

**Diastereoselective tandem oxidation/Michael/aldol reaction:
Unprecedented formation of dispirocyclopentanebisoxindoles and
dispiro[acenaphthylene-1,1'-cyclopentane-3',1''-acenaphthylene]-
2,2''diones**

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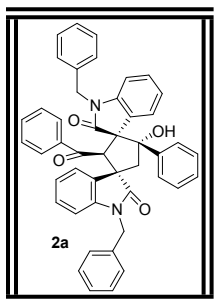
General methods

All the reagents were purchased from Sigma-Aldrich and used without further purification. Pre-coated plates (Merck, silica gel 60 GF₂₅₄, 0.25 mm) were used for TLC analysis. The ¹H and ¹³C NMR spectra were recorded on Bruker Avance 400 MHz Spectrometer. The DEPT-135 experiments were carried out on Bruker Avance 400 MHz Spectrometer. Mass spectra were recorded under EI/HRMS at 60,000 resolution using Thermo Scientific Exactive mass spectrometer. The ¹H and ¹³C chemical shift values (δ) are given in ppm with reference to TMS as internal standard (zero ppm). Coupling constants are given in Hertz.

General Procedure:

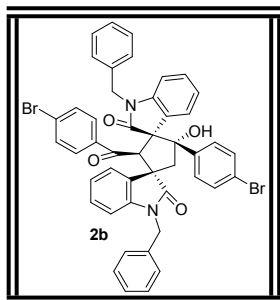
In an oven dried 50-mL round-bottom flask 1.0 mmol 3-phenacyloxindole/phenacylacenaphthylene, 10 mL ethanol and 15 mol % DIPEA were taken and the contents of the flask were heated under reflux ~80 °C until the starting materials were consumed. The reaction mixture was allowed to cool to room temperature. The crude product was separated by filtration, washed with 10-15 mL of ethanol to obtain pure white solid that did not require further purification.

2'-benzoyl-1,1''-dibenzyl-5'-hydroxy-5'-phenyl-1,1'',2,2''-tetrahydrodispiro[indole-3,1'-cyclopentane-3',3''-indole]-2,2''-dione (2a): The title compound was prepared according to the



general procedure as a white solid in 78 % yield; mp = 248-250 °C; IR (KBr): 3307, 3064, 3025, 2922, 1709, 1686, 1609, 1493, 1470, 1389, 1351, 1301, 1231, 1181, 1100, 1012, 931, 862, 804, 758, 696, 604, 554, 457 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.21 (d, *J* = 7.4 Hz, 1H), 7.97 (d, *J* = 6.8 Hz, 1H), 7.37 – 7.21 (m, 9H), 7.19 – 7.06 (m, 10H), 7.01 (t, *J* = 9.5 Hz, 3H), 6.94 (t, *J* = 7.7 Hz, 1H), 6.53 (d, *J* = 7.2 Hz, 2H), 6.40 (d, *J* = 7.5 Hz, 1H), 6.30 (d, *J* = 7.8 Hz, 1H), 5.38 (s, 1H), 5.24 (d, *J* = 15.3 Hz, 1H), 5.17 (d, *J* = 16.1 Hz, 1H), 4.51 (d, *J* = 14.9 Hz, 1H), 4.47 (d, *J* = 16.8 Hz, 1H), 4.26 (d, *J* = 15.3 Hz, 1H), 2.57 (d, *J* = 13.9 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 196.46, 183.88, 176.83, 143.79, 137.11, 135.71, 134.88, 132.29, 128.98, 128.67, 128.52, 128.33, 128.04, 127.83, 127.75, 127.65, 127.08, 126.81, 126.39, 126.10, 125.73, 124.26, 121.93, 108.78, 108.52, 84.55, 66.62, 65.29, 54.28, 46.70, 44.53, 43.80. HRMS Calcd for [C₄₆H₃₆N₂O₄+Na]: 703.25728; found: 703.25772.

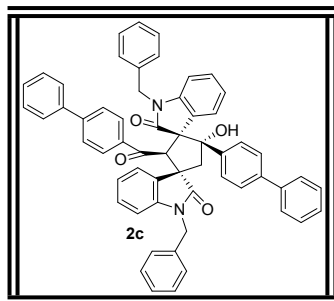
1,1''-dibenzyl-2'-(4-bromobenzoyl)-5'-(4-bromophenyl)-5'-hydroxy-1,1'',2,2''-tetrahydrodispiro[indole-3,3'-cyclopentane-1',3''-indole]-2,2''-dione (2b) : The title



compound was prepared according to the general procedure as a white solid in 73 % yield; mp = 234-236 °C; IR (KBr): 3318, 3068, 2933, 1689, 1605, 1489, 1431, 1343, 1231, 1085, 996, 915, 815, 750, 696, 577, 465 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.15 (d, *J* = 8.1 Hz, 1H), 7.92 (d, *J* = 7.3 Hz, 1H), 7.37 (dt, *J* = 11.1, 7.3 Hz, 5H), 7.23 (dd, *J* = 14.7, 7.8 Hz, 5H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.10 – 7.05 (m, 1H), 7.05 – 6.99 (m, 6H), 6.99 – 6.93 (m, 3H), 6.60 (d, *J* = 7.0 Hz, 2H), 6.46 (t, *J* = 6.1 Hz, 2H), 5.25 (s, 1H), 5.22 (d, *J* = 16.3 Hz, 1H), 5.08 (d, *J* = 15.1 Hz, 1H), 4.50 (d, *J* = 15.3 Hz, 1H), 4.46 (d, *J* = 15.8 Hz, 1H), 4.42 (d, *J* = 13.5 Hz, 1H), 2.53 (d, *J* = 13.9 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 195.28, 183.61, 176.59, 143.71, 141.58, 137.34, 135.61, 135.45, 134.67, 131.07, 130.78, 130.03, 129.13, 128.91, 128.64, 128.38, 128.25, 128.07, 128.00, 127.35, 127.11, 126.99, 126.37, 126.11, 125.74, 124.35, 122.14, 122.04, 108.89, 108.62, 84.01, 66.53, 65.01, 54.08, 46.76, 44.79, 43.91. HRMS (EI) Calcd for [C₄₆H₃₄Br₂N₂O₄+Na]: 859.07830; found: 859.07831

1,1''-dibenzyl-5'-hydroxy-2'-(4-phenylbenzoyl)-5''-(4-phenylphenyl)-1,1'',2,2''-

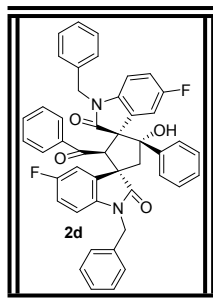
tetrahydrodispiro[indole-3,3'-cyclopentane-1',3''-indole]-2,2''-dione (2c) : The title compound



was prepared according to the general procedure as a white solid in 70 % yield; mp = 240-242 °C; IR (KBr): 3287, 3060, 2902, 1709, 1686, 1609, 1585, 1482, 1428, 1352, 1274, 1239, 1104, 1096, 1070, 1000, 846, 811, 731, 692, 573, 554, 534, 453 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, J = 7.5 Hz, 1H), 8.02 (d, J = 7.3 Hz, 1H), 7.57 (d, J = 7.6 Hz, 2H), 7.46(d, J=4.0 Hz, 4H), 7.41 (d, J=7.3Hz, 4H), 7.35 (d, J = 7.6 Hz, 1H), 7.33–7.21 (m, 10H), 7.19 (d, J = 8.3 Hz, 2H), 7.15 – 7.10 (m, 2H), 7.05 (s, 2H), 6.98–6.94 (dd, J = 9.9, 7.4 Hz, 4H), 6.59 (d, J = 7.0 Hz, 2H), 6.43 (d, J = 7.2 Hz, 1H), 6.34 (d, J = 7.7 Hz, 1H), 5.42 (s, 1H), 5.23 (dd, J = 23.1, 15.7 Hz, 2H), 4.56 (d, J = 13.9 Hz, 1H), 4.47 (d, J = 16.1 Hz, 1H), 4.36 (d, J = 15.2 Hz, 1H), 2.61 (d, J = 13.9 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 195.97, 183.96, 176.95, 144.92, 143.92, 141.72, 140.54, 140.28, 139.59, 137.55, 135.80, 135.69, 134.89, 130.49, 128.99 (2C), 128.94 (2C), 128.80, 128.74, 128.51 (2C), 128.39, 128.29, 128.09, 127.83 (2C), 127.67, 127.35, 127.31, 127.13 (2C), 127.04 (2C), 126.84, 126.68, 126.39 (2C), 126.24, 125.82, 124.31, 121.97, 108.88, 108.51, 84.44, 66.75, 65.44, 54.42, 47.04, 44.72, 43.97; HRMS (EI) Calcd for [C₅₈H₄₄N₂O₄+Na]: 855.31988; found: 855.32002.

2'-benzoyl-1,1''-dibenzyl-5,5''-difluoro-5'-hydroxy-5''-phenyl-1,1'',2,2''-

tetrahydrodispiro[indole-3,1'-cyclopentane-3',3''-indole]-2,2''-dione (2d) : The title

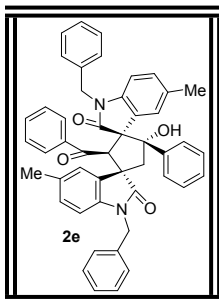


compound was prepared according to the general procedure as a white solid in 71 % yield; mp = 244-246 °C; IR (KBr): 3245, 3056, 2914, 1695, 1635, 1534, 1475, 1421, 1563, 1275, 1225, 1100, 821, 715, 689, 570, 545 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, J = 6.8 Hz, 1H), 7.73 (d, J = 6.5 Hz, 1H), 7.31 (m, 8H), 7.16 (m 8H), 7.04 (t, J = 7.6 Hz, 2H), 6.96 (s, 1H), 6.83 (t, J = 7.8 Hz, 1H), 6.65 (t, J = 7.7 Hz, 1H), 6.50 (d, J = 7.0 Hz, 2H), 6.30 (dd, J = 8.2, 4.2 Hz, 1H), 6.22 (dd, J = 8.5, 3.9 Hz, 1H), 5.30 (s, 1H), 5.25 (d, J = 15.4 Hz, 1H), 5.18 (d, J = 16.2 Hz, 1H), 4.47 (d, J = 2.0 Hz, 1H), 4.43 (d, J = 5.2 Hz, 1H), 4.23 (d, J = 15.4 Hz, 1H), 2.57 (d, J = 14.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 196.08, 183.51, 176.56, 161.27, 159.92, 158.86, 157.55, 139.75, 137.78, 137.54, 136.84, 135.30, 134.48, 132.59, 131.91, 129.07, 128.59, 128.20, 128.01, 127.95, 127.87, 127.62, 127.09, 126.97, 126.33, 126.02, 115.30, 115.13, 114.98, 114.89, 114.74,

113.94, 113.69, 109.22, 84.50, 66.99, 65.33, 54.51, 46.56, 44.70, 43.94, 29.70. HRMS (EI) Calcd for $[C_{46}H_{34}F_2N_2O_4+Na]$: 739.23843; found: 739.23888.

2'-benzoyl-1,1''-dibenzyl-5'-hydroxy-5,5''-dimethyl-5'-phenyl-1,1'',2,2''-

tetrahydrodispiro[indole-3,1'-cyclopentane-3',3''-indole]-2,2''-dione (2e) : The title compound

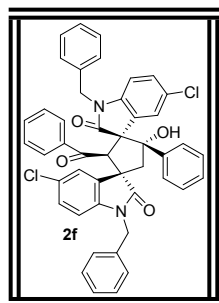


was prepared according to the general procedure as a white solid in 76 % yield; mp = 255-257 °C; IR (KBr): 3349, 3129, 2929, 2852, 1705, 1682, 1609, 1497, 1381, 1347, 1197, 1004, 811, 758, 696, 554 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.78 (s, 1H), 7.34 – 7.22 (m, 7H), 7.18 – 7.05 (m, 10H), 7.01 (t, $J = 7.6$ Hz, 2H), 6.92 (d, $J = 7.8$ Hz, 1H), 6.74 (d, $J = 7.8$ Hz, 1H), 6.46 (d, $J = 7.0$ Hz, 2H), 6.29 (d, $J = 7.9$ Hz, 1H), 6.18 (d, $J = 7.9$ Hz, 1H),

5.34 (s, 1H), 5.23 (d, $J = 15.0$ Hz, 2H), 4.50 (d, $J = 13.8$ Hz, 1H), 4.41 (d, $J = 16.2$ Hz, 1H), 4.23 (d, $J = 15.3$ Hz, 1H), 2.56 (d, $J = 13.9$ Hz, 1H), 2.38 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.59, 183.79, 176.77, 141.47, 139.21, 138.48, 137.32, 135.84, 134.97, 134.00, 132.14, 131.25, 130.43, 129.02, 128.95, 128.53, 128.47, 127.98, 127.78, 127.72, 127.63, 127.54, 127.08, 126.73, 126.53, 126.34, 126.13, 108.43, 108.28, 84.51, 66.60, 65.45, 54.34, 46.74, 44.52, 43.88, 21.32, 21.30. HRMS (EI) Calcd for $[C_{48}H_{40}N_2O_4+Na]$: 731.28858; found: 731.28961.

2'-benzoyl-1,1''-dibenzyl-5,5''-dichloro-5'-hydroxy-5'-phenyl-1,1'',2,2''-

tetrahydrodispiro[indole-3,1'-cyclopentane-3',3''-indole]-2,2''-dione (2f) : The title compound

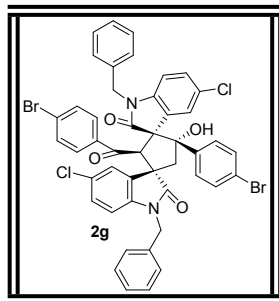


was prepared according to the general procedure as a white solid in 68 % yield; mp = 250-252 °C; IR (KBr): 3310, 3068, 2933, 1697, 1609, 1485, 1431, 1343, 1181, 1081, 992, 915, 815, 750, 700, 619, 580, 554 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.95 (s, 1H), 7.32 (t, $J = 8.6$ Hz, 3H), 7.29 – 7.23 (m, 3H), 7.22 – 7.15 (m, 7H), 7.10 (t, $J = 7.7$ Hz, 4H), 7.03 (t, $J = 7.5$ Hz, 2H), 6.93 (d, $J = 8.4$ Hz, 1H), 6.90 (s, 1H), 6.47 (d, $J = 7.3$ Hz, 2H), 6.30 (d, $J = 8.3$ Hz,

1H), 6.22 (d, $J = 8.4$ Hz, 1H), 5.28 (s, 1H), 5.24 (d, $J = 8.4$ Hz, 1H), 5.20 (d, $J = 9.2$ Hz, 1H), 4.46 (d, $J = 4.4$ Hz, 1H), 4.42 (d, $J = 6.8$ Hz, 1H), 4.24 (d, $J = 15.3$ Hz, 1H), 2.55 (d, $J = 14.0$ Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.08, 183.38, 176.36, 142.44, 140.15, 137.75, 136.92, 135.16, 134.35, 132.53, 131.96, 129.79, 129.09, 128.70, 128.60, 128.46, 128.29, 128.26, 128.02, 127.98, 127.91, 127.64, 127.27, 127.08, 126.99, 126.29, 126.05, 109.76, 109.54, 84.48, 66.82, 65.49, 54.30, 46.56, 44.68, 43.95. HRMS (EI) Calcd for $[C_{46}H_{34}Cl_2N_2O_4+Na]$: 771.17933; found: 771.17953.

1,1''-dibenzyl-2'-(4-bromobenzoyl)-5'-(4-bromophenyl)-5,5''-dichloro-5'-hydroxy-

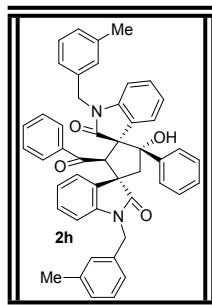
1,1'',2,2''-tetrahydrodispiro[indole-3,1'-cyclopentane-3',3''-indole]-2,2''-dione (2g) : The title



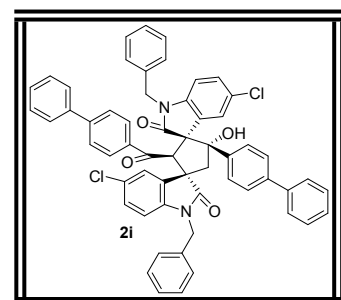
compound was prepared according to the general procedure as a white solid in 70 % yield; mp = 256-258 °C; IR (KBr): 3283, 3064, 2898, 1713, 1686, 1609, 1585, 1482, 1431, 1351, 1274, 1235, 1177, 1096, 1070, 1000, 931, 846, 808, 731, 692, 573, 550, 534, 453 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.17 (s, 1H), 7.90 (s, 1H), 7.45 – 7.18 (m, 10H), 7.15 – 6.96 (m, 7H), 6.91 (s, 1H), 6.54 (d, *J* = 6.3 Hz, 2H), 6.38 (dd, *J* = 15.9, 8.3 Hz, 2H), 5.26 (d, *J* = 16.0 Hz, 1H), 5.16 (s, 1H), 5.05 (d, *J* = 15.2 Hz, 1H), 4.52 (d, *J* = 15.1 Hz, 1H), 4.42 (d, *J* = 16.1 Hz, 1H), 4.36 (d, *J* = 14.0 Hz, 1H), 2.52 (d, *J* = 13.9 Hz, 1H), 1.25 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 195.00, 183.13, 176.17, 142.36, 140.13, 136.81, 134.91, 134.18, 131.63, 131.29, 130.99, 129.92, 129.30, 128.97, 128.75, 128.51, 128.38, 128.14, 127.97, 127.71, 127.41, 127.31, 127.25, 126.28, 126.08, 122.43, 109.93, 109.65, 83.96, 66.73, 65.21, 54.10, 46.63, 45.00, 44.08. HRMS (EI) Calcd for [C₄₆H₃₂Br₂Cl₂N₂O₄+Na]: 927.00036; found: 927.00075.

2'-benzoyl-5'-hydroxy-1,1''-bis[(3-methylphenyl)methyl]-5'-phenyl-1,1'',2,2''-

tetrahydrodispiro[indole-3,1'-cyclopentane-3',3''-indole]-2,2''-dione (2h) : The title



compound was prepared according to the general procedure as a white solid in 74 % yield; mp = 249-251 °C; IR (KBr): 3320, 2975, 2860, 1711, 1684, 1601, 1575, 1480, 1421, 1347, 1311, 1245, 1150, 1065, 927, 805, 775, 690, 650, 550, 511 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, *J* = 6.8 Hz, 1H), 7.96 (d, *J* = 6.1 Hz, 1H), 7.38 – 6.91 (m, 21H), 6.85 (s, 1H), 6.42 (d, *J* = 6.9 Hz, 1H), 6.30 (d, *J* = 6.8 Hz, 1H), 6.11 (s, 1H), 5.36 (s, 1H), 5.23 (d, *J* = 15.1 Hz, 1H), 5.06 (d, *J* = 16.0 Hz, 1H), 4.48 (t, *J* = 14.4 Hz, 2H), 4.16 (d, *J* = 15.1 Hz, 1H), 2.57 (d, *J* = 13.8 Hz, 1H), 2.33 (s, 3H), 2.27 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 196.38, 183.88, 176.87, 143.96, 141.70, 138.75, 138.22, 137.92, 137.13, 135.76, 134.81, 132.23, 130.40, 128.84, 128.64, 128.55, 128.35, 128.31, 127.81, 127.78, 127.72, 127.63, 127.38, 127.07, 127.02, 126.72, 126.05, 125.69, 124.72, 124.21, 123.45, 121.86, 108.84, 108.53, 84.54, 66.63, 65.38, 54.29, 46.67, 44.53, 43.95, 21.45, 21.43. HRMS (EI) Calcd for [C₄₈H₄₀N₂O₄+Na]: 731.28858; found: 731.28998.



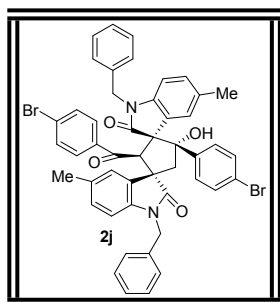
1,1''-dibenzyl-5,5''-dichloro-5'-hydroxy-2'-(4-phenylbenzoyl)-5'-(4-phenylphenyl)-1,1'',2,2''-tetrahydrodispiro[indole-3,1'-

cyclopentane-3',3''-indole]-2,2''-dione (2i) : The title compound was prepared according to the general procedure as a white solid in 64 % yield; mp = 238-240 °C; IR (KBr): 3312, 3062, 2925, 1687, 1605, 1481, 1431, 1340, 1221, 1086, 986, 910, 812, 750, 696, 575, 463 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.27 (d, *J* = 2.0 Hz, 1H), 7.99 (d, *J* = 2.0 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.50 – 7.38 (m, 9H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.31 – 7.18 (m, 11H), 7.11 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.95 (dq, *J* = 9.7, 7.2 Hz, 5H), 6.53 (d, *J* = 7.1 Hz, 2H), 6.33 (d, *J* = 8.3 Hz, 1H), 6.26 (d, *J* = 8.4 Hz, 1H), 5.32 (s, 1H), 5.29 (d, *J* = 16.3 Hz, 1H), 5.18 (d, *J* = 15.3 Hz, 1H), 4.49 (d, *J* = 14.0 Hz, 1H), 4.44 (d, *J* = 16.2 Hz, 1H), 4.36 (d, *J* = 15.2 Hz, 1H), 2.59 (d, *J* = 14.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 196.14, 184.08, 177.09, 145.06, 140.41, 139.70, 137.65, 135.89, 135.79, 135.00, 130.59, 129.13, 129.07, 128.88, 128.64, 128.53, 128.22, 127.95, 127.80, 127.45, 127.26, 127.17, 126.97, 126.79, 126.50, 126.39, 125.95, 124.45, 122.12, 109.02, 108.65, 84.57, 66.86, 65.56, 54.53, 44.83, 44.08, 29.84.

HRMS (EI) Calcd for [C₅₈H₄₂Cl₂N₂O₄+Na]: 923.24193; found: 923.24227.

1,1''-dibenzyl-2'-(4-bromobenzoyl)-5'-(4-bromophenyl)-5'-hydroxy-5,5''-dimethyl-

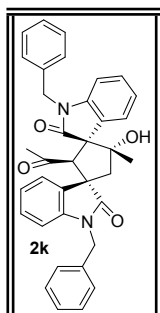
1,1'',2,2''-tetrahydrodispiro[indole-3,1'-cyclopentane-3',3''-indole]-2,2''-dione (2j) : The title



compound was prepared according to the general procedure as a white solid in 67 % yield; mp = 258-260 °C; IR (KBr): 3280, 2964, 2910, 2856, 1709, 1686, 1616, 1585, 1493, 1431, 1351, 1324, 1258, 1204, 1162, 1100, 1070, 1008, 931, 808, 777, 692, 657, 561, 534 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.96 (s, 1H), 7.73 (s, 1H), 7.40 – 7.32 (m, 5H), 7.29 – 7.18 (m, 5H), 7.06 – 6.92 (m, 8H), 6.81 (d, *J* = 7.6 Hz, 1H), 6.55 (d, *J* = 6.9 Hz,

2H), 6.33 (d, *J* = 7.9 Hz, 2H), 5.26 (d, *J* = 16.1 Hz, 1H), 5.21 (s, 1H), 5.07 (d, *J* = 15.1 Hz, 1H), 4.48 (d, *J* = 15.1 Hz, 1H), 4.41 (d, *J* = 13.8 Hz, 1H), 4.39 (d, *J* = 2.4 Hz, 1H), 2.51 (d, *J* = 13.9 Hz, 1H), 2.37 (s, 3H), 2.29 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 195.42, 183.55, 176.53, 141.42, 139.21, 137.59, 135.86, 135.61, 134.80, 134.14, 131.41, 131.04, 130.82, 130.12, 129.27, 129.11, 128.86, 128.61, 128.41, 128.20, 128.05, 127.52, 127.19, 127.04, 126.52, 126.33, 126.19, 122.11, 108.57, 108.40, 84.00, 66.56, 65.16, 54.18, 46.83, 44.79, 44.01, 21.29. HRMS (EI) Calcd for [C₄₈H₃₈Br₂N₂O₄+Na]: 887.10960; found: 887.10953.

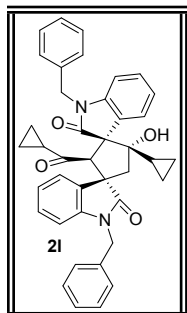
2'acetyl-1,1''-dibenzyl-4'-hydroxy-4'-methyl-1,1'',2,2''-



tetrahydrodispiro[indole-3,3'-cyclopentane-1',3''-indole]-2,2''-dione (2k): The title compound was prepared according to the general procedure as a white solid in

48 % yield; mp = 218-220 °C; IR (KBr): 3335, 3056, 1702, 1676, 1611, 1411, 1367, 1183, 805, 772, 690, 647, 506, 537. ¹H NMR (400 MHz, CDCl₃) δ 8.15 (d, *J* = 7.1 Hz, 1H), 7.59 (d, *J* = 7.1 Hz, 1H), 7.48 (d, *J* = 7.4 Hz, 2H), 7.36 (ddd, *J* = 28.6, 13.6, 7.9 Hz, 6H), 7.29 – 7.24 (m, 2H), 7.24 – 7.20 (m, 1H), 7.14 (dd, *J* = 16.6, 8.1 Hz, 2H), 7.02 (t, *J* = 7.3 Hz, 1H), 6.88 (d, *J* = 7.7 Hz, 1H), 6.71 (d, *J* = 7.7 Hz, 1H), 6.11 (s, 1H), 5.17 – 5.05 (m, 2H), 5.03 (t, *J* = 17.2 Hz, 2H), 4.43 (s, 1H), 3.51 (d, *J* = 14.1 Hz, 1H), 2.32 (d, *J* = 14.1 Hz, 1H), 1.22 (s, 3H), 1.05 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 201.60, 183.96, 178.00, 143.78, 141.97, 136.31, 135.29, 131.03, 129.05, 128.74, 128.39, 128.21, 127.61, 127.41, 127.30, 127.04, 126.95, 125.87, 124.72, 122.07, 109.31, 108.76, 82.48, 69.97, 65.07, 54.19, 49.81, 44.69, 44.15, 28.32, 20.02. HRMS (EI) Calcd for [C₃₆H₃₂N₂O₄]⁺: 556.2362; found: 556.2760.

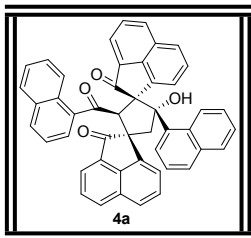
1,1''-dibenzyl-2'-cyclopropanecarbonyl-4'-cyclopropyl-4'-hydroxy-1,1'',2,2''-



tetrahydrodispiro[indole-3,3'-cyclopentane-1',3''-indole]-2,2''-dione (21): The title compound was prepared according to the general procedure as a white solid in 43 % yield; mp = 235-237 °C; IR (KBr): 3332, 3049, 1701, 1671, 1601, 1410, 1360, 1173, 805, 770, 690, 640, 507, 532 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, *J* = 7.7 Hz, 1H), 7.59–7.57 (d, *J* = 7.6 Hz, 1H), 7.48–7.46 (d, *J* = 8.0 Hz, 1H), 7.43–7.17 (m, 12H), 7.14–7.10 (t, *J* = 8.0 Hz, 1H), 7.04–7.00 (t, *J* = 8.0 Hz, 1H), 6.90–6.88 (d, *J* = 8.0 Hz, 1H), 6.75–6.73 (d, *J* = 8.0 Hz, 1H), 6.08 (s, 1H), 5.32–5.28 (d, *J* = 16.0 Hz, 1H), 5.18 – 5.14 (d, *J* = 16.0 Hz, 1H), 4.95 – 4.91 (d, *J* = 16.0 Hz, 1H), 4.87– 4.83 (d, *J* = 16.0 Hz, 1H), 3.47–3.36 (m, 2H), 3.29–3.23 (m, 1H), 2.92–2.88 (m, 1H), 2.67– 2.63 (m, 1H), 2.34– 2.30 (d, *J* = 16.0 Hz, 1H), 1.83–1.78 (m, 2H), 1.72–1.66 (m, 1H), 1.48–1.36 (m, 1H), 1.22–1.19 (m, 1H), 0.99–0.97 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 202.90, 183.87, 177.63, 143.68, 142.07, 136.25, 135.17, 130.54, 129.10 (2C), 128.97, 128.81 (2C), 128.57, 128.31, 127.76 (3C), 127.54, 127.49 (2C), 127.22, 127.02, 125.83, 124.70, 122.20, 109.59, 108.81, 84.37, 69.06, 64.99, 54.09, 45.36, 44.79, 44.22, 43.71, 38.86, 31.40, 27.18, 25.62; HRMS (EI) Calcd for [C₄₀H₃₆N₂O₄]⁺: 608.2675; found: 608.2674.

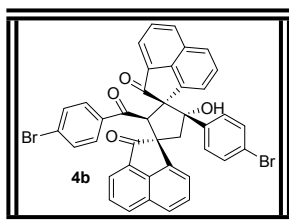
4'-hydroxy-4'-(naphthalen-1-yl)-2'-(naphthalene-1-carbonyl)-2H,2''H-

dispiro[acenaphthylene-1,3'-cyclopentane-1',1''-acenaphthylene]-2,2''-dione (4a) :



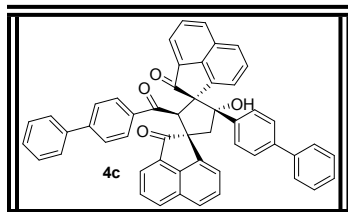
compound was prepared according to the general procedure as a white solid in 77 % yield; mp = 254-256 °C; IR (KBr): 3372, 3072, 2918, 1701, 1682, 1605, 1482, 1424, 1366, 1339, 1274, 1231, 1174, 1077, 1000, 927, 815, 765, 746, 700, 580, 554 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.46 (d, J=6.0 Hz, 1H), 8.25 (d, J=7.2 Hz, 1H), 8.07 (d, J=6.8 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.86–7.83 (dd, J = 5.2, 5.6 Hz, 2H), 7.80 (d, J = 6.8 Hz, 1H), 7.75–7.72 (dd, J=7.2, 8.0 Hz, 1H), 7.66–7.54 (m, 3H), 7.39–7.29 (m, 4H), 7.24 (merged dd, 1H), 7.16–7.12 (m, 3H), 7.06 (d, J=8.1 Hz, 2H), 6.94 (d, J = 8.4 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 6.72 (s, 1H), 5.63 (s, 1H), 5.30 (s, 1H), 4.61 (d, J = 14.0 Hz, 1H), 2.73 (d, J = 14.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 213.12, 204.61, 197.05, 144.42, 142.24, 141.78, 140.56, 139.98, 139.78, 139.56, 137.86, 137.49, 134.84, 134.39, 133.13, 131.47, 130.74, 130.24, 130.01, 129.55, 128.72 (2C), 128.55 (2C), 128.18, 128.00, 127.76, 127.71, 127.18, 127.09, 126.97 (2C), 126.86 (2C), 126.58, 125.87 (3C), 124.84, 124.53, 122.85, 122.81, 120.79, 84.62, 71.86, 67.90, 59.84, 47.28; HRMS (EI) Calcd for [C₄₈H₃₀O₄+Na]: 693.20418; found: 693.20439.

