Highly Regioselective Ring-Opening Coupling of Diarylmethylenecyclopropa[*b*]naphthalenes with Grignard Reagents

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§ Prof. Huang passed away on March 6, 2010. He had been fully in charge of this project. At this moment, Prof. Luling Wu is helping him to finish all the projects with the help from Prof. Shengming Ma

Supporting Information

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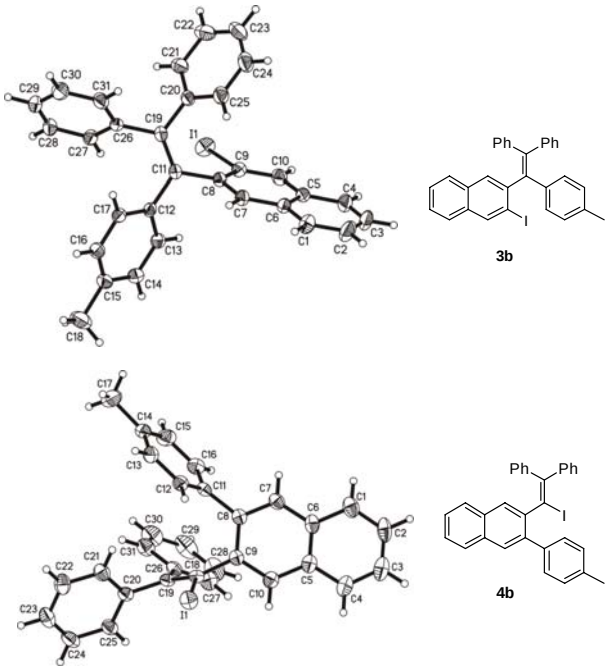


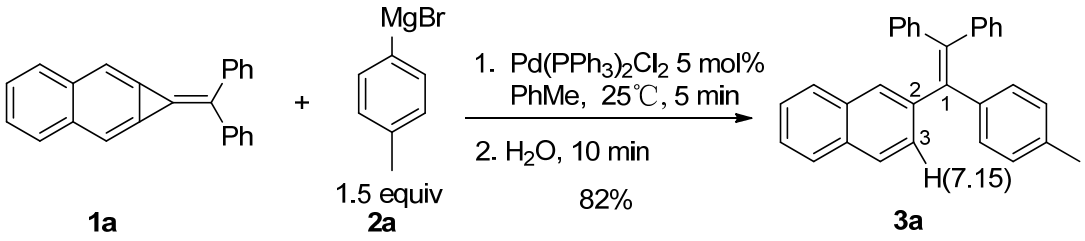
Figure S1. ORTEP representation of **3b** and **4b**.

General Experimental Procedures:

1,4-Dioxane, PhMe and THF were distilled from Na/benzophenone immediately prior to use. Petroleum ether refers to the fraction with the boiling point in the range 60℃-90℃. All ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured in $CDCl_3$ with TMS as the internal standard unless noted otherwise. Chemical shifts are expressed in ppm, and *J* values are given in Hz. The other commercially available chemicals were purchased and used without further purification unless noted otherwise.

General Experimental Procedures:

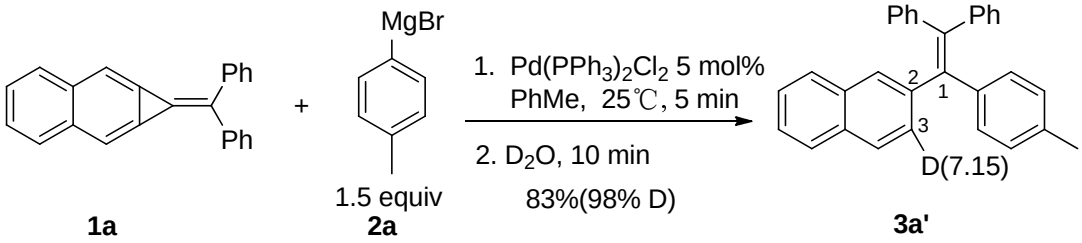
(1) 2-(2,2-Diphenyl-1-(*p*-tolyl)vinyl)naphthalene (3a)



Typical procedure: A rubber-capped Schlenk vessel containing $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol) and 1-(diphenylmethylene)-1*H*-cyclopropa[*b*]naphthalene (**1a,** 61 mg, 0.2 mmol) was degassed and backfilled with nitrogen for three times, then PhMe (2 mL) and *p*-tolylmagnesium bromide (**2a,** 1 M in THF, 0.3 mL, 0.3 mmol) was added to the Schlenk vessel. The resulting mixture was then allowed to stir at 25 °C. After the reaction was completed as monitored by TLC, the reaction mixture was quenched subsequently by H_2O (0.1 mL) and allowed to stir for another 10 min. The reaction mixture was filtered through a short pad of silica gel. The filtrate was concentrated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/CH_2Cl_2 = 10:1) and recrystallization (petroleum ether/CH_2Cl_2) to afford **3a** (65 mg, 82%) as a white solid: m.p. 125-127 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.78 (d, J = 8.0Hz, 1H), 7.57-7.48 (m, 3H), 7.36-7.30 (m,2H), 7.15(d, J = 8.4Hz, 1H, H^3), 7.14-6.99 (m, 10H), 6.96-6.87 (m, 4H), 2.24 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 144.0, 143.8, 141.5, 141.0, 140.8, 140.7, 136.1, 133.1, 132.0, 131.4(broad peak, 3C), 131.3, 130.4, 129.6, 128.4, 127.9, 127.70, 127.66, 127.4, 126.8, 126.4, 126.3, 125.6, 21.2 ppm; MS(EI): *m*/*z* (%) = 395 (M^+, 100); IR (neat): 3053, 1596, 1491, 1444, 1266, 1185, 1112, 1075, 1027 cm^{-1}; HRMS calcd. for $C_{31}H_{24}$ (M^+): 396.1878; found: 396.1875.

The following compounds were prepared according to this procedure.

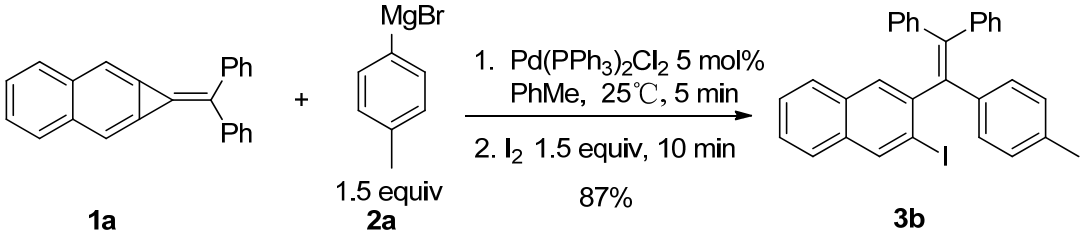
(2) 2-(2,2-Diphenyl-1-(*p*-tolyl)vinyl)-3-deuteriumnaphthalene (3a')



1a **2a** **3a'**

The reaction of **1a** (61 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), **2a** (1 M in THF, 0.3 mL, 0.3 mmol) and H_2O (0.1 mL) in PhMe (2 mL) afforded **3a'** (66 mg, 83%, 98% D)as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1): m.p. 118-120 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.80 (d, *J* = 7.6Hz, 1H), 7.57-7.48 (m, 3H), 7.37-7.31 (m, 2H), 7.15(d, *J* = 8.4Hz, 0.02H, H^3), 7.12-6.99 (m, 10H), 6.98-6.87 (m, 4H), 2.24 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): *δ* = 144.0, 143.8, 141.5, 141.0, 140.8, 140.7, 136.1, 133.1, 132.0, 131.4(broad peak, 3C), 131.3, 130.4, 129.3(t, *J* = 3.3Hz)126.4, 127.9, 127.7, 127.6, 127.4, 126.7, 126.4, 126.3, 125.6, 125.6 , 21.2 ppm; MS(EI): *m*/*z* (%) = 397 (M^+, 100); IR (neat): 3051, 1594, 1491, 1442, 1265, 1183, 1112, 1074, 1026 cm^{-1}; HRMS calcd. for $C_{31}H_{23}D$ (M^+): 397.1941; found: 397.1943.

(3) 2-(2,2-Diphenyl-1-(*p*-tolyl)vinyl)-3-iodonaphthalene (3b)

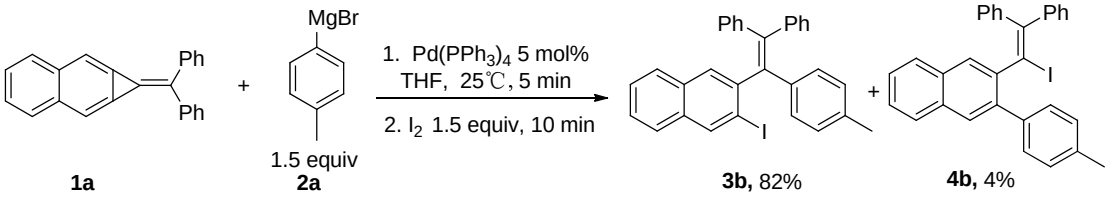


1a **2a** **3b**

The reaction of **1a** (61 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), **2a** (1 M in THF, 0.3 mL, 0.3 mmol) and I_2 (76 mg, 0.3 mmol) in PhMe (2 mL) afforded **3b** (91 mg, 87%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1): m.p. 191-193 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.26 (s, 1H),

7.66-7.58 (m, 3H), 7.39-7.34 (m, 2H), 7.19-7.10 (m, 7H), 6.99-6.83 (m, 7H), 2.20 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 144.5, 143.3, 143.2, 142.0, 141.8, 138.8, 138.5, 136.2, 133.4, 132.5, 131.3(broad peak, 2C), 131.2, 130.7, 128.2, 127.8, 127.7, 127.3, 126.7, 126.5, 126.34(broad peak, 2C), 126.31, 99.0, 21.2 ppm; MS(EI): *m*/*z* (%) = 522 (M^+, 100); IR (neat): 3051, 1577, 1509, 1488, 1442, 1264 1184, 1116, 1074, 1026 cm^{-1}; HRMS calcd. for $C_{31}H_{23}I$ (M^+):522.0845; found: 522.0856.

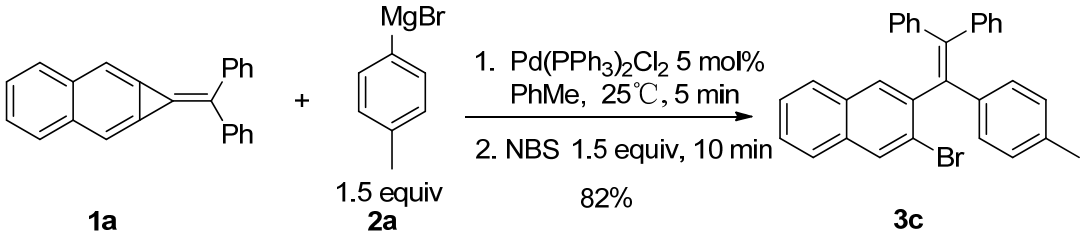
(4) 2-(1-iodo-2,2-diphenylvinyl)-3-(p-tolyl)naphthalene (4b)



1a **2a** **3b,** 82% **4b,** 4%

The reaction of **1a** (61 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11 mg, 0.01 mmol), **2a** (1 M in THF, 0.3 mL, 0.3 mmol) and I_2 (76 mg, 0.3 mmol) in THF (2 mL) afforded **3b** (86 mg, 82%) and **4b** (4 mg, 4%) as a white solid (eluent: petroleum ether): m.p. 168-170 °C (petroleum ether/CH_2Cl_2);^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.21 (s, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.51-7.42 (m, 3H), 7.33-7.25 (m, 3H), 7.14-7.05 (m, 6H), 6.94-6.88 (m, 1H), 6.81-6.75 (m, 2H), 6.45 (d, *J* = 8.4 Hz, 2H), 2.39 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 149.7, 147.5, 141.3, 139.0, 138.6, 137.8, 136.4, 133.1, 132.0, 131.4, 130.1, 129.3, 129.0, 128.9, 128.3, 128.1, 127.8, 127.7, 127.4, 127.2, 127.6, 126.1, 100.8, 21.3 ppm; MS(EI): *m*/*z* (%) = 522 (M^+, 24.00), 302(100); IR (neat): 3052, 1595, 1513, 1490, 1442, 1265, 1184, 1148, 1114, 1074, 1030 cm^{-1}; HRMS calcd. for $C_{31}H_{23}I$ (M^+):522.0845; found: 522.0851.

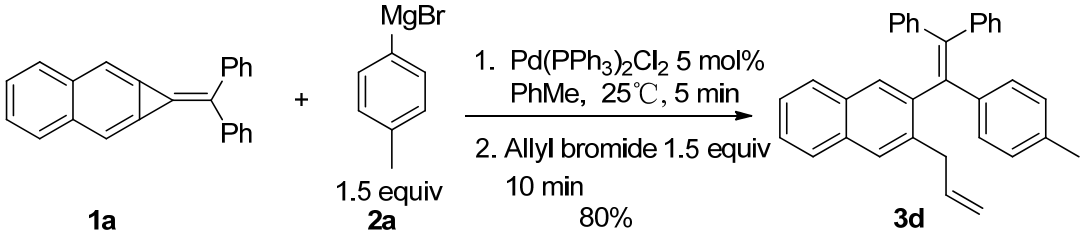
(5) 2-Bromo-3-(2,2-diphenyl-1-(*p*-tolyl)vinyl)naphthalene (3c)



1a **2a** **3c**

The reaction of **1a** (61 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), **2a** (1 M in THF, 0.3 mL, 0.3 mmol) and NBS (53 mg, 0.3 mmol) in PhMe (2 mL) afforded **3c** (78 mg, 82%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1): m.p. 166-168 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.96 (s, 1H), 7.68-7.61 (m, 3H), 7.41-7.35 (m, 2H), 7.16-7.09 (m, 7H), 7.00-6.85 (m, 7H), 2.21 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 143.4, 143.0, 142.4, 141.8, 139.4, 138.6, 136.1, 133.2, 132.0, 131.9, 131.4(broad peak, 2C), 131.3, 130.9, 130.4, 128.2, 127.8, 127.7, 127.5, 126.7, 126.6, 126.5, 126.4, 126.1, 21.2 ppm; MS(EI): *m*/*z* (%) = 474 (M^+(^{79}Br), 19.00), 476 (M^+(^{81}Br), 21.00), 83 (100); IR (neat): 3052, 1594, 1509, 1490, 1443, 1265, 1184, 1118, 1075, 1015 cm^{-1}; HRMS calcd. for $C_{31}H_{23}{}^{79}Br$ (M^+): 474.0983; found:. 474.0989.

(6) 2-Allyl-3-(2,2-diphenyl-1-(*p*-tolyl)vinyl)naphthalene (3d)

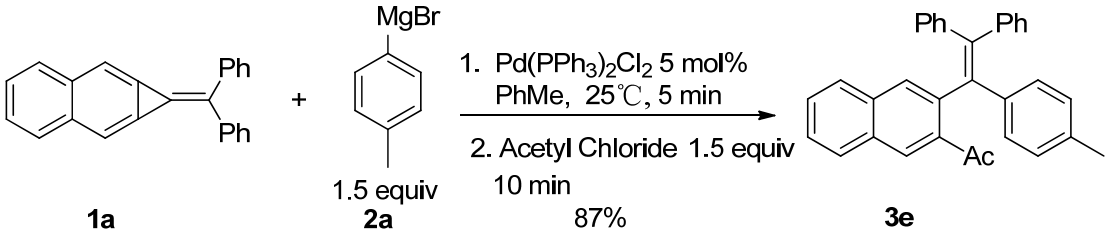


1a **2a** **3d**

The reaction of **1a** (61 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), **2a** (1 M in THF, 0.3 mL, 0.3 mmol) and Allyl Bromide (36 mg, 0.3 mmol) in PhMe (2 mL) afforded **3d** (70 mg, 80%) as oil (eluent: petroleum ether/CH_2Cl_2 = 10:1); ^{1}H NMR

(400 MHz, $CDCl_3$, 25 °C): δ = 7.68 (d, *J* = 7.2Hz, 1H), 7.60(d, *J* = 7.6Hz, 1H), 7.55 (d, *J* = 9.2Hz, 2H), 7.37-7.28 (m, 2H), 7.17-7.10 (m, 5H), 6.99-6.91 (m, 5H), 6.89-6.81 (m, 4H), 5.79-5.68 (m, 1H), 5.06 (d, *J* = 7.6Hz, 1H), 5.03 (s, 1H), 3.38 (d, *J* = 7.2Hz, 2H), 2.21 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): *δ* = 143.6, 143.5, 141.7, 141.4, 139.8, 139.6, 137.3, 137.1, 136.0, 132.6, 131.9, 131.4, 130.8, 130.6, 128.3, 127.8, 127.6, 127.48, 127.45, 127.1, 126.5, 126.3, 125.5, 125.1, 116.2, 37.6, 21.1 ppm; MS(EI): *m*/*z* (%) = 436 (M^+, 18.00), 57 (100); IR (neat): 3053, 1596, 1491, 1442, 1266, 1184, 1075, 1025 cm^{-1}; HRMS calcd. for $C_{34}H_{28}$ (M^+): 436.2191; found: 436.2187.

(7) 1-(3-(2,2-Diphenyl-1-(*p*-tolyl)vinyl)naphthalen-2-yl)ethanone (3e)

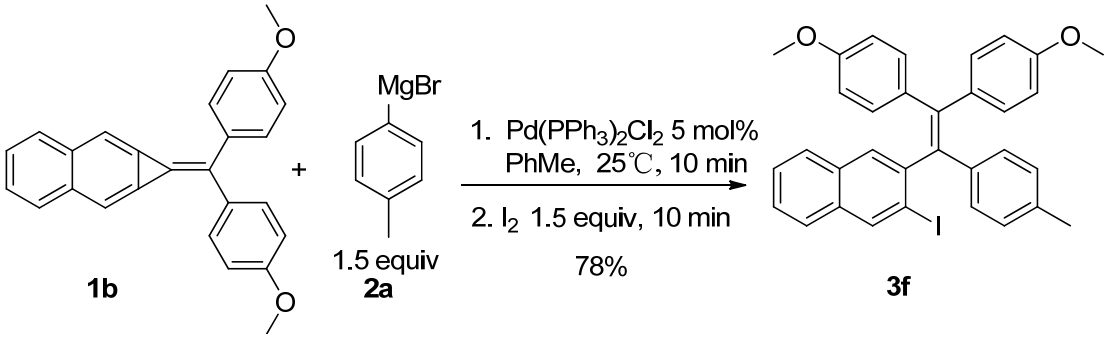


1a **2a** **3e**

The reaction of **1a** (61 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), **2a** (1 M in THF, 0.3 mL, 0.3 mmol) and Acetyl Chloride (24 mg, 0.3 mmol) in PhMe (2 mL) afforded **3e** (78 mg, 82%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1): m.p. 204-206 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.87 (s, 1H), 7.80-7.76 (m, 1H), 7.65-7.59 (m, 2H), 7.47-7.42 (m, 2H), 7.19-7.08 (m, 5H), 7.05-6.92 (m, 7H), 6.88-6.84 (m, 2H), 2.21 (s, 3H), 2.09 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): *δ* = 200.9, 143.8, 143.3, 140.45, 140.39, 139.7, 139.4, 139.1, 135.9, 134.0, 132.2, 131.5, 131.34, 131.31, 131.1, 128.4, 128.2, 128.1, 127.7(broad peak, 3C), 127.5, 126.5, 126.31, 126.26, 28.2, 21.1 ppm; MS(EI): *m*/*z* (%)

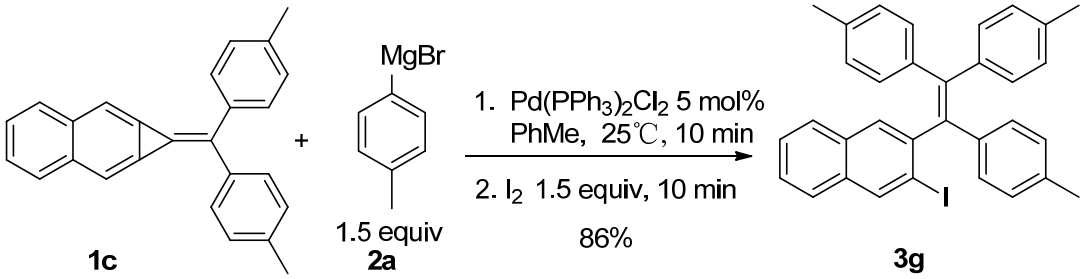
= 438 (M^+, 100); IR (neat): 3053, 1688, 1491, 1441, 1354, 1268, 1197 cm^{-1}; HRMS calcd. for $C_{33}H_{26}O$ (M^+): 438.1984 ; found: 438.1989.

(8) 2-(2,2-Bis(4-methoxyphenyl)-1-(*p*-tolyl)vinyl)-3-iodonaphthalene (3f)



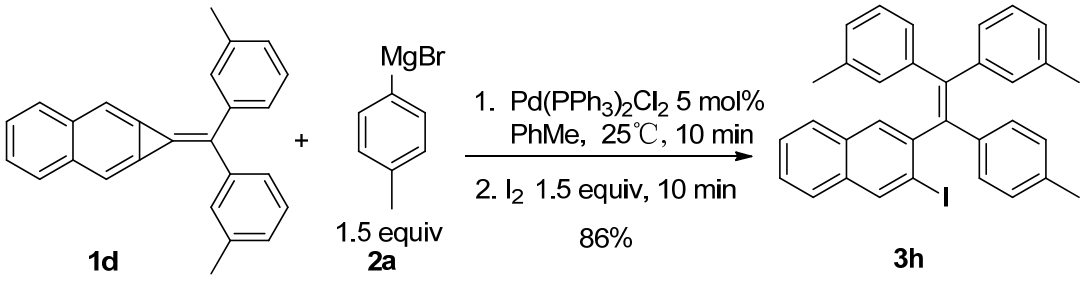
The reaction of **1b** (73 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), **2a** (1 M in THF, 0.3 mL, 0.3 mmol) and I_2 (76 mg, 0.3 mmol) in PhMe (2 mL) afforded **3f** (91 mg, 78%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 5:1): m.p. 208-210 °C (petroleum ether/CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.23 (s, 1H), 7.65-7.59 (m, 3H), 7.40-7.35 (m, 2H), 7.08 (d, *J* = 9.2 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.92-6.84 (m, 4H), 6.70 (d, *J* = 8.8 Hz, 2H), 6.51 (d, *J* = 8.4 Hz, 2H), 3.75 (s, 3H), 3.60 (s, 3H), 2.21 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): *δ* = 158.4, 158.0, 145.1, 141.3, 140.1, 139.2, 138.7, 135.94, 135.90, 135.7, 133.4, 132.6(broad peak, 2C), 132.1, 131.3, 131.1, 128.2, 127.7, 126.4, 126.3, 126.2, 113.2, 112.7, 99.5, 55.1, 54.9, 21.2 ppm; MS(EI): *m/z* (%) = 582 (M^+, 100); IR (neat): 3053, 2997, 1604, 1508, 1460, 1245, 1175, 1111, 1034 cm^{-1}; HRMS calcd. for $C_{33}H_{27}IO_2$ (M^+): 582.1056; found: 582.1053.

(9) 2-Iodo-3-(1,2,2-tri-*p*-tolylvinyl)naphthalene (3g)



The reaction of **1c** (66 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), **2a** (1 M in THF, 0.3 mL, 0.3 mmol) and I_2 (76 mg, 0.3 mmol) in PhMe (2 mL) afforded **3g** (95 mg, 86%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1): m.p. 176-178 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.25 (s, 1H), 7.65-7.58 (m, 3H), 7.38-7.33 (m, 2H), 7.05 (d, *J* = 7.2Hz, 2H), 7.01-6.94 (m, 4H), 6.91 (d, *J* = 7.6Hz, 2H), 6.84 (d, *J* = 7.6Hz, 2H), 6.77 (d, *J* = 8.0Hz, 2H), 2.27 (s, 3H)), 2.20 (s, 3H)), 2.10 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): *δ* = 145.0, 142.0, 140.8, 140.55, 140.50, 138.9, 138.7, 136.3, 136.0, 135.9, 133.4, 132.6, 131.2, 131.2(broad peak, 2C), 130.7, 128.5, 128.2, 128.1, 127.8, 126.4, 126.23, 126.19, 99.3, 21.3, 21.2, 21.1 ppm; MS(EI): *m*/*z* (%) = 550 (M^+, 100); IR (neat): 3022, 2918, 1510, 1450, 1265, 1183, 1113, 1022 cm^{-1}; HRMS calcd. for $C_{33}H_{27}I$ (M^+): 550.1158; found: 550.1157.

