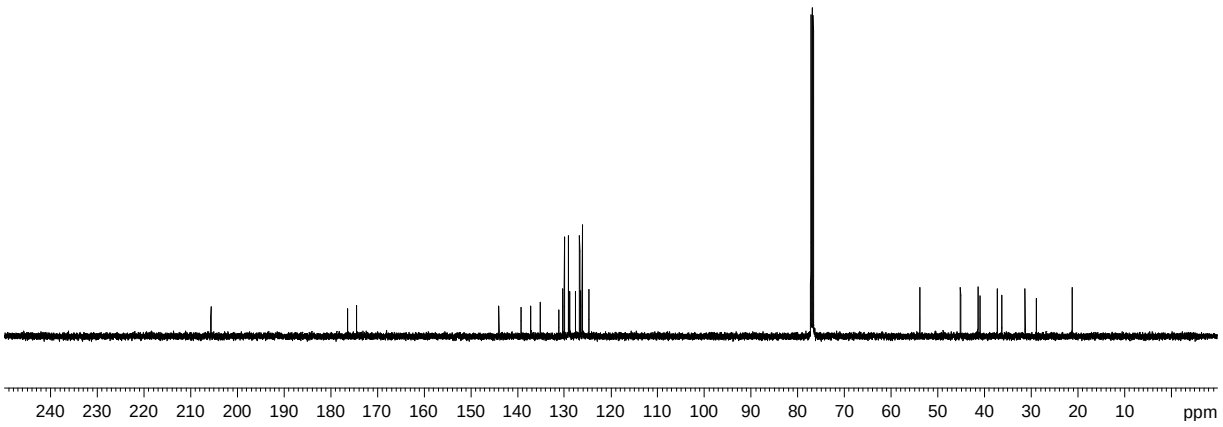
2.01
5.23
1.03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60
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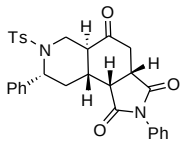
40
30
20
10
ppm


Ts
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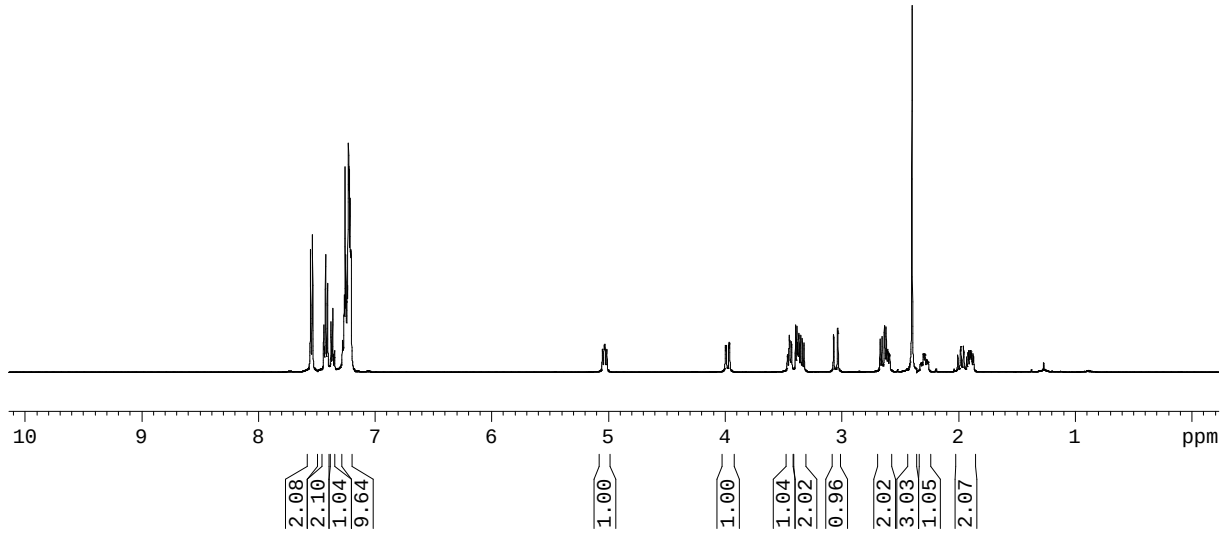
O
H
H
Ph
H
O
O
N
Ph

17d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5
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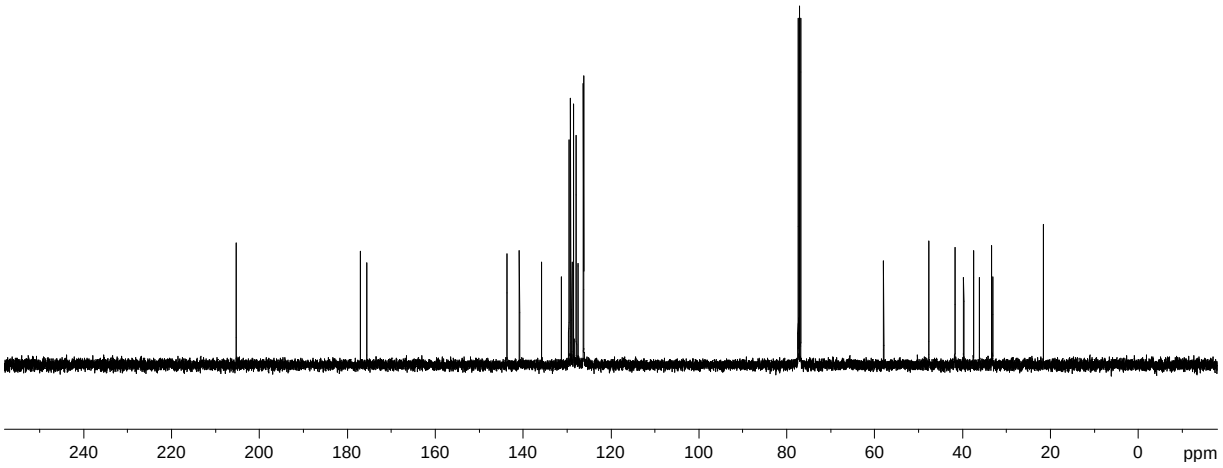
1.00
1.04
2.02
0.96
2.02
3.03
1.05
2.07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160
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120
100
80
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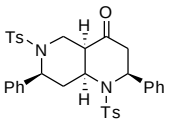
40
20
0
ppm


