Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Cascade Radical Cyclization on 3-Propargyl-2-Alkenyl Indole Gives Stereoselective Access to Cyclohepta[*b*]indole over Carbazole

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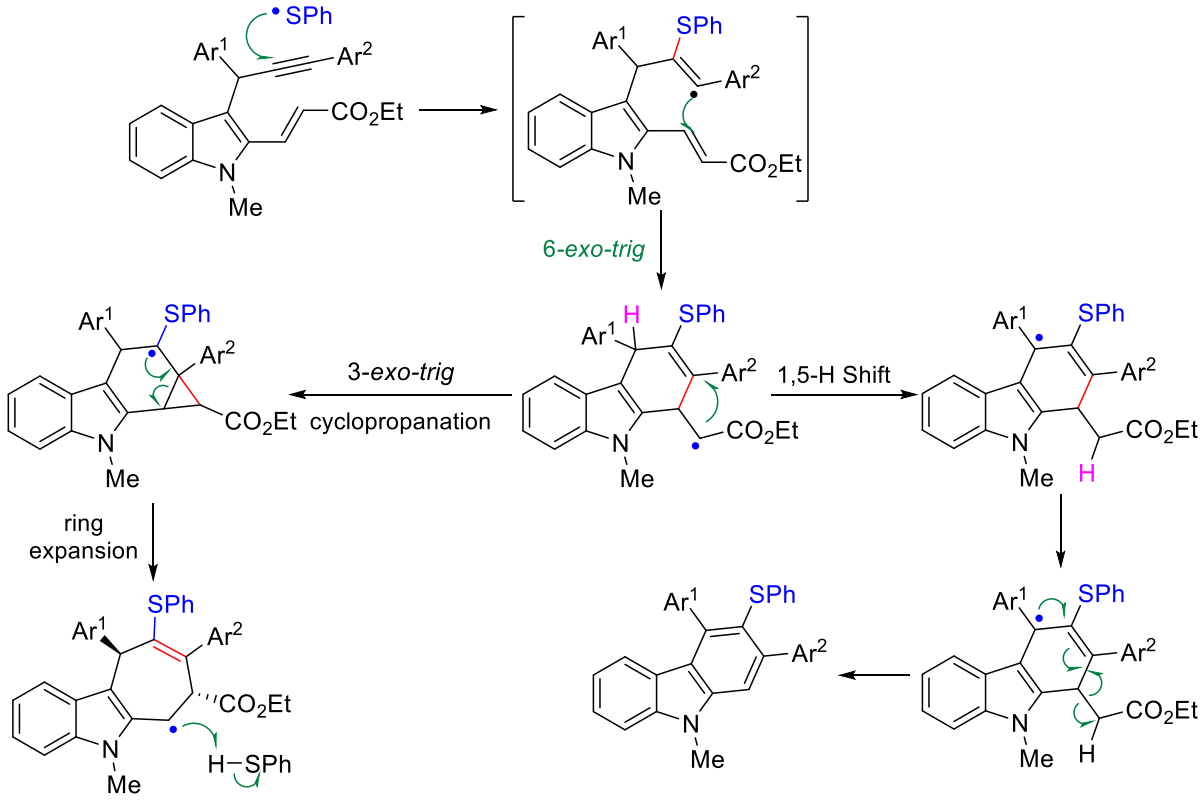
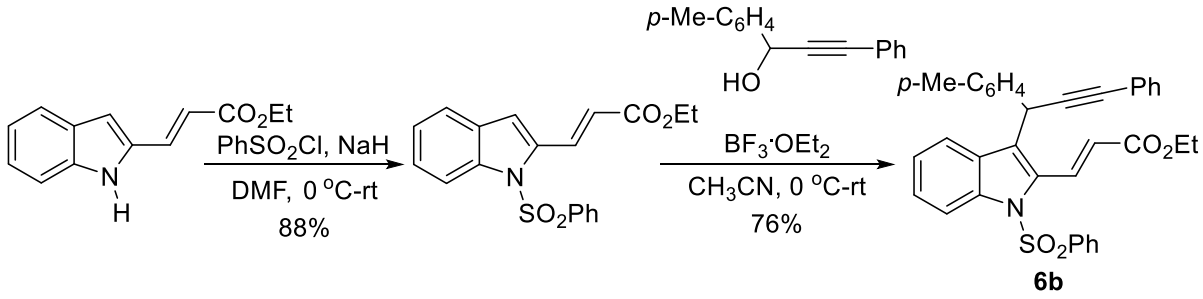
General

IR spectra were recorded on Nicolet 6700 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 400 and 500 spectrophotometers. The chemical shifts (δ, ppm) and coupling constants (Hz) are reported in the standard fashion with reference to residual $CHCl_3$ at (7.26 ppm for ^{1}H) and the central line (77.16 ppm for ^{13}C) of $CDCl_3$. In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2 or CH_3) was determined by recording the DEPT-135 experiment, and are given in parentheses. NOE spectrum was recorded on Bruker Avance 400 and 500 MHz spectrophotometer. Analytical thin-layer chromatography (TLC) was performed on glass plates (7.5 × 2.5 and 9 × 5.0 cm) coated with Merck or Acme's silica gel G containing 13% calcium sulphate as binder or on pre-coated 0.2 mm thick Merck 60 F245 silica plates and various combinations of ethyl acetate and petroleum ether were used as eluent. Visualization of spots was accomplished by either exposure to iodine vapour or $KMnO_4$ and vanillin stain. Acme's silica gel (100-200 mesh) was used for column chromatography (approximately 15-20 g per 1 g of the crude reaction mixture. All small-scale dry reactions were carried out using standard syringe septum technique. Dry THF, ether, benzene was obtained by distillation over sodium-benzophenone ketyl. Dry dichloromethane and dry DMF, dry acetonitrile, dry toluene was prepared by distilling over calcium hydride. PhSH and AIBN were obtained from Spectrochem. AIBN was recrystallize from methanol before using. All the commercial reagents were used as such without further purification. All the 3-propargyl-2-alkenyl indole derivatives were prepared following the known literature protocol[1]

Plausible Mechanism for Cyclohepta[b]indole and Carbazole Formation



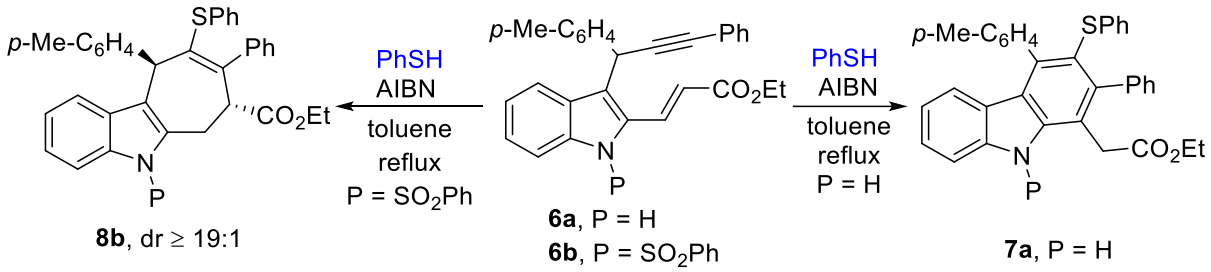
General procedure for the Synthesis of 3-propargyl-2-alkenyl indole derivatives 6



To a magnetically stirred solution of alkenyl indole (200 mg, 0.563 mmol) and propargylic alcohol (187 mg, 0.844 mmol) in dry acetonitrile (7 mL) was added $BF_3{\cdot}OEt_2$ (10 mol%) at 0 ^oC and the reaction mixture was allowed to stirred at room temperature until the completion of starting material (TLC controlled) The reaction was quenched with saturated solution of $NaHCO_3$, extracted with EtOAc (3 × 25 mL). The combine organic layer was washed with brine and dried over Na_2SO_4, evaporated under reduced pressure. The crude product was subjected to purification by silica gel column chromatography using EtOAc:Petroleum ether as eluent, furnished the 3-propargyl-2-alkenyl indole[1] **6b** (240 mg, 76%) as a sticky solid.

1. Reddy, C. R.; Reddi, R. V.; Uredi, D. *Chem. Eur. J.* **2016**, *22*, 2501.

General procedure for the synthesis of carbazole and cyclohepta[b]indole derivatives (7/8):



ethyl 2-(2-phenyl-3-(phenylthio)-4-(p-tolyl)-9H-carbazol-1-yl)acetate (7a):

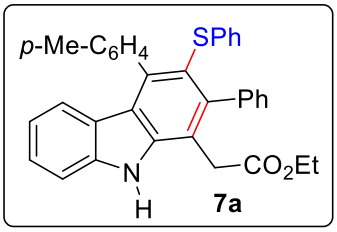
To a magnetically stirred solution of the 3-propargyl-2-alkenyl indole **6a** (84 mg, 0.200 mmol) in dry toluene (4 mL) was added thiophenol (51 µL, 0.500 mmol) and AIBN (39 mg, 0.200 mmol). The reaction mixture was allowed to reflux at 110 ^{o}C in an oil bath until the completion of starting material (TLC control). Solvent was evaporated under reduced pressure and the reaction mixture was subjected to purification on silica gel column chromatography by using DCM:Petroleum ether as eluent furnished tetra substituted carbazole **7a** (22 mg, 21%) as a sticky solid.

ethyl (7R,10R)-8-phenyl-5-(phenylsulfonyl)-9-(phenylthio)-10-(p-tolyl)-5,6,7,10-tetrahydrocyclohepta[b]indole-7-carboxylate (8b):

To a magnetically stirred solution of 3-propargyl-2-alkenyl indole **6b** (114 mg, 0.205 mmol) in dry toluene (4 mL) was added thiophenol (53 µL, 0.512 mmol) and AIBN (34 mg, 0.205 mmol). The reaction mixture was allowed to reflux at 110 ^{o}C in an oil bath until the completion of starting material (TLC control). Solvent was evaporated under reduced pressure and the reaction mixture was subjected to purification on silica gel column chromatography by using using EtOAc:Petroleum ether as eluent furnished cyclohepta[*b*]indole derivative **8b** (92 mg, 67%) as a crystalline solid.

ethyl 2-(2-phenyl-3-(phenylthio)-4-(p-tolyl)-9H-carbazol-1-yl)acetate (7a):

To a magnetically stirred solution of the 3-propargyl-2-alkenyl indole **6a** (84 mg, 0.200 mmol) in dry toluene (4 mL) was added thiophenol (51 µL, 0.500 mmol) and AIBN (39 mg, 0.200 mmol). The reaction mixture was allowed to reflux at 110 ^{o}C in an oil bath until the completion of starting material (TLC control). Solvent was evaporated under reduced pressure and the reaction mixture was subjected to purification on silica gel column chromatography by using DCM:Petroleum ether as eluent furnished tetra substituted carbazole **7a** (22 mg, 21%) as a sticky solid.



Physical appearance: sticky solid.

R$_f$: 0.3 (3:7, DCM:Petroleum ether).

IR (neat): 3374, 2928, 2874, 1714, 1596, 1582, 1476, 1386, 1217, 1024, 757 cm^{-1}.

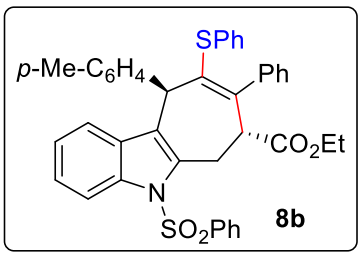
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.11 (bs, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 8.0, Hz, 1H), 7.29- 7.19 (m, 7H), 7.9 (d, *J* = 8.0 Hz, 2H), 7.00-6.92 (m, 4H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.67 (d, *J* = 4.0 Hz, 2H), 4.13 (q, *J* = 8.0 Hz, 2H), 3.69 (s, 2H), 2.44 (s, 3H), 1.23 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 171.9 (C), 145.4 (C), 142.9 (C), 141.2 (C), 140.5 (C), 140.1 (C), 140.0 (C), 137.1 (C), 137.0 (C), 130.0 (2 × CH), 129.1 (2 × CH), 128.9 (2 × CH), 128.1 (2 × CH), 127.4 (2 × CH), 127.1 (CH), 126.9 (2 × CH), 126.1 (CH), 124.2 (CH), 123.6 (C), 122.9 (C), 122.6 (CH), 121.8 (C), 120.0 (CH), 115.7 (C), 111.1 (CH), 61.5 (CH_2), 36.9 (CH_2), 21.5 (CH_3), 14.2 (CH_3).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{35}H_{29}NNaO_2S$, 550.1811 found 550.1807.

ethyl (7R*,10R*)-8-phenyl-5-(phenylsulfonyl)-9-(phenylthio)-10-(p-tolyl)-5,6,7,10-tetrahydrocyclohepta[b]indole-7-carboxylate (8b):

To a magnetically stirred solution of 3-propargyl-2-alkenyl indole **6b** (114 mg, 0.205 mmol) in dry toluene (4 mL) was added thiophenol (53 µL, 0.512 mmol) and AIBN (34 mg, 0.205 mmol). The reaction mixture was allowed to reflux at 110 ^oC in an oil bath until the completion of starting material (TLC control). Solvent was evaporated under reduced pressure and the reaction mixture was subjected to purification on silica gel column chromatography by using using EtOAc:Petroleum ether as eluent furnished cyclohepta[*b*]indole derivative **8b** (92 mg, 67%) as a crystalline solid.



Physical appearance: crystalline solid.

MP.: 178-180 ^oC.

R_f: 0.7 (1.5:8.5, EtOAc:Petroleum ether).

IR (neat): 3047, 3023, 2989, 2345, 1737, 1582, 1509, 1447, 1376, 1175, 745 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.5 Hz, 1H), 7.82 (dd, *J* = 8.5, 1.0 Hz, 2H), 7.56 (td, *J* = 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.35-7.27 (m, 4H), 7.15 (d, *J* = 8.0 Hz, 4H), 7.05 (d, *J* = 8.5 Hz, 2H), 7.01 (td, *J* = 8. 0.5 Hz, 1H), 6.92 (td, *J* = 7.5, 1.5 Hz, 1H), 6.84 (*J* = 8, 1 Hz, 2H), 6.70 (t, *J* = 7.5 Hz, 2H), 6.56 (d, J = 5.0 Hz, 1H), 5.00 (s, 1H), 4.04 (dd, *J* = 11.5, 4.5 Hz, 1H), 3.68-3.57 (m, 4H), 2.30 (s, 3H), 0.79 (t, *J* = 7.5 Hz, 3H).

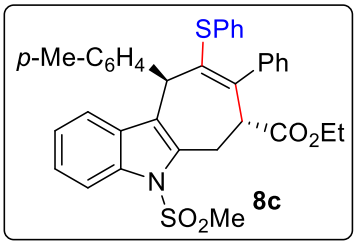
^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 171.4 (C), 141.4 (C), 139.4 (C), 139.2 (C), 138.6 (C), 138.5 (C), 136.4 (C), 136.2 (C), 135.3 (C), 134.0 (CH), 133.9 (C), 131.5 (2 × CH), 130.7 (C), 129.4 (4 × CH), 128.8 (2 × CH), 128.0 (2 × CH), 127.9 (CH), 127.0 (CH), 126.4 (6 × CH),

124.9 (CH), 123.9 (CH), 122.3 (C), 118.2 (CH), 114.9 (CH), 60.7 (CH_2), 46.1 (CH), 43.2 (CH), 29.6 (CH_2), 21.1 (CH_3), 13.6 (CH_3).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{41}H_{35}NNaO_4S_2$ 692.1900, found 692.1891.

ethyl (7R*,10R*)-5-(methylsulfonyl)-8-phenyl-9-(phenylthio)-10-(p-tolyl)-5,6,7,10-tetrahydrocyclohepta[b]indole-7-carboxylate (8c):

The reaction of 3-propargyl-2-alkenyl indole **6c** (107 mg, 0.215 mmol), thiophenol (55 µL, 0.538 mmol) and AIBN (35 mg, 0.2152 mmol) in dry toluene (8 mL) as described for compound **8b**, followed by purification of the crude reaction mixture on silica gel column chromatography by using EtOAc: Petroleum ether as eluent furnished cyclohepta[*b*]indole derivative **8c** (85mg, 65%) as a sticky solid.



Physical appearance: sticky solid.

R$_f$: 0.4 (1:9, EtOAc:Petroleum ether).

IR (neat): 3019, 2930, 1731, 1454, 1372, 1170, 756 cm^{-1}.

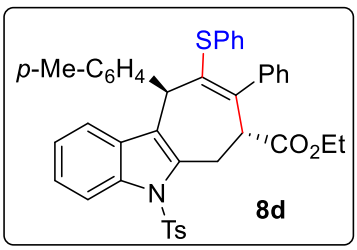
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.4 Hz, 1H), 7.38-7.34 (m, 2H), 7.31-7.25 (m, 6H), 7.11-7.05 (m, 5H), 7.02 (t, *J* = 7.2 Hz, 1H), 6.91 (t, *J* = 7.6 Hz, 2H), 6.70 (d, *J* = 8.0 Hz, 1H), 5.15 (s, 1H) 4.12 (dd, *J* = 12.4, 3.2 Hz, 1H), 3.70-3.52 (m, 4H), 3.12 (s, 3H), 2.33 (3H), 0.79 (t, 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 171.5 (C), 140.9 (C), 139.5 (C), 138.7 (C), 138.4 (C), 136.4 (C), 135.4 (C), 135.2 (C), 133.9 (C), 132.0 (3 × CH), 130.4 (C), 129.5 (2 × CH), 129.0 (3 × CH), 128.0 (2 × CH), 127.8 (CH), 127.4 (CH), 126.5 (2 × CH), 124.8 (CH), 123.8 (CH), 121.1 (C), 118.5 (CH), 114.0 (CH), 60.7 (CH_2), 46.5 (CH), 43.0 (CH), 40.8 (CH_3), 29.4 (CH_2), 21.1 (CH_3), 13.6 (CH_3).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{36}H_{33}NNaO_4S_2$ 630.1744 found 630.1744.

ethyl (7R*,10R*)-8-phenyl-9-(phenylthio)-10-(p-tolyl)-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]indole-7-carboxylate (8d):

The reaction of 3-propargyl-2-alkenyl indole **6d** (105 mg, 0.1830 mmol), thiophenol (46 µL, 0.457 mmol) and AIBN (30 mg, 0.183 mmol) in dry toluene (4 mL) as described for compound **8b**, followed by purification of the crude reaction mixture on silica gel column chromatography by using EtOAc:Petroleum ether as eluent furnished cyclohepta[*b*]indole derivative **8d** (58 mg, 46%) as a sticky solid.



Physical appearance: sticky solid.

R$_f$: 0.5, (3:7, DCM:Petroleum ether).

IR (neat): 3026, 2980, 2925, 1736, 1597, 1453, 1375, 1214, 1173, 753cm^{-1}.

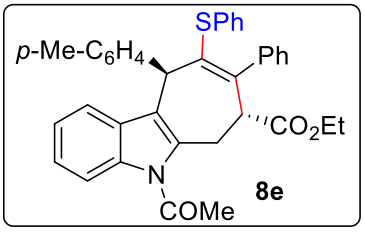
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 2H), 7.36-7.25 (m, 6H), 7.16 (d, *J* = 7.5 Hz, 4H), 7.05 (d, *J* = 7.5 Hz, 2H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.69 (t, *J* = 7.5 Hz, 2H), 6.56 (d, *J* = 8.0 Hz, 1H), 5.01 (s, 1H), 4.04 (dd, *J* = 12.5, 3.5 Hz, 1H), 3.65-3.57 (m, 4H), 2.35 (s, 3H), 2.30 (s, 3H), 0.79 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 171.4 (C), 145.1 (C), 141.5 (C), 139.4 (C), 138.6 (C), 138.5 (C), 136.3 (C), 136.3 (C), 136.2 (C), 135.4 (C), 133.9 (C), 131.5 (2 × CH), 130.7 (C), 129.9 (2 × CH), 129.4 (2 × CH), 129.1 (CH), 128.8 (2 × CH), 127.9 (2 × CH), 127.8 (CH), 127.0 (CH), 126.5 (5 × CH), 124.7 (CH), 123.8 (CH), 122.1 (C), 118.2 (CH), 114.9 (CH), 60.7 (CH_2), 46.2 (CH), 43.2 (CH), 29.6 (CH_2), 21.7 (CH_3), 21.1 (CH_3), 13.6 (CH_3).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{42}H_{37}NNaO_4S_2$ 706.2056, found 706.2049.

ethyl (7R*,10R*)-5-acetyl-8-phenyl-9-(phenylthio)-10-(p-tolyl)-5,6,7,10-tetrahydrocyclohepta[b]indole-7-carboxylate (8e):

The reaction of 3-propargyl-2-alkenyl indole **6e** (72 mg, 0.156 mmol), thiophenol (40 µL, 0.389 mmol) and AIBN (26 mg, 0.156 mmol) in dry toluene (10 mL) as described for compound **8b**, followed by purification of the crude reaction mixture on silica gel column chromatography by using EtOAc:Petroleum ether as eluent furnished cyclohepta[*b*]indole derivative **8e** (50 mg, 56%) as a sticky solid**.**



Physical appearance: sticky solid.

R_f: 0.5, (1:9, EtOAc:Petroleum ether).

IR (neat): 3019, 1733, 1709, 1461, 1307, 754 cm^{-1}.

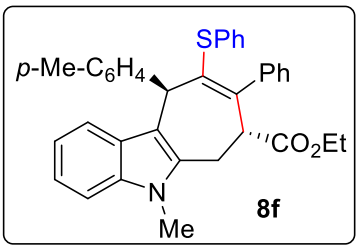
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.4 Hz, 1H), 7.36-7.24 (m, 8H), 7.12-7.07 (m, 4H), 7.04-7.00 (m, 2H), 6.91 (t, *J* = 7.2 Hz, 2H), 6.67 (d, *J* = 7.6 Hz, 1H), 5.14 (s, 1H), 4.12 (dd, *J* = 12.8, 2.4 Hz, 1H), 3.82-3.75 (m, 1H), 3.66-3.54 (m, 3H), 2.87 (s, 3H), 2.31 (s, 3H), 0.78 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): 171.8 (C), 170.6 (C), 140.7 (C), 139.6 (C), 139.0 (C), 138.2 (C), 136.2 (C), 136.1 (C), 134.9 (C), 134.0 (C), 131.9 (2 × CH), 130.6 (C), 129.3 (2 × CH), 129.2 (CH), 129.0 (2 × CH), 128.0 (2 × CH), 127.8 (2 × CH), 127.2 (CH), 126.7 (2 × CH), 124.2 (CH), 123.0 (CH), 120.0 (C), 118.4 (CH), 114.5 (CH), 60.6 (CH_2), 46.7 (CH), 42.8 (CH), 31.0 (CH_2), 28.2 (CH_3), 21.1 (CH_3), 13.6 (CH_3)

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{37}H_{34}NO_3S$ 572.2285 found 572.2285.

ethyl (7R*,10R*)-5-methyl-8-phenyl-9-(phenylthio)-10-(p-tolyl)-5,6,7,10-tetrahydrocyclohepta[b]indole-7-carboxylate (8f):

The reaction of 3-propargyl-2-alkenyl indole **6f** (41 mg, 0.095 mmol), thiophenol (24 µL, 0.236 mmol) and AIBN (16 mg, 0.095 mmol) in dry toluene (3 mL) as described for compound **8b**, followed by purification of the crude reaction mixture on silica gel column chromatography by using EtOAc:Petroleum ether as eluent furnished cyclohepta[*b*]indole derivative **8f** (36 mg, 70%) and **7f** (14%) as a crystalline solid.



Physical appearance: crystalline solid.

MP.: 169-171 °C.

R_f: 0.6, (1:9, EtOAc:Petroleum ether).

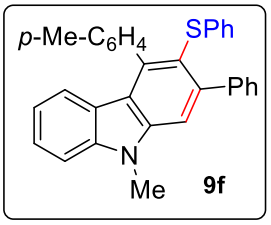
IR (neat): 3021, 2928, 2854, 1732, 1582, 1508, 1471, 757 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.32 (m, 8H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.13-7.06 (m, 5H), 6.96-6.91 (m, 3H), 6.80 (d, *J* = 8.0 Hz, 1H), 5.22 (s, 1H), 4.18 (dd, *J* = 13.2, 3.2 Hz, 1H), 3.78 (s, 3H), 3.73-3.58 (m, 2H), 3.39 (dd, *J* = 17.2, 13.6 Hz, 1H), 3.22 (dd, *J* = 17.2, 3.2 Hz, 1H), 2.32 (s, 3H), 0.86 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 172.4 (C), 140.6 (C), 140.2 (C), 139.9 (C), 138.2 (C), 136.1 (C), 135.7 (C), 134.7 (C), 134.0 (C), 132.1 (2 × CH), 129.4 (CH), 129.1 (2 × CH), 129.0 (2 × CH), 128.0 (C), 127.9 (2 × CH), 127.7 (CH), 127.1 (CH), 126.8 (3 × CH), 121.1 (CH), 119.1 (CH), 118.1 (CH), 112.0 (C), 108.4 (CH), 60.6 (CH_2), 46.2 (CH), 42.5 (CH), 29.7 (CH_3), 27.3 (CH_2), 21.1 (CH_3), 13.7 (CH_3).

HRMS (ESI, M+K^+): m/z calcd. for $C_{36}H_{33}KNO_2S$ 582.1864, found 582.1861.

9-methyl-2-phenyl-3-(phenylthio)-4-(p-tolyl)-9H-carbazole (9f):



Physical appearance: sticky solid.

R_f: 0.9, (1:9, EtOAc:Petroleum ether).

IR (neat): 3011, 2928, 2857, 1585, 1476, 1216, 755 cm^{-1}.

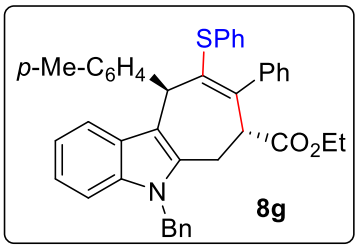
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (s, 1H), 7.41-7.36 (m, 4H), 7.29-7.27 (m, 3H), 7.24-7.18 (m, 4H), 6.99-6.90 (m, 4H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 7.2 Hz, 2H), 3.89 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 145.8 (C), 143.9 (C), 142.8 (C), 141.7 (C), 141.2 (2 × C), 137.2 (C), 137.1 (C), 129.8 (2 × CH), 129.1 (2 × CH), 128.9 (2 × CH), 128.2 (2 × CH), 127.4 (2 × CH), 126.9 (CH), 126.8 (2 × CH), 126.0 (CH), 124.3 (CH), 122.8 (C), 122.6 (CH), 122.2 (C), 120.2 (C), 119.5 (CH), 110.5 (CH), 108.4 (CH), 29.3 (CH_3), 21.6 (CH_3).

HRMS (ESI, M+K^+): m/z calcd. for $C_{32}H_{25}KNS$ 494.1339, found 494.1336.

ethyl (7R*,10R*)-5-benzyl-8-phenyl-9-(phenylthio)-10-(p-tolyl)-5,6,7,10-tetrahydrocyclohepta[b]indole-7-carboxylate (8g):

The reaction of 3-propargyl-2-alkenyl indole **6g** (100 mg, 0.203 mmol) with thiophenol (52 µL, 0.508 mmol) and AIBN (33 mg, 0.2034 mmol) in dry toluene (8 mL) as described for compound **8b**, followed by purification of crude reaction mixture on silica gel column chromatography by using EtOAc:Petroleum ether as eluent furnished cyclohepta[*b*]indole derivative **8g** (95 mg, 75 %), **9g** (13 mg 14%) as a sticky solid.



Physical appearance: sticky solid.

R_f: 0.5 (1:9, EtOAc:Petroleum ether).

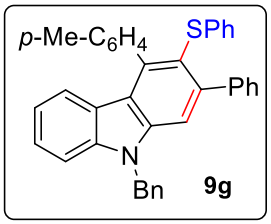
IR (neat): 3019, 2831, 1729, 1466, 1216, 1027, 759 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 (d, *J* = 7.5 Hz, 2H), 7.32-7.25 (m, 7H), 7.20 (d, *J* = 7.0 Hz, 2H), 7.14-7.09 (m, 5H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 2H), 6.94-6.90 (m, 3H), 6.84 (d, *J* = 8.0 Hz, 1H), 5.43 (dd, *J* = 22.0, 17.5 Hz, 2H), 5.26 (s, 1H), 4.17 (dd, 13.0, 3.0 Hz, 1H), 3.66-3.53 (m, 2H), 3.32 (dd, *J* = 17.0, 13.0 Hz, 1H), 3.13 (dd, *J* = 17.5, 3.0 Hz, 1H), 2.32 (s, 3H), 0.81 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 172.2 (C), 140.5 (C), 140.1 (C), 139.8 (C), 139.4 (C), 137.8 (C), 136.1 (C), 135.8 (C), 134.6 (C), 134.1 (C), 131.8 (2 × CH), 129.2 (2 × CH), 129.0 (2 × CH), 128.9 (3 × CH), 128.3 (C), 127.9 (2 × CH), 127.6 (CH), 127.5 (CH), 127.0 (CH), 126.7 (2 × CH), 125.9 (3 × CH), 121.6 (CH), 119.5 (CH), 118.2 (CH), 113.1 (C), 109.0 (CH), 60.6 (CH_2), 46.5 (CH_2), 46.0 (CH), 43.1 (CH), 27.0 (CH_2), 21.1 (CH_3), 13.6 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{42}H_{38}NO_2S$ 620.2639 found 620.2639.

9-benzyl-2-phenyl-3-(phenylthio)-4-(p-tolyl)-9H-carbazole (9g):



Physical appearance: sticky solid.

R_f: 0.8 (1:9, EtOAc:Petroleum ether).

IR (neat): 3017, 1586, 1415, 1215, 756 cm^{-1}.

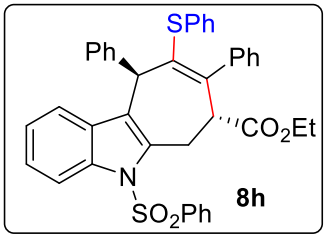
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (s, 1H), 7.36-7.29 (m, 5H), 7.28-7.20 (m, 11H), 7.00-6.91 (m, 4H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 7.2 Hz, 2H), 5.55 (s, 2H), 2.47 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 145.9 (C), 144.0 (C), 142.7 (C), 141.4 (C), 141.1 (C), 141.0 (C), 137.2 (2 × C), 136.8 (C), 129.8 (2 × CH), 129.1 (2 × CH), 129.1 (2 × CH), 128.9 (2 × CH), 128.2 (2 × CH), 127.7 (CH), 127.4 (2 × CH), 127.0 (2 × CH), 126.9 (CH), 126.6 (2 × CH), 126.1 (CH), 124.3 (CH), 123.0 (C), 122.7 (CH), 122.4 (C), 120.7 (C), 119.8 (CH), 110.6 (CH), 109.0 (CH), 46.8 (CH_2), 21.6 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{38}H_{30}NS$ 532.2092 found 532.2092.

ethyl (7R*,10R*)-8,10-diphenyl-5-(phenylsulfonyl)-9-(phenylthio)-5,6,7,10-tetrahydrocyclohepta[b]indole-7-carboxylate (8h):

The reaction of 3-propargyl-2-alkenyl indole **6h** (62 mg, 0.114 mmol), thiophenol (29 µL, 0.2840 mmol) and AIBN (19 mg, 0.1136 mmol) in dry toluene (3 mL) as described for compound **8b**, followed by purification of the crude reaction mixture on silica gel column chromatography by using EtOAc:Petroleum ether as eluent furnished cyclohepta[*b*]indole derivative **8h** (50 mg, 67%) as a sticky solid.



Physical appearance: sticky solid.

R_f: 0.6, (1:9, EtOAc:Petroleum ether).

IR (neat): 3058, 3027, 2922, 1735, 1597, 1582, 1474, 1447, 1376, 1217, 1173, 754 cm^{-1}.

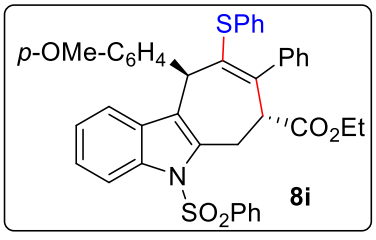
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.35-7.20 (m, 9H), 7.14 (d, *J* = 6.8 Hz, 2H), 7.01 (t, *J* = 7.2 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 2H), 6.70 (t, *J* = 7.6 Hz, 2H), 6.57 (d, *J* = 8.0 Hz, 1H), 5.04 (s, 1H), 4.00 (dd, *J* = 10.4, 5.2 Hz, 1H), 3.69-3.56 (m, 4H), 0.79 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 171.4 (C), 141.7 (C), 141.5 (C), 139.3 (C), 139.2 (C), 138.7 (C), 136.2 (C), 135.4 (C), 134.0 (CH), 133.8 (C), 131.5 (2 × CH), 130.6 (C), 129.4 (3 × CH), 129.0 (CH), 128.9 (2 × CH), 128.7 (2 × CH), 128.0 (2 × CH), 127.9 (CH), 127.1 (CH), 126.8 (CH), 126.6 (2 × CH), 126.4 (2 × CH), 124.9 (CH), 123.9 (CH), 122.1 (C), 118.2 (CH), 114.9 (CH), 60.7 (CH_2), 46.1 (CH), 43.5 (CH), 29.6 (CH_2), 13.6 (CH_3).

HRMS (ESI, M+K^+): m/z calcd. for $C_{40}H_{33}KNO_4S_2$ 694.1483, found 694.1479.

ethyl (7R*,10R*)-10-(4-methoxyphenyl)-8-phenyl-5-(phenylsulfonyl)-9-(phenylthio)-5,6,7,10-tetrahydrocyclohepta[b]indole-7-carboxylate (8i):

The reaction of 3-propargyl-2-alkenyl indole **6i** (102 mg, 0.177 mmol), thiophenol (45 µL, 0.443 mmol) and AIBN (30 mg, 0.177 mmol) in dry toluene (4 mL) as described for compound **8b**, followed by purification of the crude reaction mixture on silica gel column chromatography by using EtOAc:Petroleum ether as eluent furnished cyclohepta[*b*]indole derivative **8i** (76 mg, 62%) as a sticky solid.



Physical appearance: sticky solid.

R_f: 0.6 (1.5:8.5, EtOAc:Petroleum ether).

IR (neat): 2928, 2849, 1733, 1608, 1508, 1453, 1376, 1249, 1175, 756 cm^{-1}.

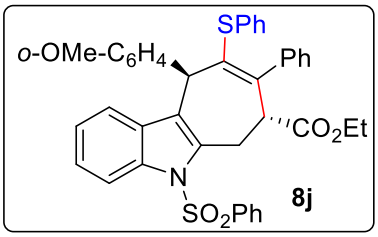
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.48 (t, 8.0 Hz, 2H), 7.36-7.27 (m, 4H), 7.18 (d, *J* = 8.8 Hz, 2H) 7.14 (d, *J* = 7.6 Hz, 2H), 7.01 (t, *J* = 7.2 Hz, 1H), 6.92 (t, *J* = 7.2 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 6.70 (t, *J* = 7.6 Hz, 2H), 6.57 (d, *J* = 7.6 Hz, 1H), 4.99 (s, 1H), 4.07 (dd, *J* = 9.6, 6.4 Hz, 1H), 3.77 (s, 3H), 3.67-3.61 (m, 4H), 0.80 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 171.4 (C), 158.4 (C), 141.6 (C), 139.4 (C), 139.1 (C), 138.6 (C), 136.2 (C), 135.4 (C), 134.0 (CH), 133.9 (C), 133.5(C), 131.4 (2 × CH), 130.6 (C), 129.4 (3 × CH), 129.0 (CH), 128.8 (2 × CH), 127.9 (2 × CH), 127.8 (CH), 127.6 (2 × CH), 127.0 (CH), 126.4 (2 × CH), 124.9 (CH), 123.9 (CH), 122.4 (C), 118.2 (CH), 114.9 (CH), 114.1 (2 × CH), 60.7 (CH_2), 55.4 (CH_3), 46.0 (CH), 42.9 (CH), 29.7 (CH_2), 13.6 (CH_3).

HRMS (ESI, M+K$^+$): m/z calcd. for $C_{41}H_{35}KNO_5S_2$ 724.1588, found 724.1585

ethyl (7R*,10S*)-10-(2-methoxyphenyl)-8-phenyl-5-(phenylsulfonyl)-9-(phenylthio)-5,6,7,10-tetrahydrocyclohepta[b]indole-7-carboxylate (8j):

The reaction of 3-propargyl-2-alkenyl indole **6j** (100 mg, 0.174 mmol), thiophenol (44 µL, 0.435 mmol) and AIBN (28 mg, 0.174 mmol) in dry toluene (12 mL) as described for compound **8b**, followed by purification of the crude reaction mixture on silica gel column chromatography by using EtOAc:Petroleum ether as eluent furnished cyclohepta[*b*]indole derivative **8j** (50 mg, 42%) as a sticky solid.



Physical appearance: sticky solid.

R_f: 0.4 (1:9, EtOAc:Petroleum ether).

IR (neat): 2928, 2850, 1733, 1598, 1583, 1487, 1453, 1374, 1249, 1174, 754 cm^{-1}.

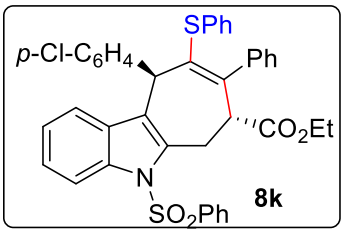
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 (d, *J* = 8.5 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.27-7.19 (m, 5H), 7.06-7.00 (m, 3H), 6.92-6.84 (m, 5H), 6.78-6.73 (m, 4H), 5.24 (s, 1H), 4.29 (dd, *J* = 10.0, 5.0 Hz, 1H), 3.72 (s, 3H), 3.70-3.64 (m, 4H), 0.77 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 171.4 (C), 157.5 (C), 142.2 (C), 140.8 (C), 138.9 (C), 137.6 (C), 136.3 (C), 135.4 (C), 135.4 (C), 133.7 (CH), 131.0 (2 × CH), 130.2 (C), 129.2 (C), 129.2 (2 × CH), 128.6 (CH), 128.5 (3 × CH), 128.2 (CH), 127.7 (2 × CH), 127.3 (CH), 126.3 (3 × CH), 126.2 (CH), 124.5 (CH), 123.5 (CH), 122.5 (C), 120.1 (CH), 118.7 (CH), 114.8 (CH), 111.2 (CH), 60.7 (CH_2), 54.9 (CH_3), 46.2 (CH), 42.2 (CH), 28.7 (CH_2), 13.5 (CH_3).

HRMS (ESI, M+K$^+$): m/z calcd. for $C_{41}H_{35}KNO_5S_2$ 724.1588, found 724.1578.

ethyl (7R*,10R*)-10-(4-chlorophenyl)-8-phenyl-5-(phenylsulfonyl)-9-(phenylthio)-5,6,7,10-tetrahydrocyclohepta[b]indole-7-carboxylate (8k):

The reaction of 3-propargyl-2-alkenyl indole **6k** (87 mg, 0.150 mmol), thiophenol (38 µL, 0.375 mmol) and AIBN (25 mg, 0.150 mmol) in dry toluene (10 mL) as described for compound **8b**, followed by purification of the crude reaction mixture on silica gel column chromatography by using EtOAc:Petroleum ether as eluent furnished cyclohepta[*b*]indole derivative **8k** (60 mg, 58%) sticky solid.



Physical appearance: sticky solid.

R_f: 0.5 (1:9, EtOAc:Petroleum ether).

IR (neat): 2931, 1738, 1448, 1375, 1246, 1176, 755 cm^{-1}.

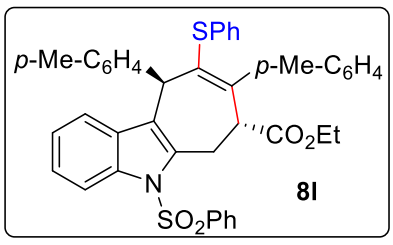
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.36-7.29 (m, 5H), 7.21 (bs, 3H), 7.12 (d, *J* = 7.0 Hz, 2H), 7.02 (t, *J* = 8.0 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 2H), 6.72 (t, *J* = 7.5 Hz, 2H), 6.52 (d, *J* = 7.5 Hz, 1H), 4.97 (s, 1H), 3.92 (dd, *J* = 10.5, 5.5 Hz, 1H), 3.68-3.58 (m, 4H), 0.79 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 171.2 (C), 141.7 (C), 140.2 (C), 139.1 (2 × C), 138.3 (C), 136.2 (C), 135.6 (C), 134.1 (CH), 133.6 (C), 132.7 (C), 131.6 (2 × CH), 130.3 (C), 129.4 (2 × CH), 128.9 (2 × CH), 128.8 (2 × CH), 128.0 (2 × CH), 128.0 (5 × CH), 127.2 (CH), 126.4 (2 × CH), 125.1 (CH), 124.0 (CH), 121.5 (C), 118.0 (CH), 115.0 (CH), 60.9 (CH_2), 46.2 (CH), 43.0 (CH), 29.6 (CH_2), 13.6 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{40}H_{33}ClNO_4S_2$ 690.1497 found 690.1497.

ethyl (7R*,10R*)-5-(phenylsulfonyl)-9-(phenylthio)-8,10-di-p-tolyl-5,6,7,10-tetrahydrocyclohepta[b]indole-7-carboxylate (8l):

The reaction of 3-propargyl-2-alkenyl indole **6l** (52 mg, 0.091 mmol), thiophenol (23 µL, 0.226 mmol) and AIBN (15 mg, 0.091 mmol) in dry toluene (3 mL) as described for compound **8b**, followed by purification of the crude reaction mixture on silica gel column chromatography by using EtOAc:Petroleum ether as eluent furnished the product **8l** (40 mg, 65%) as a sticky solid.



Physical appearance: sticky solid.

R_f: 0.8 (1:9, EtOAc:Petroleum).

IR (neat): 3020, 1735, 1448, 1375, 1174, 754 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.4 Hz, 1H), 7.82 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.59-7.55 (m, 1H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.29 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.16-7.13 (m, 4H), 7.05-6.98 (m, 5H), 6.91 (t, *J* = 7.2 Hz, 1H), 6.82 (dd, *J* = 8.4, 1.2 Hz, 2H), 6.89 (t, *J* = 8.0 Hz, 2H),

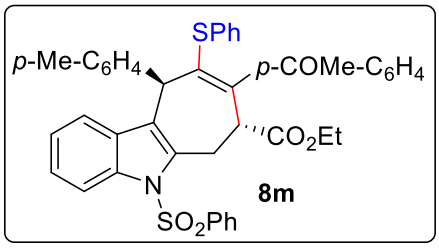
6.56 (d, *J* = 7.6 Hz, 1H), 4.99 (s, 1H), 4.02 (dd, *J* = 10.8, 5.2 Hz, 1H), 3.69-3.59 (m, 4H), 2.34 (s, 3H), 2.30 (s, 3H), 0.82 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 171.5 (C), 141.5 (C), 139.2 (C), 138.6 (C), 138.3 (C), 137.6 (C), 136.4 (C), 136.3 (C), 136.2 (C), 135.4 (C), 134.0 (C), 134.0 (CH), 131.5 (2 × CH), 130.7 (C), 129.4 (4 × CH), 128.9 (CH), 128.8 (2 × CH), 128.7 (2 × CH), 127.0 (CH), 126.5 (2 × CH), 126.4 (3 × CH), 124.8 (CH), 123.9 (CH), 122.4 (C), 118.2 (CH), 114.9 (CH), 60.7 (CH_2), 46.2 (CH), 43.2 (CH), 29.6 (CH_2), 21.5 (CH_3), 21.1 (CH_3), 13.6 (CH_3).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{42}H_{37}NNaO_4S_2$ 706.2056 found 706.2057.

ethyl (7R*,10R*)-8-(4-acetylphenyl)-5-(phenylsulfonyl)-9-(phenylthio)-10-(p-tolyl)-5,6,7,10-tetrahydrocyclohepta[b]indole-7-carboxylate (8m):

The reaction of 3-propargyl-2-alkenyl indole **6m** (63 mg, 0.105 mmol), thiophenol (27 µL, 0.262 mmol) and AIBN (17 mg, 0.105 mmol) in dry toluene (5 mL) as described for compound **8b**, followed by purification of the crude reaction mixture on silica gel column chromatography by using DCM:Petroleum ether as eluent furnished the product **8m** in 63% yield as a sticky solid.



Physical appearance: sticky solid.

R_f: 0.2 (4:6, DCM:Petroleum).

IR (neat): 3018, 2929, 1733, 1683, 1602, 1757 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.31-7.24 (m, 3H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.95 (t, *J* = 7.5 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.74 (t, *J* = 7.5 Hz, 2H), 6.55 (d, *J* = 8.0 Hz, 1H), 5.02 (s, 1H), 4.07 (dd, *J* = 10.5, 6.0 Hz, 1H), 3.68-3.60 (m, 4H), 2.61 (s, 3H), 2.30 (s, 3H), 0.81 (t, *J* = 7.5 Hz, 3H).

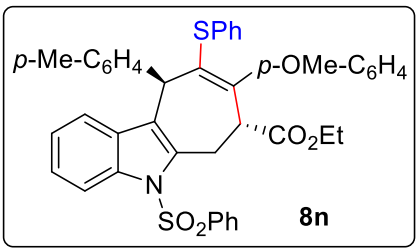
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 197.7 (C), 171.1 (C), 144.4 (C), 140.1 (C), 139.8 (C), 139.2 (C), 138.2 (C), 136.6 (C), 136.3 (C), 136.2 (C), 135.1 (C), 134.0 (CH), 133.3 (C), 131.7 (2 × CH), 130.5 (C), 129.5 (2 × CH), 129.5 (2 × CH), 129.0 (2 × CH), 128.1 (2 × CH), 127.4 (CH), 126.4 (6 × CH), 125.0 (CH), 123.9 (CH), 122.0 (C), 118.2 (CH), 114.9 (CH), 60.9 (CH_2), 45.9 (CH), 43.3 (CH), 29.6 (CH_2), 26.8 (CH_3) 21.1 (CH_3), 13.7 (CH_3).

HRMS (ESI, M+K$^+$): m/z calcd. for $C_{43}H_{37}KNO_5S_2$,750.1745 found 750.1744.

ethyl (7R*,10R*)-8-(4-methoxyphenyl)-5-(phenylsulfonyl)-9-(phenylthio)-10-(p-tolyl)-5,6,7,10-tetrahydrocyclohepta[b]indole-7-carboxylate (8n):

The reaction of 3-propargyl-2-alkenyl indole **6n** (63 mg, 0.107 mmol), thiophenol (27 µL, 0.267 mmol) and AIBN (18 mg, 0.107 mmol) in dry toluene (10 mL) as described for compound **8b**, followed by purification of the crude reaction mixture on silica gel column

chromatography by using EtOAc:Petroleum ether as eluent furnished the product **8n** (39 mg, 52%) as a sticky solid.