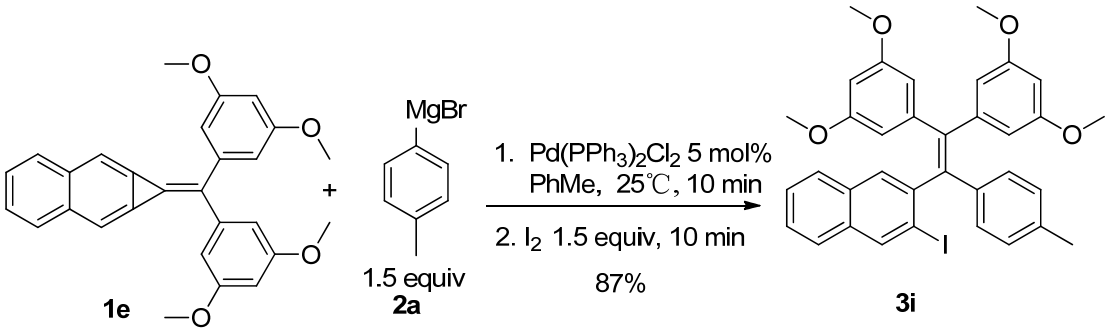
(10) 2-(2,2-Di-*m*-tolyl-1-(*p*-tolyl)vinyl)-3-iodonaphthalene (3h)



The reaction of **1d** (66 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), **2a** (1 M in THF, 0.3 mL, 0.3 mmol) and I_2 (76 mg, 0.3 mmol) in PhMe (2 mL) afforded **3h** (95

mg, 86%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1): m.p. 162-164 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.25 (s, 1H), 7.65-7.57 (m, 3H), 7.38-7.33 (m, 2H), 7.05-6.81 (m, 11H), 6.75 (d, *J* = 6.8 Hz, 1H), 2.20 (s, 3H), 2.19 (s, 3H), 2.03 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): *δ* = 144.7, 143.2, 143.1, 142.2, 141.5, 138.6, 138.5, 137.2, 136.6, 136.0, 133.4, 132.5, 131.8, 131.4, 131.2, 131.2, 128.4, 128.1, 127.8, 127.7, 127.6, 127.5, 127.3, 127.2, 126.33, 126.27, 126.2, 99.1, 21.4, 21.2 ppm; MS(EI): *m*/*z* (%) = 550 (M^+, 91.00), 316 (100); IR (neat): 3022, 1600, 1509, 1485, 1421, 1264, 1184, 1092, 1021 cm^{-1}; HRMS calcd. for $C_{33}H_{27}I$ (M^+): 550.1158; found: 550.1150.

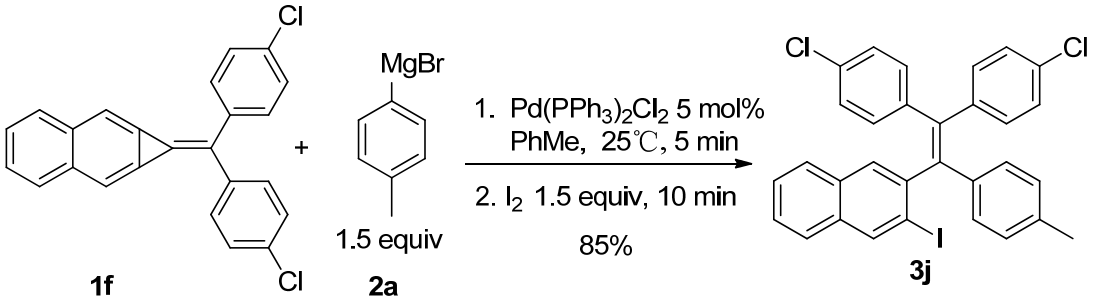
(11) 2-(2,2-Bis(3,5-dimethoxyphenyl)-1-(*p*-tolyl)vinyl)-3-iodonaphthalene (3i)



The reaction of **1e** (85 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), **2a** (1 M in THF, 0.3 mL, 0.3 mmol) and I_2 (76 mg, 0.3 mmol) in PhMe (2 mL) afforded **3i** (112 mg, 87%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 3:1): m.p. 193-195 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.29 (s, 1H), 7.68-7.60 (m, 3H), 7.41-7.37 (m, 2H), 6.96 (d, *J* = 7.6 Hz, 2H), 6.88 (d, *J* = 7.6 Hz, 2H), 6.36-6.33 (m, 4H), 6.30 (s,1H), 6.09 (s, 1H), 3.59 (s, 6H), 3.48 (s, 6H), 2.22 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): *δ* = 160.1, 159.7, 144.8, 144.51, 144.49, 142.1, 141.8, 138.7, 138.1, 136.3, 133.4, 132.6, 131.0, 130.8, 128.2, 127.7,

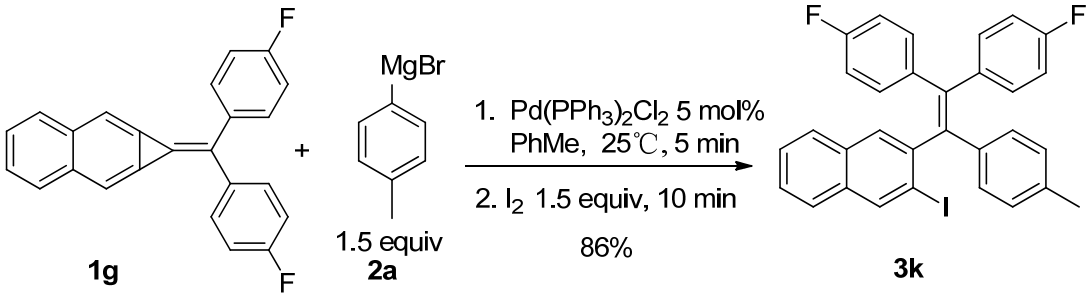
126.45, 126.39, 126.3, 109.5, 108.7, 99.6, 99.4, 98.8, 55.2, 55.1, 21.2 ppm; MS(EI): *m*/*z* (%) = 642 (M^+, 2.00), 515 (100); IR (neat): 2936, 2835, 1587, 1509, 1455, 1421, 1345, 1264, 1202, 1152 1064, 1025 cm^{-1}; HRMS calcd. for $C_{35}H_{31}IO_4$ (M^+): 642.1267; found: 642.1265.

(12) 2-(2,2-Bis(4-chlorophenyl)-1-(*p*-tolyl)vinyl)-3-iodonaphthalene (3j)



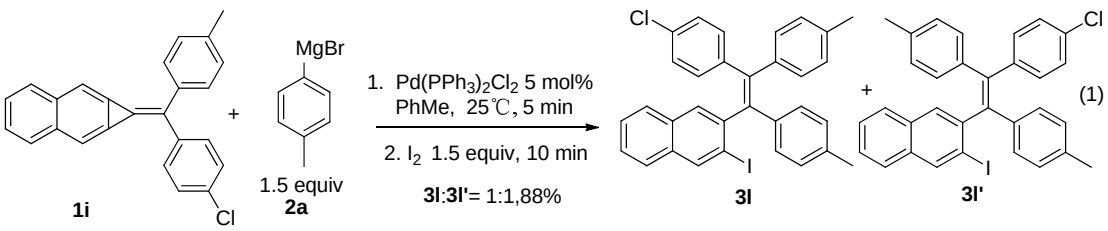
The reaction of **1f** (75 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), **2a** (1 M in THF, 0.3 mL, 0.3 mmol) and I_2 (76 mg, 0.3 mmol) in PhMe (2 mL) afforded **3j** (100 mg, 85%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1): m.p. 192-194 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.28 (s, 1H), 7.64-7.60 (m, 3H), 7.44-7.40 (m, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.92-6.84 (m, 4H), 2.23 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): *δ* = 147.3, 145.2, 140.7, 138.2, 137.6, 137.2, 136.6, 133.5, 133.2, 132.7, 131.9, 131.4(broad peak, 3C), 130.4, 129.2(broad peak, 2C), 128.6, 128.4, 127.8, 127.4, 126.9, 126.3, 101.7, 21.2 ppm; MS(EI): *m*/*z* (%) = 590 (M^+(^{35,35}Cl), 64.00), 592 (M^+(^{35,37}Cl), 45.00), 590 (M^+(^{37,37}Cl), 9.00), 428 (100); IR (neat): 3050, 1584, 1487, 1421, 1397, 1264, 1183, 1089, 1015 cm^{-1}; HRMS calcd. for $C_{31}H_{21}{}^{35,35}Cl_2I$ (M^+):590.0065; found: 590.0063.

(13) 2-(2,2-Bis(4-fluorophenyl)-1-(*p*-tolyl)vinyl)-3-iodonaphthalene (3k)



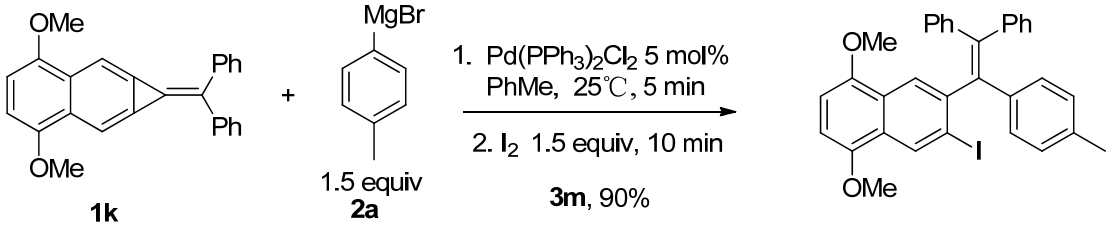
The reaction of **1g** (68 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), **2a** (1 M in THF, 0.3 mL, 0.3 mmol) and I_2 (76 mg, 0.3 mmol) in PhMe (2 mL) afforded **3k** (96 mg, 86%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1): m.p. 167-169 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.28 (s, 1H), 7.66-7.60 (m, 3H), 7.44-7.39 (m, 2H), 7.15-7.04 (m, 4H), 6.91-6.83 (m, 6H), 6.71-6.65 (m, 2H), 2.23 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 161.7(d, J = 246.1Hz), 161.3 (d, J = 245.3Hz), 144.2, 142.1, 139.8, 138.99(broad peak, 2C), 138.92, 138.2, 136.4, 133.5, 132.8 (d, J = 8.2 Hz), 132.5, 132.4 (d, J = 8.3 Hz), 131.1, 131.0(broad peak, 2C), 128.3, 127.6, 126.5, 126.4, 114.9 (d, J = 21.0 Hz), 114.4 (d, J = 21.6 Hz), 99.5, 21.1 ppm; MS(EI): m/z (%) = 558 (M^+, 100); IR (neat): 3053, 1600, 1506, 1273, 1226, 1157 cm^{-1}; HRMS calcd. for $C_{31}H_{21}F_2I$ (M^+): 558.0656; found: 558.0660.

(14) (Z)-2-(2-(4-chlorophenyl)-1,2-di-p-tolylvinyl)-3-iodonaphthalene (3l) and (E)-2-(2-(4-chlorophenyl)-1,2-di-p-tolylvinyl)-3-iodonaphthalene (3l')



The reaction of **1i** (71 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), **2a** (1 M in THF, 0.3 mL, 0.3 mmol) and I_2 (76 mg, 0.3 mmol) in PhMe (2 mL) afforded **3k** (100 mg, 88%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1): m.p. 190-192 °C ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.26 (s, 2H), 7.66-7.60 (m, 6H), 7.42-7.35 (m, 4H), 7.15-7.07 (m, 4H), 7.06-7.01 (m, 4H), 6.99-6.83 (m, 14H), 6.78 (d, *J* = 8.0 Hz, 2H), 2.28 (s, 3H), 2.219 (s, 3H), 2.216 (s, 3H), 2.11 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): *δ* = 144.5, 144.4, 142.0, 141.8, 140.74, 140.68, 139.9, 139.8, 138.9, 138.8, 138.44, 138.37, 136.6, 136.40, 136.37, 136.3, 133.47, 133.45, 132.7, 132.50, 132.49, 132.4, 132.2, 132.1, 131.2, 131.13, 131.08, 130.6, 128.7, 128.4, 128.3, 128.0, 127.8, 127.7, 127.6, 126.5, 126.4, 126.3, 98.9, 98.8, 21.3, 21.2, 21.1 ppm; MS(EI): *m/z* (%) = 570 (M^+(^{35}Cl), 100), 577 (M^+(^{37}Cl), 40.00); IR (neat): 3025, 2246, 1904, 1582, 1509, 1485, 1420, 1271, 1183, 1069, 1016cm^{-1}.

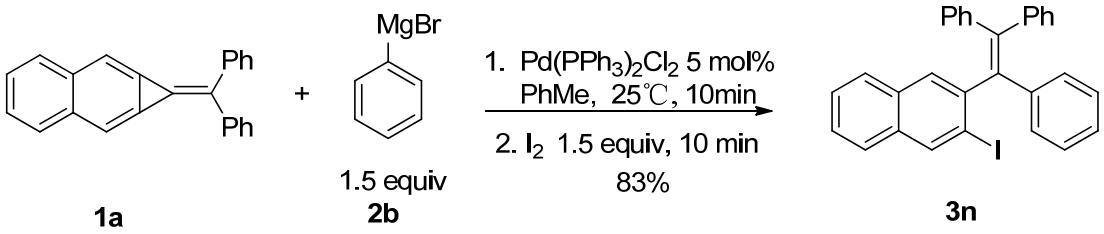
(15) 6-(2,2-diphenyl-1-(p-tolyl)vinyl)-7-iodo-1,4-dimethoxynaphthalene (3m)



The reaction of **1k** (73 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), **2a** (1 M in THF, 0.3 mL, 0.3 mmol) and I_2 (76 mg, 0.3 mmol) in PhMe (2 mL) afforded **3k** (105 mg, 90%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1): m.p. 230-232 °C ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.61 (s, 1H), 8.00 (s, 1H), 7.20-7.09 (m, 7H), 6.99-6.94 (m, 3H), 6.91 (d, *J* =8.0Hz,2H), 6.84 (d, *J* =8.4Hz,2H), 6.58 (s, 2H), 3.87 (s, 3H), 3.82 (s, 3H), 2.21 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): *δ* = 149.3,

148.1, 144.6, 143.4, 143.2, 142.0, 141.8, 138.6, 136.0, 133.1, 131.3, 131.2, 130.8, 128.1, 127.8, 127.3, 126.6, 126.4, 126.2, 125.6(broad peak, 2C), 103.8, 103.6, 99.4, 55.7, 55.6, 21.2 ppm; MS(EI): *m/z* (%) = 582 (M^+, 100); IR (neat): 3022, 2362, 1623, 1904, 1623, 1575, 1458, 1316, 1267, 1236, 1131, 1099 cm^{-1}; HRMS calcd. for $C_{33}H_{27}IO_2$ (M^+): 582.1056; found: 582.1050.

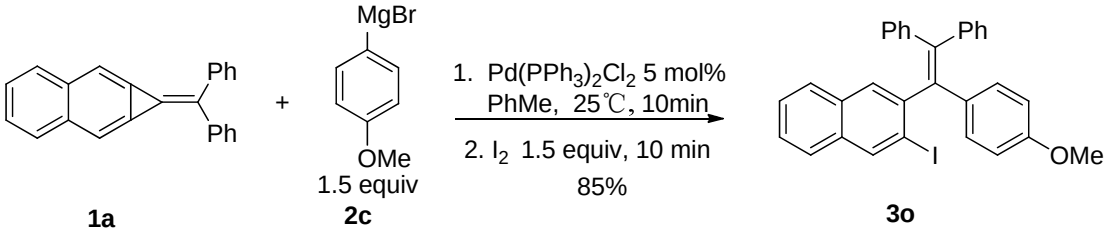
(16) 2-Iodo-3-(1,2,2-triphenylvinyl)naphthalene (3n)



1a 1.5 equiv **2b** **3n**

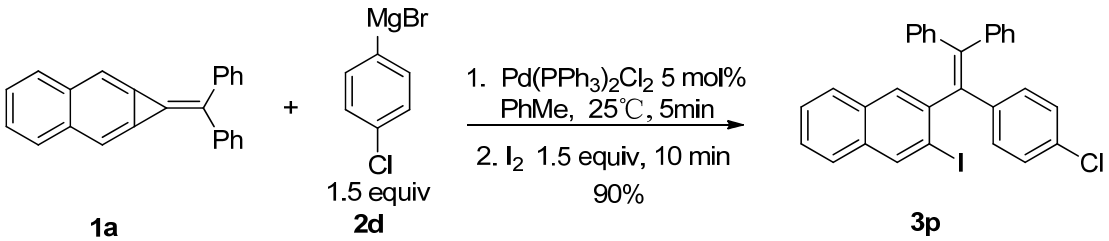
The reaction of **1a** (61 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), **2b** (1 M in THF, 0.3 mL, 0.3 mmol) and I_2 (76 mg, 0.3 mmol) in PhMe (2 mL) afforded **3n** (84 mg, 83%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1): m.p. 190-192 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.27 (s, 1H), 7.66-7.60 (m, 3H), 7.39-7.35 (m, 2H), 7.17-7.11 (m, 7H), 7.06-6.96 (m, 8H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): *δ* = 144.4, 143.09, 143.05, 142.7, 141.8, 141.5, 138.8, 133.5, 132.5, 131.4(broad peak, 3C), 131.3, 130.7, 127.8, 127.7, 127.44, 127.41, 126.8, 126.6, 126.5, 126.4(broad peak, 2C), 98.8 ppm; MS(EI): *m/z* (%) = 508 (M^+, 100); IR (neat): 3052, 1575, 1490, 1442, 1264, 1075, 1029 cm^{-1}; HRMS calcd. for $C_{30}H_{21}I$(M^+): 508.0688; found: 508.0687.

(17) 2-Iodo-3-(1-(4-methoxyphenyl)-2,2-diphenylvinyl)naphthalene (3o)



The reaction of **1a** (61 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), **2c** (1 M in THF, 0.3 mL, 0.3 mmol) and I_2 (76 mg, 0.3 mmol) in PhMe (2 mL) afforded **3o** (91 mg, 85%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 5:1): m.p. 188-190 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.27 (s, 1H), 7.65-7.58 (m, 3H), 7.39-7.34 (m, 2H), 7.20-7.10 (m, 7H), 6.98-6.91 (m, 5H), 6.58 (d, *J* = 8.8Hz, 2H), 3.66 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): *δ* = 158.1, 144.5, 143.3, 141.4, 138.8, 133.8, 133.4, 132.6(broad peak, 3C), 132.5, 131.31(broad peak, 2C), 131.27, 130.7, 127.9, 127.7, 127.4, 126.7, 126.4, 126.3(broad peak, 2C), 112.8, 99.0, 55.0 ppm; MS(EI): *m/z* (%) = 538 (M^+, 100); IR (neat): 3052, 2834, 1602, 1574, 1507, 1441, 1247, 1177, 1115, 1033 cm^{-1}; HRMS calcd. for $C_{31}H_{23}IO$ (M^+): 538.0794; found: 538.0793.

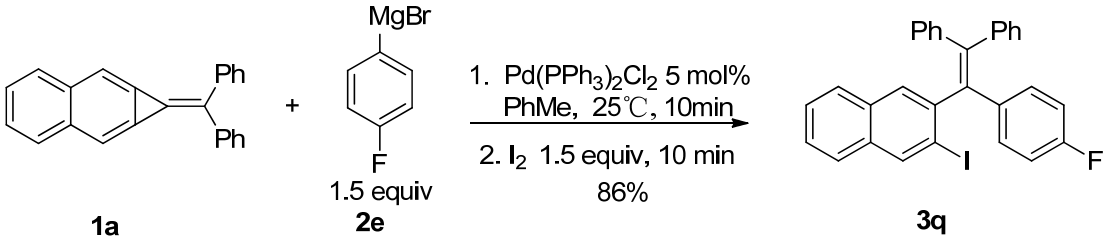
(18) 2-(1-(4-Chlorophenyl)-2,2-diphenylvinyl)-3-iodonaphthalene (3p)



The reaction of **1a** (61 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), **2d** (1 M in THF, 0.3 mL, 0.3 mmol) and I_2 (76 mg, 0.3 mmol) in PhMe (2 mL) afforded **3p** (98 mg, 90%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1): m.p. 185-187 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.27 (s, 1H),

7.65-7.59 (m, 3H), 7.39-7.36 (m, 2H), 7.18-7.09 (m, 7H), 7.02-6.92 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 143.9, 143.2, 142.8, 142.6, 140.6, 139.9, 138.9, 133.5, 132.6, 132.4, 132.2, 131.4, 131.2, 130.6, 128.0, 127.7, 127.5, 127.1, 126.8, 126.53, 126.50, 126.4, 98.6 ppm; MS(EI): *m*/*z* (%) = 542 (M^+(^{35}Cl), 93.00), 544 (M^+(^{37}Cl), 38.00), 380 (100); IR (neat): 3053, 1575, 1488, 1441, 1396, 1264, 1090, 1012 cm^{-1}; HRMS calcd. for $C_{30}H_{20}ClI$ (M^+): 542.0298; found: 542.0300.