Ts
N
H
O
Ph
H
N
Ts
Ph

18a

10
9
8
7
6
5
4
3
2
1
ppm
1.99
2.07
4.02
2.20
2.88
2.98
1.98
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1.00
1.01
0.99
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0.99
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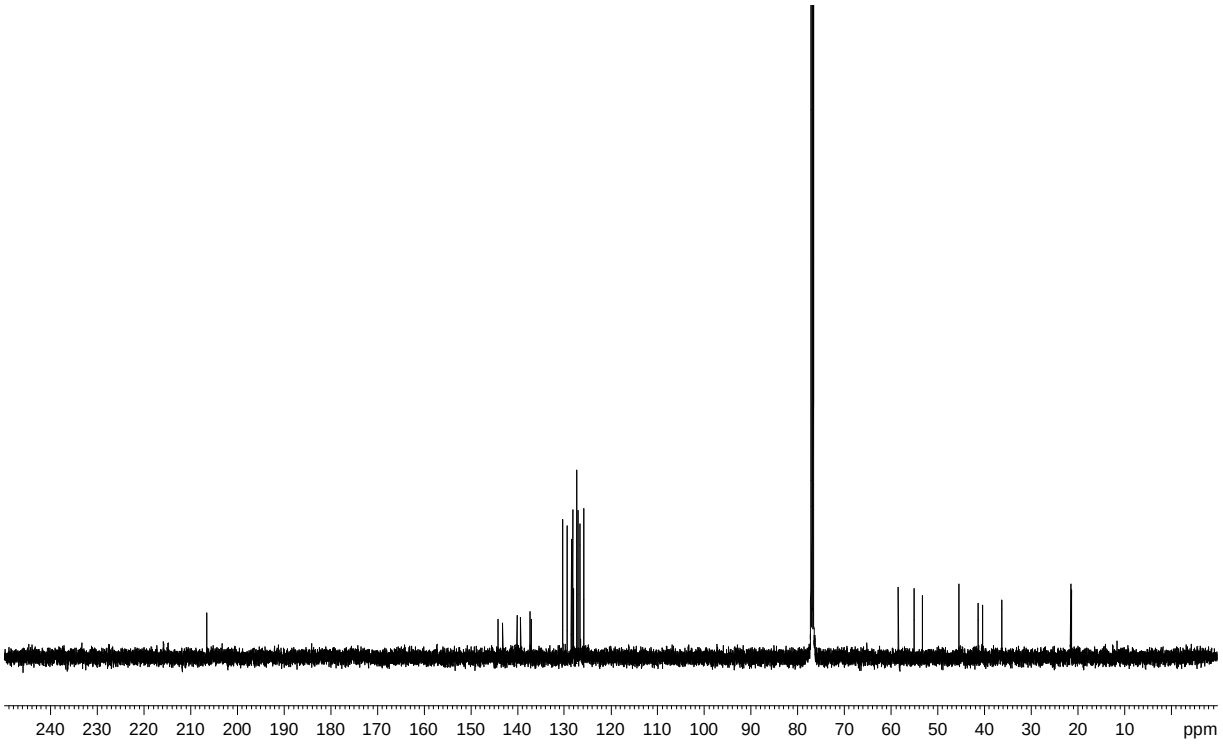
2.97
2.96
1.03
1.01
1.01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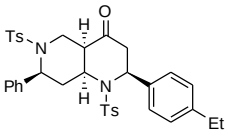
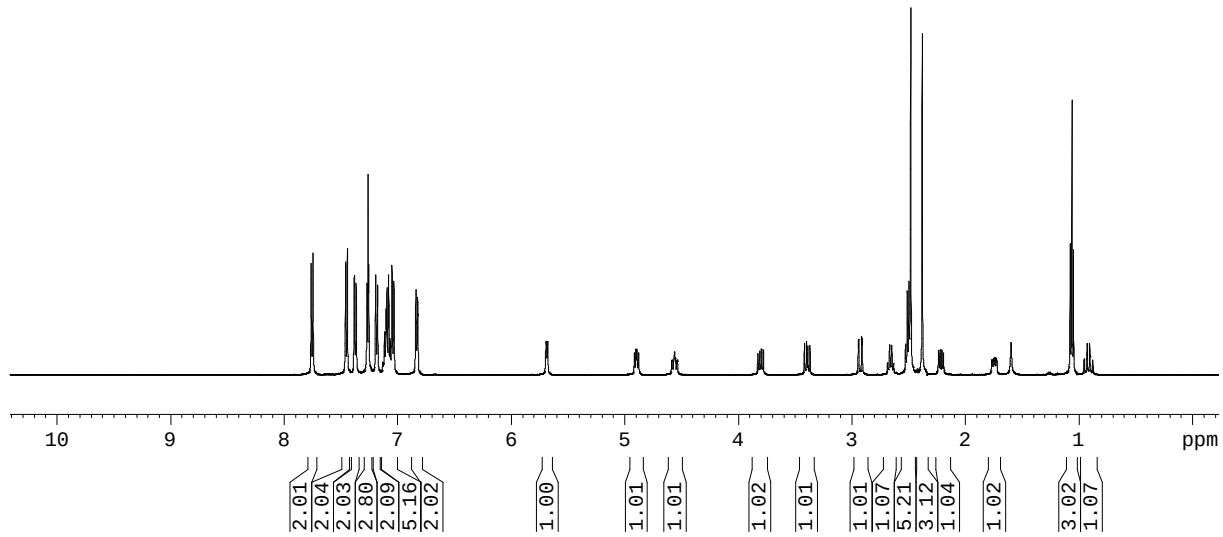
30
20
10
ppm