2'-(4-bromobenzoyl)-4'-(4-bromophenyl)-4'-hydroxy-2H,2''H-dispiro[acenaphthylene-1,3'-cyclopentane-1',1''-acenaphthylene]-2,2''-dione (4b) :



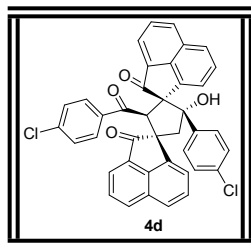
according to the general procedure as a white solid in 74 % yield; mp = 250-252 °C; IR (KBr): 3334, 3056, 2925, 1713, 1693, 1605, 1562, 1497, 1435, 1393, 1324, 1270, 1235, 1096, 1077, 1012, 838, 777, 700, 538 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.39 (d, J = 6.7 Hz, 1H), 8.17 (d, J = 6.8 Hz, 1H), 8.06 (d, J = 7.0 Hz, 1H), 7.98 (d, J = 8.0 Hz, 2H), 7.83 (dd, J = 11.3, 7.8 Hz, 2H), 7.74 – 7.65 (m, 3H), 7.61 (dd, J = 11.9, 7.2 Hz, 2H), 7.01 (d, J = 8.2 Hz, 2H), 6.88 (d, J = 8.1 Hz, 2H), 6.71 (q, J = 8.2 Hz, 4H), 6.66 (s, 1H), 5.47 (s, 1H), 4.48 (d, J = 14.3 Hz, 1H), 2.64 (d, J = 14.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 212.77, 204.32, 196.46, 141.63, 139.53, 137.40, 137.23, 134.78, 134.10, 133.47, 131.00, 130.41, 130.32, 130.02, 129.50, 128.17, 127.99, 127.92, 126.62, 125.04, 124.79, 124.46, 123.08, 122.86, 121.64, 120.97, 84.25, 71.67, 67.70, 59.62, 47.03. HRMS (EI) Calcd for [C₄₀H₂₄Br₂O₄+Na]: 748.99390; found: 748.99408.

4'-hydroxy-2'-(4-phenylbenzoyl)-4'-(4-phenylphenyl)-2H,2''H-dispiro[acenaphthylene-1,3'-cyclopentane-1',1''-acenaphthylene]-2,2''-dione (4c) :



compound was prepared according to the general procedure as a white solid in 71 % yield; mp = 244-246 °C; IR (KBr): 3372, 3045, 2925, 1716, 1689, 1601, 1493, 1424, 1343, 1270, 1231, 1096, 1008, 919, 842, 777, 700, 646 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.47 (d, *J* = 5.6 Hz, 1H), 8.25 (d, *J* = 6.9 Hz, 1H), 8.07 (d, *J* = 7.0 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 5.5 Hz, 1H), 7.84 (d, *J* = 5.2 Hz, 1H), 7.80 (d, *J* = 6.9 Hz, 1H), 7.77 – 7.70 (m, 1H), 7.62 (td, *J* = 14.9, 7.8 Hz, 3H), 7.58 – 7.53 (m, 1H), 7.38 – 7.30 (m, 6H), 7.29 – 7.21 (m, 3H), 7.16 – 7.11 (m, 4H), 7.06 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 8.3 Hz, 2H), 6.81 (d, *J* = 8.3 Hz, 1H), 6.72 (s, 1H), 5.63 (s, 1H), 4.61 (d, *J* = 14.2 Hz, 1H), 2.73 (d, *J* = 14.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 213.12, 204.61, 197.05, 144.42, 142.24, 140.56, 139.98, 139.78, 139.56, 137.86, 137.49, 134.84, 134.39, 133.13, 131.47, 130.74, 130.24, 130.01, 129.55, 128.72, 128.55, 128.18, 128.00, 127.76, 127.71, 127.18, 127.09, 126.97, 126.86, 126.58, 125.87, 124.84, 124.53, 122.85, 122.81, 120.79, 84.62, 71.86, 67.90, 59.84, 47.28. HRMS (EI) Calcd for [C₅₂H₃₄O₄+Na]: 745.23548; found: 745.23567.

2'-(4-chlorobenzoyl)-4'-(4-chlorophenyl)-4'-hydroxy-2H,2''H-dispiro[acenaphthylene-1,3'-cyclopentane-1',1''-acenaphthylene]-2,2''-dione (4d) : The title compound was prepared



according to the general procedure as a white solid in 64 % yield; mp = 240-242 °C; IR (KBr): 3368, 3045, 2929, 1720, 1682, 1601, 1489, 1428, 1343, 1270, 1227, 1093, 1008, 923, 846, 777, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.38 (d, *J* = 6.7 Hz, 1H), 8.16 (d, *J* = 6.8 Hz, 1H), 8.05 (d, *J* = 7.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 7.1 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.60 (dd, *J* = 11.9, 7.2 Hz, 2H), 7.25 (s, 1H), 7.00 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 8.1 Hz, 2H), 6.71 (q, *J* = 8.2 Hz, 4H), 6.66 (s, 1H), 5.46 (s, 1H), 4.48 (d, *J* = 14.3 Hz, 1H), 2.63 (d, *J* = 14.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 212.76, 204.31, 196.45, 141.63, 139.53, 137.39, 137.23, 134.78, 134.09, 133.46, 131.00, 130.41, 130.31, 130.01, 129.50, 128.17, 127.98, 127.92, 126.62, 125.03, 124.79, 124.46, 123.07, 122.86, 121.63, 120.97, 84.25, 71.66, 67.70, 59.61, 47.02. HRMS (EI) Calcd for [C₄₀H₂₄Cl₂O₄+Na]: 661.09493; found: 661.09497.