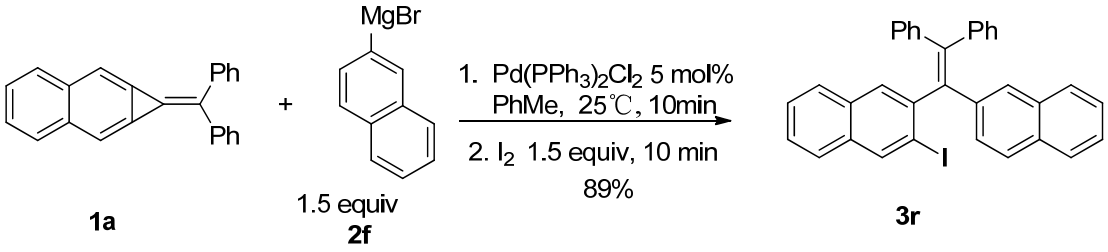
(19) 2-(1-(4-Fluorophenyl)-2,2-diphenylvinyl)-3-iodonaphthalene (3q)



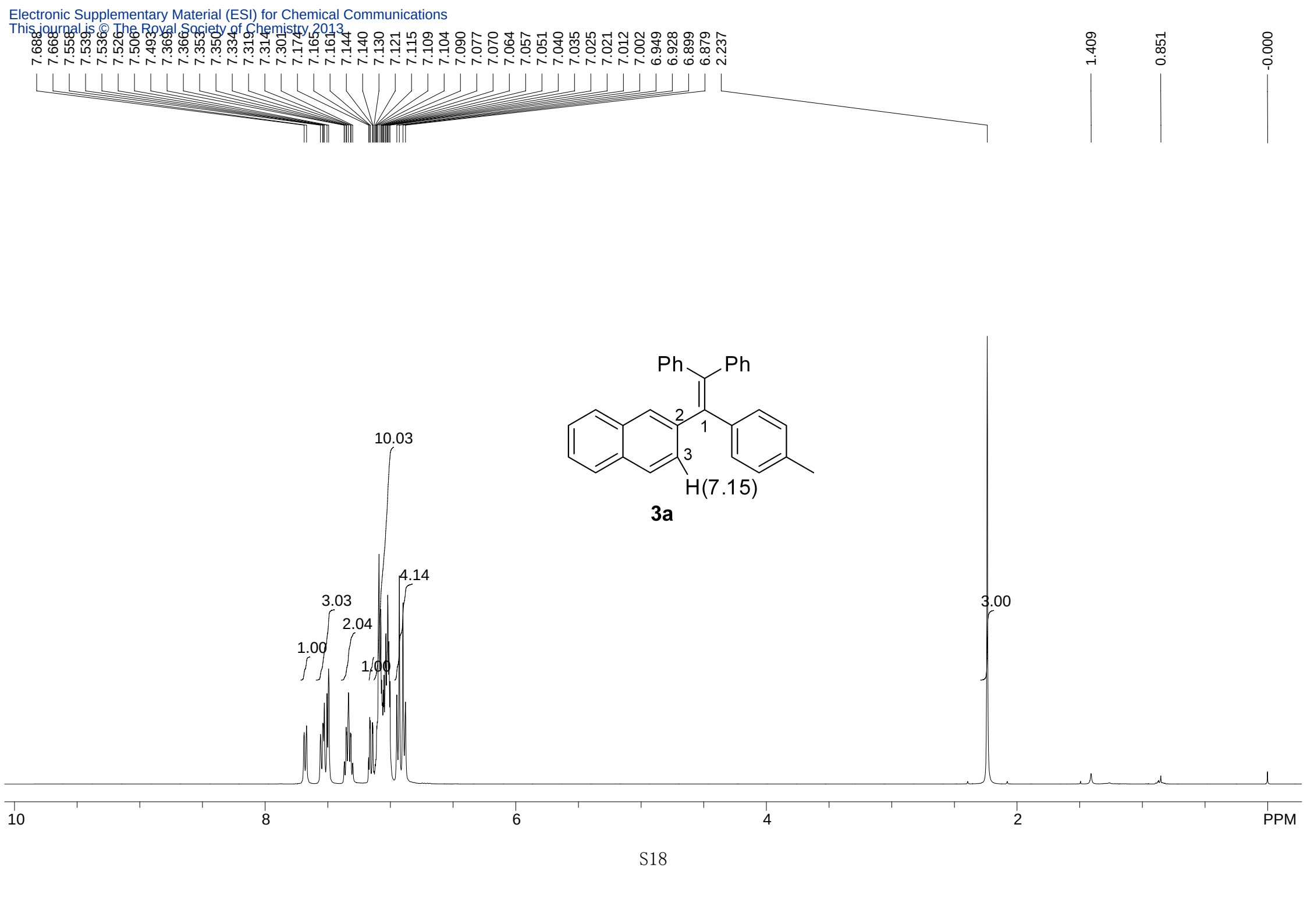
1a **2e** **3q**

The reaction of **1a** (61 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), **2e** (1 M in THF, 0.3 mL, 0.3 mmol) and I_2 (76 mg, 0.3 mmol) in PhMe (2 mL) afforded **3q** (91 mg, 86%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1): m.p. 153-155 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.28 (s, 1H), 7.65-7.58 (m, 3H), 7.39-7.36 (m, 2H), 7.20-7.09 (m, 7H), 7.02-6.95 (m, 5H), 6.76-6.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 161.3 (d, *J* = 245.6 Hz), 144.1, 142.9, 142.8, 142.8, 140.8, 138.9, 137.4 (d, *J* = 3.2 Hz), 133.5, 133.0 (d, *J* = 7.5 Hz), 132.5, 131.4, 131.3, 130.6, 127.9, 127.7, 127.5, 127.0, 126.7, 126.5, 126.4, 114.4 (d, *J* = 21.6 Hz), 98.6 ppm; MS(EI): *m*/*z* (%) = 526 (M^+, 100); IR (neat): 3053, 1597, 1504, 1442, 1420, 1264, 1225, 1157, 1097, 1075, 1009 cm^{-1}; HRMS calcd. for $C_{30}H_{20}FI$ (M^+): 526.0594; found: 526.0593.

(20) 2-Iodo-3-(1-(naphthalen-2-yl)-2,2-diphenylvinyl)naphthalene (3r)



The reaction of **1a** (61 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), **2f** (1 M in THF, 0.3 mL, 0.3 mmol) and I_2 (76 mg, 0.3 mmol) in PhMe (2 mL) afforded **3r** (99 mg, 89%) as a white solid (eluent: petroleum ether/ CH_2Cl_2 = 10:1): m.p. 224-226 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.28 (s, 1H), 7.72-7.62 (m, 4H), 7.53-7.28 (m, 7H), 7.23-7.13 (m, 8H), 7.02-6.99 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 144.6, 143.2, 143.1, 142.9, 141.7, 139.2, 138.8, 133.5, 133.0, 132.5, 132.0, 131.6, 131.5, 130.7, 130.1, 130.0, 128.0, 127.9, 127.8, 127.5, 127.4, 127.0, 126.7, 126.4(broad peak, 3C), 125.8, 125.6, 99.0 ppm; MS(EI): *m*/*z* (%) = 558 (M^+, 100); IR (neat): 3053, 1596, 1489, 1441, 1420, 1266, 1186, 1135, 1075, 1029 cm^{-1}; HRMS calcd. for $C_{34}H_{23}I$ (M^+): 558.0845; found: 558.0853.



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127.945
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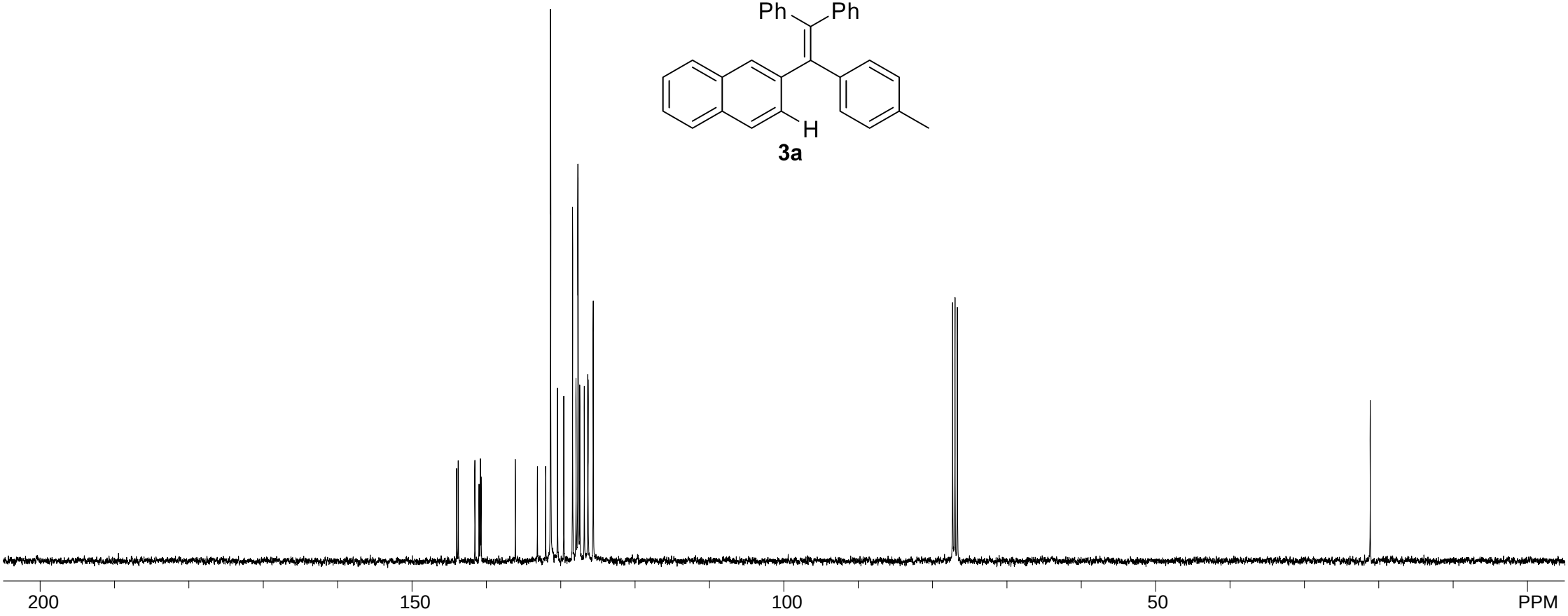
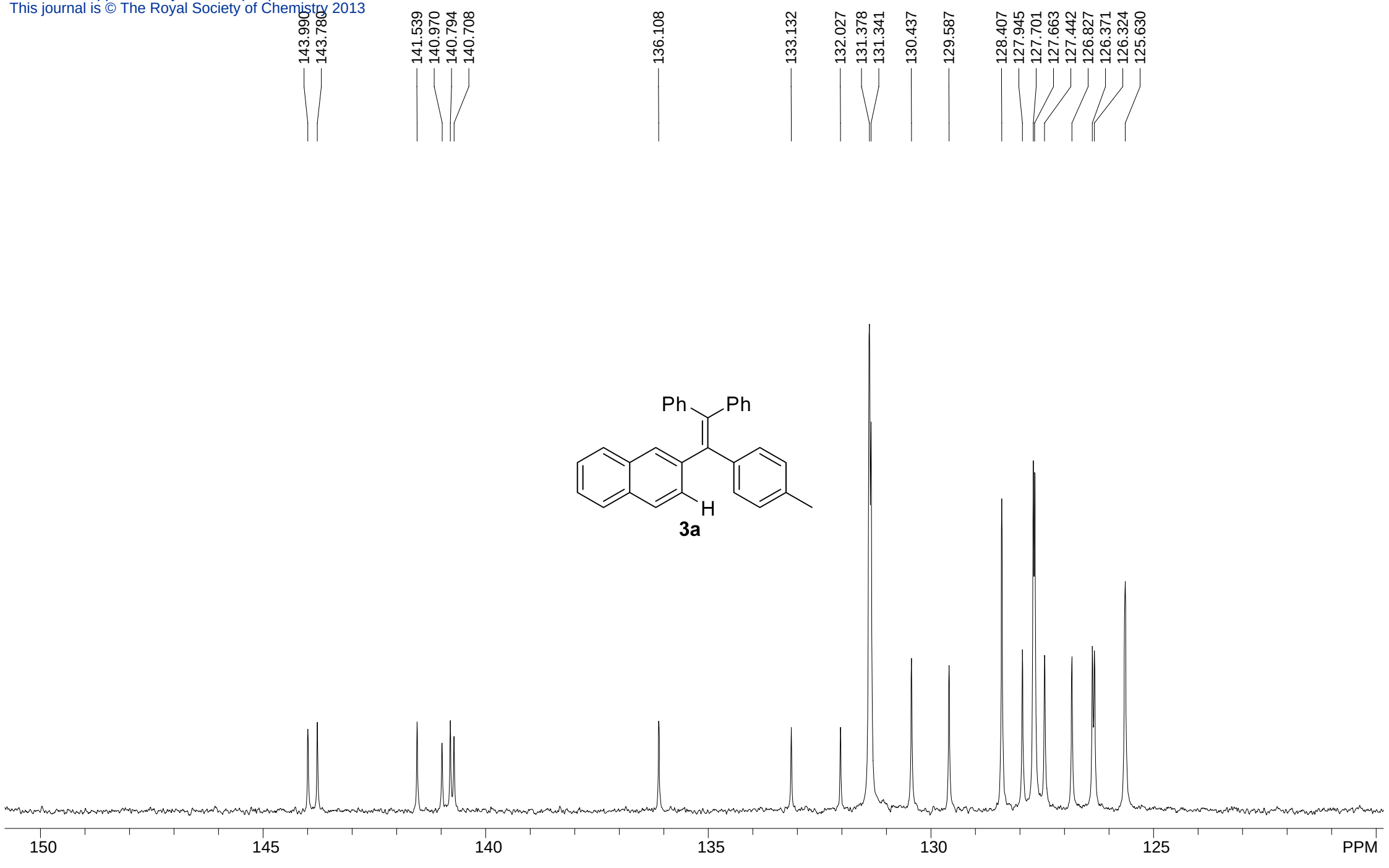
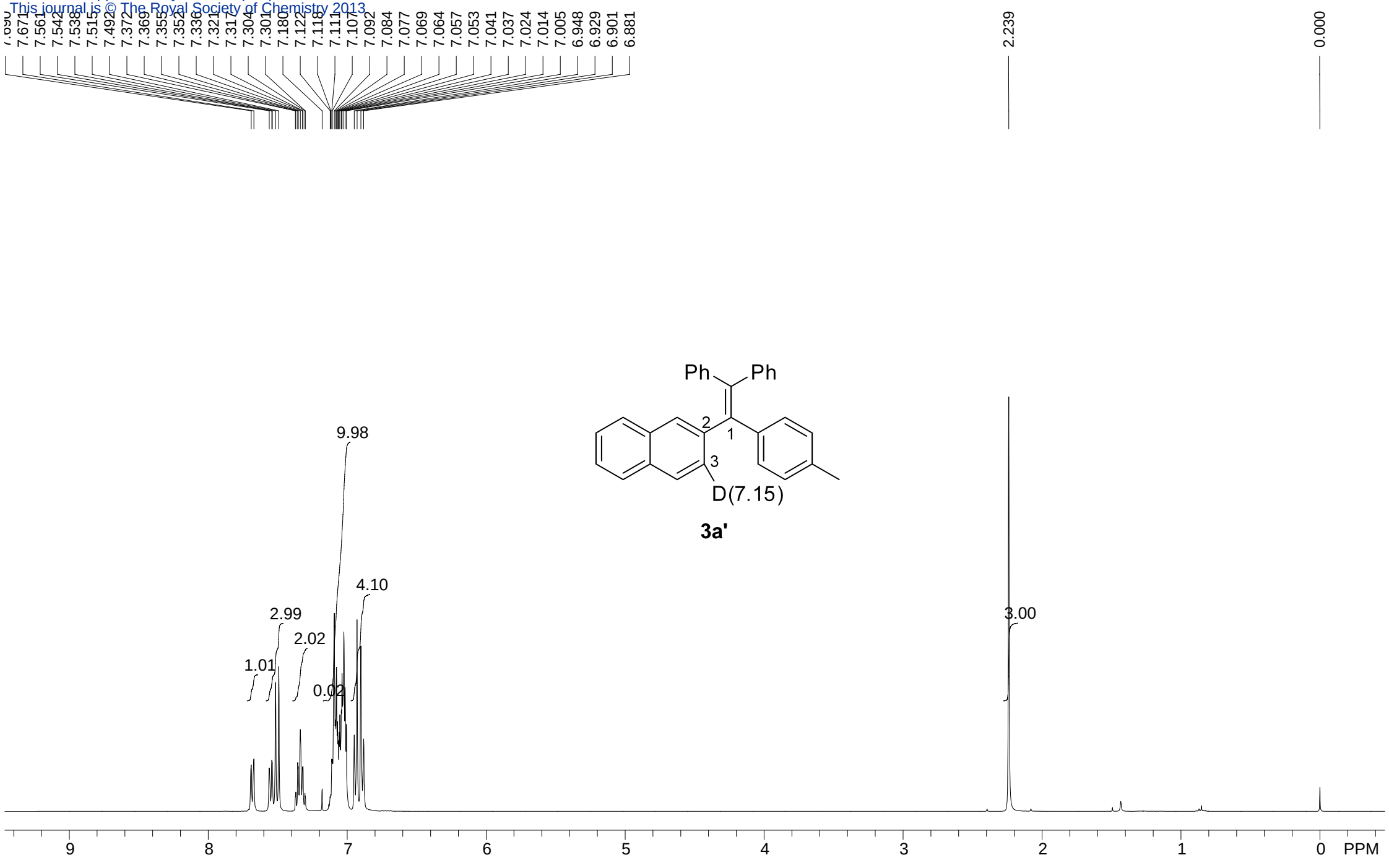
77.000
76.686
21.182

3a







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129.286
129.050
128.404
127.944
127.691
127.653
127.441
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126.311
125.634
125.620
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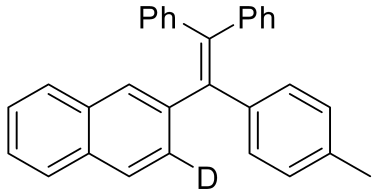
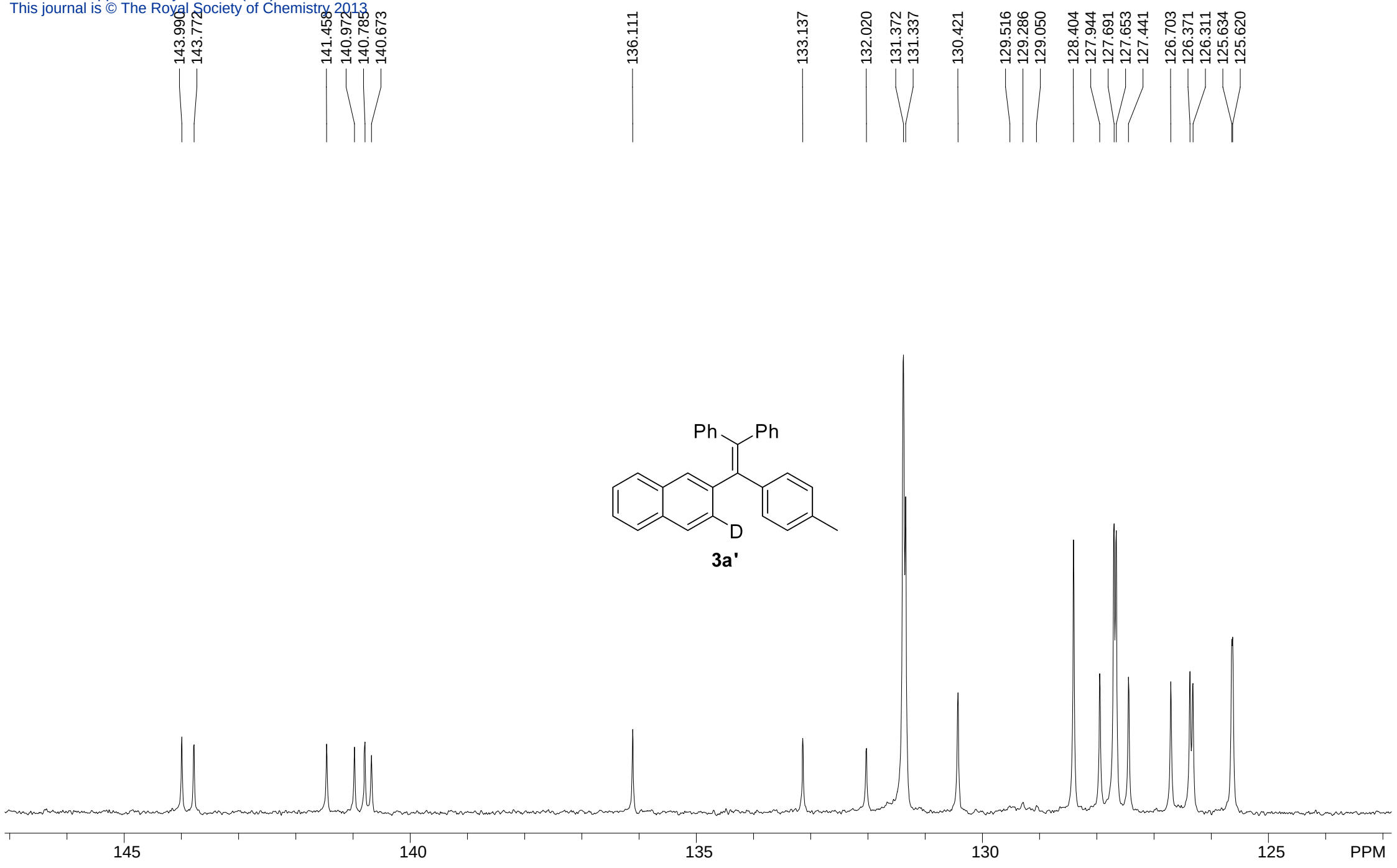
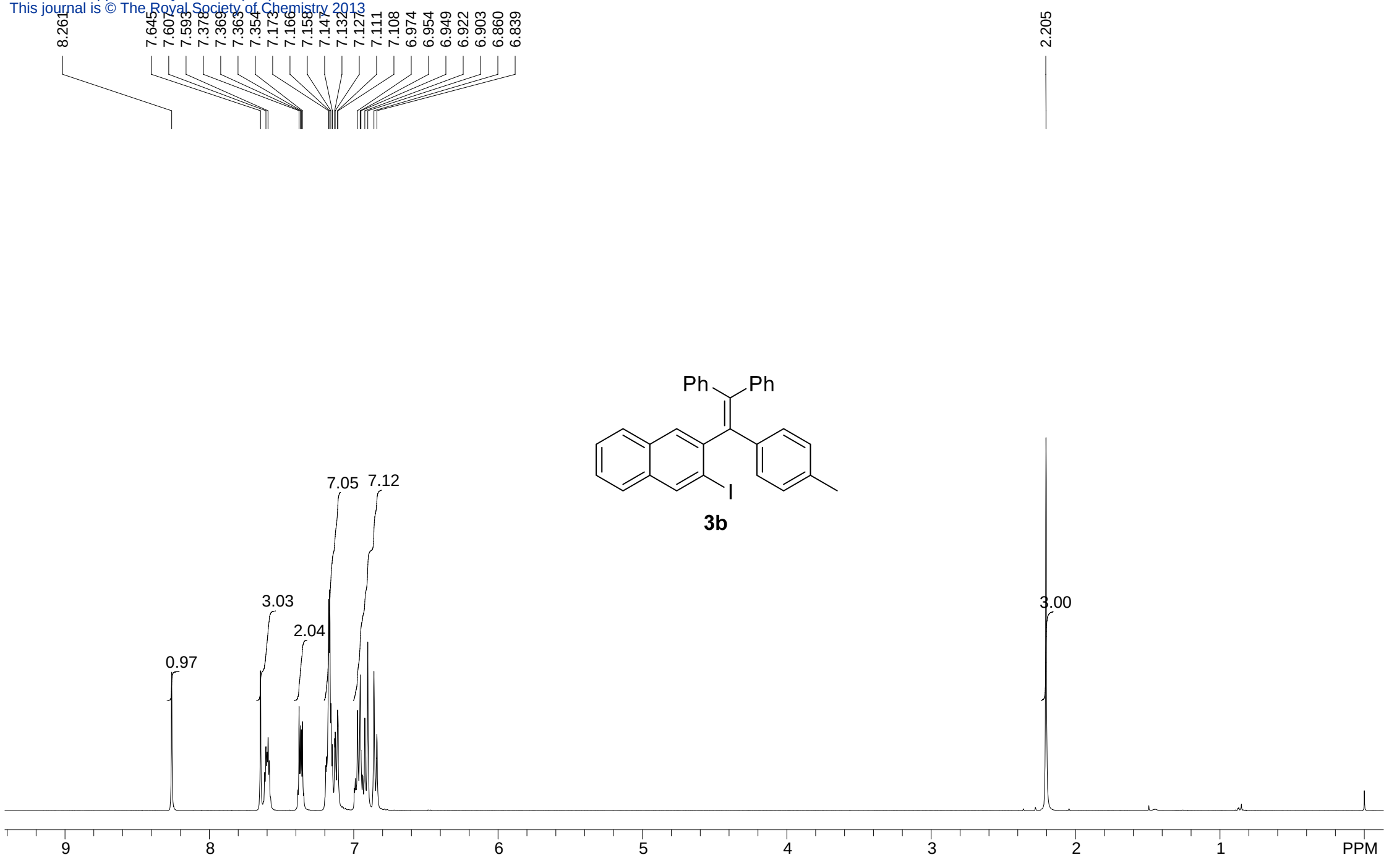
77.000
76.676
21.181