Ts
N
H
O
Ph
H
N
Ts
Et

18b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6
5
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ppm
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2.04
2.03
2.80
2.09
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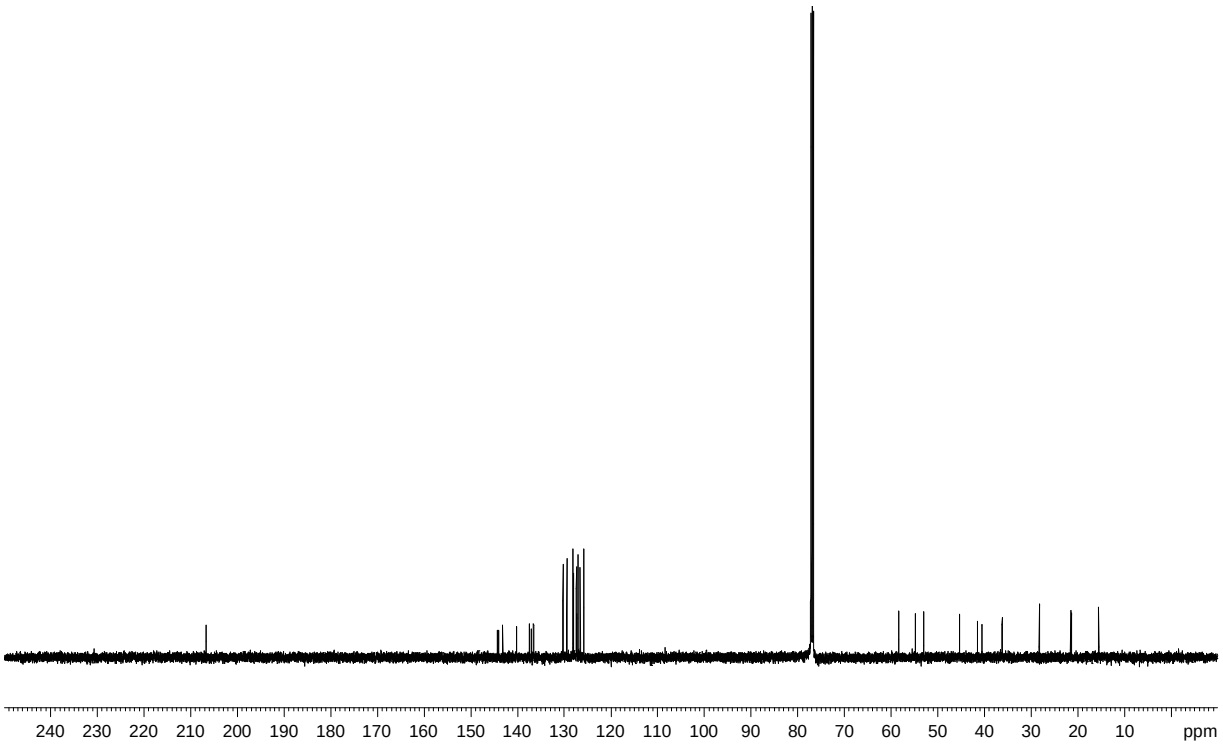
3.12
1.04
1.02
3.02
1.07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230
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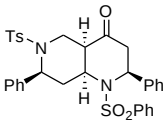
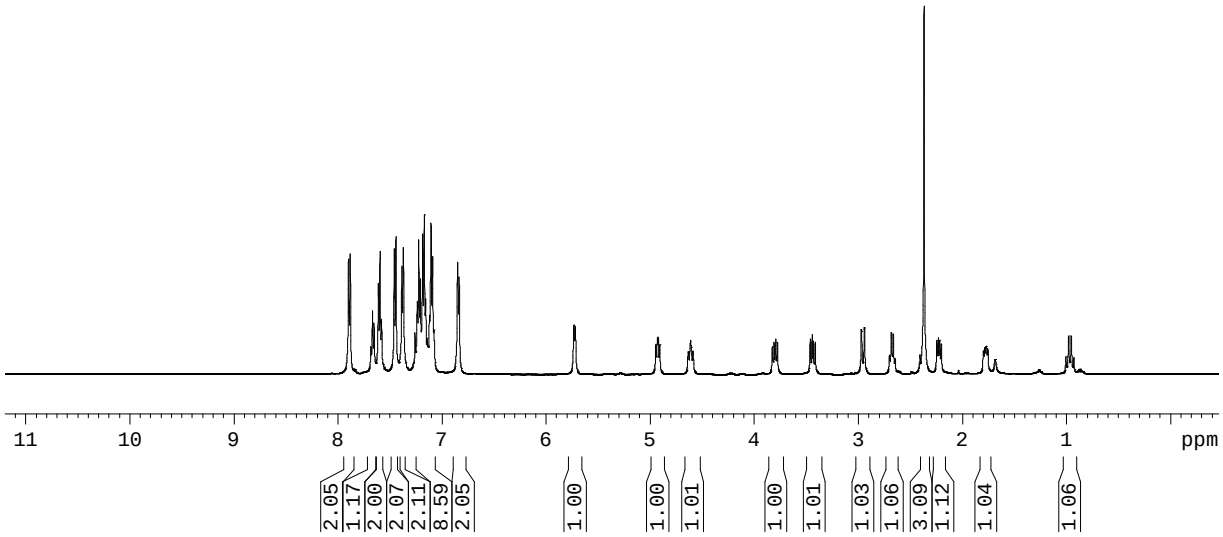
110
100
90
80
70
60
50
40
30
20
10
ppm


Ts
N
H
O
Ph
H
N
Ph
SO2Ph

18c


11
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7
6
5
4
3
2
1
ppm
2.05
1.17
2.00
2.07
2.11
8.59
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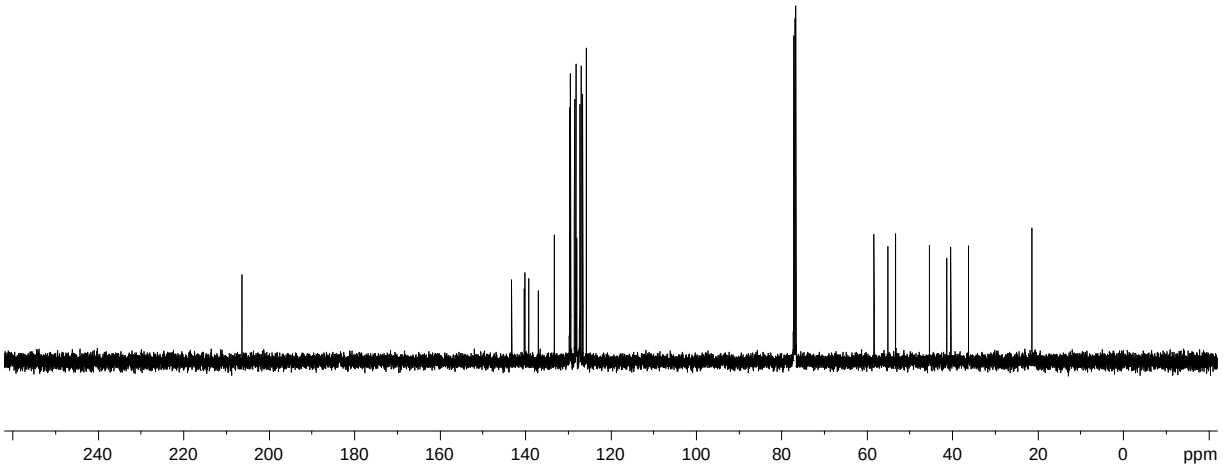
1.00
1.01
1.00
1.01
1.03
1.06
3.09
1.12
1.04
1.06