Physical appearance: sticky solid.

R_f: 0.2 (4:6, DCM:Petroleum ether).

IR (neat): 3019, 1732, 1508, 1375, 1246, 1177, 756 cm^{-1}.

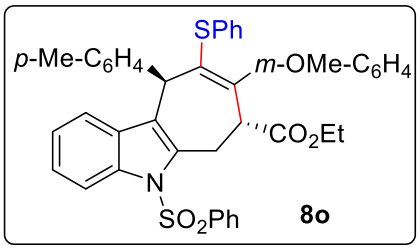
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.10–6.98 (m, 5H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.88–6.83 (m, 4H), 6.70 (t, *J* = 7.6 Hz, 2H), 6.56 (d, *J* = 8.0 Hz, 1H), 4.99 (s, 1H), 4.04–4.00 (m, 1H), 3.81 (s, 3H), 3.66 (q, *J* = 7.2 Hz, 2H), 3.62–3.56 (m, 2H), 2.30 (s, 3H), 0.84 (q, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 171.6 (C), 159.1 (C), 141.0 (C), 139.2 (C), 138.5 (C), 138.5 (C), 136.3 (C), 136.2 (C), 135.4 (C), 134.0 (CH), 131.8 (C), 131.5 (2 × CH), 130.7 (C), 130.2 (CH), 129.4 (6 × CH), 128.8 (2 × CH), 127.0 (C), 126.5 (2 × CH), 126.4 (2 × CH), 124.8 (CH), 123.9 (CH), 122.4 (C), 118.2 (CH), 114.9 (CH), 113.3 (2 × CH), 60.7 (CH_2), 55.3 (CH_3), 46.2 (CH), 43.2 (CH), 29.6 (CH_2), 21.1 (CH_3), 13.7 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{42}H_{38}NO_5S_2$ 700.2179 found 700.2179.

ethyl (7R*,10R*)-8-(3-methoxyphenyl)-5-(phenylsulfonyl)-9-(phenylthio)-10-(p-tolyl)-5,6,7,10-tetrahydrocyclohepta[b]indole-7-carboxylate (8o):

The reaction of 3-propargyl-2-alkenyl indole **6o** (100 mg, 0.169 mmol), thiophenol (43 µL, 0.424 mmol) and AIBN (28 mg, 0.169 mmol) in dry toluene (10 mL) as described for compound **8b**, followed by purification of the crude reaction mixture on silica gel column chromatography by using EtOAc:Petroleum ether as eluent furnished the product **8o** (44 mg, 43%) as a sticky solid.



Physical appearance: sticky solid.

R_f: 0.2 (1:9, EtOAc:Petroleum ether).

IR (neat): 3027, 1738, 1582, 1376, 755 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.31-7.23 (m, 3H), 7.14 (d, *J* = 7.5 Hz, 3H), 7.04 (d, *J* = 8.0 Hz, 2H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.92 (t, *J* = 7.0 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 2H), 6.34-6.68 (m, 2H), 6.56 (d, *J* = 5.7 Hz, 1H), 6.49 (t, *J* = 7.5 Hz, 1H), 4.99 (s, 1H), 4.05-4.02 (m, 1H), 3.83 (s, 3H), 3.68 (q, *J* = 7.0 Hz, 2H), 3.63-3.60 (m, 2H), 2.30 (s, 3H), 0.83 (t, *J* = 7.0 Hz, 3H).

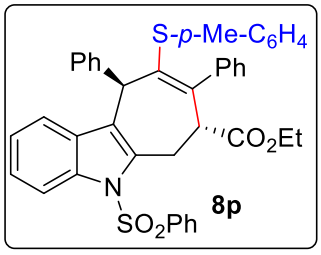
^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 171.3 (C), 159.2 (C), 141.2 (C), 140.6 (C), 139.1 (C), 138.6 (C), 138.5 (C), 136.4 (C), 136.2 (C), 135.4 (C), 134.0 (CH), 134.0 (C), 131.5 (2 × CH),

130.7 (C), 129.4 (3 × CH), 129.4 (2 × CH), 129.0 (CH), 128.8 (2 × CH), 127.0 (CH), 126.5 (2 × CH), 126.4 (3 × CH), 124.9 (CH), 123.9 (CH), 122.3 (C), 118.2 (CH), 114.9 (CH), 112.8 (CH), 60.7 (CH_2), 55.4 (CH_3), 46.1 (CH), 43.2 (CH), 29.6 (CH_2), 21.1 (CH_3), 13.6 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{42}H_{38}NO_5S_2$ is 700.2186 found 700.2186.

ethyl (7R*,10R*)-8,10-diphenyl-5-(phenylsulfonyl)-9-(p-tolylthio)-5,6,7,10-tetrahydrocyclohepta[b]indole-7-carboxylate (8p):

The reaction of 3-propargyl-2-alkenyl indole **6h** (129 mg, 0.236 mmol), 4-methyl thiophenol (73 mg, 0.591 mmol) and AIBN (39 mg, 0.236 mmol) in dry toluene (12 mL) as described for compound **8b**, followed by purification of the crude reaction mixture on silica gel column chromatography by using EtOAc: Petroleum ether as eluent furnished cyclohepta[*b*]indole derivative **8p** (96 mg, 60%) as a sticky solid.



Physical appearance: sticky solid.

R$_f$: 0.5 (4:6, DCM:Petroleum ether).

IR (neat): 3027, 1733, 1491, 1447, 1376, 1174, 756 cm^{-1}.

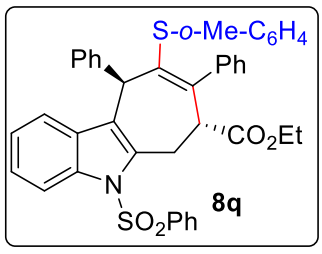
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.36-7.19 (m, 9H), 7.15 (d, *J* = 6.8 Hz, 2H), 7.08-6.97 (m, 2H) 6.77 (d, *J* = 8.0 Hz, 2H), 6.51 (d, *J* = 8.0 Hz, 2H), 5.00 (s, 1H), 3.98 (dd, *J* = 10.8, 5.6, Hz, 1H), 3.66-3.54 (m, 4H), 2.09 (s, 3H), 0.77 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 171.4 (C), 141.9 (C), 140.0 (C), 139.5 (C), 139.3 (C), 139.2 (C), 137.6 (C), 136.1 (C), 135.4 (C), 134.0 (CH), 132.5 (2 × CH), 130.7 (C), 129.9 (C), 129.6 (2 × CH), 129.4 (2 × CH), 129.1 (CH), 128.7 (2 × CH), 127.9 (2 × CH), 127.8 (CH), 126.7 (CH), 126.5 (2 × CH), 126.4 (3 × CH), 124.8 (CH), 123.5 (CH), 122.0 (C), 118.2 (CH), 114.8 (CH), 60.6 (CH_2), 45.9 (CH), 42.9 (CH), 29.6 (CH_2), 21.0 (CH_3), 13.5 (CH_3).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{41}H_{35}NNaO_4S_2$ 692.1900, found 692.1899.

ethyl (7R*,10R*)-8,10-diphenyl-5-(phenylsulfonyl)-9-(o-tolylthio)-5,6,7,10-tetrahydrocyclohepta[b]indole-7-carboxylate (8q):

The reaction of 3-propargyl-2-alkenyl indole **6h** (56 mg, 0.1023 mmol), with 2-methylthiophenol (30 µL, 0.2557 mmol) and AIBN (17 mg, 0.1023 mmol) in dry toluene (8 mL) as described for compound **8b**, followed by purification of crude product on silica gel column chromatography by using EtOAc:Petroleum ether as eluent furnished cyclohepta[*b*]indole derivative **8q** (29 mg, 42%) as a sticky solid.



Physical appearance: sticky solid.

R$_f$: 0.4 (5:5, DCM:Petroleum ether).

IR (neat): 2926, 1733, 1448, 1377, 1217, 1174, 1029, 756 cm^{-1}.

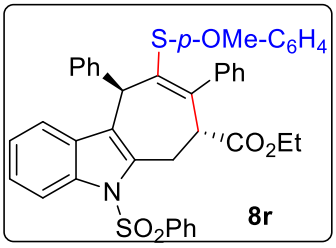
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.35-7.20 (m, 9H), 7.15 (d, *J* = 7.0 Hz, 2H), 6.99-6.90 (m, 3H), 6.77 (d, *J* = 7.5 Hz, 1H), 6.56 (t, *J* = 7.0 Hz, 1H), 6.44 (d, *J* = 7.5 Hz, 1H), 4.90 (s, 1H), 3.97 (dd, *J* = 11.0, 5.0 Hz, 1H), 3.66-3.56 (m, 4H), 1.82 (s, 3H), 0.78 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 171.5 (C), 141.9 (C), 140.9 (C), 139.5 (C), 139.3 (2 × C), 138.9 (C), 136. 0 (C), 135.2 (C), 134.0 (CH), 133.9 (CH), 132.4 (2 × C), 130.6 (2 × CH), 129.4 (2 × CH), 128.9 (CH), 128.7 (2 × CH), 128.2 (CH), 127.9 (2 × CH), 127.9 (CH), 126.7 (CH), 126.6 (2 × CH), 126.5 (2 × CH), 126.4 (CH), 124.9 (CH), 123.8 (CH), 121.3 (C), 118.1 (CH), 114.7 (CH), 60.7 (CH_2), 46.0 (CH), 42.5 (CH), 29.6 (CH_2), 20.5 (CH_3), 13.6 (CH_3).

HRMS (ESI, M+K^+): m/z calcd. for $C_{41}H_{35}KNO_4S_2$, 708.1639, found 708.1639.

ethyl (7R*,10R*)-9-((4-methoxyphenyl)thio)-8,10-diphenyl-5-(phenylsulfonyl)-5,6,7,10-tetrahydrocyclohepta[b]indole-7-carboxylate (8r):

The reaction of 3-propargyl-2-alkenyl indole **6h** (64 mg, 0.117 mmol), with and 4-methoxythiophenol (36 µL, 0.293 mmol) and AIBN (19 mg, 0.117 mmol) in dry toluene (7 mL) as described for compound **8b**, followed by purification of crude product on silica gel column chromatography by using EtOAc:Petroleumether as eluent furnished cyclohepta[*b*]indole derivative **8r** (36 mg, 45%) as a sticky solid.



Physical appearance: sticky solid.

R_f: 0.3 (3:7, DCM:Petroleum ether).

IR (neat): 3024, 2932, 2837, 1732, 1592, 1492, 1376, 1248, 1029, 756 cm^{-1}.

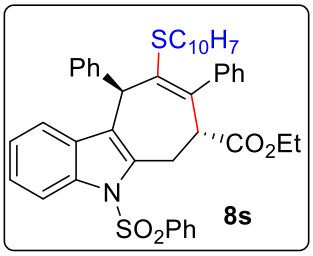
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.34-7.16 (m, 11H), 7.01 (t, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 8.0 Hz, 2H), 6.53 (d, *J* = 8.0 Hz, 1H), 6.25 (d, *J* = 8.0 Hz, 2H), 5.00 (s, 1H), 3.96 (d, *J* = 8.0 Hz, 1H), 3.61-3.55 (m, 6H), 0.75 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 171.5 (C), 159.5 (C), 142.0 (C), 140.1 (C), 139.3 (C), 139.2 (C), 139.0 (C), 136.1 (C), 135.5 (C), 134.7 (2 × CH), 134.0 (CH), 130.9 (C), 129.4 (3 × CH), 128.7 (2 × CH), 128.0 (2 × CH), 127.8 (CH), 126.7 (CH), 126.5 (2 × CH), 126.5 (3 × CH), 124.8 (CH), 123.9 (C), 123.7 (CH), 121.9 (C), 118.1 (CH), 114.8 (CH), 114.5 (2 × CH), 60.7 (CH_2), 55.3 (CH_3), 46.0 (CH), 42.6 (CH), 29.7 (CH_2), 13.6 (CH_3).

HRMS (ESI, M+K^+): m/z calcd. for $C_{41}H_{35}KNO_5S_2$, 724.1588, found 724.1582.

ethyl (7R*,10R*)-9-(naphthalen-1-ylthio)-8,10-diphenyl-5-(phenylsulfonyl)-5,6,7,10-tetrahydrocyclohepta[b]indole-7-carboxylate (8s):

The reaction of 3-propargyl-2-alkenyl indole **6h** (127 mg, 0.233 mmol), napthol (93 mg, 0.582 mmol) and AIBN (38 mg, 0.233 mmol) in dry toluene (12 mL) as described for compound **8b**, followed by purification of crude product on silica gel column chromatography by using EtOAc:Petroleum ether as eluent furnished cyclohepta[*b*]indole derivative **8s** (97 mg, 59%) as a crystalline solid.



Physical appearance: crystalline solid.

MP.: 192-193 ^{o}C.

R*f*: 0.4 (3:7, DCM:Petroleum ether).

IR (neat): 3058, 3028, 1737, 1447, 1376, 1173, 756 cm^{-1}.

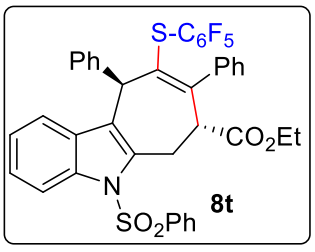
^{1}H NMR (500 MHz, CDCl$_3$): δ 8.27 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 2H), 7.59-7.49 (m, 4H), 7.38-7.15 (m, 15H), 6.89 (dd, *J* = 8.5, 1.5 Hz, 1H), 6.76 (d, *J* = 8.5 Hz, 1H), 6.59 (t, *J* = 7.5 Hz, 1H), 6.28 (d, *J* = 7.5 Hz, 1H), 5.13 (s, 1H), 4.06 (dd, *J* = 13.0, 3.5 Hz, 1H), 3.76-3.61 (m, 4H), 0.80 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, CDCl$_3$, DEPT): δ 171.4 (C), 141.9 (C), 141.7 (C), 139.3 (C), 139.2 (C), 138.5 (C), 136.0 (C), 135.4 (C), 134.1 (CH), 133.5 (C), 132.0 (C), 131.5 (C), 130.5 (C), 130.2 (CH), 129.5 (2 × CH), 129.0 (CH), 128.7 (2 × CH), 128.5 (CH), 128.3 (CH), 128.0 (2 × CH), 127.9 (CH), 127.5 (CH), 127.0 (CH), 126.8 (CH), 126.6 (2 × CH), 126.5 (2 × CH), 126.4 (2 × CH), 126.0 (CH), 124.8 (CH), 123.7 (CH), 121.9 (C), 118.0 (CH), 114.7 (CH), 60.7 (CH_2), 46.2 (CH), 43. 4 (CH), 29.6 (CH_2), 13.6 (CH_3).

HRMS (ESI, M+Na^{+}): m/z calcd. for $C_{44}H_{35}NNaO_4S_2$, 728.1900, found 728.1898.

ethyl (7R*,10R*)-9-((perfluorophenyl)thio)-8,10-diphenyl-5-(phenylsulfonyl)-5,6,7,10-tetrahydrocyclohepta[b]indole-7-carboxylate (8t):

The reaction of 3-propargyl-2-alkenyl indole **6h** (131 mg, 0.240 mmol), with and penta fluorothiophenol (74 µL, 0.600 mmol) and AIBN (39 mg, 0.240 mmol) in dry toluene (12 mL) as described for compound **8b**, followed by purification of crude product on silica gel column chromatography by using EtOAc:Petroleum ether as eluent furnished cyclohepta[*b*]indole derivative **8t** (130 mg, 72%) as a sticky solid and **10t** (19 mg, 11%) as a white solid.



Physical appearance: sticky solid.

R*f*: 0.9 (1:9, EtOAc:Petroleum ether).

IR (neat): 3031, 1738, 1510, 1488, 1449, 1378, 1173, 981, 756 cm^{-1}.

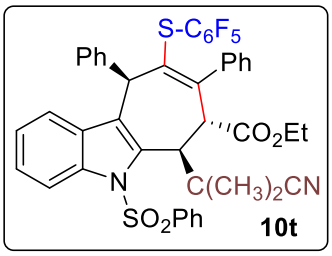
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.2 Hz, 2H), 7.63-7.59 (m, 1H), 7.51 (t, *J* = 8.0 Hz, 2H), 7.37-7.23 (m, 9H), 7.12 (t, *J* = 7.2 Hz, 1H), 7.05 (bs, 2H), 6.74 (d, *J* = 8.0 Hz, 1H), 4.87 (s, 1H), 4.02 (dd, *J* = 13.6, 3.6 Hz, 1H), 3.68-3.59 (m, 3H), 3.45 (dd, *J* = 18.8, 13.6 Hz, 1H), 0.76 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 170.9 (C), 148.5 (2 × C), 145.9 (C), 143.3 (C), 141.0 (C), 139.2 (C), 138.8 (C), 136.1 (C), 135.3 (C), 135.0 (C), 134.0 (CH), 129.7 (C), 129.5 (3 × CH), 129.0 (2 × CH), 128.5 (C), 128.3 (2 × C), 128.1 (CH), 128.1 (2 × CH), 127.2 (CH), 126.6 (3 × CH), 126.4 (2 × CH), 125.3 (CH), 123.7 (CH), 118.9 (C), 116.3 (CH), 115.0 (CH), 107.7 (C), 60.8 (CH_2), 45.8 (CH), 44.5 (CH), 29.0 (CH_2), 13.5 (CH_3).

^{19}F NMR ($CDCl_3$, 470.5 MHz): δ -131.4 (dd, J_{F-F} = 23.5, 4.7 Hz), -151.7 (t, J_{F-F} = 37.0 Hz), -160.9 (td, J_{F-F} = 23.5, 4.7 Hz).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{40}H_{28}F_5NNaO_4S_2$ 768.1272 found 768.1267.

ethyl (6S*,7R*,10R*)-6-(2-cyanopropan-2-yl)-9-((perfluorophenyl)thio)-8,10-diphenyl-5-(phenylsulfonyl)-5,6,7,10-tetrahydrocyclohepta[b]indole-7-carboxylate (10t):



Physical appearance: white solid.

MP.: 212-214 °C.

R_f: 0.8 (1:9, EtOAc:Petroleum ether).

IR (neat): 3012, 1737, 1511, 1488, 1090, 757 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 7.5 Hz, 2H), 7.54 (t, *J* = 7.0 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.39-7.32 (m, 9H), 7.16-7.10 (m, 2H), 6.79 (d, *J* = 7.5 Hz, 1H), 5.01-4.97 (m, 2H), 4.32 (d, *J* = 10.5 Hz, 1H), 3.76-3.65 (m, 2H), 1.32 (s, 3H), 1.24 (s, 3H), 0.96 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 171.2 (C), 147.9 (2 × C), 145. (C), 140.0 (C), 139.7 (C), 139.2 (C), 138.7 (C), 138.5 (C), 136.5 (2 × C), 135.9 (C), 134.9 (C), 134.0 (CH), 130.6 (C), 129.4 (2 × CH), 129.3 (3 × CH), 128.1 (CH), 128.0 (3 × CH), 127.9 (CH), 127.6 (2 × CH), 127.4 (C), 127.0 (2 × CH), 126.0 (CH), 124.3 (CH), 117.2 (CH), 116.5 (CH). 61.6 (CH_2), 51.9 (CH), 45.3 (CH), 43.6 (CH), 39.3 (C), 27.4 (CH_3), 27.2 (CH_3), 13.7 (CH_3).

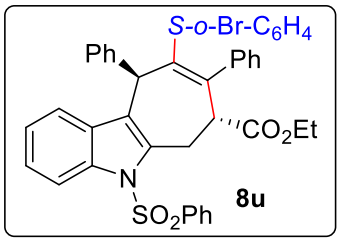
^{19}F NMR ($CDCl_3$, 376.5 MHz): δ -131.0 (dd, J_{F-F} = 22.6, 7.5 Hz), -151.8 (t, J_{F-F} = 22.6 Hz), -160.7 (td, J_{F-F} = 26.4, 7.53 Hz).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{44}H_{34}F_5N_2O_4S_2$ 813.1875 found 813.1871.

ethyl (7R*,10R*)-9-((2-bromophenyl)thio)-8,10-diphenyl-5-(phenylsulfonyl)-5,6,7,10-tetrahydrocyclohepta[b]indole-7-carboxylate (8u):

The reaction of 3-propargyl-2-alkenyl indole **6h** (53 mg, 0.097 mmol), 2-bromothiophenol (29 µL, 0.242 mmol) and AIBN (16 mg, 0.097 mmol) in dry toluene (7 mL) as described for

compound **8b**, followed by purification of crude product on silica gel column chromatography by using EtOAc:Petroleum ether as eluent furnished cyclohepta[*b*]indole derivative **8u** (30 mg, 42%) and **10u** (23 mg, 30%) as a pale yellow solid.



Physical appearance: pale yellow solid.

MP.: 190-192 ºC.

R*f*: 0.3 (1:9, EtOAc:Petroleum ether).

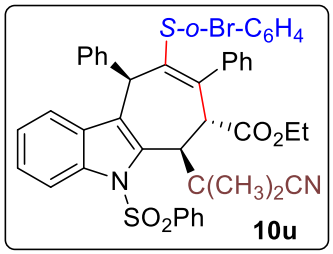
IR (neat): 3059, 1737, 1447, 1376, 1174, 754 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.35-7.30 (m, 4H), 7.28-7.21 (m, 6H), 7.14-7.12 (m, 2H), 7.01 (t, *J* = 8.0 Hz, 1H), 6.79-6.73 (m, 2H), 6.62 (d, *J* = 8.0 Hz, 1H), 6.35 (t, *J* = 8.0 Hz, 1H), 4.94 (s, 1H), 4.02 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.68-3.57 (m, 4H), 0.78 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 171.3 (C), 143.1 (C), 141.5 (C), 139.4 (C), 139.2 (C), 137.6 (C), 136.2 (C), 135.4 (C), 135.3 (C), 134.0 (CH), 133.3 (CH), 133.0 (CH), 130.5 (C), 129.5 (3 × CH), 128.8 (2 × CH), 128.4 (CH), 128.0 (CH), 128.0 (2 × CH), 127.5 (CH), 126.9 (CH), 126.7 (2 × CH), 126.6 (3 × CH), 126.2 (C), 125.0 (CH), 123.9 (CH), 121.6 (C), 118.1 (CH), 114.9 (CH), 60.8 (CH_2), 46.2 (CH), 44.0 (CH), 29.5 (CH_2), 13.6 (CH_3).

HRMS (ESI, M+2): m/z calcd. for $C_{40}H_{33}BrNO_4S_2$ 736.1006 found 736.1006.

ethyl (6S*,7R*,10R*)-9-((2-bromophenyl)thio)-6-(2-cyanopropan-2-yl)-8,10-diphenyl-5-(phenylsulfonyl)-5,6,7,10-tetrahydrocyclohepta[b]indole-7-carboxylate (10u):



Physical appearance: pale yellow solid.

MP.: 241-243 ºC.

R*f*: 0.6 (1:9, EtOAc:Petroleum ether).

IR (neat): 3059, 1738, 1446, 1376, 1186, 754 cm^{-1}.

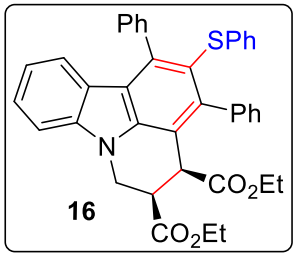
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.41-7.35 (m, 9H), 7.30-7.26 (m, 5H), 7.06 (t, *J* = 8.0 Hz, 1H), 6.77-6.71 (m, 2H), 6.17 (d, *J* = 4.0 Hz, 1H), 5.91 (t, *J* = 8.0 Hz, 1H), 5.13 (d, *J* = 12.0 Hz, 1H), 5.00 (s, 1H), 4.31 (d, *J* = 12.0 Hz, 1H), 3.72-3.57 (m, 2H), 1.38 (s, 3H), 1.06 (s, 3H), 0.96 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 171.5 (C), 141.5 (C), 140.5 (C), 139.6 (C), 138.9 (C), 138.0 (C), 136.3 (C), 135.3 (C), 134.9 (C), 134.1 (CH), 133.2 (CH), 132.7 (CH), 131.7 (C), 130.9 (C), 129.3 (3 × CH), 129.2 (2 × CH), 128.2 (CH), 128.0 (CH), 127.8 (2 × CH), 127.6 (CH), 127.4 (CH), 127.2 (2 × CH), 127.1 (3 × CH), 125.8 (CH), 125.7 (C), 124.7 (CH), 124.4 (C), 118.8 (CH), 116.7 (CH), 61.4 (CH_2), 51.6 (CH), 43.9 (CH), 43.8 (CH), 39.3 (C), 27.6 (CH_3), 26.5 (CH_3), 13.6 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{44}H_{38}BrN_2O_4S_2$ 801.1451, found 801.1466.

diethyl (4S*,5R*)-1,3-diphenyl-2-(phenylthio)-5,6-dihydro-4H-pyrido[3,2,1-jk]carbazole-4,5-dicarboxylate (16):

Oven dried two necked RB was charged with indole derivative **15** (80 mg, 0.159 mmol) under nitrogen atmosphere then toluene (3 mL) was added to this. In another RB a solution of thiophenol (48 µL, 0.476 mmol) and AIBN (34 mg, 0.207 mmol) in toluene (10 mL) was prepared. Then solution of indole derivative was kept at 110 ^oC and to this a solution of thiophenol and AIBN in toluene was added dropwise over a period of 2h by using syringe pump. After the completion of reaction (monitored by TLC), solvent was evaporated under reduced pressure and the crude reaction mixture was subjected to purification by silica gel column chromatography using CH_2Cl_2:Petroleum ether (20:80) as eluent furnished dihydropyrrole **16 (**49 mg, 50%) as a sticky solid.



Physical appearance: sticky solid.

R$_f$: 0.4 (3:7, DCM:Petroleum ether).

IR (neat): 3022, 2933, 1734, 1475, 1373, 1216, 1025, 755 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45-7.37 (m, 5H), 7.34-7.33 (m, 1H), 7.30-7.27 (m, 3H), 7.24-7.21 (m, 1H), 7.11 (d, *J* = 7.5 Hz, 1H), 7.07-7.06 (m, 1H), 6.98-6.91 (m, 4H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 7.5 Hz, 2H), 4.65 (dd, *J* = 17.5, 5.0 Hz, 1H), 4.84 (t, *J* = 12.0 Hz, 1H), 4.32 (d, *J* = 3.0 Hz, 1H), 4.29-4.20 (m, 2H), 4.05-3.93 (m, 2H), 3.34 (dt, *J* = 12.0, 4.5 Hz, 1H), 1.30 (t, *J* = 7.5 Hz, 3H), 1.11 (t, *J* = 7. Hz, 3H).

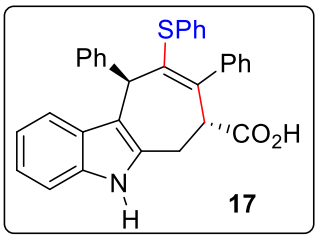
^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 171.3 (C), 170.9 (C), 144.0 (C), 143.0 (C), 141.3 (2 × C), 140.6 (C), 139.9 (C), 139.0 (C), 137.3 (C), 130.6 (CH), 129.12 (CH), 129.11 (CH), 129.06 (CH), 128.3 (CH), 128.2 (C), 128.1 (2 × CH), 127.7 (CH), 127.6 (CH), 127.4 (CH), 127.2 (CH), 126.8 (2 × CH), 126.2 (CH), 124.5 (CH), 123.0 (CH), 122.7 (CH), 120.9 (C), 120.7 (C), 119.8 (CH), 115.7 (CH), 108.6 (CH), 61.6 (CH_2), 61.4 (CH_2), 42.7 (CH), 41.9 (CH), 39.6 (CH_2), 14.3 (CH_3), 14.1 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{39}H_{34}NO_4S$ 612.2203 found 612.2210.

(7R*,10R*)-8,10-diphenyl-9-(phenylthio)-5,6,7,10-tetrahydrocyclohepta[b]indole-7-carboxylic acid (17):

To a solution of compound **8h** (123 mg, 0.187 mmol) in EtOH:H_2O (1:1) (16 mL) was added 10% NaOH solution and reaction mixture was allowed to reflux for overnight. After the completion of reaction, the solution was neutralized with dilute HCl and extracted with EtOAc,

dried over anhydrous Na_2SO_4 and combine organic layer was evaporated under reduced pressure. The crude reaction mixture was subjected to purification using silica gel column chromatography to furnish product **17** (67 mg, 73%) as a sticky solid.



Physical appearance: sticky solid.

R_f: 0.1 (2:8, EtOAc:Petroleum ether).

IR (neat): 3395, 3058, 2919, 1712, 1460, 1218, 755 cm^{-1}.

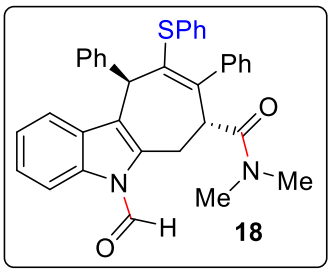
^{1}H NMR (100 MHz, $CDCl_3$): δ 7.99 (bs, 1H), 7.42 (d, *J* = 6.8 Hz, 2H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.27-7.14 (m, 8H), 7.12-7.06 (m, 4H), 6.95 (t, *J* = 7.6 Hz, 3H), 6.80 (d, *J* = 7.6 Hz, 1H), 5.24 (s, 1H), 4.13 (d, *J* = 12.8 Hz, 1H), 3.39 (t, *J* = 14.8 Hz, 1H), 3.14 (d, *J* = 17.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 176.1 (C), 143.4 (C), 140.9 (C), 139.3 (C), 137.9 (C), 134.9 (C), 133.8 (C), 133.0 (C), 132.0 (3 × CH), 129.2 (CH), 129.0 (3 × CH), 128.6 (C), 128.5 (2 × CH), 128.1 (2 × CH), 127.8 (CH), 127.2 (CH), 126.8 (2 × CH), 126.5 (CH), 121.8 (CH), 119.7 (CH), 118.1 (CH), 112.6 (C), 110.3 (CH), 46.1 (CH), 42.8 (CH), 27.6 (CH_2).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{32}H_{26}NO_2S$ 488.1679 found 488.1677.

(7R*,10R*)-5-formyl-N,N-dimethyl-8,10-diphenyl-9-(phenylthio)-5,6,7,10-tetrahydrocyclohepta[b]indole-7-carboxamide(18):

To a solution of compound **17** (55 mg, 0.113 mmol) in dry CH_2Cl_2 (4 mL) was added oxalyl chloride (49 µL, 0.564 mmol), a drop of DMF (7 µL) at 0 ^{o}C and reaction mixture was allowed to stirred at room temperature for 2 h. After the completion of reaction solvent was evaporated using vacuum pump under N_2 condition. The residue was dissolved in dry CH_2Cl_2 (4 mL) and to this $AlCl_3$ (30 mg, 0.225) was added at 0 ^{o}C, reaction mixture was allowed to stirred overnight. After the completion solvent was evaporate under reduce pressure and crude reaction mixture was subjected to purification using silica gel column chromatography to furnish **18** (30 mg, 49%) as a sticky solid.



Physical appearance: sticky solid.

R_f: 0.2 (2:8, EtOAc:Petroleum ether).

IR (neat): 3027, 2930, 1703, 1650, 1460, 1359, 750 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.47 (s, 1H), 8.44 (bs, 1H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.36-7.27 (m, 6H), 7.24-7.22 (m, 3H), 7.15 (d, *J* = 7.2 Hz, 2H), 7.07-7.01 (m, 2H), 6.93 (t, *J* = 7.6 Hz, 2H), 6.55 (d, *J* = 8.0 Hz, 1H), 5.19 (s, 1H), 4.20 (dd, *J* = 12.4, 2.8 Hz, 1H), 3.72 (t, *J* = 17.2 Hz, 1H), 3.44 (d, *J* = 16.8 Hz, 1H), 2.39 (s, 3H), 2.08 (s, 3H).

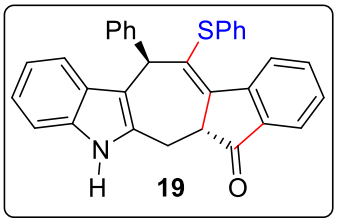
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 170.7 (C), 158.6 (CH), 141.6 (C), 140.4 (C), 139.2 (C), 138.3 (C), 134.2 (C), 133.3 (C), 132.4 (2 × CH), 130.0 (C), 129.2 (3 × CH), 128.6 (4 ×

CH), 128.2 (CH), 127.9 (CH), 127.7 (CH), 127.2 (3 × CH), 127.0 (CH), 125.3 (CH), 124.3 (CH), 118.7 (C). 117.8 (CH), 115.9 (C), 43.7 (CH), 42.8 (CH), 35.9 (CH_3), 35.3 (CH_3), 28.6 (CH_2).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{35}H_{31}N_2O_2S$ 543.2092 found 543.2091.

ethyl 2-((1R*,3R*,E)-4-methyl-2-((phenylthio)methylene)-1-(p-tolyl)-1,2,3,4-tetrahydrocyclopenta[b]indol-3-yl)acetate (19):

To a solution of compound **17** (110 mg, 0.226 mmol) in dry CH_2Cl_2 (6 mL) was added oxalyl chloride (97 µL, 1.129 mmol) at 0 °C and reaction mixture was allowed to stirred at room temperature for 2 h. After the completion of reaction solvent was evaporated using vacuum pump under N_2 condition. The residue was dissolved in dry CH_2Cl_2 (5 mL) and to this $AlCl_3$ (60 mg, 0.452) was added at 0 °C, reaction mixture was allowed to stirred for 20 mint. After the completion solvent was evaporate under reduce pressure and crude reaction mixture was subjected to purification using silica gel column chromatography to furnish **19** (20 mg, 19%) as a sticky solid.



Physical appearance: sticky solid.

R_f: 0.5 (3:7, EtOAc:Petroleum ether).

IR (neat): 3222, 3059, 2932, 1660, 1473, 1452, 755 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.18 (bs, 1H), 8.03-8.01 (m, 1H), 7.45 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.36 (d, *J* = 4.0 Hz, 2H), 7.33-7.30 (m, 2H), 7.22-7.19 (m, 5H), 7.11-7.01 (m, 4H), 6.95-6.92 (m, 1H), 6.84-6.82 (m, 2H), 4.95 (dd, *J* = 8.0, 4.0 Hz, 1H), 4.55 (s, 1H), 3.48 (dd, *J* = 20.0, 8.0 Hz, 1H), 3.35 (dd, *J* = 20.0, 4.0 Hz, 1H).

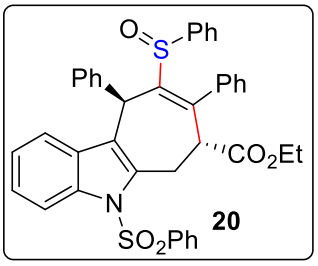
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 194.2 (C), 165.1 (C), 148.8 (C), 145.7 (C), 143.1 (C), 142.1 (C), 141.7 (C), 139.2 (C), 135.5 (C), 130.8 (2 × CH), 129.1 (2 × CH), 128.74 (C), 128.7 (2 × CH), 128.6 (2 × CH), 127.2 (CH), 127.1 (CH), 126.9 (CH), 126.4 (CH), 124.5 (CH), 124.3 (CH), 122.8 (CH), 121.7 (C), 121.4 (CH), 119.7 (CH), 112.2 (CH), 57.8 (CH), 51.9 (CH), 28.3 (CH_2).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{32}H_{24}NOS$ 470.1573 found 470.1575.

ethyl (7R*,10R*)-8,10-diphenyl-9-(phenylsulfinyl)-5-(phenylsulfonyl)-5,6,7,10-tetrahydrocyclohepta[b]indole-7-carboxylate (20):

To a solution of compound **8h** (35 mg, 0.053 mmol) in CH_2Cl_2 (1 mL), was added *m*-CPBA (14 mg, 0.053 mmol) at 0 °C and reaction mixture was allowed to stir for 1 h. After the completion of starting material (monitored by TLC), the reaction quenched with saturated solution of $NaHCO_3$ at 0 °C and extract with CH_2Cl_2 (3 × 20 mL). The combine organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure, crude product was

subjected to purification by silica gel column chromatography to by using EtOAc:Petroleum ether (30:70) as eluent to furnished the product **20** (20 mg, 56%) as a white sticky solid.



Physical appearance: white sticky solid.

R_f: 0.2 (2:8, EtOAc:Petroleum ether).

IR (neat): 3022, 1737, 1599, 1447, 1375, 1174, 755, cm^{-1}.

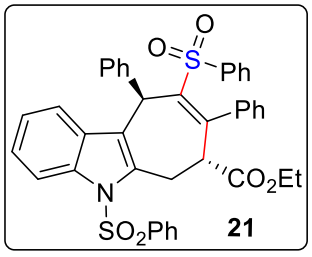
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.43-7.35 (m, 5H), 7.25-7.18 (m, 6H), 7.08-7.05 (m, 2H), 7.01 (t, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.74-6.72 (m, 3H), 5.20 (s, 1H), 4.03 (dd, *J* = 16.0, 4.0 Hz, 1H), 3.68-3.46 (m, 4H), 0.68 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 170.4 (C),149.8 (C), 147.8 (C), 142.0 (C), 141.1 (C), 139.3 (C), 136.3 (C), 135.5 (C), 134.3 (C), 134.1 (CH), 129.8 (CH), 129.5 (2 × CH), 129.3 (C), 128.8 (CH), 128.7 (2 × CH), 128.6 (2 × CH), 128.4 (2 × CH), 127.3 (2 × CH), 126.9 (CH), 126.6 (3 × CH), 124.8 (CH), 123.9 (2 × CH), 123.5 (CH), 120.2 (CH), 118.3 (CH), 114.4 (CH), 61.0 (CH_2), 45.6 (CH), 35.1 (CH), 28.6 (CH_2), 13.4 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{40}H_{34}NO_5S_2$ 672.1858 found 672.1858.

ethyl (7R*,10R*)-8,10-diphenyl-5,9-bis(phenylsulfonyl)-5,6,7,10-tetrahydrocyclohepta[b]indole-7-carboxylate (21):

To a solution of compound **8h** (35 mg, 0.053 mmol) in CH_2Cl_2 (1 mL), was added *m*-CPBA (28 mg, 0.106 mmol) at 0 ^oC and reaction mixture was allowed to stir for 1 h. After the completion of starting material (monitored by TLC), the reaction quenched with saturated solution of $NaHCO_3$ at 0 ^oC and extract with CH_2Cl_2 (3 × 20 mL). The combine organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure, crude product was subjected to purification by silica gel column chromatography to by using EtOAc:Petroleum ether (30:70) as eluent to furnished the product **21** (29 mg, 80%) as a white sticky solid.



Physical appearance: white sticky solid.

R_f: 0.2 (2:8, EtOAc:Petroleum ether).

IR (neat): 2925, 2850, 1742, 1598, 1446, 1303, 1144, 755 cm^{-1}.

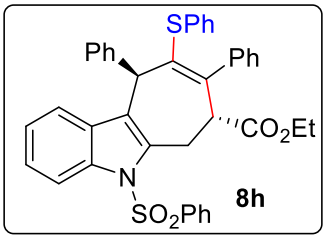
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 8.4 Hz, 1H), 7.82 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.65 (tt, *J* = 8.0, 7.6 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 2H), 7.41-7.37 (m, 2H), 7.34-7.29 (m, 6H), 7.28-7.19 (m, 5H), 7.12 (dd, *J* = 8.4, 1.2 Hz, 2H), 6.96 (t, *J* = 7.6 Hz, 2H), 6.41 (d, *J* = 5.6 Hz, 1H), 6.04 (s, 1H), 4.10 (dd, *J* = 13.6, 3.6 Hz, 1H), 3.63-3.55 (m, 2H), 3.51-3.52 (m, 2H), 0.80 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 169.8 (C), 150.7 (C), 146.2 (C), 140.7 (C), 140.5 (C), 139.3 (C), 135.8 (C), 135.1 (C), 134. 5 (C), 134.1 (CH), 132.6 (CH), 130.4 (C), 129.6 (2 × CH), 129.0 (2 × CH), 128.5 (4 × CH), 128.45 (CH), 127.3 (2 × CH), 127.2 (CH), 126.9 (2 × CH), 126.5 (4 × CH), 125. 4 (CH), 124.2 (CH), 119.5 (C), 118.4 (CH), 114.7 (CH), 61.0 (CH_2), 47.0 (CH), 38.8 (CH), 27.7 (CH_2), 13.5 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{40}H_{34}NO_6S_2$ 688.1822 found 688.1831.

ethyl (7R*,10R*)-8,10-diphenyl-5-(phenylsulfonyl)-9-(phenylthio)-5,6,7,10-tetrahydrocyclohepta[b]indole-7-carboxylate (8h): (Gram scale synthesis)

The reaction of 3-propargyl-2-alkenyl indole **6h** (1.0 g, 1.832 mmol), thiophenol (466 µL, 4.580 mmol) and AIBN (300 mg, 1.832 mmol) in dry toluene (60 mL) as described for compound **8b**, followed by purification of the crude reaction mixture on silica gel column chromatography by using EtOAc:Petroleum ether as eluent furnished cyclohepta[*b*]indole derivative **8h** (787 mg, 66%) as a sticky solid.



Physical appearance: sticky solid.

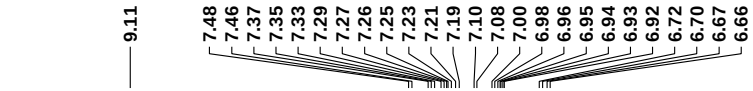
R_f: 0.6, (1:9, EtOAc:Petroleum ether).

IR (neat): 3058, 3027, 2922, 1735, 1597, 1582, 1474, 1447, 1376, 1217, 1173, 754 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.34-7.20 (m, 9H), 7.14 (d, *J* = 6.4 Hz, 2H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 2H), 6.70 (t, *J* = 6.8 Hz, 2H), 6.57 (d, *J* = 7.6 Hz, 1H), 5.04 (s, 1H), 4.00 (dd, *J* = 11.5, 10 Hz, 1H), 3.69-3.58 (m, 4H), 0.79 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 171.4 (C), 141.7 (C), 141.5 (C), 139.3 (C), 139.2 (C), 138.7 (C), 136.2 (C), 135.4 (C), 134.0 (CH), 133.8 (C), 131.5 (2 × CH), 130.6 (C), 129.4 (3 × CH), 129.0 (CH), 128.9 (2 × CH), 128.7 (2 × CH), 128.0 (2 × CH), 127.9 (CH), 127.1 (CH), 126.8 (CH), 126.6 (2 × CH), 126.4 (2 × CH), 124.9 (CH), 123.9 (CH), 122.1 (C), 118.2 (CH), 114.9 (CH), 60.7 (CH_2), 46.1 (CH), 43.5 (CH), 29.6 (CH_2), 13.6 (CH_3).

HRMS (ESI, M+K$^+$): m/z calcd. for $C_{40}H_{33}KNO_4S_2$ 694.1483, found 694.1479.