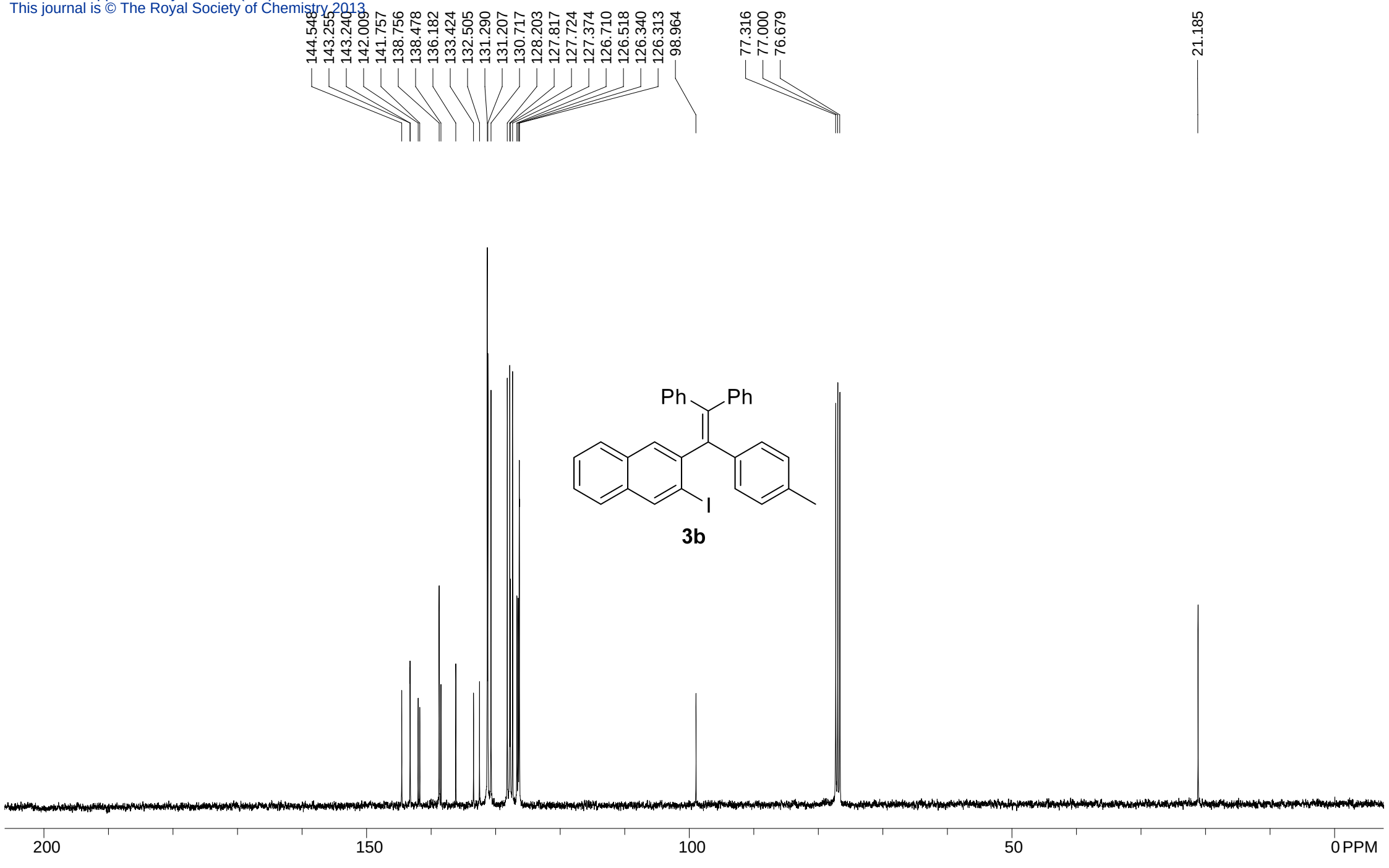


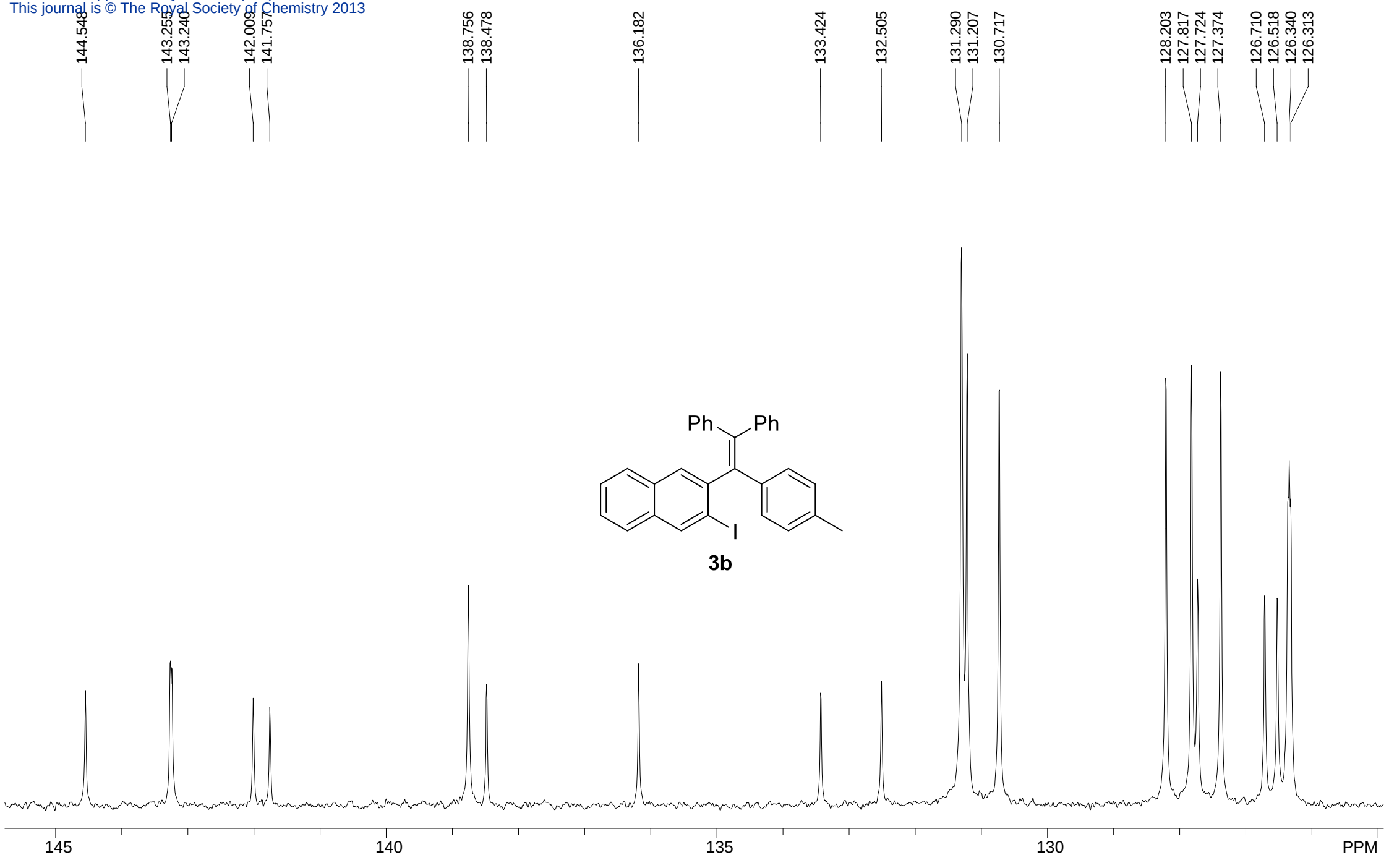
3a'

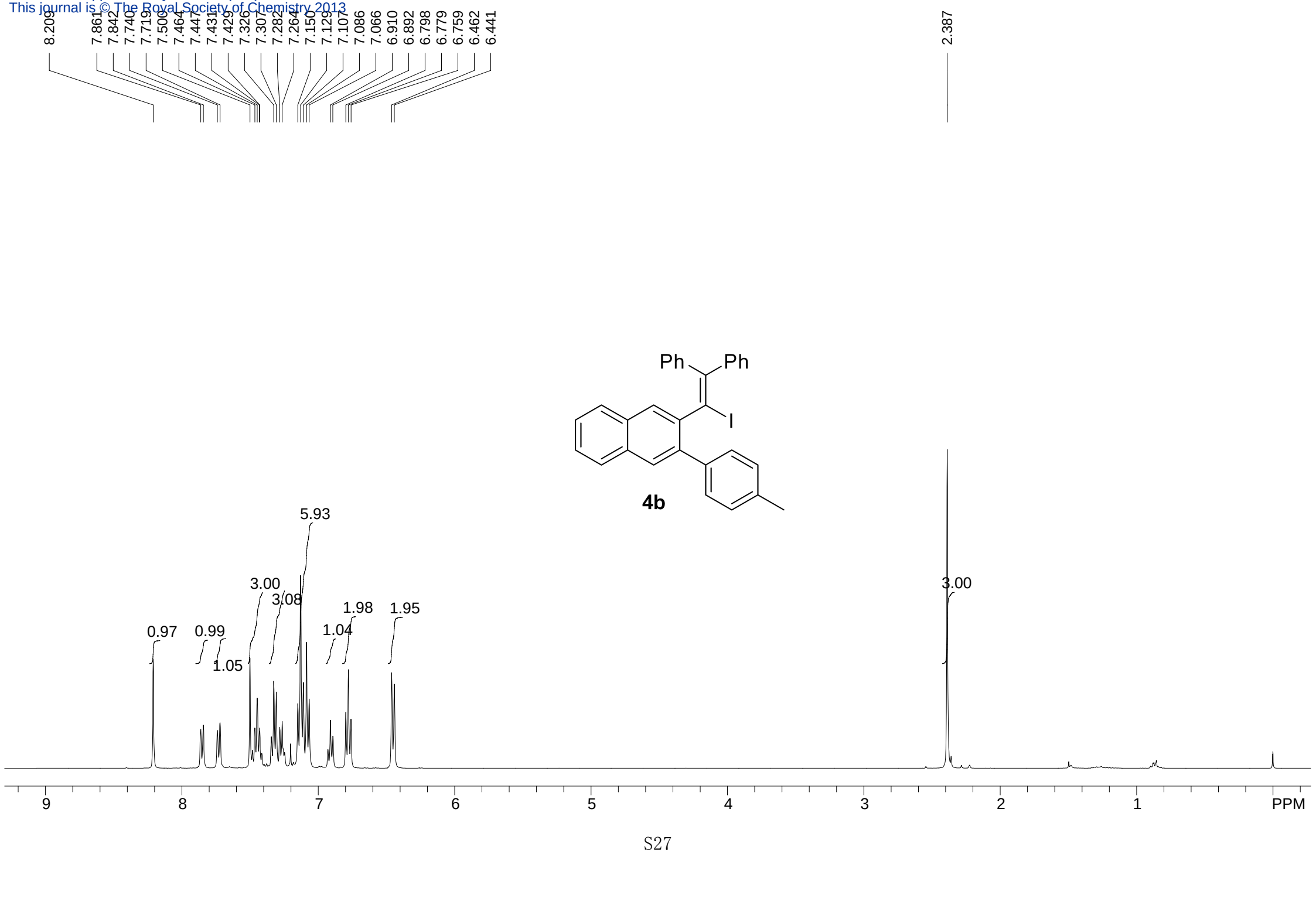
200
150
100
50
PPM

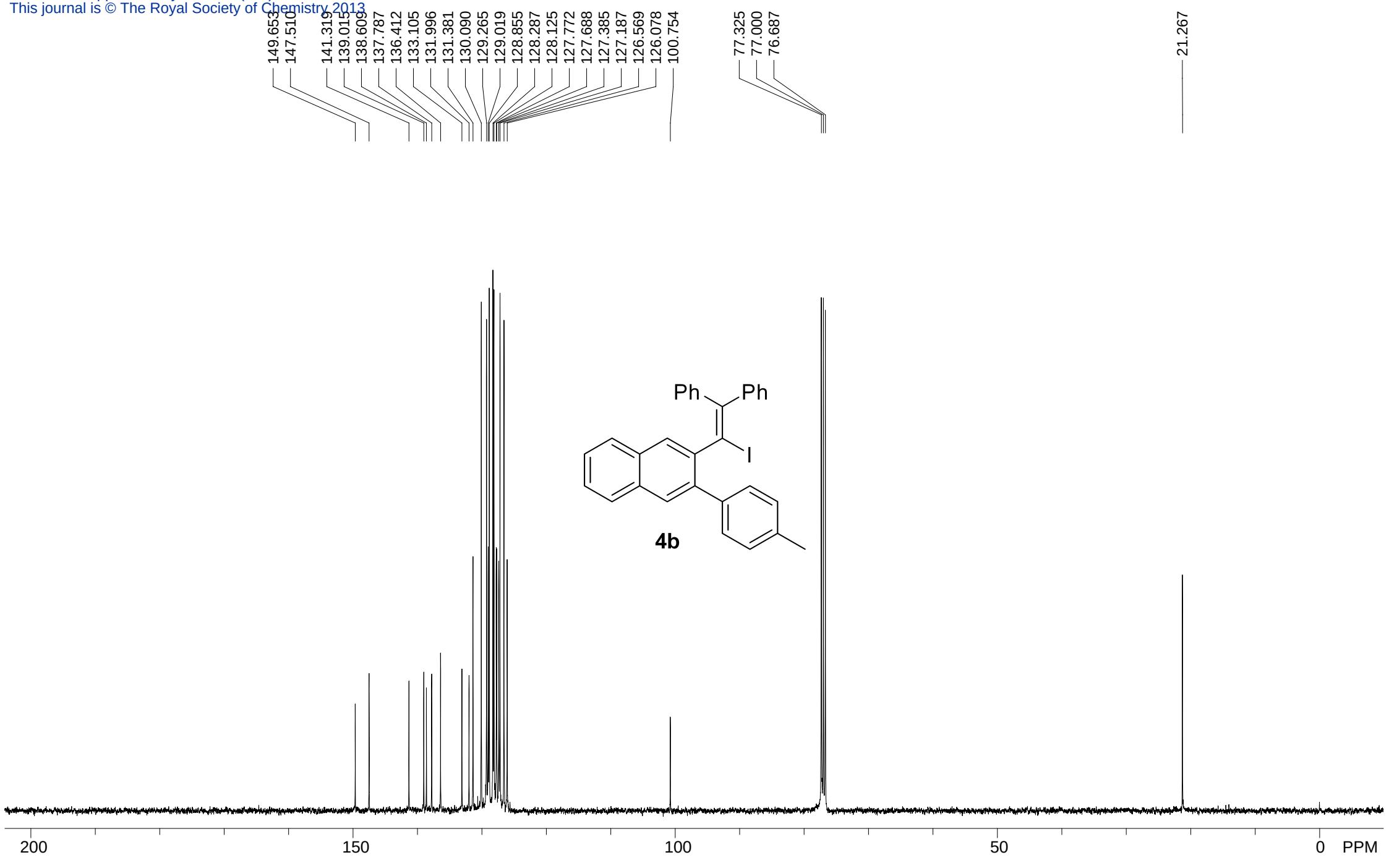


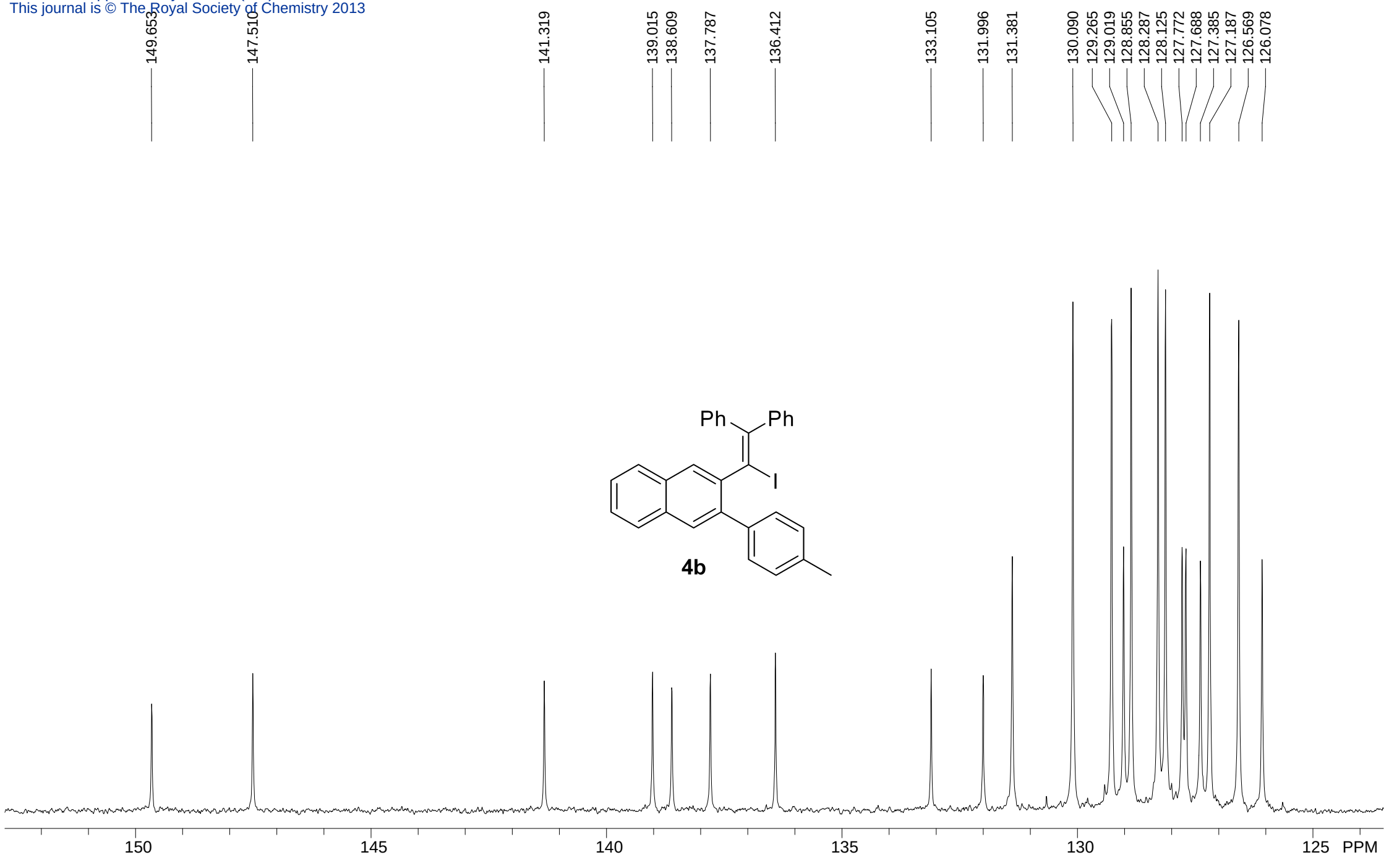


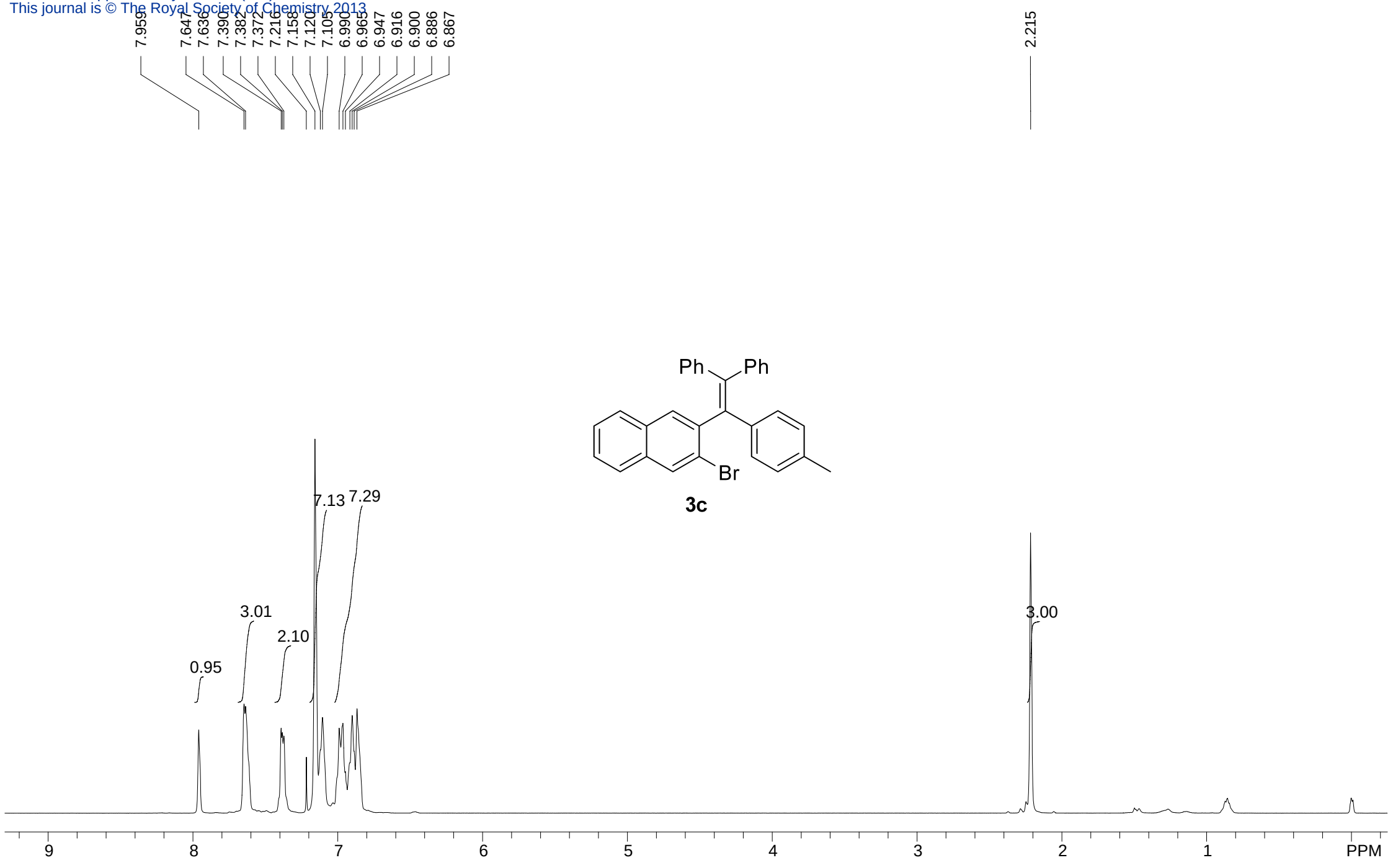


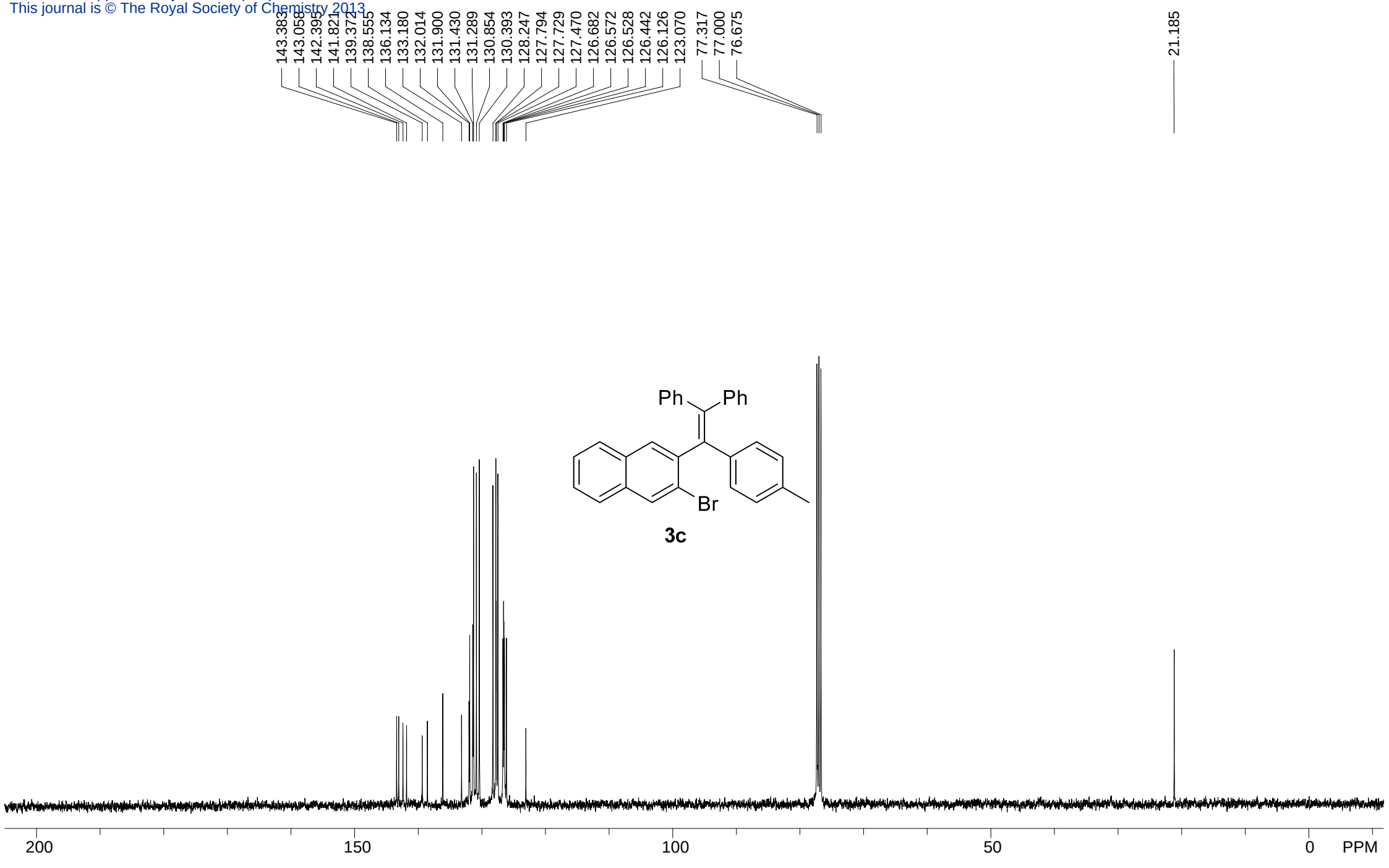












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126.682
126.572
126.528
126.442
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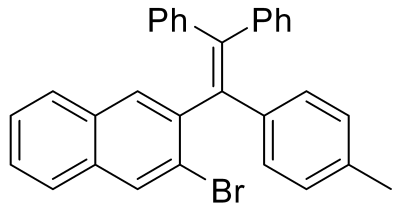