240
220
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180
160
140
120
100
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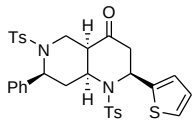
40
20
0
ppm


Ts
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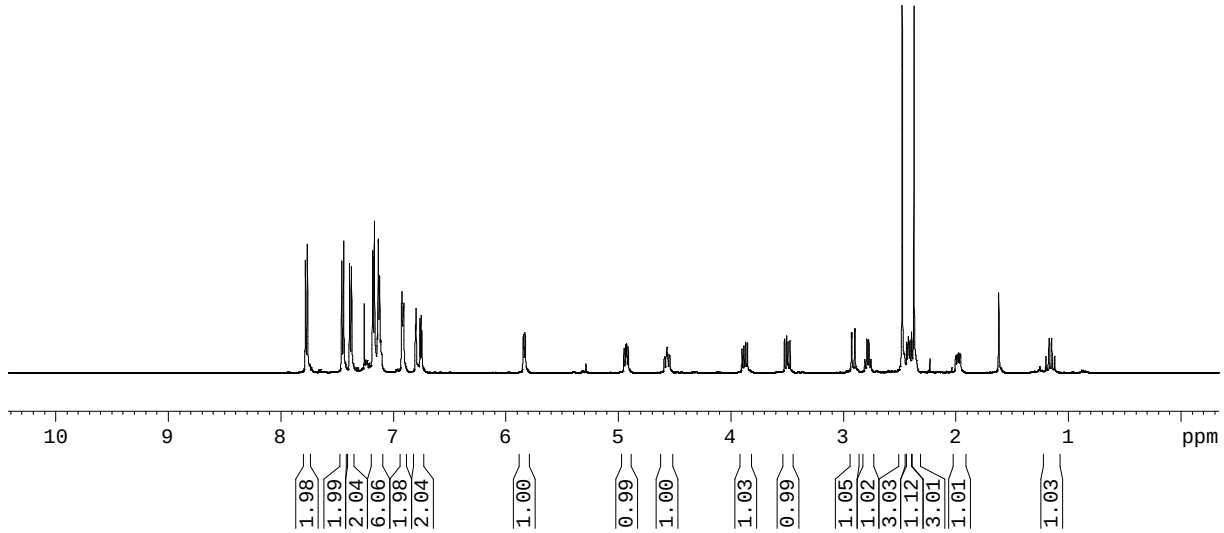
O
Ph
H
N
Ts
S

18d


10
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6
5
4
3
2
1
ppm
1.98
1.99
2.04
6.06
1.98
2.04
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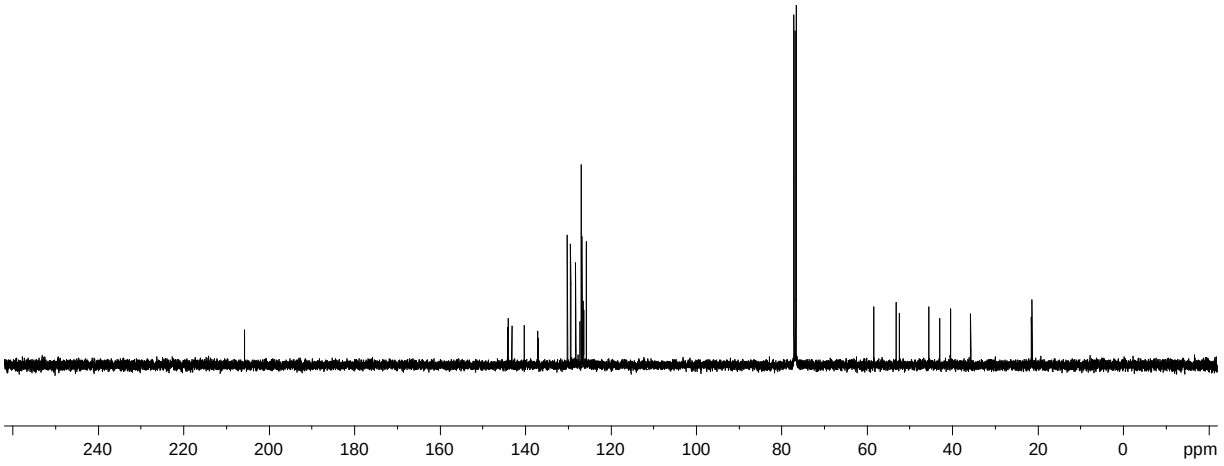
0.99
1.00
1.03
0.99
1.05
1.02
3.03
1.12
3.01
1.01
1.03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120
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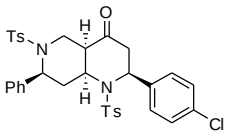
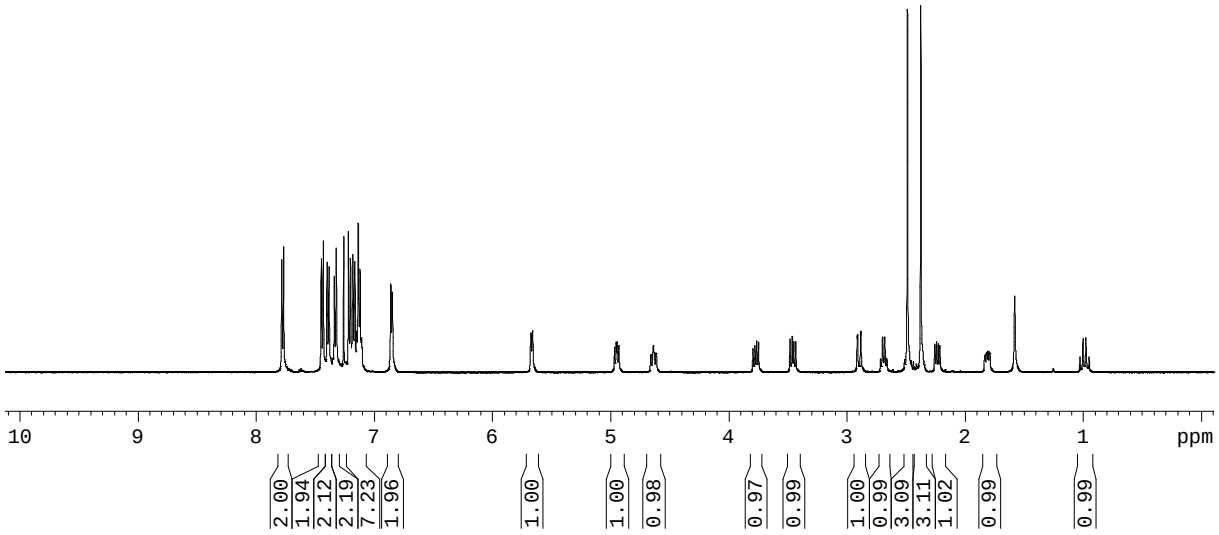
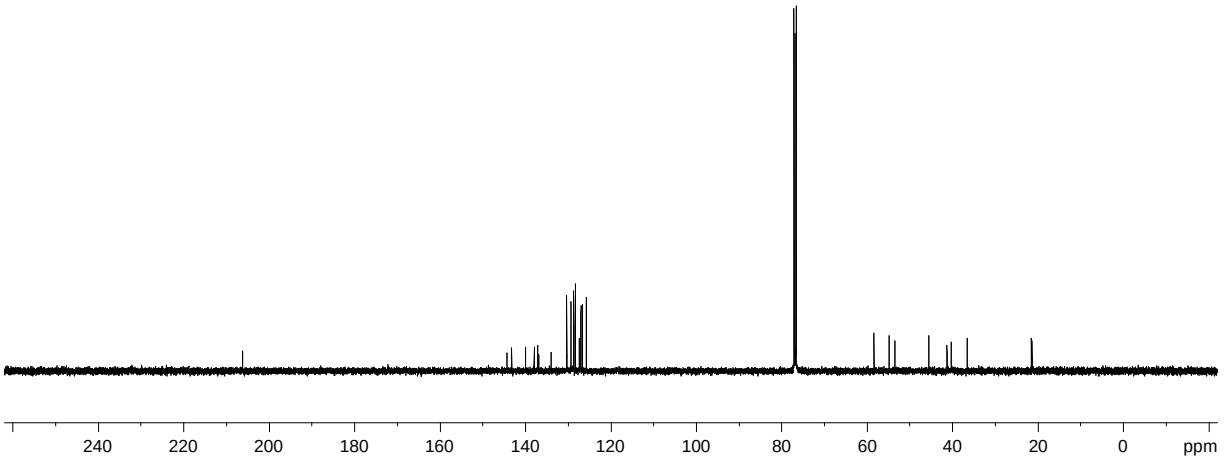
80
60
40
20
0
ppm