NMR Spectra of compounds 2a-j and 4a-d

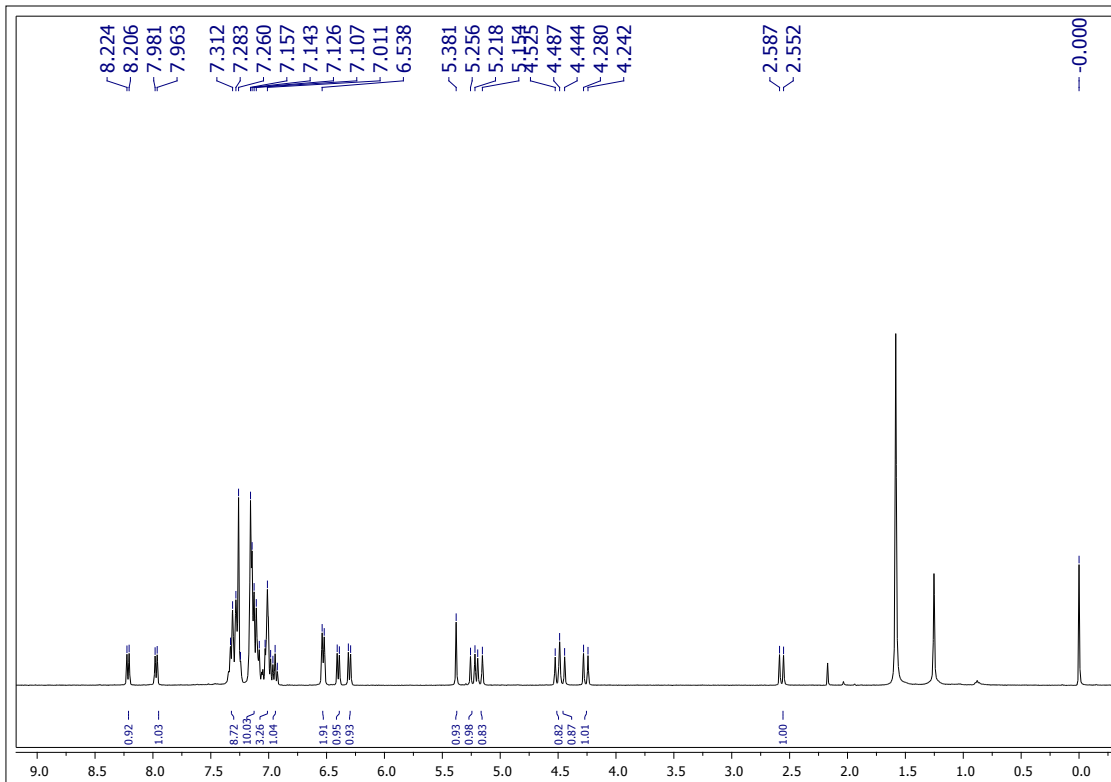


Figure S1. ^1H NMR spectrum of compound **2a**

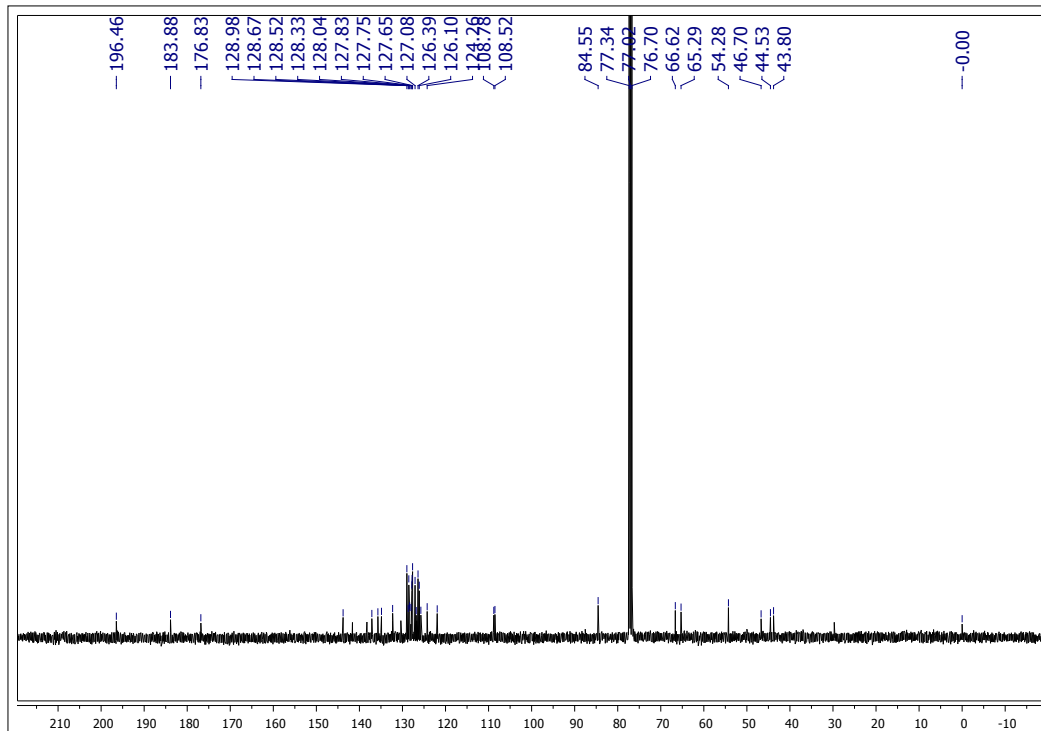


Figure S2. ^{13}C NMR spectrum of compound **2a**

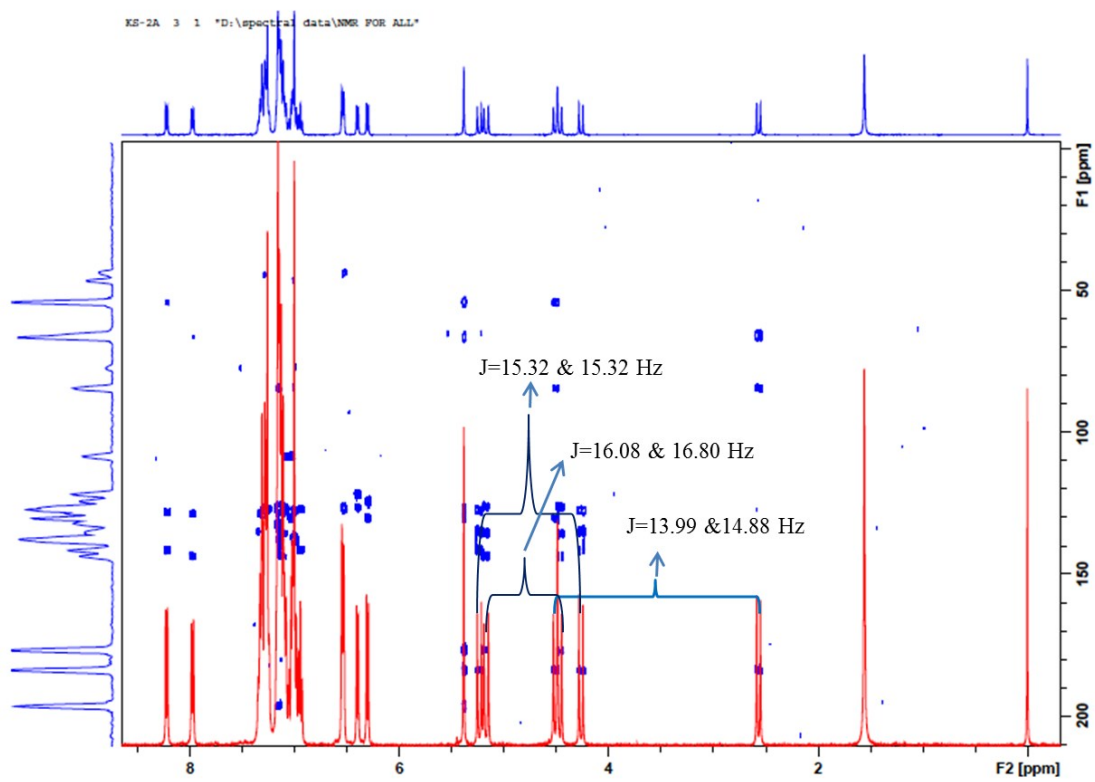


Figure S3. HMBC spectrum of compound **2a**

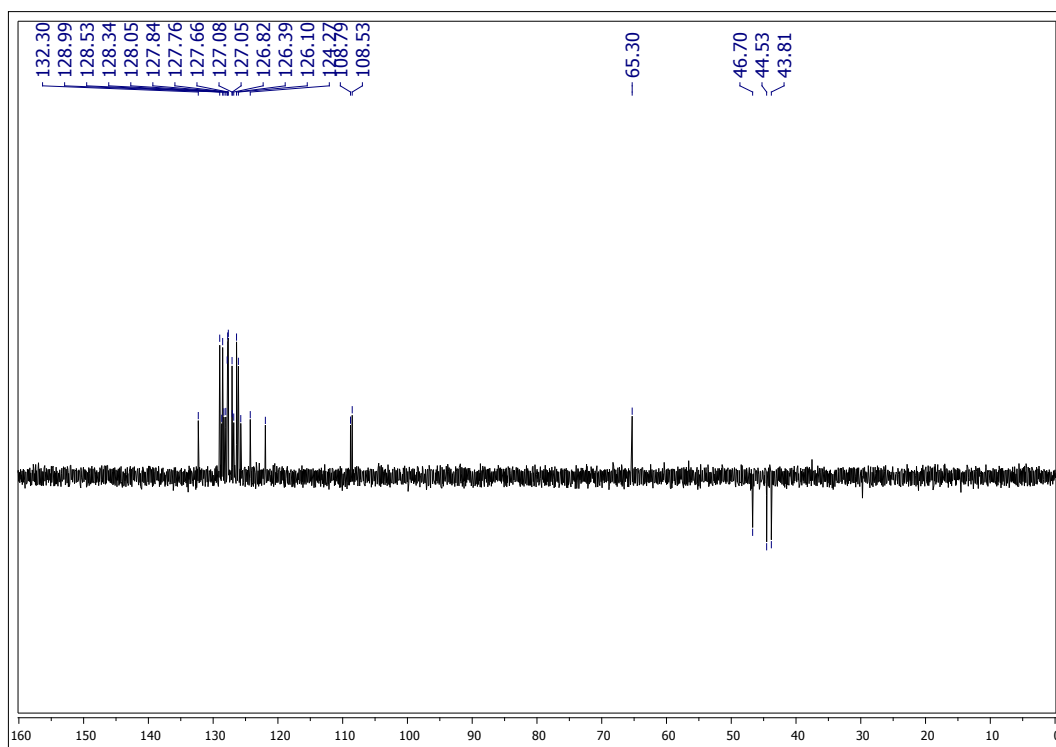


Figure S4. DEPT-135 spectrum of compound **2a**

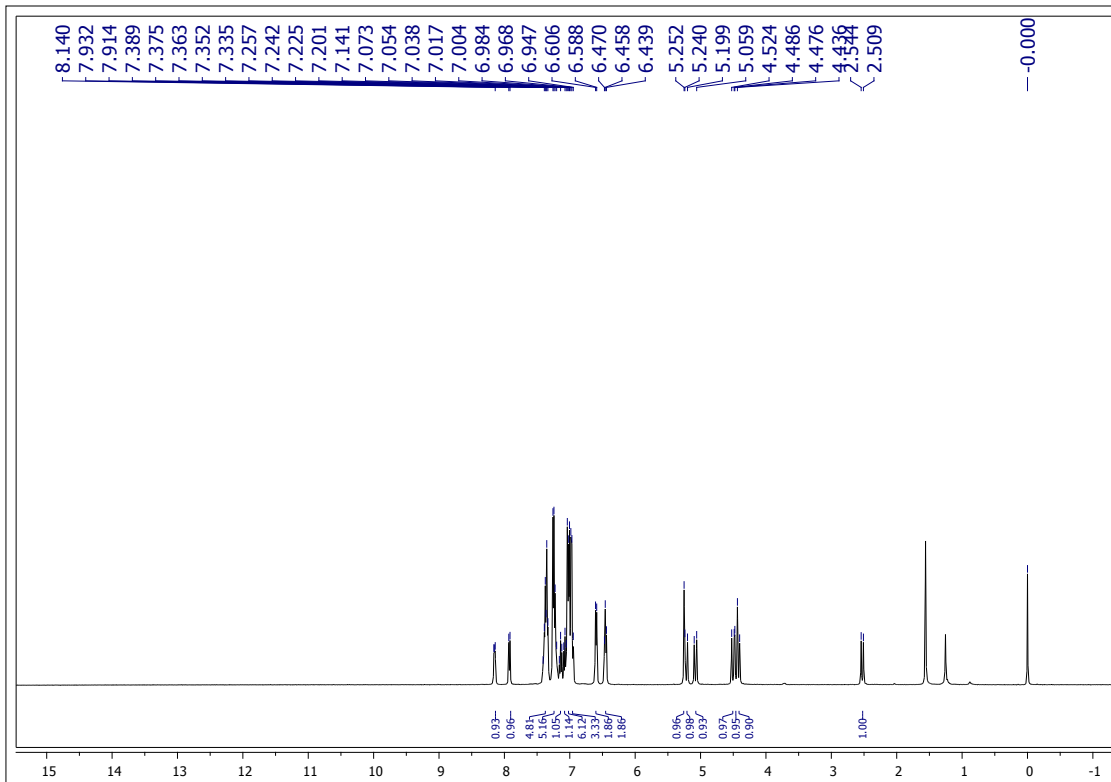


Figure S5. ^1H NMR spectrum of compound **2b**

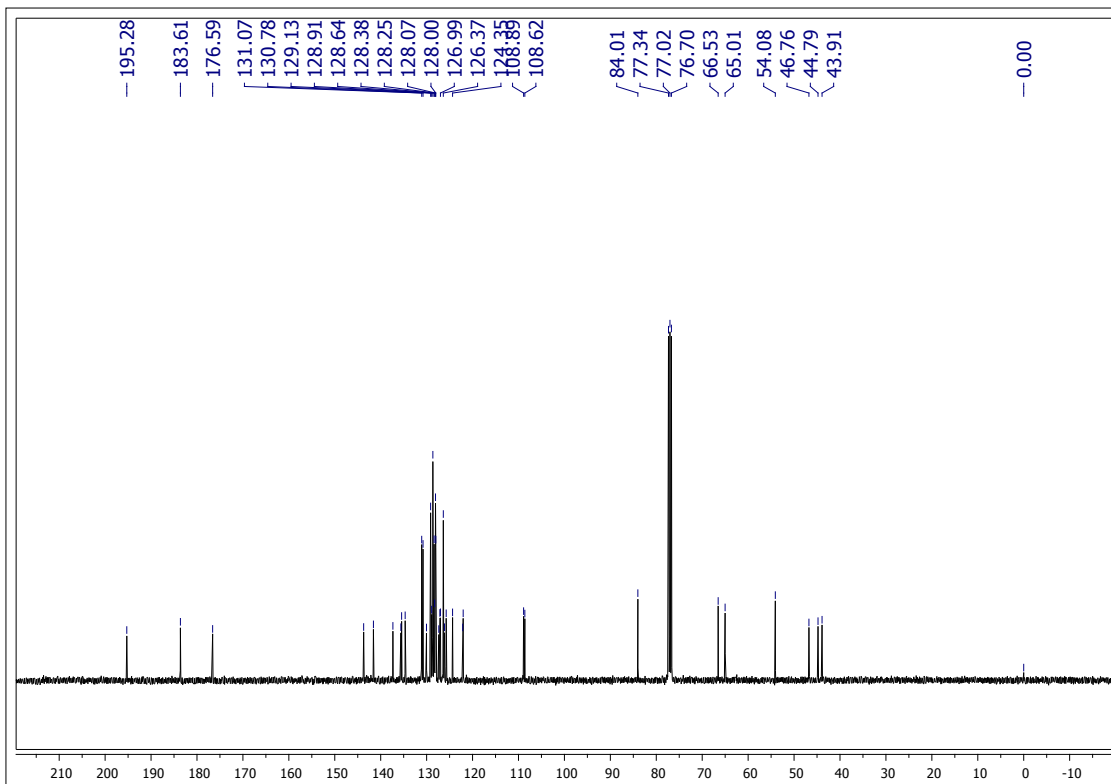


Figure S6. ^{13}C NMR spectrum of compound **2b**

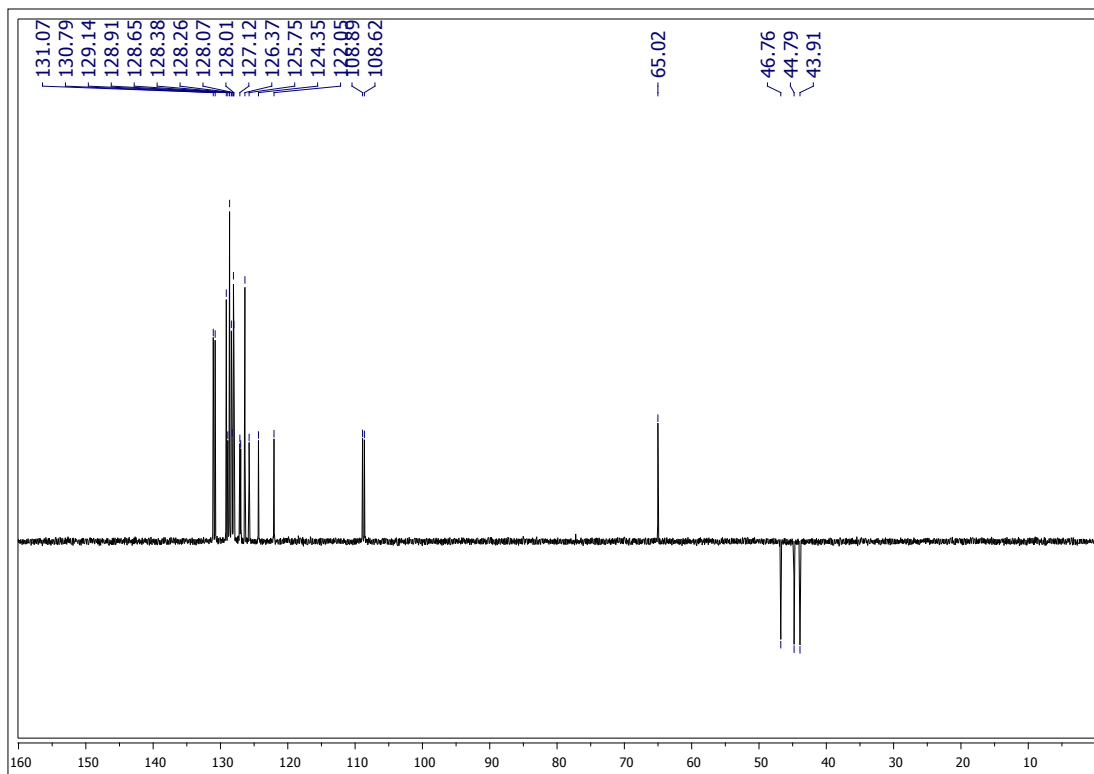


Figure S7. DEPT-135 spectrum of compound **2b**

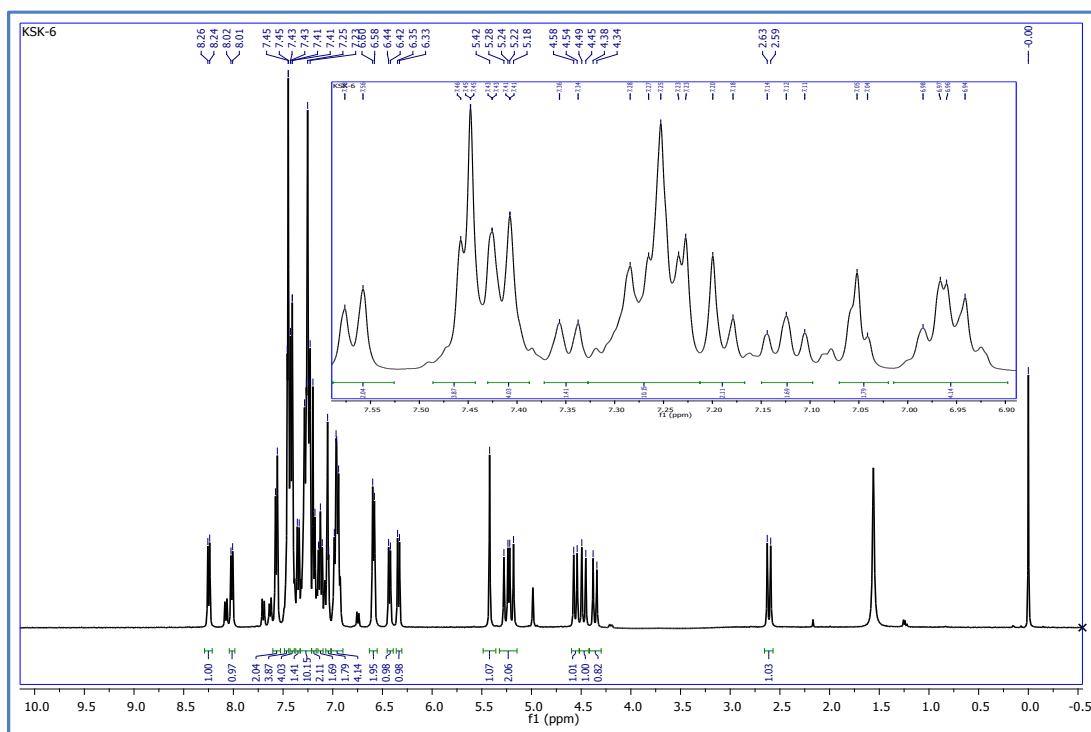


Figure S8. ¹H NMR spectrum of compound **2c**

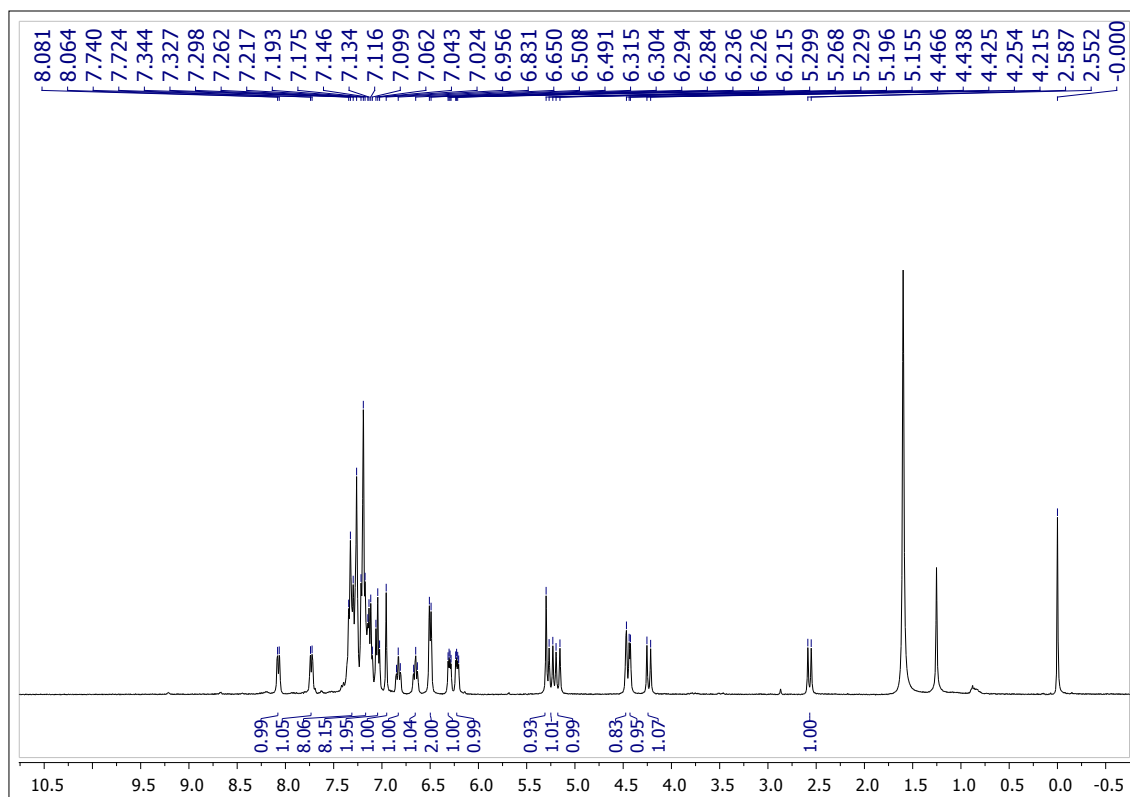


Figure S11. ¹H NMR spectrum of compound 2d

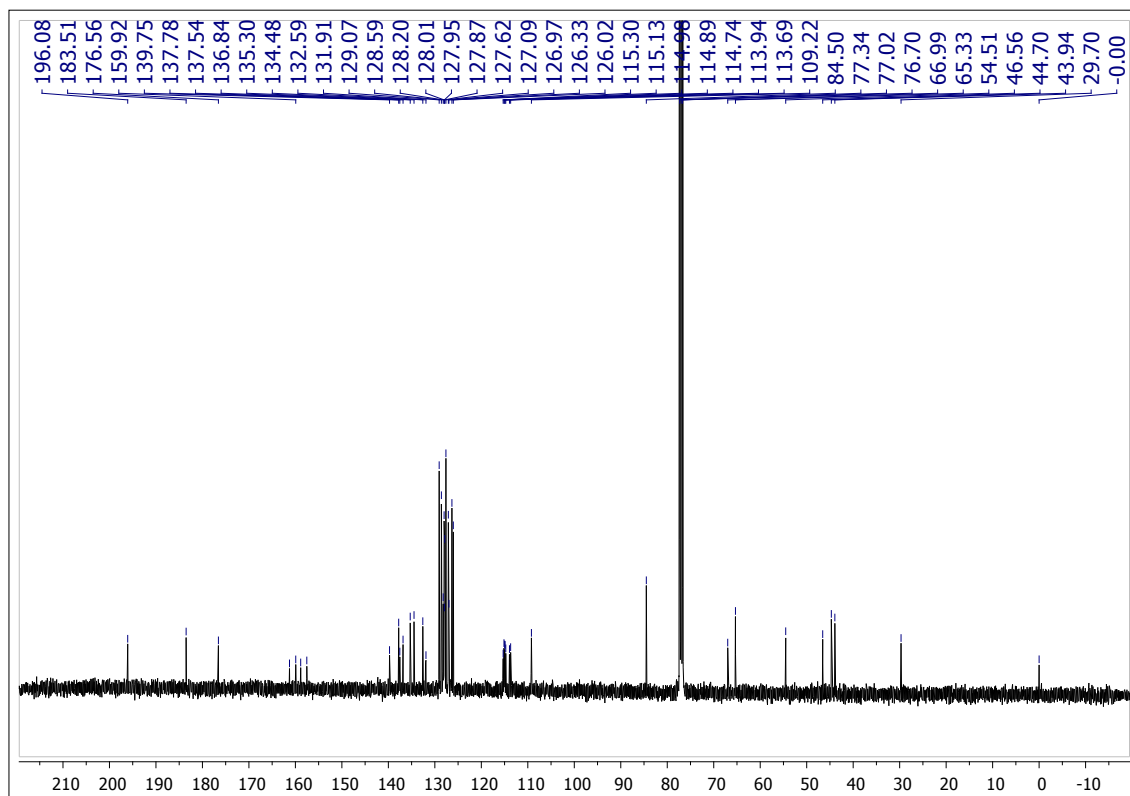


Figure S12. ¹³C NMR spectrum of compound 2d

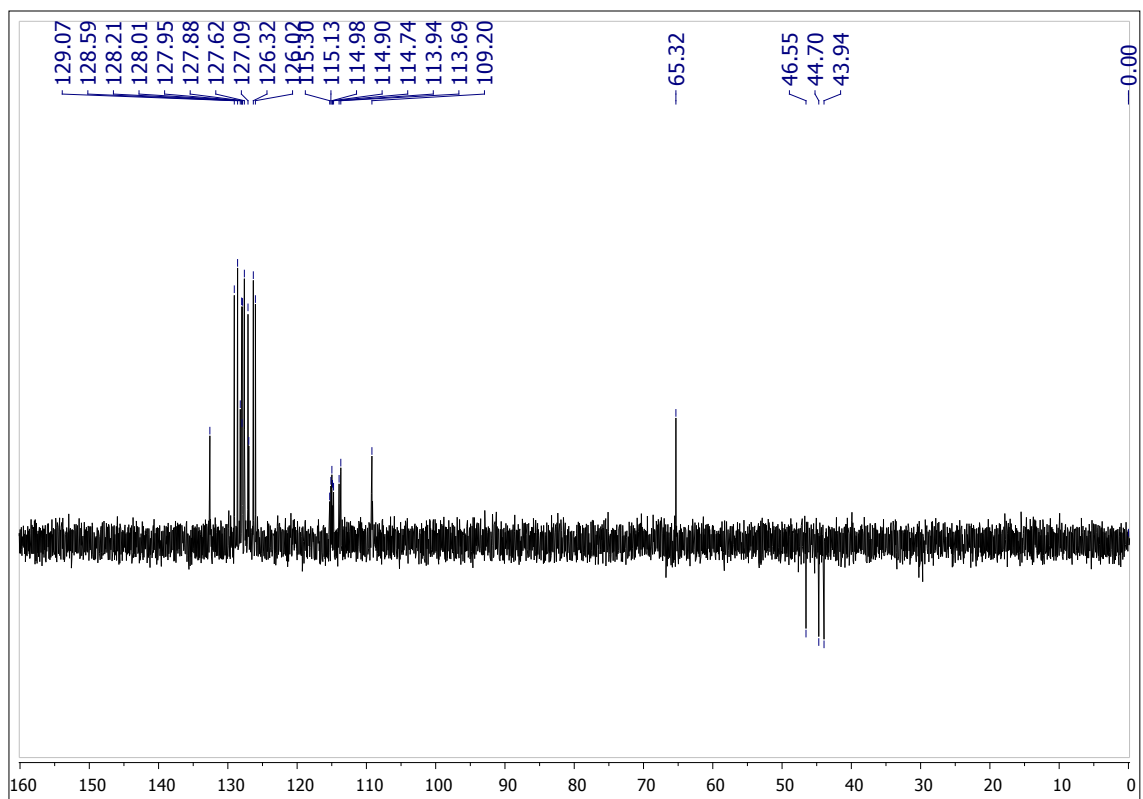


Figure S13. DEPT-135 spectrum of compound 2d

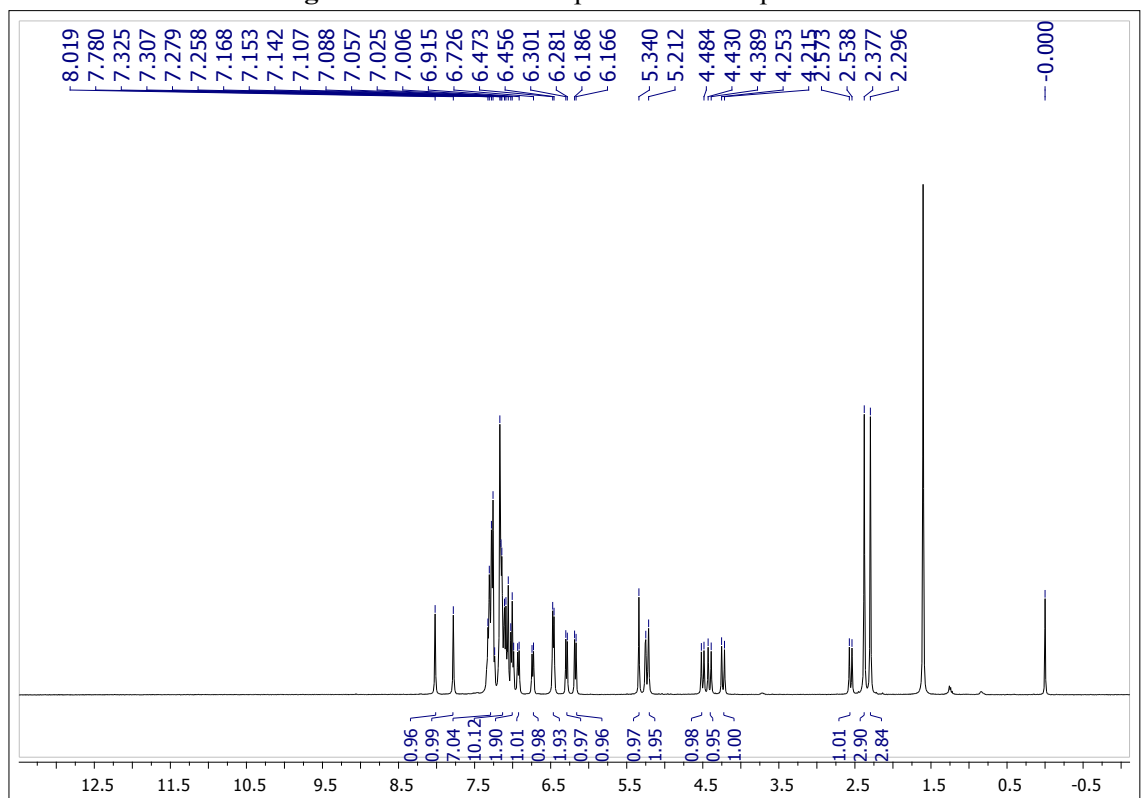


Figure S14. ¹H NMR spectrum of compound 2e

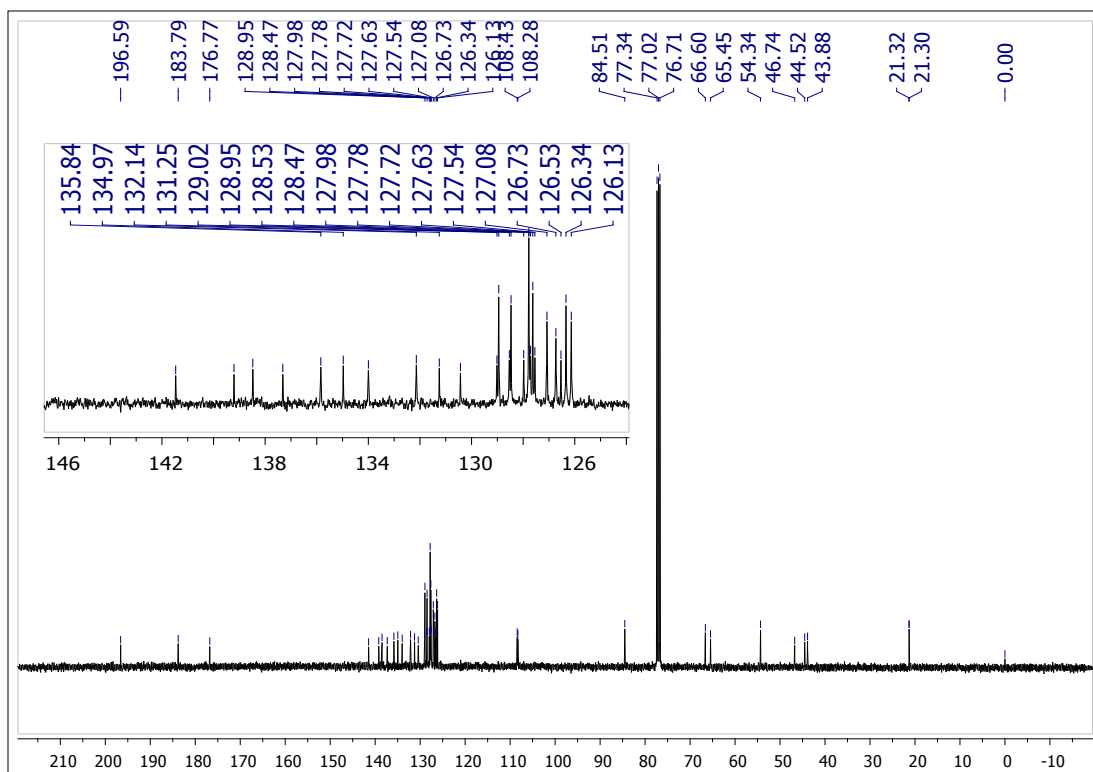


Figure S15. ^{13}C NMR spectrum of compound **2e**

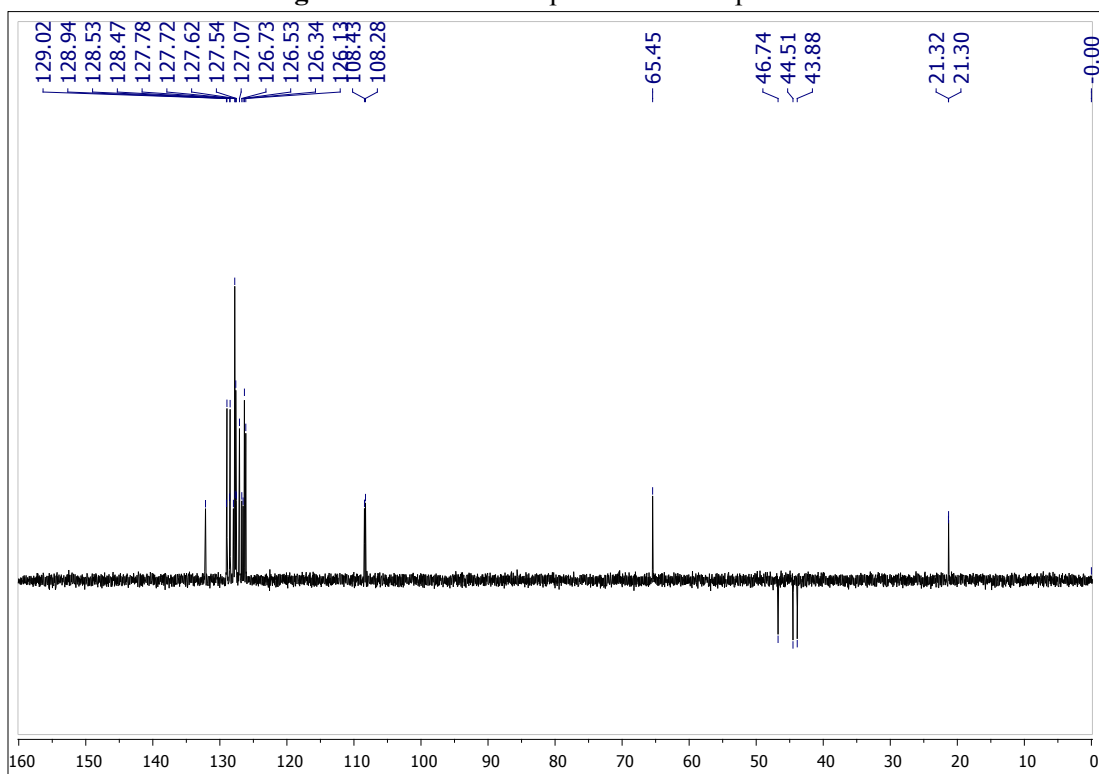


Figure S16. DEPT-135 spectrum of compound **2e**

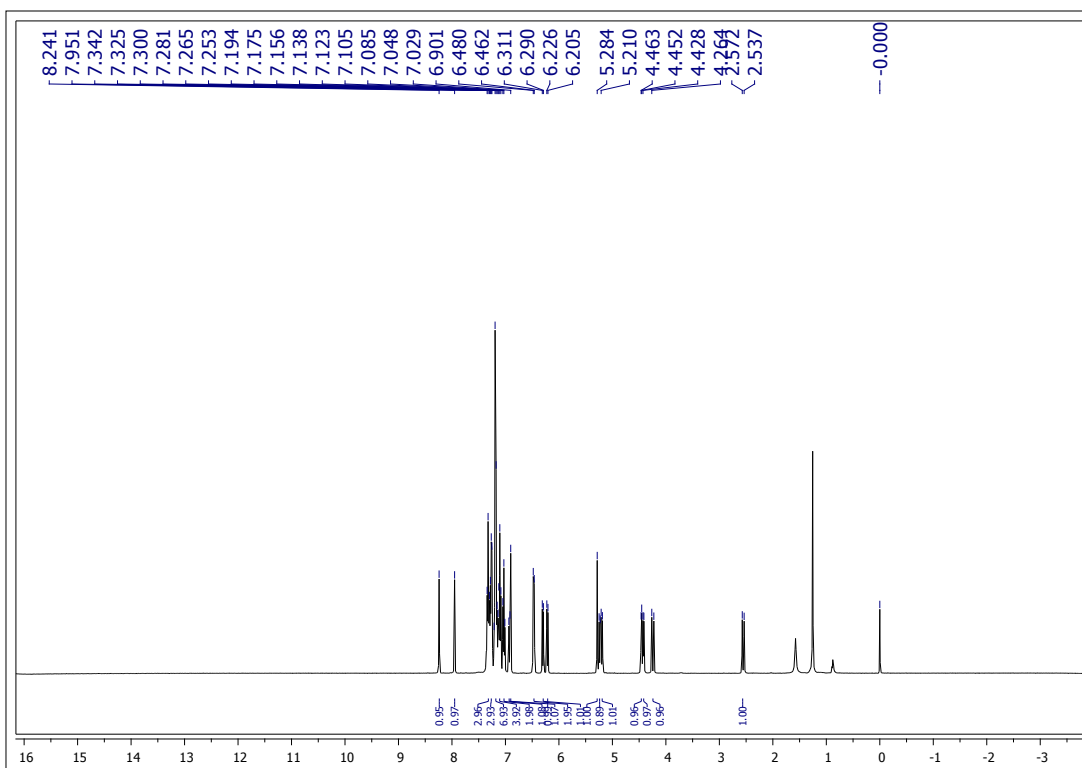


Figure S17. ^1H NMR spectrum of compound **2f**

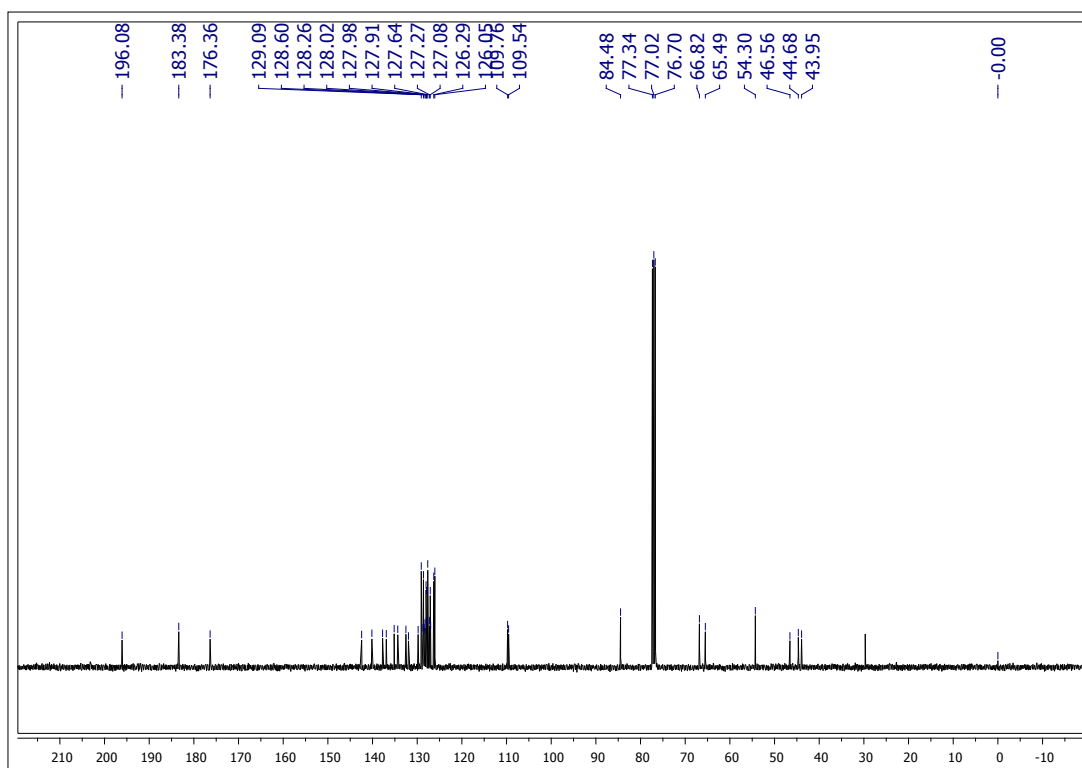


Figure S18. ^{13}C NMR spectrum of compound **2f**

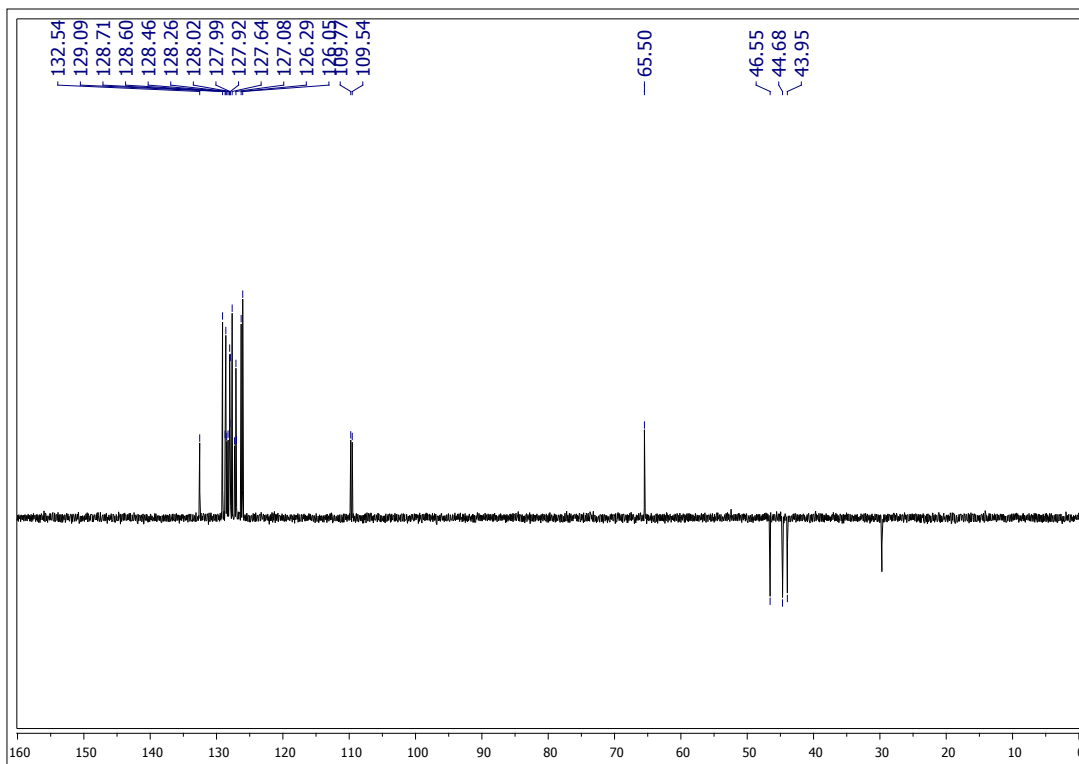


Figure S19. DEPT-135 spectrum of compound 2f

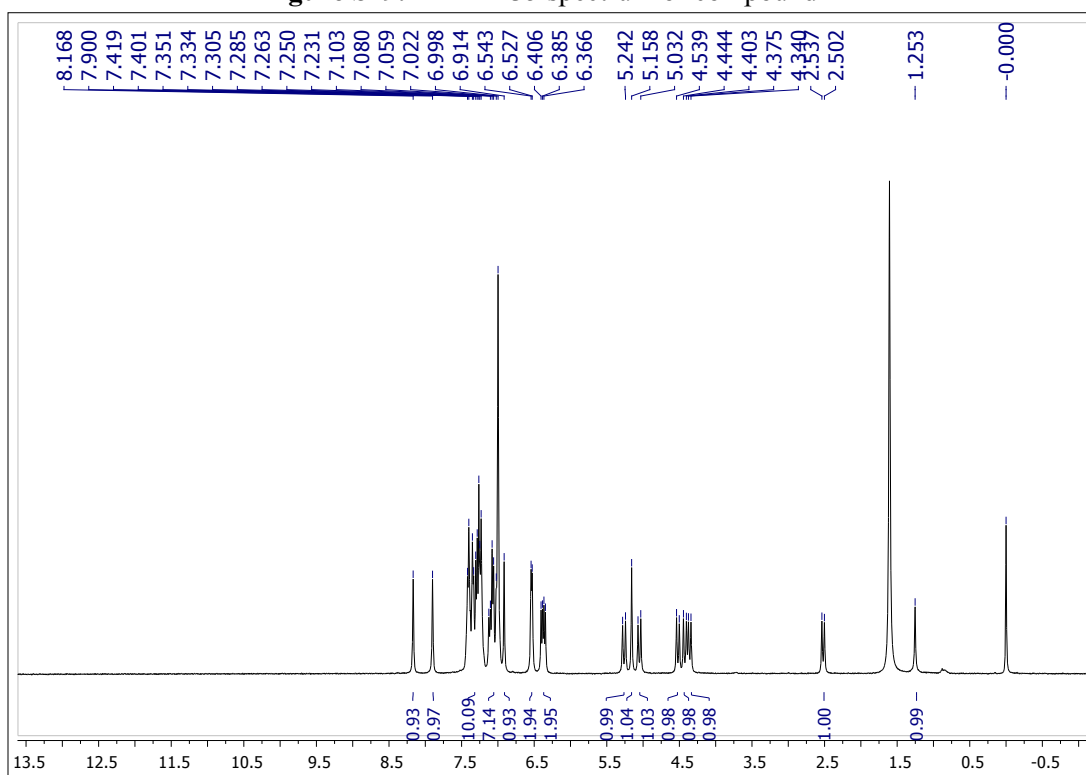