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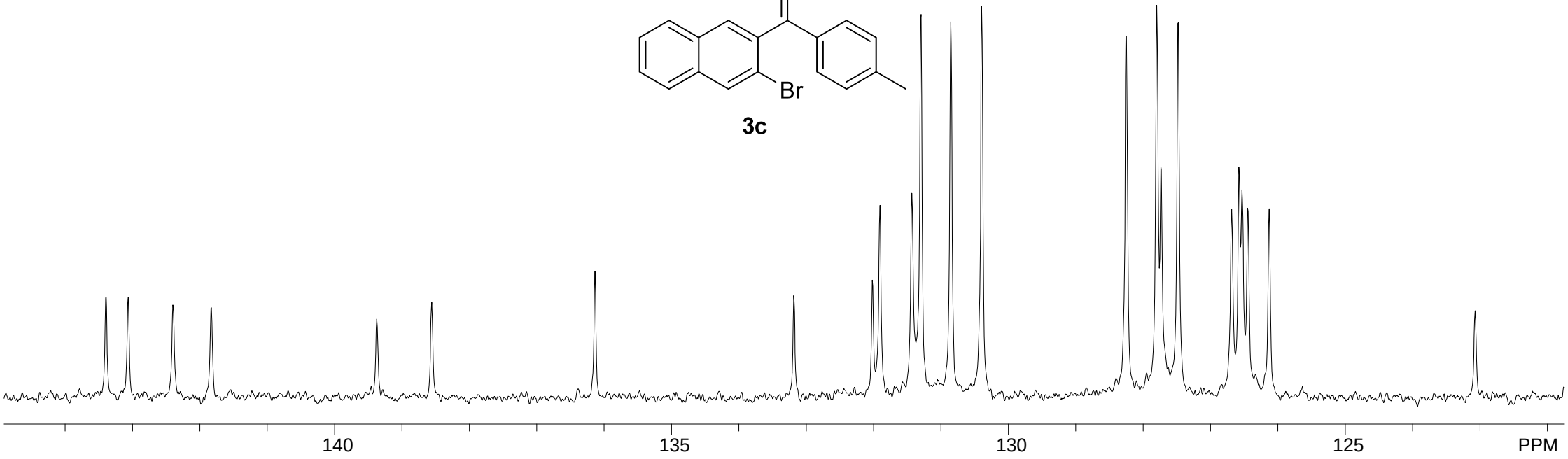

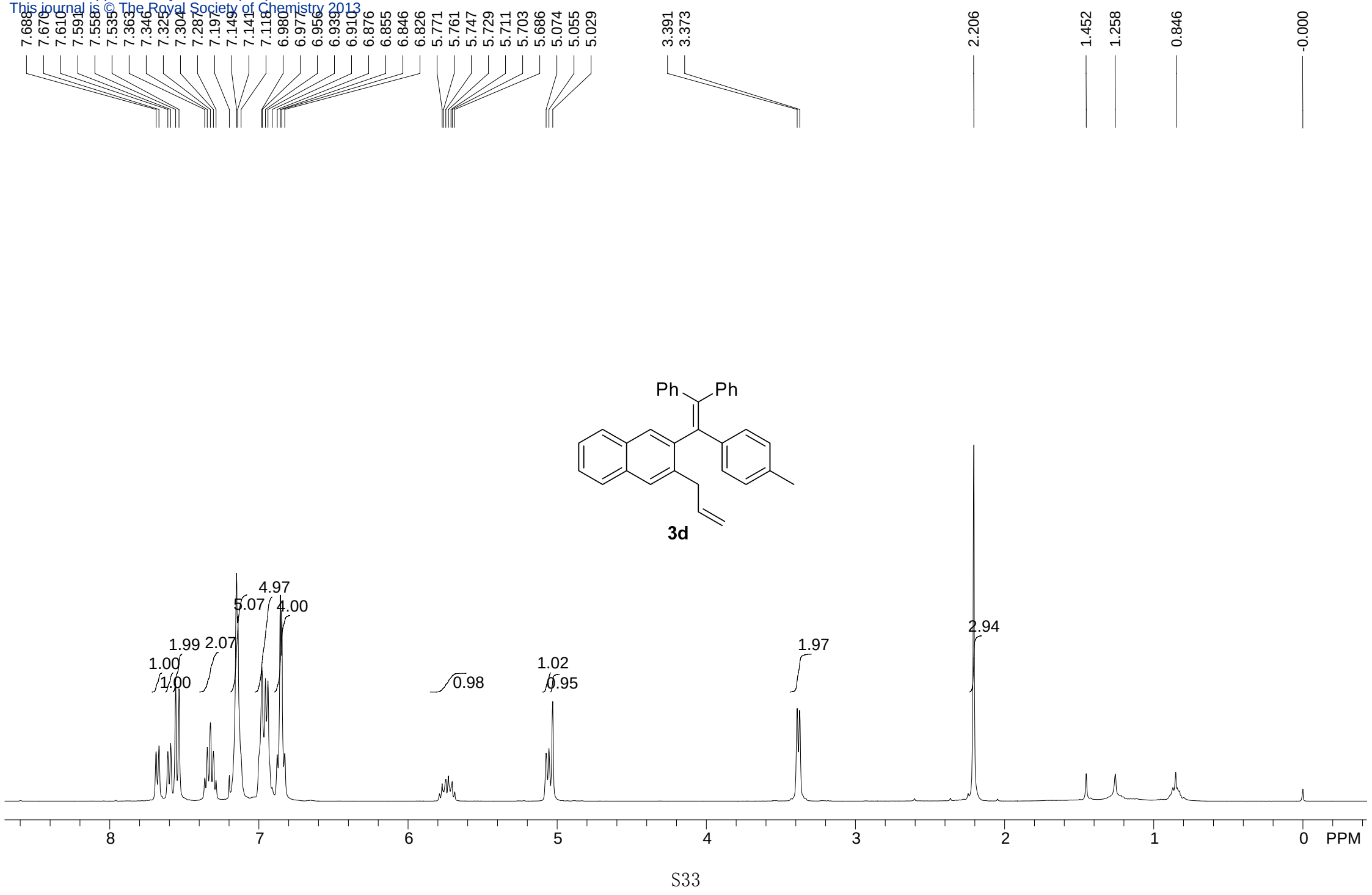

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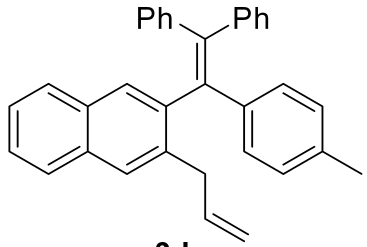

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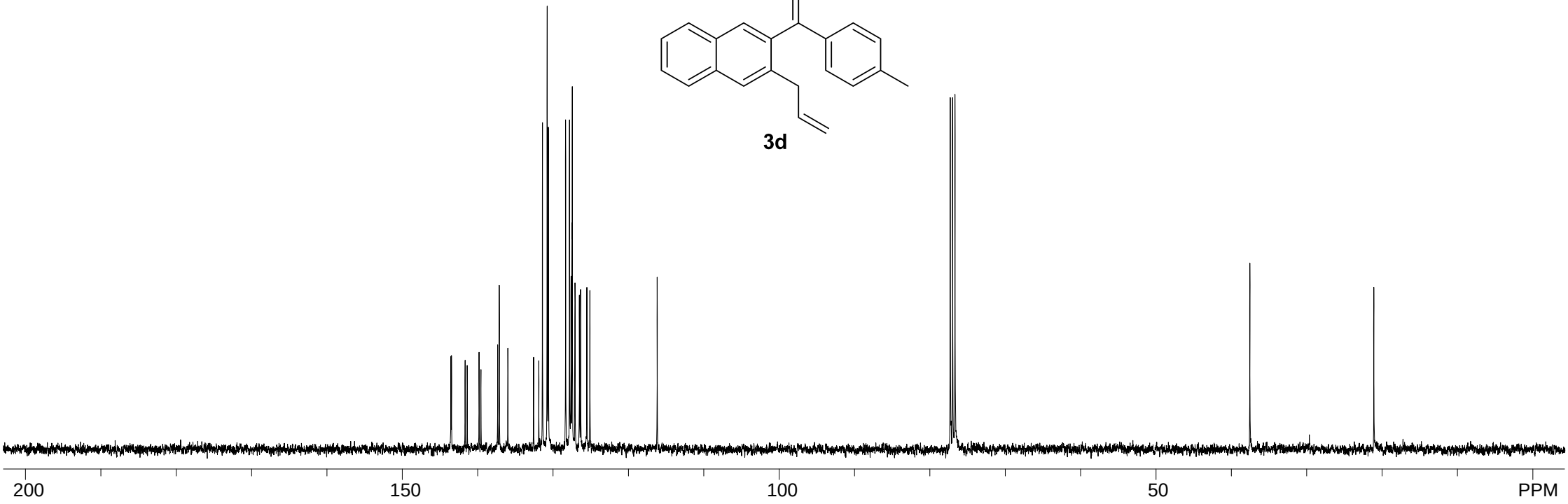