Ts
N
H
O
Ph
H
N
Ts
Cl

18e


10
9
8
7
6
5
4
3
2
1
ppm
2.00
1.94
2.12
2.19
7.23
1.96
1.00
1.00
0.98
0.97
0.99
1.00
0.99
3.09
3.11
1.02
0.99
0.99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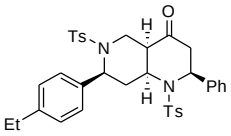
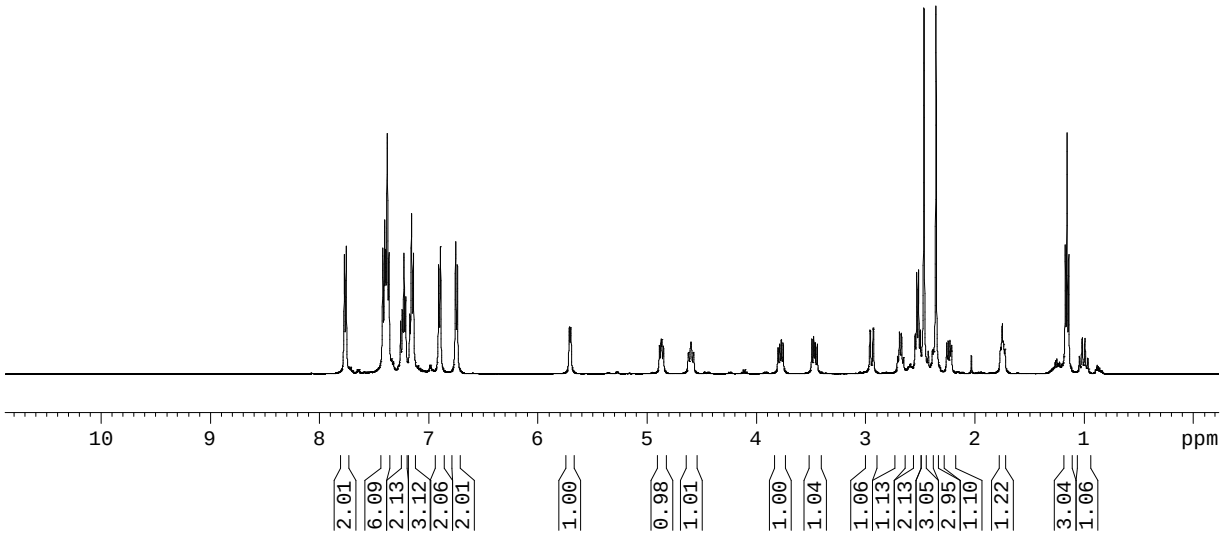
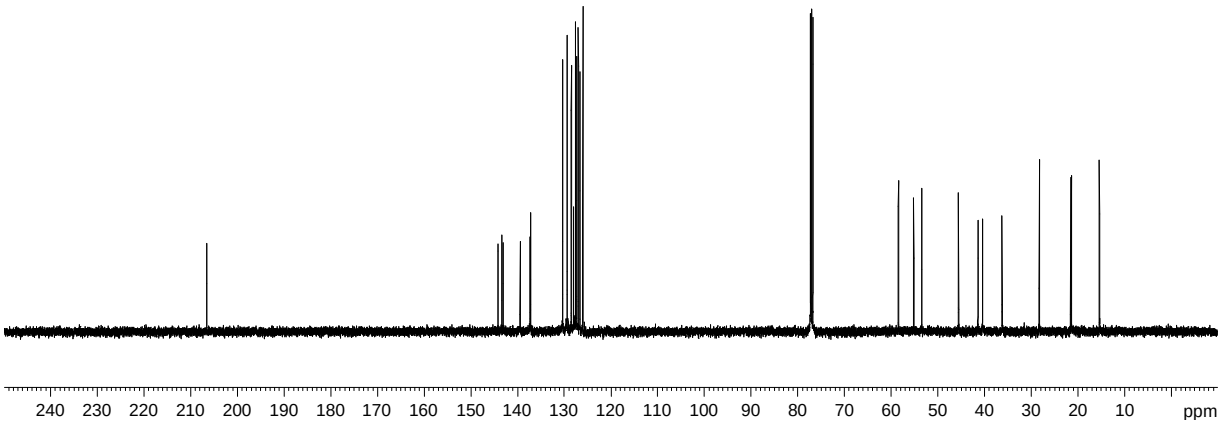
120
100
80
60
40
20
0
ppm