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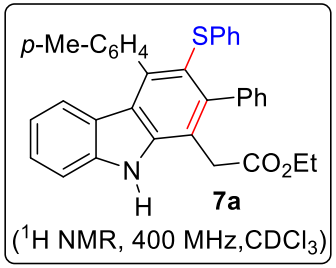

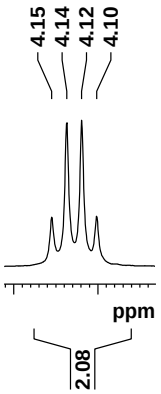

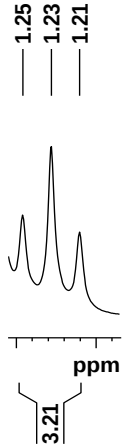

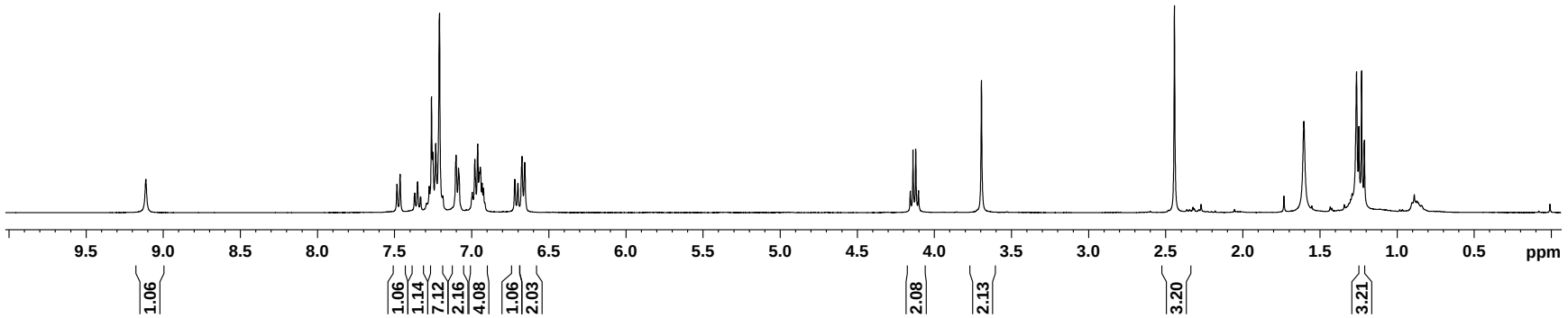

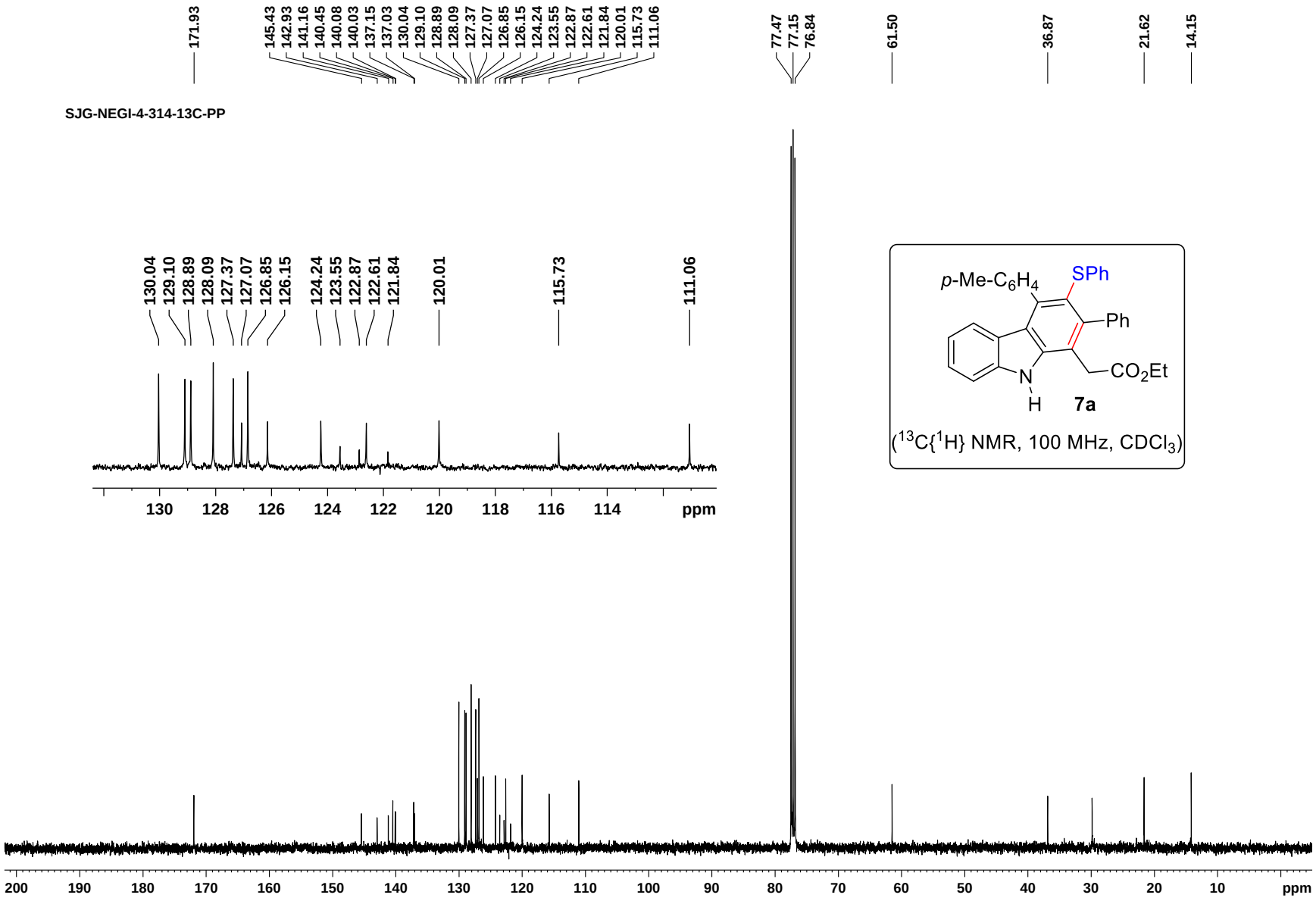
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76.84
61.50
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14.15
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126
124
122
120
118
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114
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Ph
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7a
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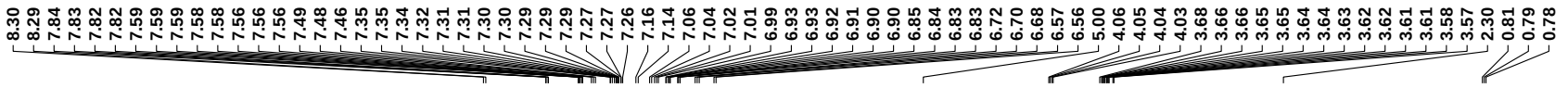
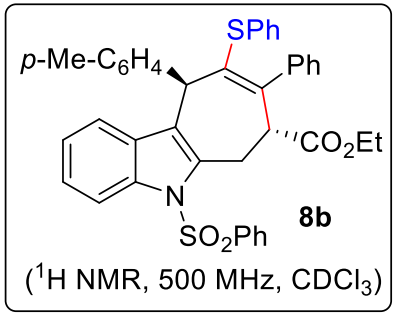
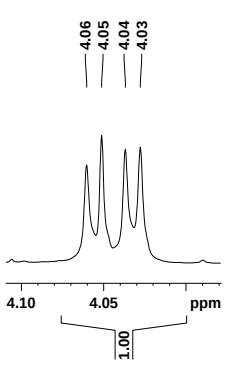
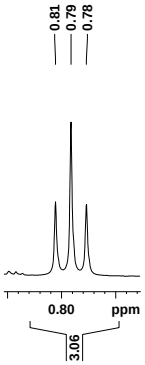
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

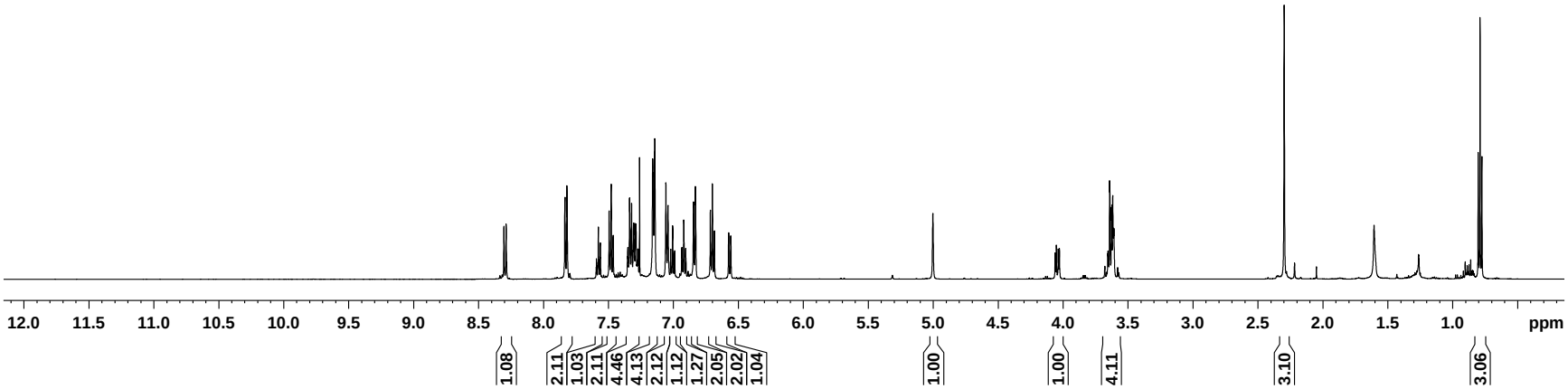


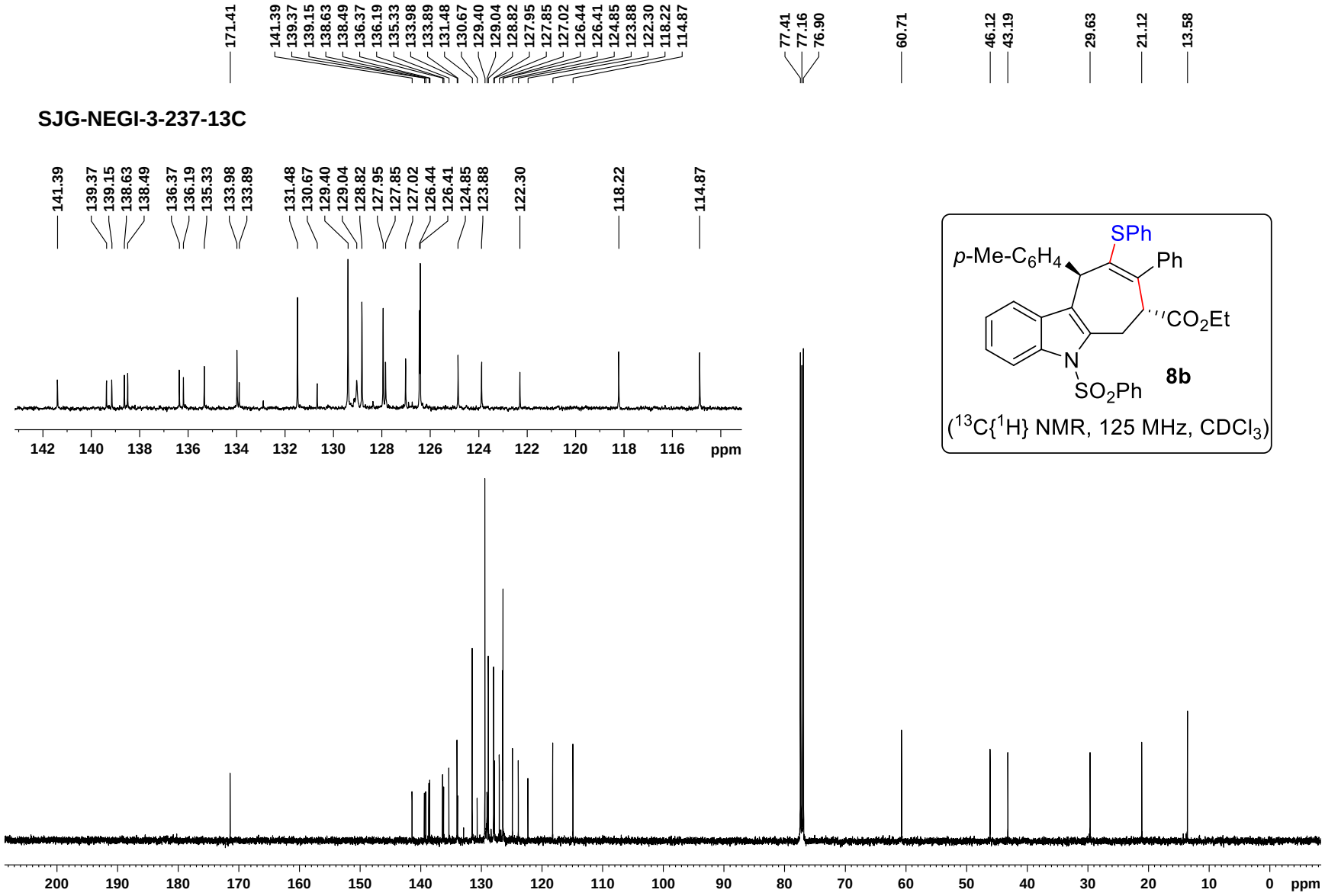
SJG-NEGI-3-237-1H,

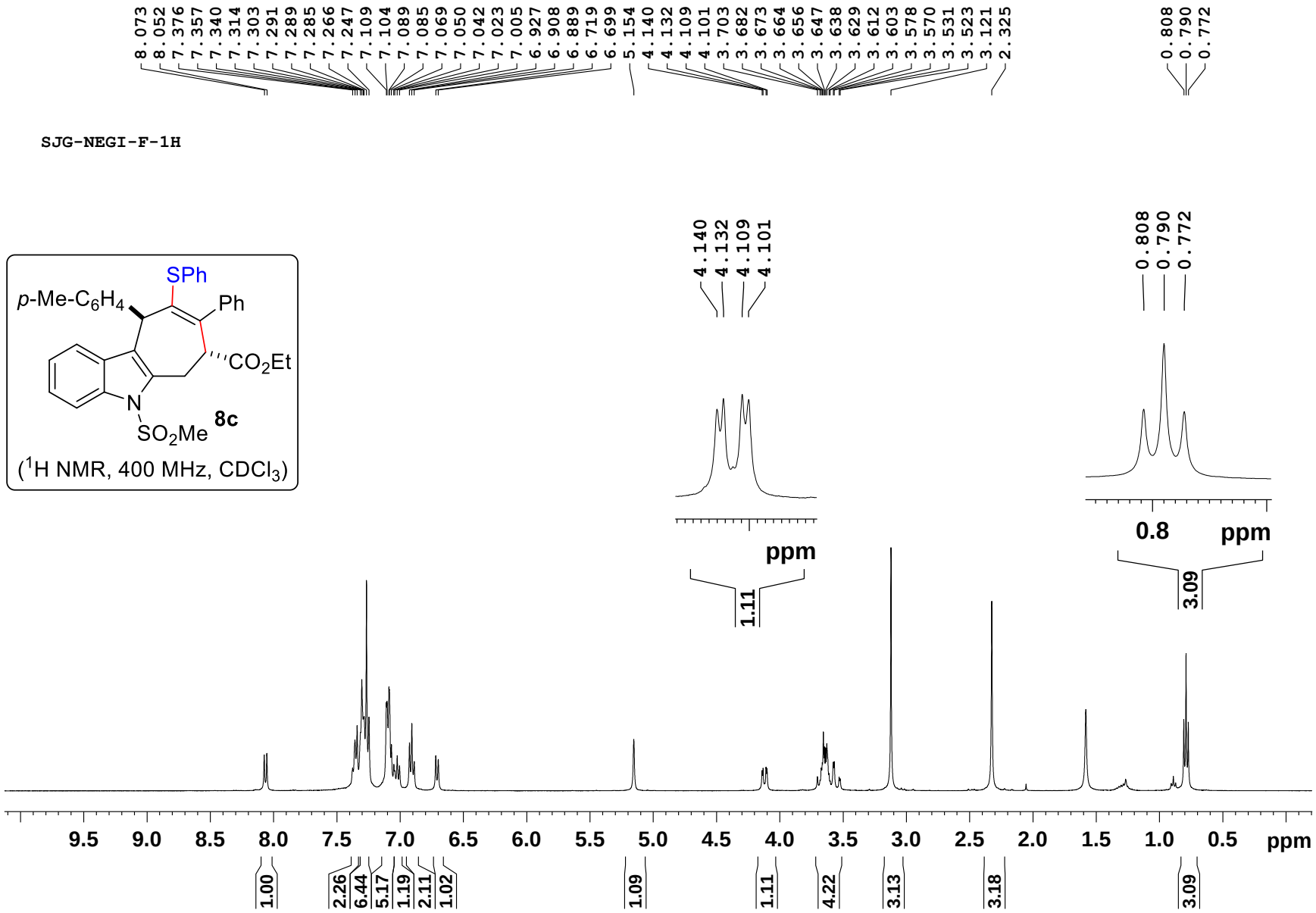


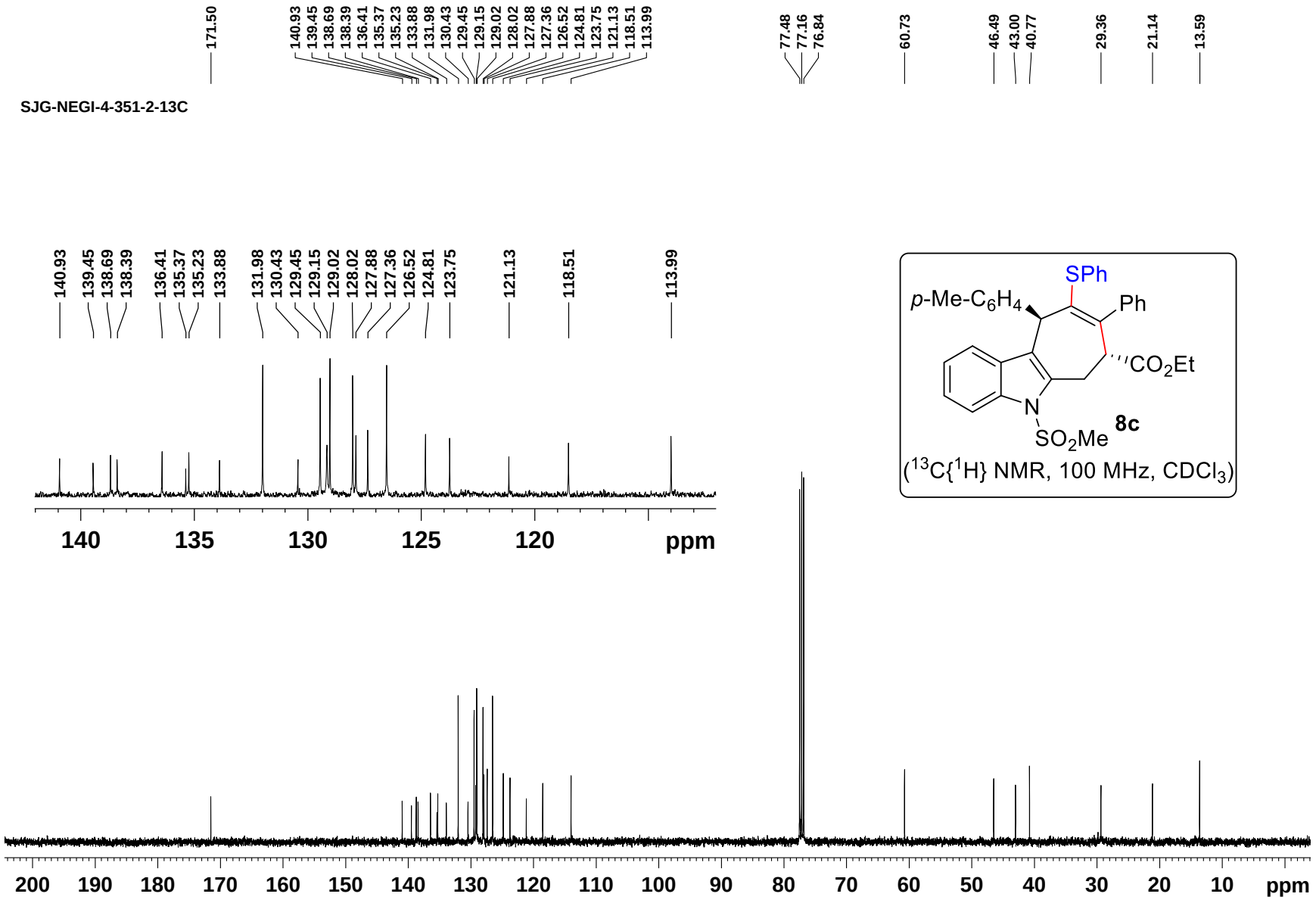




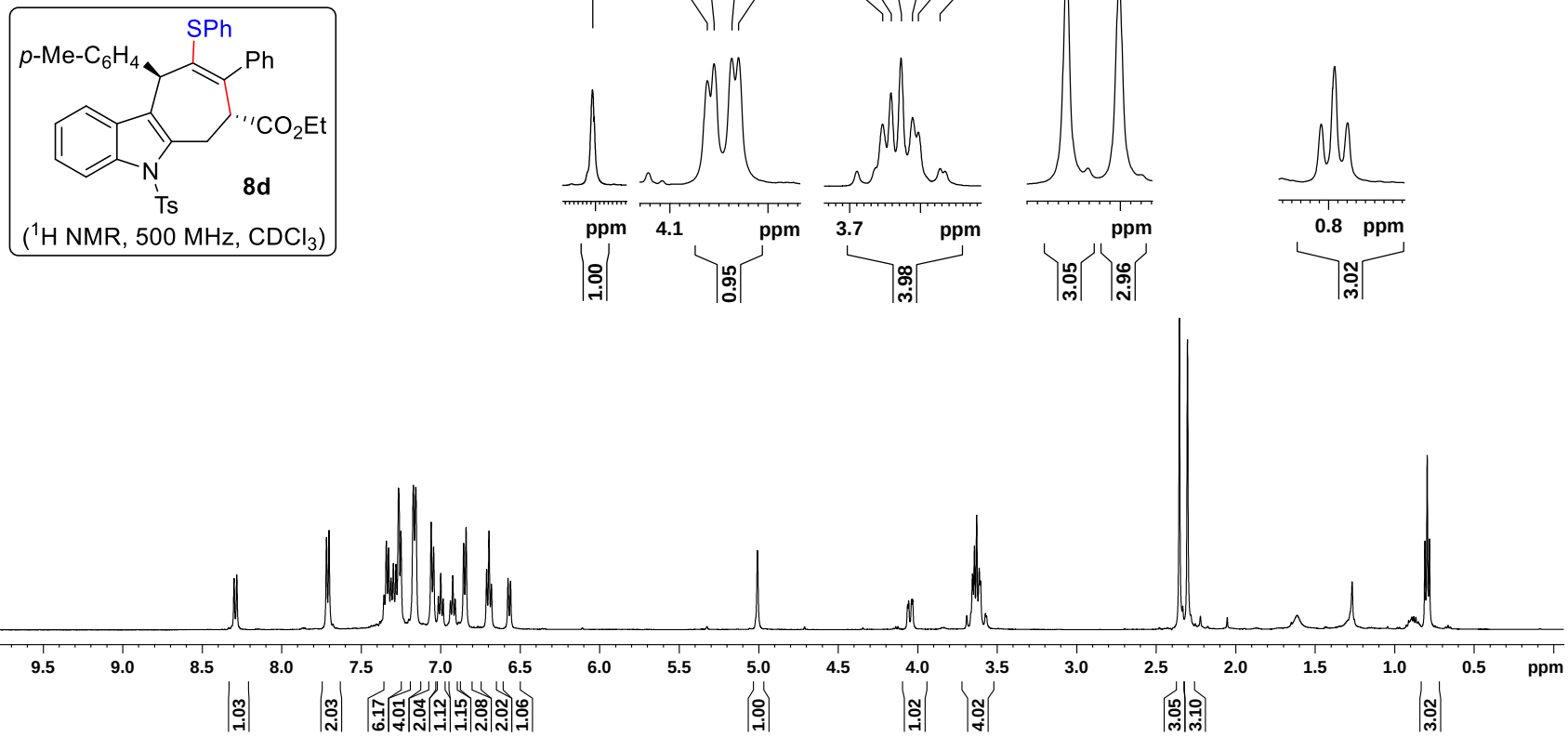


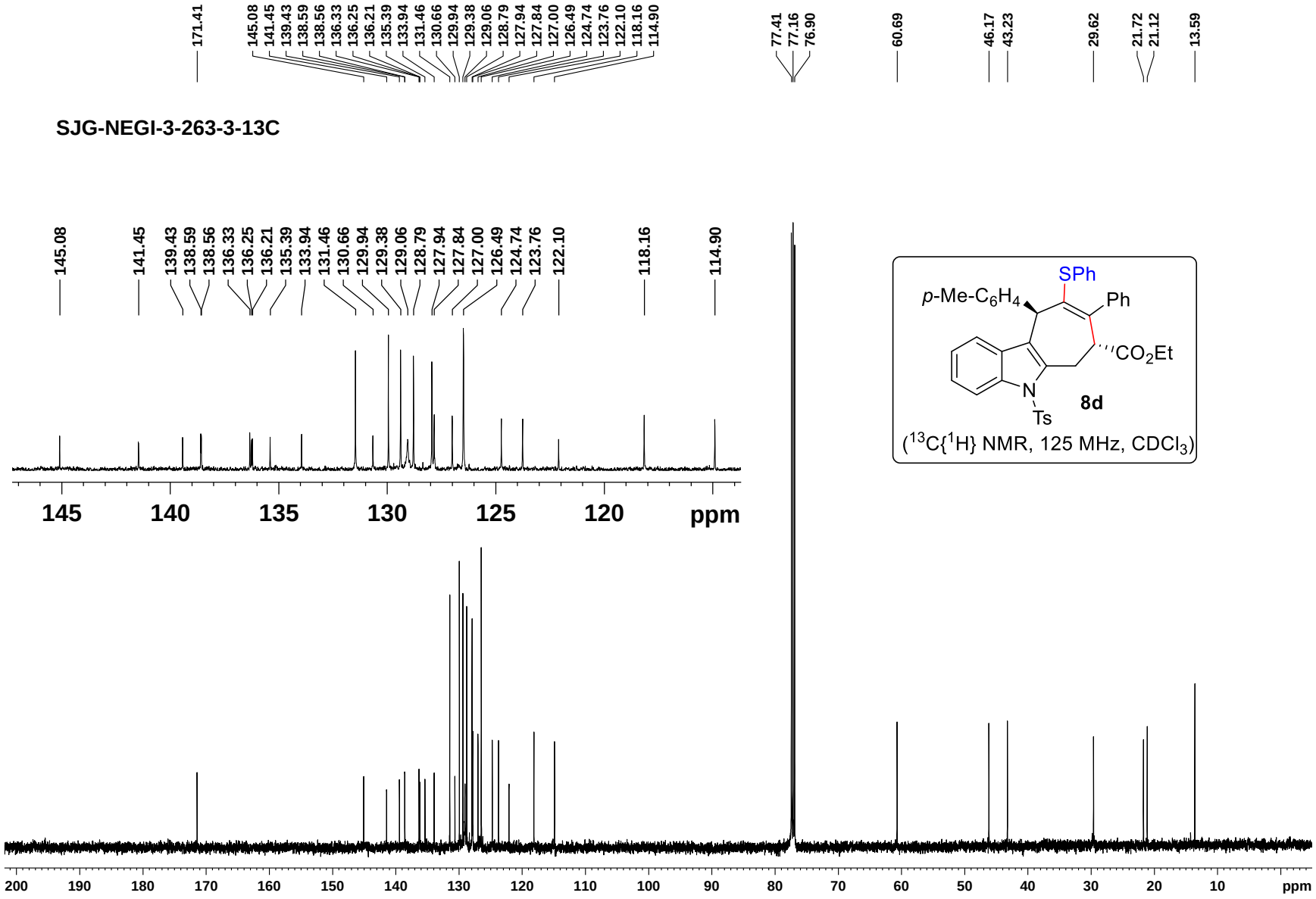

171.41
141.39
139.37
139.15
138.63
138.49
136.37
136.19
135.33
133.98
133.89
131.48
130.67
129.40
129.04
128.82
127.95
127.85
127.02
126.44
126.41
124.85
123.88
122.30
118.22
114.87
77.41
77.16
76.90
60.71
46.12
43.19
29.63
21.12
13.58
SJG-NEGI-3-237-13C
SPh
p-Me-C6H4
Ph
CO2Et
N
SO2Ph
8b
(13C{1H} NMR, 125 MHz, CDCl3)
ppm

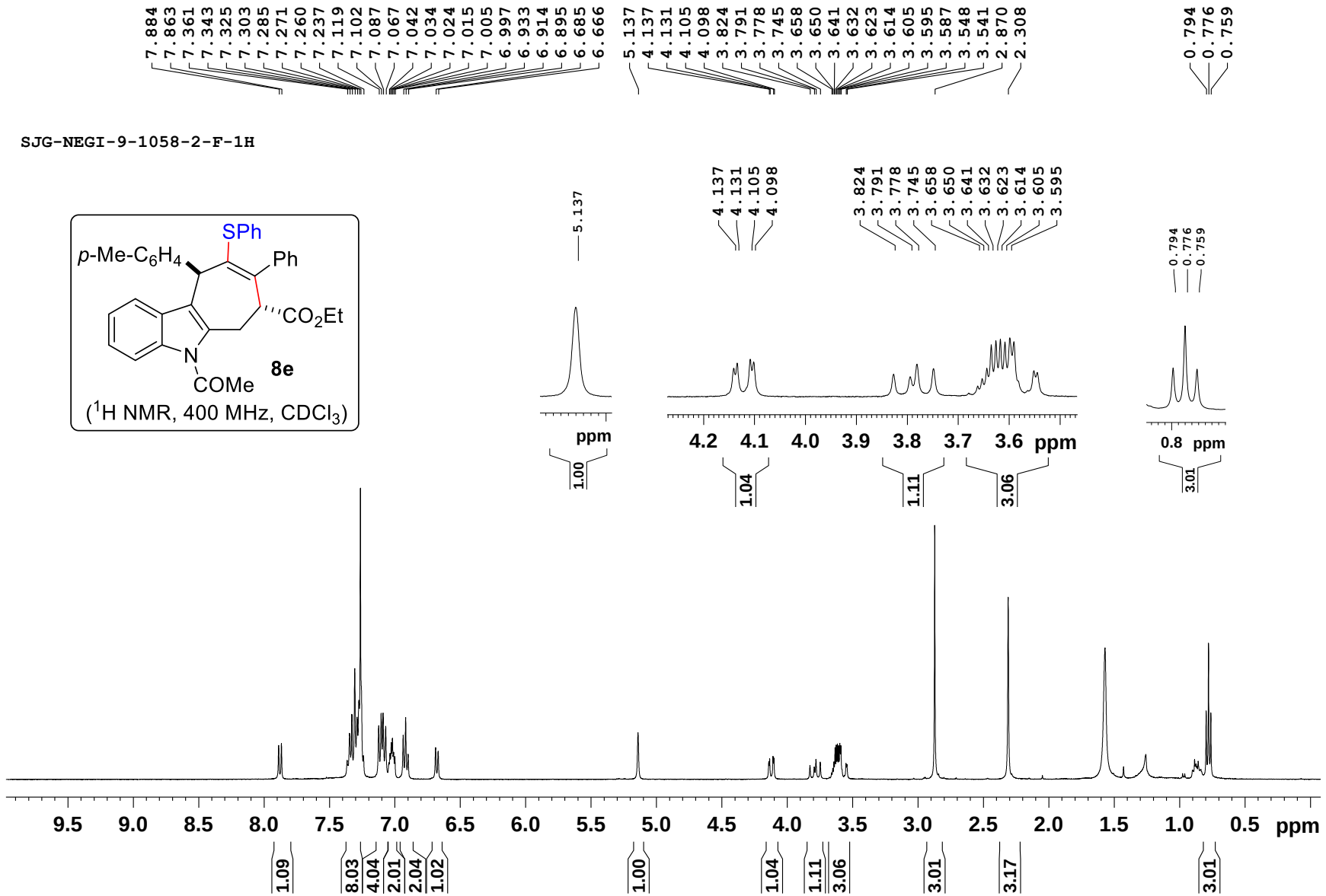

8.073
8.052
7.376
7.357
7.340
7.314
7.303
7.291
7.289
7.285
7.266
7.247
7.109
7.104
7.089
7.085
7.069
7.050
7.042
7.023
7.005
6.927
6.908
6.889
6.719
6.699
5.154
4.140
4.132
4.109
4.101
3.703
3.682
3.673
3.664
3.656
3.647
3.638
3.629
3.612
3.603
3.578
3.570
3.531
3.523
3.121
2.325
0.808
0.790
0.772
SJG-NEGI-F-1H
SPh
p-Me-C6H4
Ph
CO2Et
N
SO2Me
8c
(1H NMR, 400 MHz, CDCl3)
ppm
1.11
0.8
ppm
3.09
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
1.00
2.26
6.44
5.17
1.19
2.11
1.02
1.09
1.11
4.22
3.13
3.18
3.09

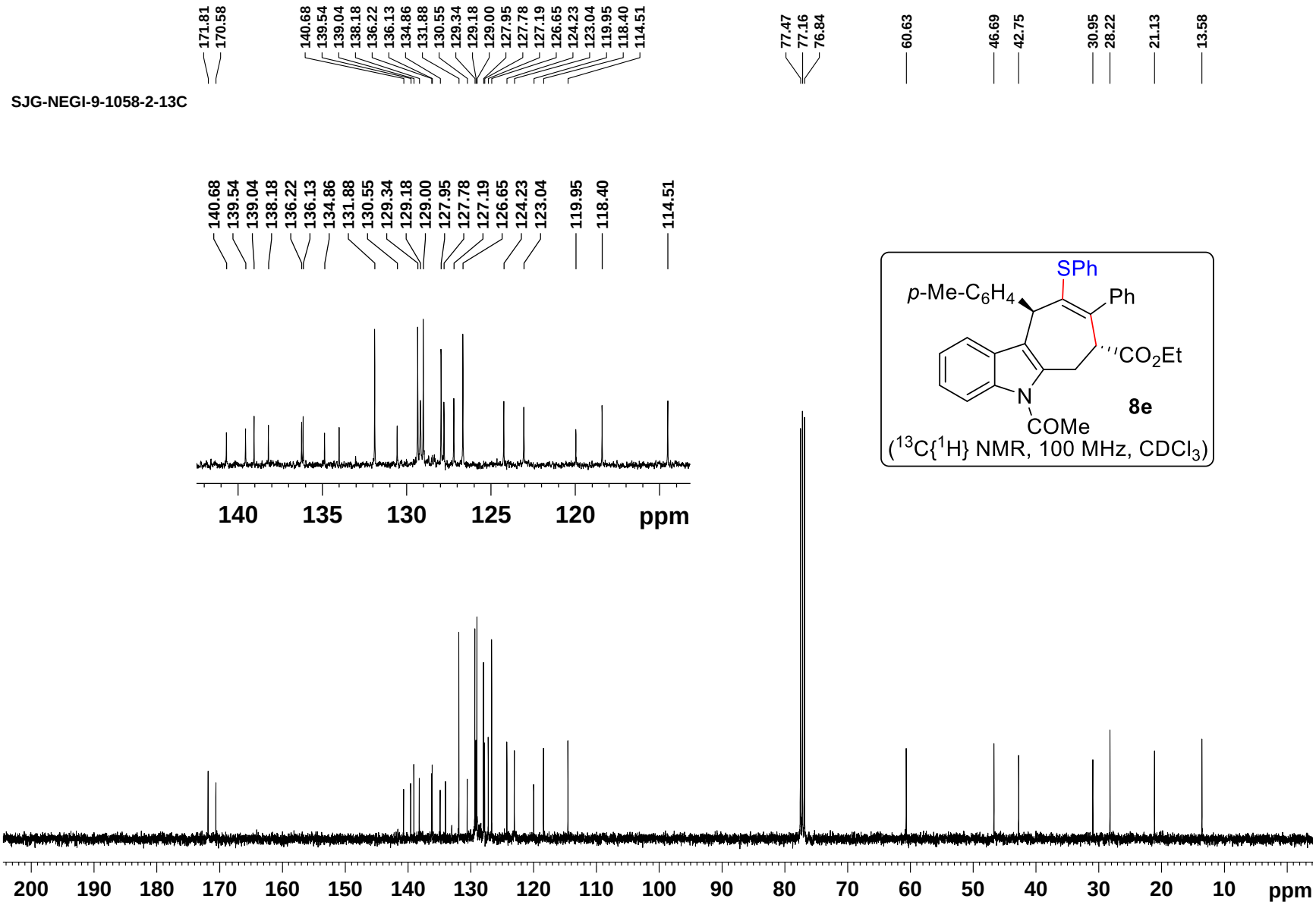

171.50
140.93
139.45
138.69
138.39
136.41
135.37
135.23
133.88
131.98
130.43
129.45
129.15
129.02
128.02
127.88
127.36
126.52
124.81
123.75
121.13
118.51
113.99
77.48
77.16
76.84
60.73
46.49
43.00
40.77
29.36
21.14
13.59
SJG-NEGI-4-351-2-13C
SPh
p-Me-C6H4
Ph
CO2Et
N
SO2Me
8c
(13C{1H} NMR, 100 MHz, CDCl3)
ppm

SJG-NEGI-3-263-3-1H

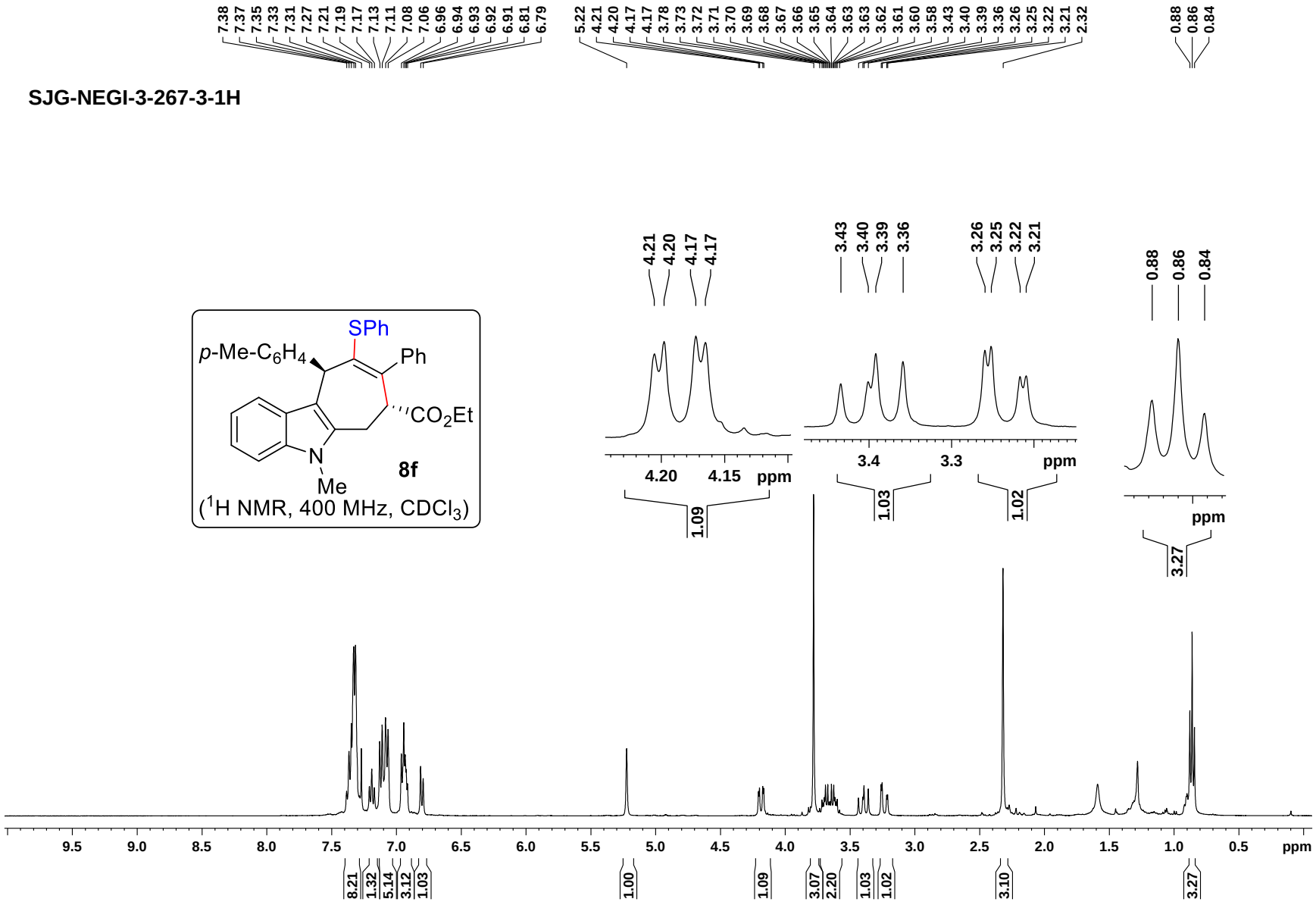


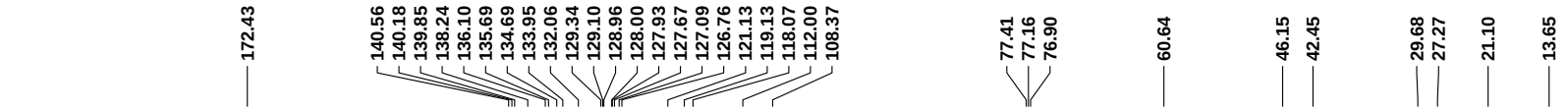

171.41
145.08
141.45
139.43
138.59
138.56
136.33
136.25
136.21
135.39
133.94
131.46
130.66
129.94
129.38
129.06
128.79
127.94
127.84
127.00
126.49
124.74
123.76
122.10
118.16
114.90
77.41
77.16
76.90
60.69
46.17
43.23
29.62
21.72
21.12
13.59
SJG-NEGI-3-263-3-13C
SPh
p-Me-C6H4
Ph
CO2Et
N
Ts
8d
(13C{1H} NMR, 125 MHz, CDCl3)
145
140
135
130
125
120
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.884
7.863
7.361
7.343
7.325
7.303
7.285
7.271
7.260
7.237
7.119
7.102
7.087
7.067
7.042
7.034
7.024
7.015
7.005
6.997
6.933
6.914
6.895
6.685
6.666
5.137
4.137
4.131
4.105
4.098
3.824
3.791
3.778
3.745
3.658
3.650
3.641
3.632
3.623
3.614
3.605
3.595
3.587
3.548
3.541
2.870
2.308
0.794
0.776
0.759
SJG-NEGI-9-1058-2-F-1H
SPh
p-Me-C6H4
Ph
CO2Et
N
COMe
8e
(1H NMR, 400 MHz, CDCl3)
ppm
4.2
4.1
4.0
3.9
3.8
3.7
3.6
0.8
1.00
1.04
1.11
3.06
3.01
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
1.09
8.03
4.04
2.01
2.04
1.02
1.00
1.04
1.11
3.06
3.01
3.17
3.01

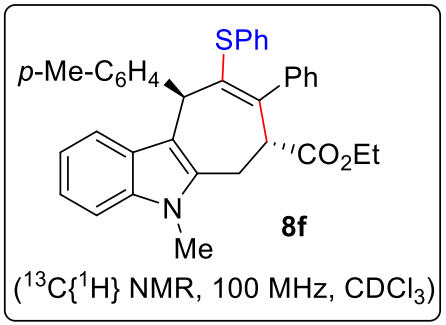

SJG-NEGI-9-1058-2-13C
171.81
170.58
140.68
139.54
139.04
138.18
136.22
136.13
134.86
131.88
130.55
129.34
129.18
129.00
127.95
127.78
127.19
126.65
124.23
123.04
119.95
118.40
114.51
77.47
77.16
76.84
60.63
46.69
42.75
30.95
28.22
21.13
13.58
SPh
p-Me-C6H4
Ph
CO2Et
N
COMe
8e
(13C{1H} NMR, 100 MHz, CDCl3)
140
135
130
125
120
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