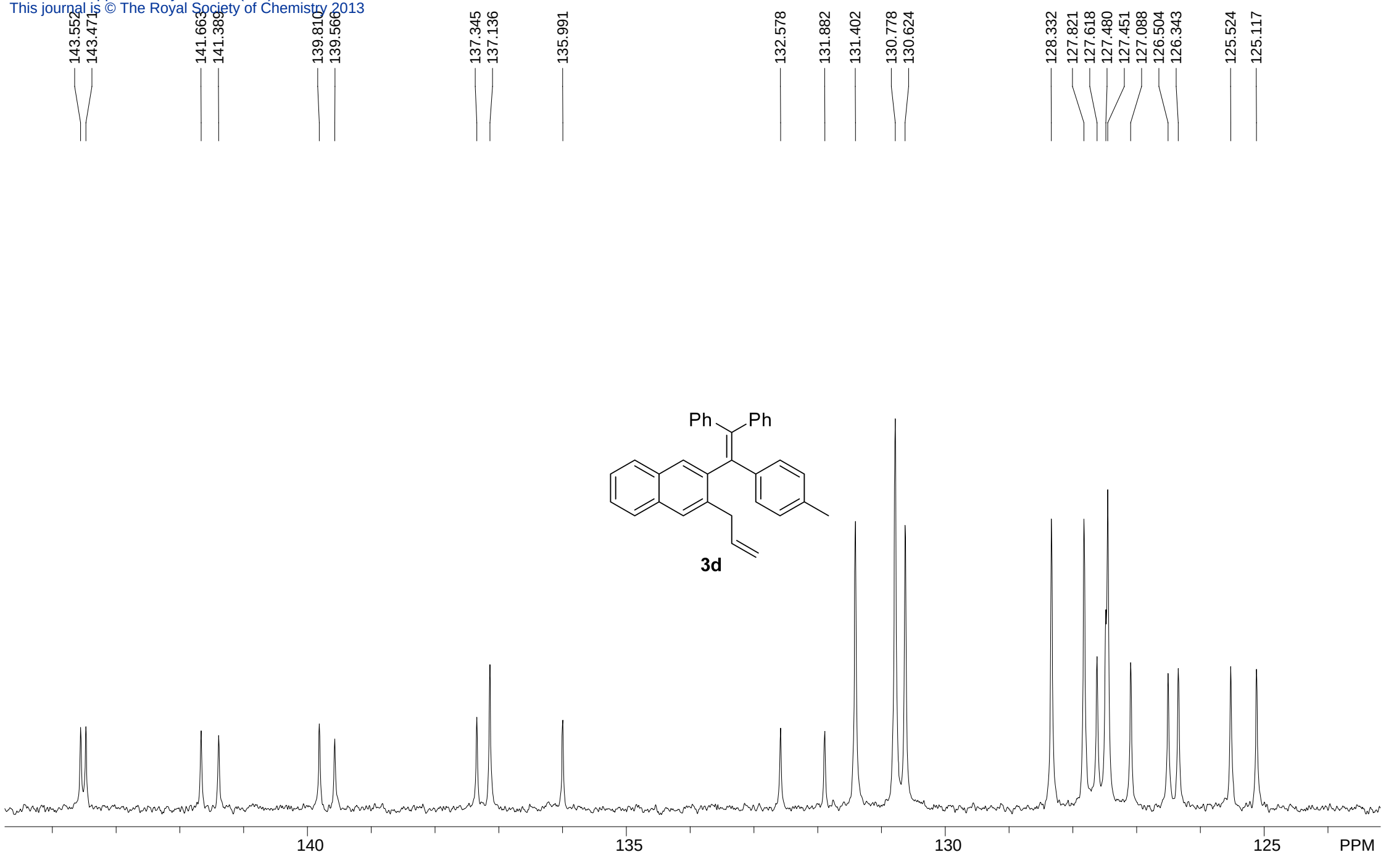

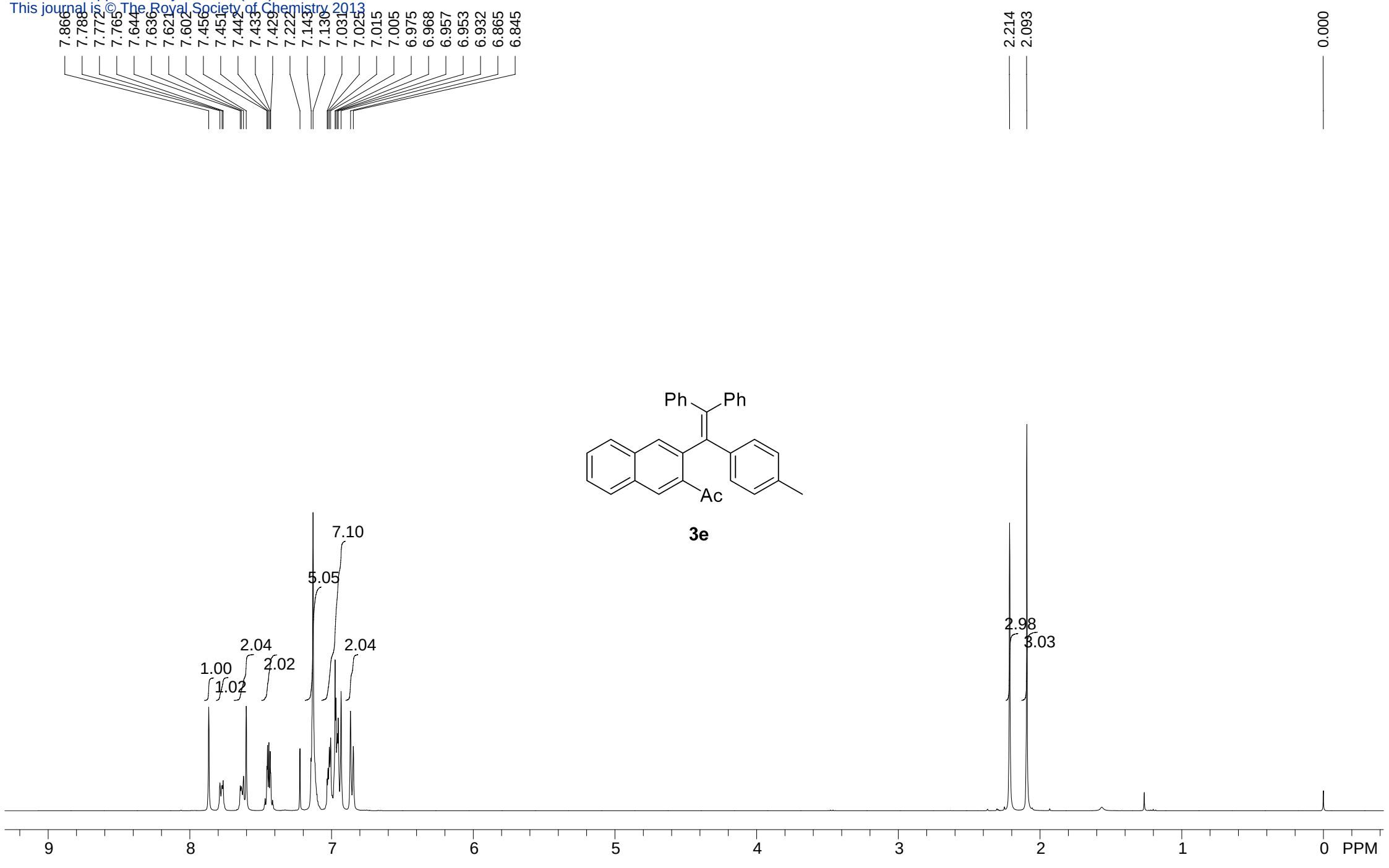

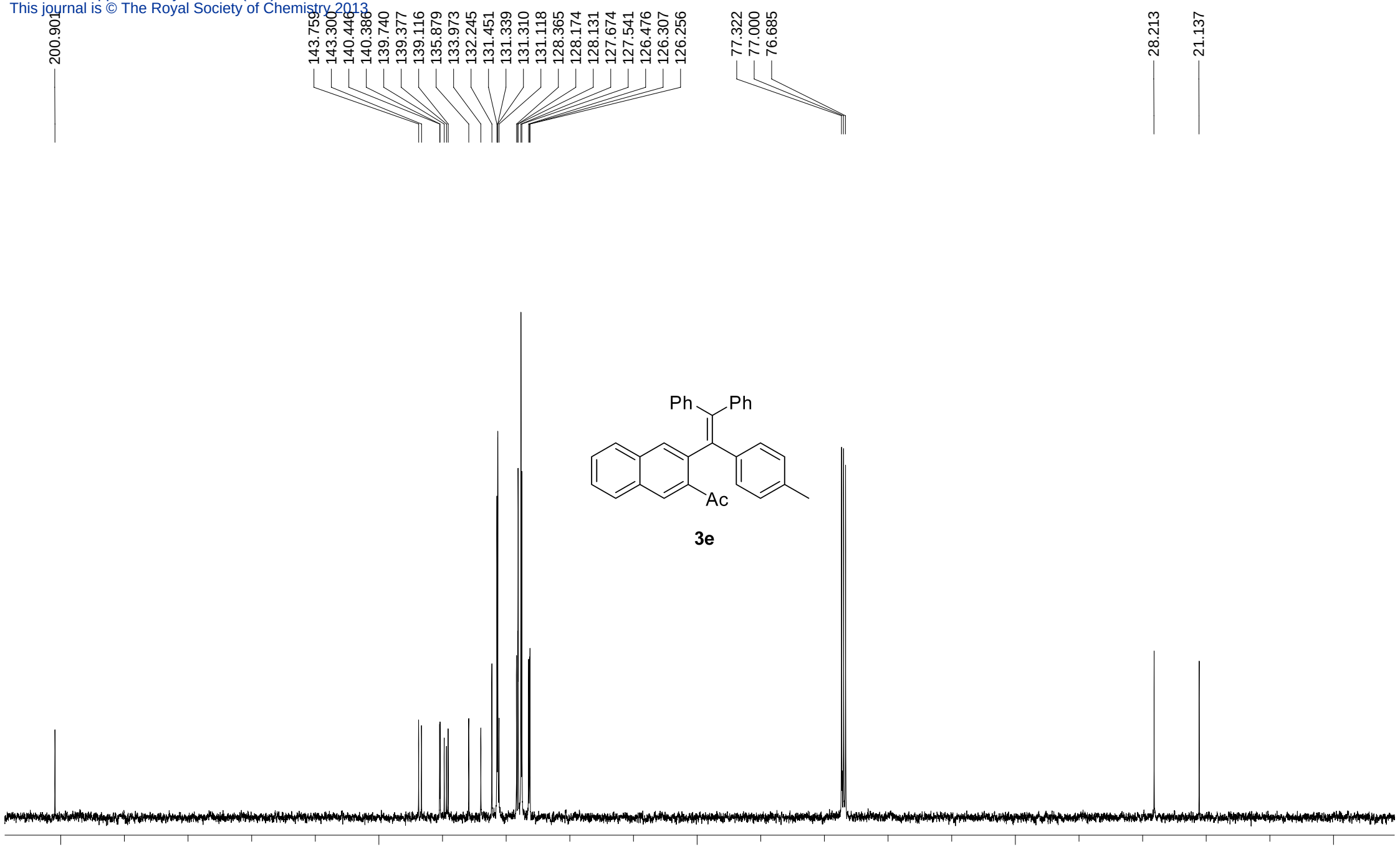

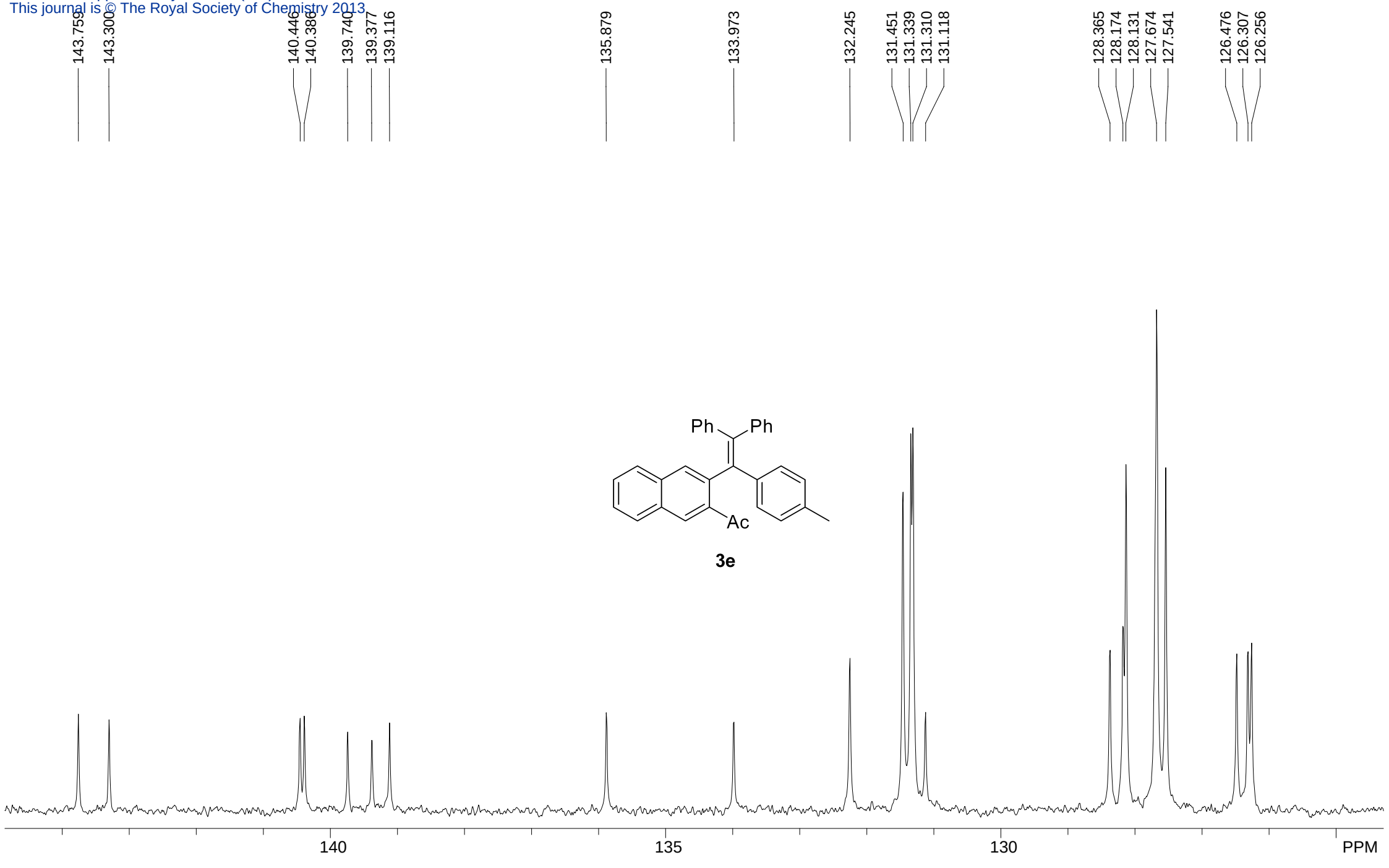

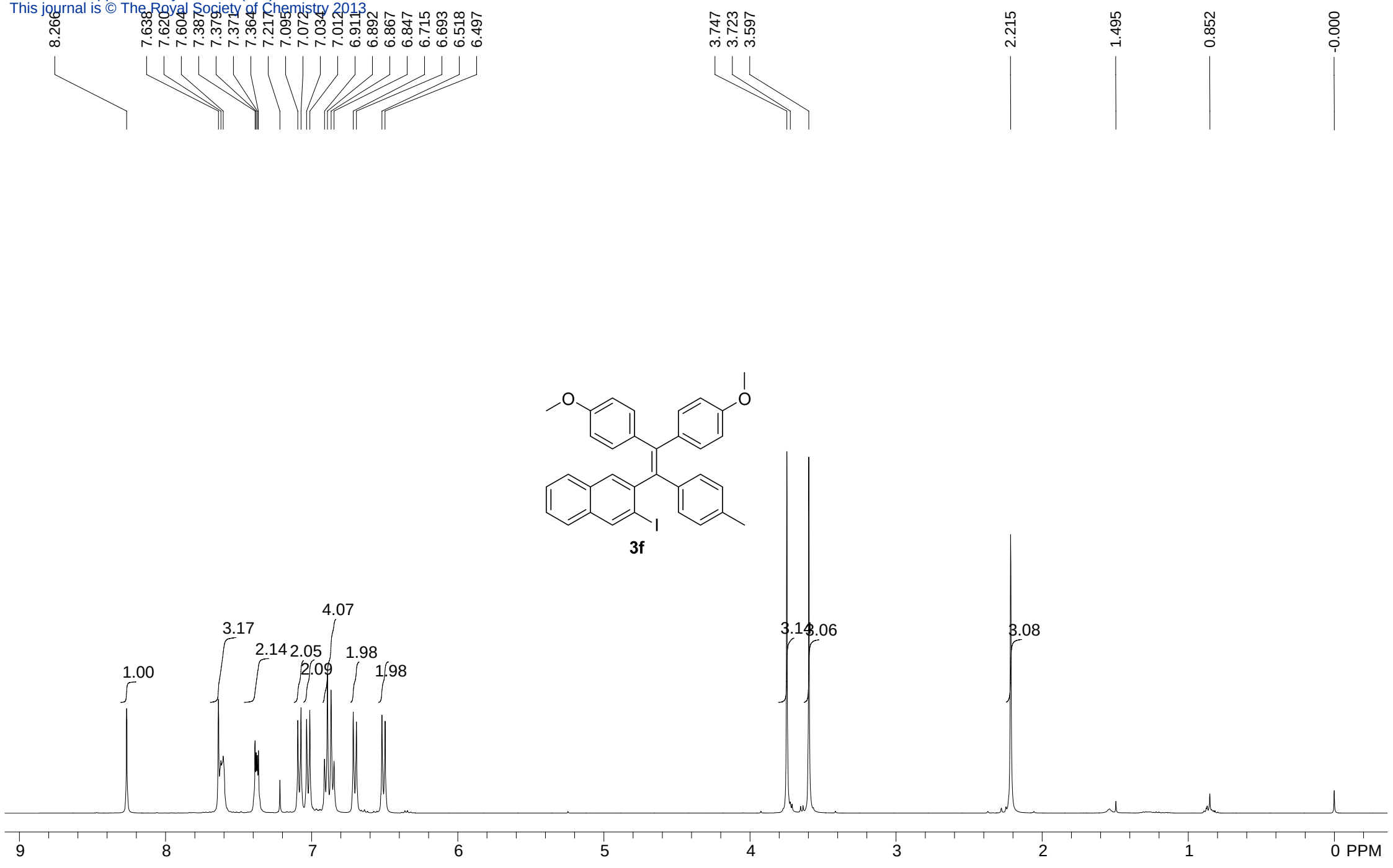

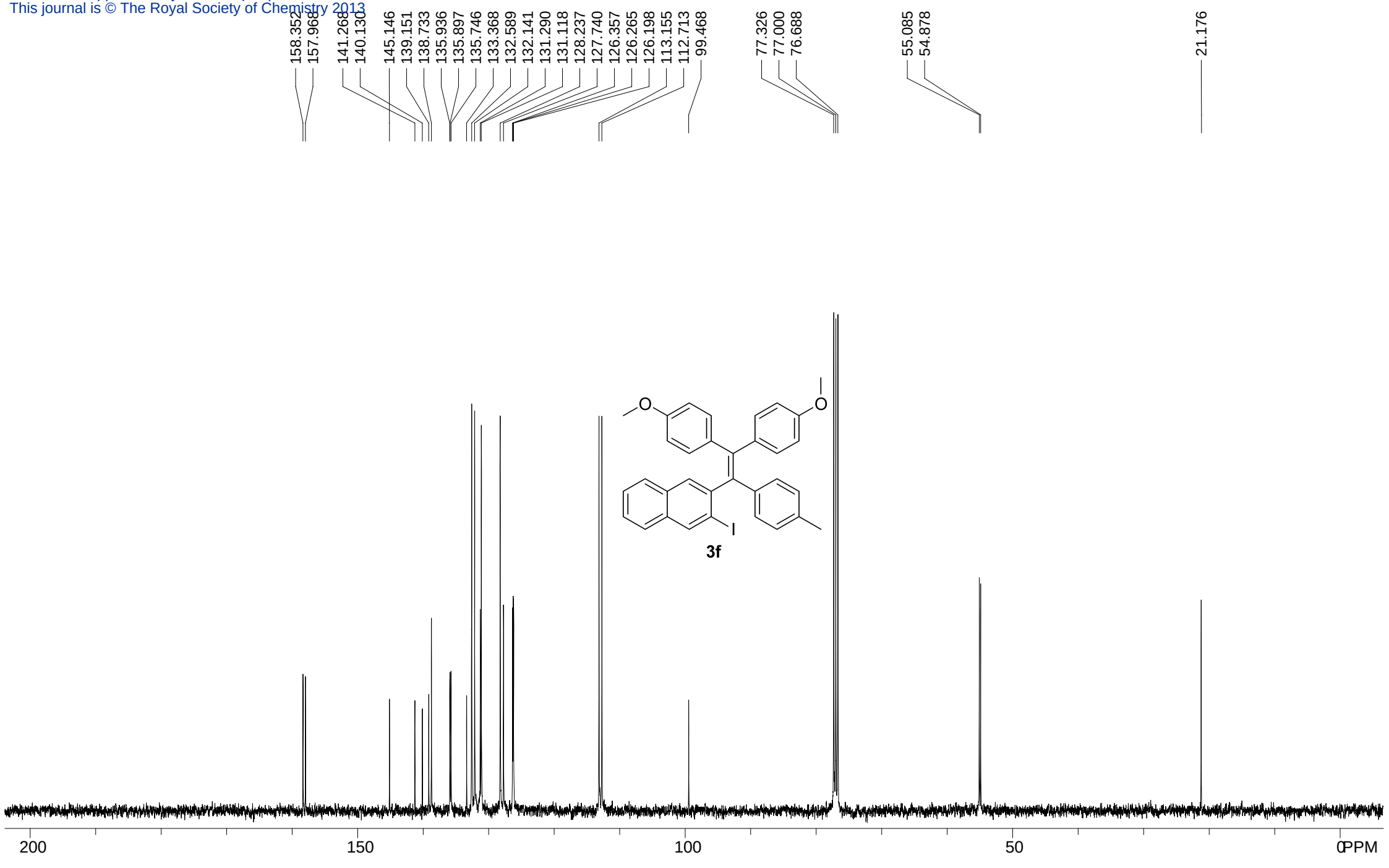

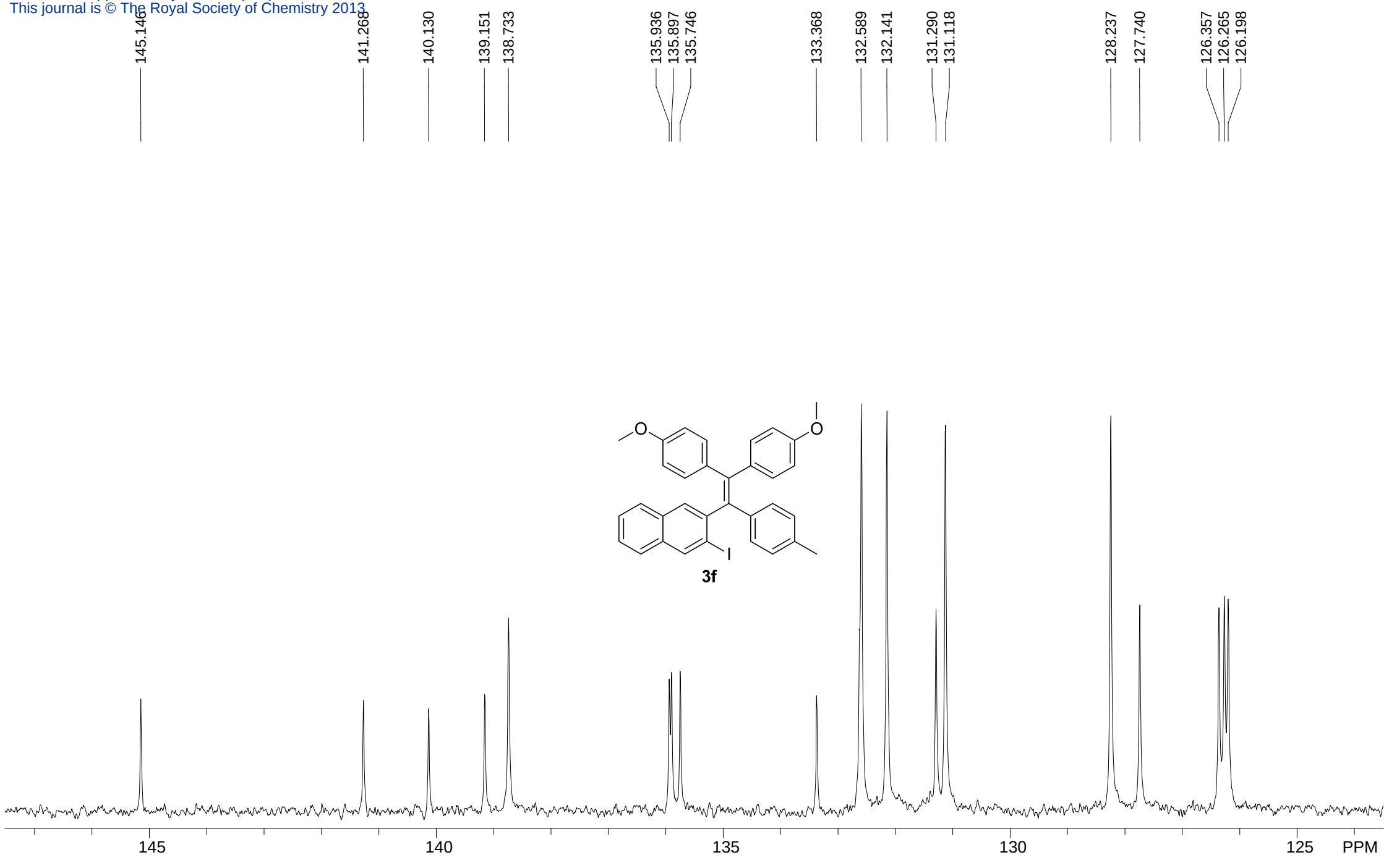

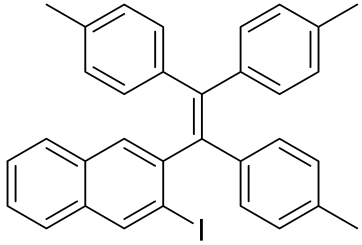

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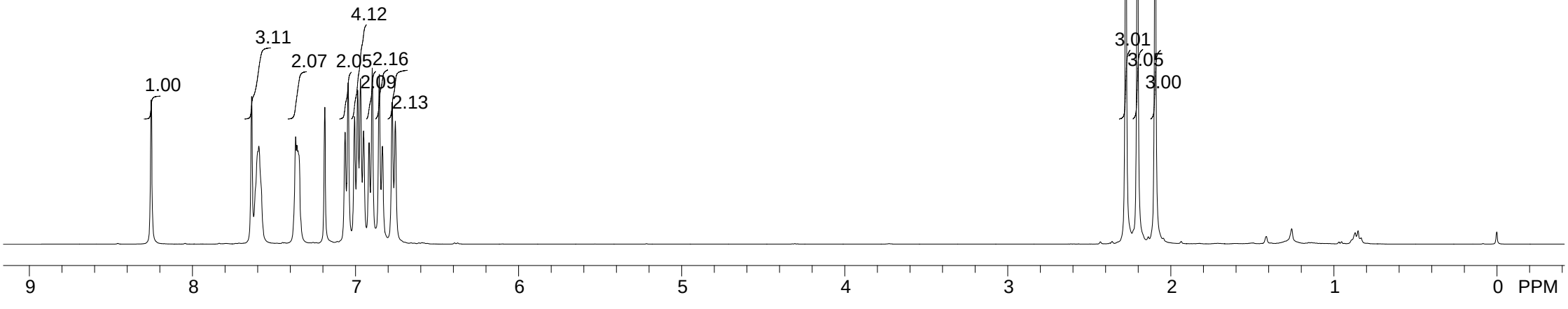