Ts
N
H
O
H
N
Ts
Ph
Et

18f


10
9
8
7
6
5
4
3
2
1
ppm
2.01
6.09
2.13
3.12
2.06
2.01
1.00
0.98
1.01
1.00
1.04
1.06
1.13
2.13
3.05
2.95
1.10
1.22
3.04
1.06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230
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210
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140
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120
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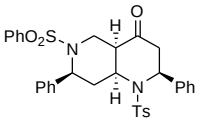
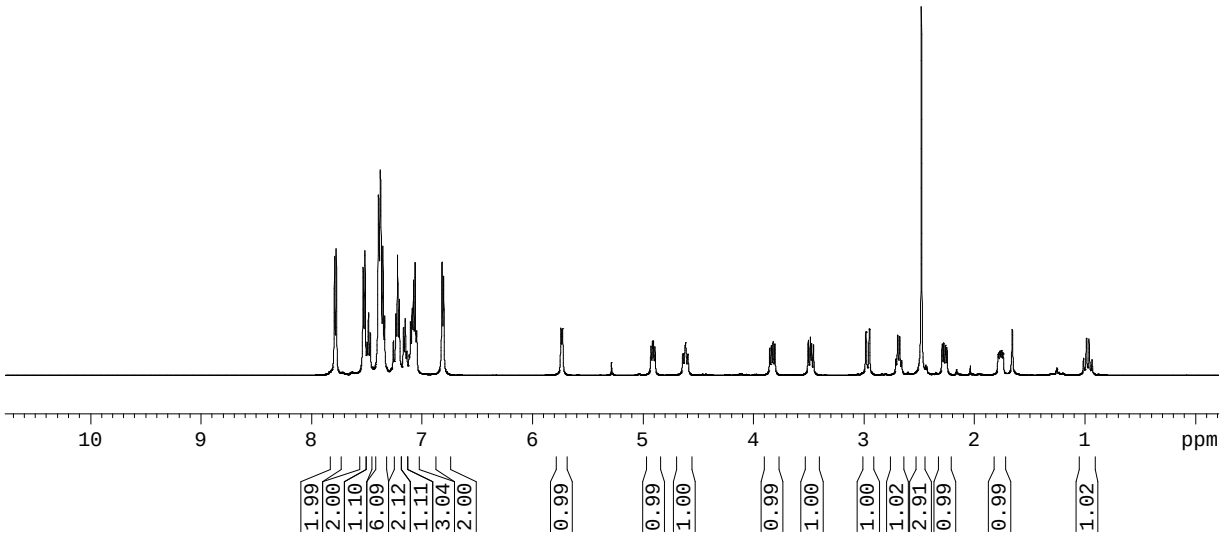
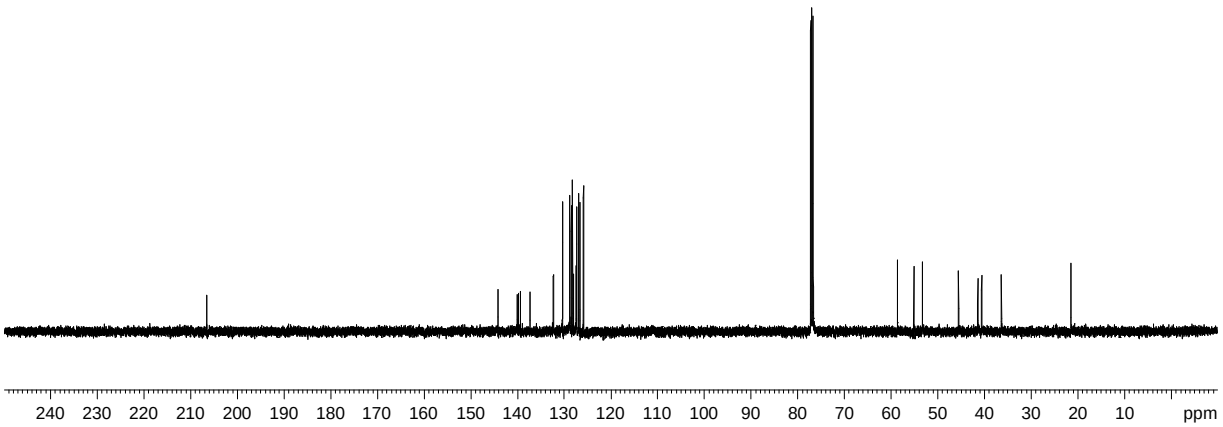
100
90
80
70
60
50
40
30
20
10
ppm