Figure S20. ¹H NMR spectrum of compound 2g

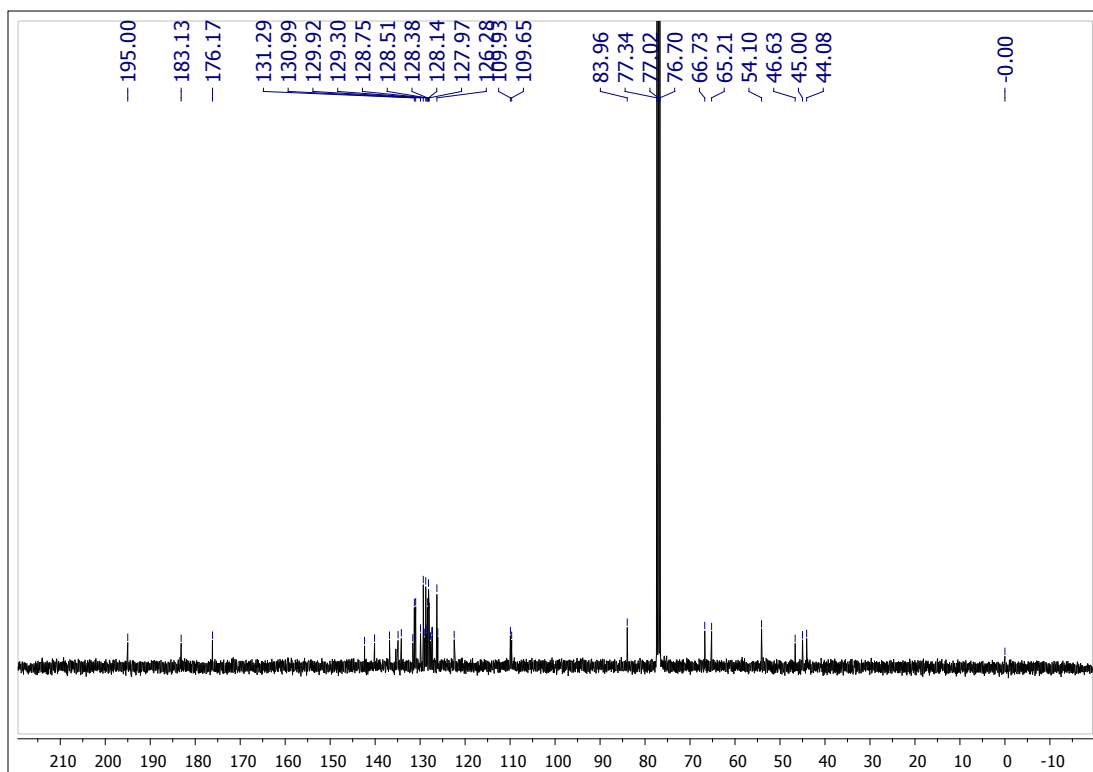


Figure S21. ^{13}C NMR spectrum of compound **2g**

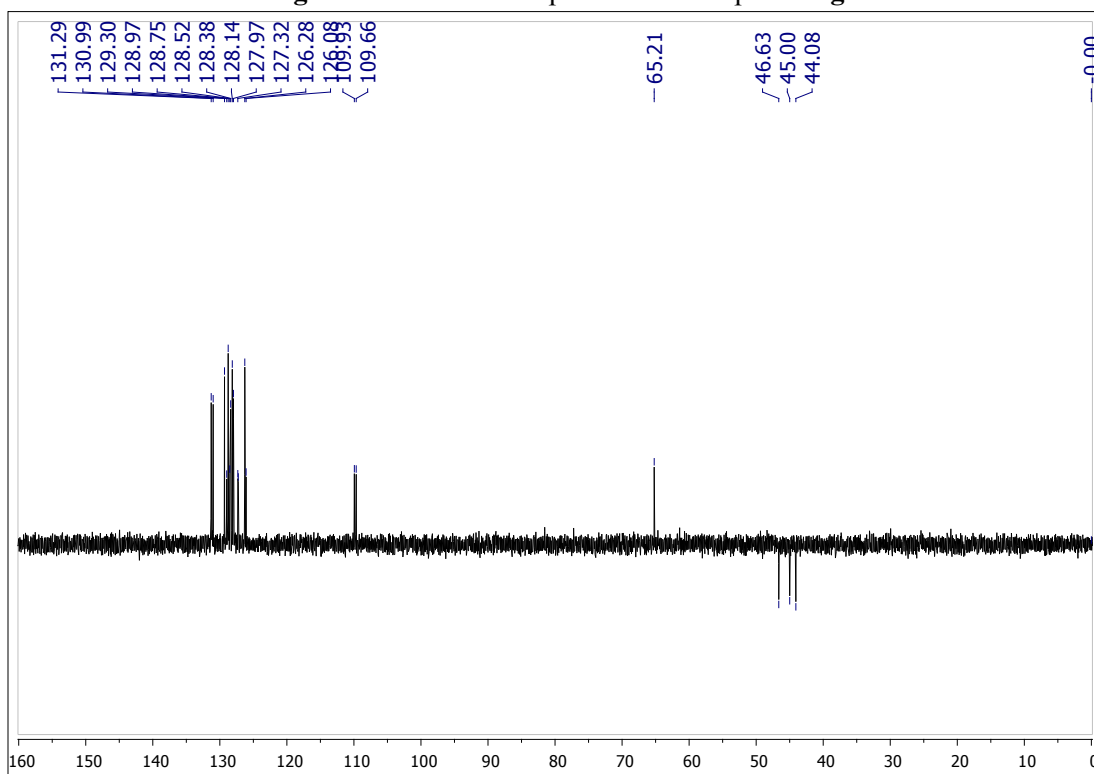


Figure S22. DEPT-135 spectrum of compound **2g**

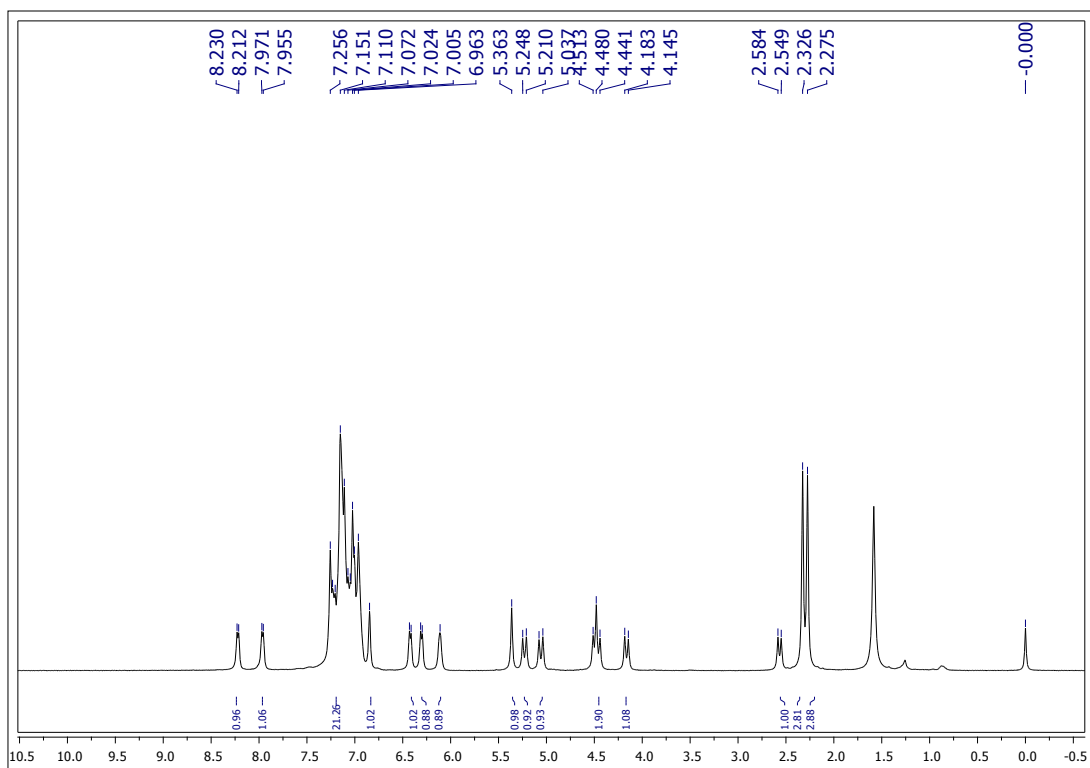


Figure S23. ¹H NMR spectrum of compound **2h**

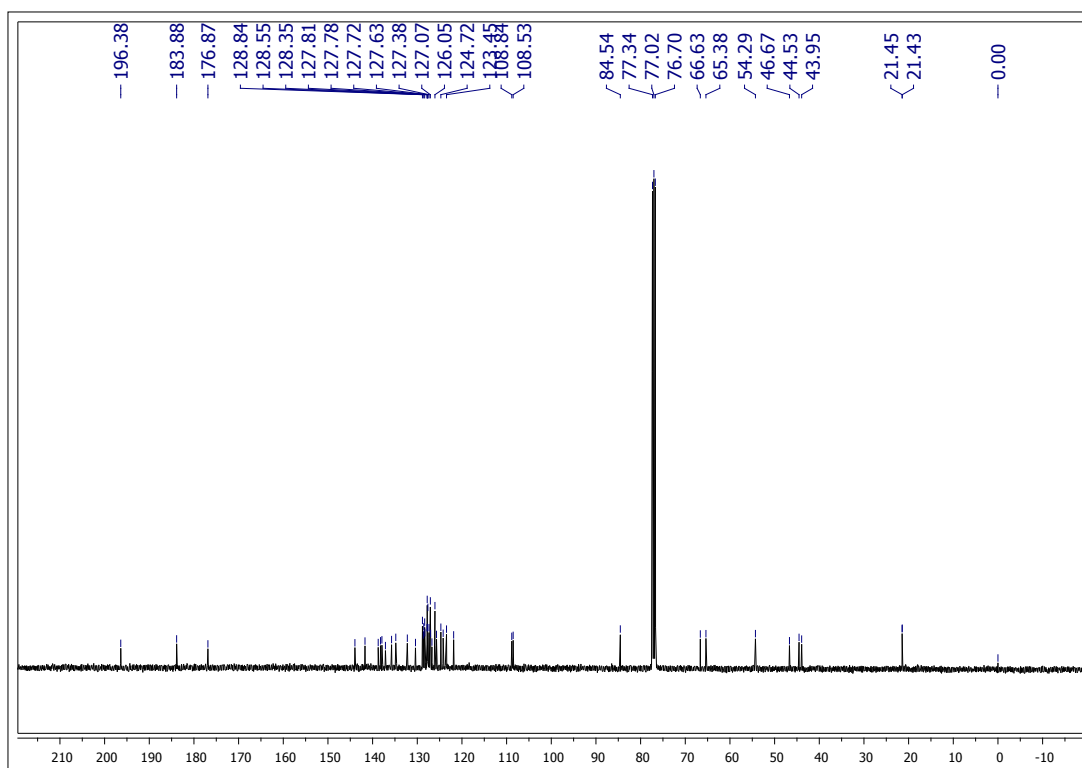


Figure S24. ¹³C NMR spectrum of compound **2h**

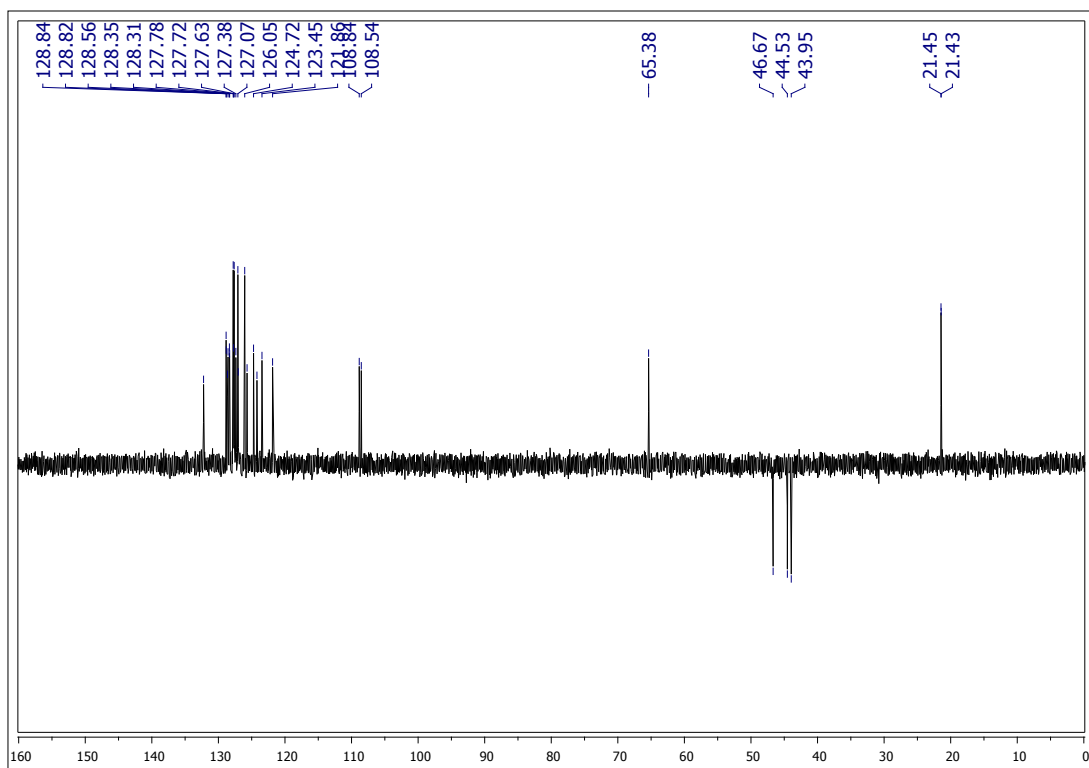


Figure S25. DEPT-135 spectrum of compound 2h

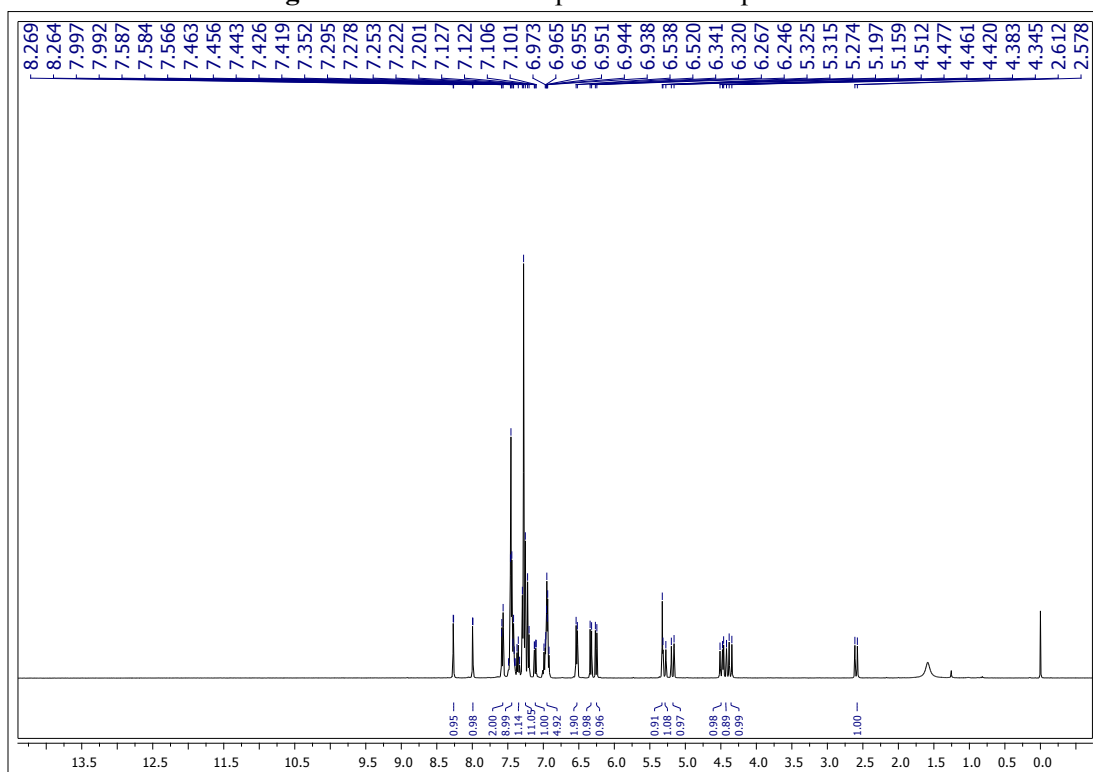


Figure S26. ¹H NMR spectrum of compound 2i

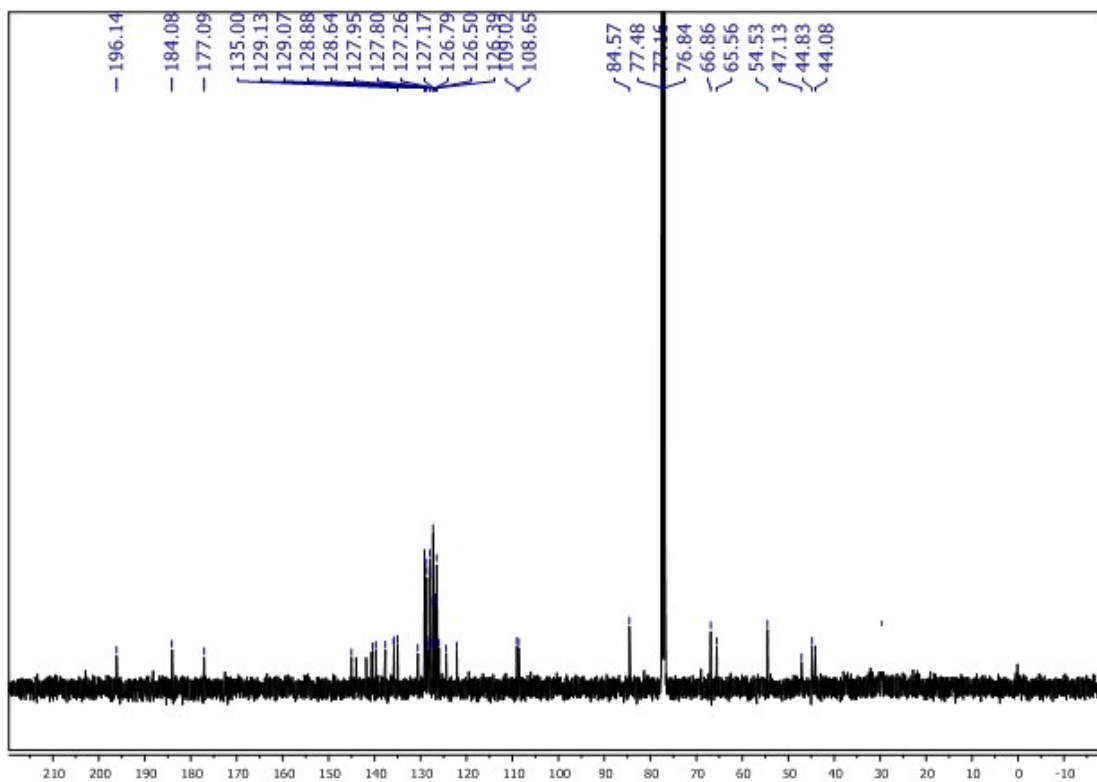


Figure S27. ^{13}C NMR spectrum of compound **2i**

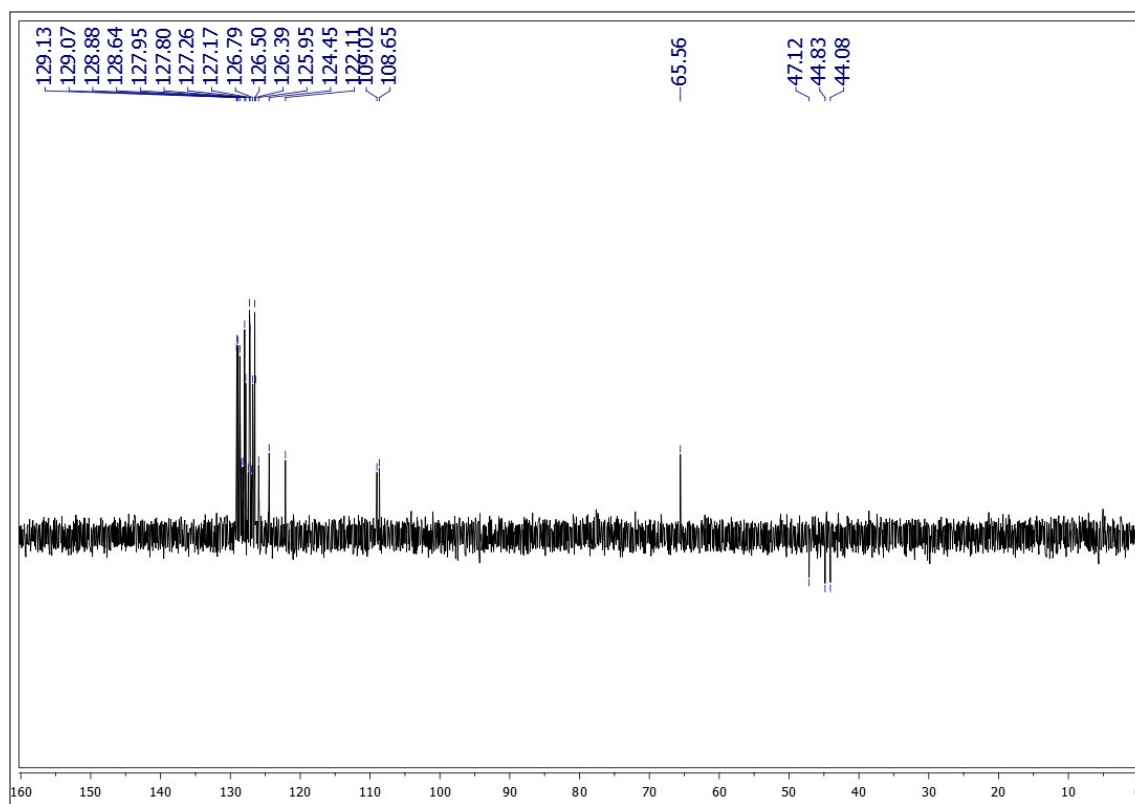


Figure S28. DEPT-135 spectrum of compound **2i**

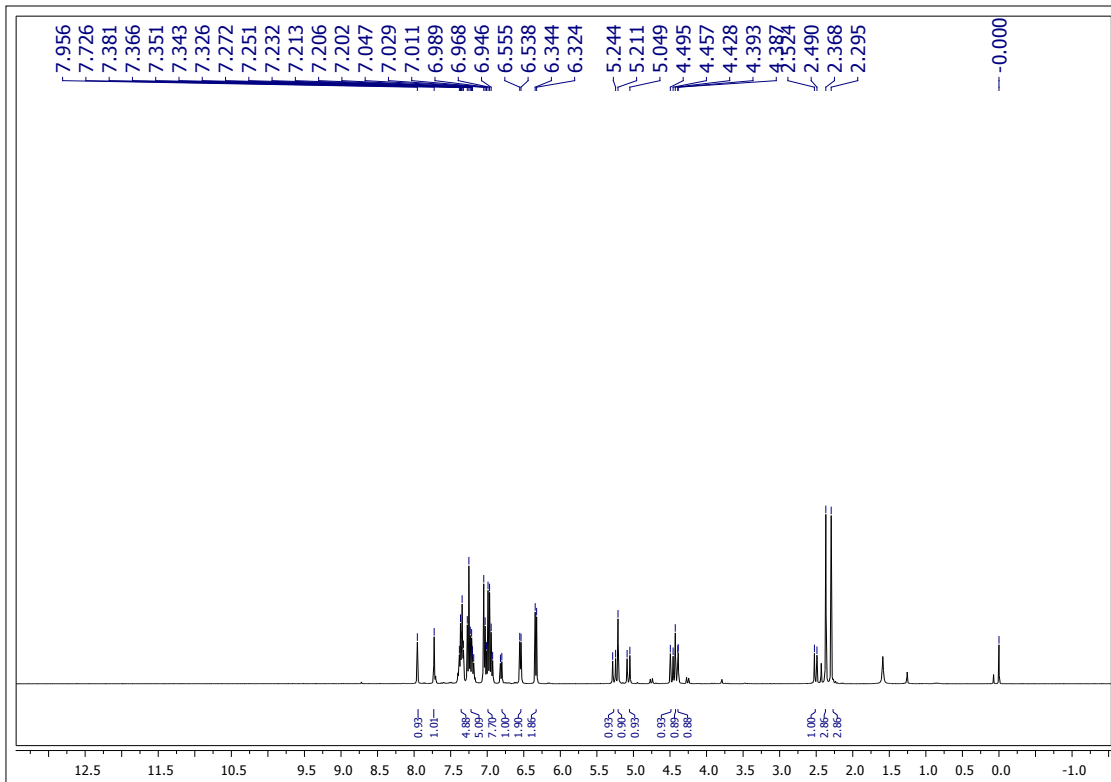


Figure S29. ¹H NMR spectrum of compound **2j**

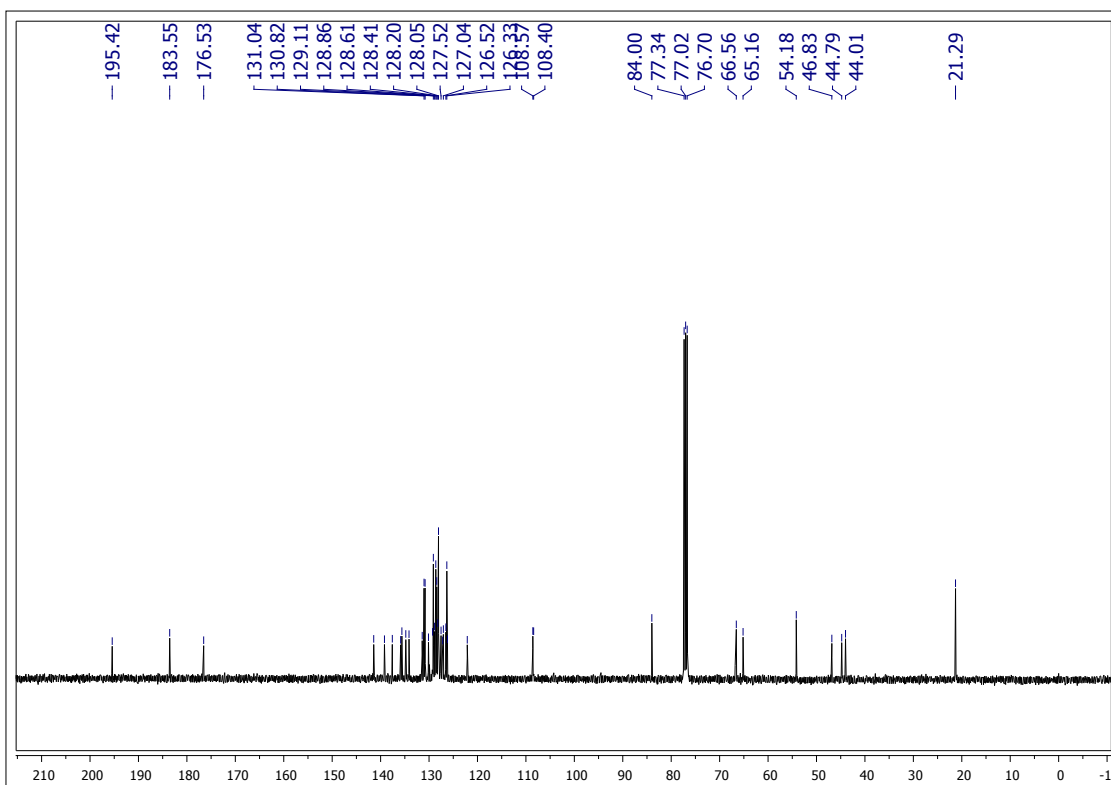


Figure S30. ¹³C NMR spectrum of compound **2j**

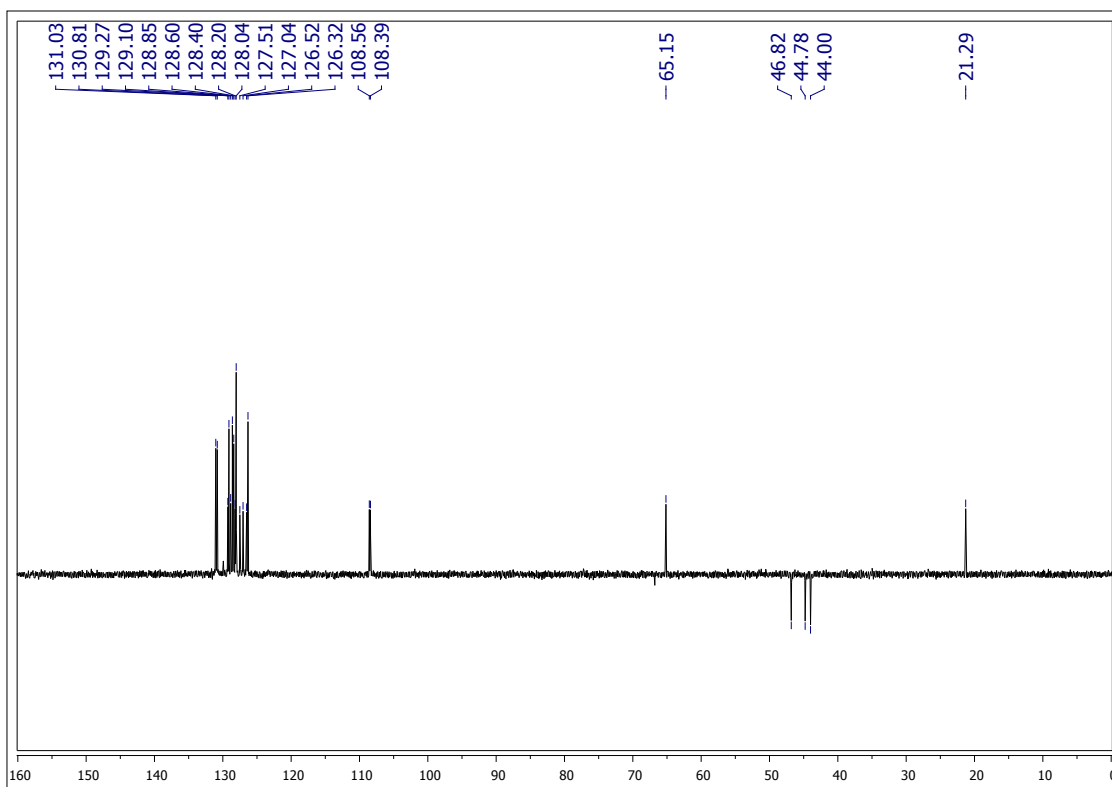


Figure S31. DEPT-135 spectrum of compound 2j

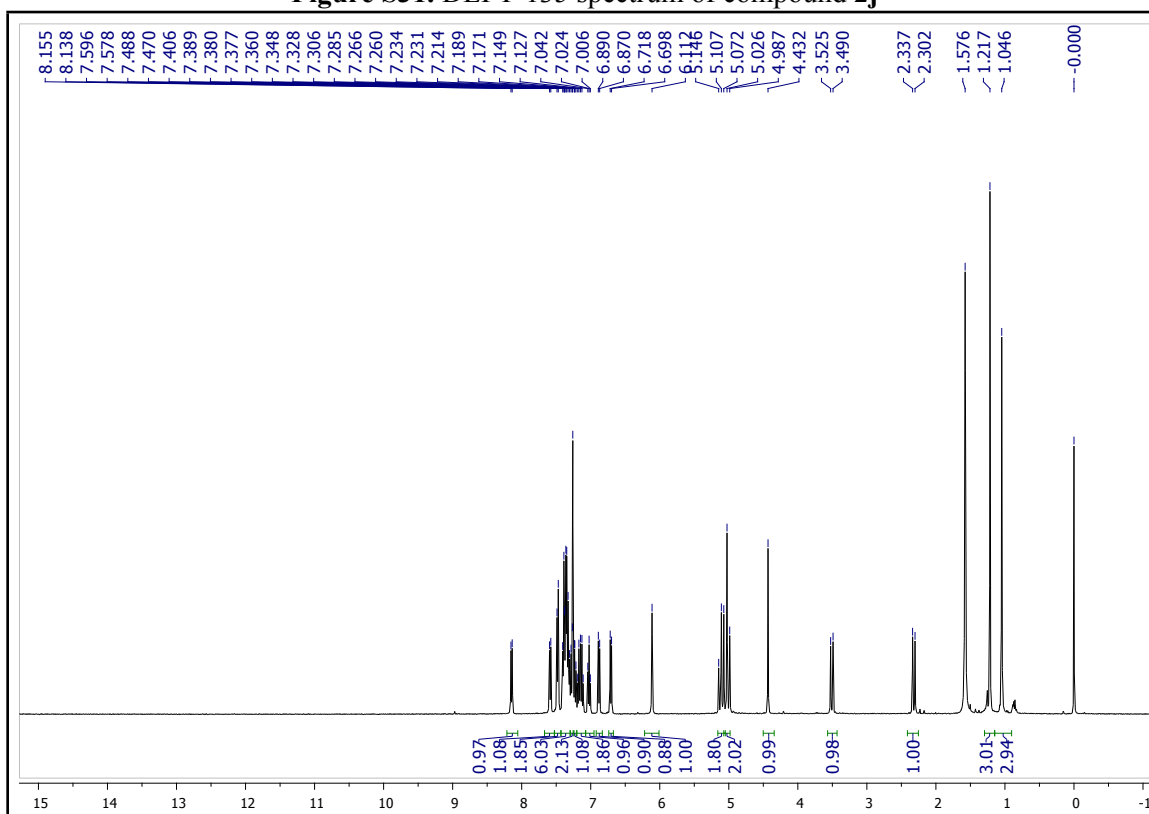


Figure S32. ¹H NMR spectrum of compound 2k

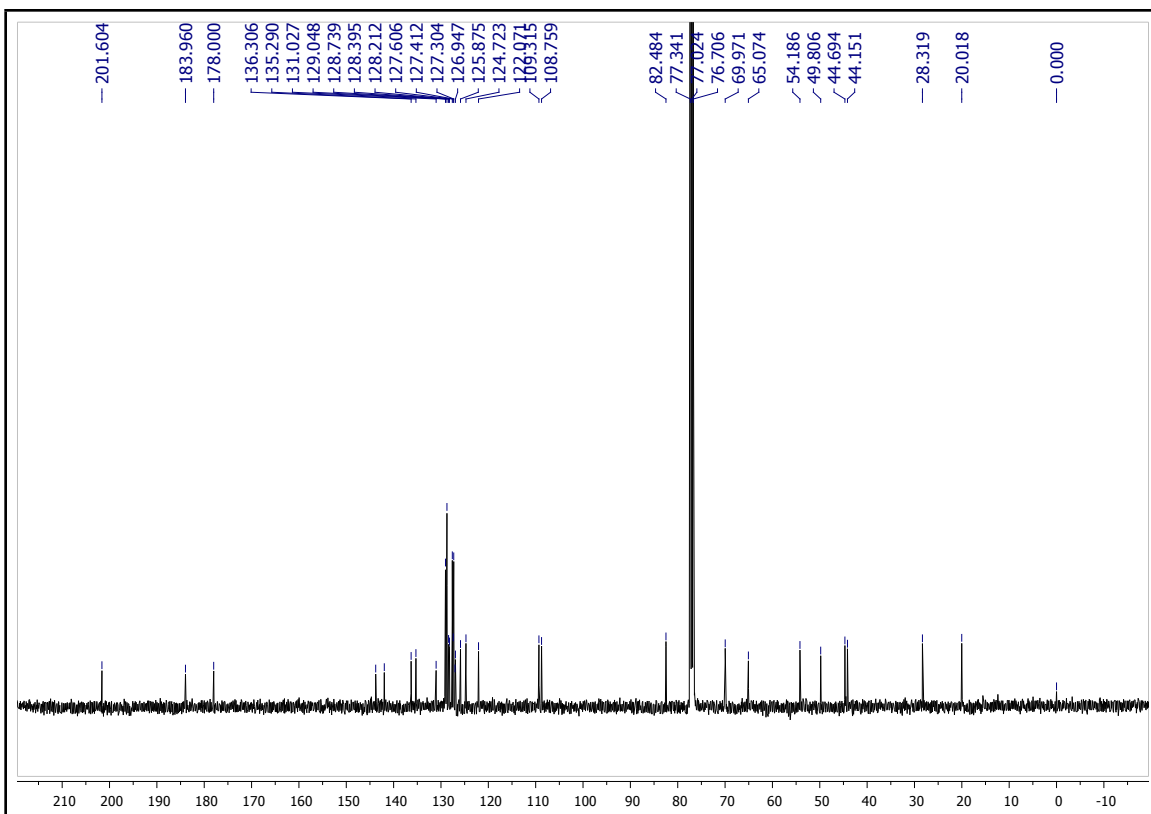


Figure S33. ^{13}C NMR spectrum of compound **2k**

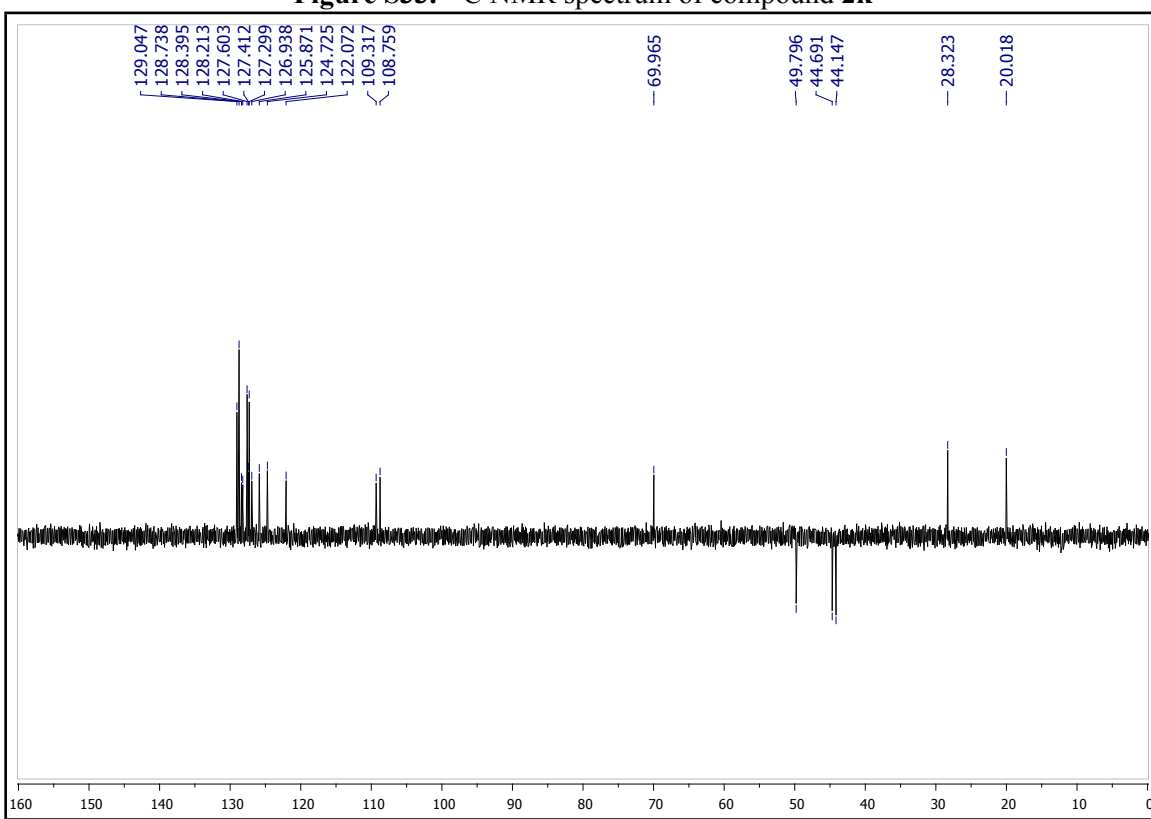


Figure S34. DEPT-135 spectrum of compound **2k**

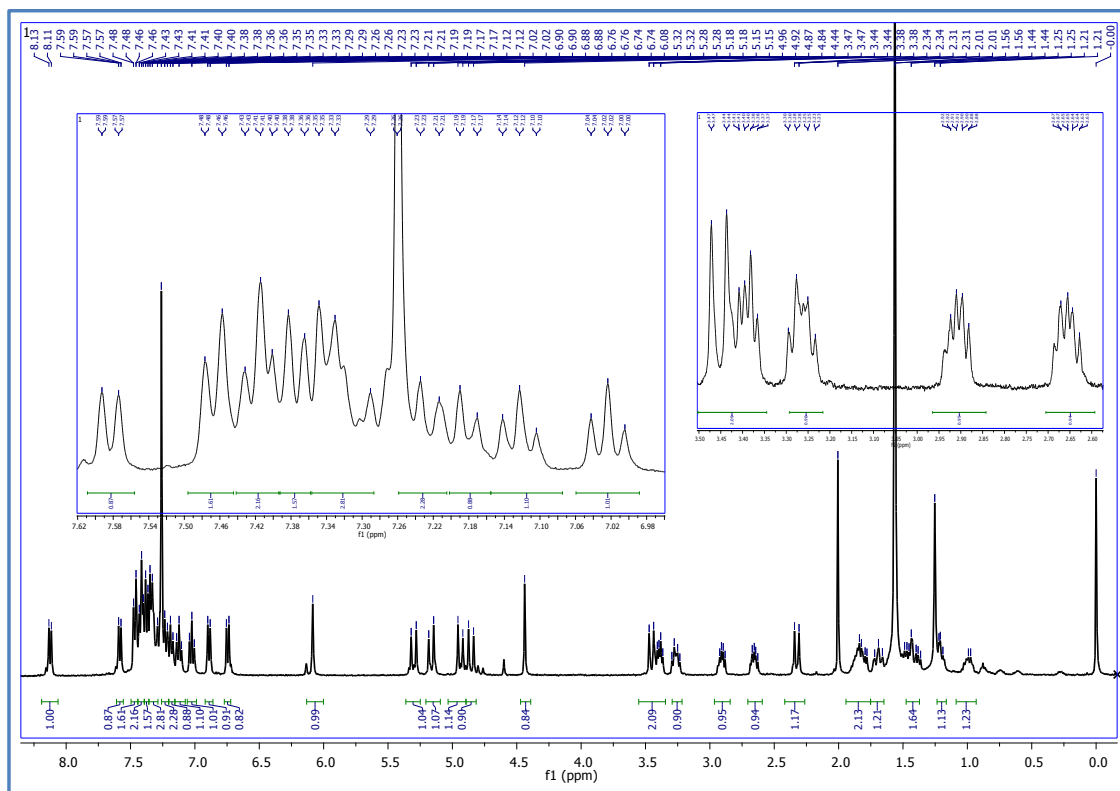


Figure S35. ^1H NMR spectrum of compound 21

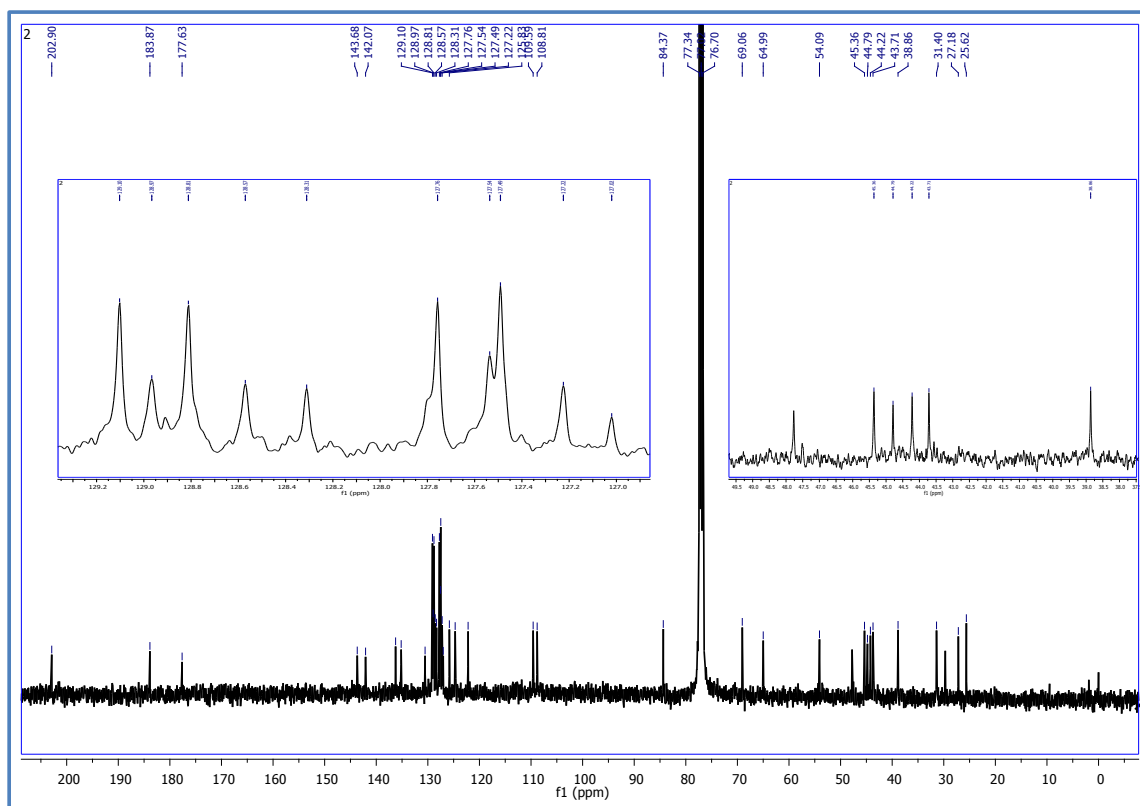


Figure S36. ^{13}C NMR spectrum of compound 21

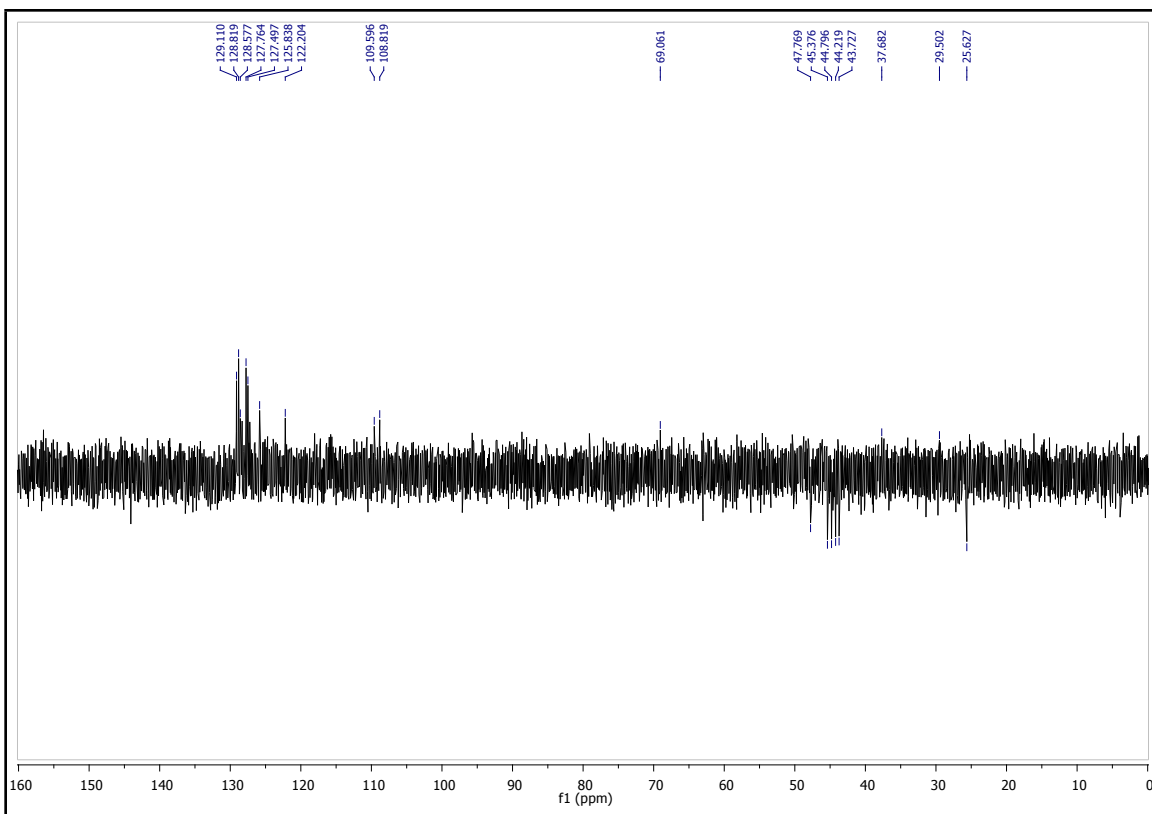


Figure S37. DEPT-135 spectrum of compound 21