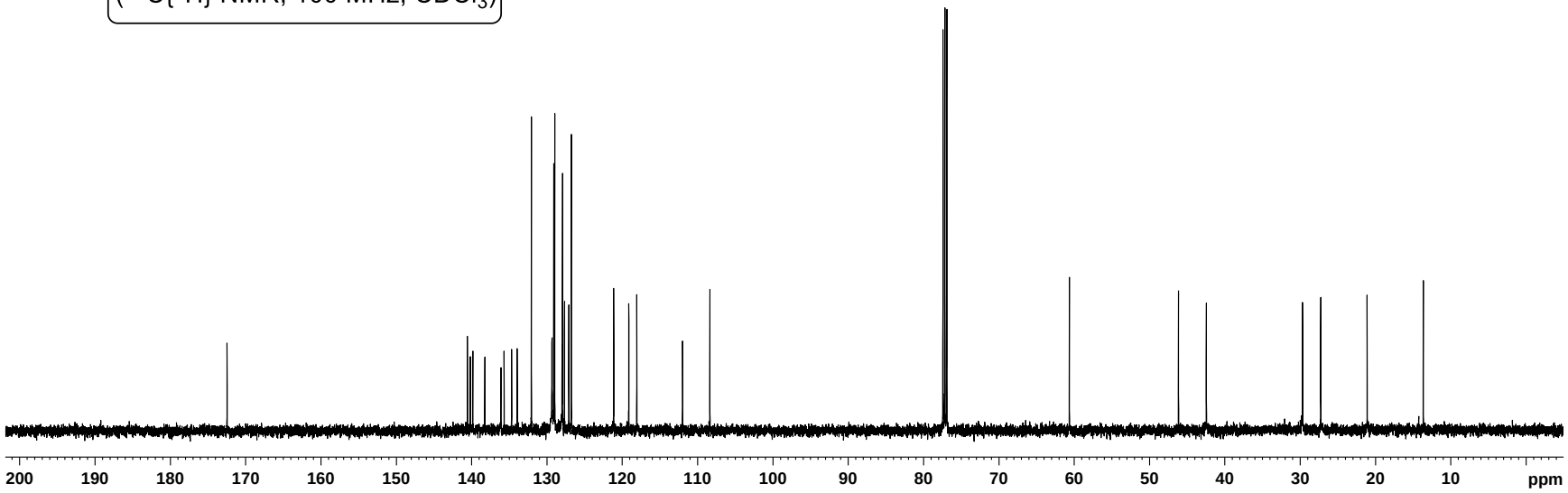
SJG-NEGI-3-267-3-1H

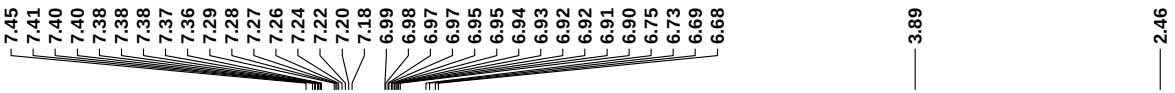




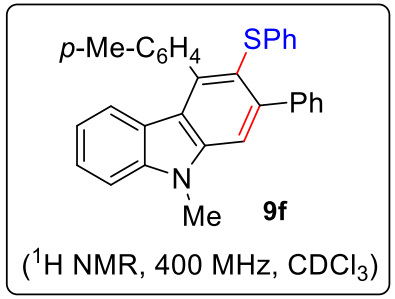
SJG-NEGI-3-267-3-13C

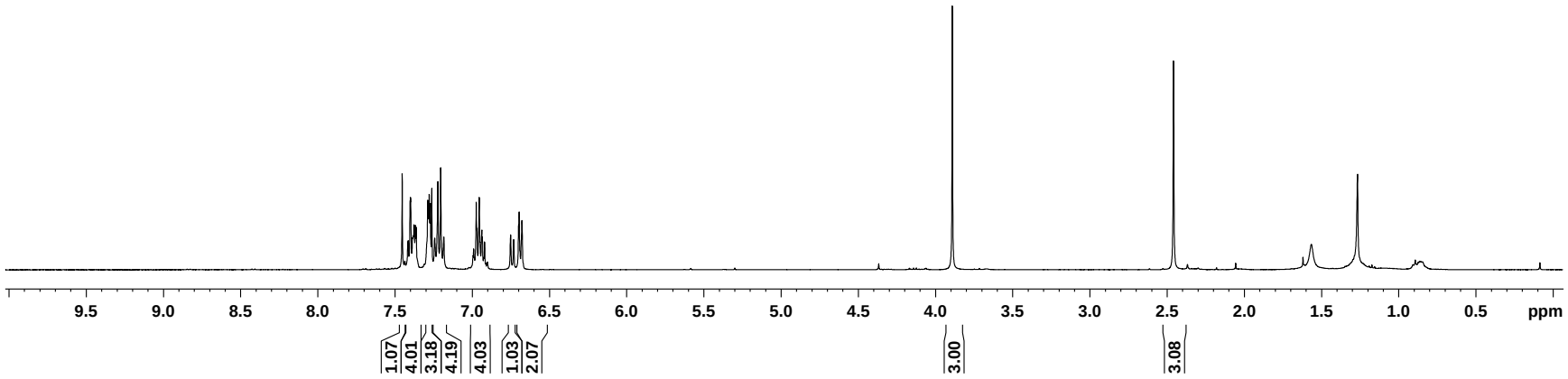


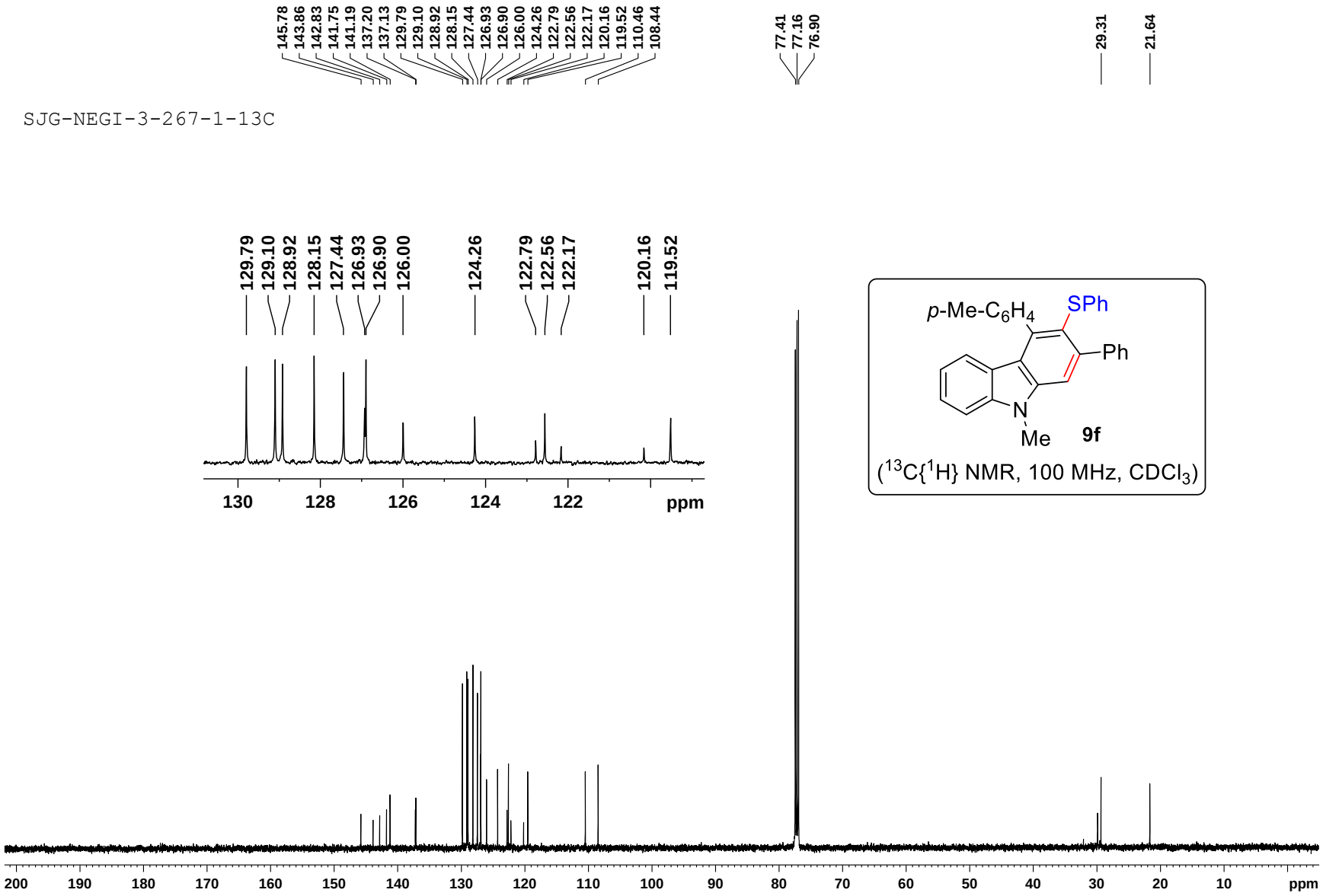


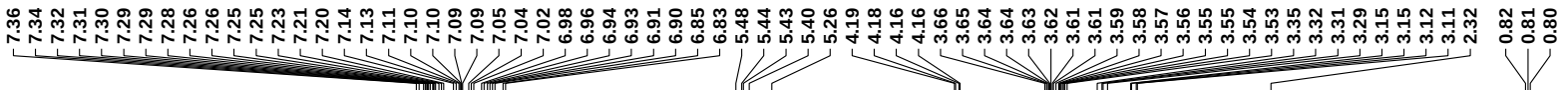


SJG-NEGI-3-267-1-1H

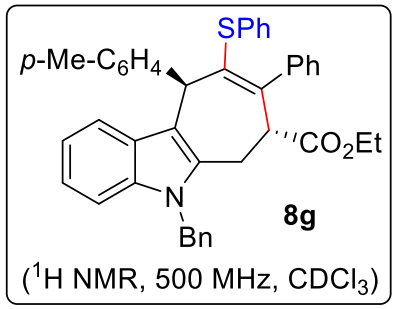


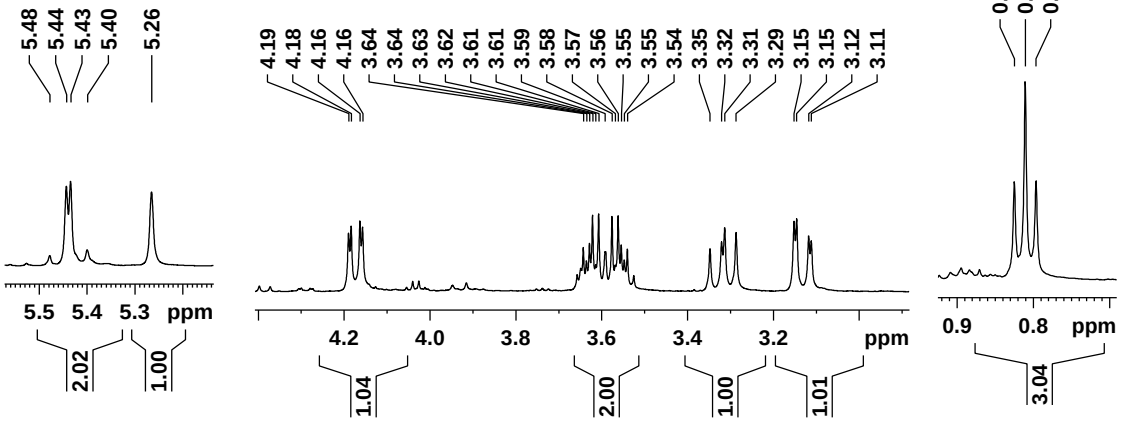


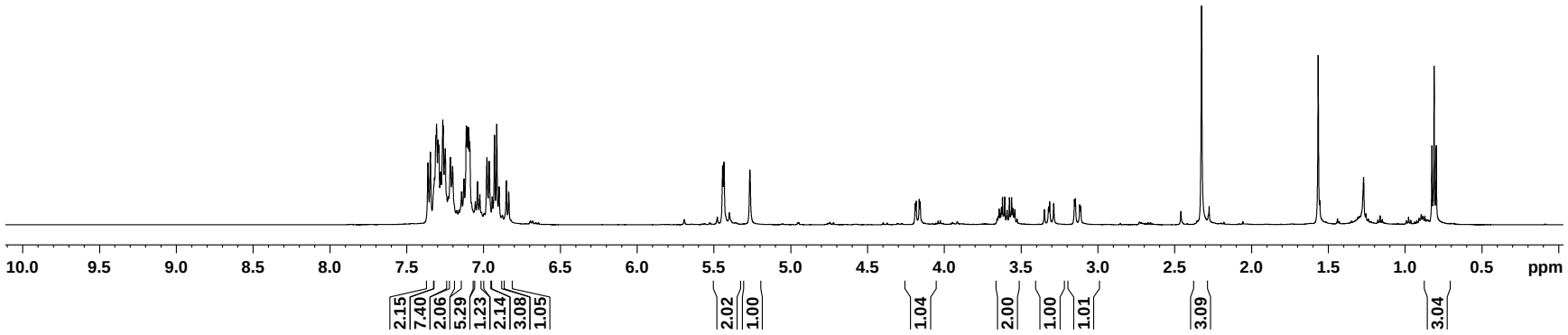

145.78
143.86
142.83
141.75
141.19
137.20
137.13
129.79
129.10
128.92
128.15
127.44
126.93
126.90
126.00
124.26
122.79
122.56
122.17
120.16
119.52
110.46
108.44
77.41
77.16
76.90
29.31
21.64
SJG-NEGI-3-267-1-13C
130
128
126
124
122
ppm
p-Me-C6H4
SPh
Ph
N
Me
9f
(13C{1H} NMR, 100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

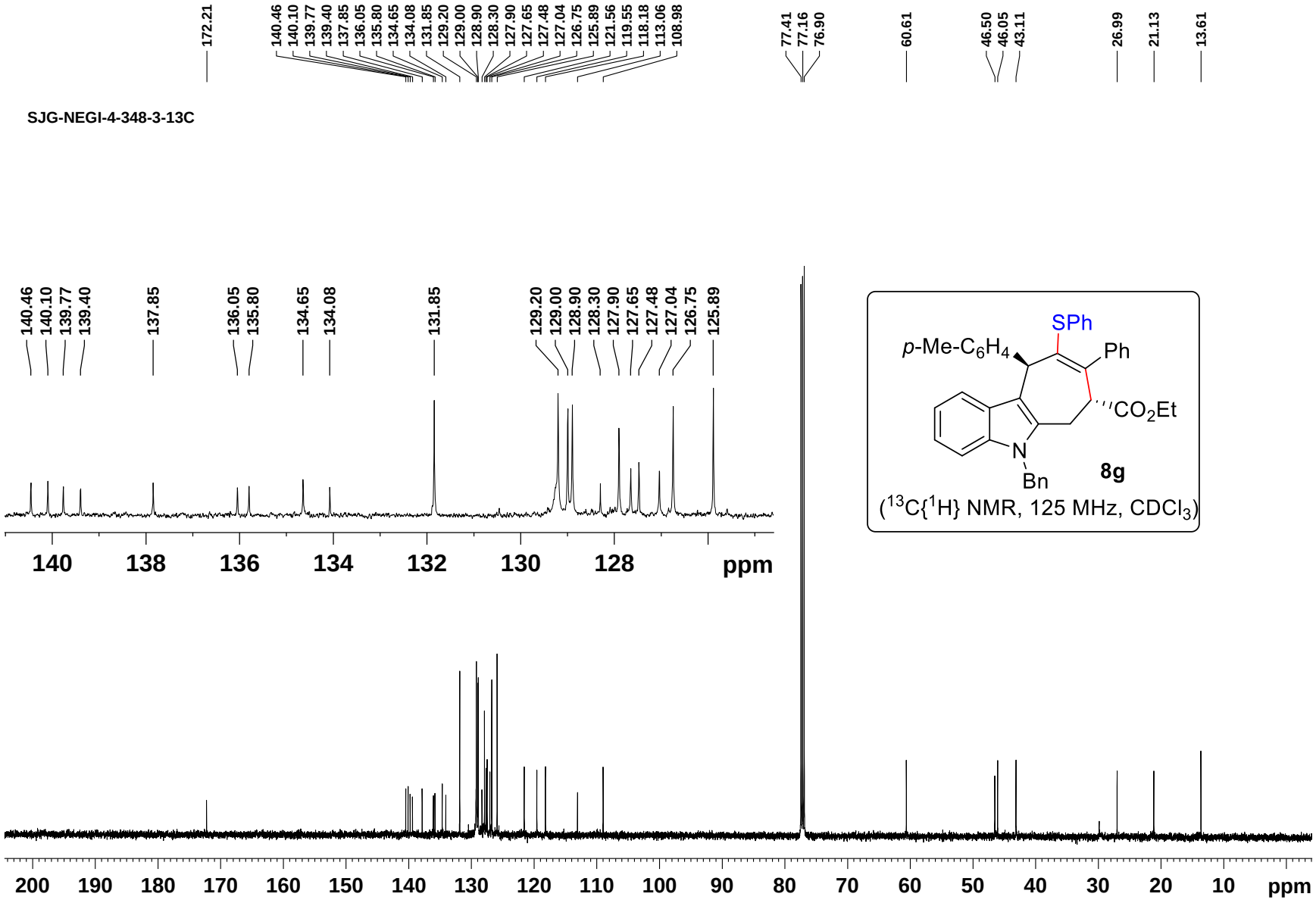


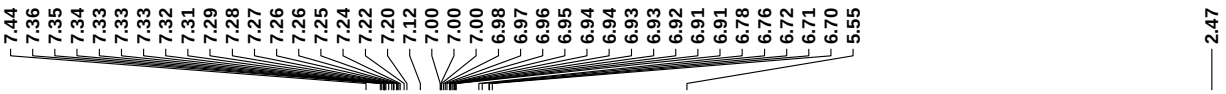
SJG-NEGI-4-348-3-1H



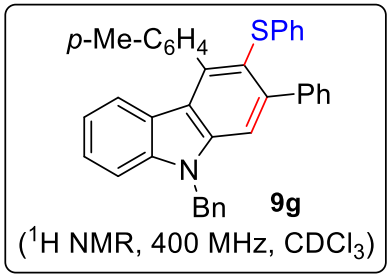


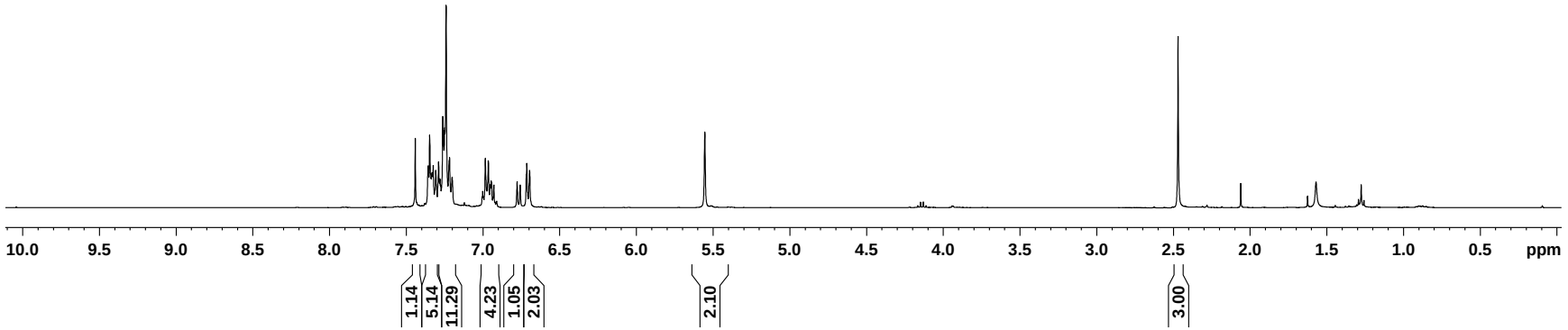


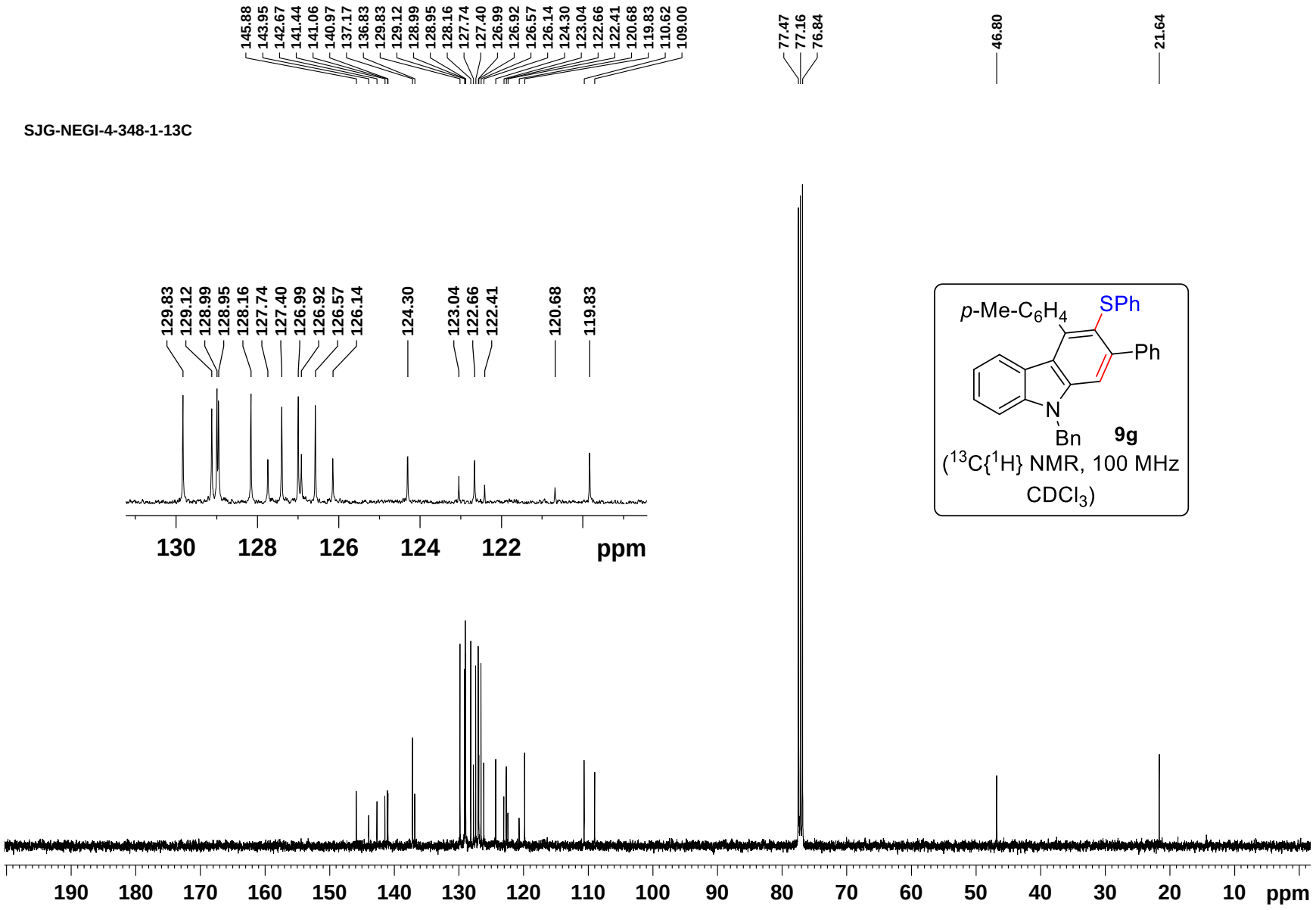

172.21
140.46
140.10
139.77
139.40
137.85
136.05
135.80
134.65
134.08
131.85
129.20
129.00
128.90
128.30
127.90
127.65
127.48
127.04
126.75
125.89
121.56
119.55
118.18
113.06
108.98
77.41
77.16
76.90
60.61
46.50
46.05
43.11
26.99
21.13
13.61
SJG-NEGI-4-348-3-13C
SPh
p-Me-C6H4
Ph
CO2Et
N
Bn
8g
(13C{1H} NMR, 125 MHz, CDCl3)
ppm

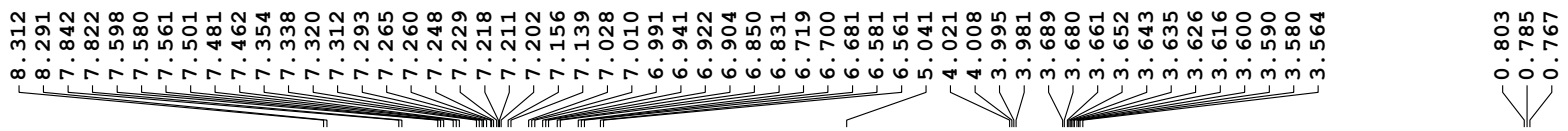


SJG-NEGI-4-348-1-1H

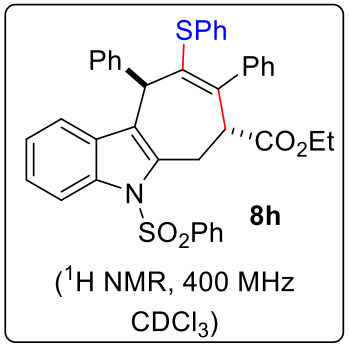


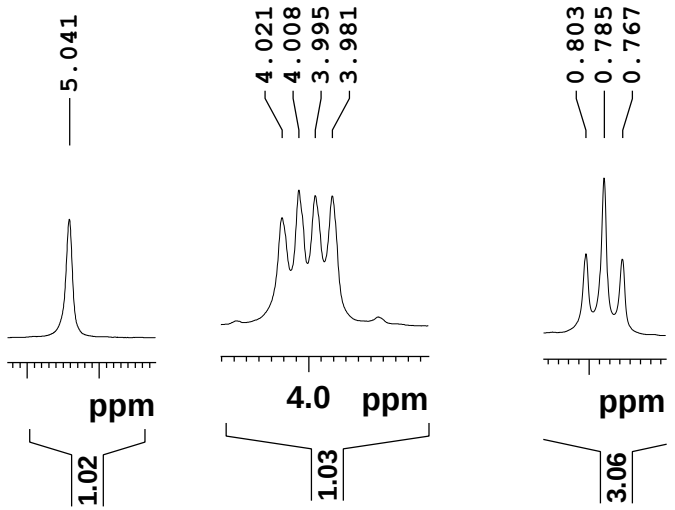


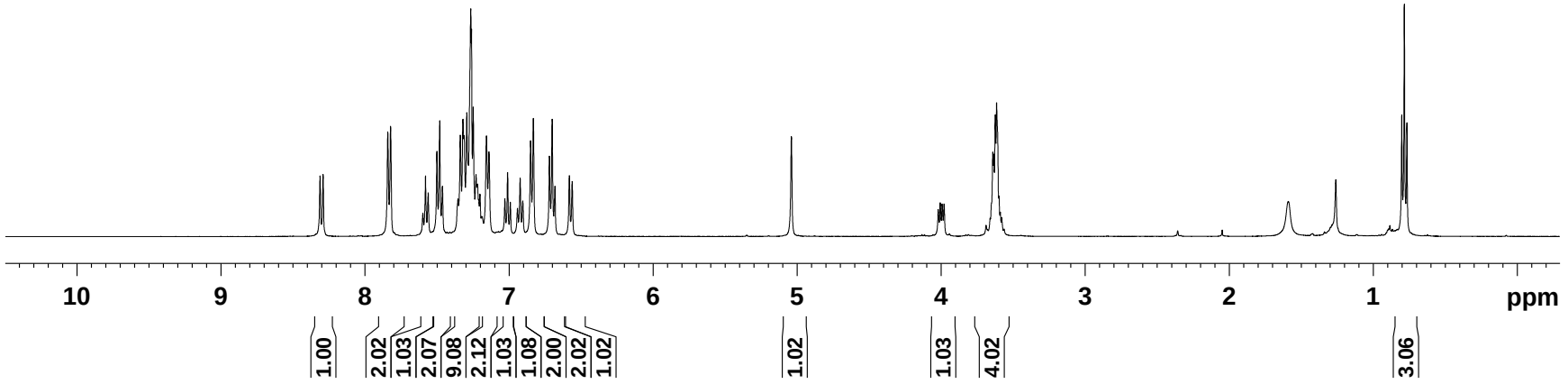

145.88
143.95
142.67
141.44
141.06
140.97
137.17
136.83
129.83
129.12
128.99
128.95
128.16
127.74
127.40
126.99
126.92
126.57
126.14
124.30
123.04
122.66
122.41
120.68
119.83
110.62
109.00
77.47
77.16
76.84
46.80
21.64
SJG-NEGI-4-348-1-13C
129.83
129.12
128.99
128.95
128.16
127.74
127.40
126.99
126.92
126.57
126.14
124.30
123.04
122.66
122.41
120.68
119.83
130
128
126
124
122
ppm
p-Me-C6H4
SPh
Ph
N
Bn
9g
(13C{1H} NMR, 100 MHz
CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

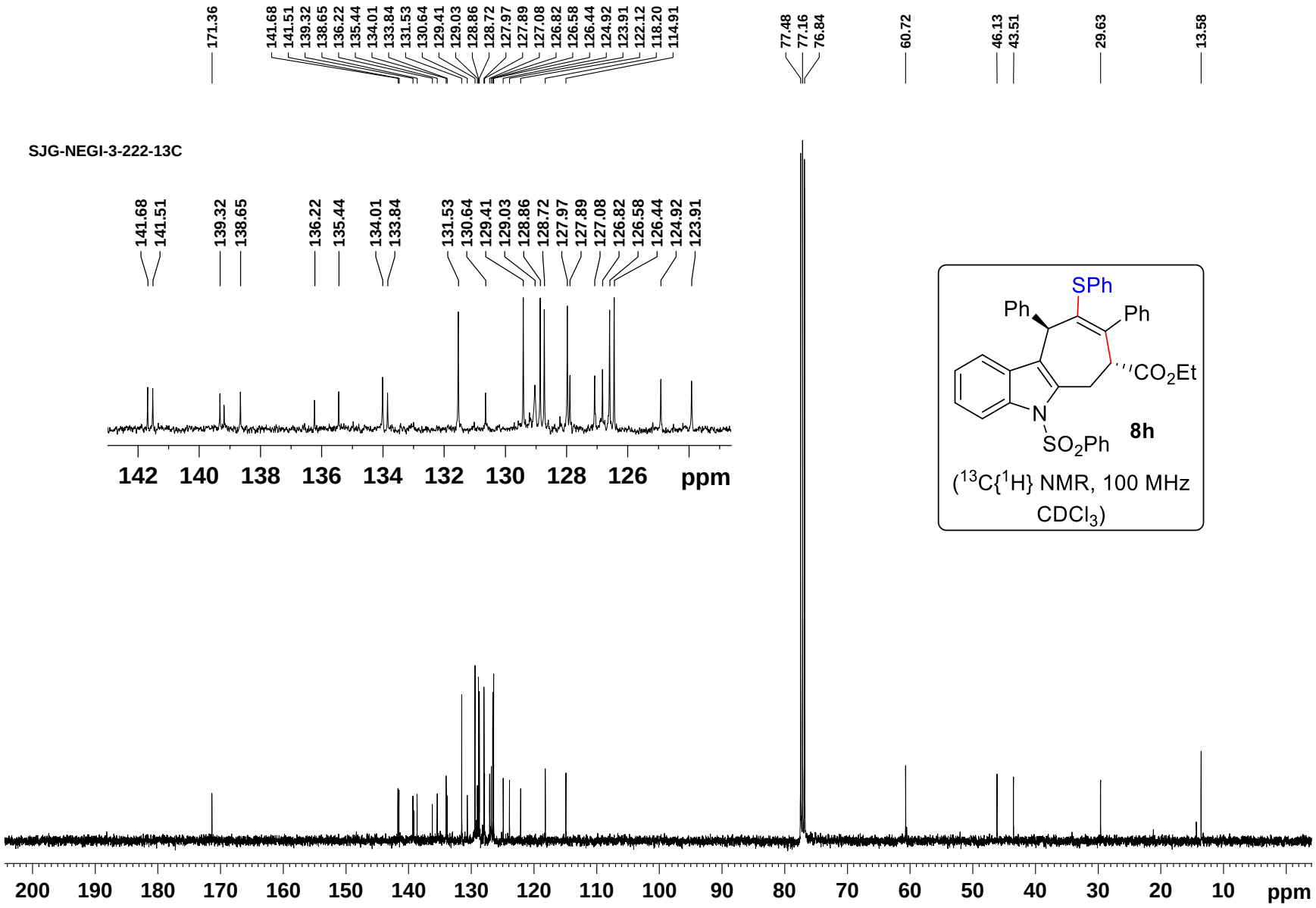


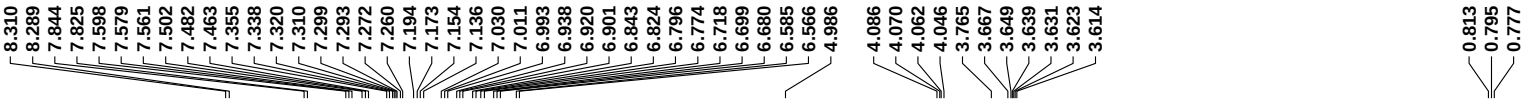
SJG-NEGI-3-222-F-1H



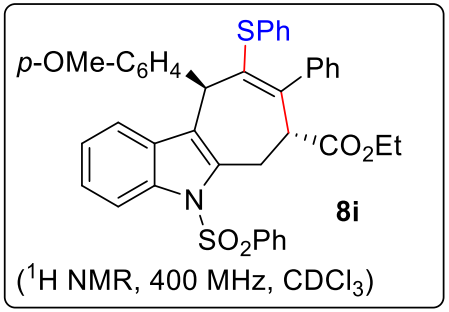


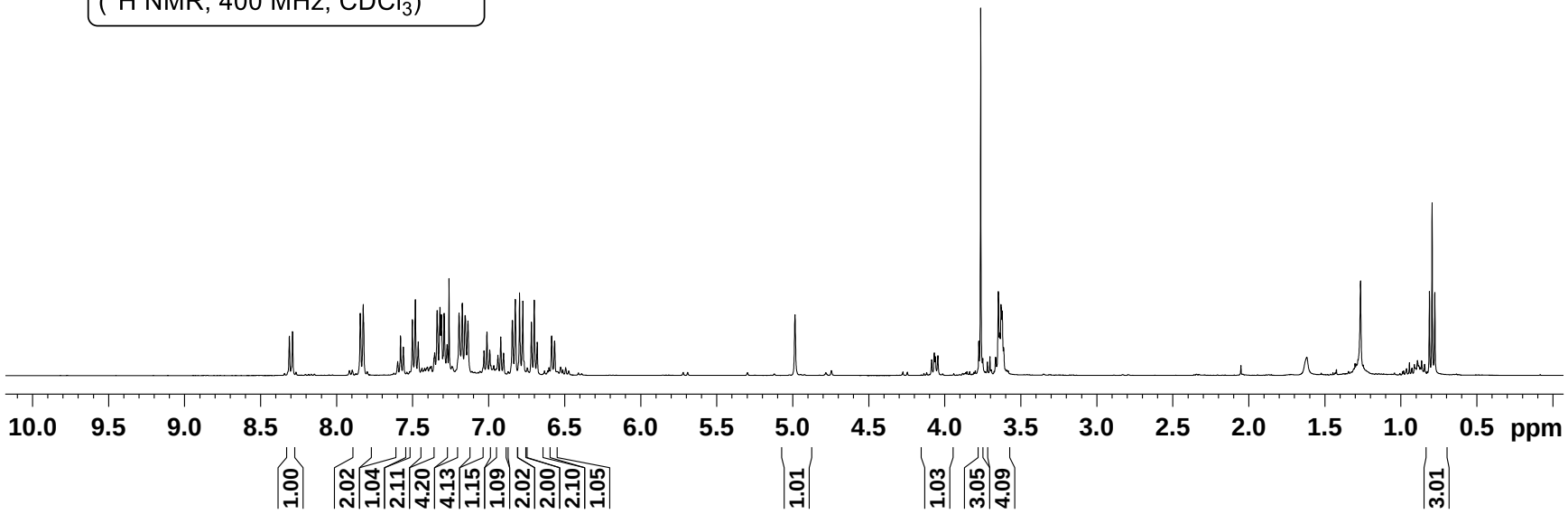


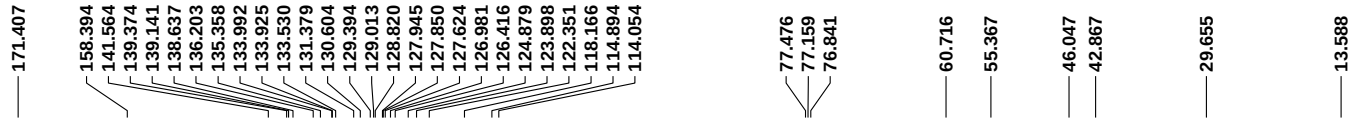

171.36
141.68
141.51
139.32
138.65
136.22
135.44
134.01
133.84
131.53
130.64
129.41
129.03
128.86
128.72
127.97
127.89
127.08
126.82
126.58
126.44
124.92
123.91
122.12
118.20
114.91
77.48
77.16
76.84
60.72
46.13
43.51
29.63
13.58
SJG-NEGI-3-222-13C
142 140 138 136 134 132 130 128 126 ppm
SPh
Ph
Ph
CO2Et
N
SO2Ph
8h
(13C{1H} NMR, 100 MHz
CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



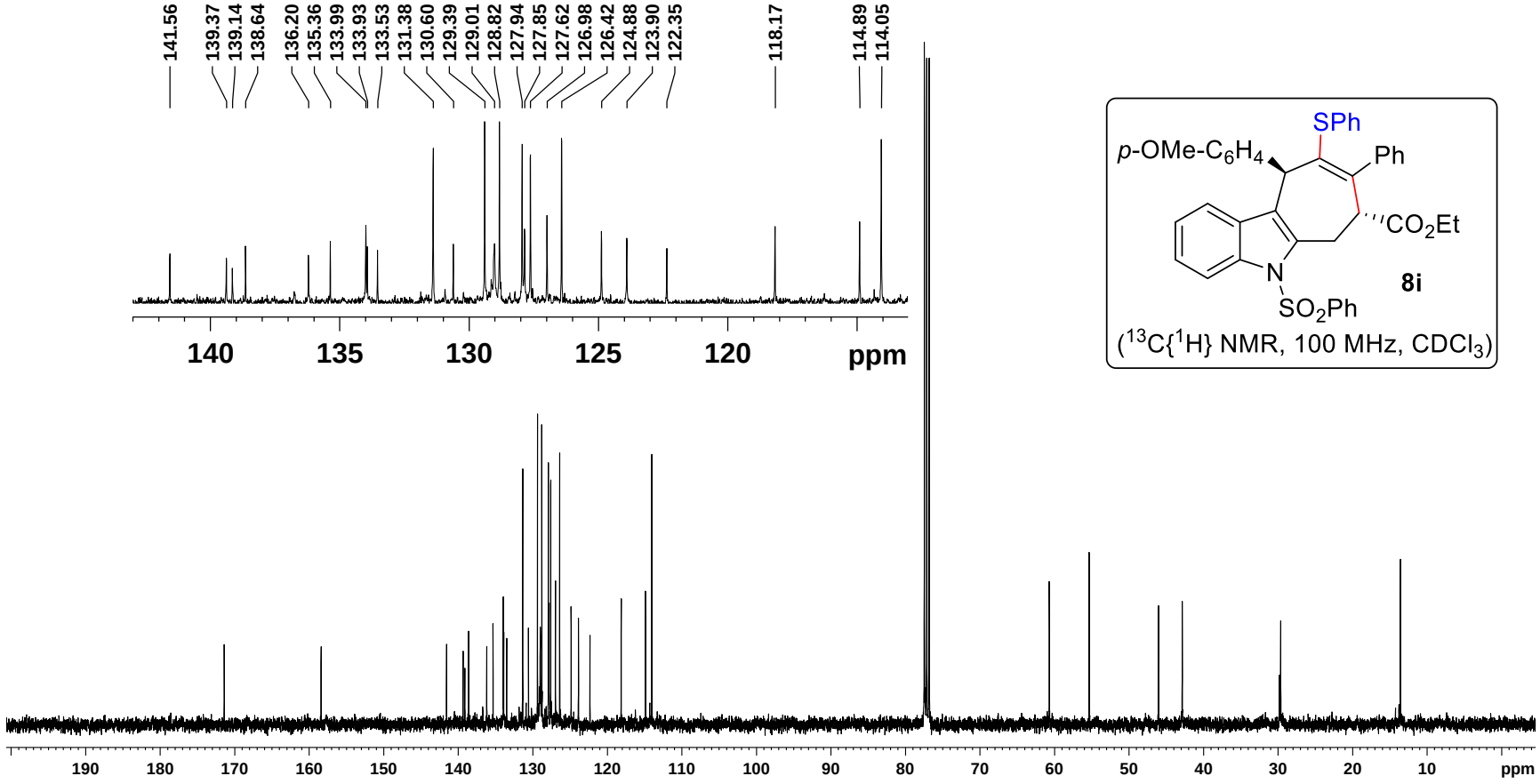
SJG-NEGI-3-239-1H

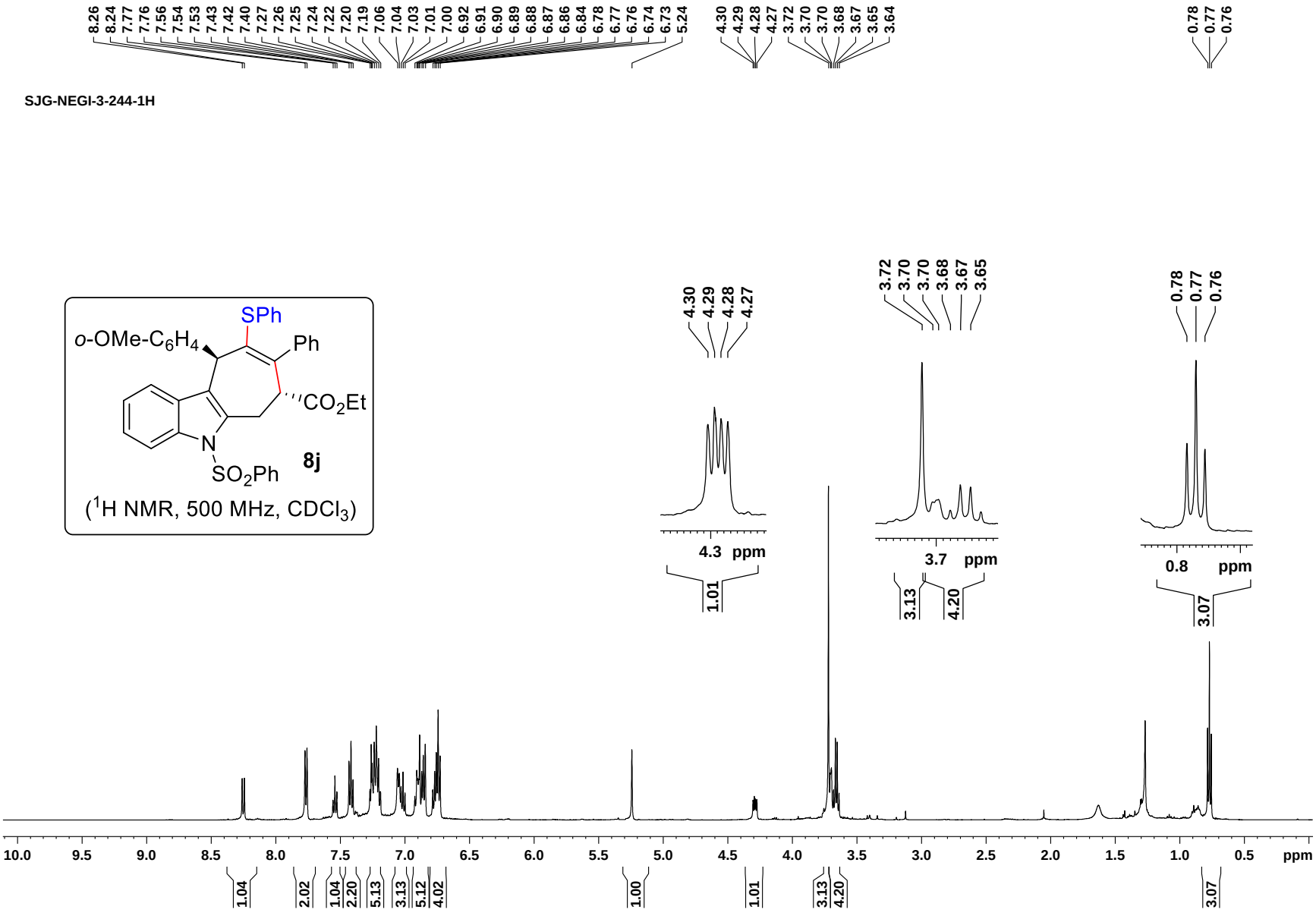


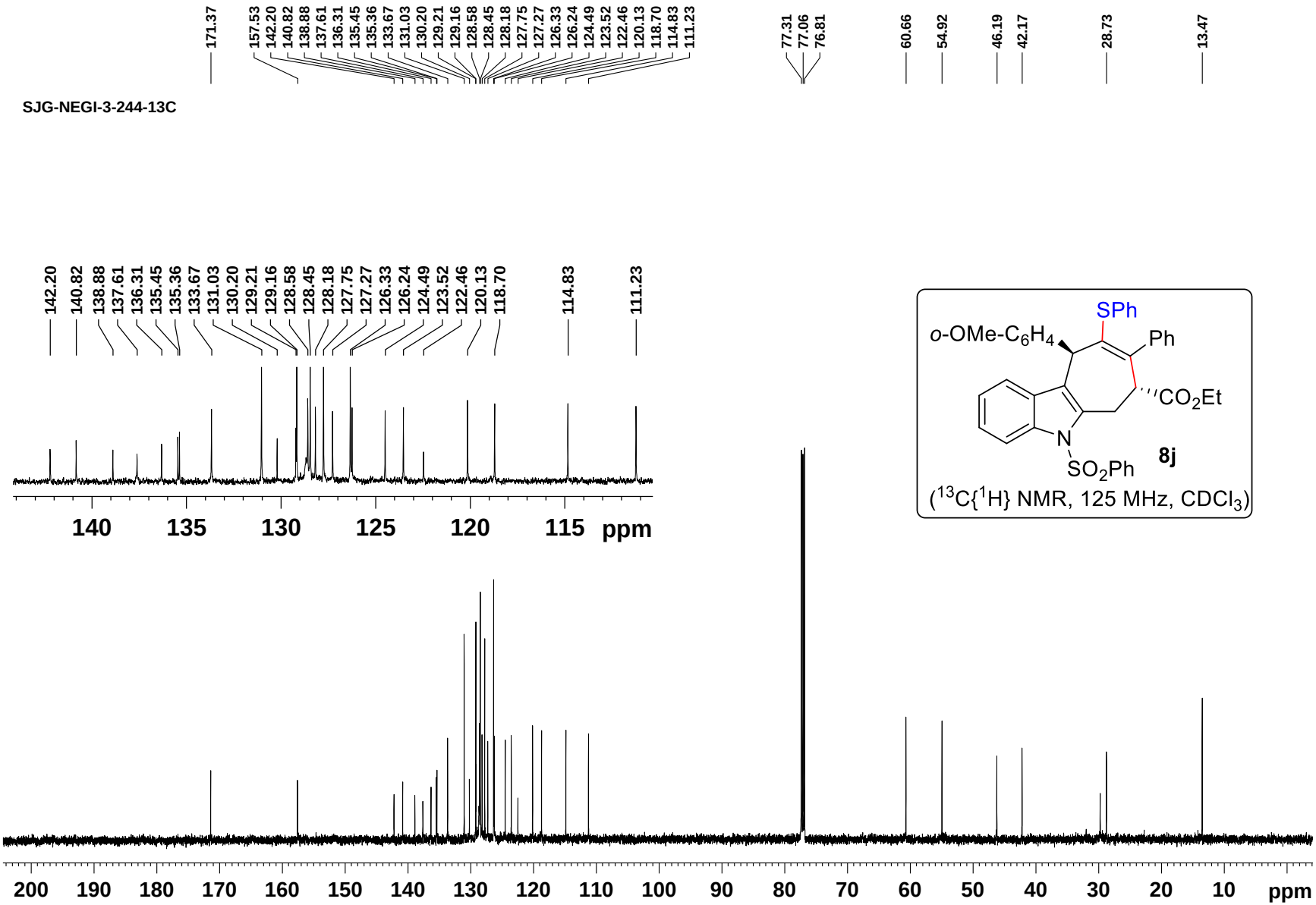


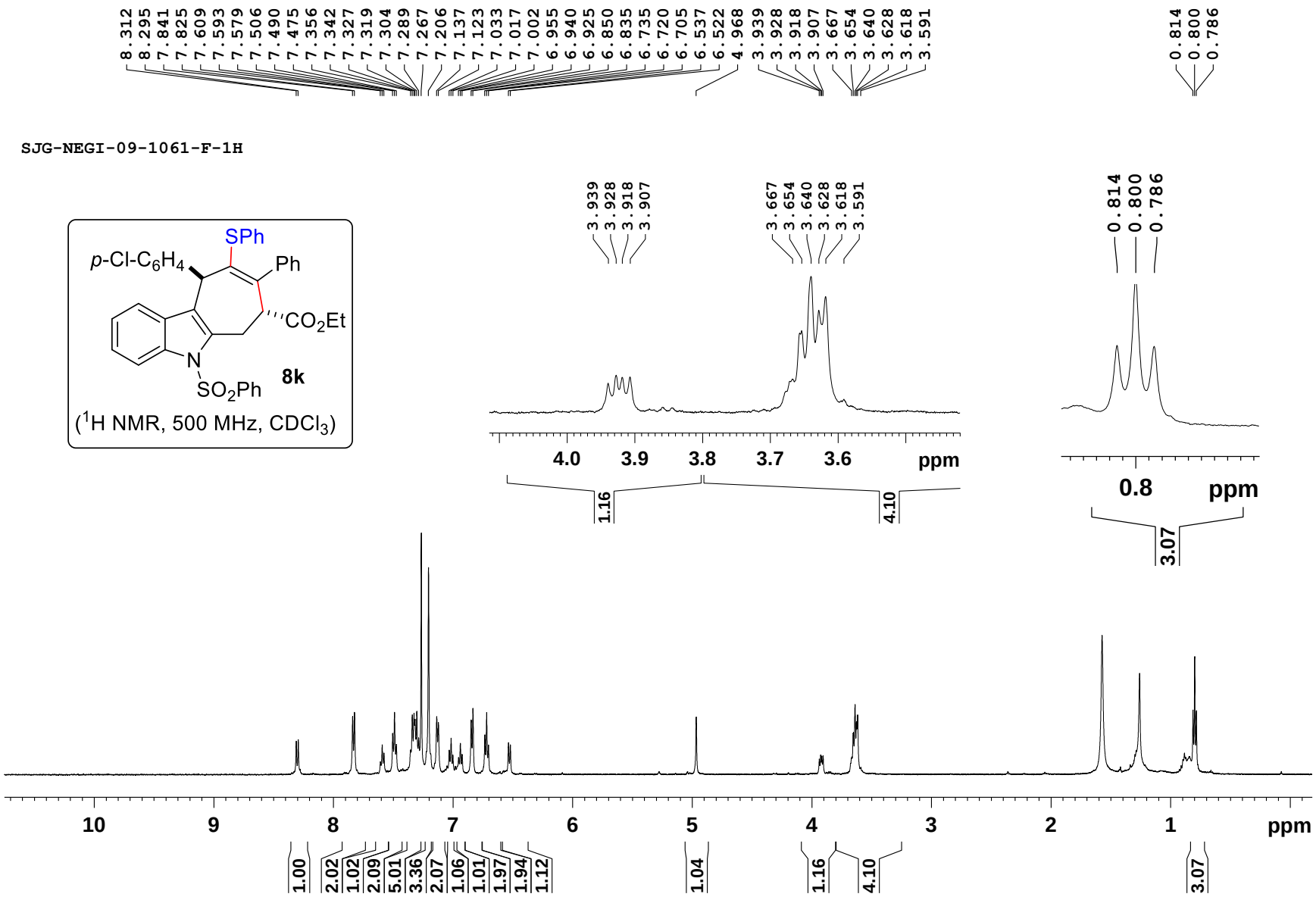


SJG-NEGI-3-239-13C



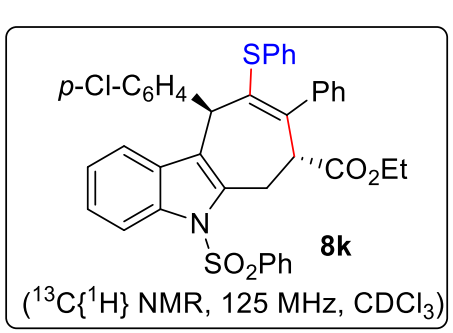

8.26 8.24 7.77 7.76 7.56 7.54 7.53 7.43 7.42 7.40 7.27 7.26 7.25 7.24 7.22 7.20 7.19 7.06 7.04 7.03 7.01 7.00 6.92 6.91 6.90 6.89 6.88 6.87 6.86 6.84 6.78 6.77 6.76 6.74 6.73 5.24
4.30 4.29 4.28 4.27
3.72 3.70 3.70 3.68 3.67 3.65
0.78 0.77 0.76
SJG-NEGI-3-244-1H
SPh
o-OMe-C6H4
Ph
CO2Et
N
SO2Ph
8j
(1H NMR, 500 MHz, CDCl3)
4.3 ppm
1.01
3.7 ppm
3.13
4.20
0.8 ppm
3.07
10.0 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
1.04 2.02 1.04 2.20 5.13 3.13 5.12 4.02 1.00 1.01 3.13 4.20 3.07