PhO2S
N
H
O
Ph
H
N
Ts
Ph

18g


10
9
8
7
6
5
4
3
2
1
ppm
1.99
2.00
1.10
6.09
2.12
1.11
3.04
2.00
0.99
0.99
1.00
0.99
1.00
1.00
1.02
2.91
0.99
0.99
1.02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210
200
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110
100
90
80
70
60
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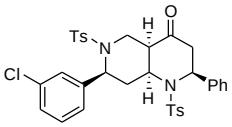
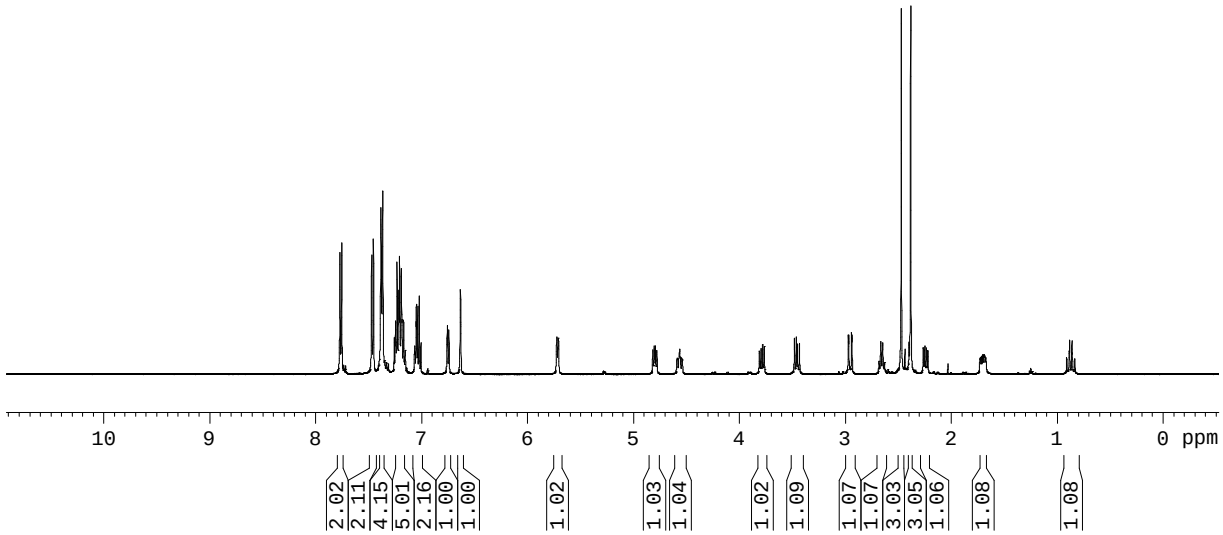
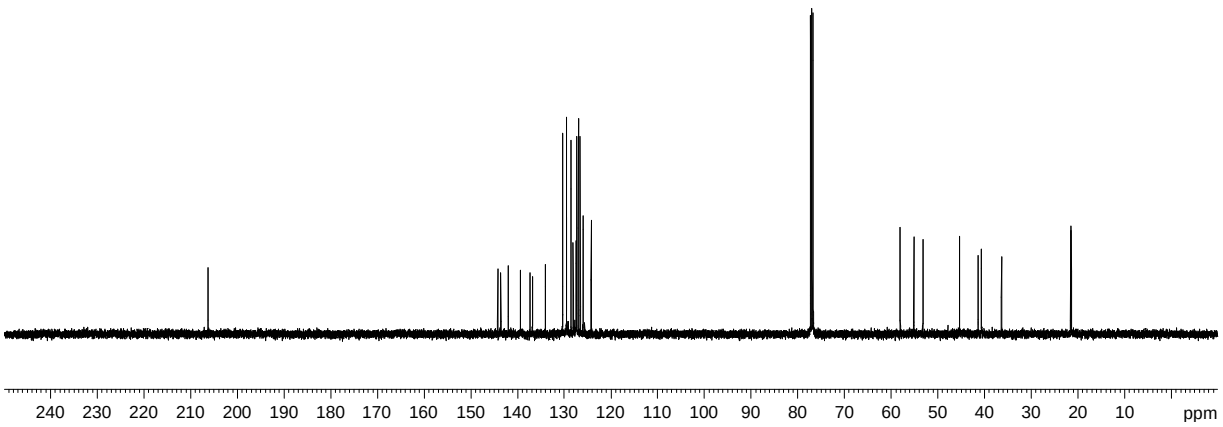
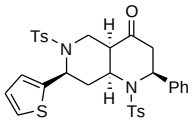
40
30
20
10
ppm


Ts
N
H
O
Cl
Ph
H
N
Ts

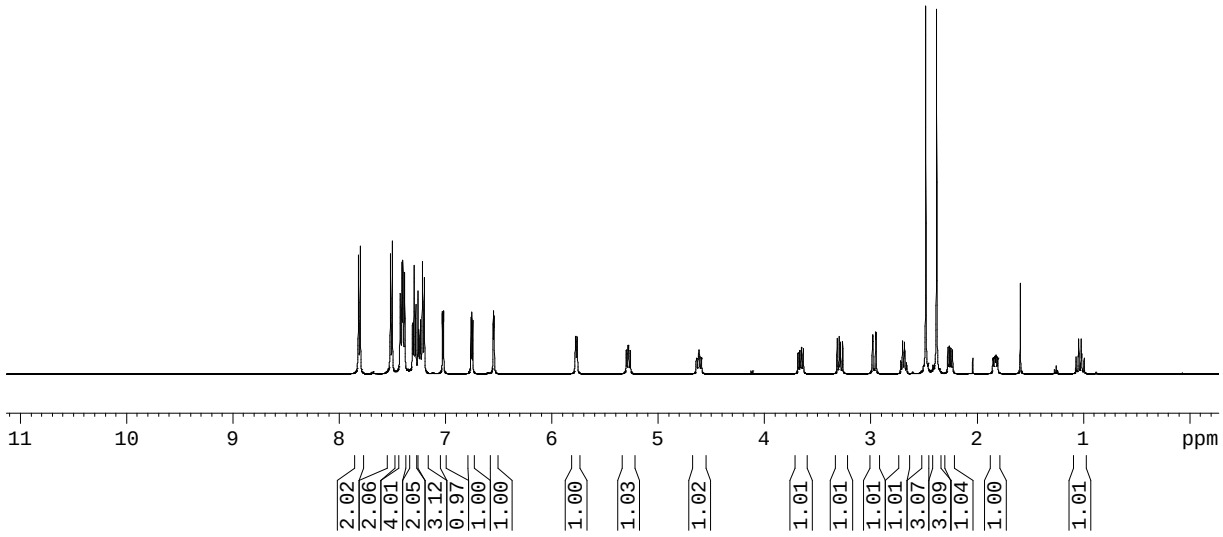
18h

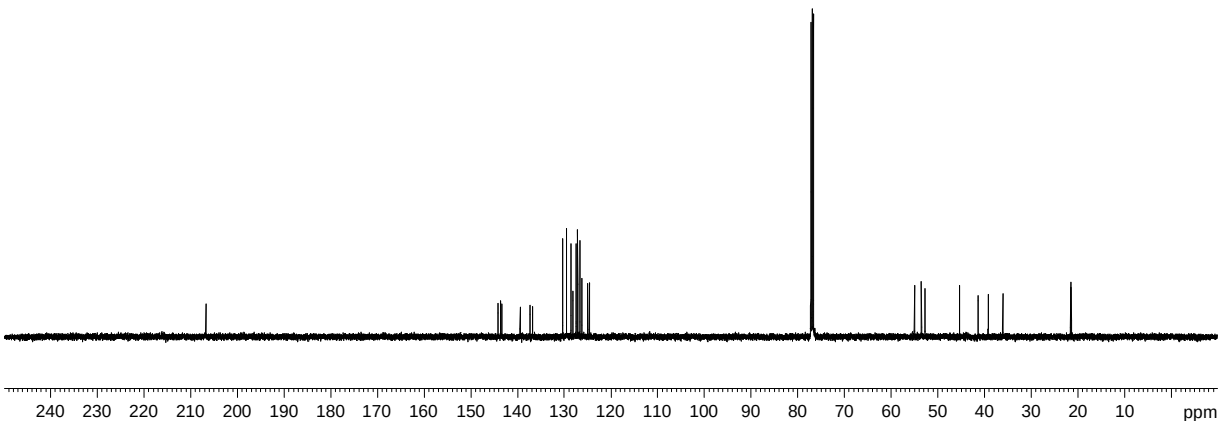

10 9 8 7 6 5 4 3 2 1 0 ppm
2.02 2.11 4.15 5.01 2.16 1.00 1.00 1.02 1.03 1.04 1.02 1.09 1.07 1.07 3.03 3.05 1.06 1.08 1.08