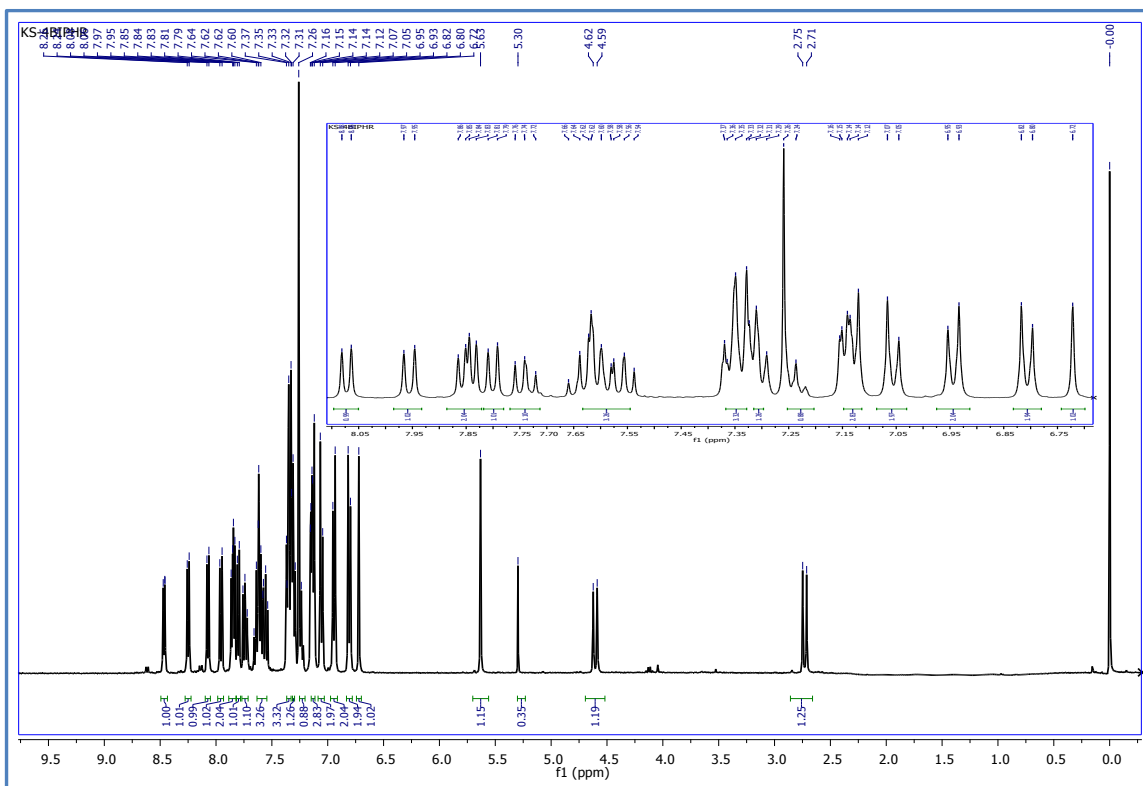


Figure S38. ¹H NMR spectrum of compound 4a

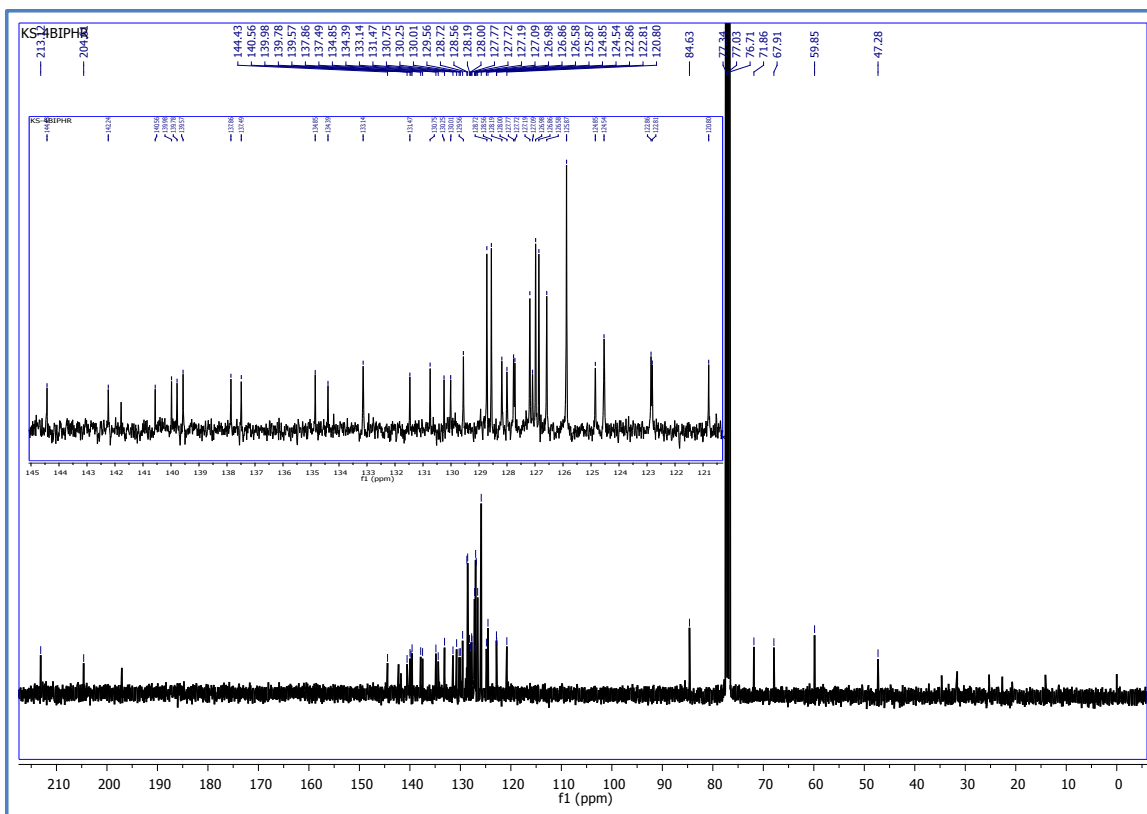


Figure S39. ^{13}C NMR spectrum of compound 4a

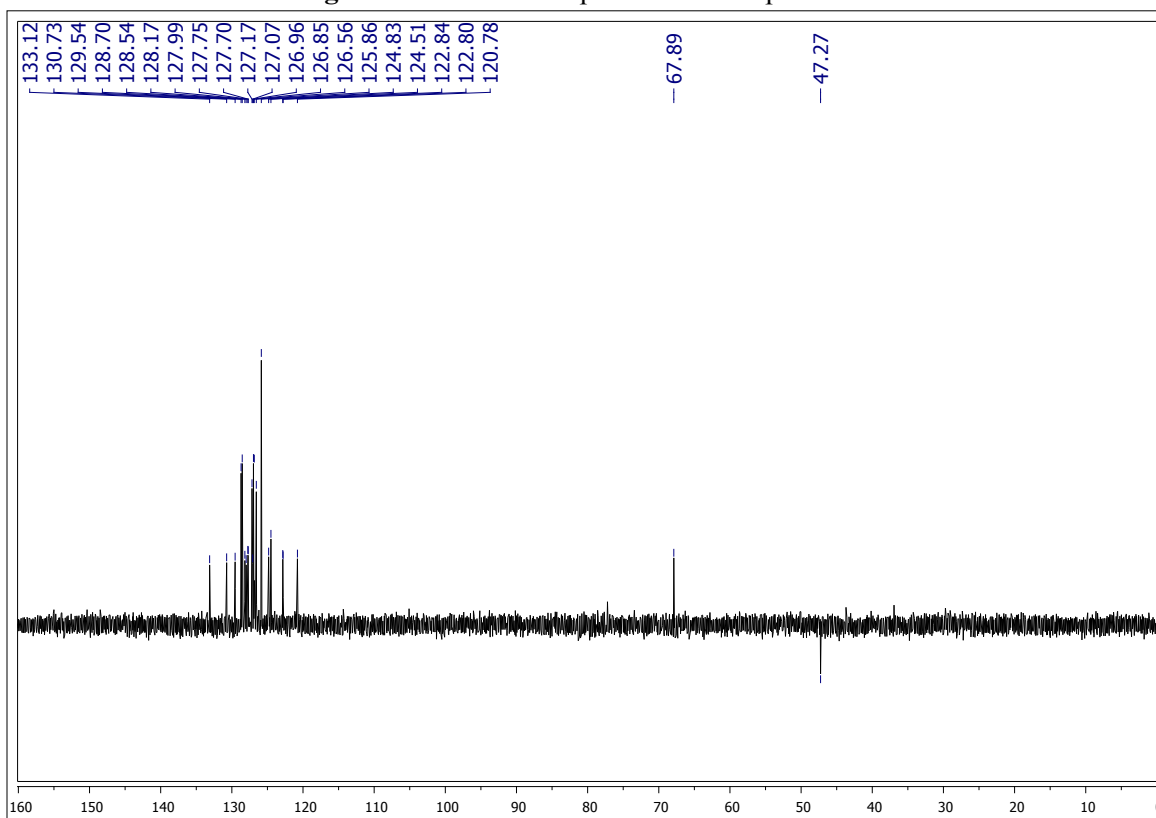


Figure S40. DEPT-135 spectrum of compound 4a

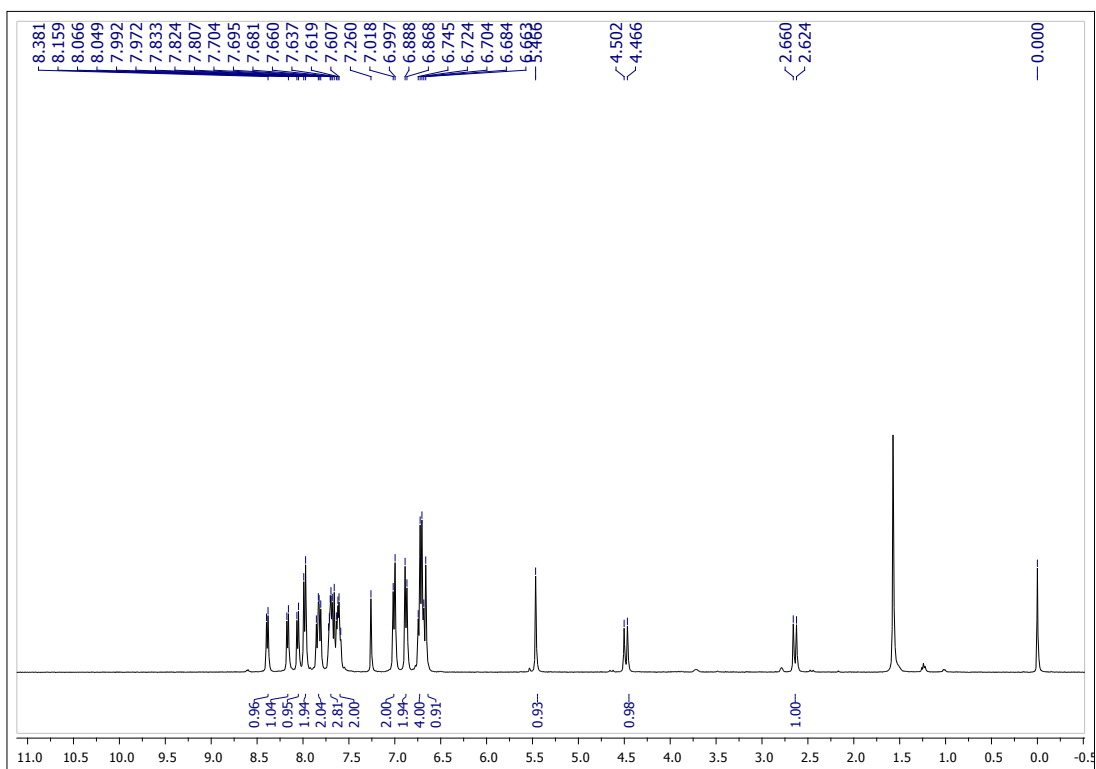


Figure S41. ^1H NMR spectrum of compound **4b**

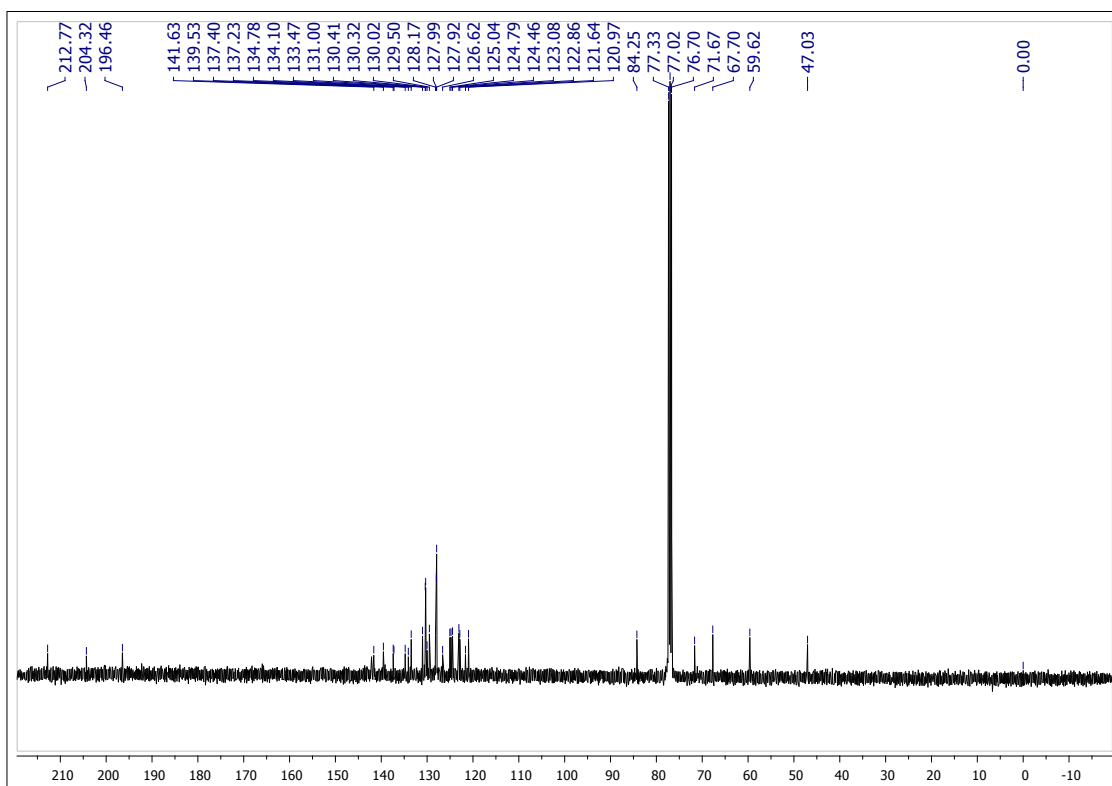


Figure S42. ^{13}C NMR spectrum of compound **4b**

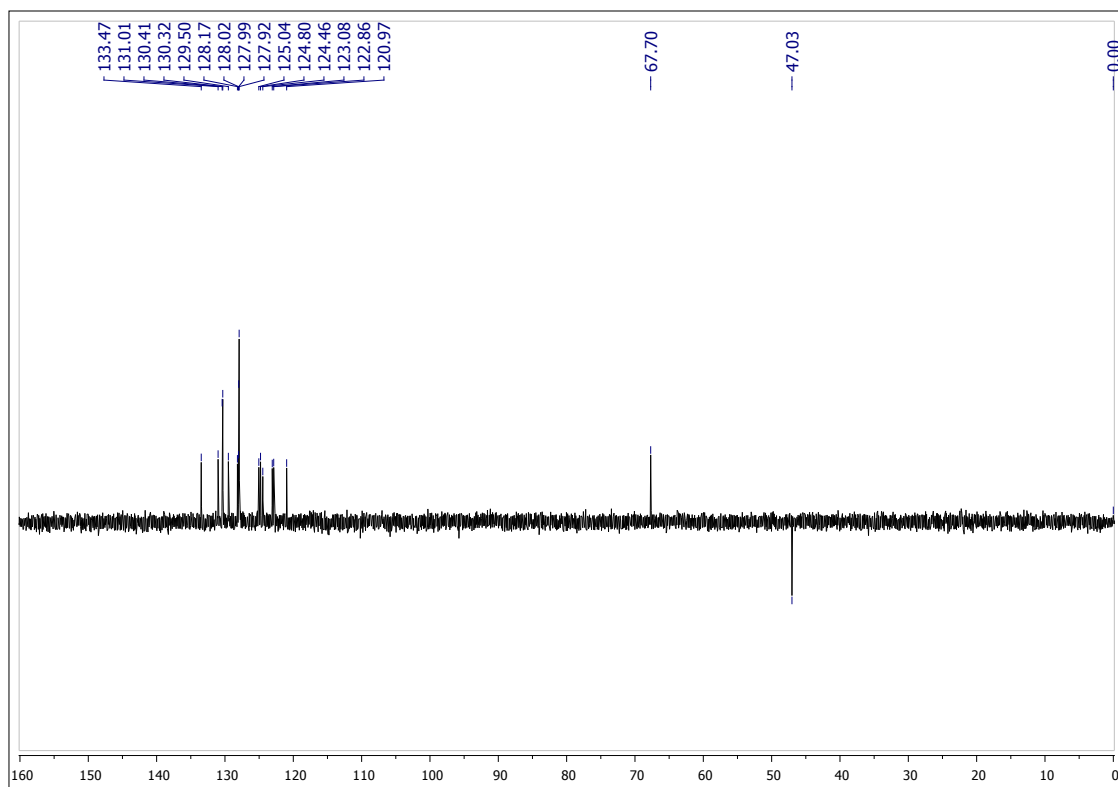


Figure S43. DEPT-135 spectrum of compound **4b**

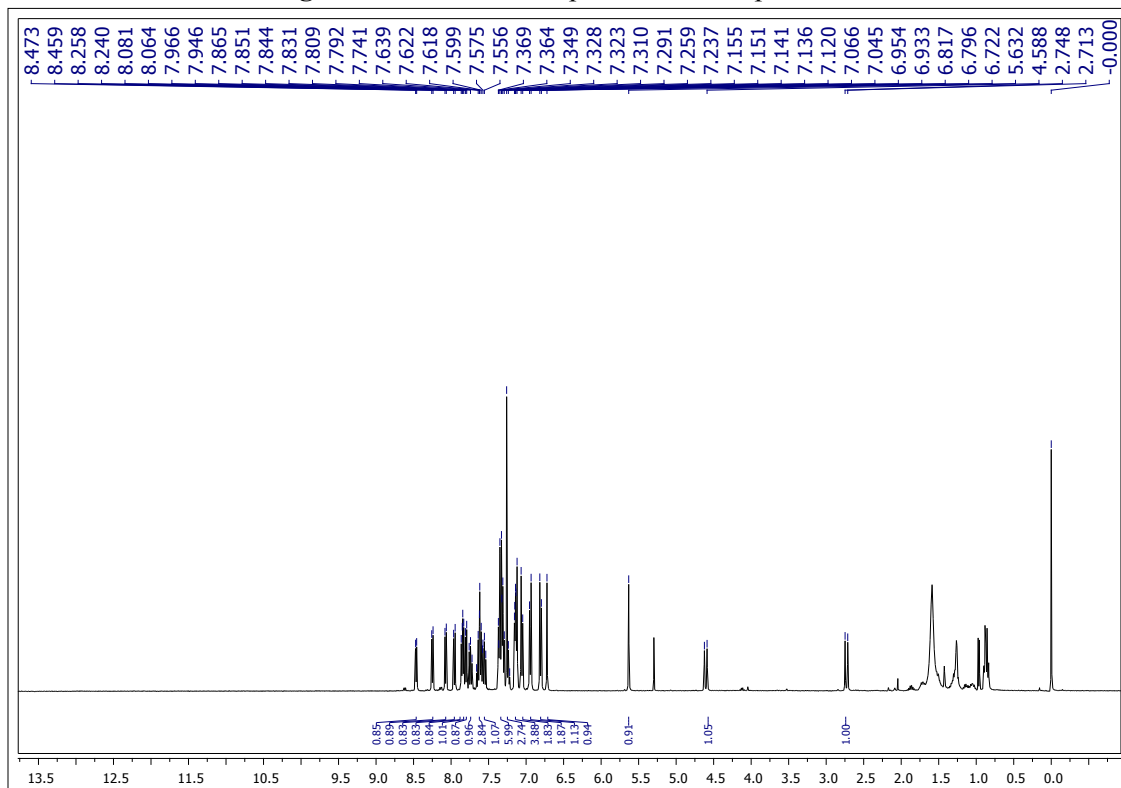


Figure S44. ¹H NMR spectrum of compound **4c**

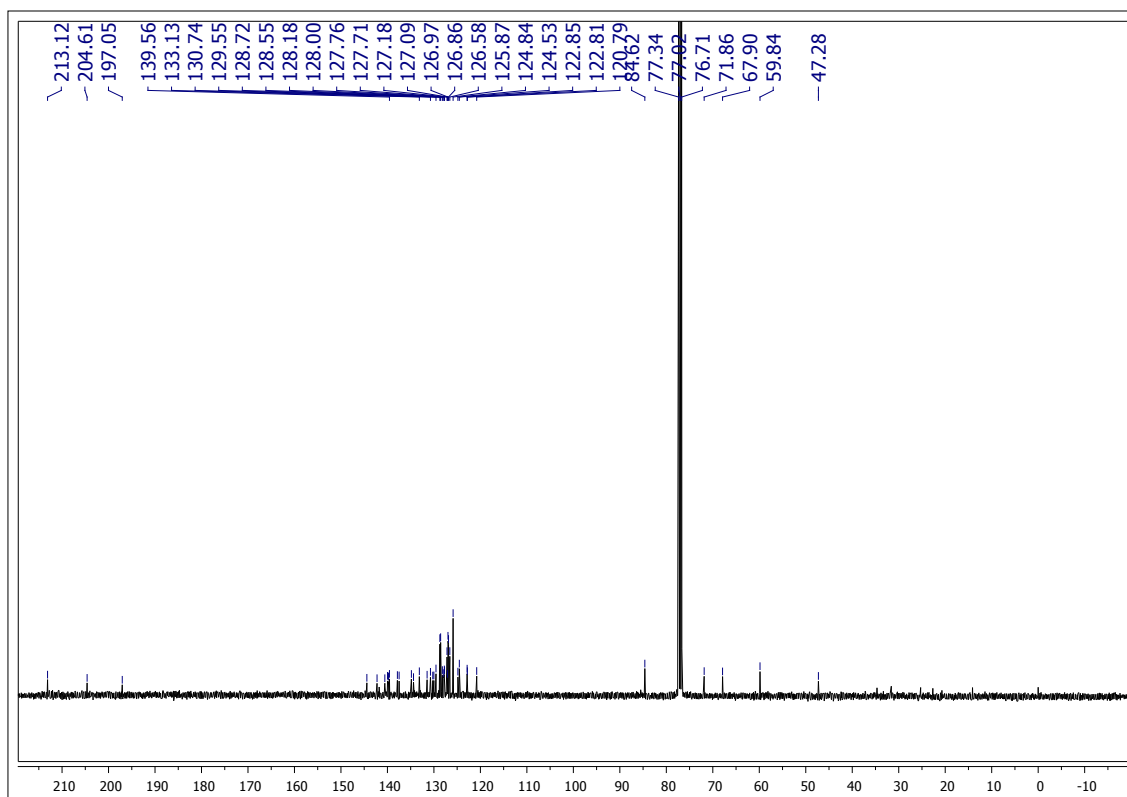


Figure S45. ^{13}C NMR spectrum of compound **4c**

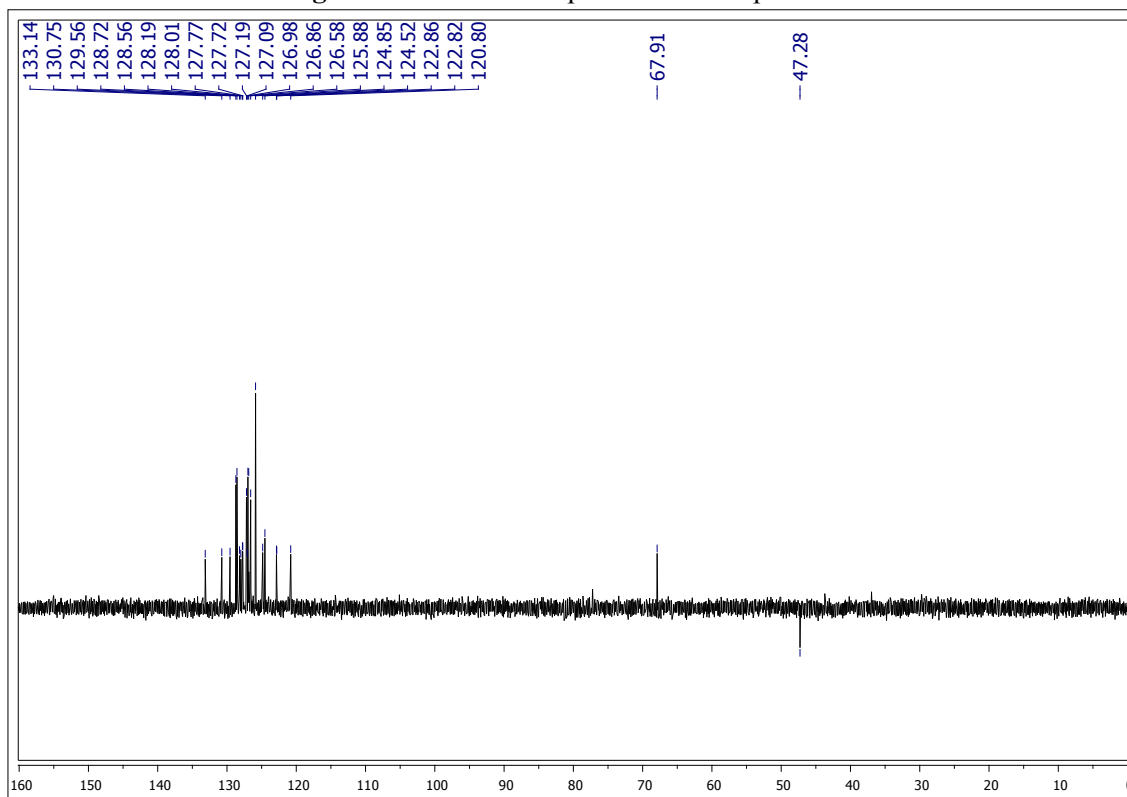


Figure S46. DEPT-135 spectrum of compound **4c**

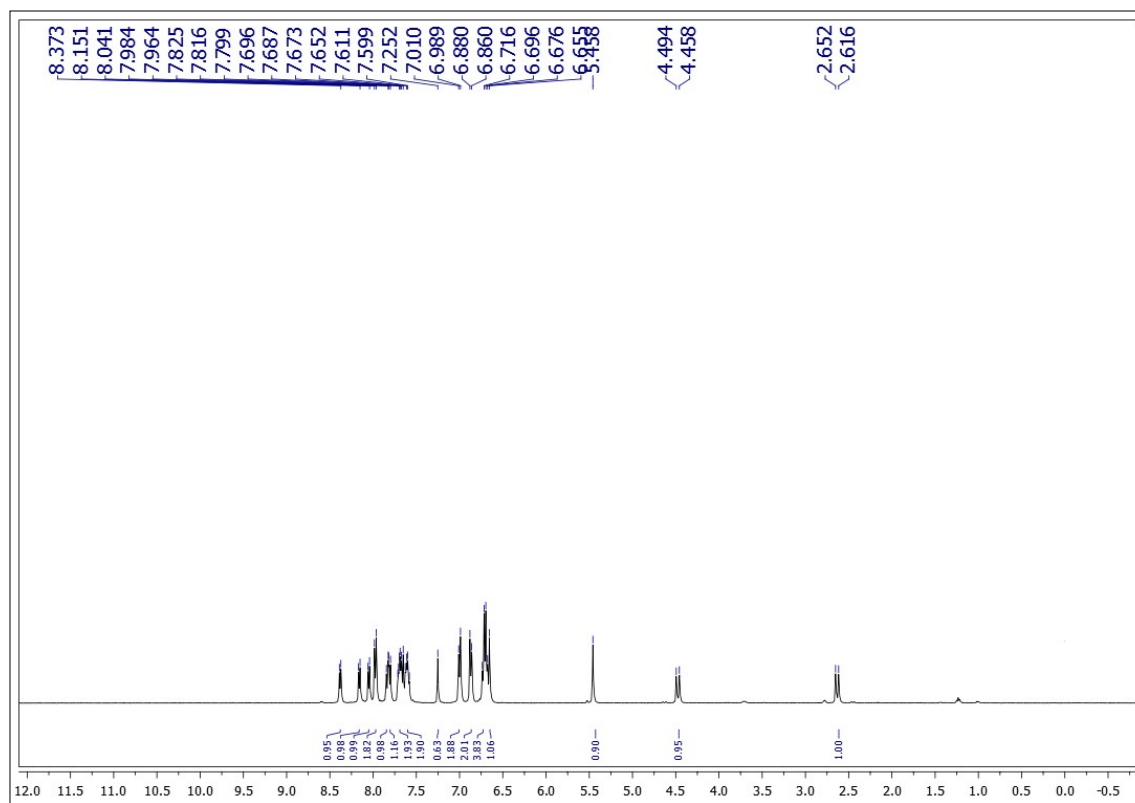


Figure S47. ¹H NMR spectrum of compound 4d

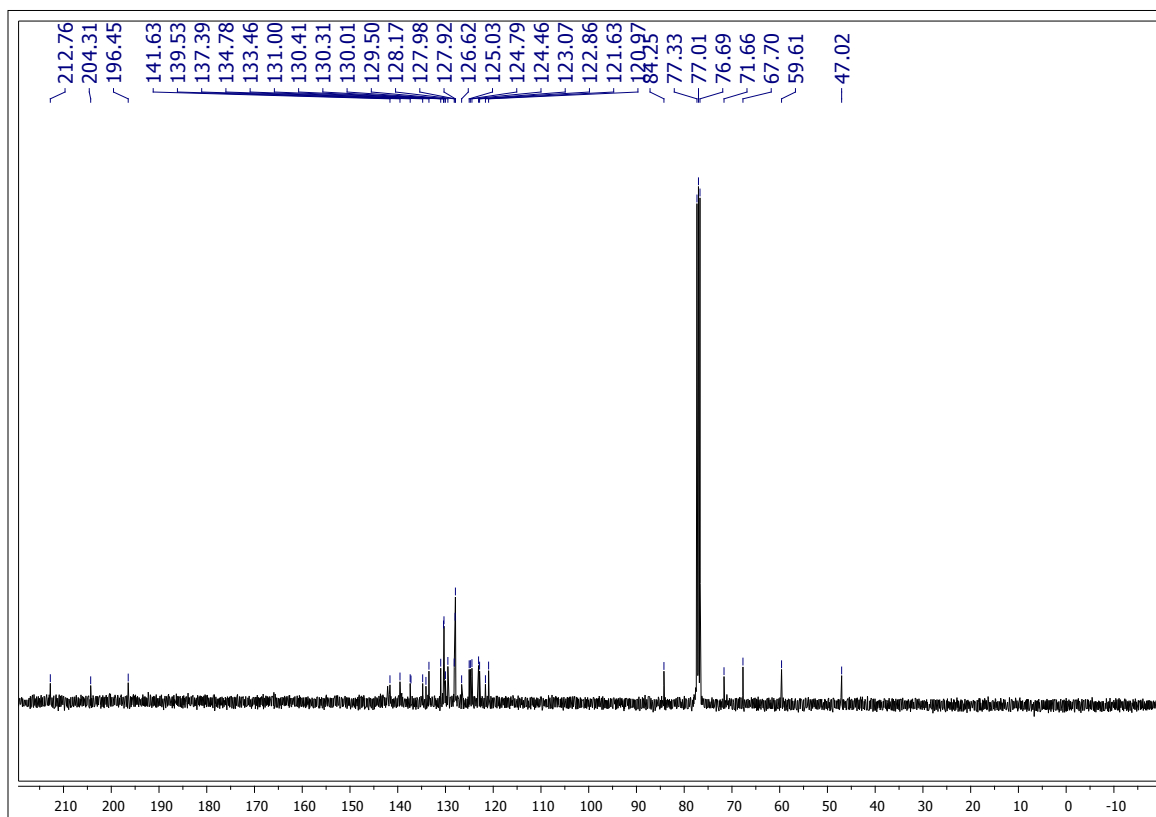


Figure S48. ¹³C NMR spectrum of compound 4d

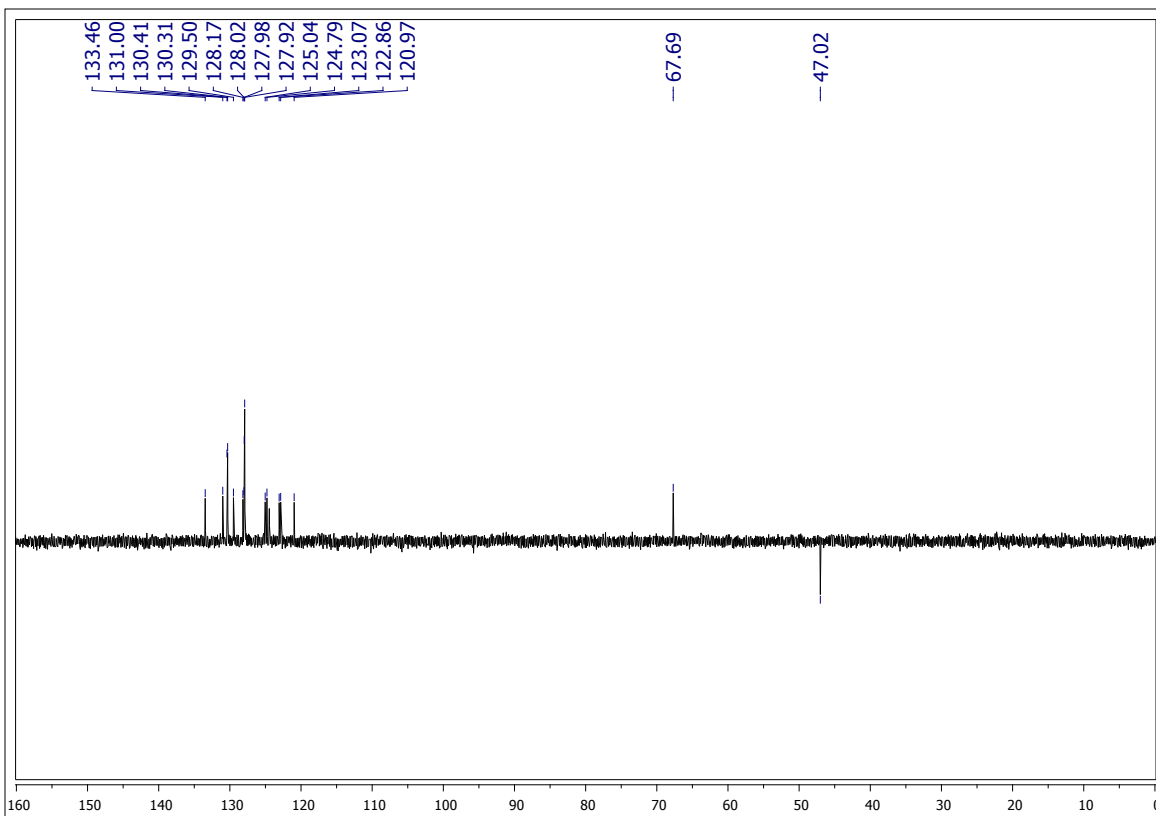


Figure S49. DEPT-135 spectrum of compound 4d

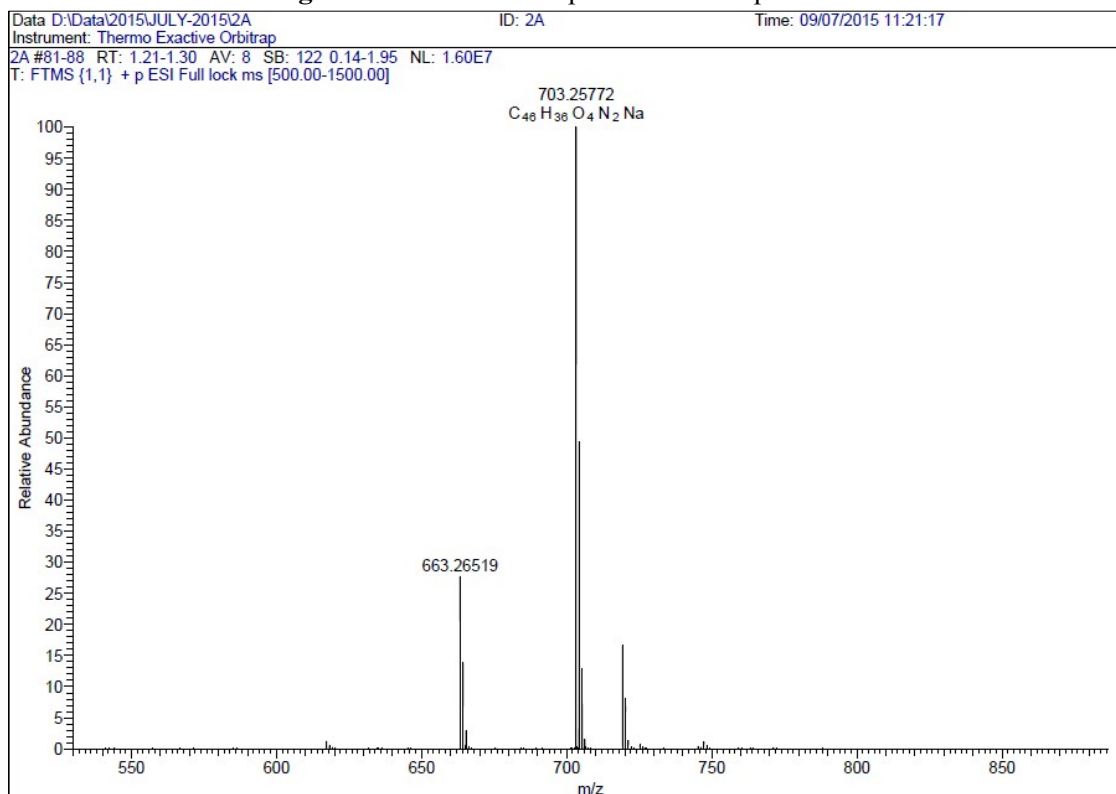


Figure S50. Mass spectrum of 2a

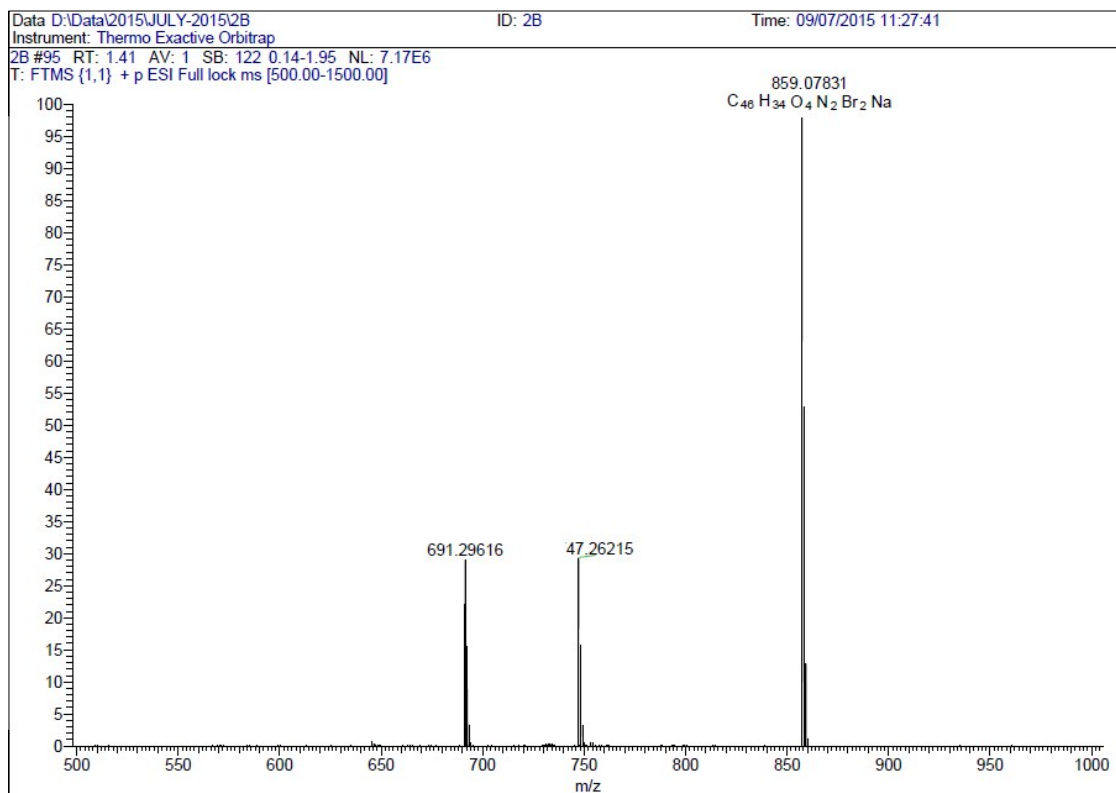


Figure S51. Mass spectrum of 2b

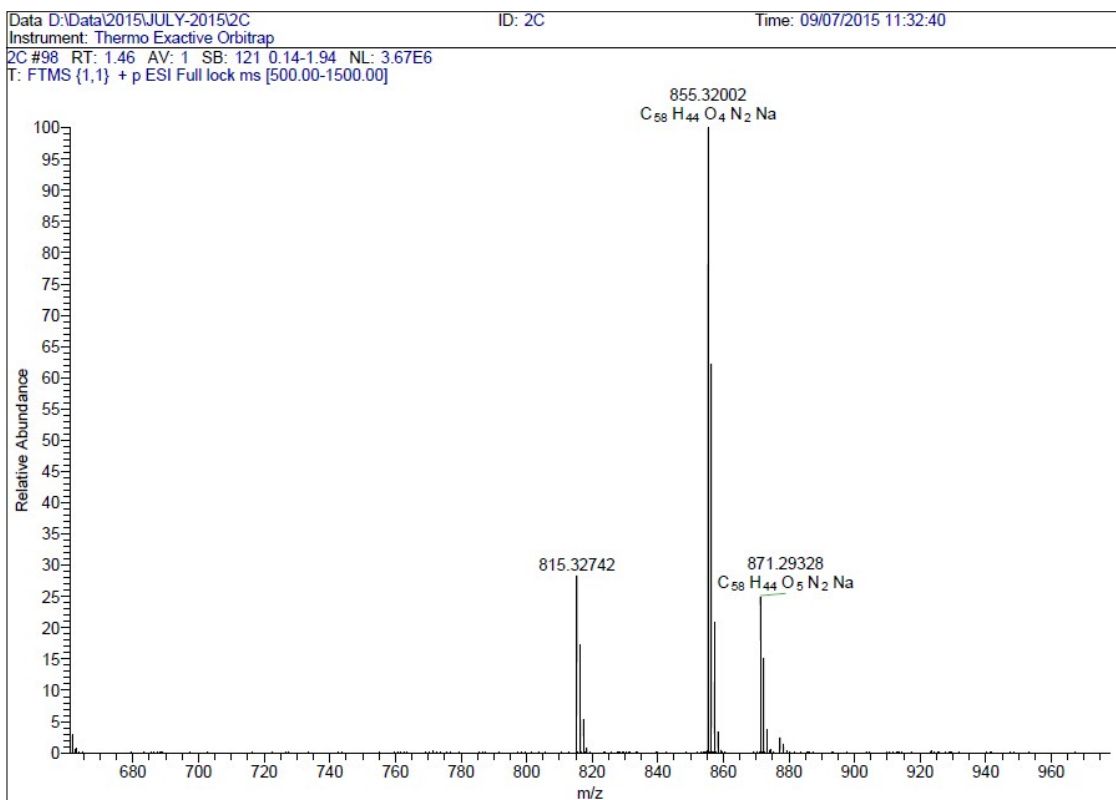


Figure S52. Mass spectrum of 2c

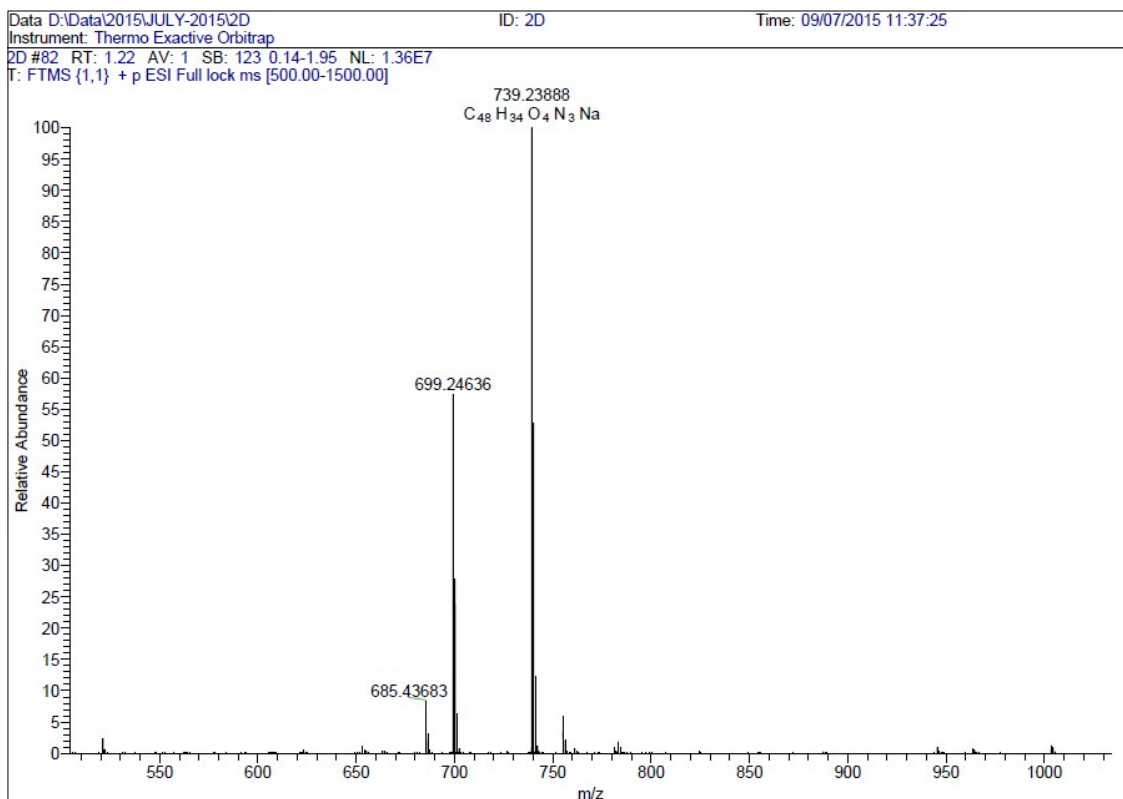


Figure S53. Mass spectrum of 2d

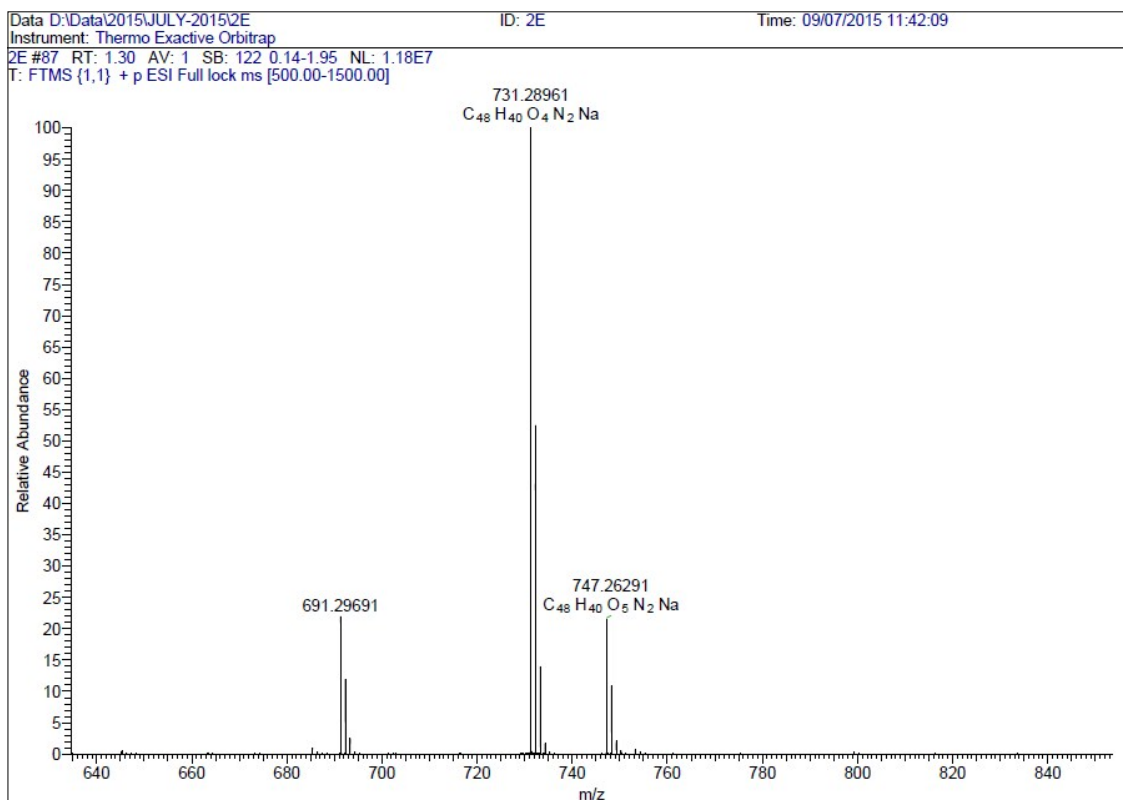


Figure S54. Mass spectrum of 2e

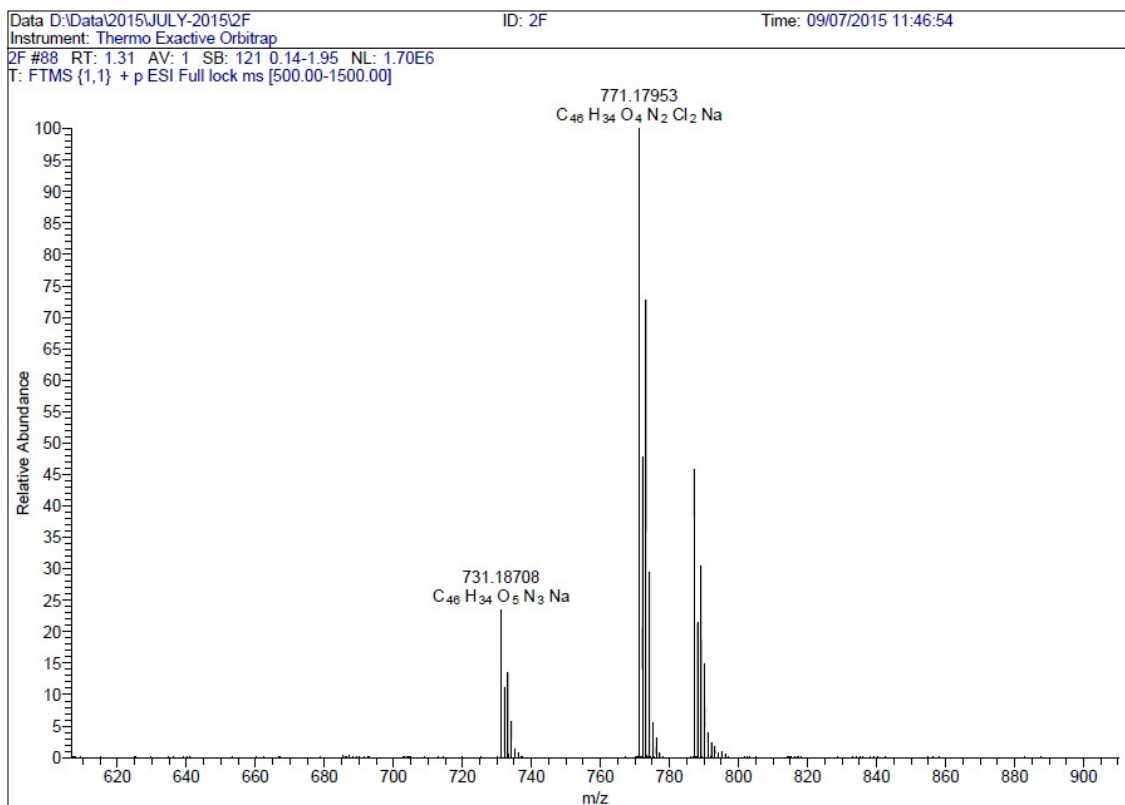


Figure S55. Mass spectrum of 2f

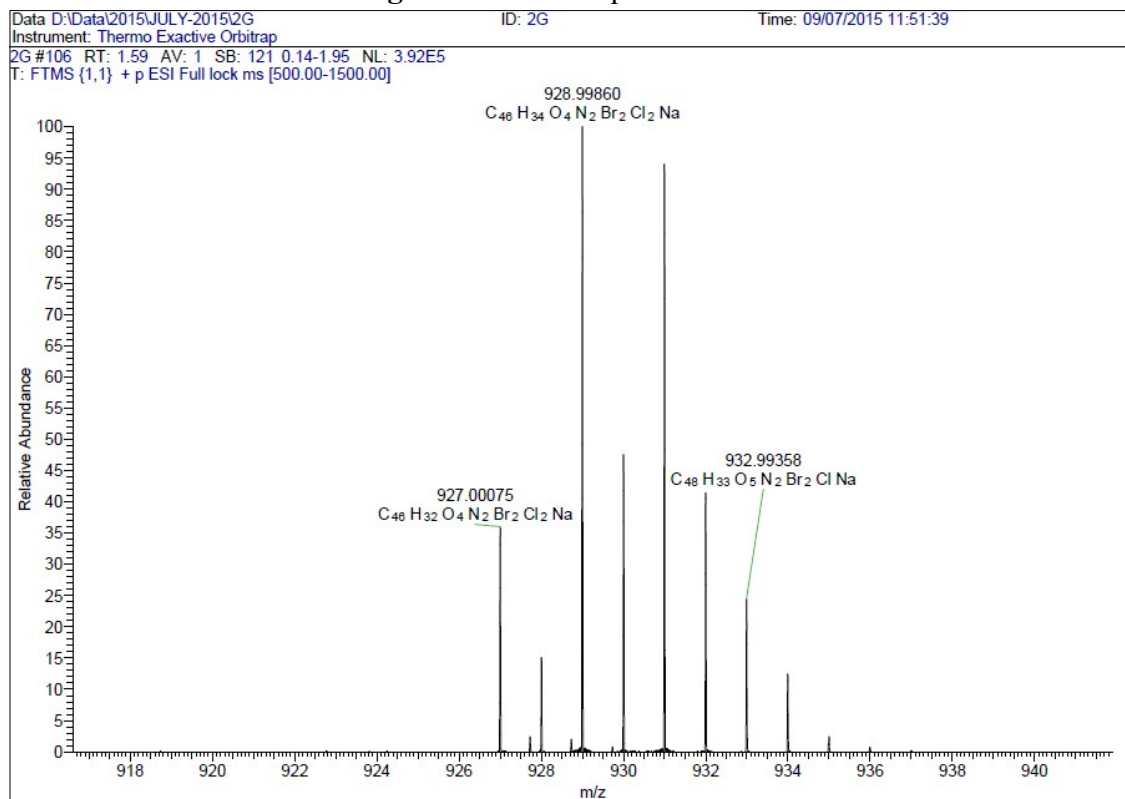


Figure S56. Mass spectrum of 2g