171.37
157.53
142.20
140.82
138.88
137.61
136.31
135.45
135.36
133.67
131.03
130.20
129.21
129.16
128.58
128.45
128.18
127.75
127.27
126.33
126.24
124.49
123.52
122.46
120.13
118.70
114.83
111.23
77.31
77.06
76.81
60.66
54.92
46.19
42.17
28.73
13.47
SJG-NEGI-3-244-13C
SPh
o-OMe-C6H4
Ph
CO2Et
N
SO2Ph
8j
(13C{1H} NMR, 125 MHz, CDCl3)
ppm

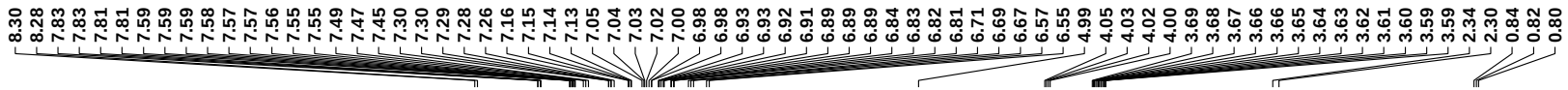

8.312
8.295
7.841
7.825
7.609
7.593
7.579
7.506
7.490
7.475
7.356
7.342
7.327
7.319
7.304
7.289
7.267
7.206
7.137
7.123
7.033
7.017
7.002
6.955
6.940
6.925
6.850
6.835
6.735
6.720
6.705
6.537
6.522
4.968
3.939
3.928
3.918
3.907
3.667
3.654
3.640
3.628
3.618
3.591
0.814
0.800
0.786
SJG-NEGI-09-1061-F-1H
SPh
p-Cl-C6H4
Ph
CO2Et
N
SO2Ph
8k
(1H NMR, 500 MHz, CDCl3)
4.0
3.9
3.8
3.7
3.6
ppm
1.16
4.10
0.8
ppm
3.07
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.02
1.02
2.09
5.01
3.36
2.07
1.06
1.01
1.97
1.94
1.12
1.04
1.16
4.10
3.07

171.16
141.68
140.20
139.13
138.28
136.21
135.57
134.07
133.61
132.68
131.55
130.33
129.68
129.44
128.93
128.84
128.02
127.99
127.23
126.43
125.05
123.98
121.48
117.95
114.97
77.41
77.15
76.90
60.85
46.20
42.98
29.58
13.60

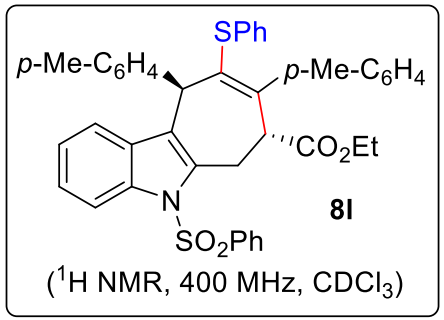
SJG-NEGI-9-1061-13C

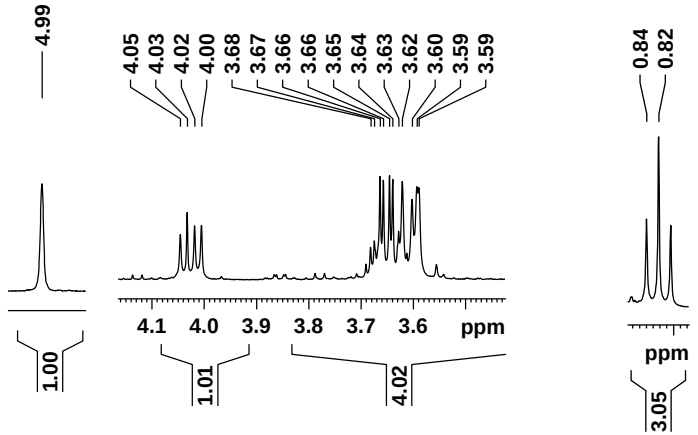


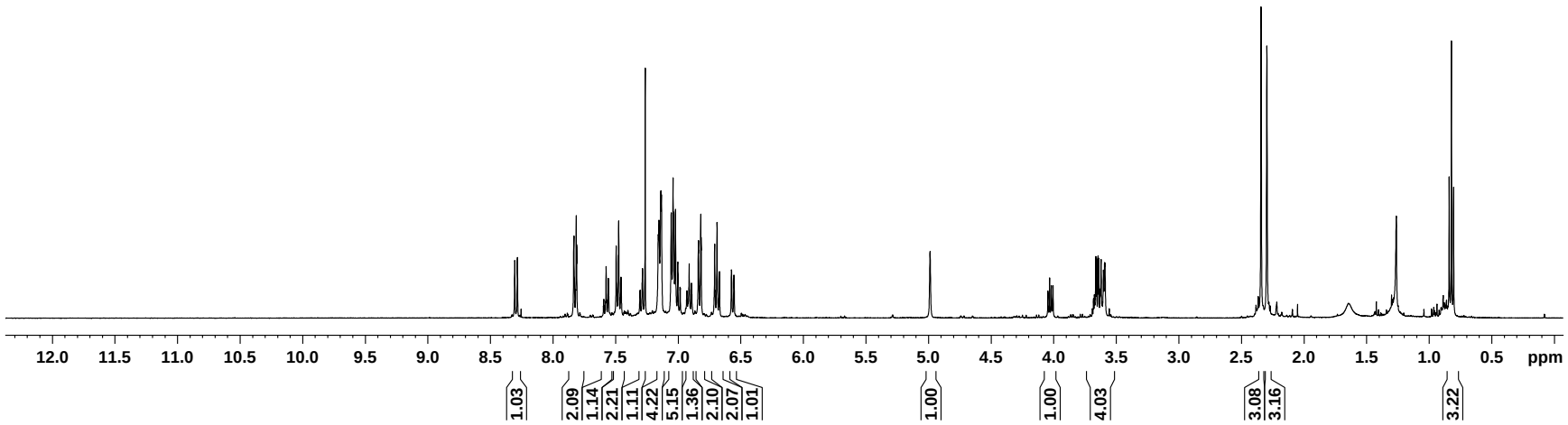
($^{13}C\{^{1}H\}$ NMR, 125 MHz, $CDCl_3$)

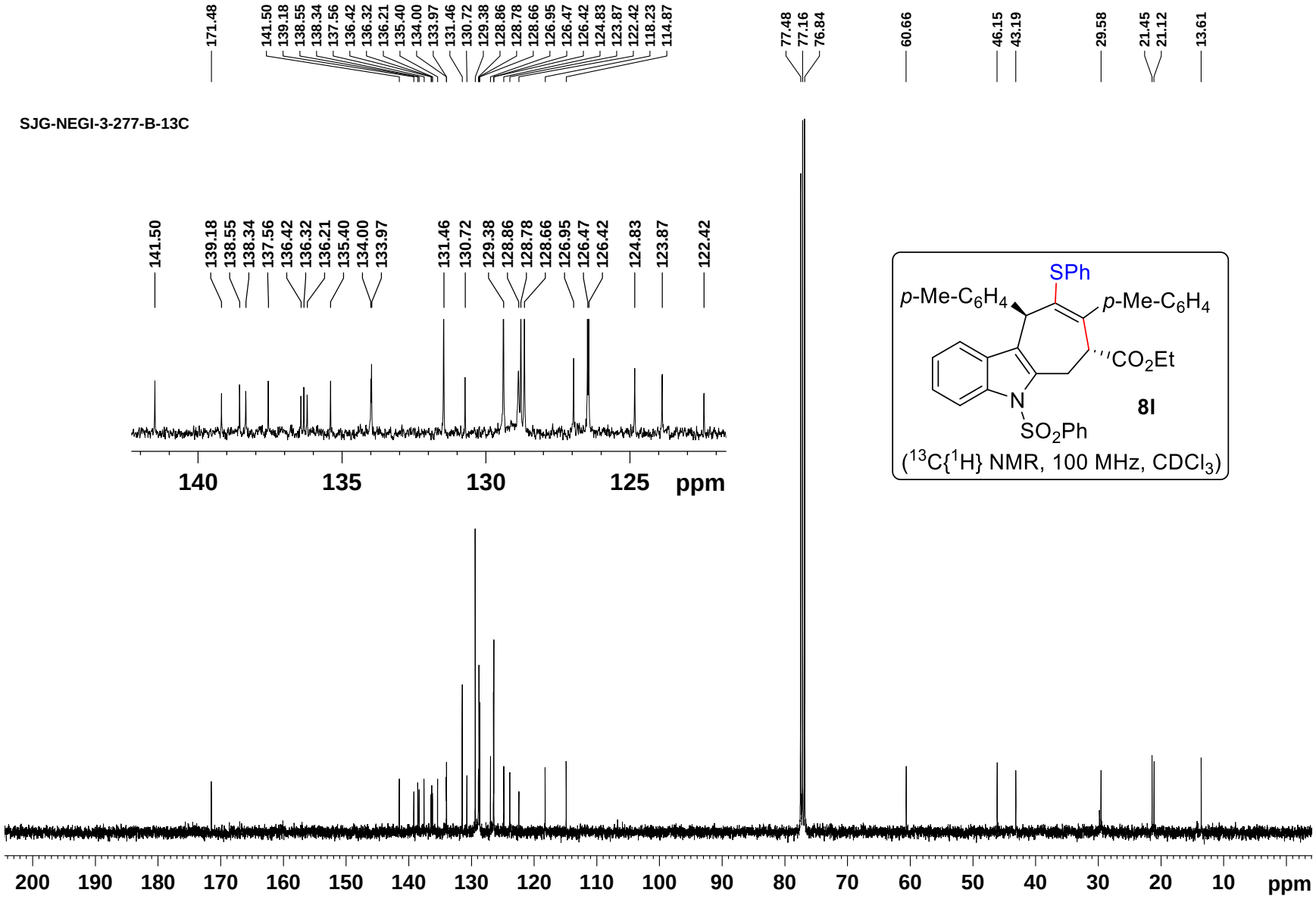


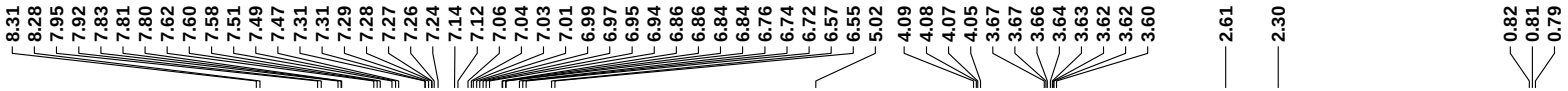
SJG-NEGI-3-277-B-1H



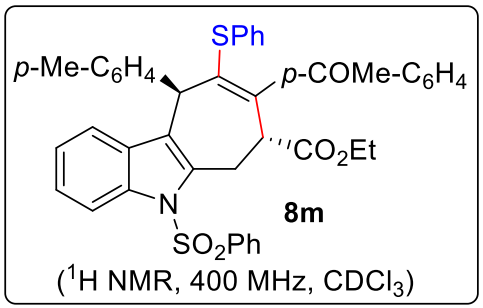


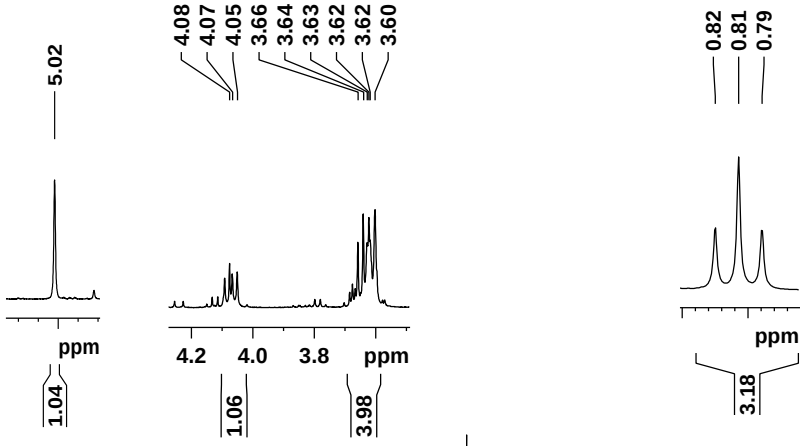


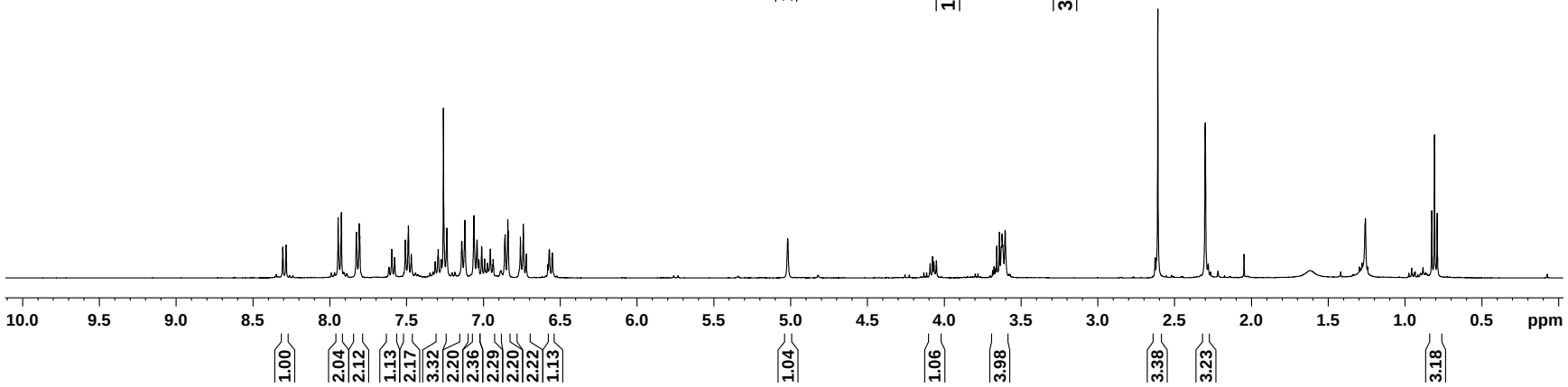

SJG-NEGI-3-277-B-13C
171.48
141.50
139.18
138.55
138.34
137.56
136.42
136.32
136.21
135.40
134.00
133.97
131.46
130.72
129.38
128.86
128.78
128.66
126.95
126.47
126.42
124.83
123.87
122.42
118.23
114.87
77.48
77.16
76.84
60.66
46.15
43.19
29.58
21.45
21.12
13.61
140
135
130
125
ppm
SPh
p-Me-C6H4
p-Me-C6H4
CO2Et
N
SO2Ph
8l
(13C{1H} NMR, 100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

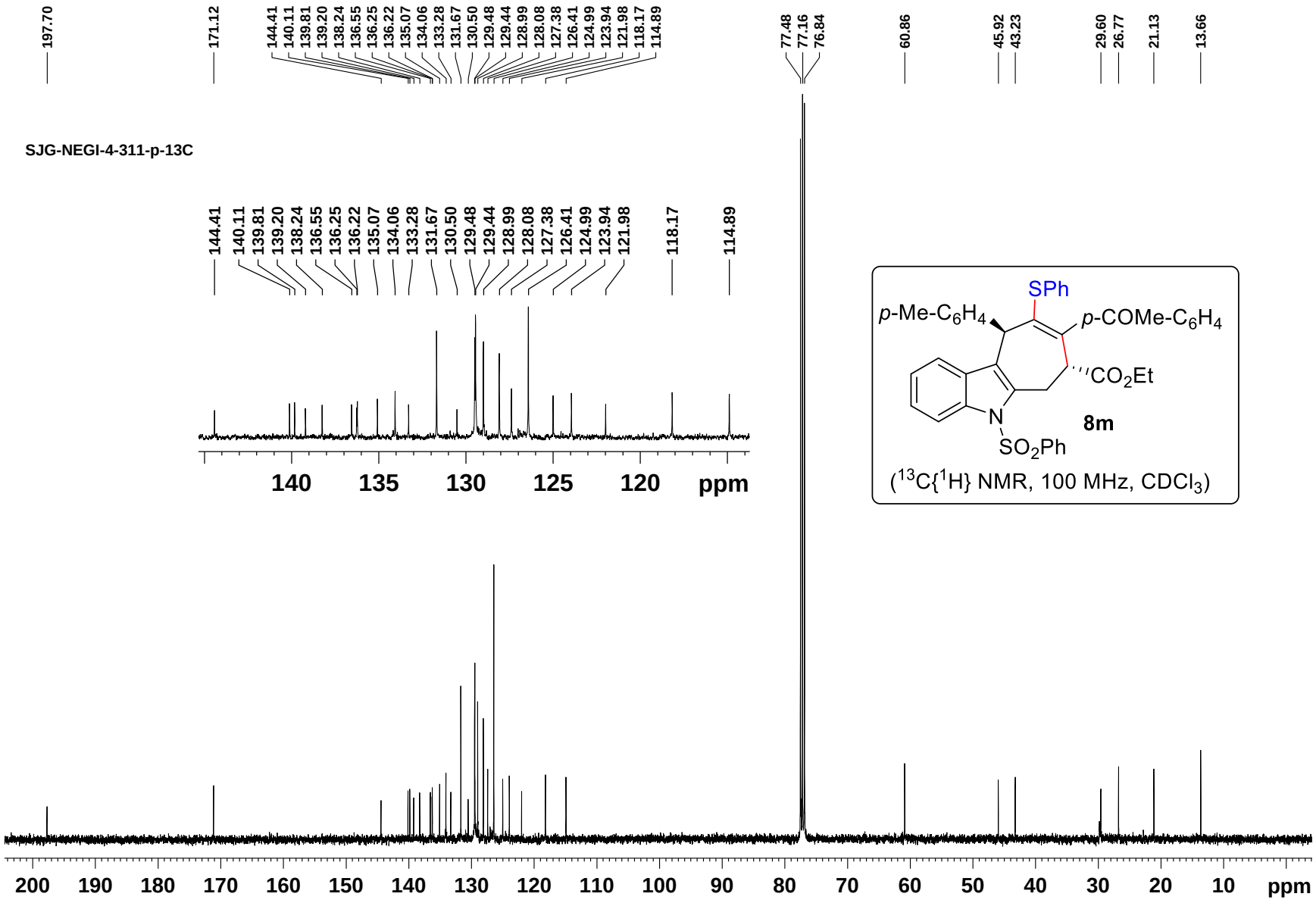


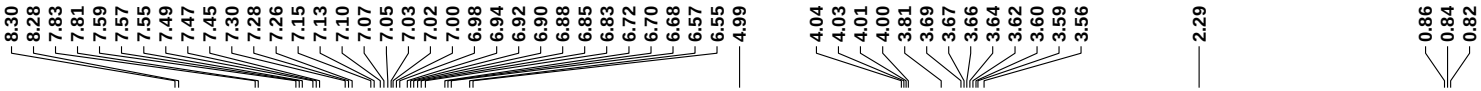
SJG-NEGI-4-311-p-1H



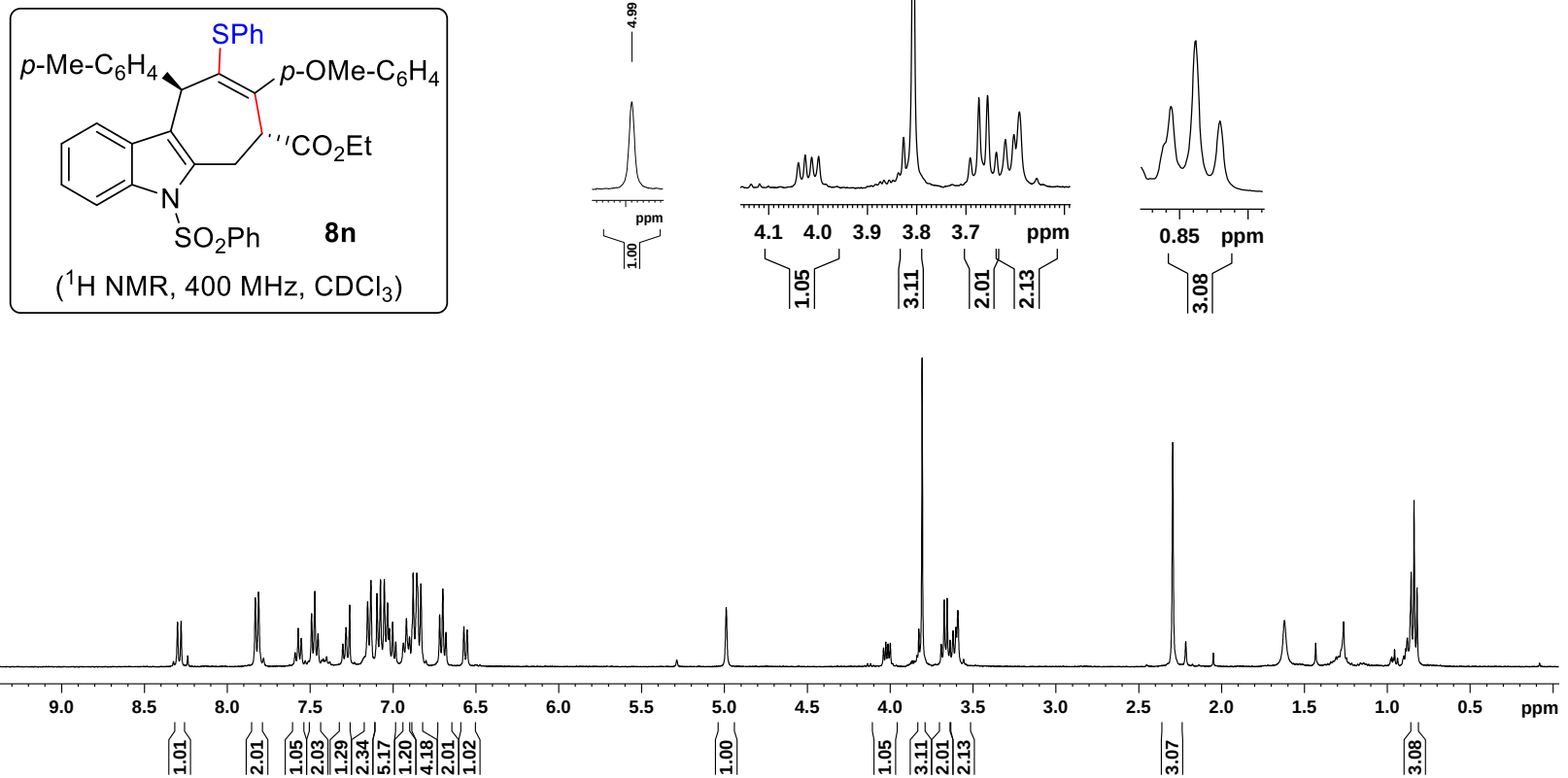


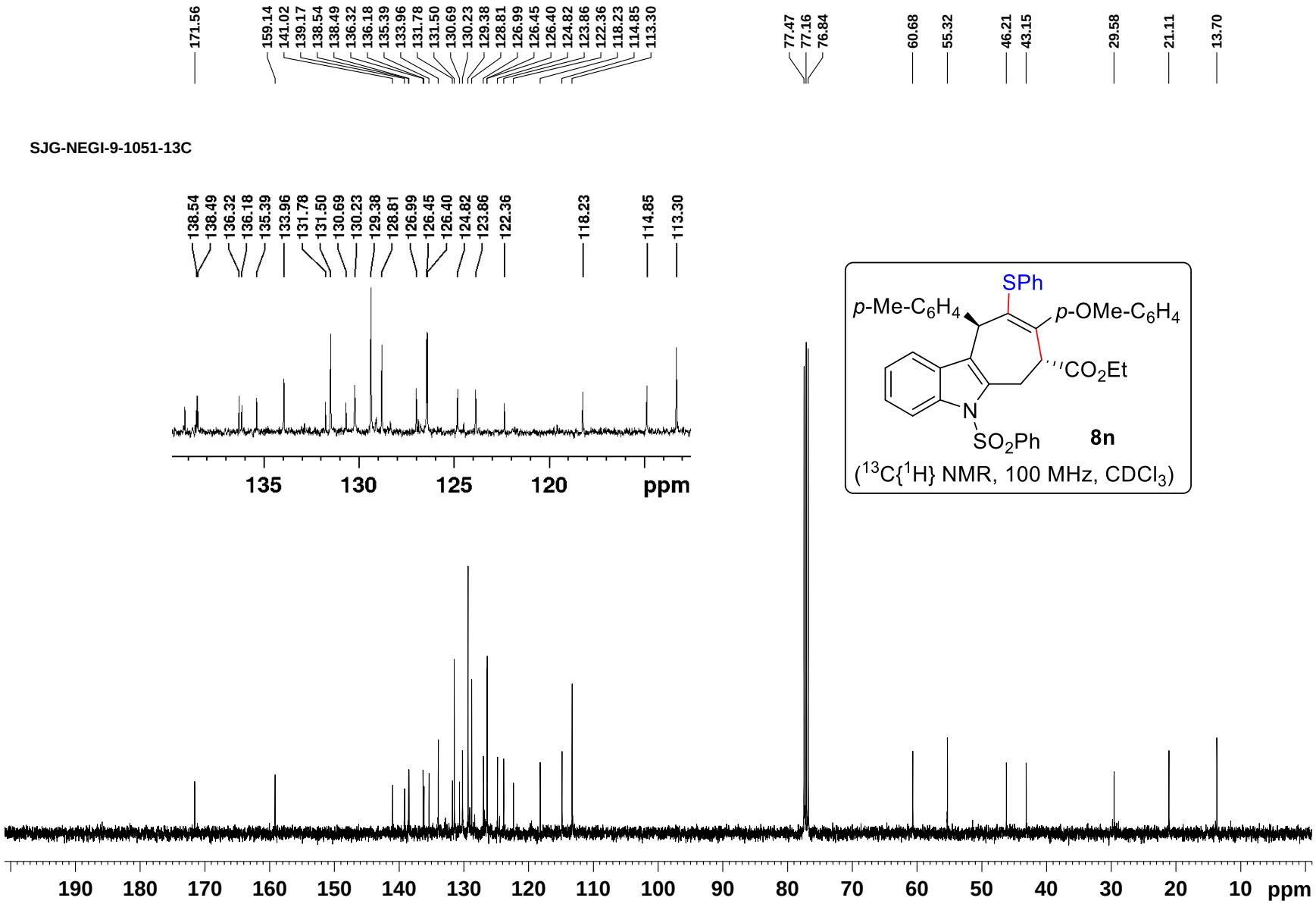


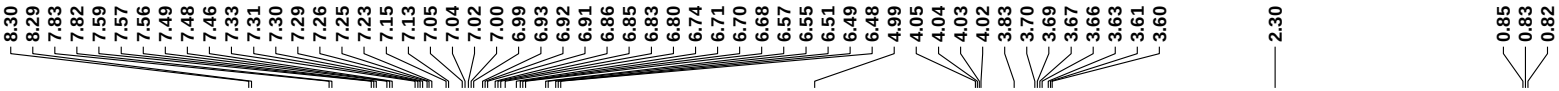

197.70
171.12
144.41
140.11
139.81
139.20
138.24
136.55
136.25
136.22
135.07
134.06
133.28
131.67
130.50
129.48
129.44
128.99
128.08
127.38
126.41
124.99
123.94
121.98
118.17
114.89
77.48
77.16
76.84
60.86
45.92
43.23
29.60
26.77
21.13
13.66
SJG-NEGI-4-311-p-13C
140
135
130
125
120
ppm
SPh
p-Me-C6H4
p-COMe-C6H4
CO2Et
N
SO2Ph
8m
(13C{1H} NMR, 100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



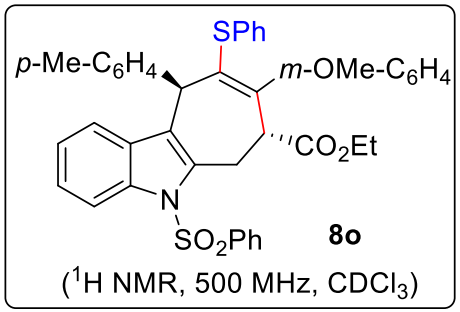
SJG-NEGI-9-1051-1H

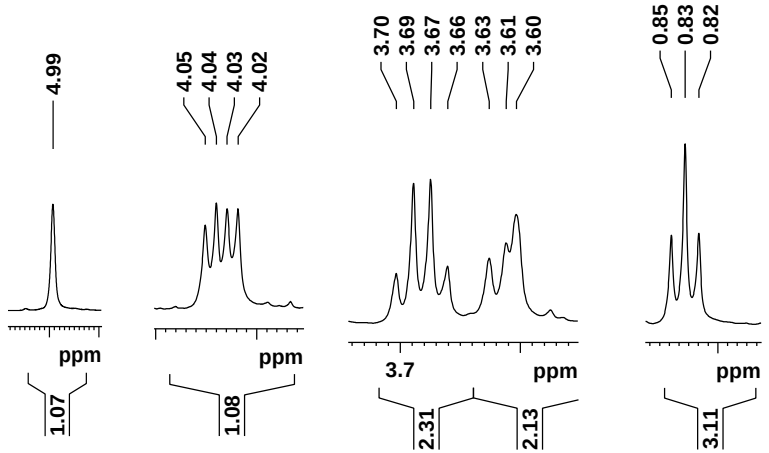


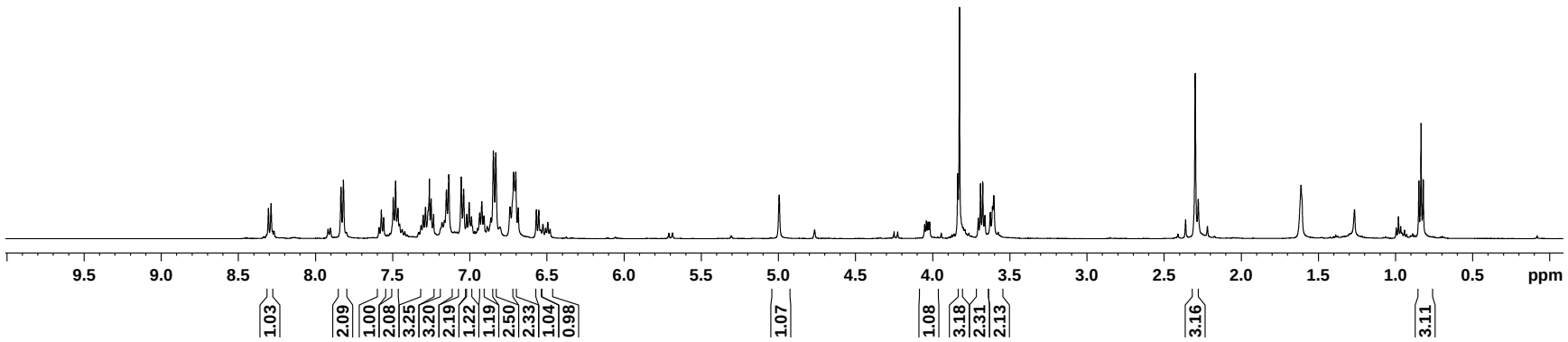

171.56
159.14
141.02
139.17
138.54
138.49
136.32
136.18
135.39
133.96
131.78
131.50
130.69
130.23
129.38
128.81
126.99
126.45
126.40
124.82
123.86
122.36
118.23
114.85
113.30
77.47
77.16
76.84
60.68
55.32
46.21
43.15
29.58
21.11
13.70
SJG-NEGI-9-1051-13C
SPh
p-Me-C6H4
p-OMe-C6H4
CO2Et
N
SO2Ph
8n
(13C{1H} NMR, 100 MHz, CDCl3)
135
130
125
120
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

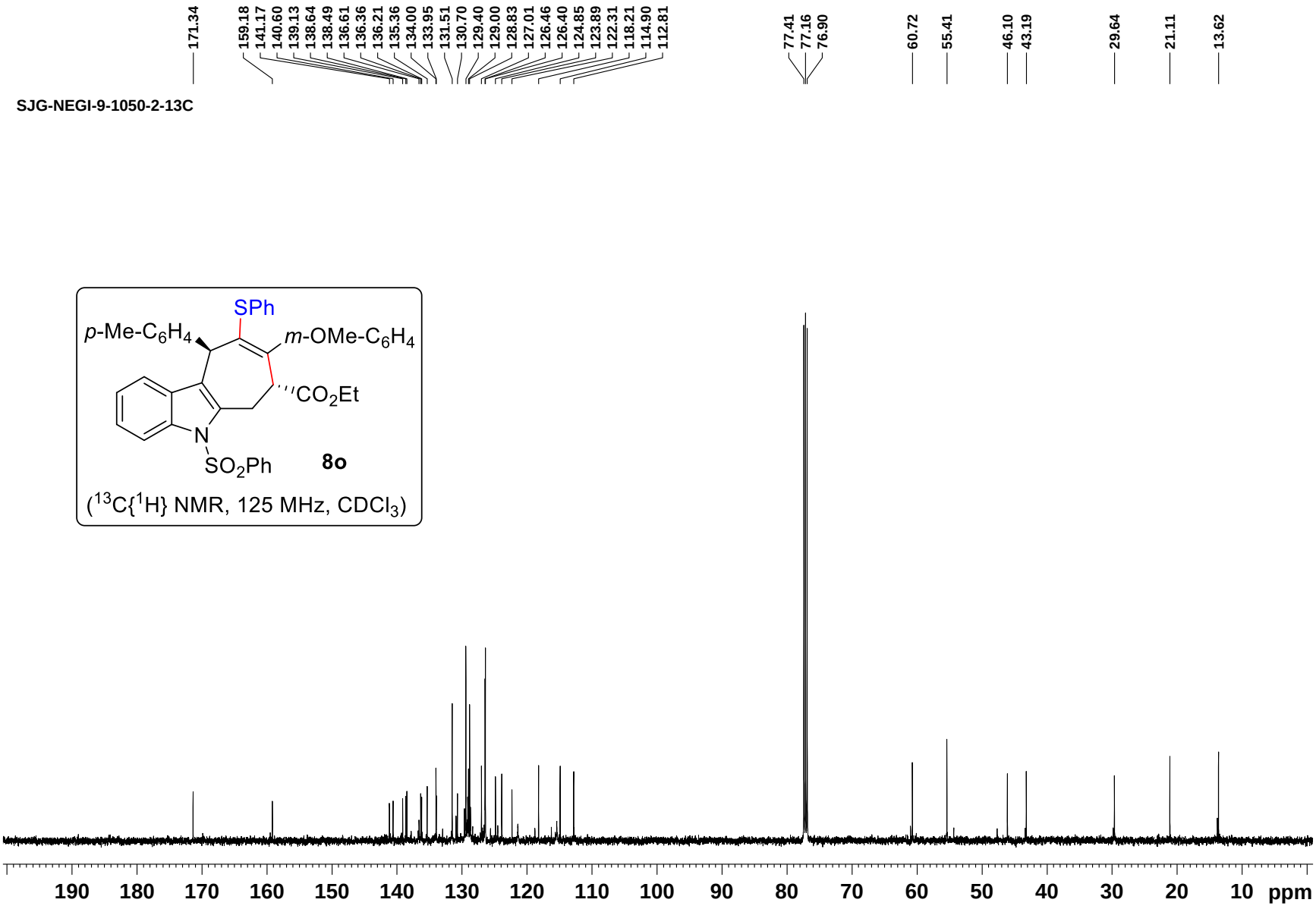


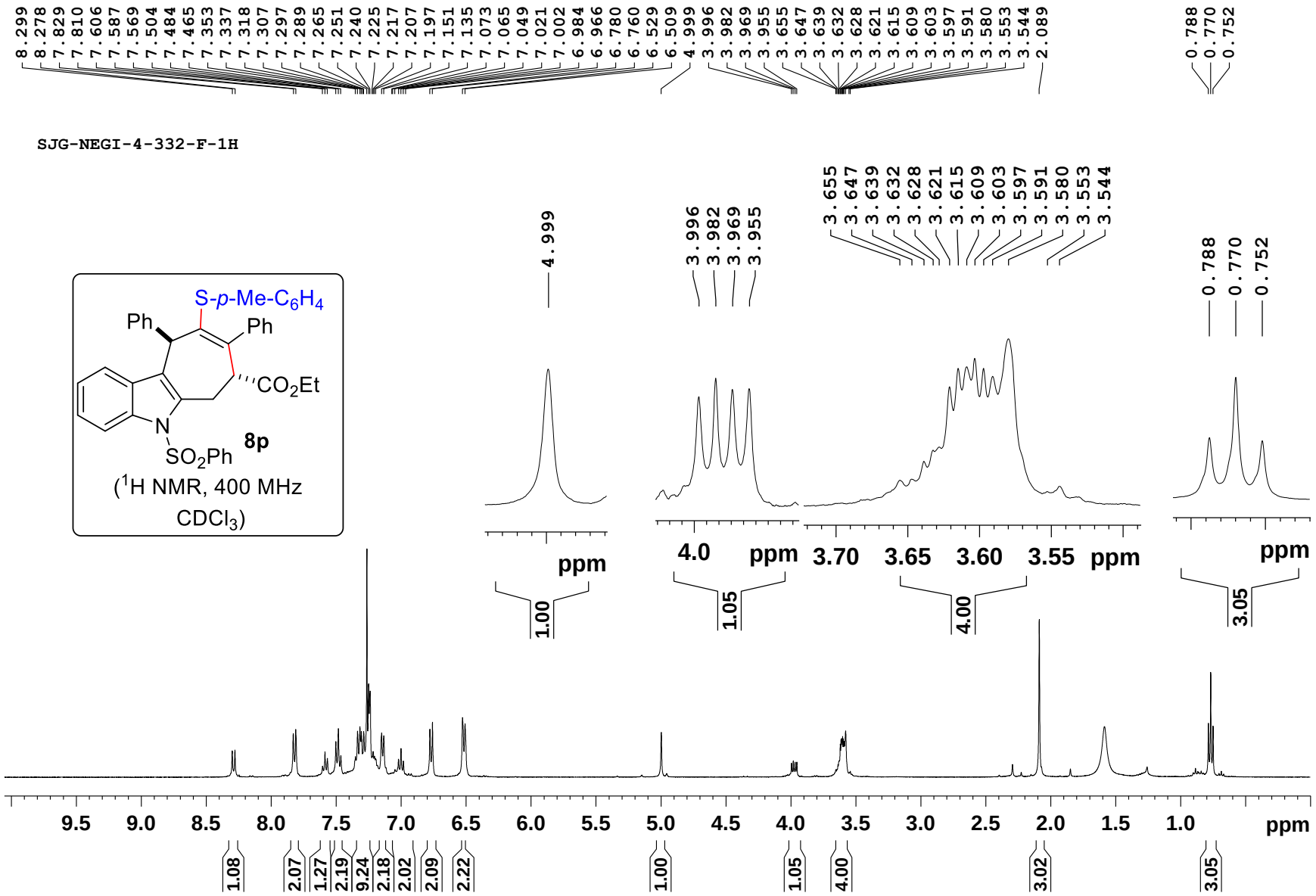
SJG-NEGI-9-1050-2-1H

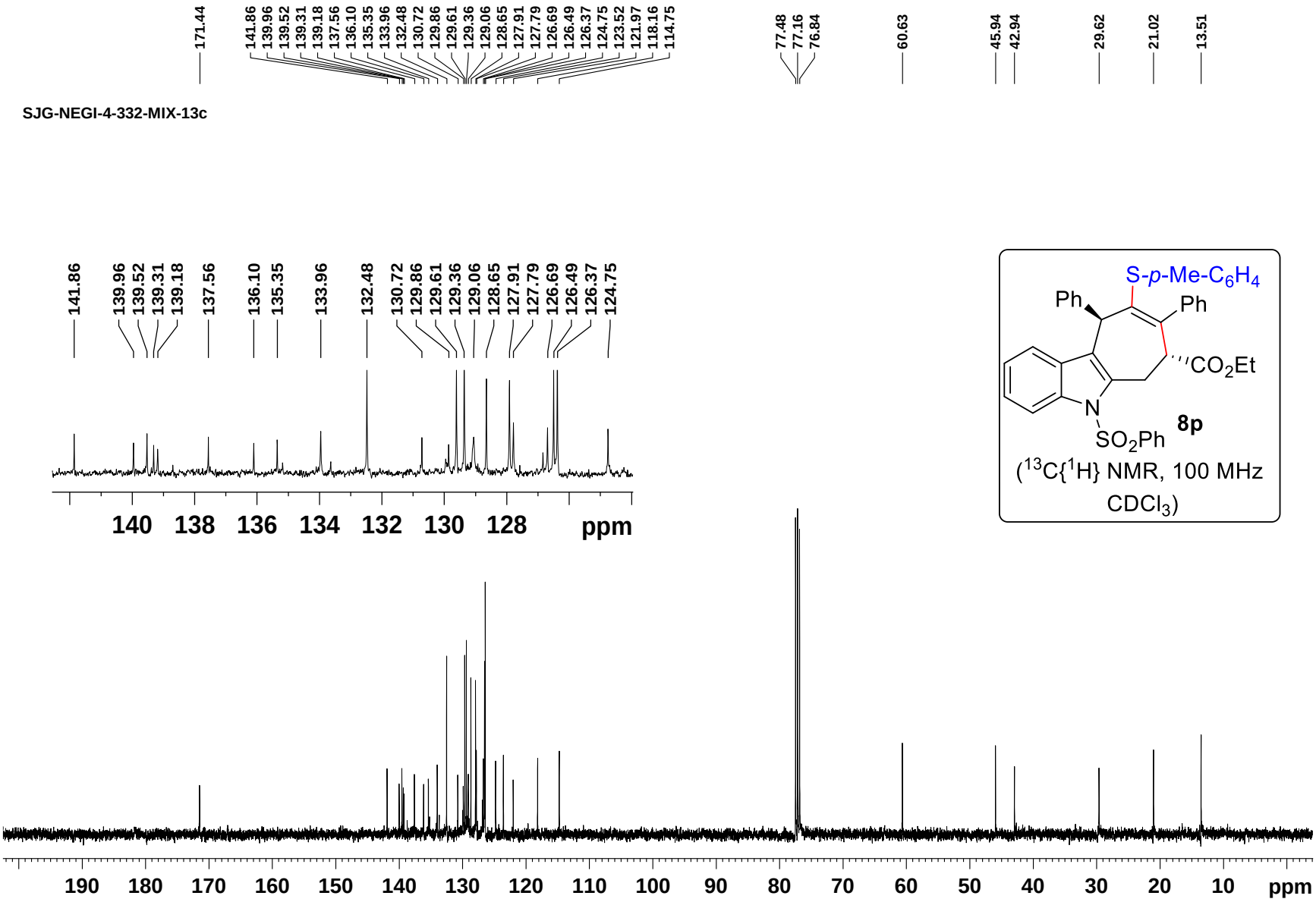


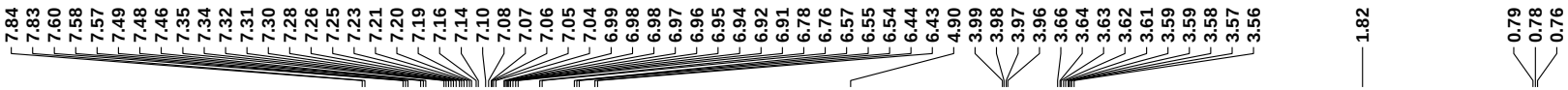




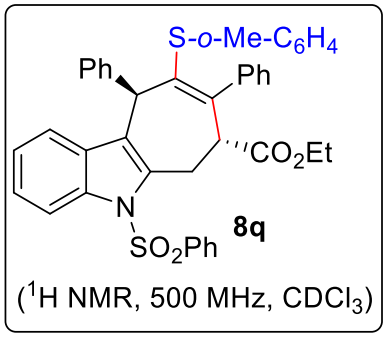

171.34
159.18
141.17
140.60
139.13
138.64
138.49
136.61
136.36
136.21
135.36
134.00
133.95
131.51
130.70
129.40
129.00
128.83
127.01
126.46
126.40
124.85
123.89
122.31
118.21
114.90
112.81
77.41
77.16
76.90
60.72
55.41
46.10
43.19
29.64
21.11
13.62
SJG-NEGI-9-1050-2-13C
SPh
p-Me-C6H4
m-OMe-C6H4
CO2Et
N
SO2Ph
8o
(13C{1H} NMR, 125 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

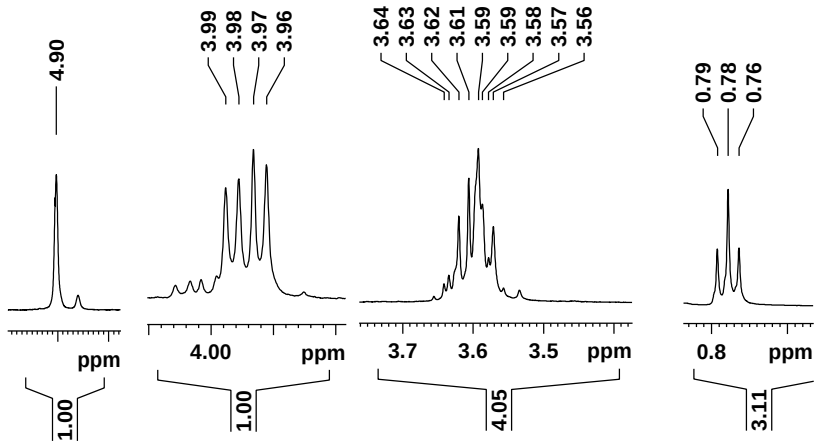

SJG-NEGI-4-332-F-1H
S-p-Me-C6H4
Ph
Ph
CO2Et
N
SO2Ph
8p
(1H NMR, 400 MHz
CDCl3)
ppm