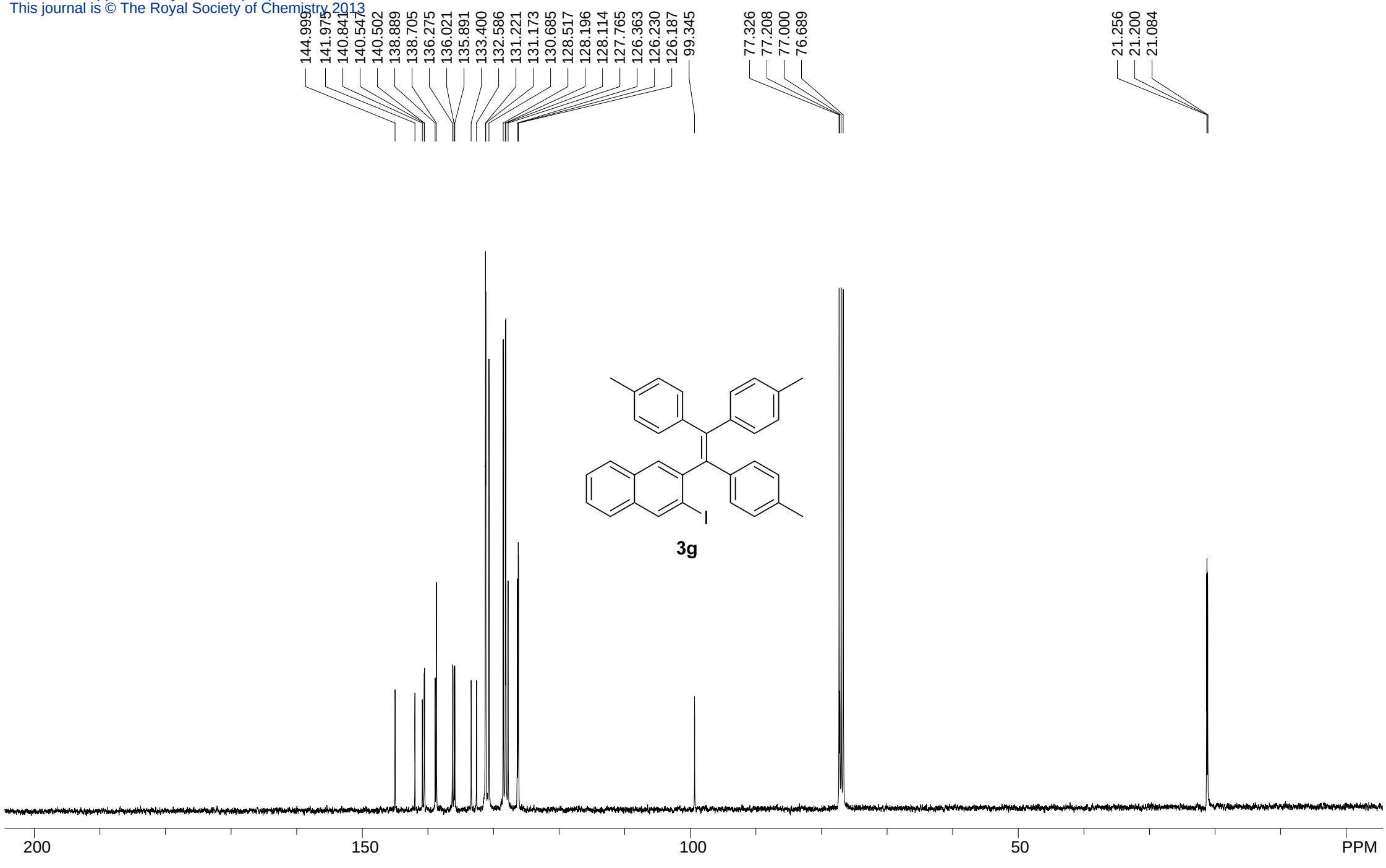

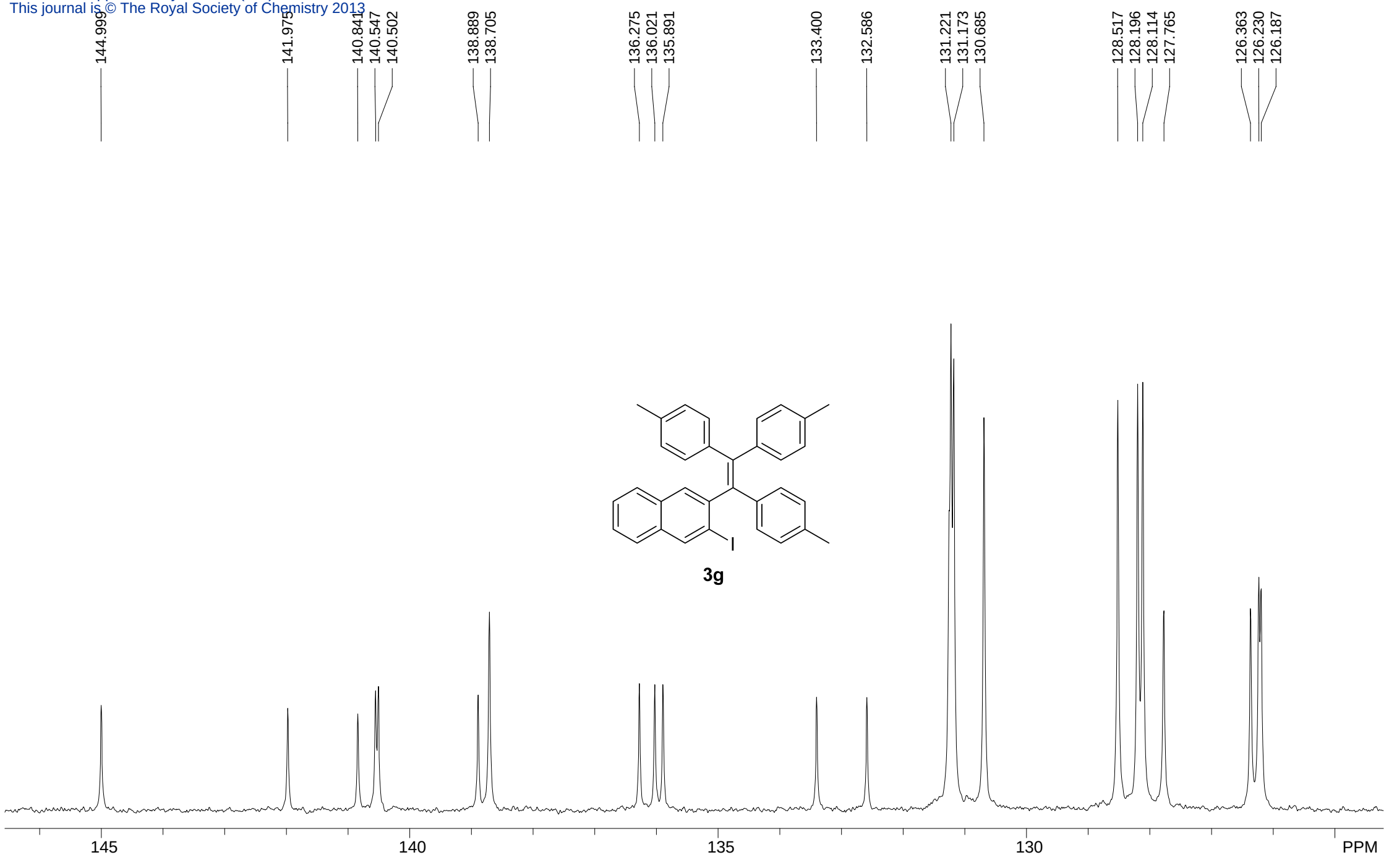

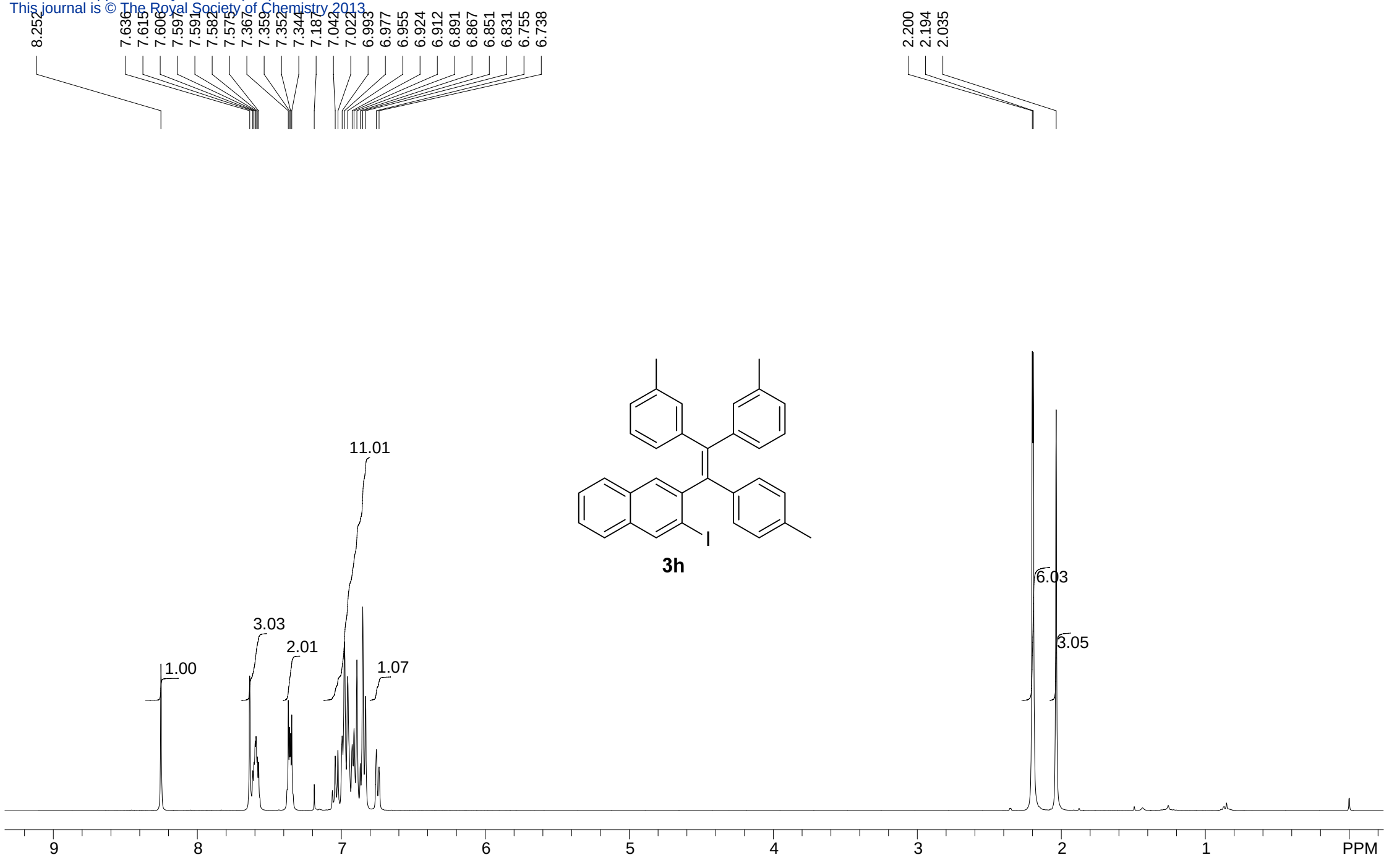

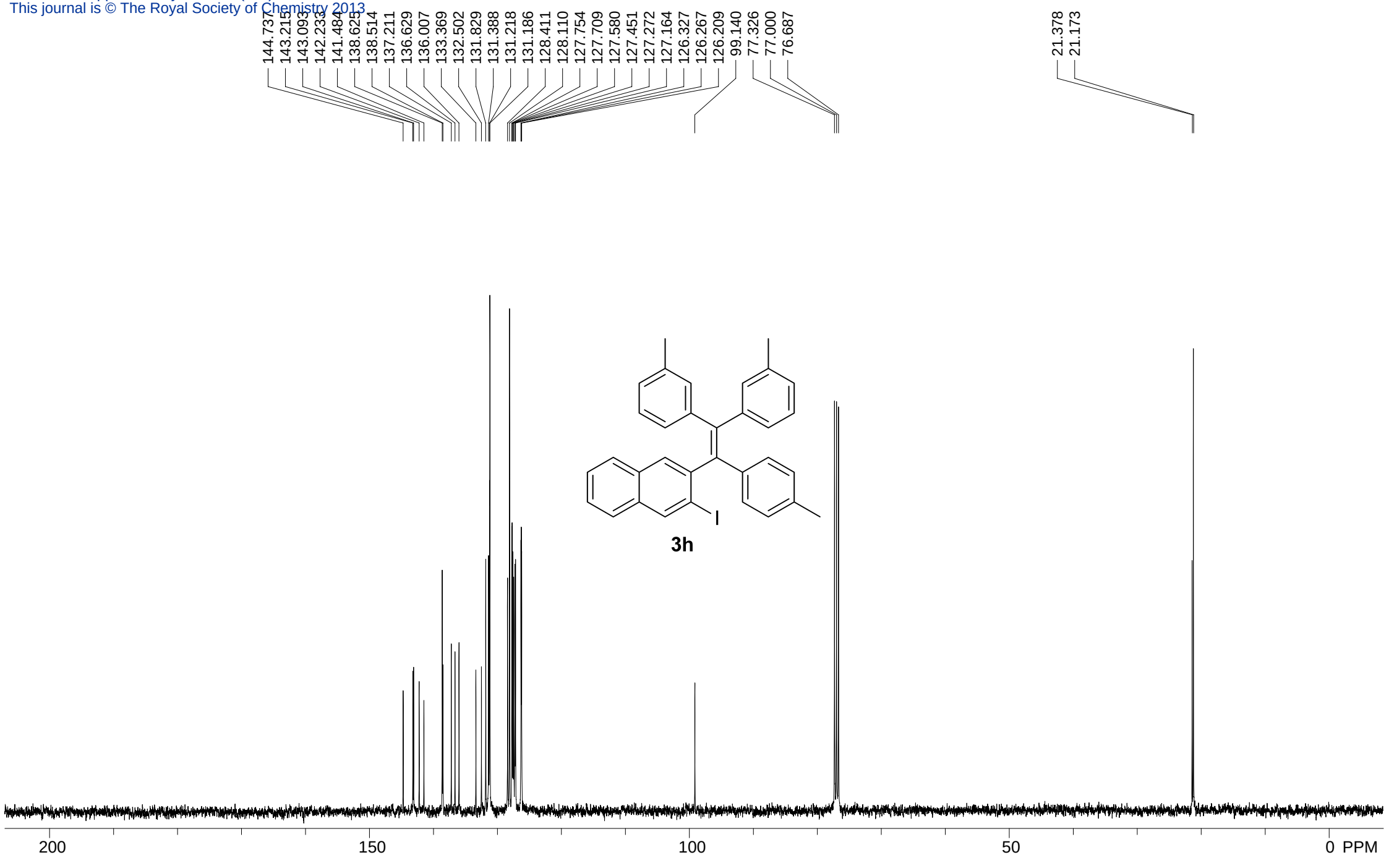

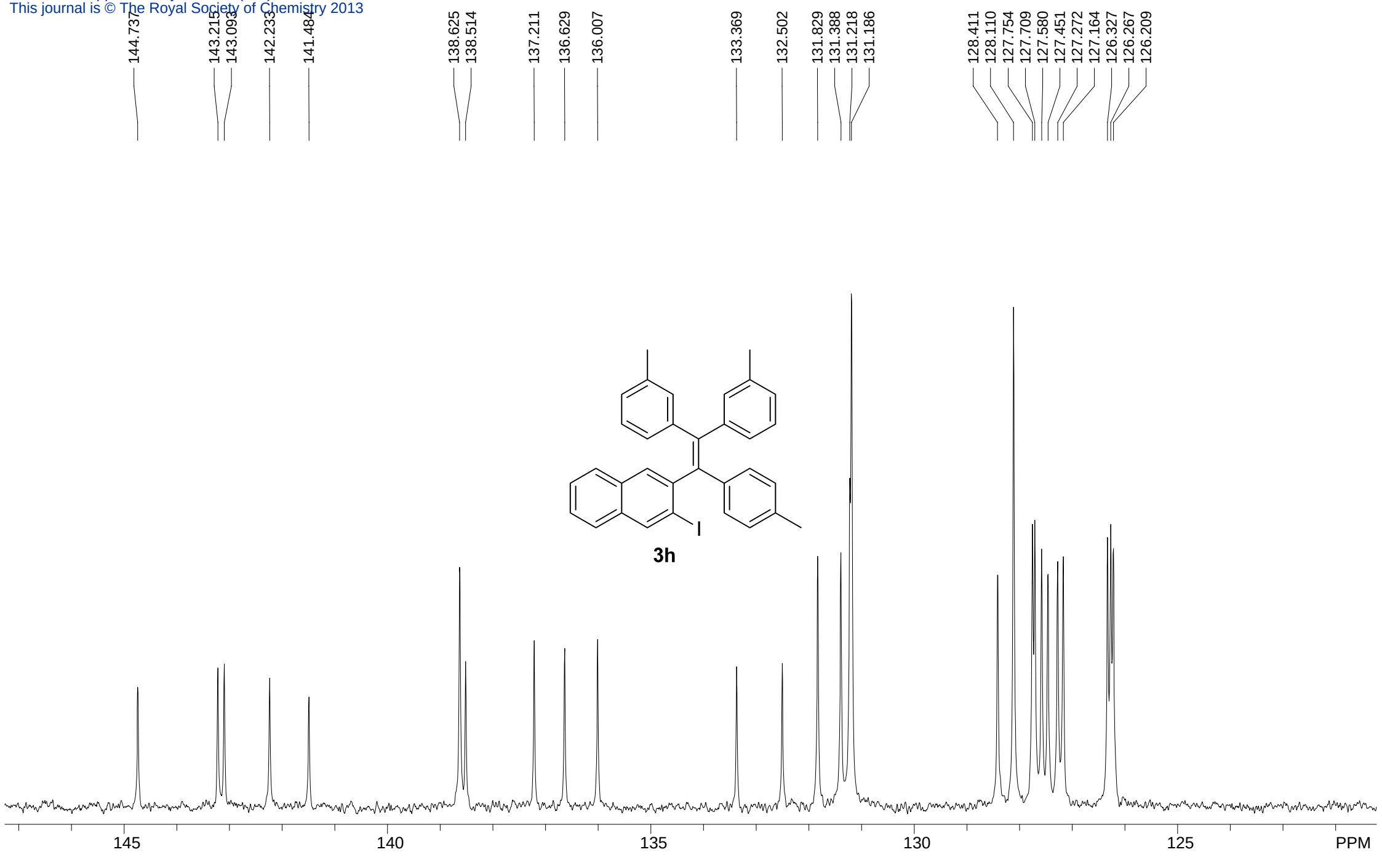

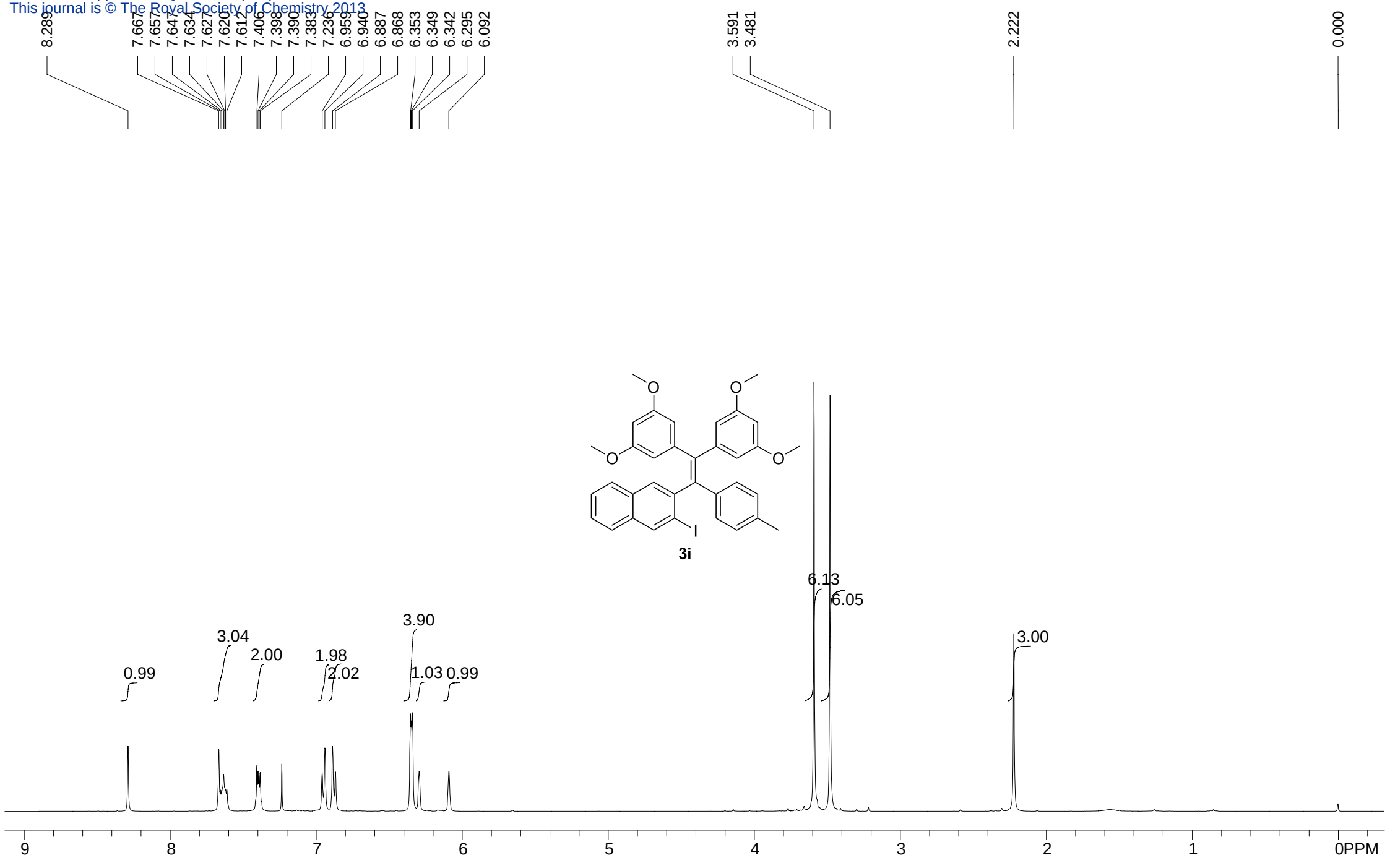

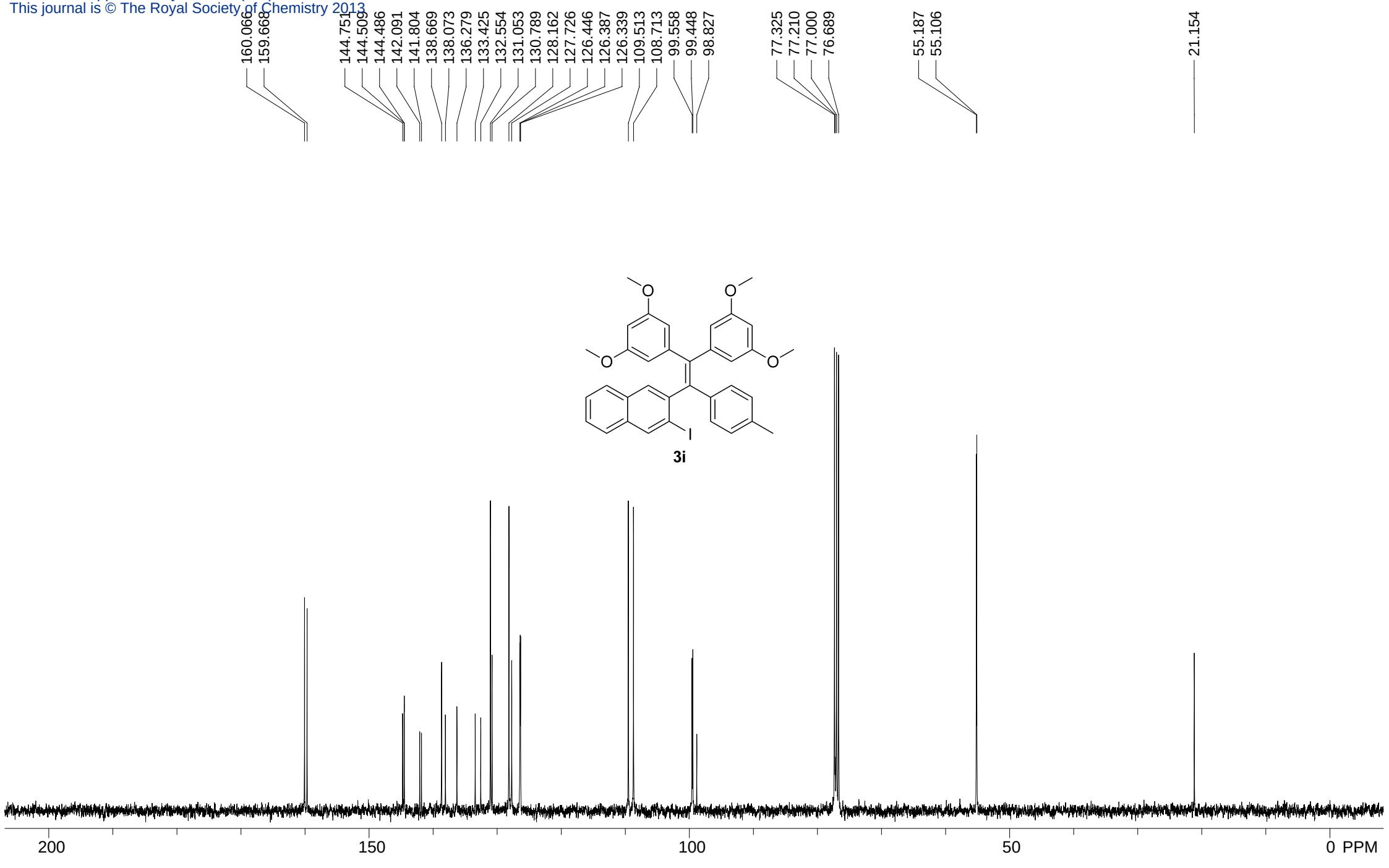

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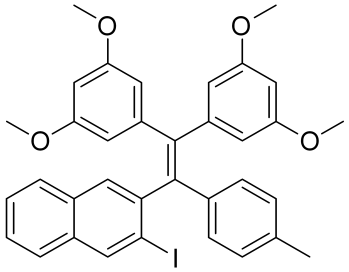

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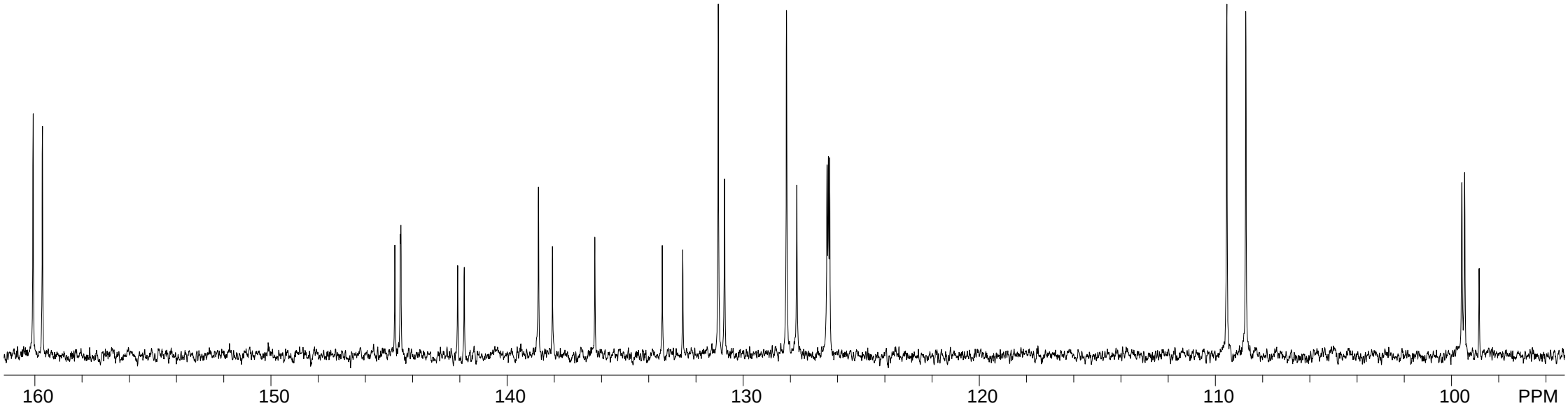