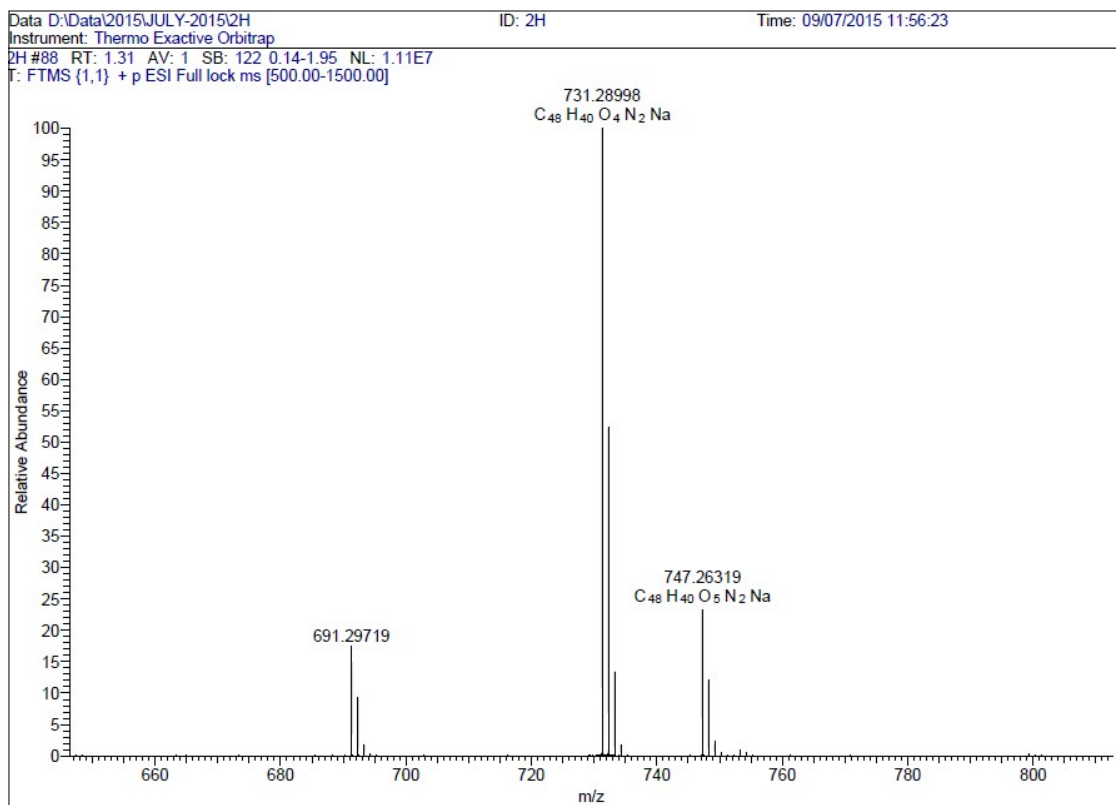


Figure S57. Mass spectrum of 2h

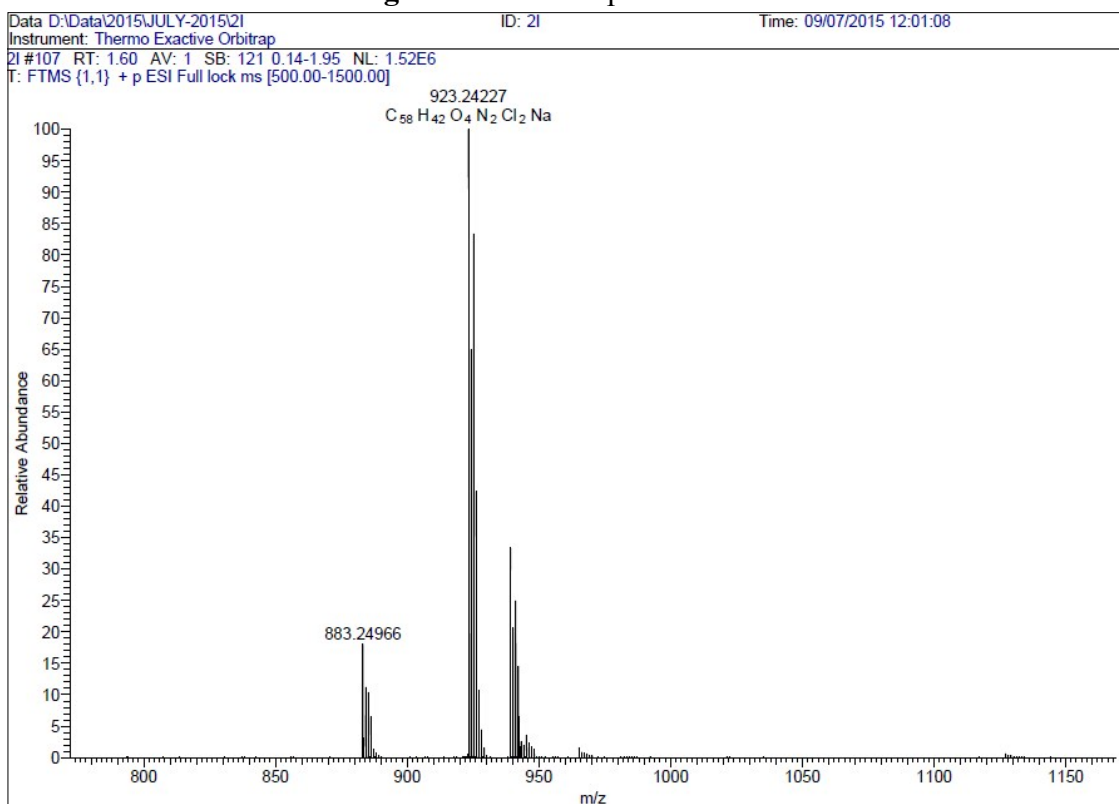


Figure S58. Mass spectrum of 2i

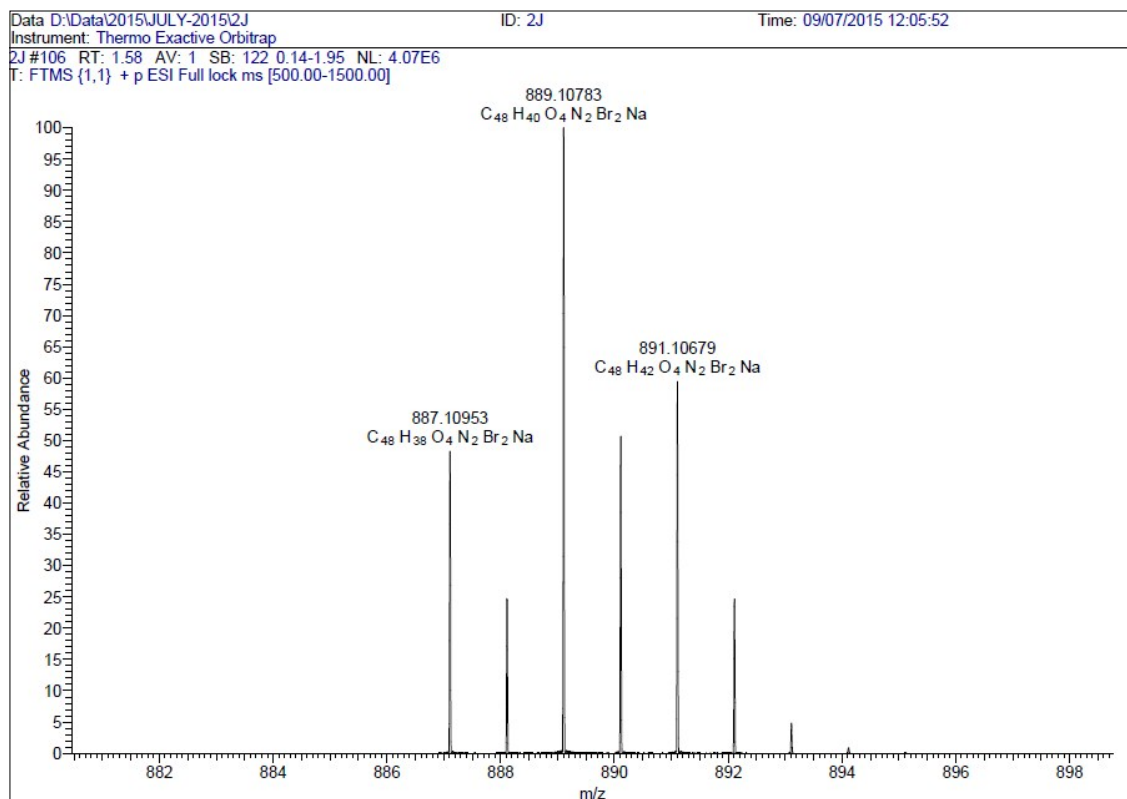


Figure S59. Mass spectrum of 2j

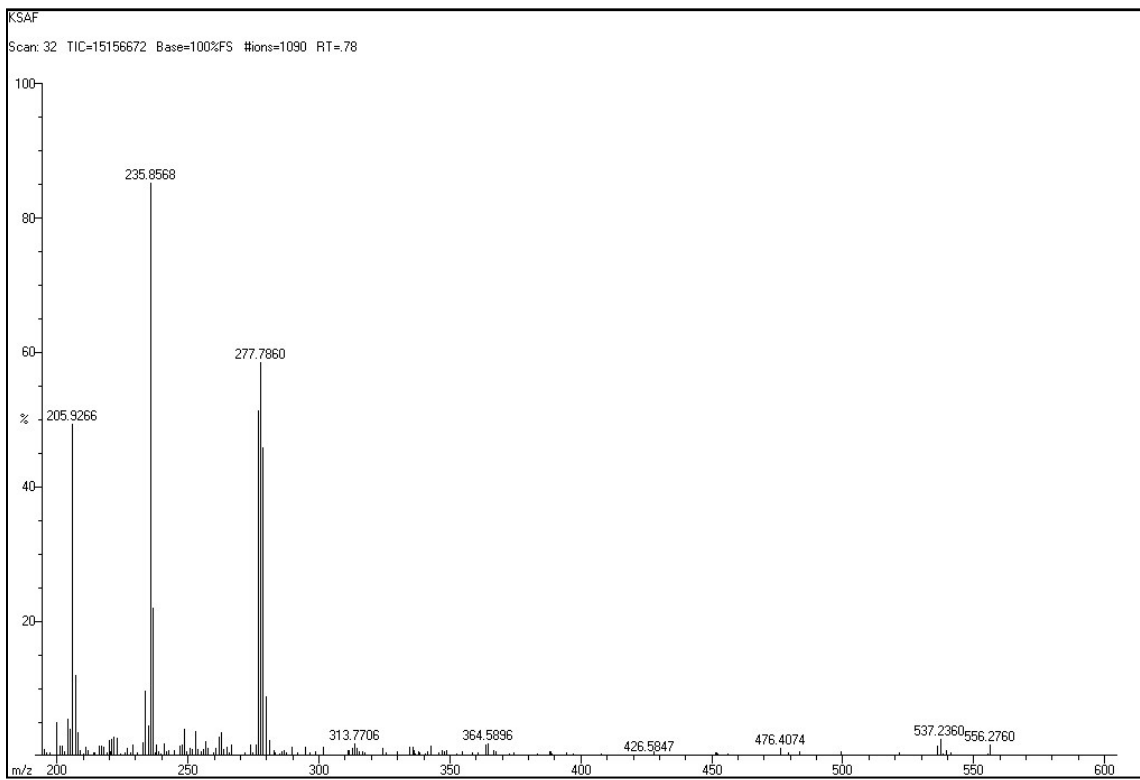


Figure S60. Mass spectrum of 2k

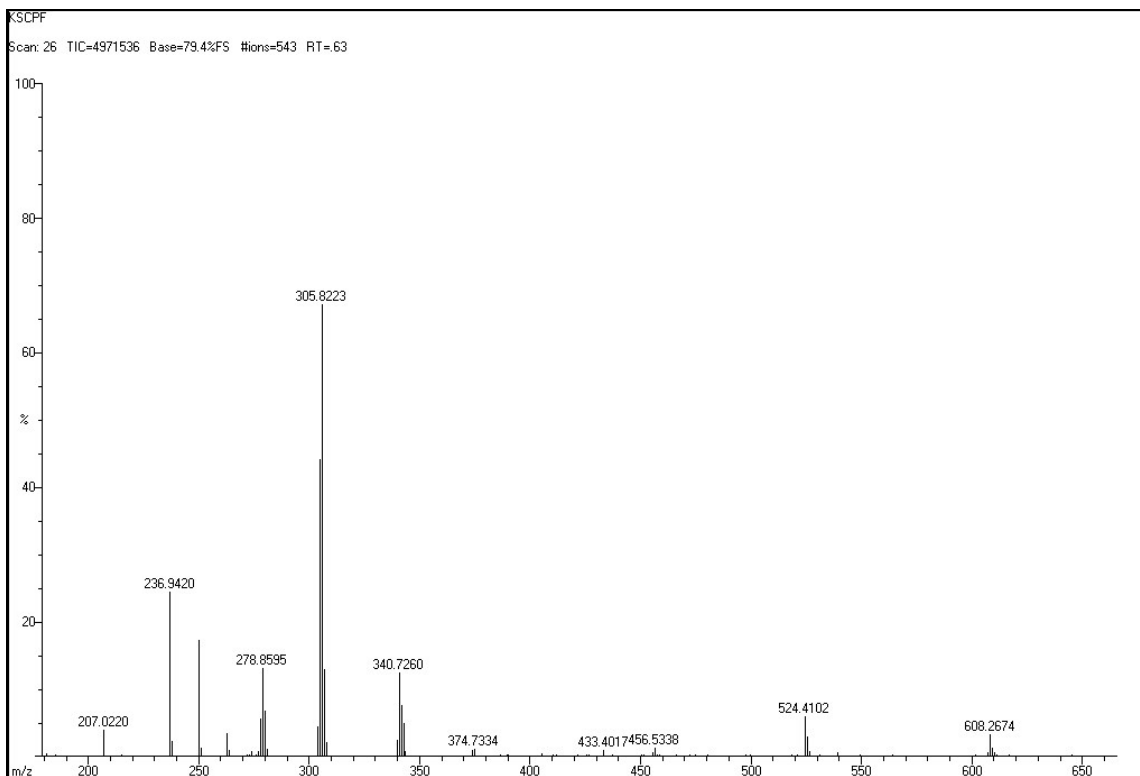


Figure S61. Mass spectrum of 21

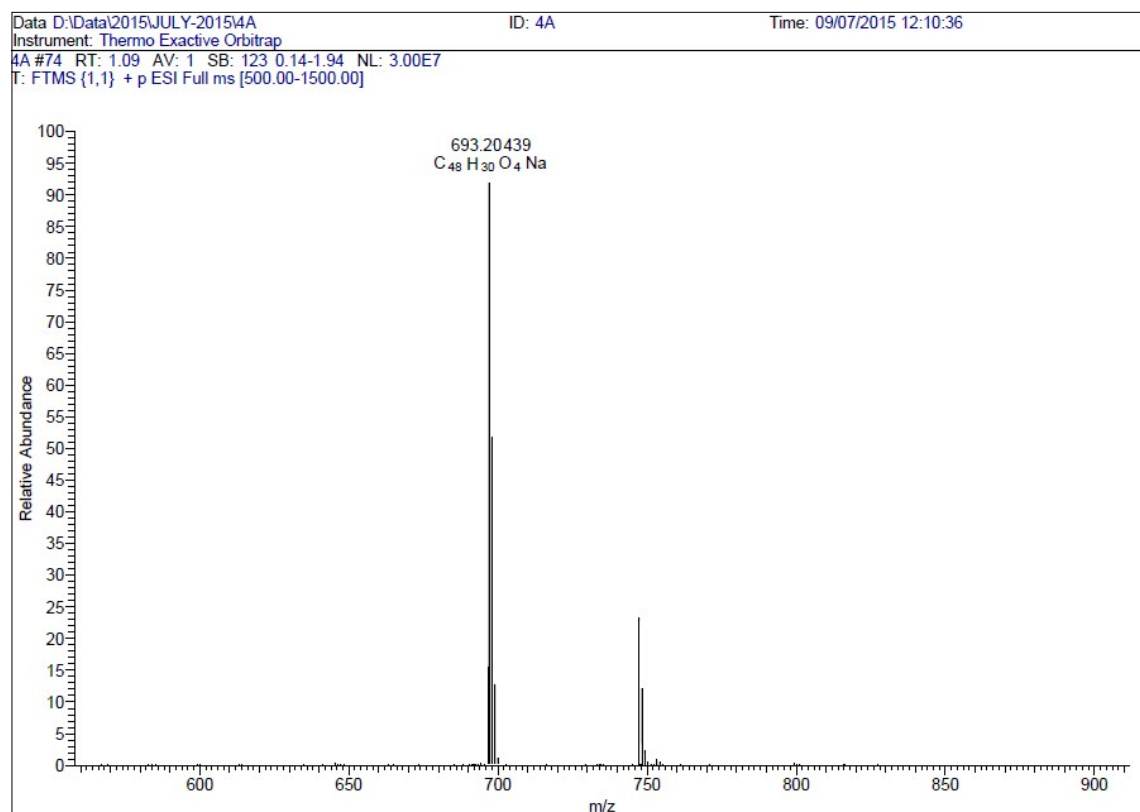


Figure S62. Mass spectrum of 4a

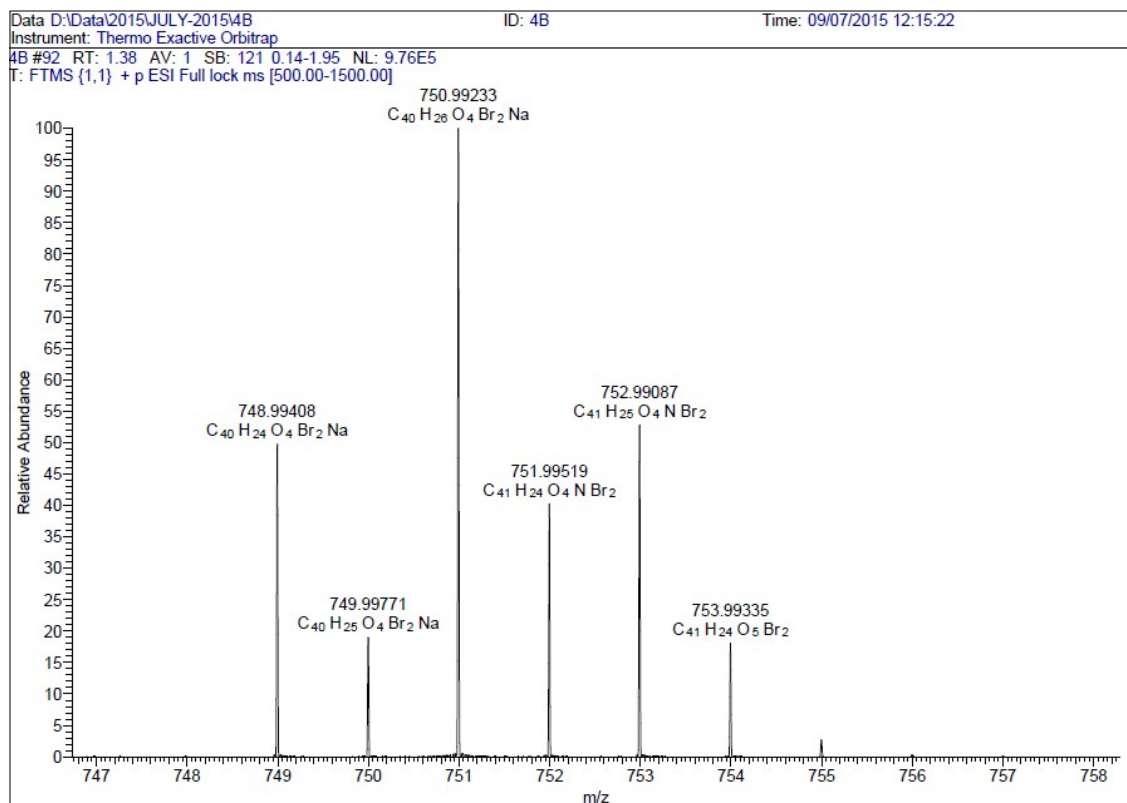


Figure S63. Mass spectrum of 4b

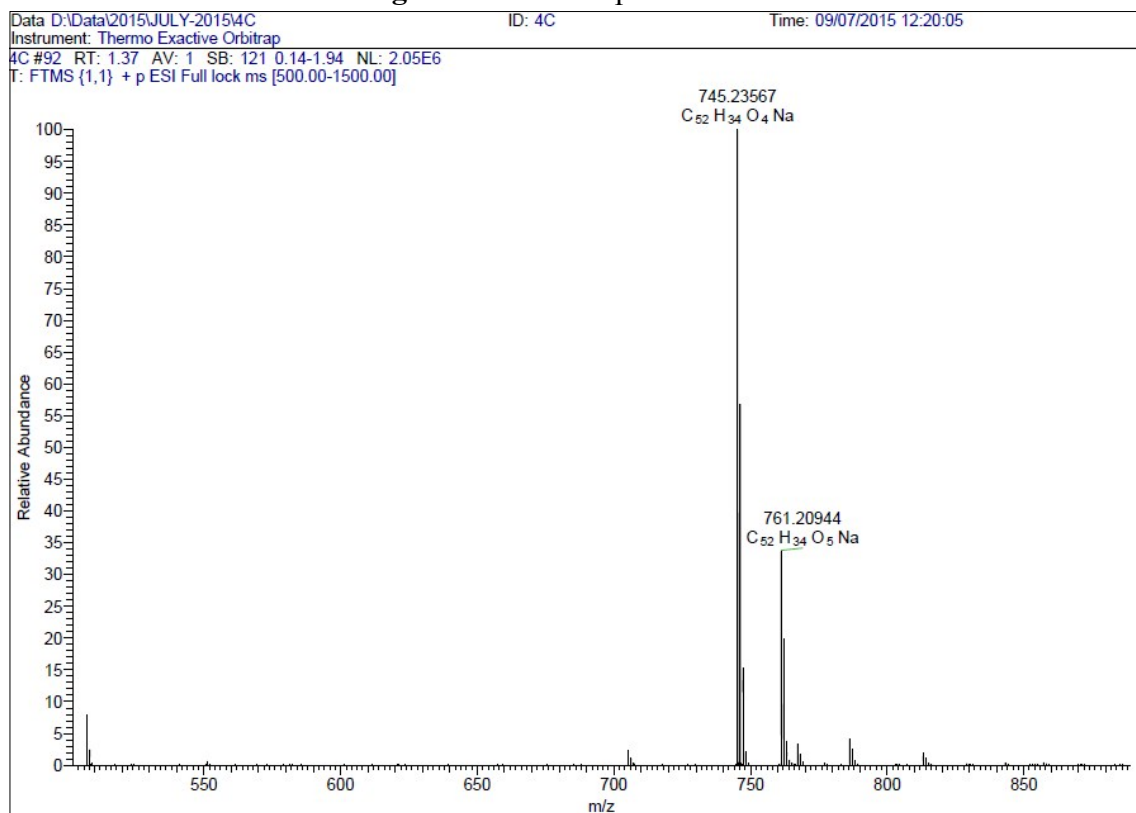


Figure S64. Mass spectrum of 4c

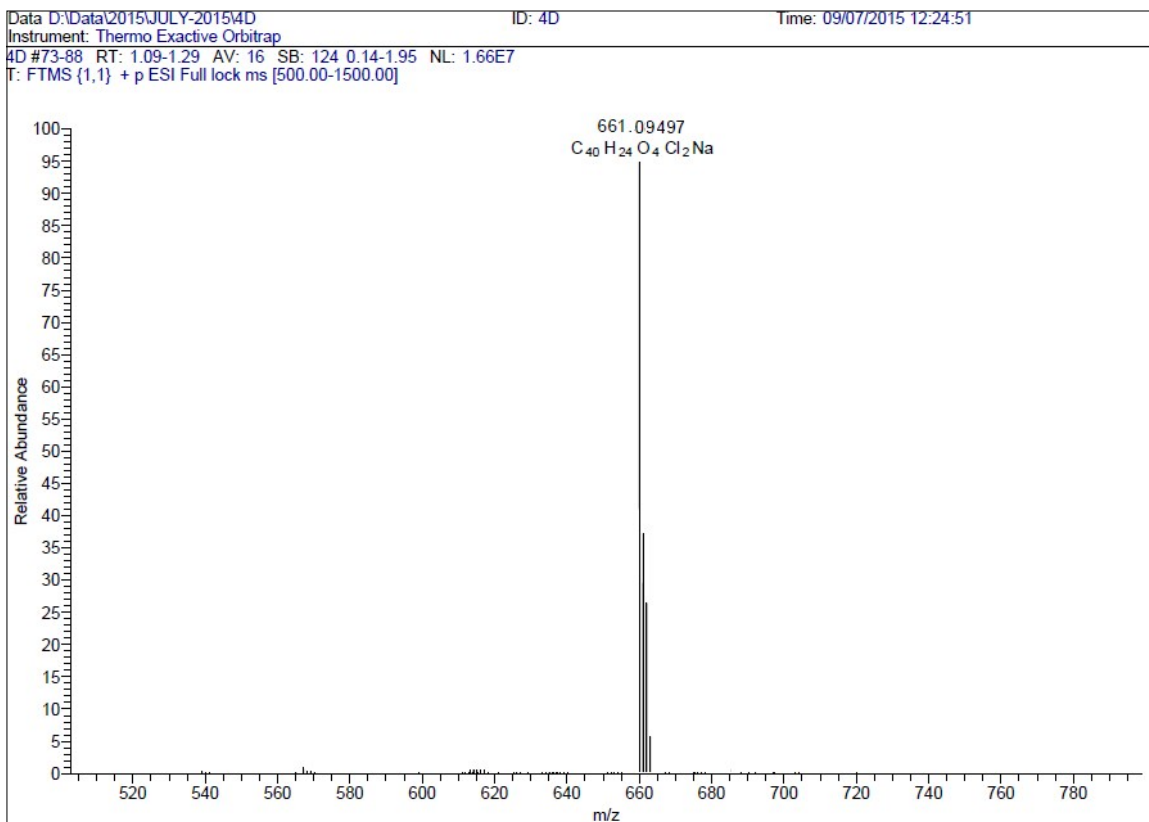


Figure S65. Mass spectrum of **4d**
 Detecting the formation of intermediate **ii** (Scheme 2) through ESI MS method

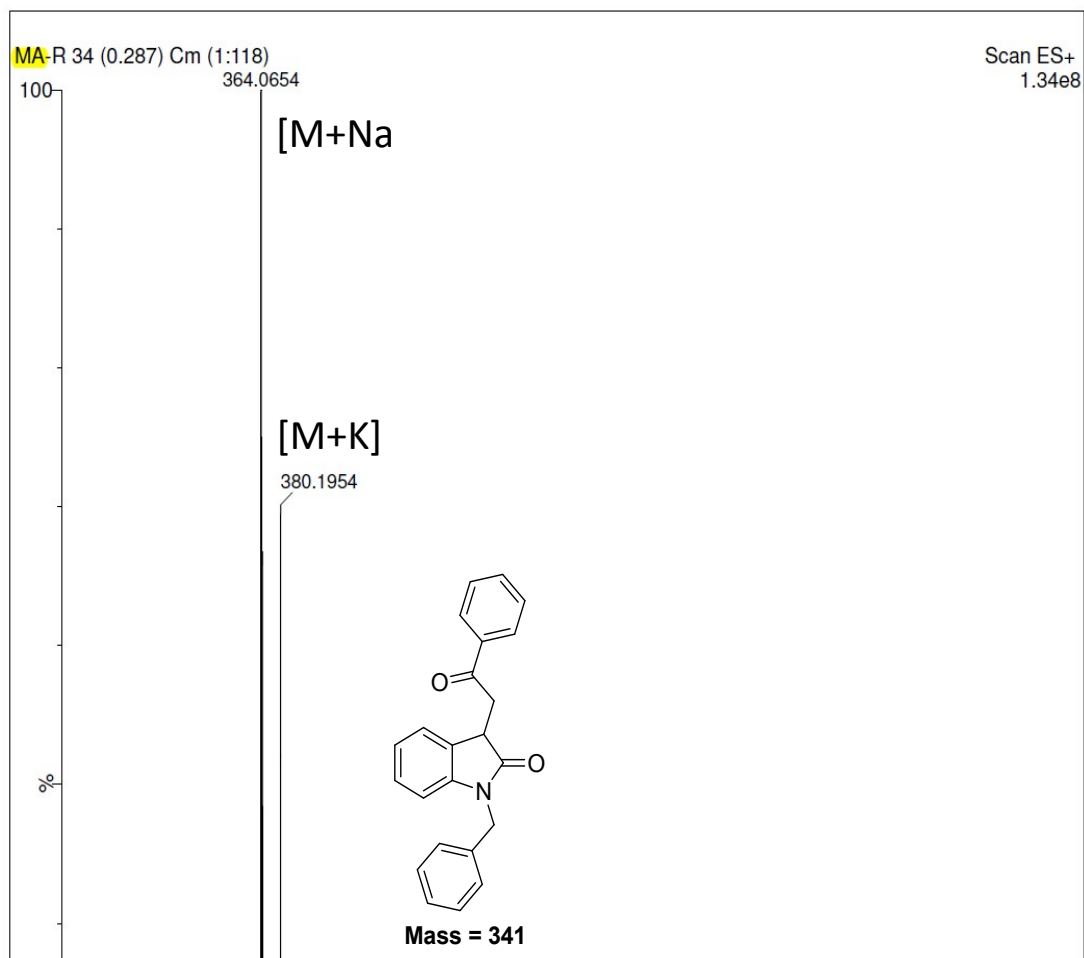


Figure S66. Mass spectrum of substrate **1a**

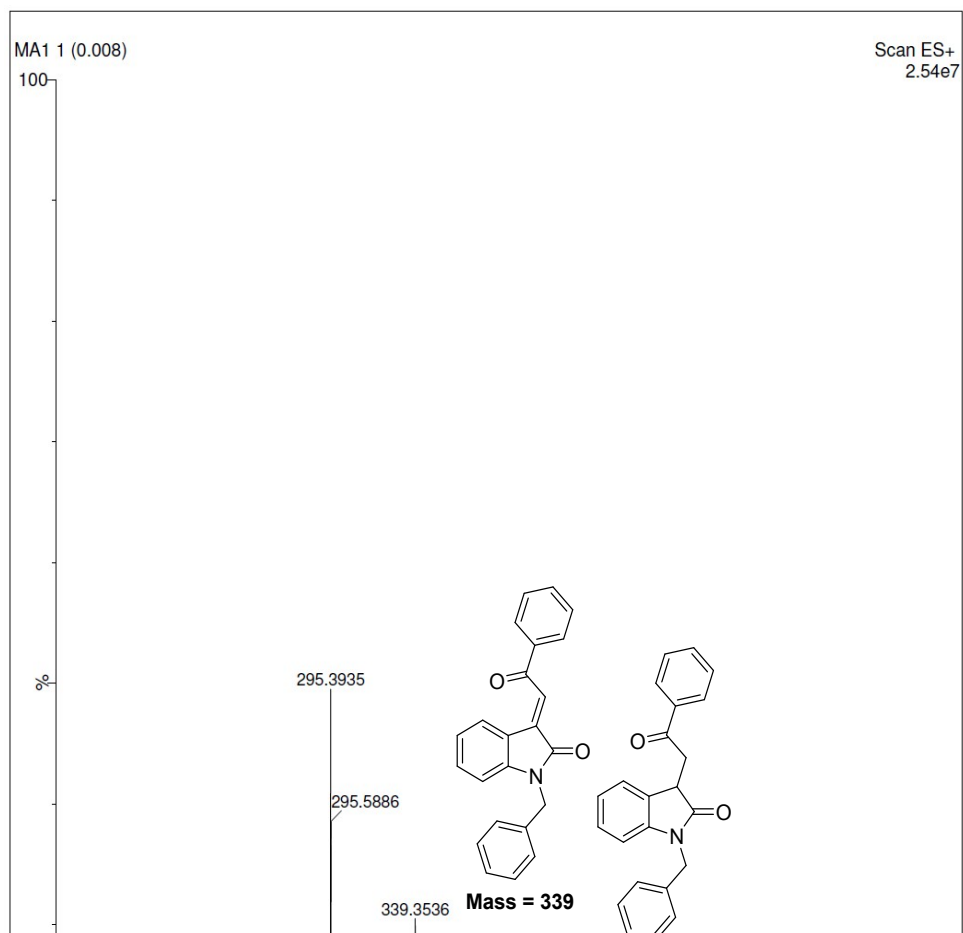


Figure S68. Mass spectrum of substrate **1a** and product **2a**

Spectrum was recorded using an aliquot withdrawn from the reaction after 5 h.

Annexure 1

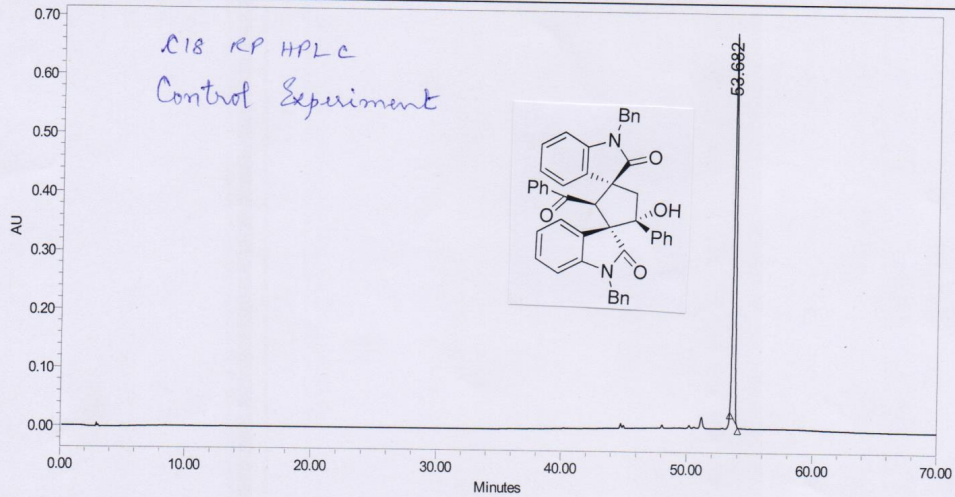
-01-

Project Name protein
Reported by User: Breeze user (Breeze)



SAMPLE INFORMATION

Sample Name: KS2A
Sample Type: Unknown
Vial: 1
Injection #: 1
Injection Volume: 20.00 ul
Run Time: 70.00 Minutes
Acquired By: Breeze
Date Acquired: 23-01-2017 17:52:36 IST
Acq. Method: 161015
Date Processed: 23-01-2017 18:50:51 IST
Channel Name: 2998 Ch1 260nm@1.2nm
Sample Set Name:



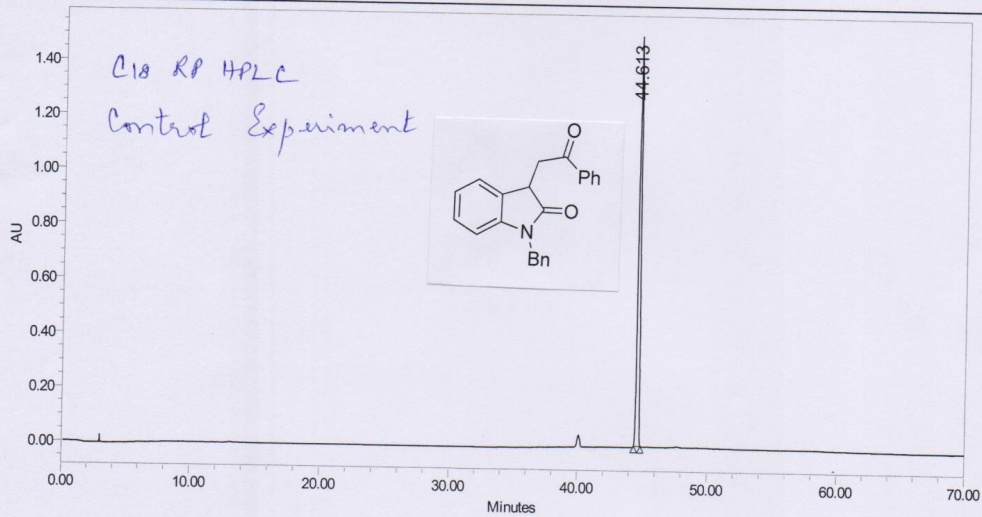
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	53.682	8605254	100.00	658150	100.00

Project Name: protein