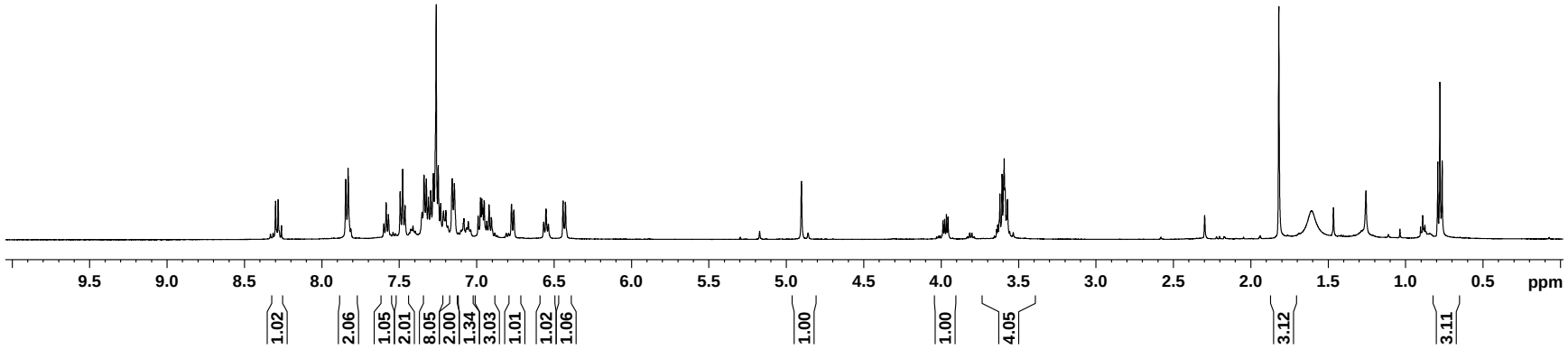

171.44
141.86
139.96
139.52
139.31
139.18
137.56
136.10
135.35
133.96
132.48
130.72
129.86
129.61
129.36
129.06
128.65
127.91
127.79
126.69
126.49
126.37
124.75
123.52
121.97
118.16
114.75
77.48
77.16
76.84
60.63
45.94
42.94
29.62
21.02
13.51
SJG-NEGI-4-332-MIX-13c
S-p-Me-C6H4
Ph
Ph
CO2Et
N
SO2Ph
8p
(13C{1H} NMR, 100 MHz
CDCl3)
ppm
ppm

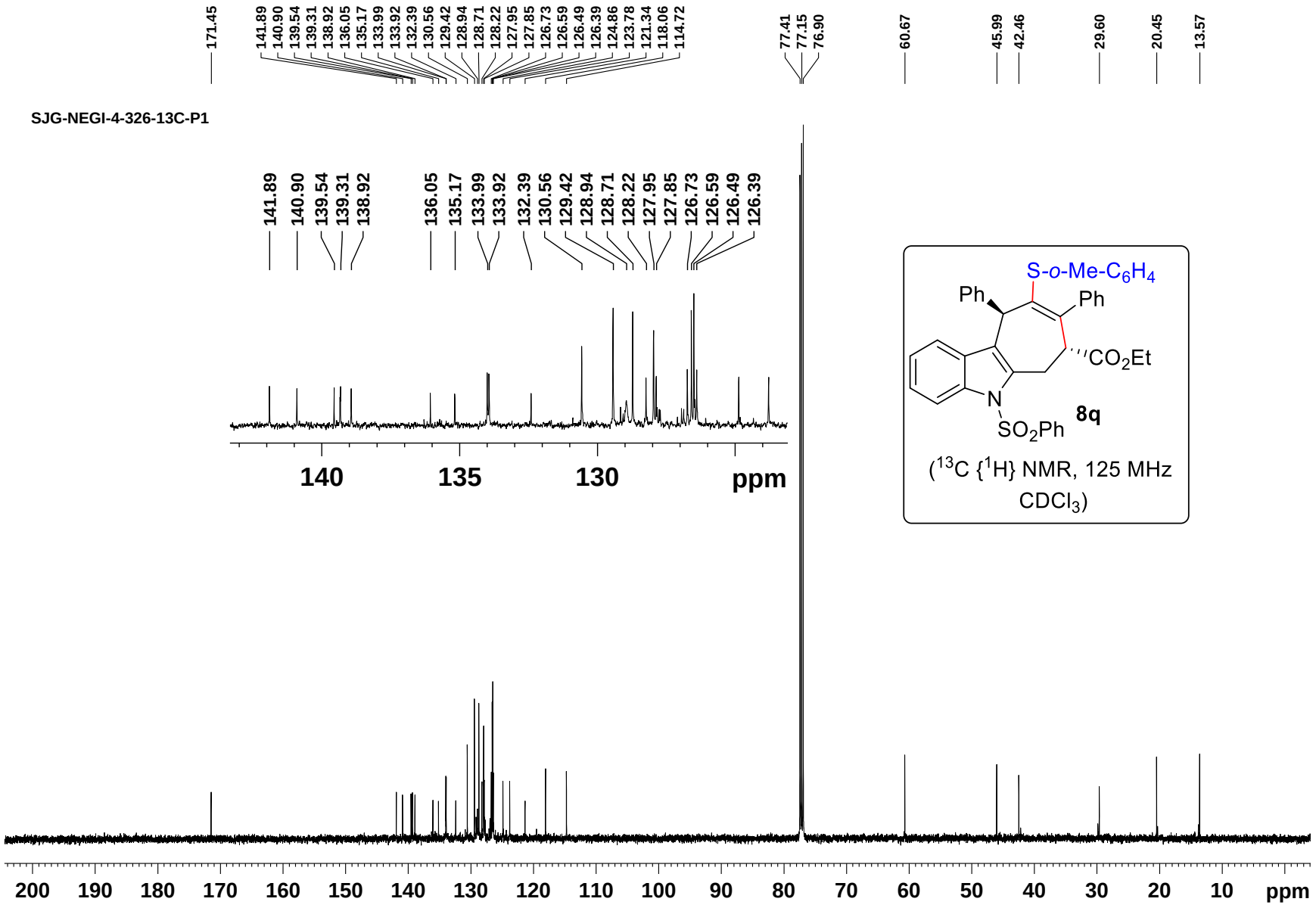


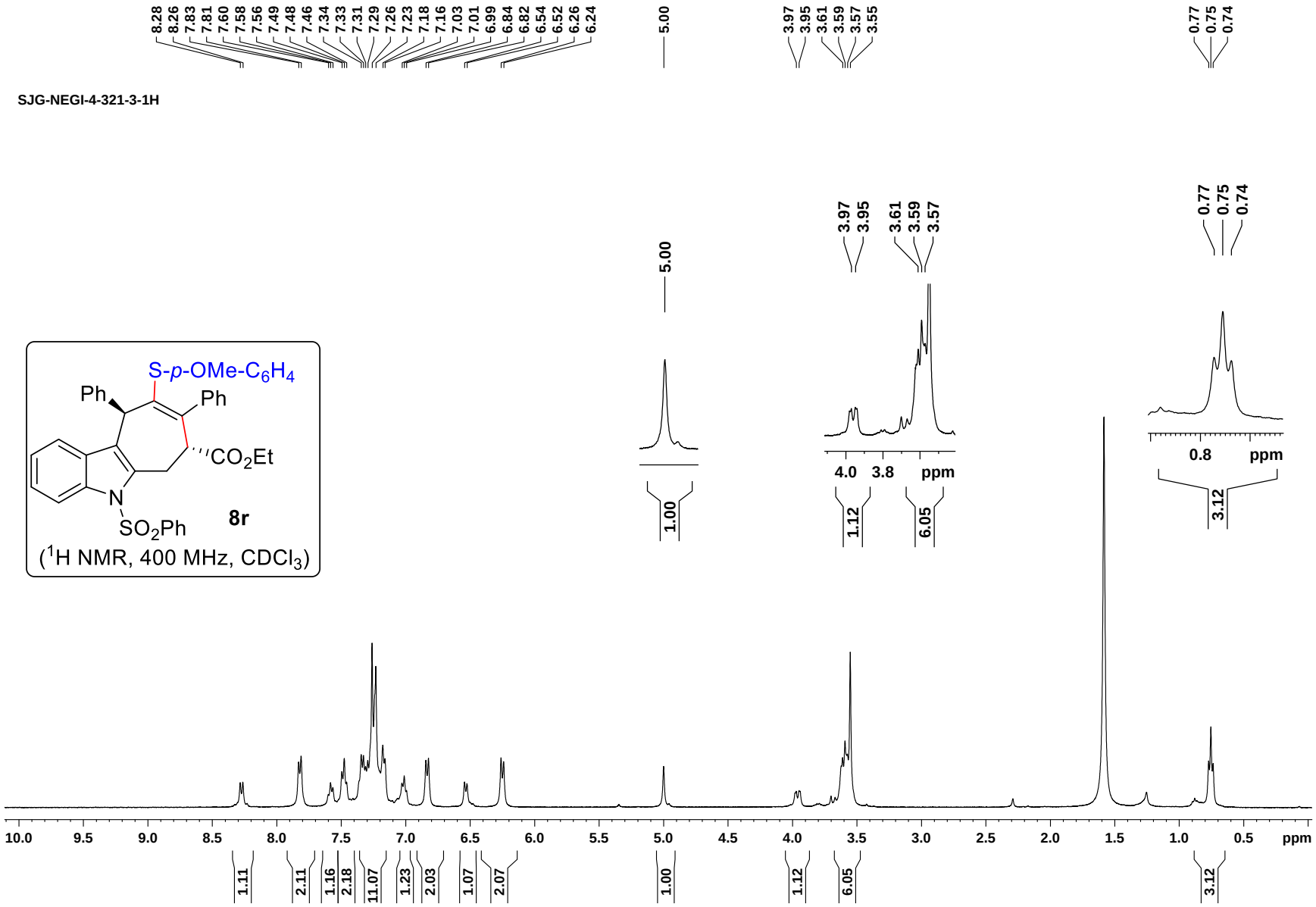
SJG-NEGI-4-326-1H

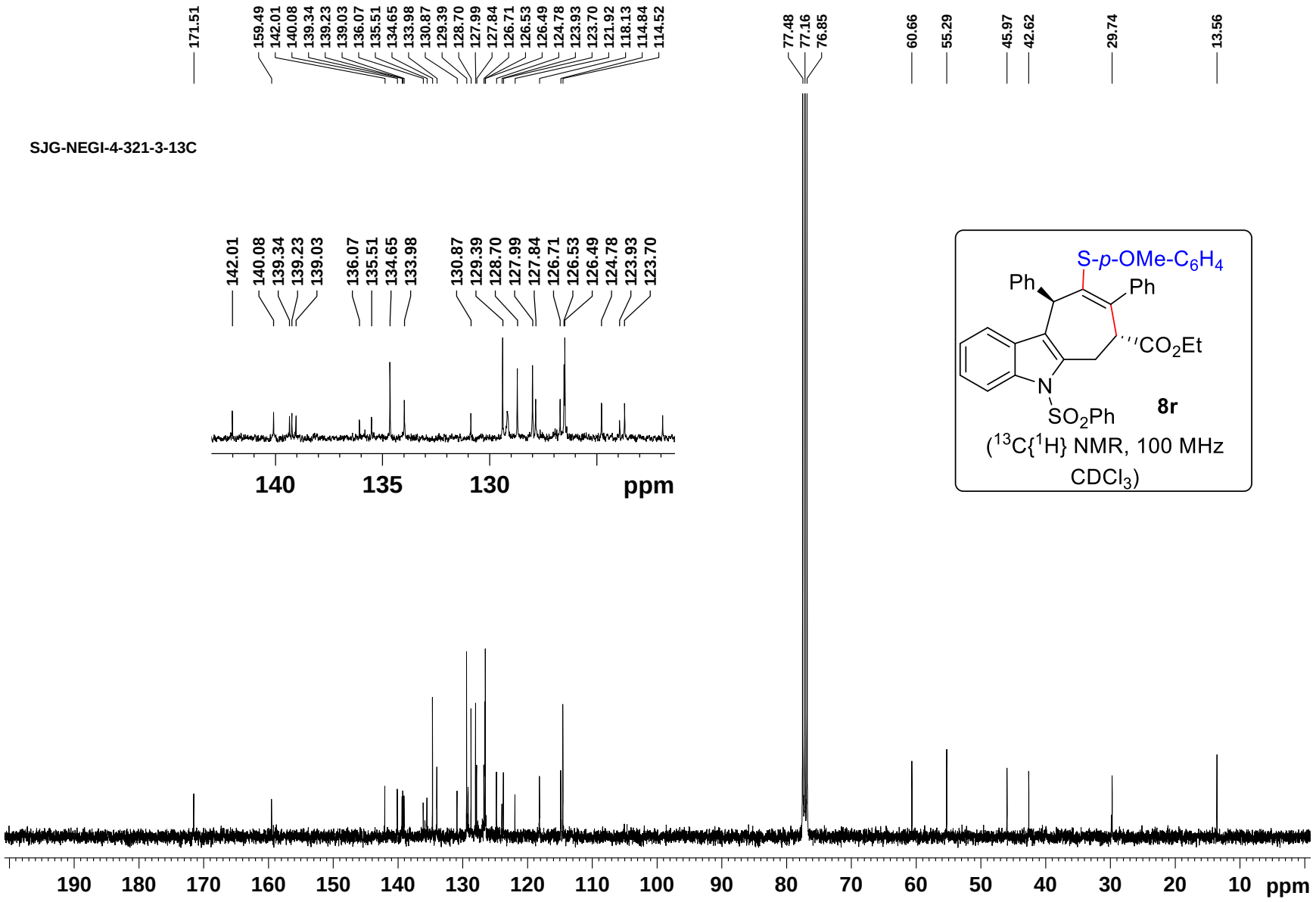


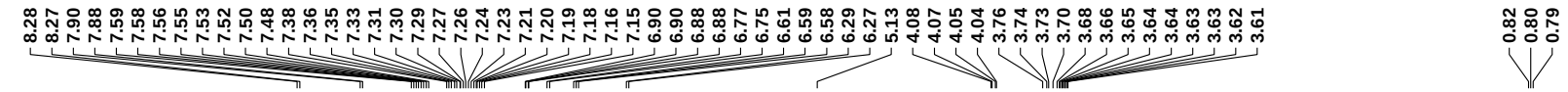


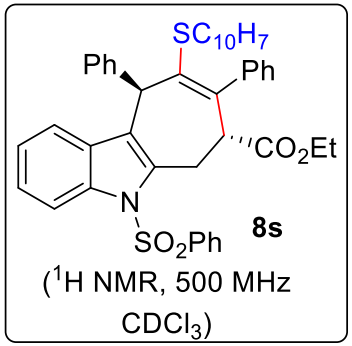


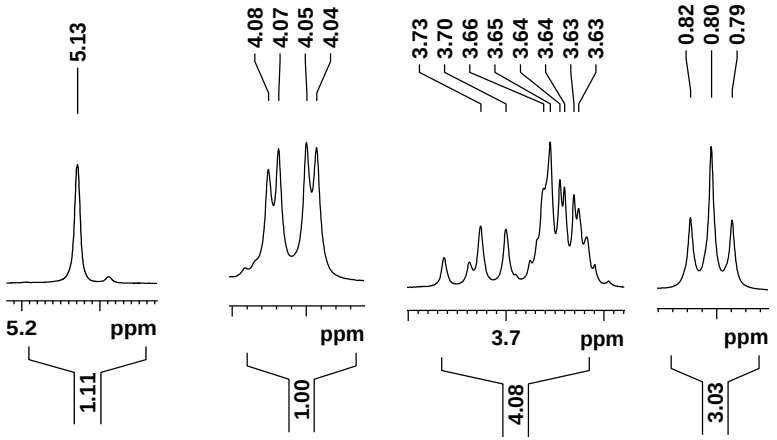

171.45
141.89
140.90
139.54
139.31
138.92
136.05
135.17
133.99
133.92
132.39
130.56
129.42
128.94
128.71
128.22
127.95
127.85
126.73
126.59
126.49
126.39
124.86
123.78
121.34
118.06
114.72
77.41
77.15
76.90
60.67
45.99
42.46
29.60
20.45
13.57
SJG-NEGI-4-326-13C-P1
140
135
130
ppm
S-o-Me-C6H4
Ph
Ph
CO2Et
N
SO2Ph
8q
(13C {1H} NMR, 125 MHz CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

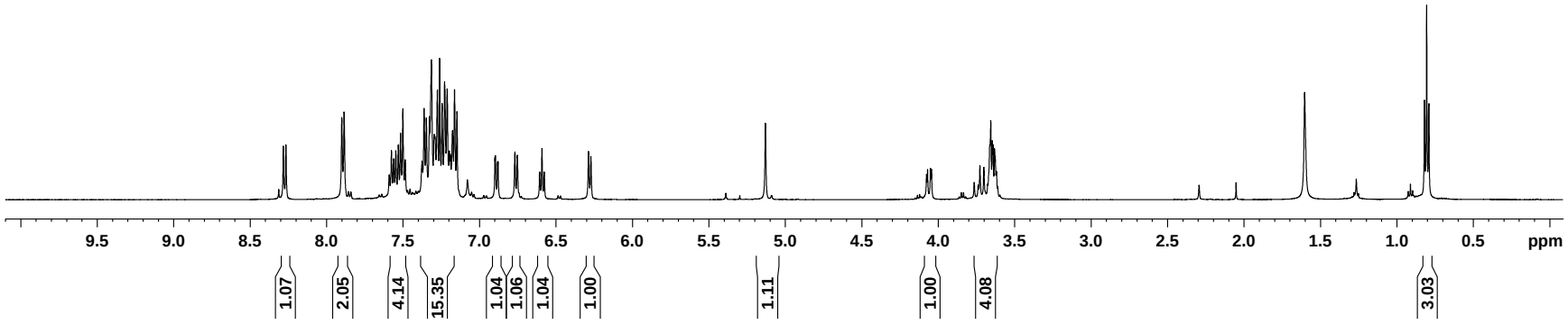

8.28
8.26
7.83
7.81
7.60
7.58
7.56
7.49
7.48
7.46
7.34
7.33
7.31
7.29
7.26
7.23
7.18
7.16
7.03
7.01
6.99
6.84
6.82
6.54
6.52
6.26
6.24
5.00
3.97
3.95
3.61
3.59
3.57
3.55
0.77
0.75
0.74
SJG-NEGI-4-321-3-1H
S-p-OMe-C6H4
Ph
Ph
CO2Et
N
SO2Ph
8r
(1H NMR, 400 MHz, CDCl3)
1.00
1.12
6.05
3.12
4.0
3.8
ppm
0.8
10.0
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
1.11
2.11
1.16
2.18
11.07
1.23
2.03
1.07
2.07

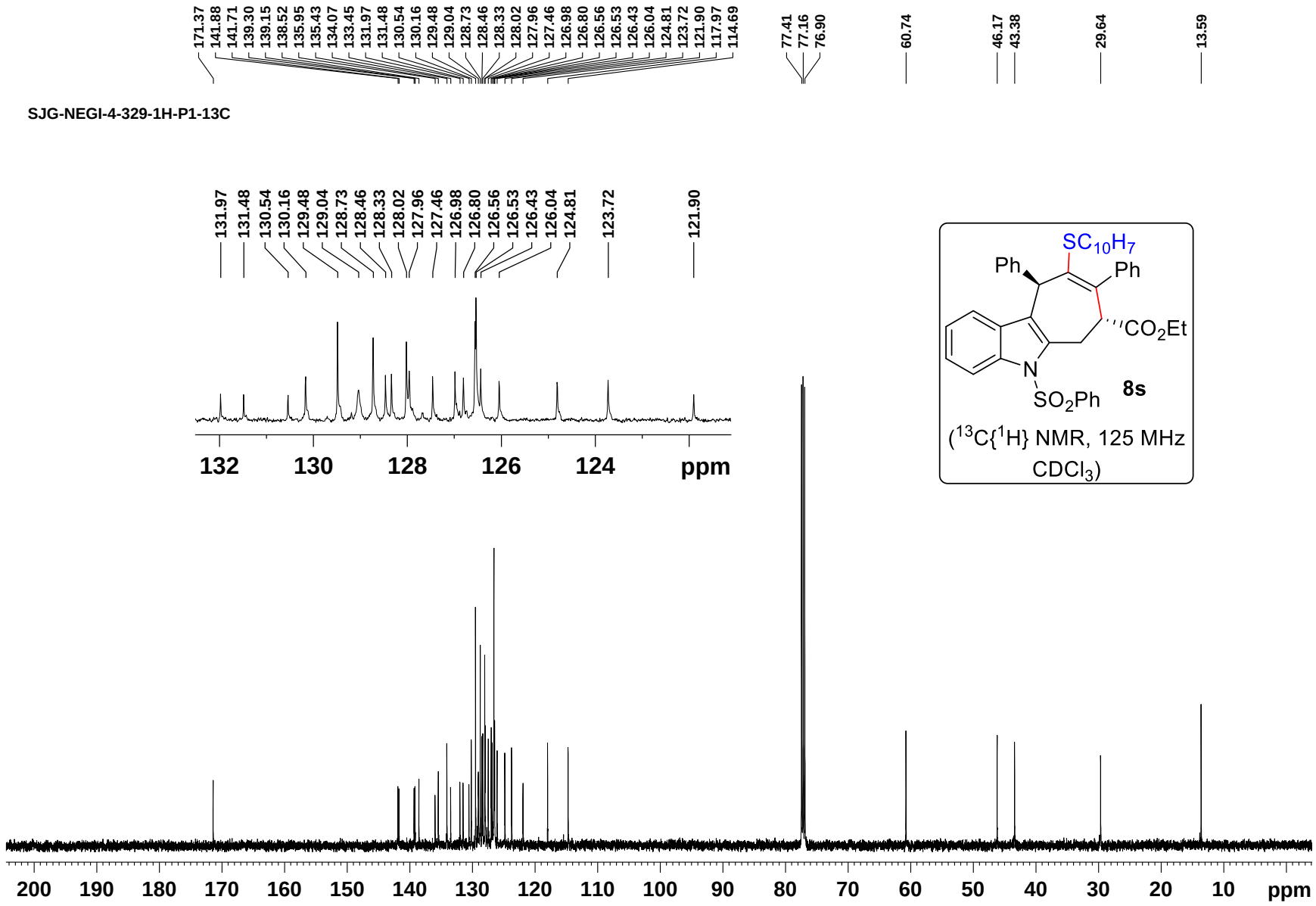

171.51
159.49
142.01
140.08
139.34
139.23
139.03
136.07
135.51
134.65
133.98
130.87
129.39
128.70
127.99
127.84
126.71
126.53
126.49
124.78
123.93
123.70
121.92
118.13
114.84
114.52
77.48
77.16
76.85
60.66
55.29
45.97
42.62
29.74
13.56
SJG-NEGI-4-321-3-13C
140
135
130
ppm
S-p-OMe-C6H4
Ph
Ph
CO2Et
N
SO2Ph
8r
(13C{1H} NMR, 100 MHz
CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

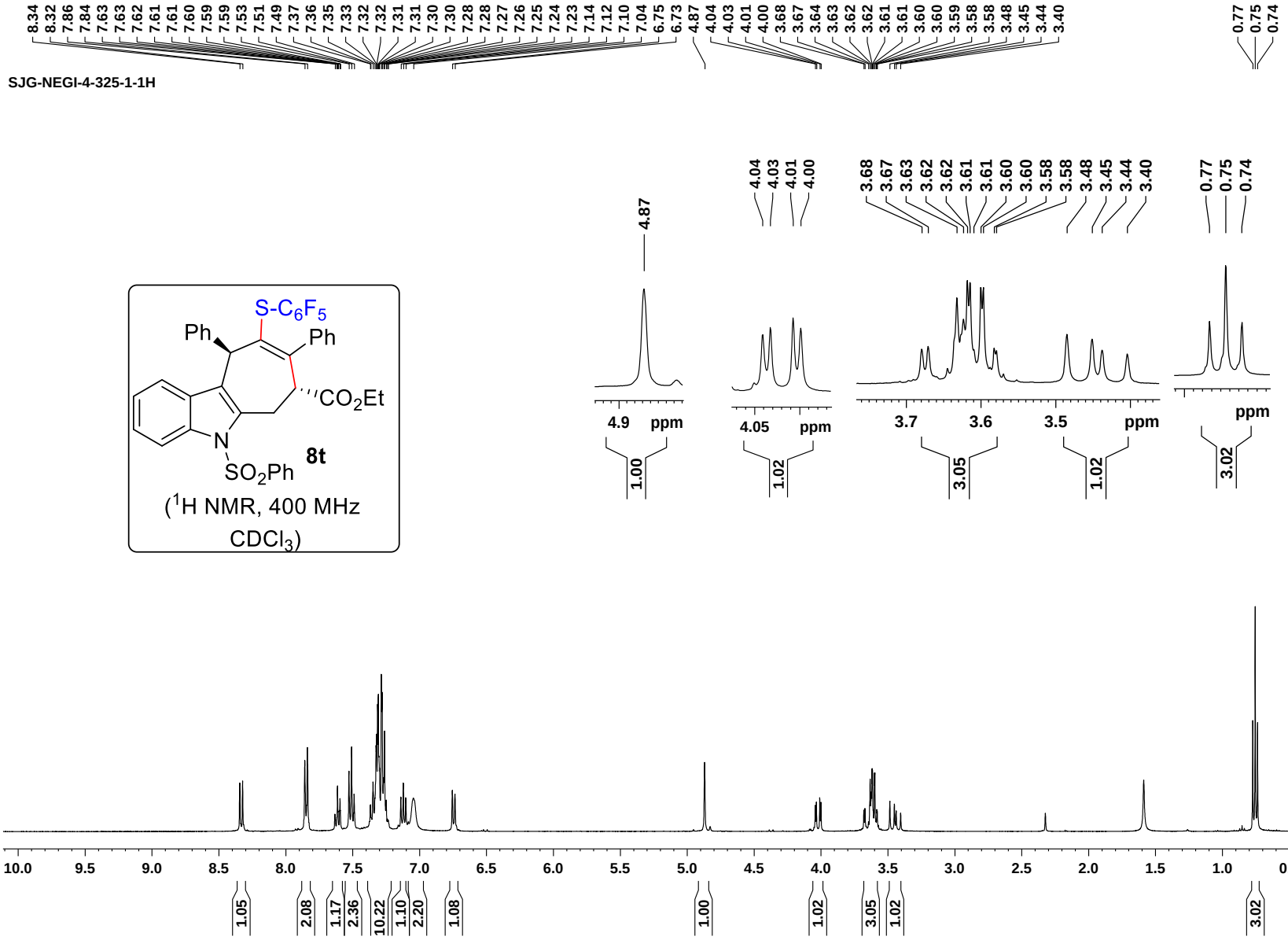

8.28 8.27 7.90 7.88 7.59 7.58 7.56 7.55 7.53 7.52 7.50 7.48 7.38 7.36 7.35 7.33 7.31 7.30 7.29 7.27 7.26 7.24 7.23 7.21 7.20 7.19 7.18 7.16 7.15 6.90 6.90 6.88 6.88 6.77 6.75 6.61 6.59 6.58 6.29 6.27 5.13 4.08 4.07 4.05 4.04 3.76 3.74 3.73 3.70 3.68 3.66 3.65 3.64 3.64 3.63 3.63 3.62 3.61
0.82 0.80 0.79
SJG-NEGI-4-329-1H-P1

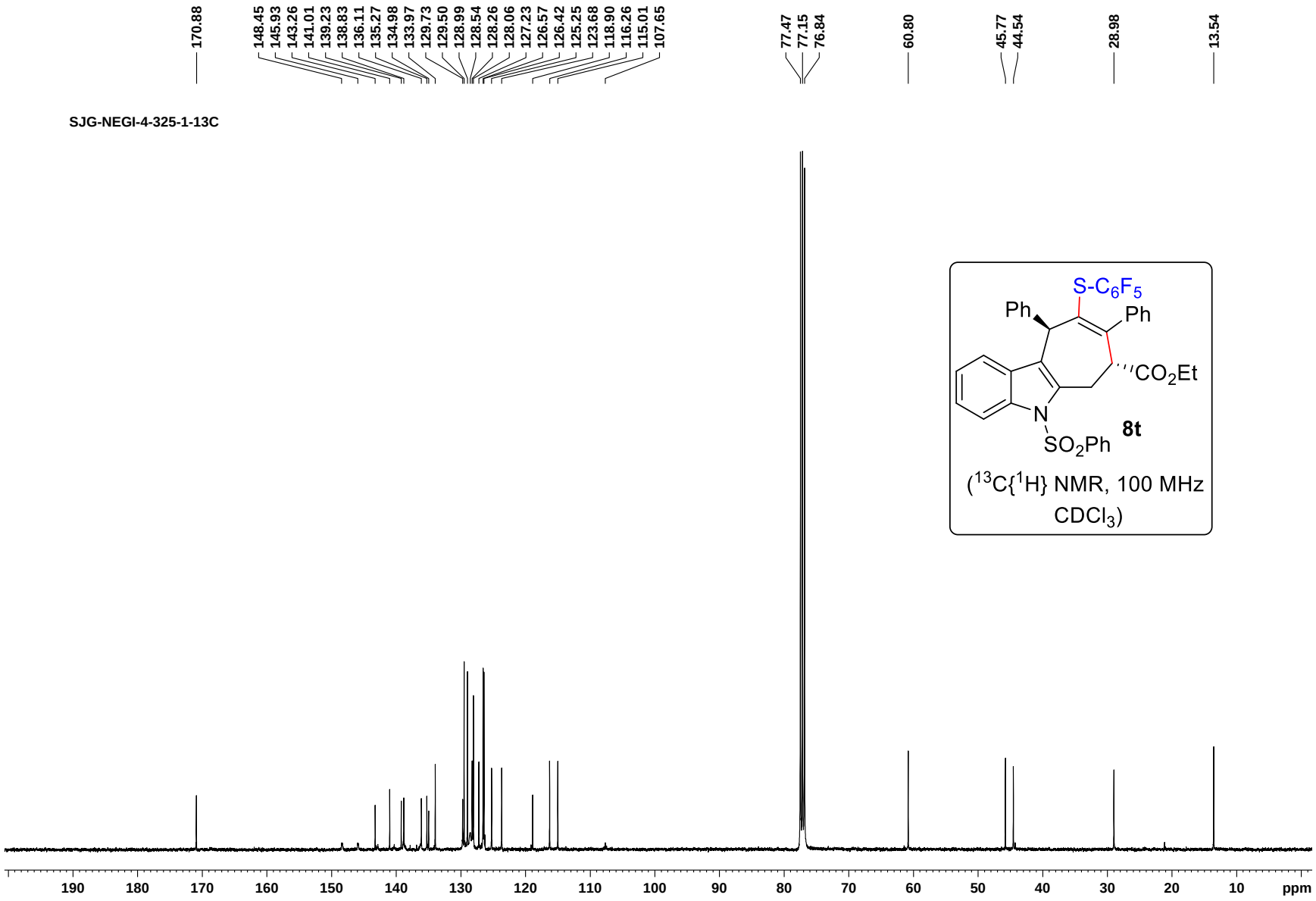

SC10H7
Ph
Ph
CO2Et
N
SO2Ph
8s
(1H NMR, 500 MHz
CDCl3)


5.13
4.08 4.07 4.05 4.04
3.73 3.70 3.66 3.65 3.64 3.64 3.63 3.63
0.82 0.80 0.79
5.2 ppm
ppm
3.7 ppm
ppm
1.11
1.00
4.08
3.03

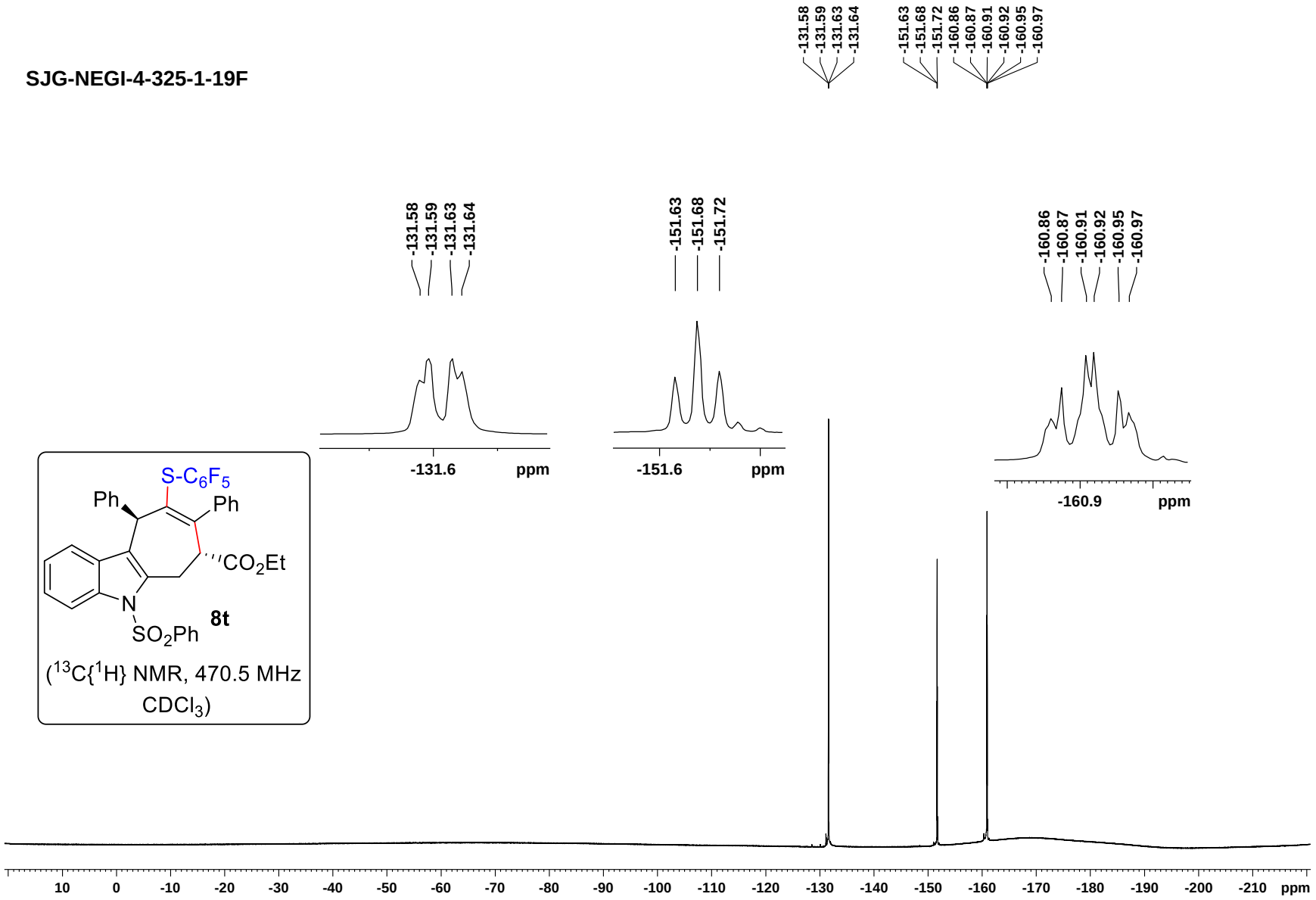

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.07 2.05 4.14 15.35 1.04 1.06 1.04 1.00 1.11 1.00 4.08 3.03


171.37
141.88
141.71
139.30
139.15
138.52
135.95
135.43
134.07
133.45
131.97
131.48
130.54
130.16
129.48
129.04
128.73
128.46
128.33
128.02
127.96
127.46
126.98
126.80
126.56
126.53
126.43
126.04
124.81
123.72
121.90
117.97
114.69
77.41
77.16
76.90
60.74
46.17
43.38
29.64
13.59
SJG-NEGI-4-329-1H-P1-13C
131.97
131.48
130.54
130.16
129.48
129.04
128.73
128.46
128.33
128.02
127.96
127.46
126.98
126.80
126.56
126.53
126.43
126.04
124.81
123.72
121.90
132
130
128
126
124
ppm
SC10H7
Ph
Ph
CO2Et
N
SO2Ph
8s
(13C{1H} NMR, 125 MHz
CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

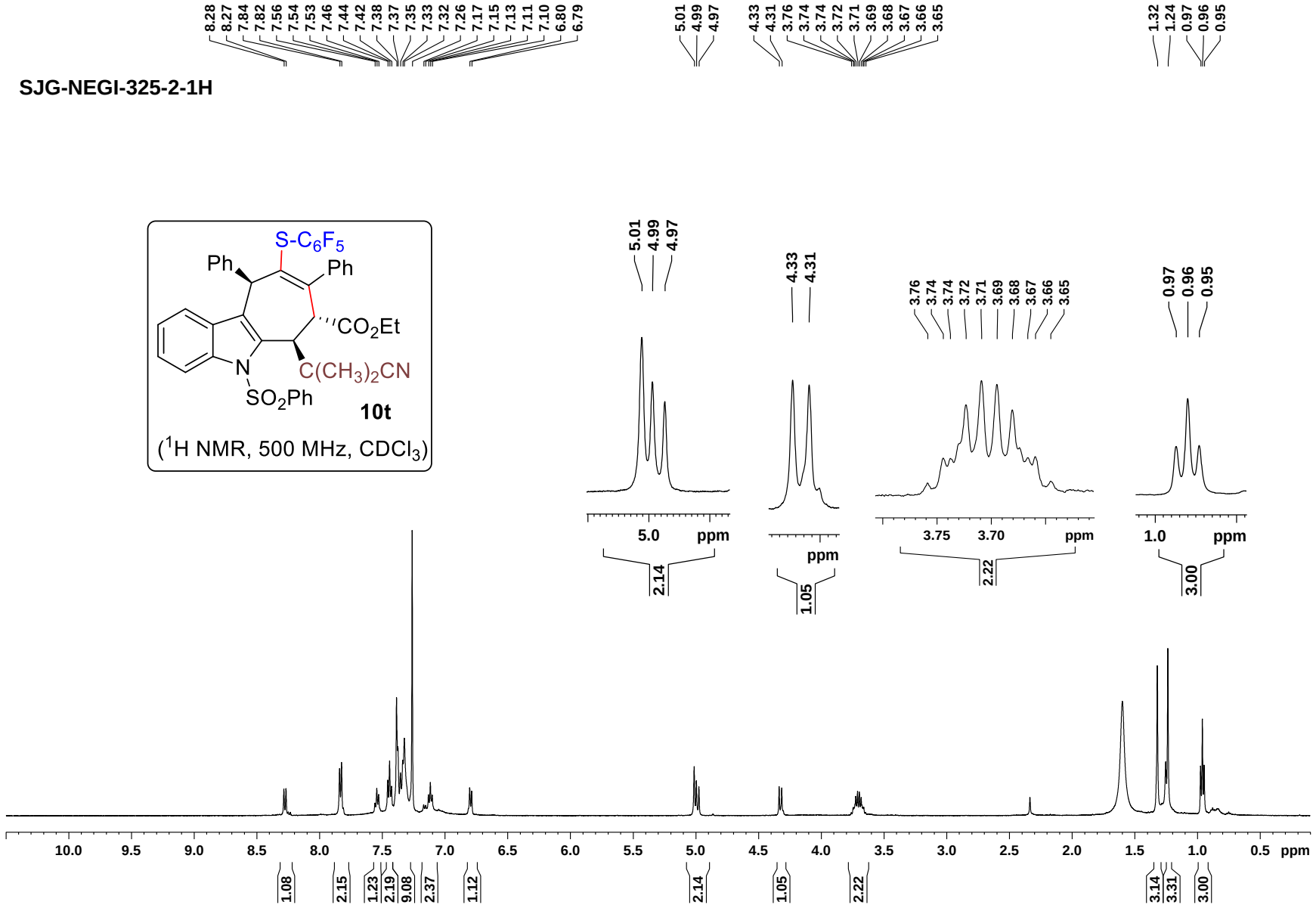

SJG-NEGI-4-325-1-1H
8.34 8.32 7.86 7.84 7.63 7.63 7.62 7.61 7.61 7.60 7.59 7.59 7.53 7.51 7.49 7.37 7.36 7.35 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.28 7.28 7.27 7.26 7.25 7.24 7.23 7.14 7.12 7.10 7.04 6.75 6.73 4.87 4.04 4.03 4.01 4.00 3.68 3.67 3.64 3.63 3.62 3.62 3.61 3.61 3.60 3.60 3.59 3.58 3.58 3.48 3.45 3.44 3.40 0.77 0.75 0.74
S-C6F5
Ph
Ph
CO2Et
N
SO2Ph
8t
(1H NMR, 400 MHz CDCl3)
4.87
4.04 4.03 4.01 4.00
3.68 3.67 3.63 3.62 3.62 3.61 3.61 3.60 3.60 3.58 3.58 3.48 3.45 3.44 3.40
0.77 0.75 0.74
4.9 ppm
4.05 ppm
3.7 3.6 3.5 ppm
ppm
1.00 1.02 3.05 1.02 3.02
10.0 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
1.05 2.08 1.17 2.36 10.22 1.10 2.20 1.08 1.00 1.02 3.05 1.02 3.02

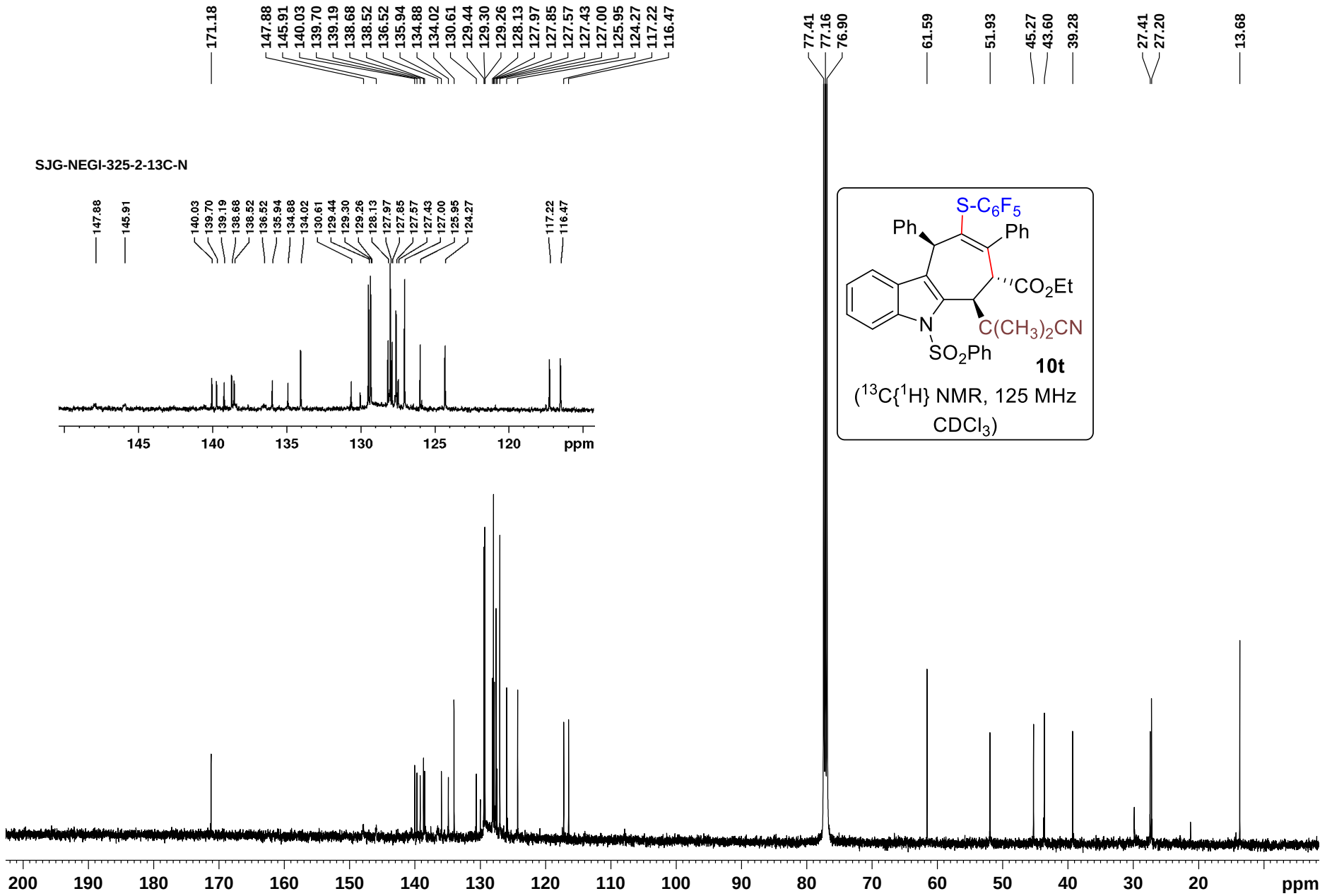

170.88
148.45
145.93
143.26
141.01
139.23
138.83
136.11
135.27
134.98
133.97
129.73
129.50
128.99
128.54
128.26
128.06
127.23
126.57
126.42
125.25
123.68
118.90
116.26
115.01
107.65
77.47
77.15
76.84
60.80
45.77
44.54
28.98
13.54
SJG-NEGI-4-325-1-13C
S-C6F5
Ph
Ph
CO2Et
N
SO2Ph
8t
(13C{1H} NMR, 100 MHz
CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

SJG-NEGI-4-325-1-19F

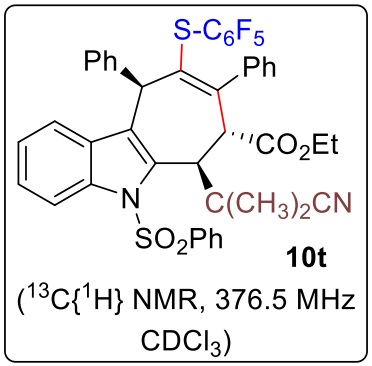


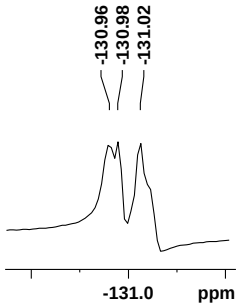
SJG-NEGI-325-2-1H

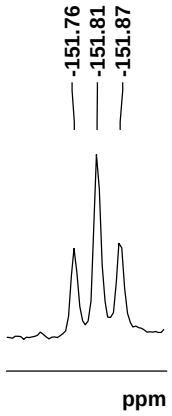


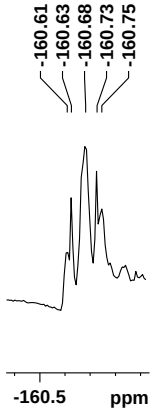

171.18
147.88
145.91
140.03
139.70
139.19
138.68
138.52
136.52
135.94
134.88
134.02
130.61
129.44
129.30
129.26
128.13
127.97
127.85
127.57
127.43
127.00
125.95
124.27
117.22
116.47
77.41
77.16
76.90
61.59
51.93
45.27
43.60
39.28
27.41
27.20
13.68
SJG-NEGI-325-2-13C-N
S-C6F5
Ph
Ph
CO2Et
C(CH3)2CN
N
SO2Ph
10t
(13C{1H} NMR, 125 MHz
CDCl3)
ppm