240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Ts
N
H
O
Ph
N
H
Ts
S

18i


11
10
9
8
7
6
5
4
3
2
1
ppm
2.02
2.06
4.01
2.05
3.12
0.97
1.00
1.00
1.00
1.03
1.02
1.01
1.01
1.01
1.01
3.07
3.09
1.04
1.00
1.01


240
230
220
210
200
190
180
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160
150
140
130
120
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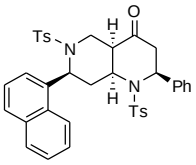
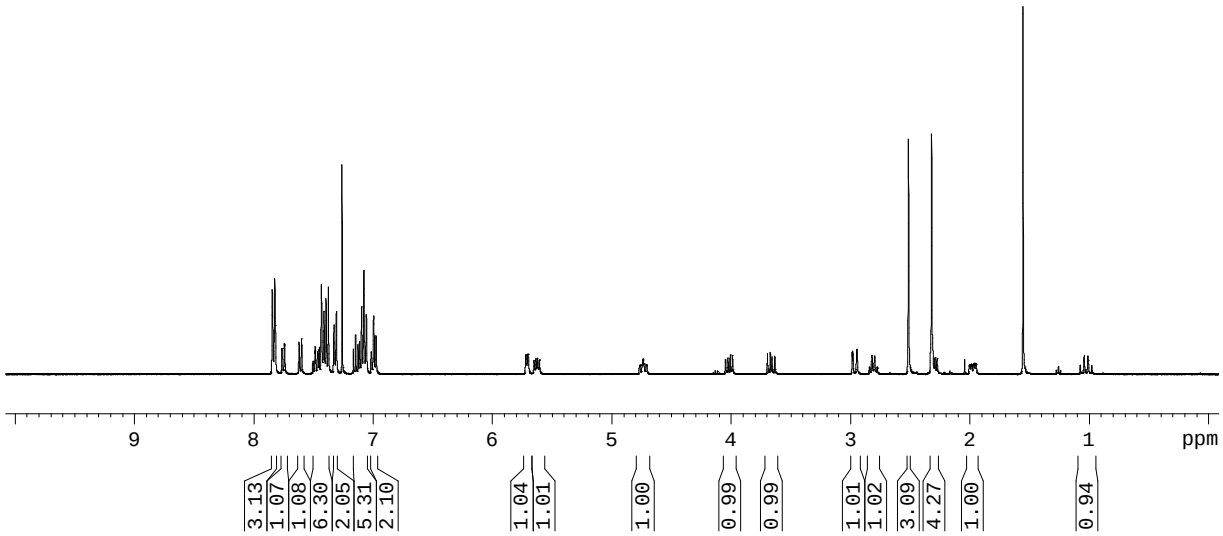
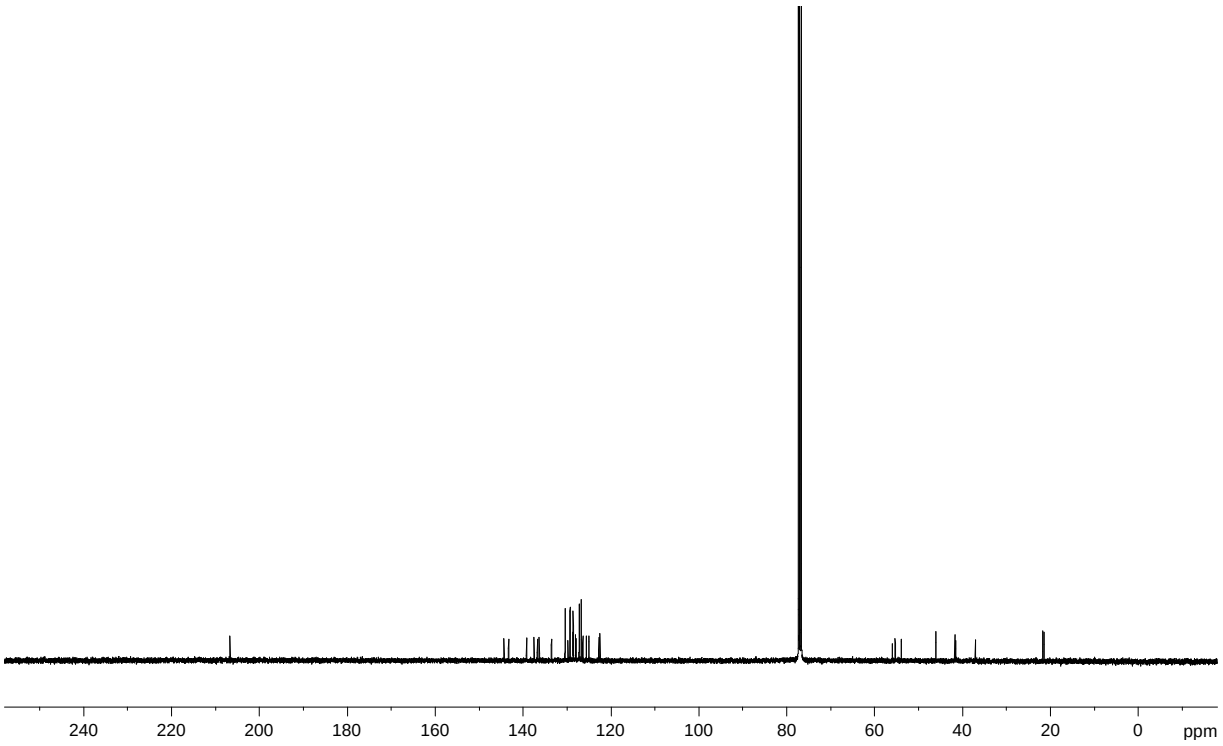
100
90
80
70
60
50
40
30
20
10
ppm


Ts
N
H
O
H
N
Ts
Ph

18j


9
8
7
6
5
4
3
2
1
ppm
3.13
1.07
1.08
6.30
2.05
5.31
2.10
1.04
1.01
1.00
0.99
0.99
1.01
1.02
3.09
4.27
1.00
0.94


240
220
200
180
160
140
120
100
80
60
40
20
0
ppm