Reported by User: Breeze user (Breeze)



SAMPLE INFORMATION

Sample Name:	ks1a	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	20-01-2017 14:24:43 IST
Vial:	1	Acq. Method:	161015
Injection #:	1	Date Processed:	20-01-2017 15:35:27 IST
Injection Volume:	25.00 ul	Channel Name:	2998 Ch1 260nm@1.2nm
Run Time:	70.00 Minutes	Sample Set Name:	



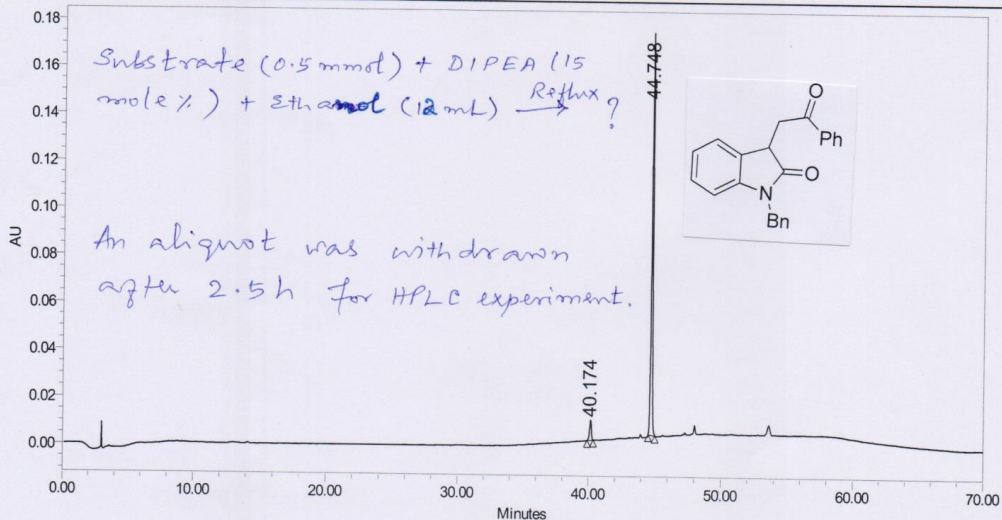
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	44.613	17136721	100.00	1502875	100.00

Project Name: protein
Reported by User: Breeze user (Breeze)



SAMPLE INFORMATION

Sample Name:	1;30 H KAUnk	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	23-01-2017 12:01:32 IST
Vial:	1	Acq. Method:	161015
Injection #:	1	Date Processed:	23-01-2017 12:46:46 IST
Injection Volume:	20.00 ul	Channel Name:	2998 Ch1 260nm@1.2nm
Run Time:	70.00 Minutes	Sample Set Name:	



	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	40.174	75991	5.88	8426	4.72
2	44.748	1215569	94.12	170196	95.28

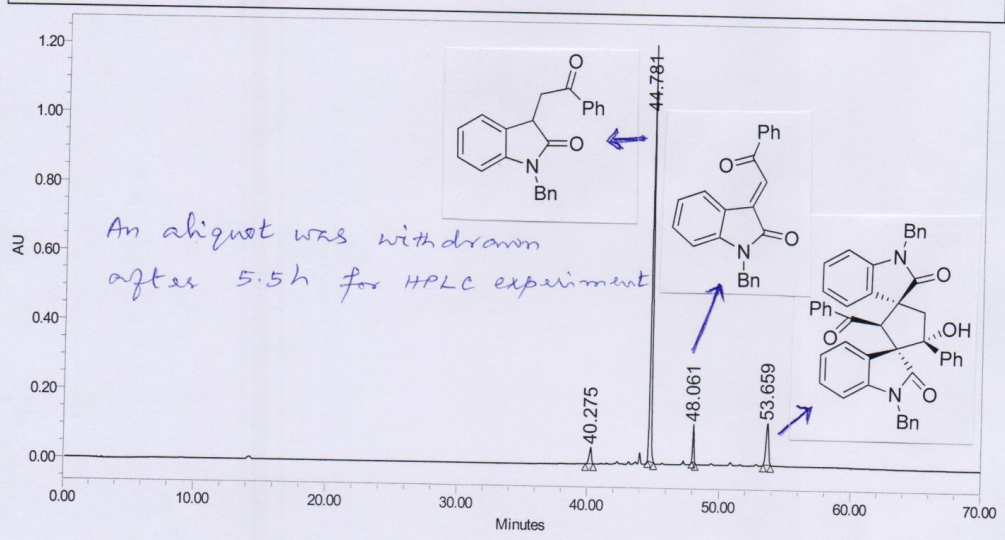
-04-

Project Name: protein
Reported by User: Breeze user (Breeze)



SAMPLE INFORMATION

Sample Name:	4H KSA	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	23-01-2017 15:03:52 IST
Vial:	1	Acq. Method:	161015
Injection #:	1	Date Processed:	23-01-2017 16:14:14 IST
Injection Volume:	20.00 ul	Channel Name:	2998 Ch1 260nm@1.2nm
Run Time:	70.00 Minutes	Sample Set Name:	



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	40.275	573823	4.74	47160	3.19
2	44.781	9164815	75.74	1203186	81.34
3	48.061	708291	5.85	108791	7.35
4	53.659	1653464	13.66	120130	8.12

Report Method: Untitled
Page: 1 of 1