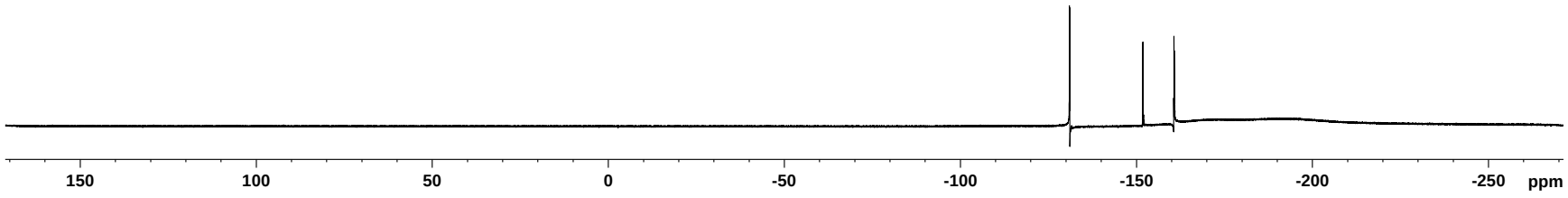
SJG-NEGI-325-2-19F

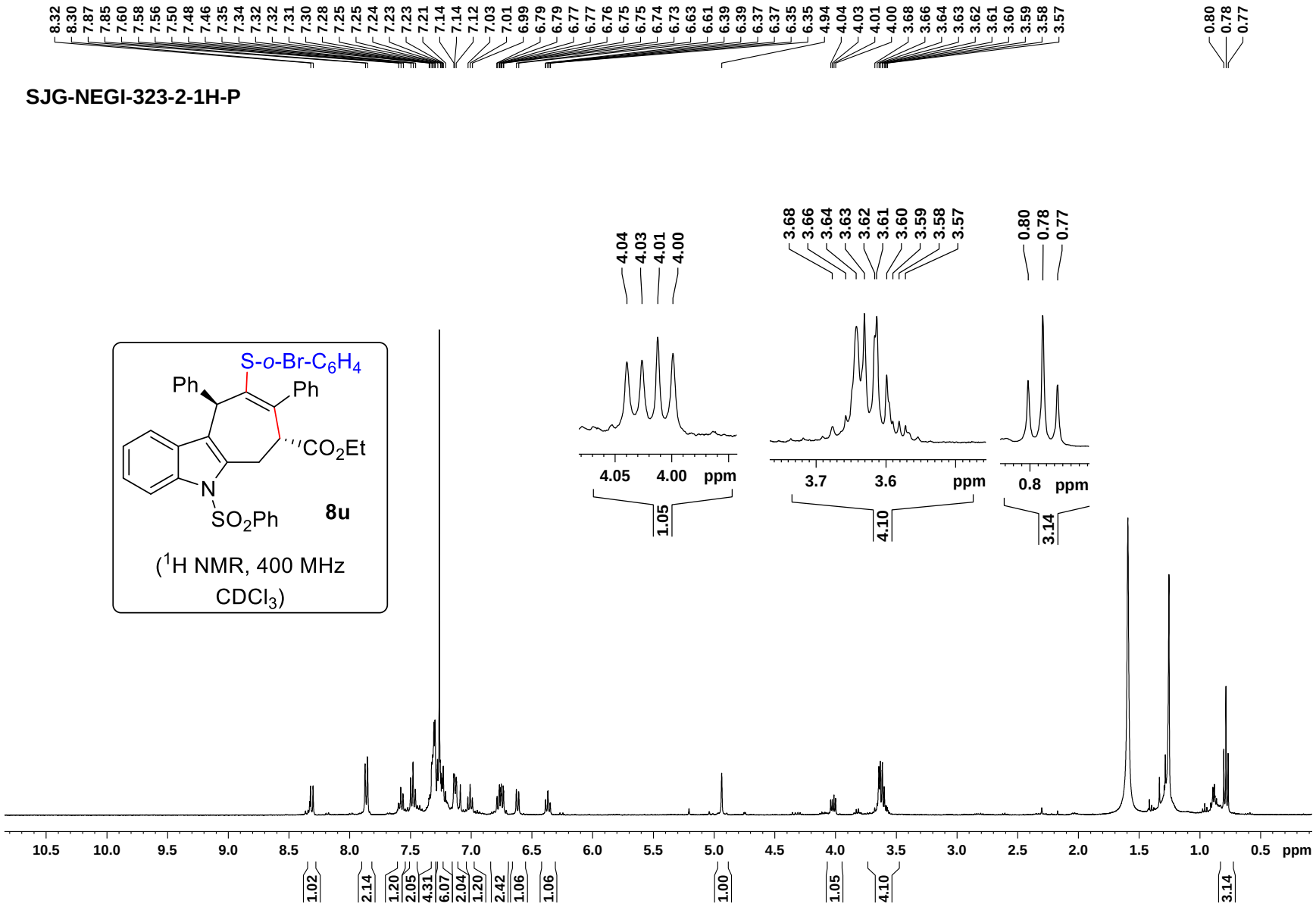


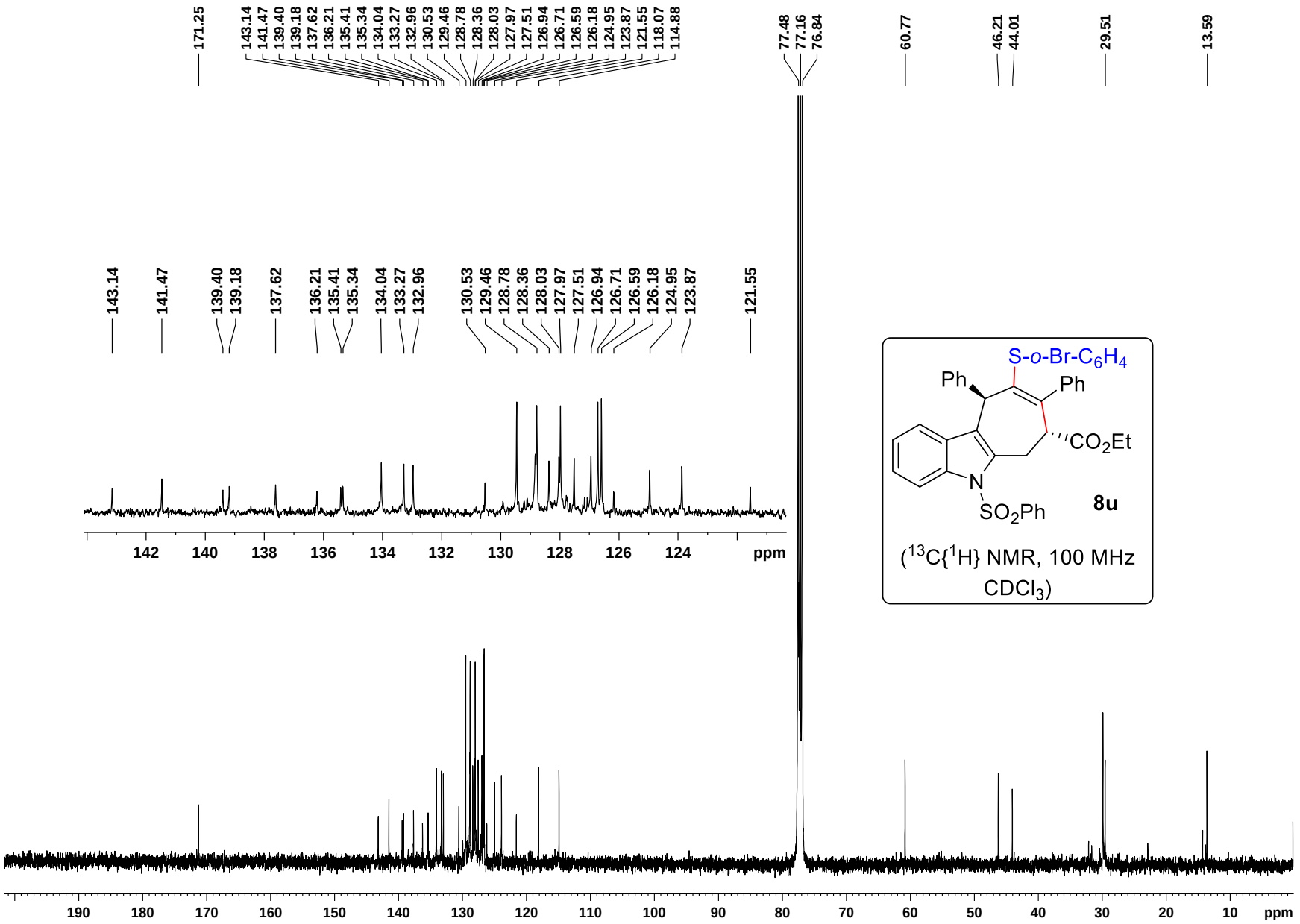


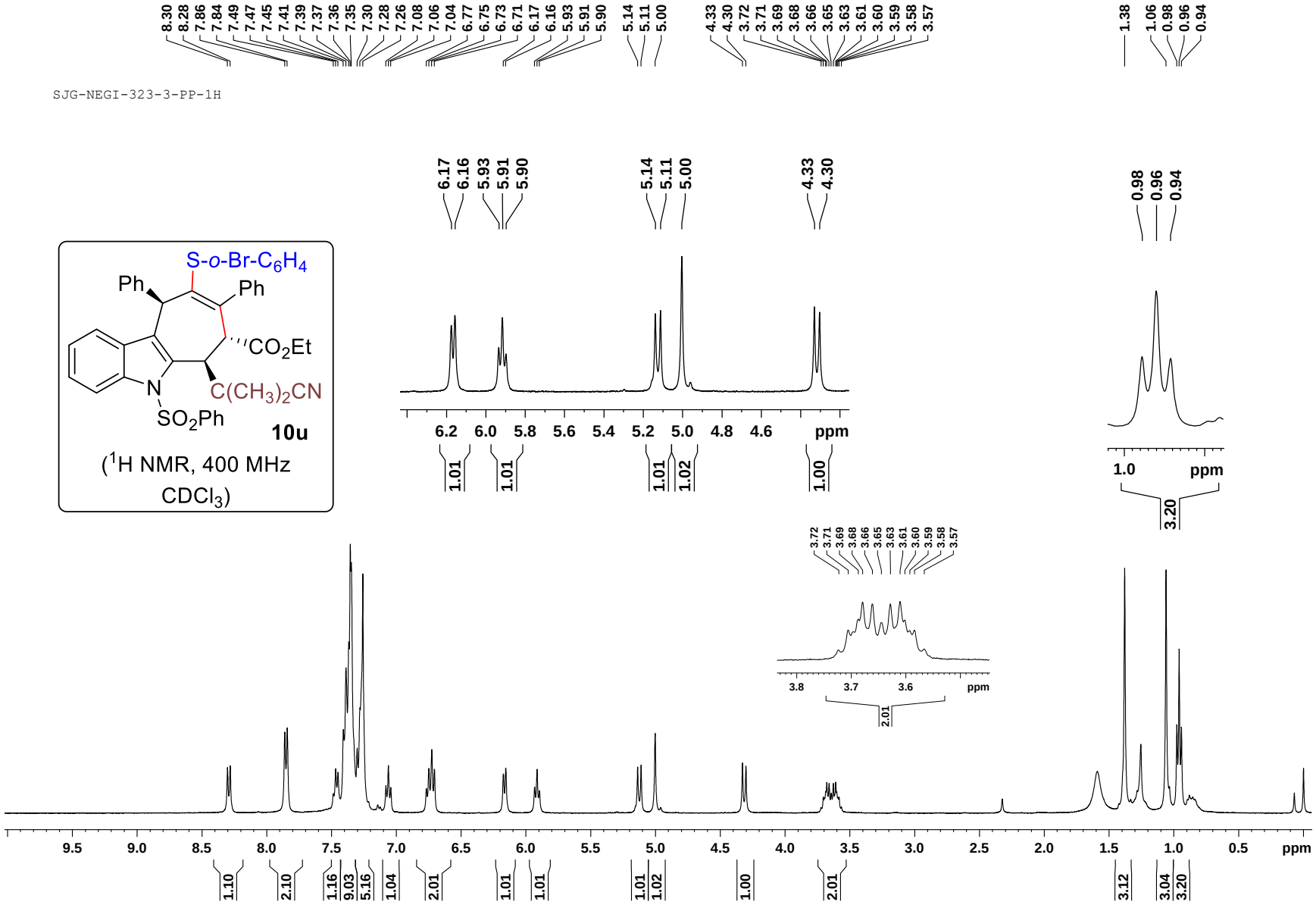


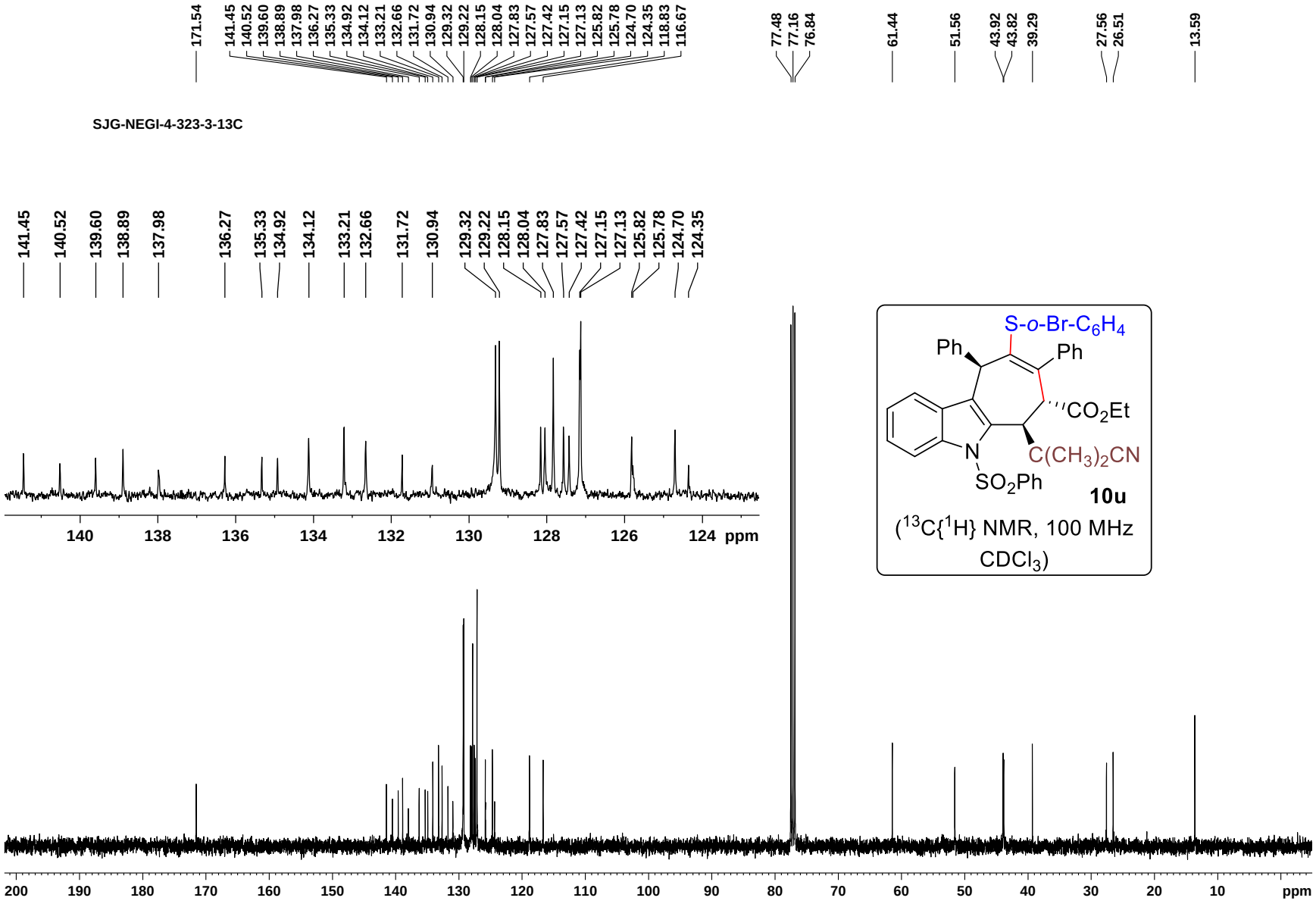


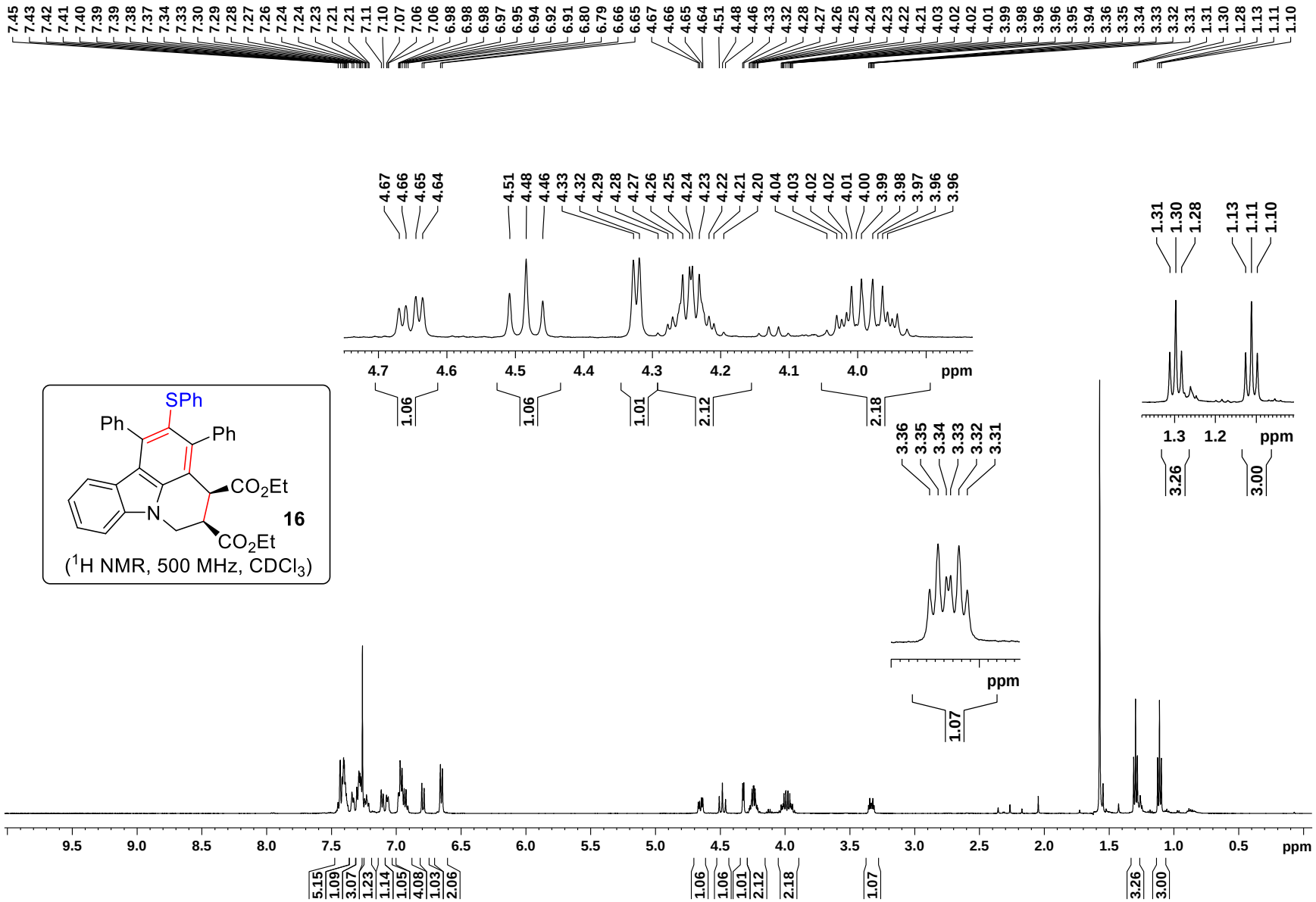


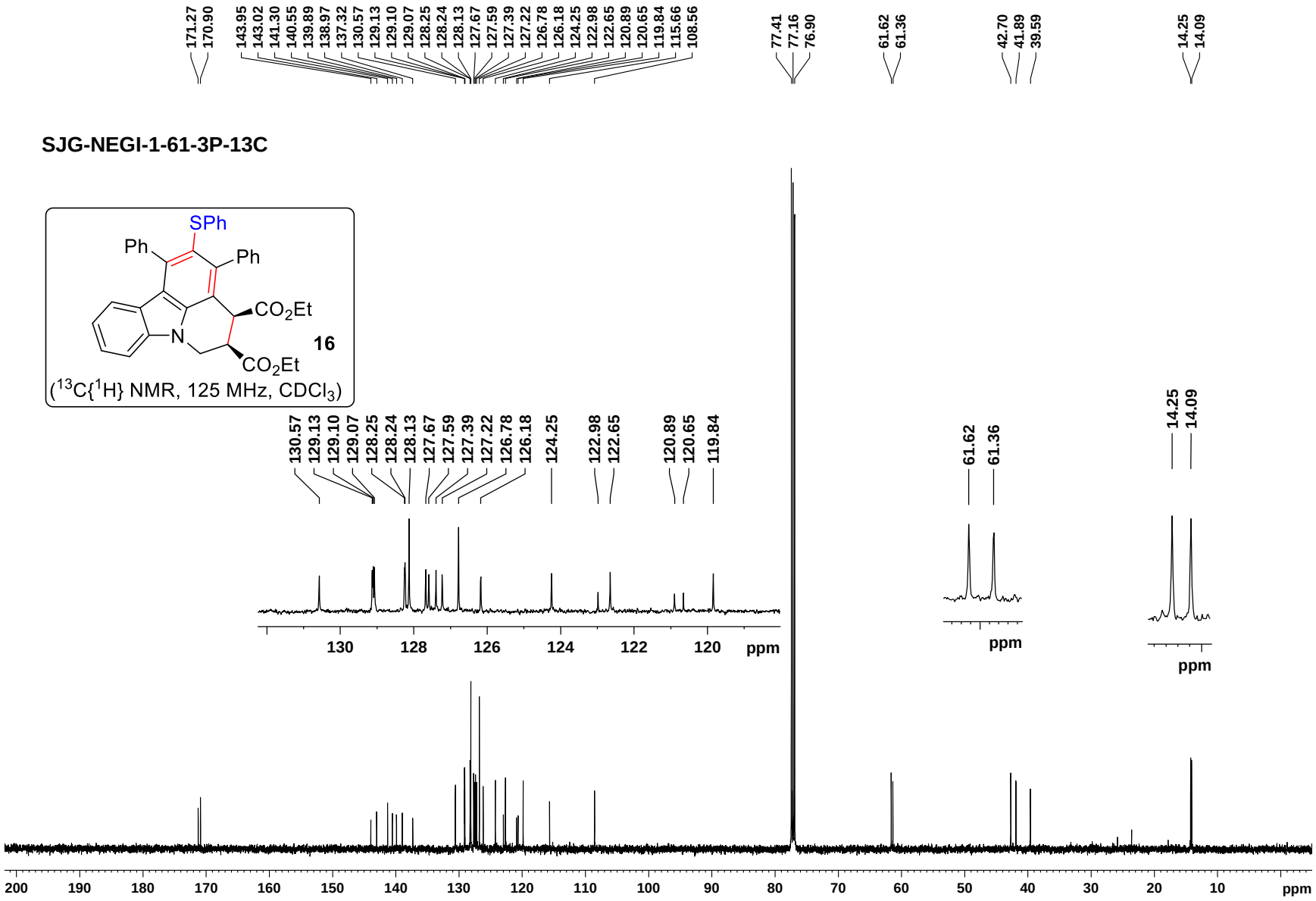

8.32 8.30 7.87 7.85 7.60 7.58 7.56 7.50 7.48 7.46 7.35 7.34 7.32 7.32 7.31 7.30 7.28 7.25 7.25 7.24 7.23 7.23 7.21 7.14 7.14 7.12 7.03 7.01 6.99 6.79 6.79 6.77 6.77 6.76 6.75 6.75 6.74 6.73 6.63 6.61 6.39 6.39 6.37 6.37 6.35 6.35 4.94 4.04 4.03 4.01 4.00 3.68 3.66 3.64 3.63 3.62 3.61 3.60 3.59 3.58 3.57 0.80 0.78 0.77
SJG-NEGI-323-2-1H-P
S-o-Br-C6H4
Ph
Ph
CO2Et
N
SO2Ph
8u
(1H NMR, 400 MHz CDCl3)
4.05 4.00 ppm
3.7 3.6 ppm
0.8 ppm
1.05
4.10
3.14
10.5 10.0 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
1.02 2.14 1.20 2.05 4.31 6.07 2.04 1.20 2.42 1.06 1.06 1.00 1.05 4.10 3.14

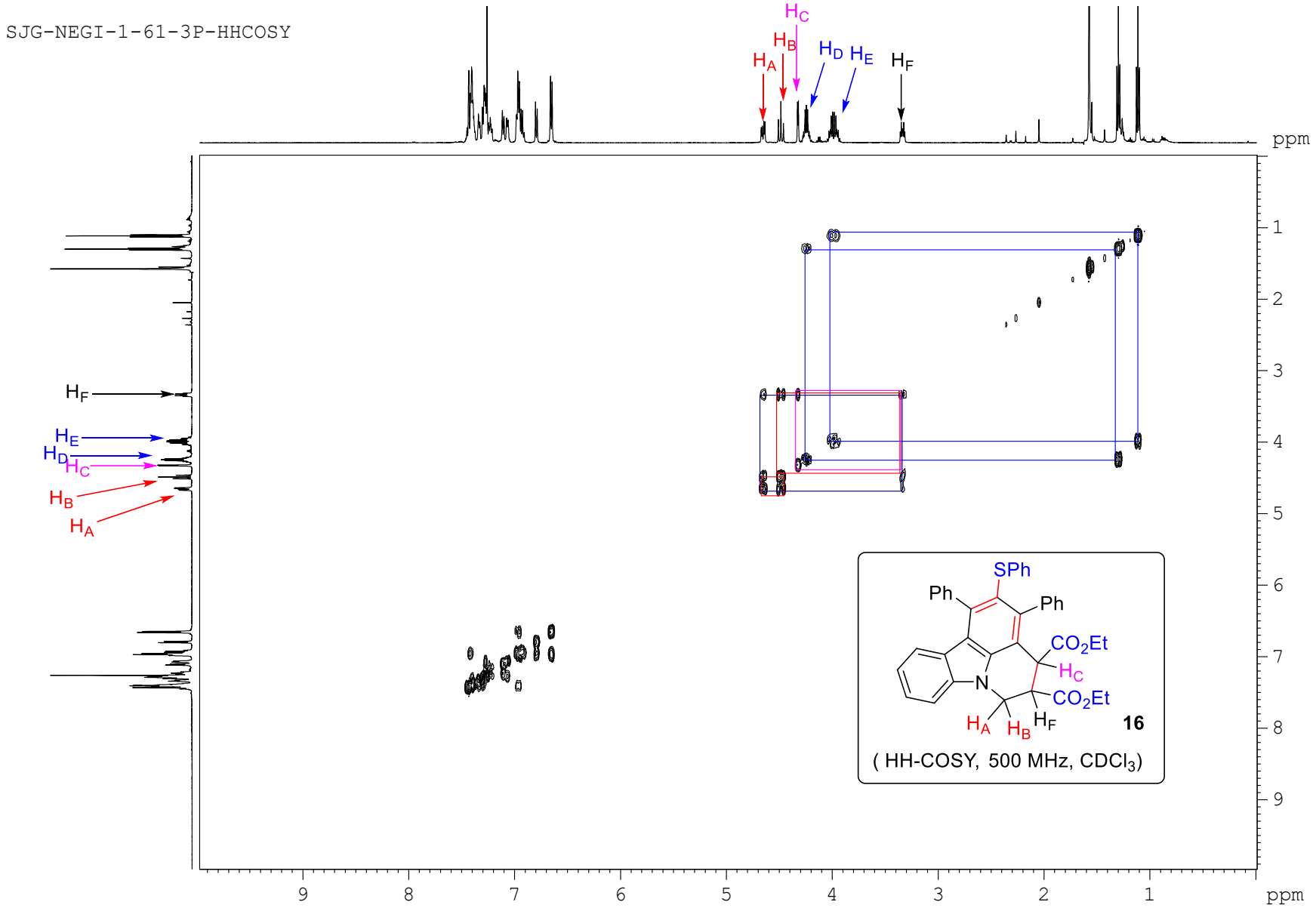

171.25
143.14
141.47
139.40
139.18
137.62
136.21
135.41
135.34
134.04
133.27
132.96
130.53
129.46
128.78
128.36
128.03
127.97
127.51
126.94
126.71
126.59
126.18
124.95
123.87
121.55
118.07
114.88
77.48
77.16
76.84
60.77
46.21
44.01
29.51
13.59
ppm
S-o-Br-C6H4
Ph
Ph
CO2Et
N
SO2Ph
8u
(13C{1H} NMR, 100 MHz CDCl3)

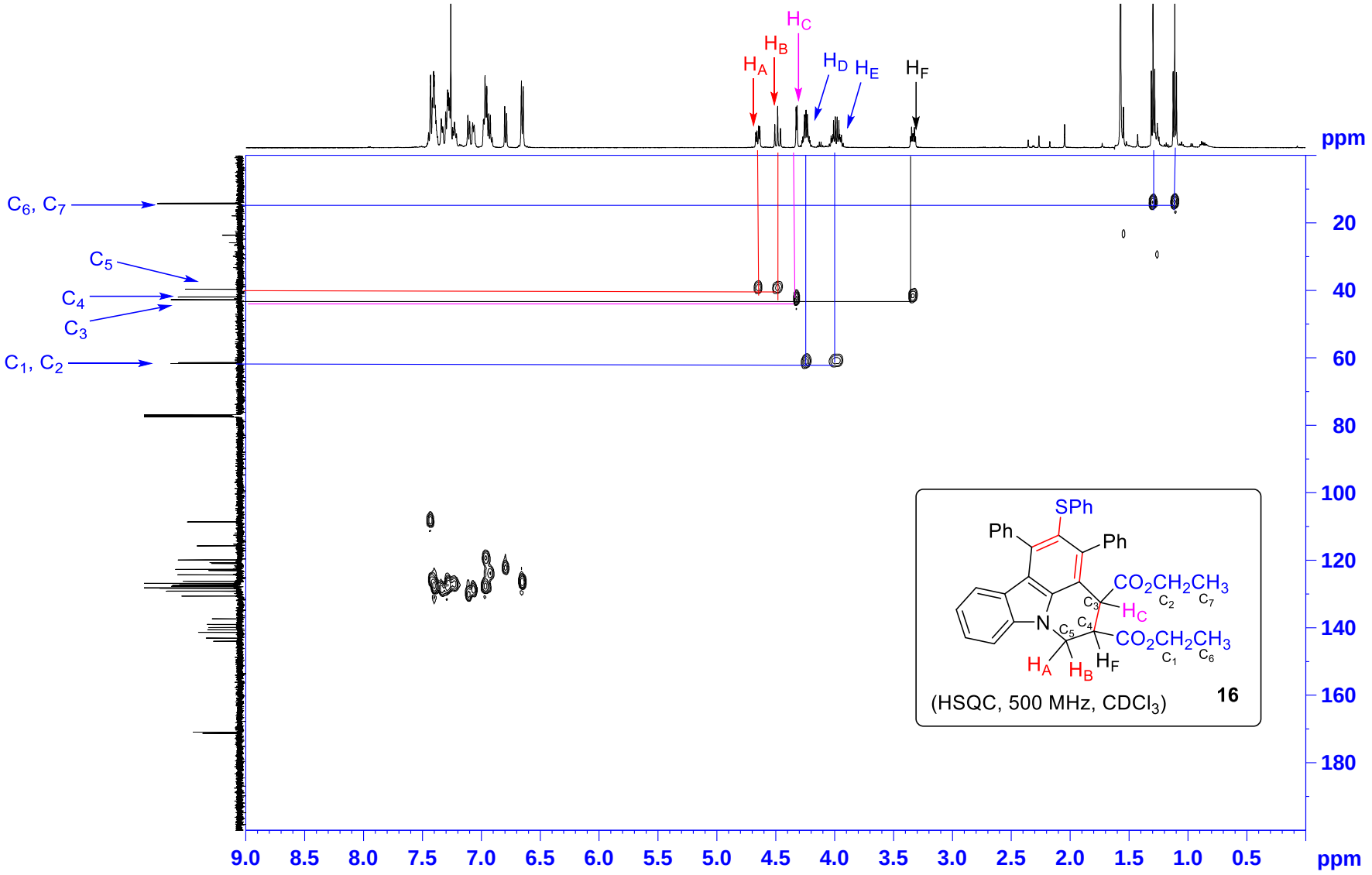

8.30 8.28 7.86 7.84 7.49 7.47 7.45 7.41 7.39 7.37 7.36 7.35 7.30 7.28 7.26 7.08 7.06 7.04 6.77 6.75 6.73 6.71 6.17 6.16 5.93 5.91 5.90 5.14 5.11 5.00 4.33 4.30 3.72 3.71 3.69 3.68 3.66 3.65 3.63 3.61 3.60 3.59 3.58 3.57 1.38 1.06 0.98 0.96 0.94
SJG-NEGI-323-3-PP-1H
S-o-Br-C6H4
Ph
Ph
CO2Et
C(CH3)2CN
N
SO2Ph
10u
(1H NMR, 400 MHz CDCl3)
6.17 6.16 5.93 5.91 5.90 5.14 5.11 5.00 4.33 4.30
6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 ppm
1.01 1.01 1.01 1.02 1.00
0.98 0.96 0.94
1.0 ppm
3.20
3.72 3.71 3.69 3.68 3.66 3.65 3.63 3.61 3.60 3.59 3.58 3.57
3.8 3.7 3.6 ppm
2.01
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
1.10 2.10 1.16 9.03 5.16 1.04 2.01 1.01 1.01 1.01 1.02 1.00 2.01 3.12 3.04 3.20

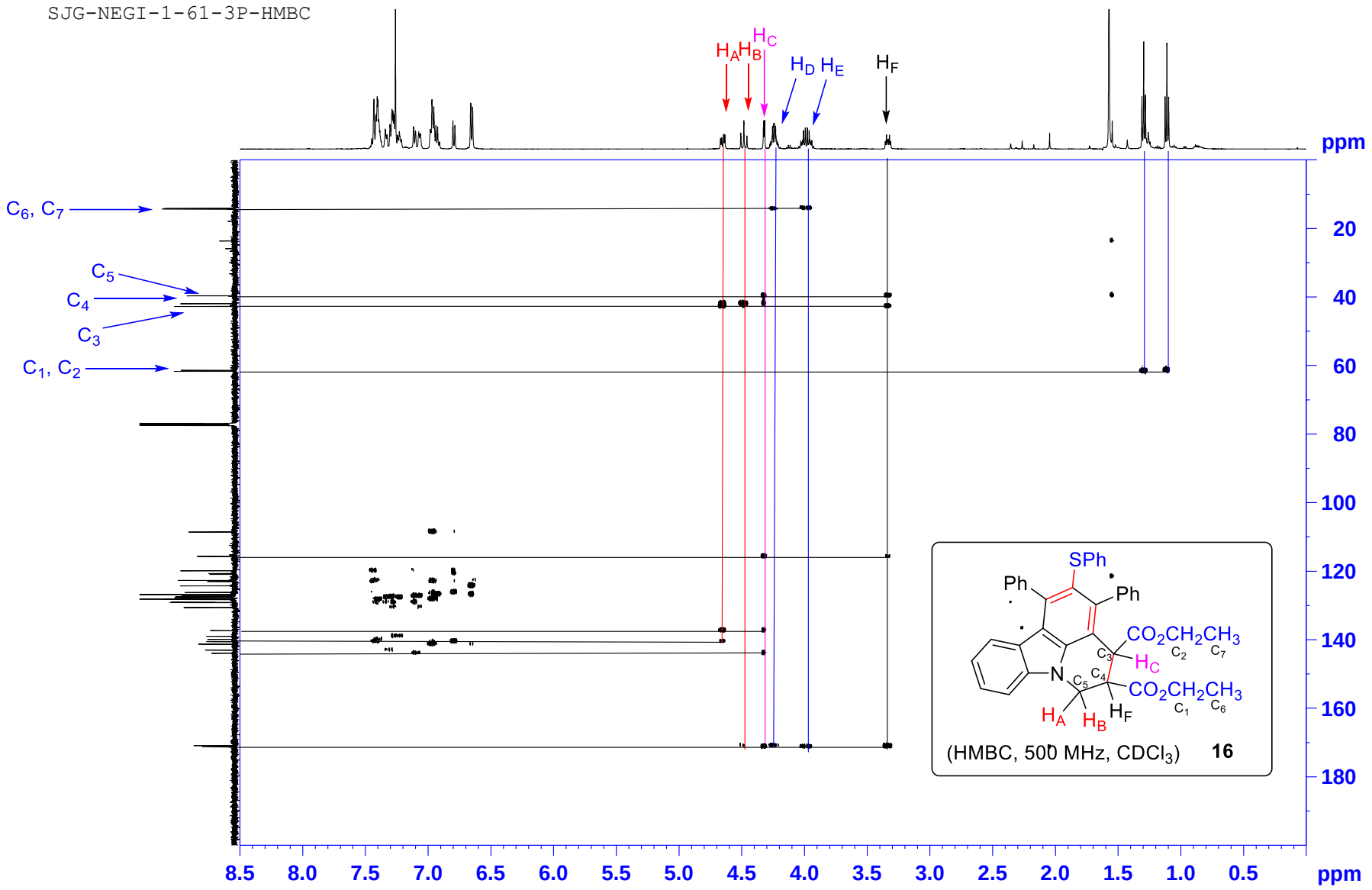

171.54
141.45
140.52
139.60
138.89
137.98
136.27
135.33
134.92
134.12
133.21
132.66
131.72
130.94
129.32
129.22
128.15
128.04
127.83
127.57
127.42
127.15
127.13
125.82
125.78
124.70
124.35
118.83
116.67
77.48
77.16
76.84
61.44
51.56
43.92
43.82
39.29
27.56
26.51
13.59
SJG-NEGI-4-323-3-13C
S-o-Br-C6H4
Ph
Ph
CO2Et
C(CH3)2CN
N
SO2Ph
10u
(13C{1H} NMR, 100 MHz CDCl3)
ppm

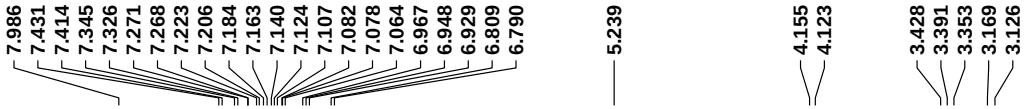

SPh
Ph
Ph
CO2Et
N
CO2Et
16
(1H NMR, 500 MHz, CDCl3)
ppm


171.27
170.90
143.95
143.02
141.30
140.55
139.89
138.97
137.32
130.57
129.13
129.10
129.07
128.25
128.24
128.13
127.67
127.59
127.39
127.22
126.78
126.18
124.25
122.98
122.65
120.89
120.65
119.84
115.66
108.56
77.41
77.16
76.90
61.62
61.36
42.70
41.89
39.59
14.25
14.09
SJG-NEGI-1-61-3P-13C
SPh
Ph
Ph
CO2Et
N
CO2Et
16
(13C{1H} NMR, 125 MHz, CDCl3)
130.57
129.13
129.10
129.07
128.25
128.24
128.13
127.67
127.59
127.39
127.22
126.78
126.18
124.25
122.98
122.65
120.89
120.65
119.84
61.62
61.36
14.25
14.09
130
128
126
124
122
120
ppm
ppm
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

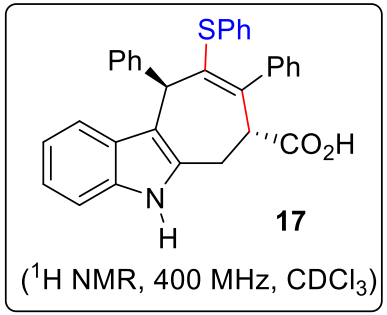

SJG-NEGI-1-61-3P-HHCOSY
HC
HB
HA
HD HE
HF
ppm
HF
HE
HD
HC
HB
HA
SPh
Ph
Ph
CO2Et
HC
CO2Et
N
HA HB HF
16
(HH-COSY, 500 MHz, CDCl3)
9 8 7 6 5 4 3 2 1
ppm

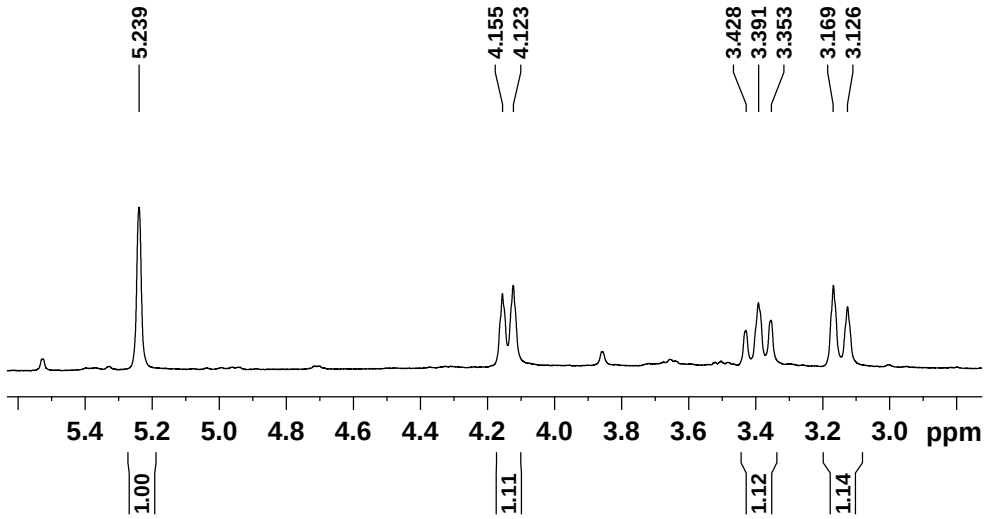

SJG-NEGI-1-61-3P-HSQC
H_C
H_B
H_A
H_D H_E
H_F
ppm
C_6, C_7
C_5
C_4
C_3
C_1, C_2
20
40
60
80
100
120
140
160
180
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm
SPh
Ph
Ph
CO2CH2CH3
CO2CH2CH3
N
H_C
H_A
H_B
H_F
(HSQC, 500 MHz, CDCl3)
16

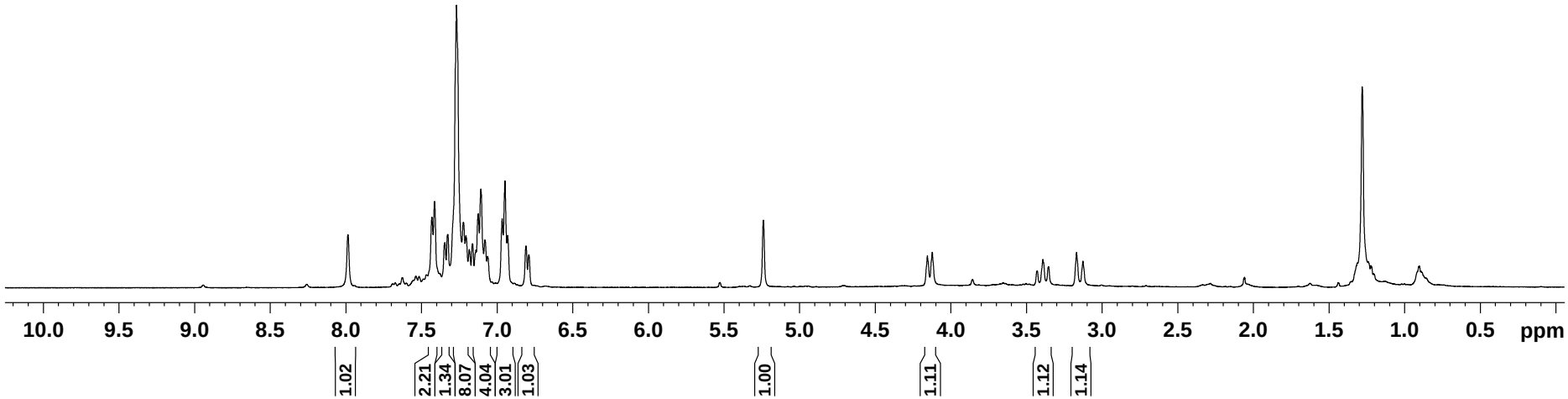

SJG-NEGI-1-61-3P-HMBC
HA HB HC
HD HE
HF
ppm
C6, C7
C5
C4
C3
C1, C2
20
40
60
80
100
120
140
160
180
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm
SPh
Ph
Ph
CO2CH2CH3
C2
C7
C3
HC
N
C4
C5
CO2CH2CH3
C1
C6
HA
HB
HF
(HMBC, 500 MHz, CDCl3) 16

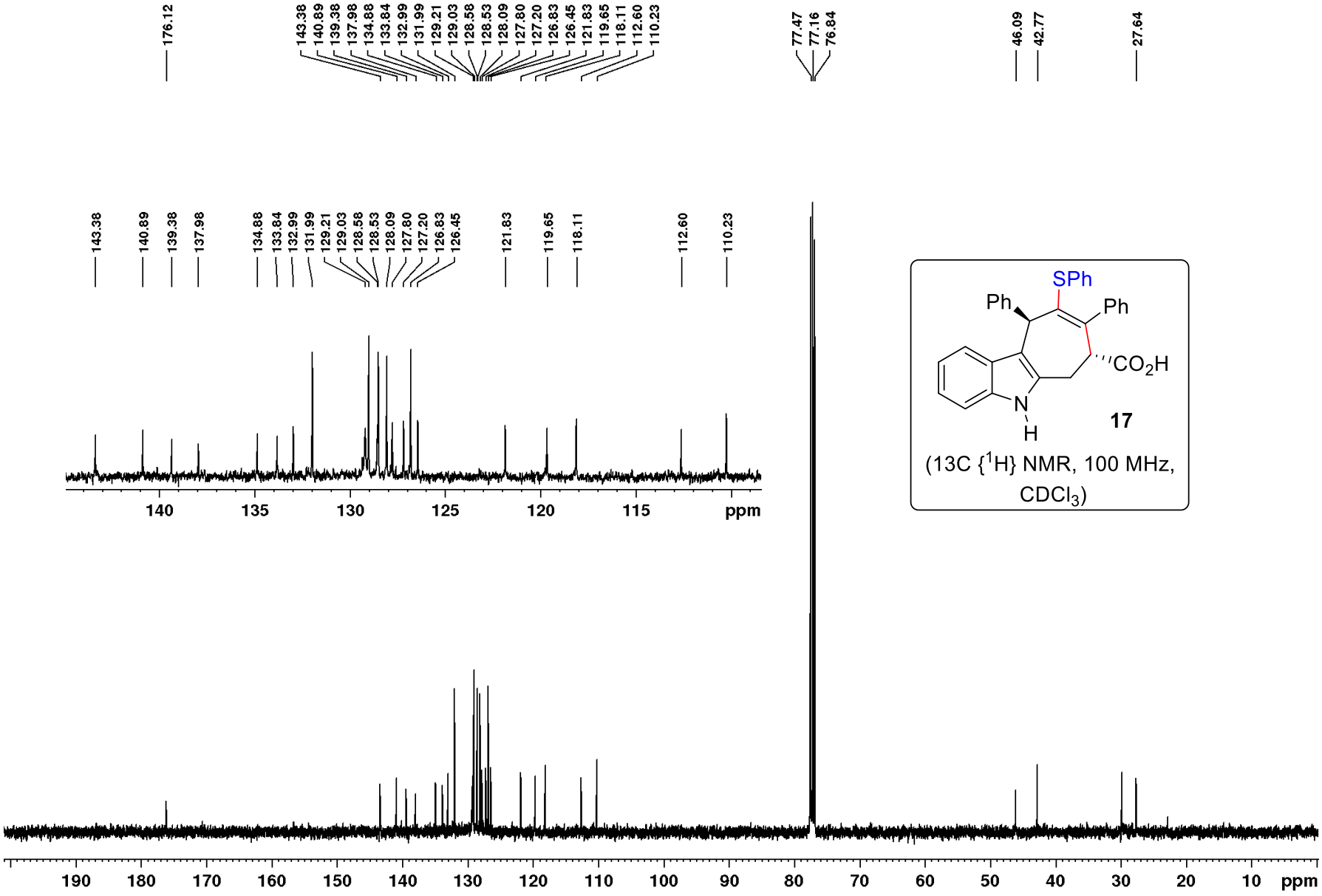


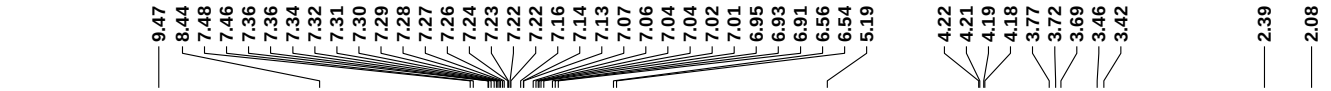
SJG-NEGI-1-66-1H



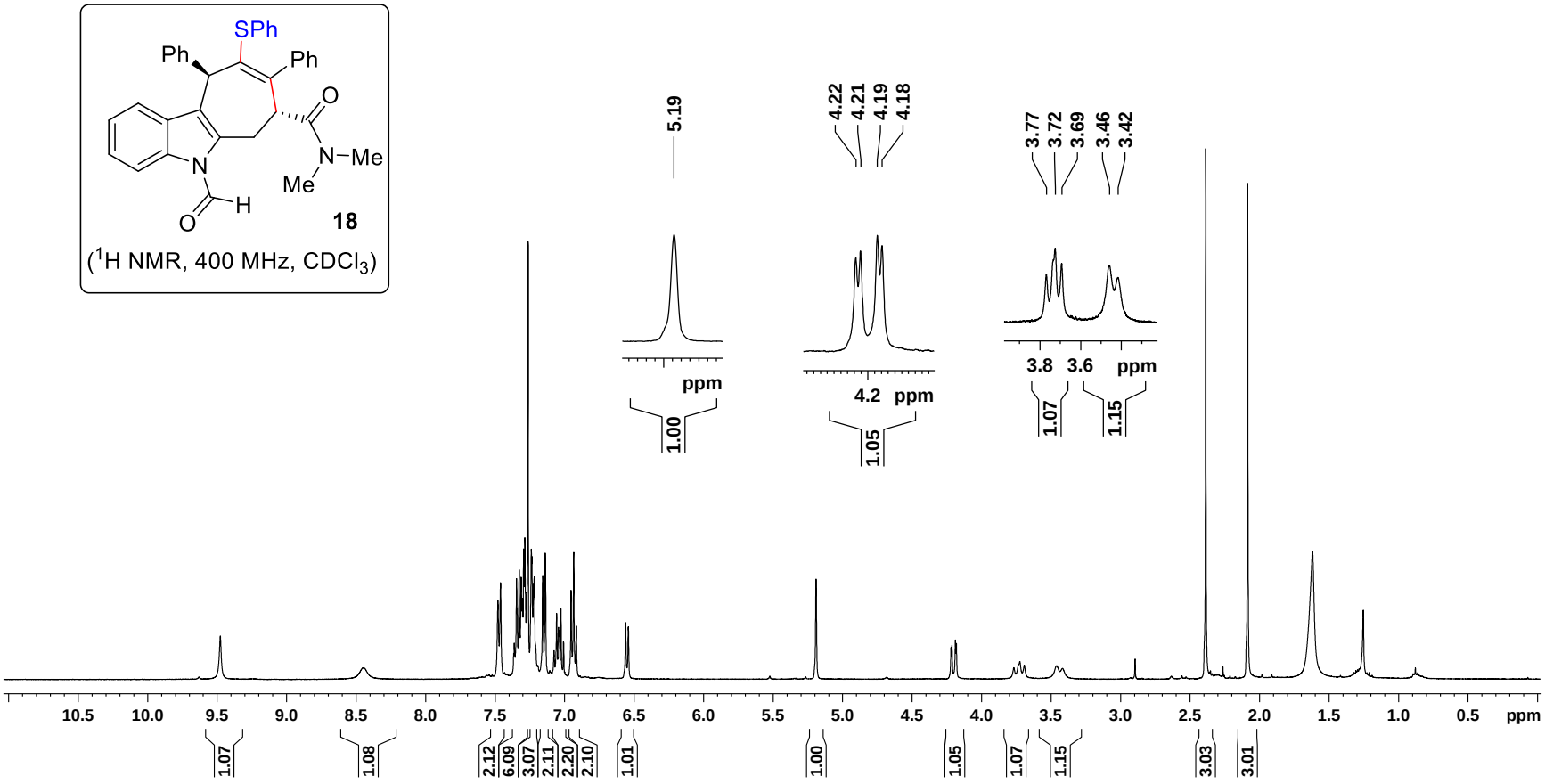


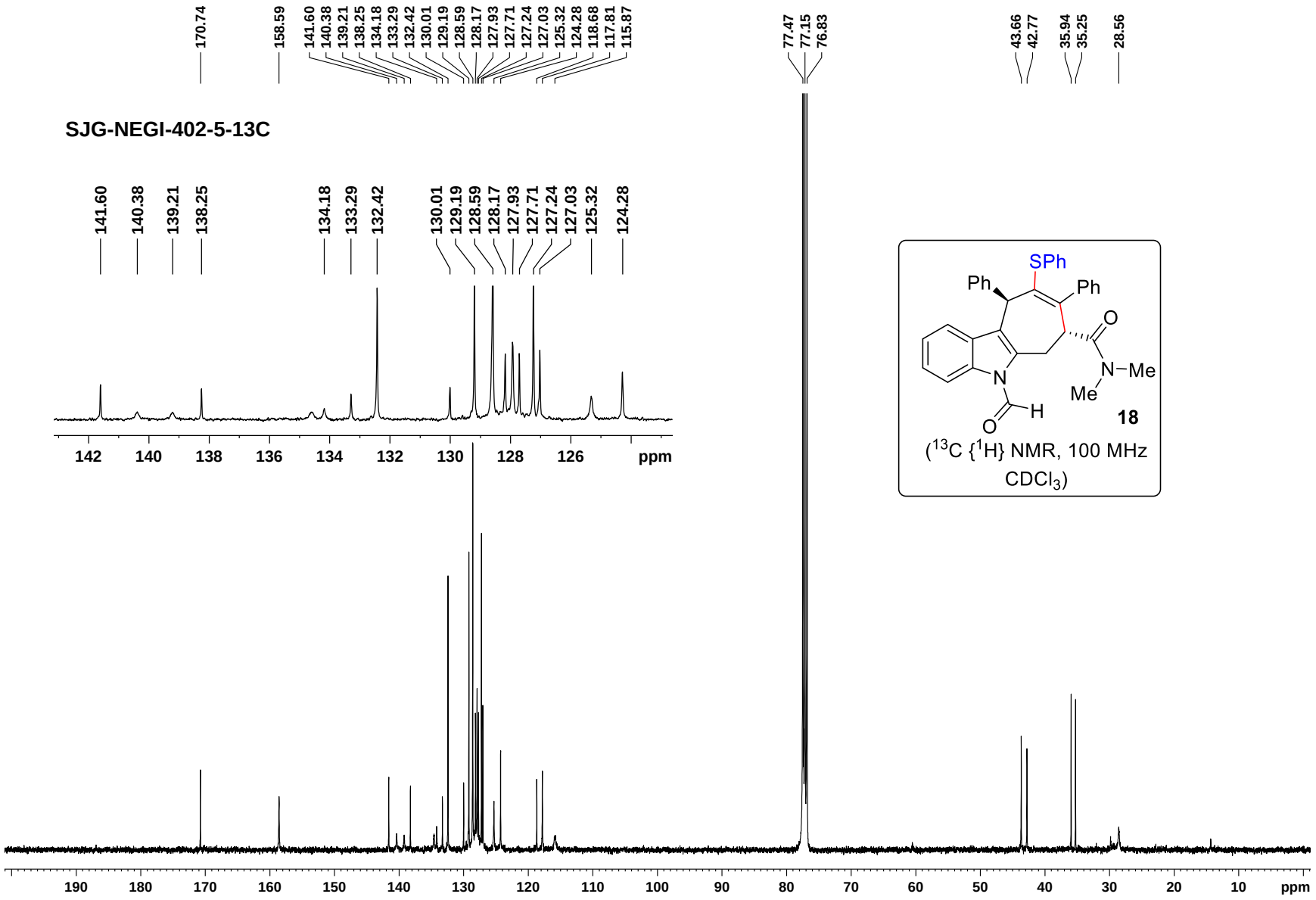


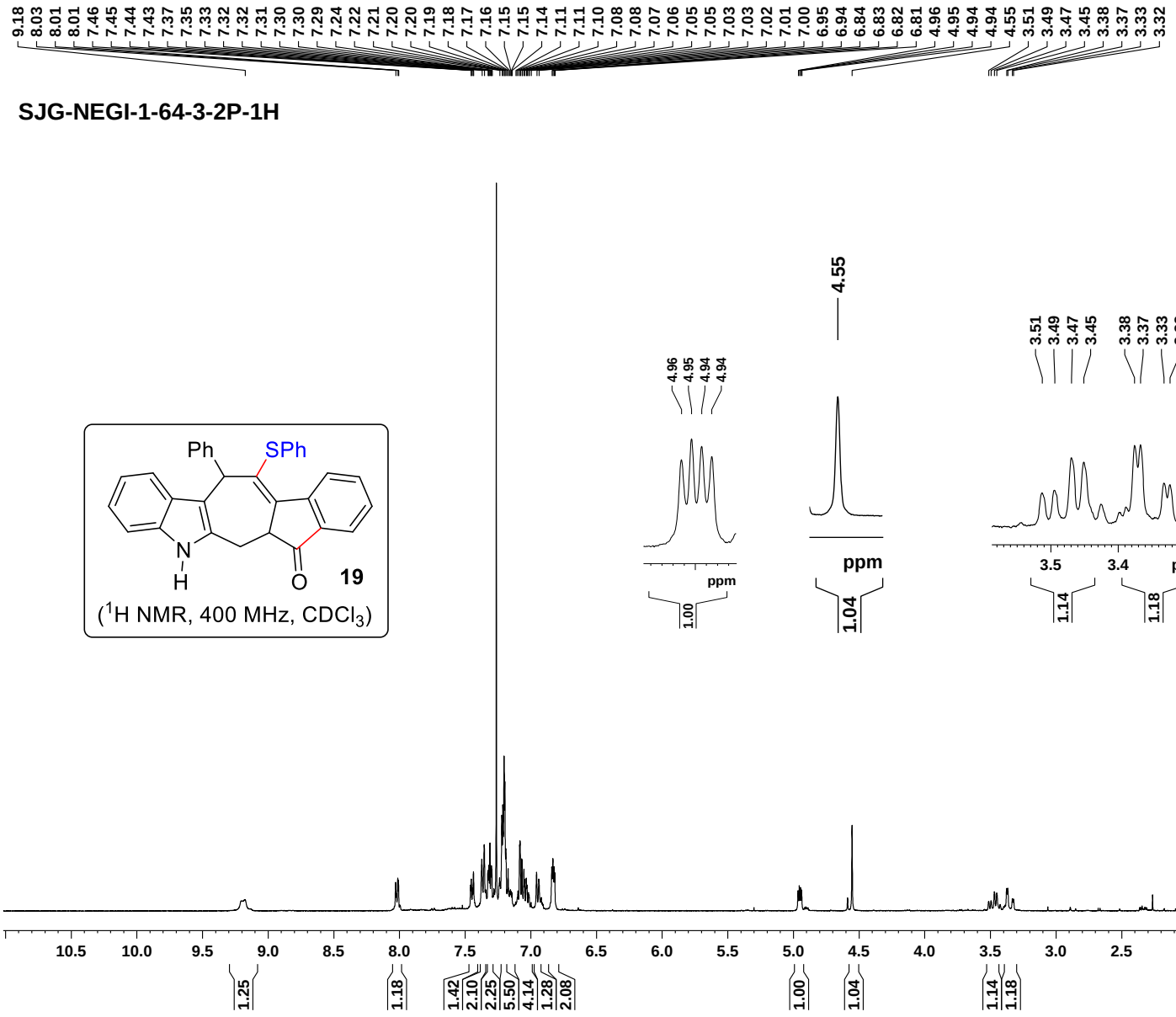

176.12
143.38
140.89
139.38
137.98
134.88
133.84
132.99
131.99
129.21
129.03
128.58
128.53
128.09
127.80
127.20
126.83
126.45
121.83
119.65
118.11
112.60
110.23
77.47
77.16
76.84
46.09
42.77
27.64
140
135
130
125
120
115
ppm
SPh
Ph
Ph
CO2H
N
H
17
(13C {1H} NMR, 100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

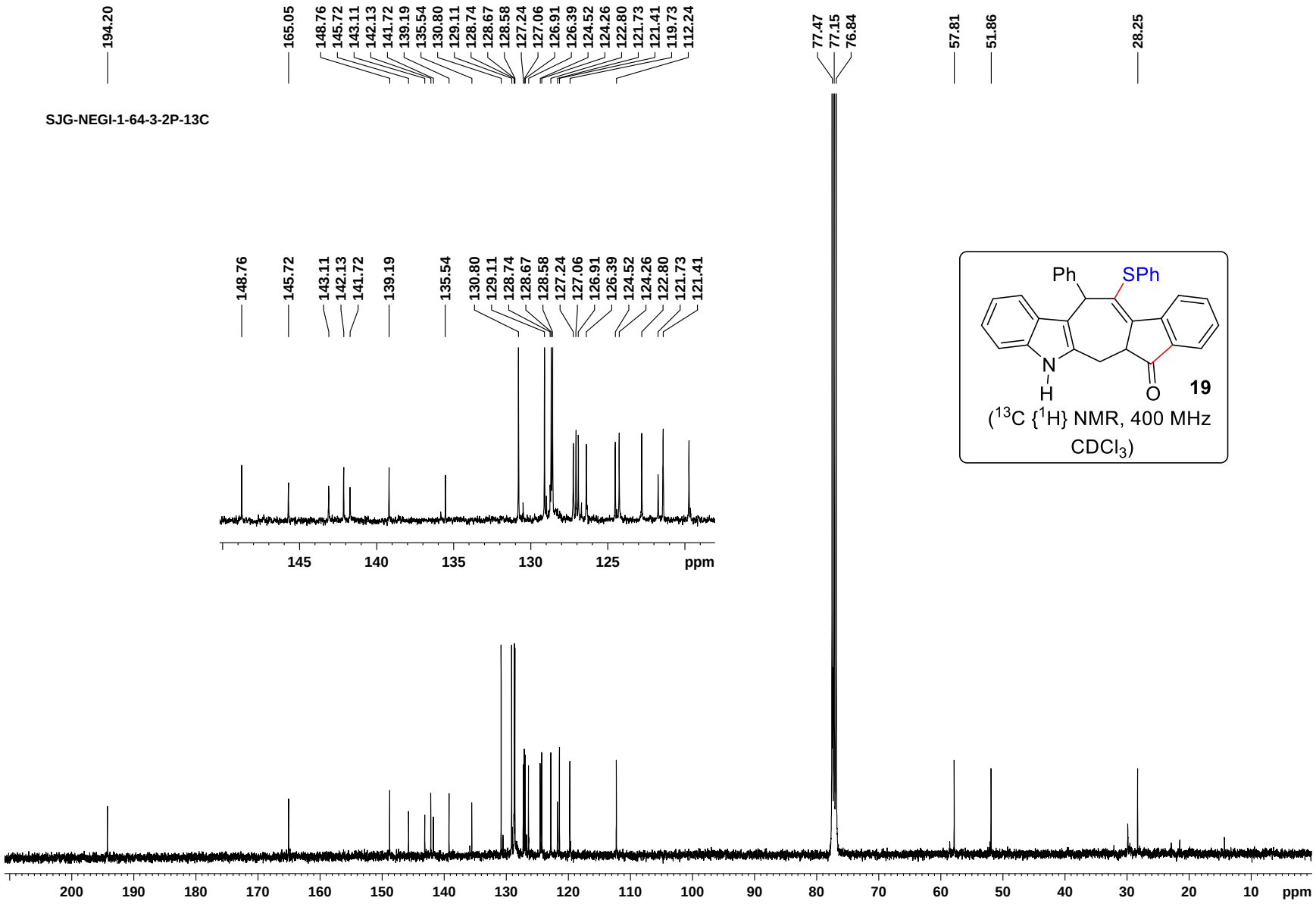


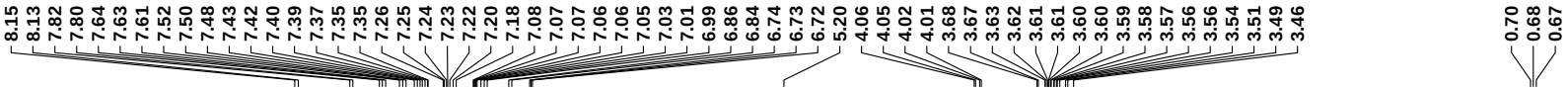
SJG-NEGI-402-5-1H



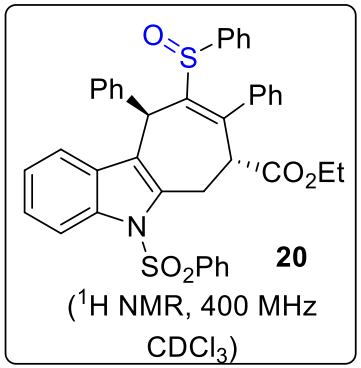

SJG-NEGI-402-5-13C
170.74
158.59
141.60
140.38
139.21
138.25
134.18
133.29
132.42
130.01
129.19
128.59
128.17
127.93
127.71
127.24
127.03
125.32
124.28
118.68
117.81
115.87
77.47
77.15
76.83
43.66
42.77
35.94
35.25
28.56
142
140
138
136
134
132
130
128
126
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
SPh
Ph
Ph
O
N
N–Me
Me
H
O
18
(^{13}C {^{1}H} NMR, 100 MHz
$CDCl_3$)

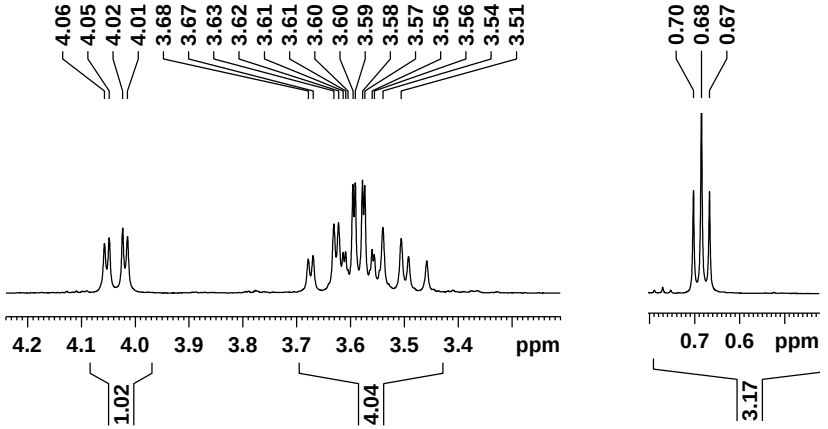

9.18 8.03 8.01 8.01 7.46 7.45 7.44 7.43 7.37 7.35 7.33 7.32 7.32 7.31 7.30 7.30 7.29 7.24 7.22 7.21 7.20 7.20 7.19 7.18 7.17 7.16 7.15 7.15 7.14 7.11 7.11 7.10 7.08 7.08 7.07 7.06 7.05 7.05 7.03 7.03 7.02 7.01 7.00 6.95 6.94 6.84 6.83 6.82 6.81 4.96 4.95 4.94 4.94 4.55 3.51 3.49 3.47 3.45 3.38 3.37 3.33 3.32
SJG-NEGI-1-64-3-2P-1H
Ph
SPh
N
H
O
19
(1H NMR, 400 MHz, CDCl3)
4.55
ppm
3.5
3.4
ppm
10.5 10.0 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
1.25 1.18 1.42 2.10 2.25 5.50 4.14 1.28 2.08 1.00 1.04 1.14 1.18

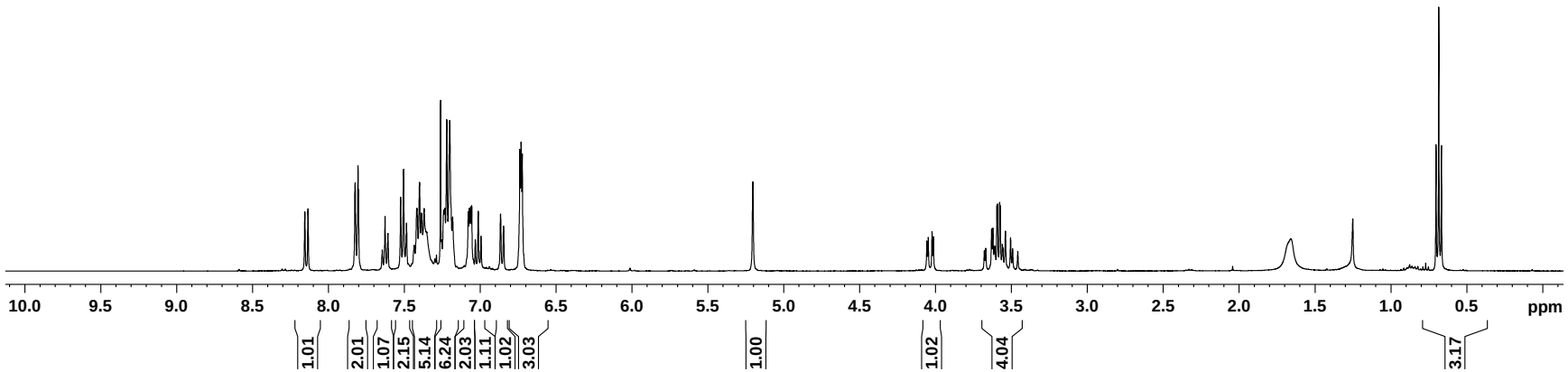

194.20
165.05
148.76
145.72
143.11
142.13
141.72
139.19
135.54
130.80
129.11
128.74
128.67
128.58
127.24
127.06
126.91
126.39
124.52
124.26
122.80
121.73
121.41
119.73
112.24
77.47
77.15
76.84
57.81
51.86
28.25
SJG-NEGI-1-64-3-2P-13C
148.76
145.72
143.11
142.13
141.72
139.19
135.54
130.80
129.11
128.74
128.67
128.58
127.24
127.06
126.91
126.39
124.52
124.26
122.80
121.73
121.41
145
140
135
130
125
ppm
Ph
SPh
N
H
O
19
(^{13}C {^{1}H} NMR, 400 MHz
$CDCl_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

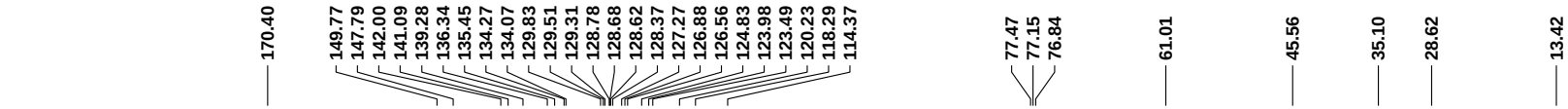


SJG-NEGI-1-62-1H

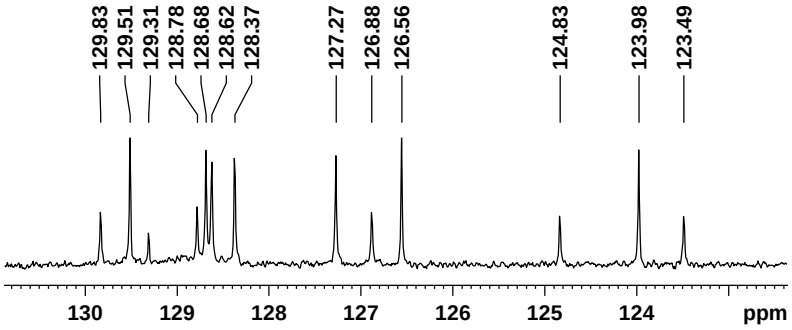


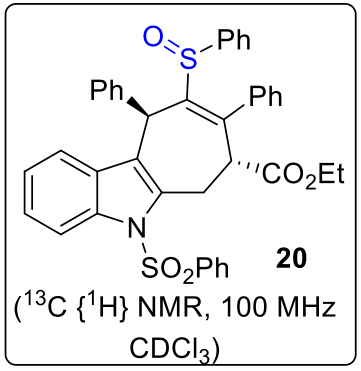


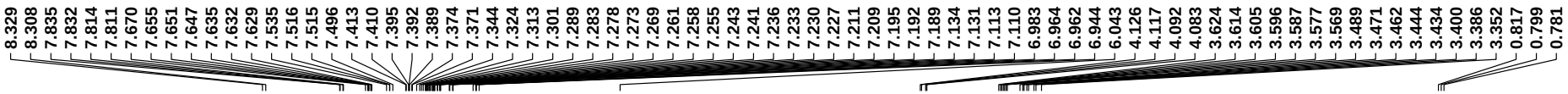




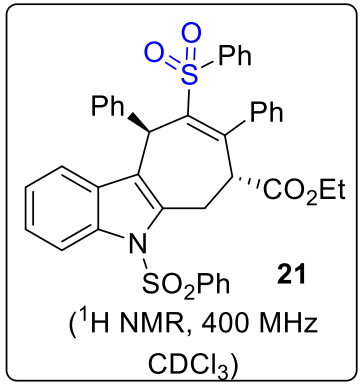
SJG-NEGI-1-62-13C

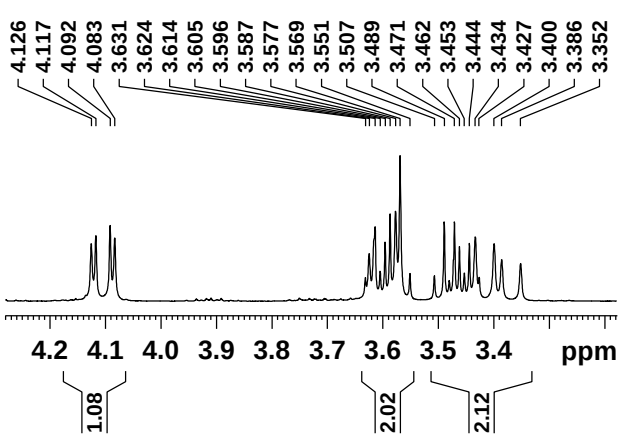


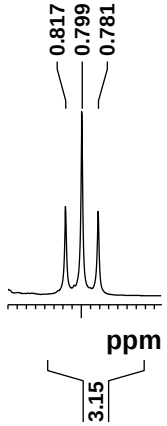


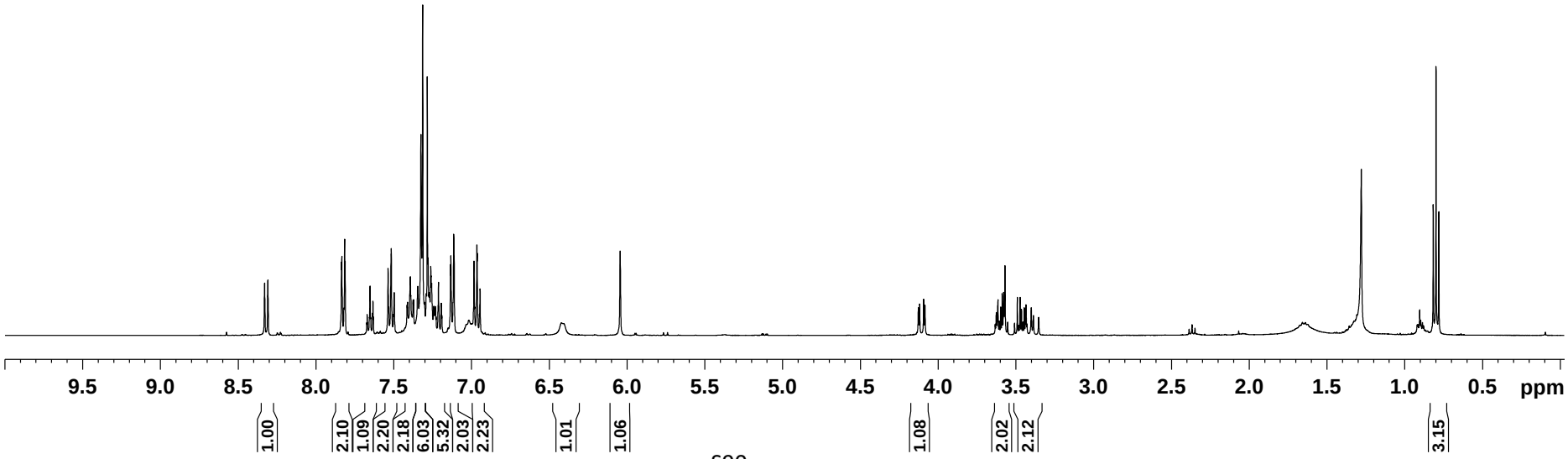


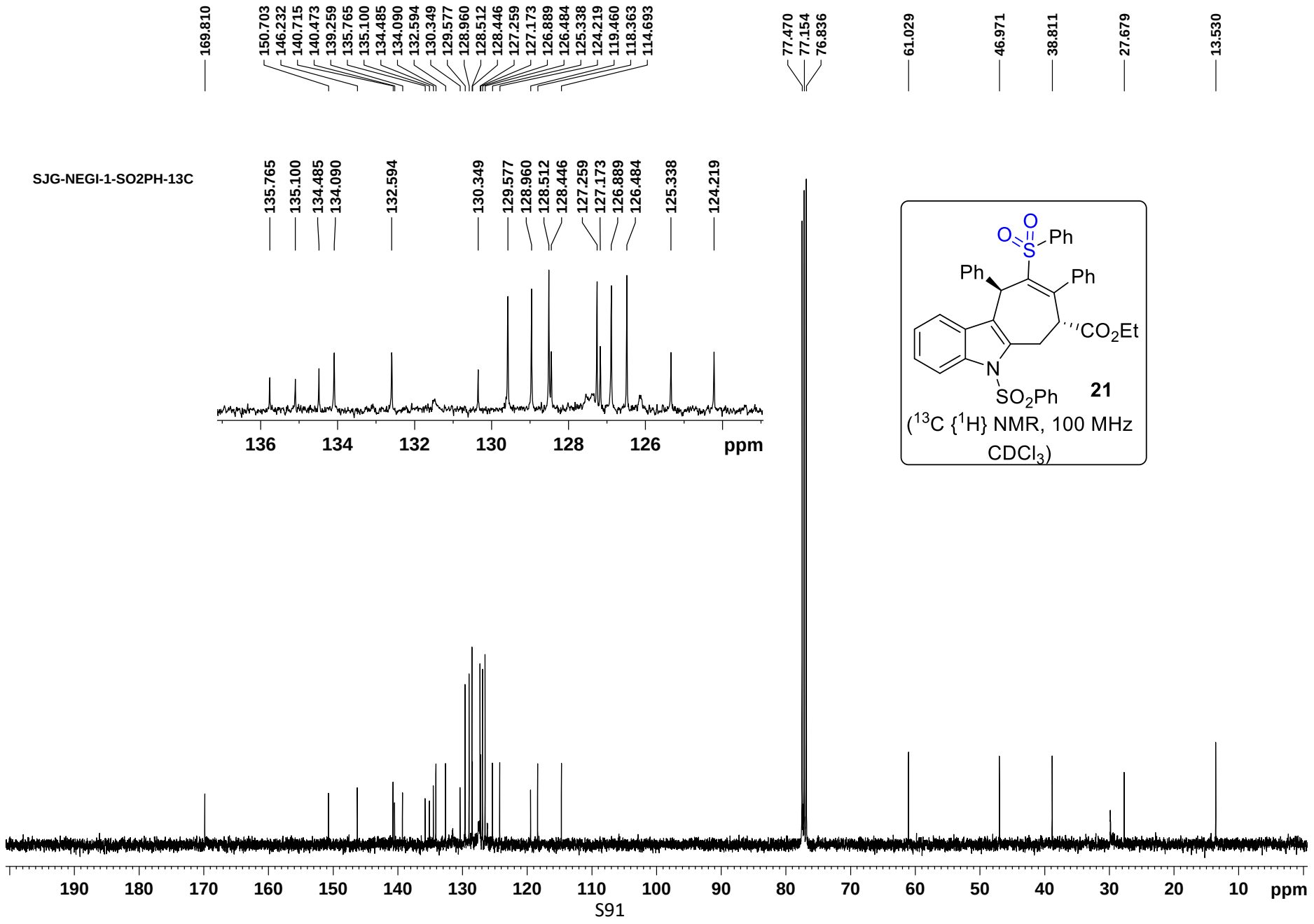
SJG-NEGI-1-SO2PH-1H



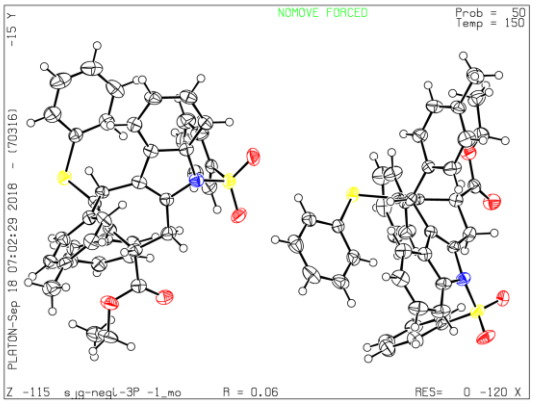







SJG-NEGI-1-SO2PH-13C
169.810
150.703
146.232
140.715
140.473
139.259
135.765
135.100
134.485
134.090
132.594
130.349
129.577
128.960
128.512
128.446
127.259
127.173
126.889
126.484
125.338
124.219
119.460
118.363
114.693
77.470
77.154
76.836
61.029
46.971
38.811
27.679
13.530
136
134
132
130
128
126
ppm
Ph
Ph
Ph
CO2Et
N
SO2Ph
21
(13C {1H} NMR, 100 MHz
CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Crystal data and structure refinement for 8b



Counter probability = 50%

Identification code	**8b**		
CCDC	2296800		
Solvent	CH_2Cl_2		
Bond precision:	C-C = 0.0051 A		Wavelength=0.71073
Cell:	a=10.5565(3)	b=17.7776(7)	c=19.8243(8)
	alpha=72.058(3)	beta=79.538(3)	gamma=73.177(3)
Temperature:	150 K		

	Calculated	Reported
Volume	3370.5(2)	3370.5(2)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C41 H35 N O4 S2	2(C41 H35 N O4 S2)
Sum formula	C41 H35 N O4 S2	C82 H70 N2 O8 S4
Mr	669.82	1339.64
Dx,g cm-3	1.320	1.320
Z	4	2
Mu (mm-1)	0.203	0.203
F000	1408.0	1408.0
F000’	1409.56	
h,k,lmax	12,21,23	12,21,23
Nref	11892	11573
Tmin,Tmax	0.971,0.994	0.854,1.000
Tmin’	0.964	

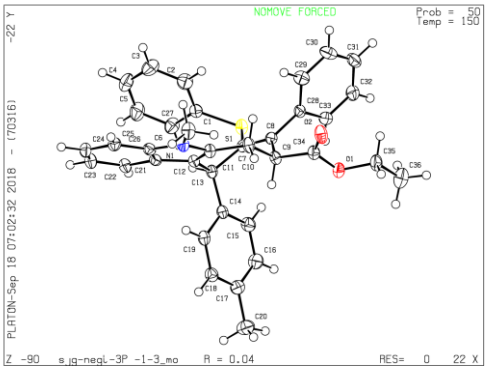
Correction method= # Reported T Limits: Tmin=0.854 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.973 Theta(max)= 24.999

R(reflections)= 0.0599 (7900) wR2(reflections)= 0.1604(11573)

S = 1.058 Npar= 869

Crystal data and structure refinement for 8f



Counter probability = 50%

Identification code	**8f**		
Solvent	CH_2Cl_2		
CCDC	2296676		
Bond precision:	C-C = 0.0029 A		Wavelength=0.71073
Cell:	a=11.0196(3)	b=11.9729(3)	c=12.4127(3)
	alpha=68.202(3)	beta=71.011(3)	gamma=87.557(2)
Temperature:	150 K		
	Calculated	Reported	
Volume	1432.13(8)	1432.12(8)	
Space group	P -1	P -1	
Hall group	-P 1	-P 1	
Moiety formula	C36 H33 N O2 S	C36 H33 N O2 S	
Sum formula	C36 H33 N O2 S	C36 H33 N O2 S	
Mr	543.69	543.69	
Dx,g cm-3	1.261	1.261	
Z	2	2	
Mu (mm-1)	0.147	0.147	
F000	576.0	576.0	
F000’	576.47		
h,k,lmax	13,14,14	13,14,14	
Nref	5036	5021	
Tmin,Tmax	0.976,0.983	0.937,1.000	
Tmin’	0.976		

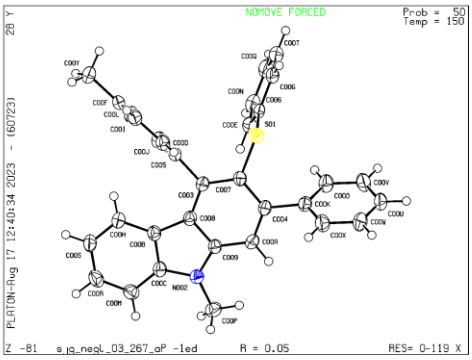
Correction method= # Reported T Limits: Tmin=0.937 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.997 Theta(max)= 25.000

R(reflections)= 0.0416(4349) wR2(reflections)= 0.1053(5021)

S = 1.041 Npar= 364

Crystal data and structure refinement for 9f



Counter probability = 50%

Identification code	**9f**		
Solvent	CH_2Cl_2		
CCDC	2296678		
Bond precision:	C-C = 0.0038 A		Wavelength=0.71073
Cell:	a=10.4151(5)	b=11.5788(8)	c=12.6011(9)
	alpha=95.743(6)	beta=112.337(6)	gamma=116.102(6)
Temperature:	150 K		

	Calculated	Reported
Volume	1195.11(18)	1195.11(15)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C32 H25 N S	C32 H25 N S
Sum formula	C32 H25 N S	C32 H25 N S
Mr	455.59	455.59
Dx,g cm-3	1.266	1.266
Z 2 2		
Mu (mm-1)	0.157	0.157
F000	480.0	480.0
F000’ 480.41		
h,k,lmax	12,13,14	12,13,14
Nref 4206 4207		
Tmin,Tmax	0.941,0.957	0.700,1.000
Tmin’	0.906	

Correction method= # Reported T Limits: Tmin=0.700 Tmax=1.000
AbsCorr = MULTI-SCAN

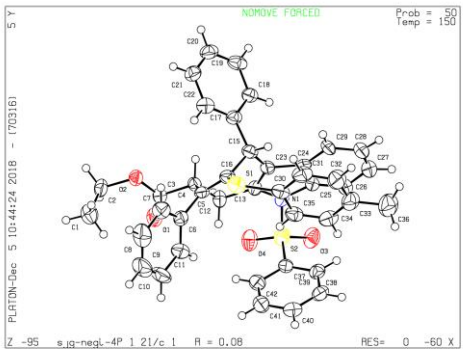
Data completeness= 1.000 Theta(max)= 24.995

R(reflections)= 0.0484(2994)

wR2(reflections)= 0.1353(4207)

S = 1.047 Npar= 310

Crystal data and structure refinement for 8p



Counter probability = 50%

Identification code	**8p**		
Solvent	CH_2Cl_2		
CCDC	2296804		
Bond precision:	C-C = 0.0075 A		Wavelength=0.71073
Cell:	a=19.4285(18)	b=11.6342(8)	c=16.4121(14)
	alpha=90	beta=113.21(1)	gamma=90
Temperature:	150 K		

	Calculated	Reported
Volume	3409.5(6)	3409.5(5)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C41 H35 N O4 S2	C41 H35 N O4 S2
Sum formula	C41 H35 N O4 S2	C41 H35 N O4 S2
Mr	669.82	669.82
Dx,g cm-3	1.305	1.305
Z	4	4
Mu (mm-1)	0.200	0.200
F000	1408.0	1408.0
F000’	1409.56	
h,k,lmax	23,13,19	23,13,19
Nref 5999 5997		
Tmin,Tmax	0.972,0.984	0.611,1.000
Tmin’	0.965	

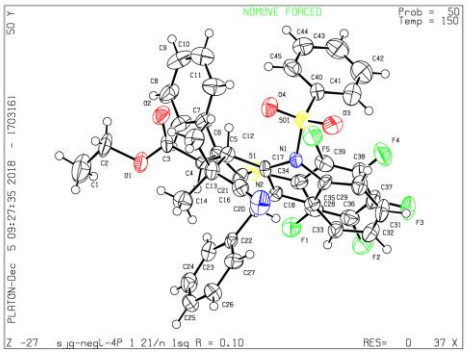
Correction method= # Reported T Limits: Tmin=0.611 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.000 Theta(max)= 24.999

R(reflections)= 0.0758 (3394) wR2(reflections)= 0.2707 (5997)

S = 1.033 Npar= 435

Crystal data and structure refinement for 10t



Counter probability = 50%

Identification code	**10t**		
Solvent	CH_2Cl_2		
CCDC	2296802		
Bond precision:	C-C = 0.0100 A		Wavelength=0.71073
Cell:	a=10.3514(6)	b=27.898(2)	c=15.1231(11)
	alpha=90	beta=101.799(7)	gamma=90
Temperature:	150 K		
	Calculated	Reported	
Volume	4275.0(5)	4275.0(6)	
Space group	P 21/n	P 1 21/n 1	
Hall group	-P 2yn	-P 2yn	
Moiety formula	C44 H33 F5 N2 O4 S2 [+ solvent]	C44 H33 F5 N2 O4 S2	
Sum formula	C44 H33 F5 N2 O4 S2 [+ Solvent]	C44 H33 F5 N2 O4 S2	
Mr	812.84	812.84	
Dx,g cm-3	1.263	1.263	
Z	4	4	
Mu (mm-1)	0.189	0.189	
F000	1680.0	1680.0	
F000’	1681.92		
h,k,lmax	12,33,17	12,33,17	
Nref	7532	7529	
Tmin,Tmax	0.967,0.981	0.365,1.000	
Tmin’	0.963		

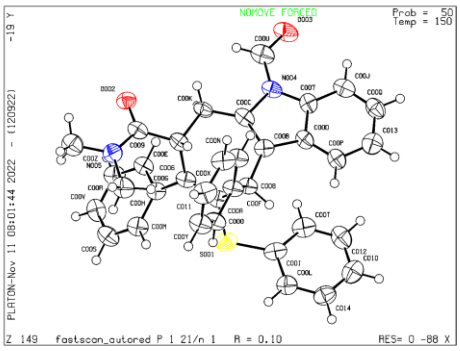
Correction method= # Reported T Limits: Tmin=0.365 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.000 Theta(max)= 24.998

R(reflections)= 0.0985(3702) wR2(reflections)= 0.3461(7529)

S = 1.030 Npar= 517

Crystal data and structure refinement for 18



Counter probability = 50%

Identification code	**18**		
Solvent	CH_2Cl_2		
CCDC	2296781		
Bond precision:	C-C = 0.0083 A		Wavelength=0.71073
Cell:	a=13.651(3)	b=8.9231(12)	c=22.780(3)
	alpha=90	beta=95.384(15)	gamma=90
Temperature:	150 K		

	Calculated	Reported
Volume	2762.6(8)	2762.6(7)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C35 H30 N2 O2 S	C35 H30 N2 O2 S
Sum formula	C35 H30 N2 O2 S	C35 H30 N2 O2 S
Mr	542.67	542.67
Dx,g cm-3	1.305	1.305
Z 4 4		
Mu (mm-1)	0.153	0.153
F000	1144.0	1144.0
F000’ 1144.93		
h,k,lmax	16,10,27	16,10,27
Nref	4871	4785
Tmin,Tmax	0.978,0.992	0.206,1.000
Tmin’	0.961	

Correction method= # Reported T Limits: Tmin=0.206 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.982 Theta(max) = 24.996

R(reflections)= 0.0979(2396) wR2(reflections)= 0.2881(4785)

S = 1.015 Npar= 363