Printed: 23-01-2017
16:15:02 Asia/Calcutta

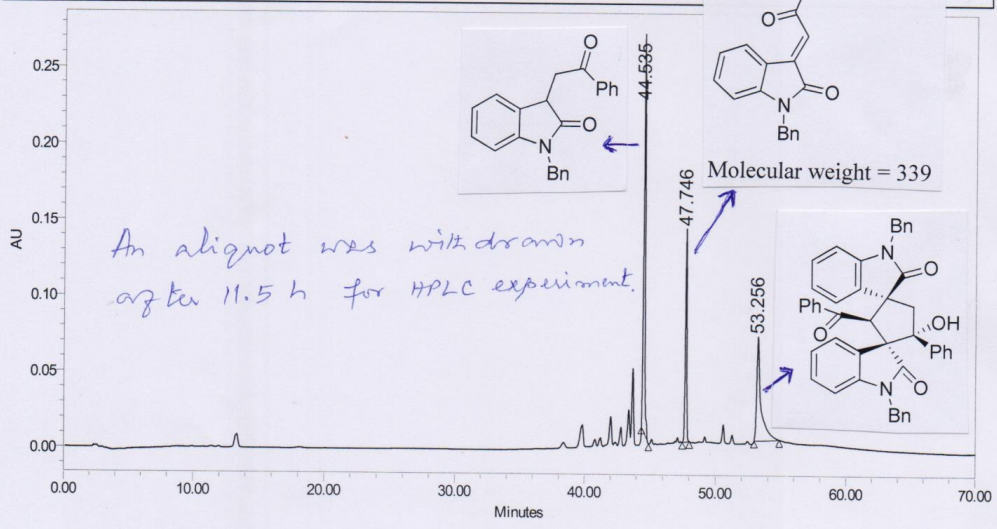
-05-

Project Name: protein
Reported by User: Breeze user (Breeze)



SAMPLE INFORMATION

Sample Name:	KS 2A 9PM	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	23-01-2017 21:01:42 IST
Vial:	1	Acq. Method:	161015
Injection #:	1	Date Processed:	23-01-2017 22:11:01 IST
Injection Volume:	20.00 ul	Channel Name:	2998 Ch1 260nm@1.2nm
Run Time:	70.00 Minutes	Sample Set Name:	



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	44.535	2141854	45.57	260817	55.67
2	47.746	998694	21.25	139660	29.81
3	53.256	1559129	33.18	68032	14.52

Report Method: Untitled
Page: 1 of 1

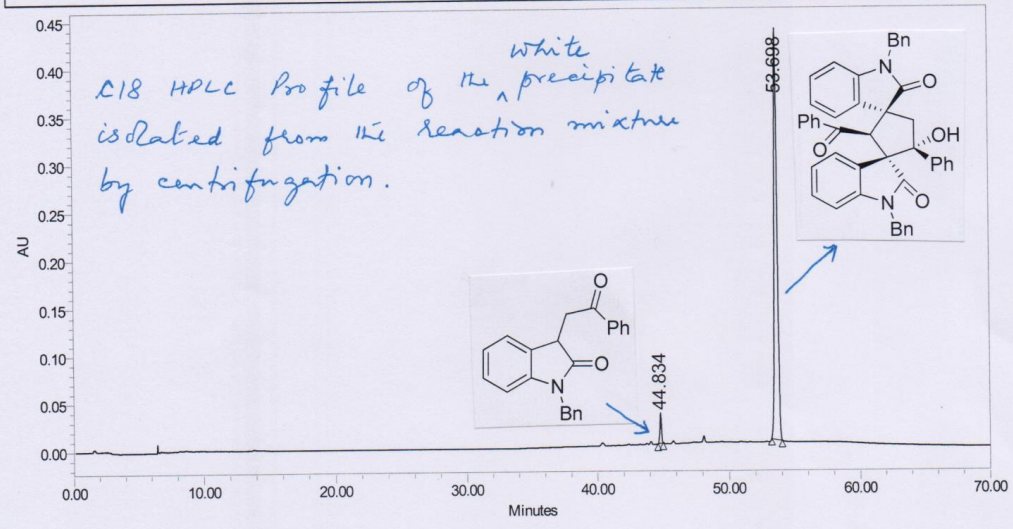
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22:12:43 Asia/Calcutta

-06-



SAMPLE INFORMATION

Sample Name:	ks 2a ppt	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	25-01-2017 15:50:38 IST
Vial:	1	Acq. Method:	161015
Injection #:	1	Date Processed:	25-01-2017 16:47:27 IST
Injection Volume:	10.00 ul	Channel Name:	2998 Ch1 260nm@1.2nm
Run Time:	70.00 Minutes	Sample Set Name:	

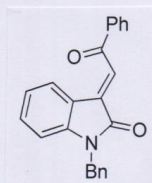


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	44.834	262634	3.63	31395	6.81
2	53.698	6965645	96.37	429357	93.19

2AD-KS48Y 76 (0.643) Sm (Mn, 10x1.00); Cm (8:119)
340.2166

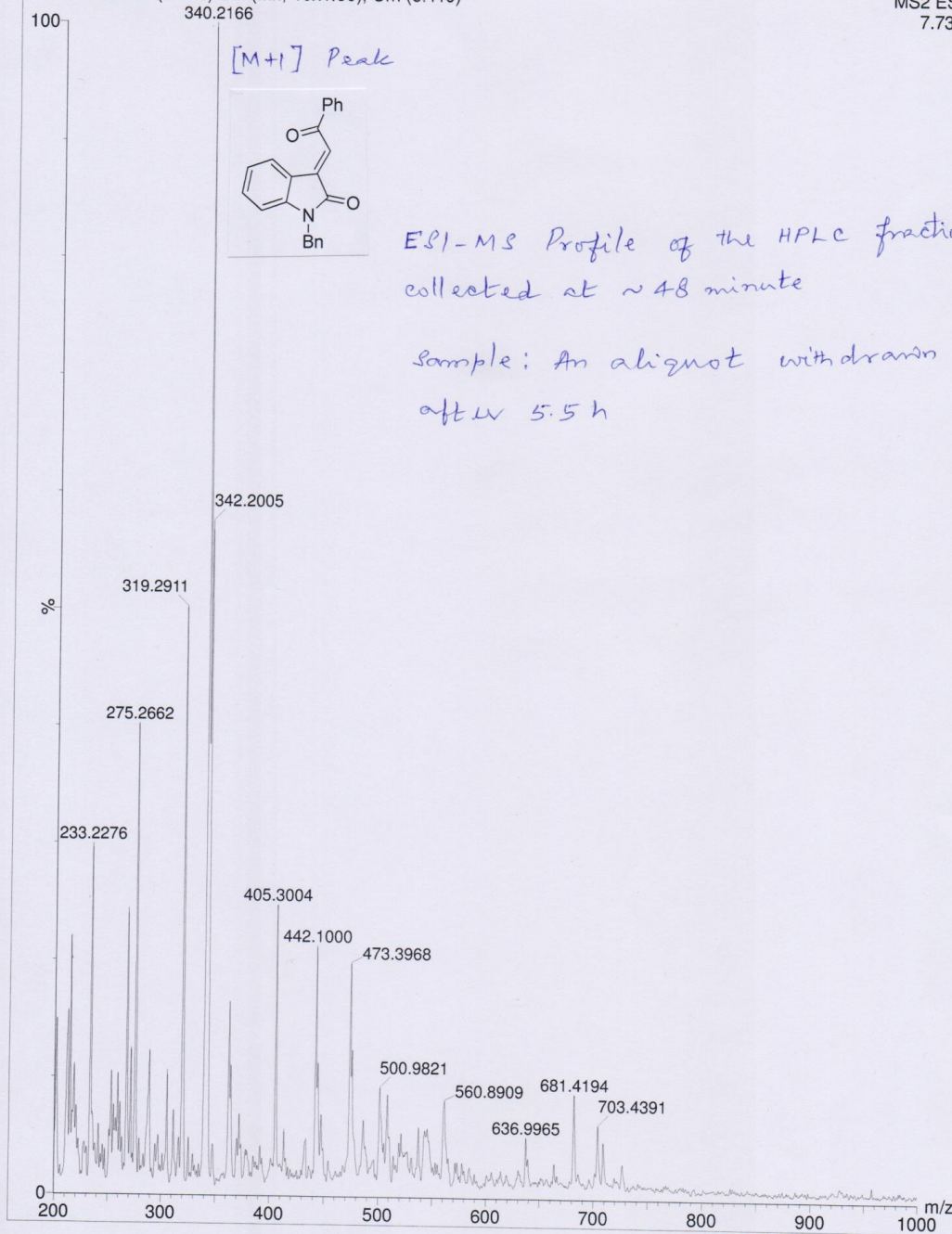
MS2 ES+
7.73e5

[M+1] Peak



ESI-MS Profile of the HPLC fraction
collected at ~48 minute

Sample: An aliquot withdrawn
after 5.5 h



2AD-KS4OT 110 (0.930) Cm (8:117)
319.2911

MS2 ES+
4.97e6

ESI-MS Profile of the fraction
collected at ~40 minute