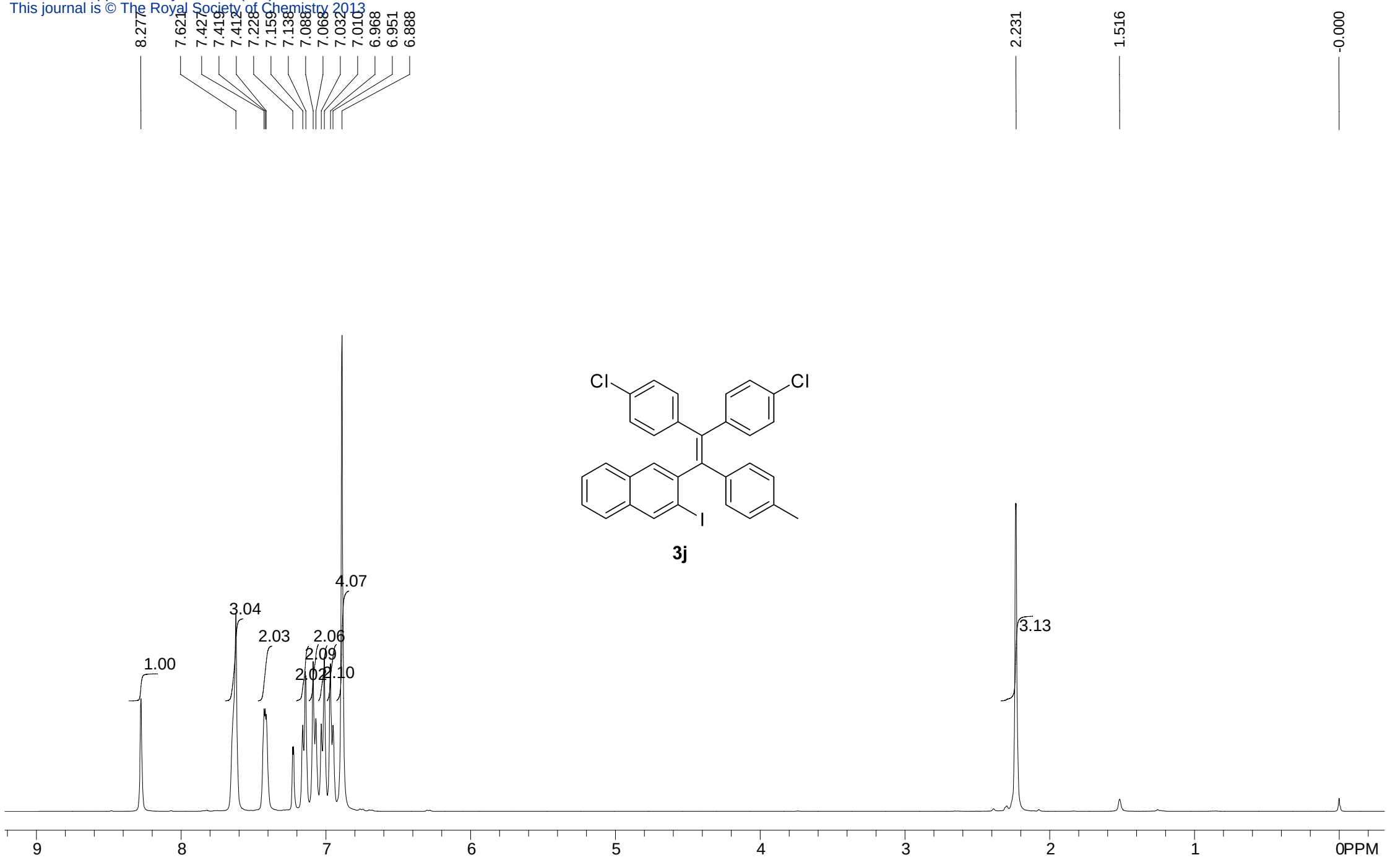

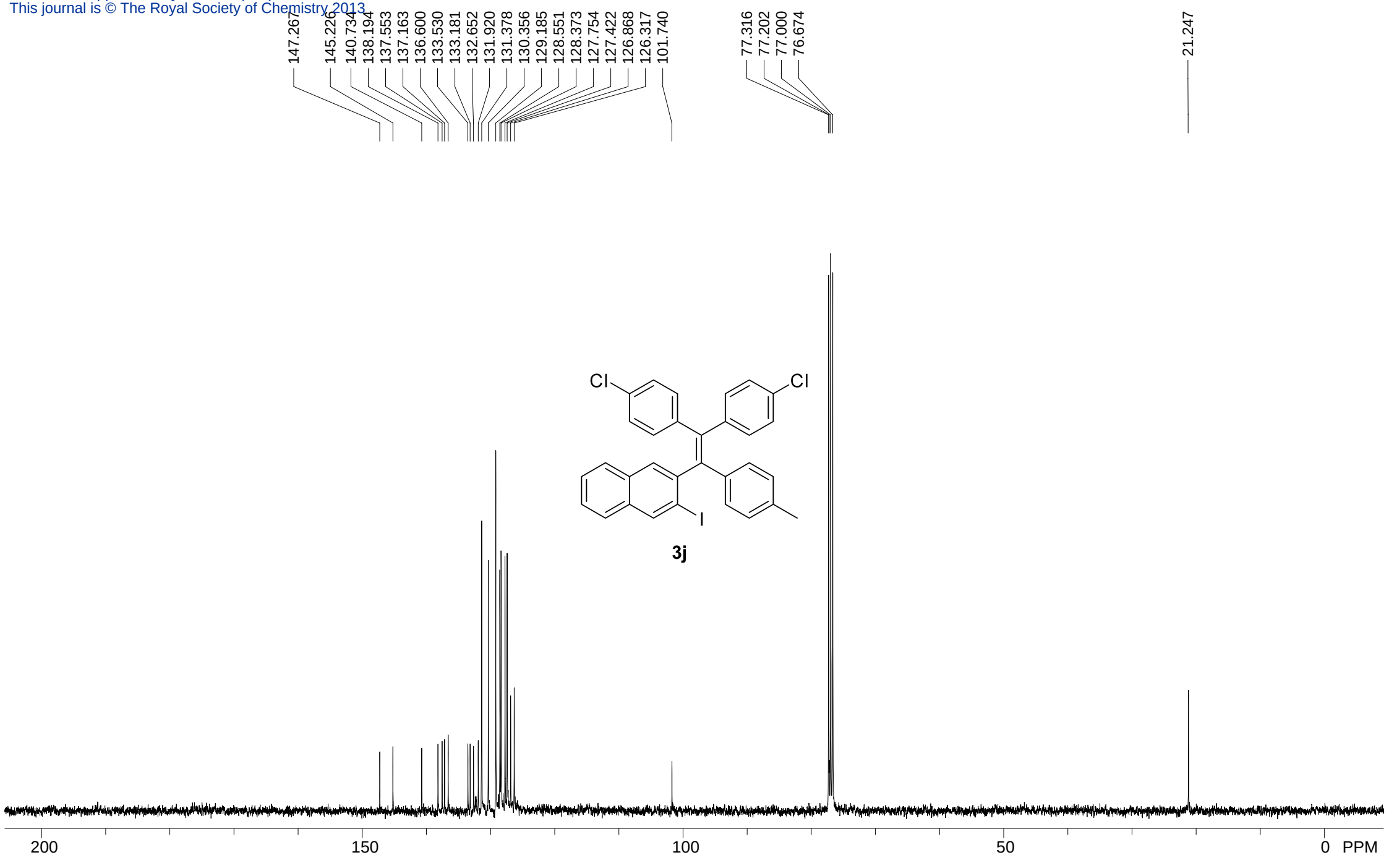

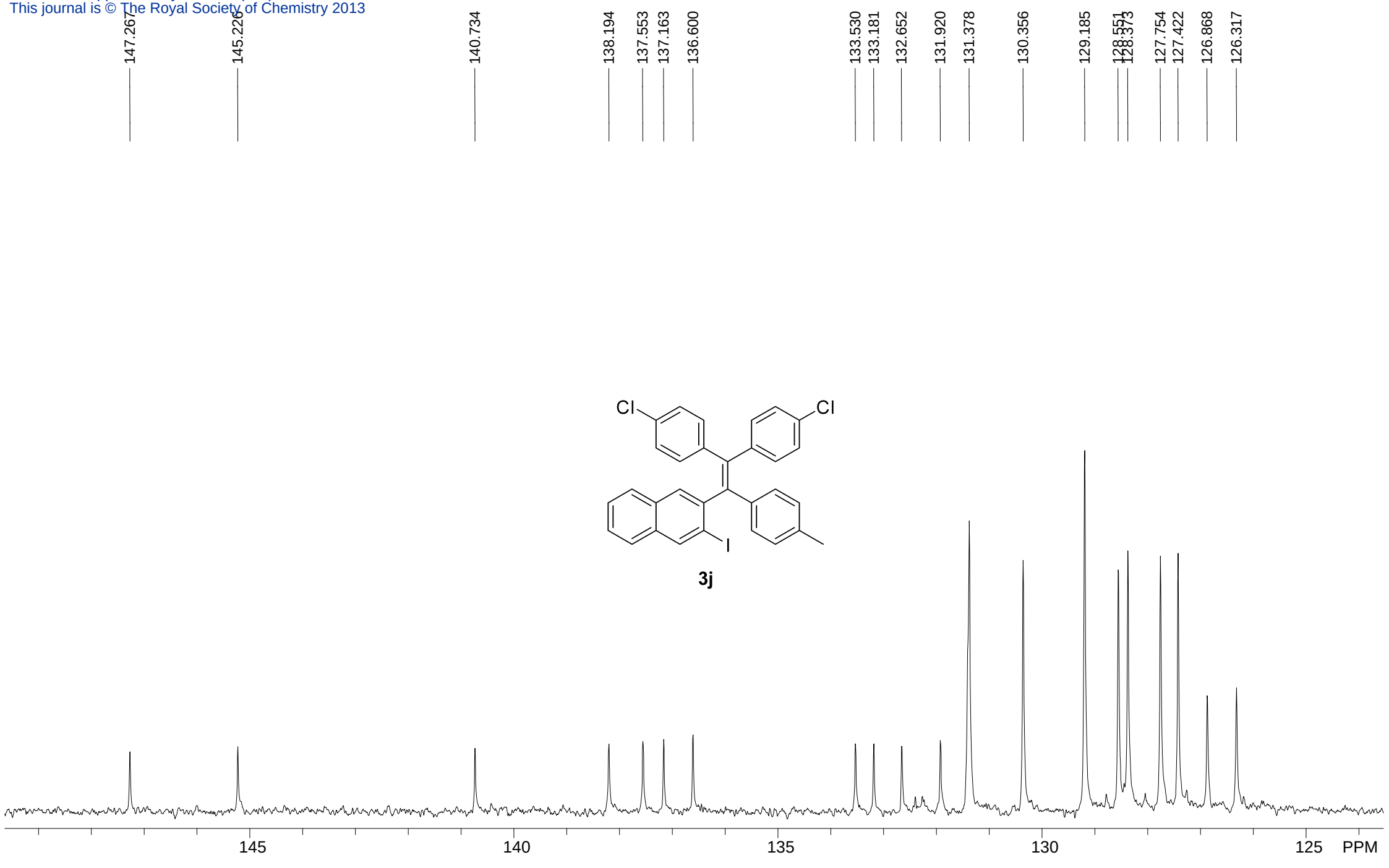

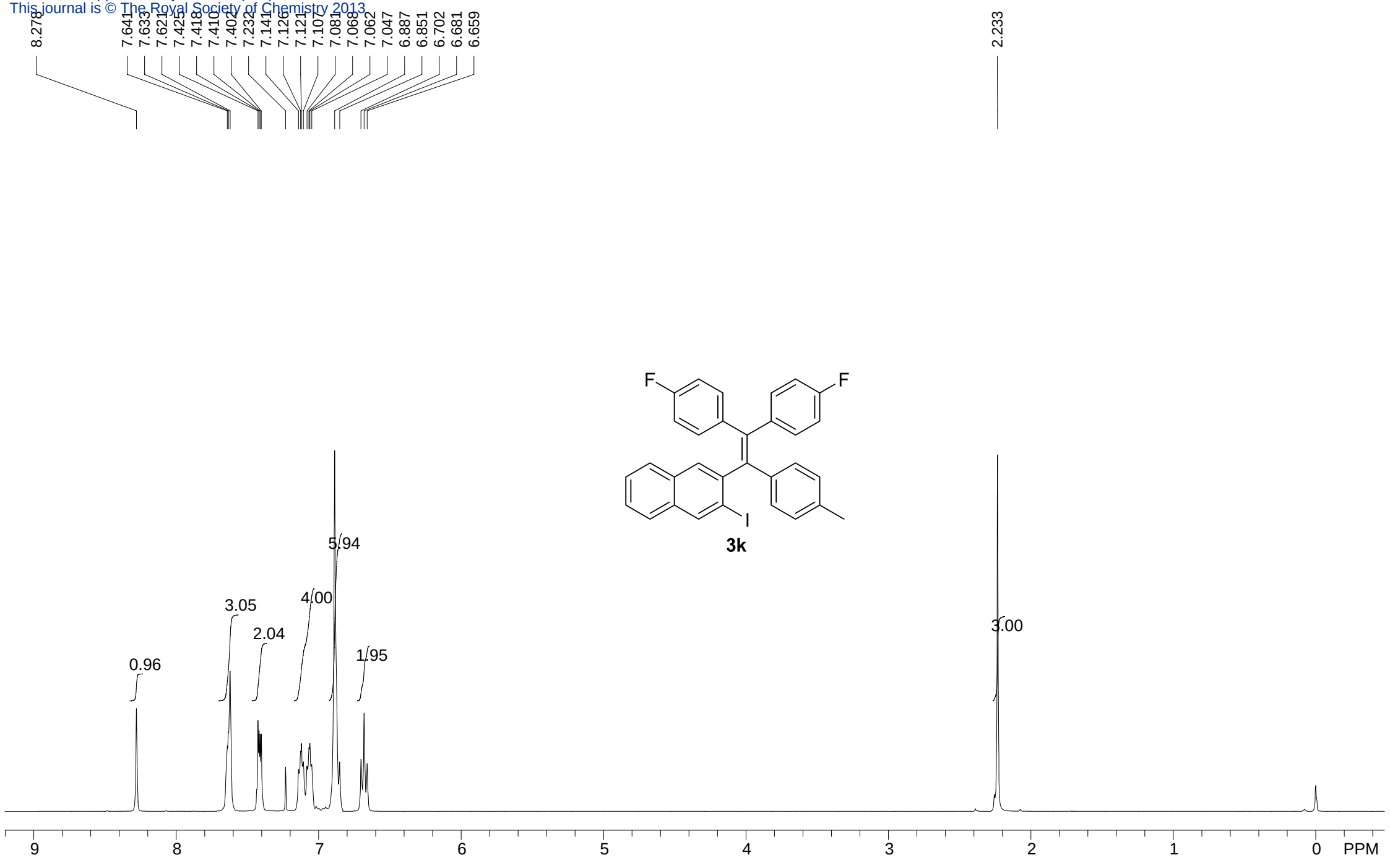

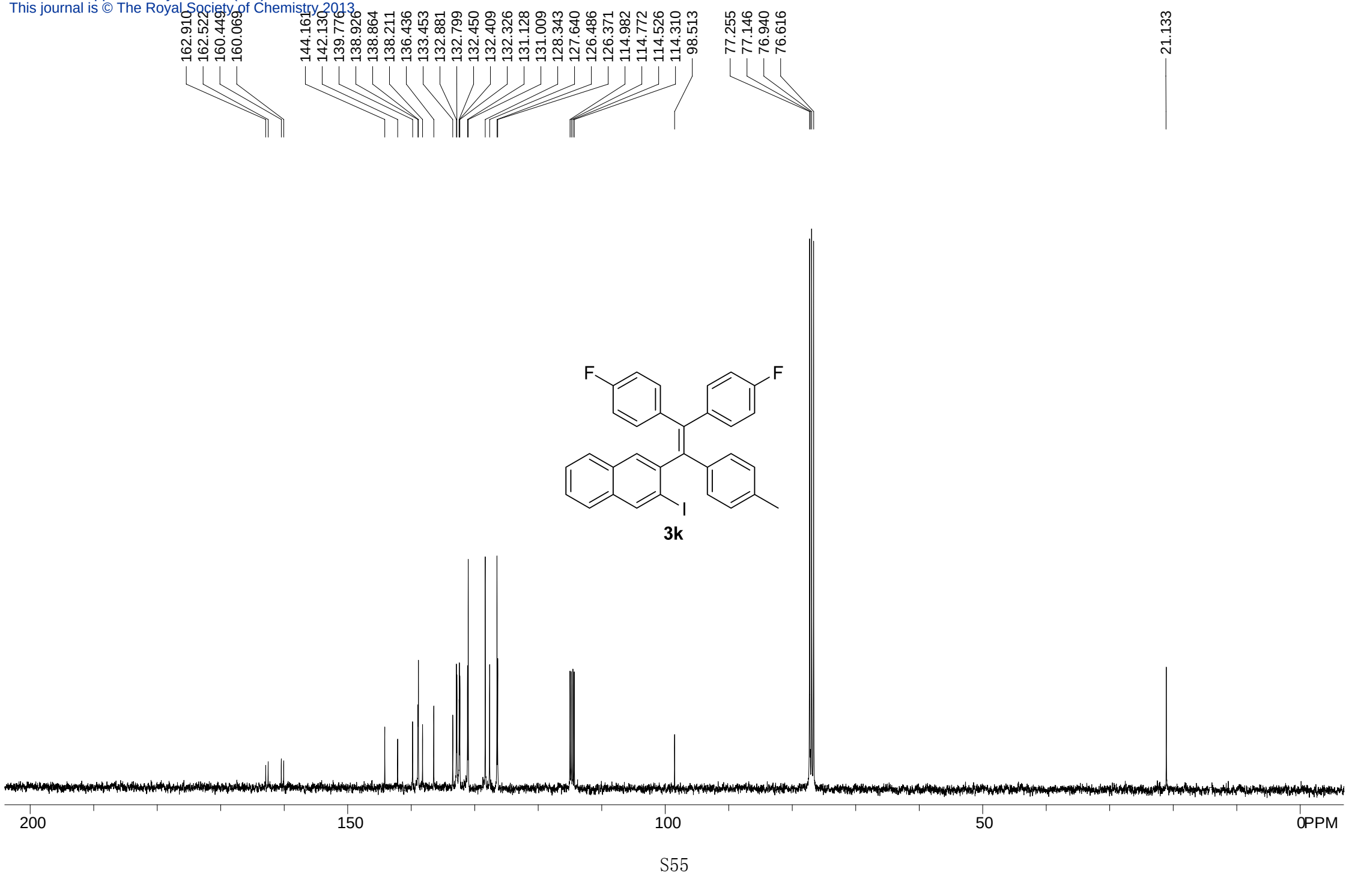

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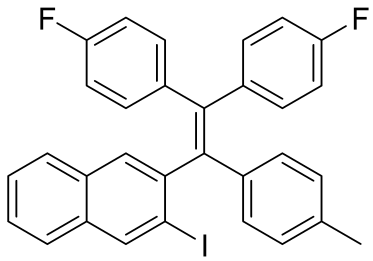

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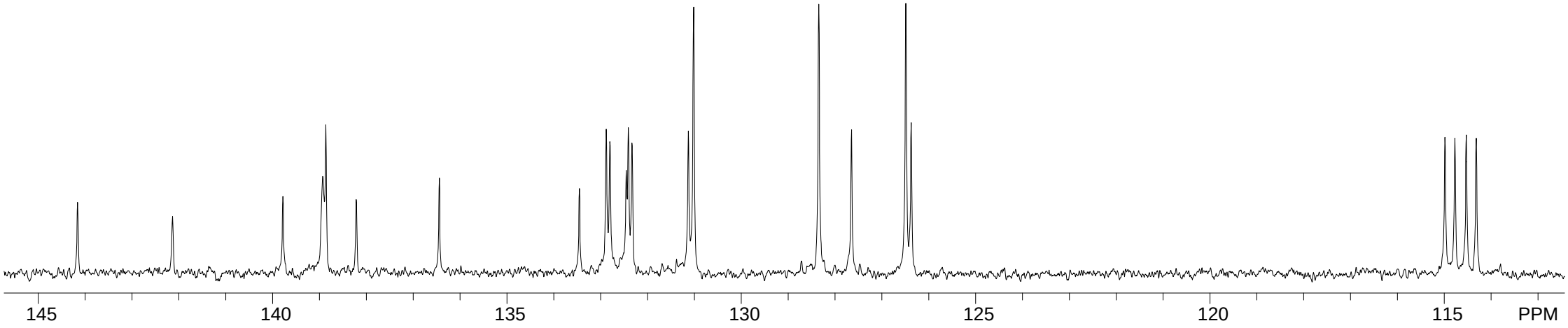

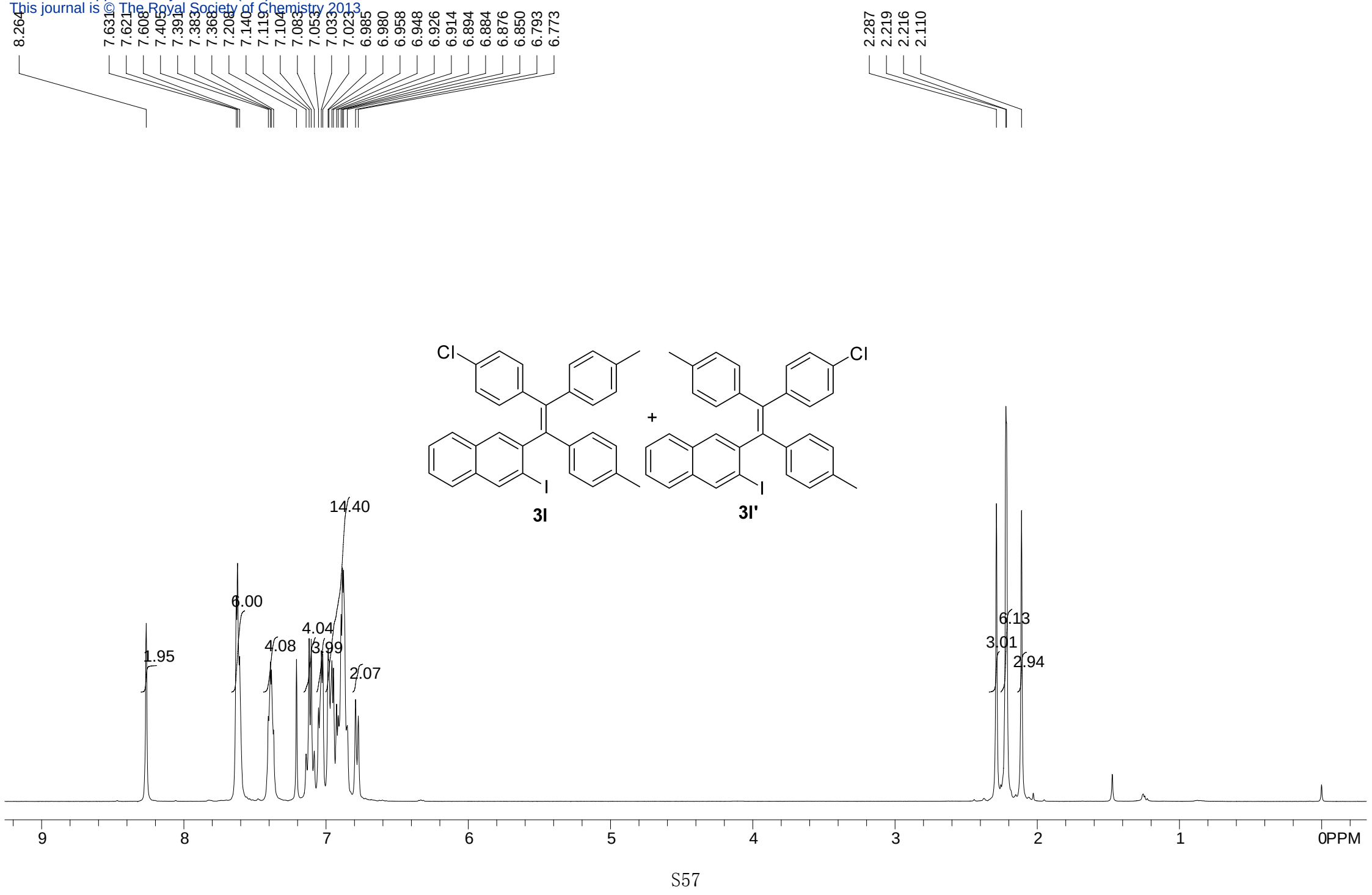

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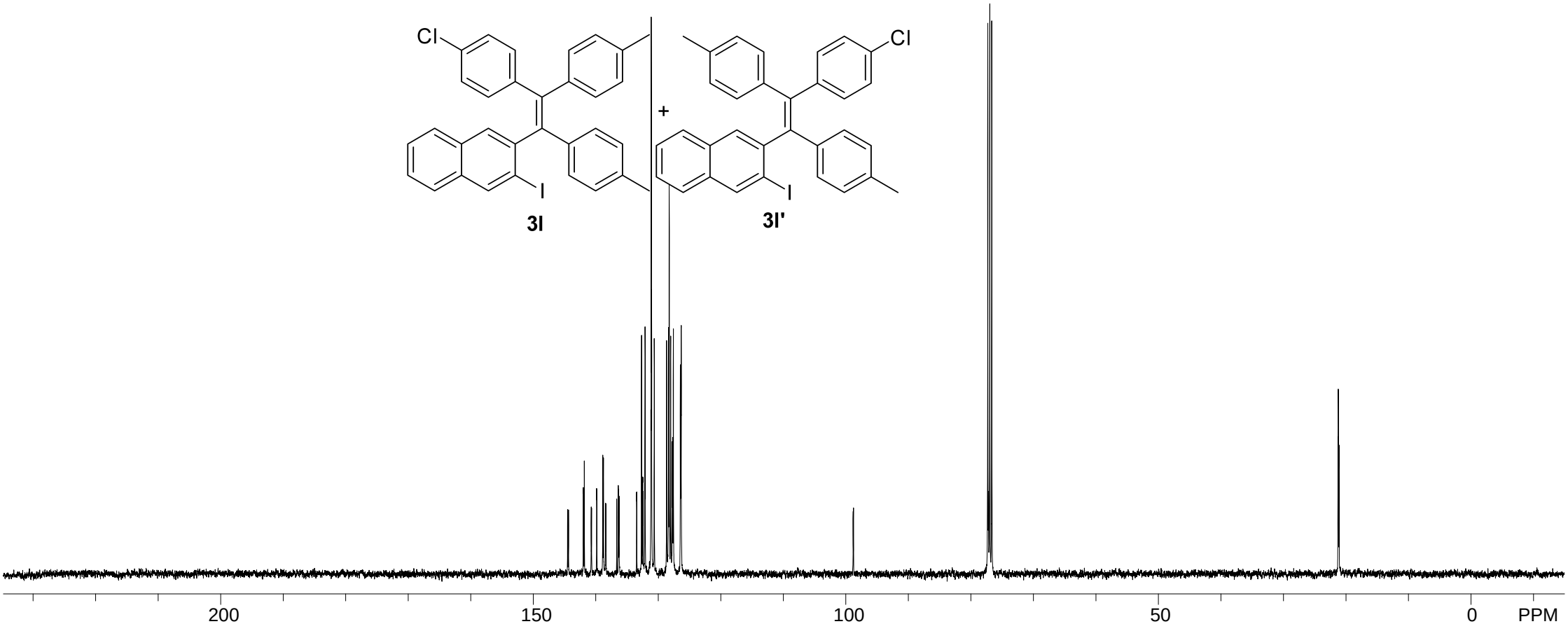
+

3l'



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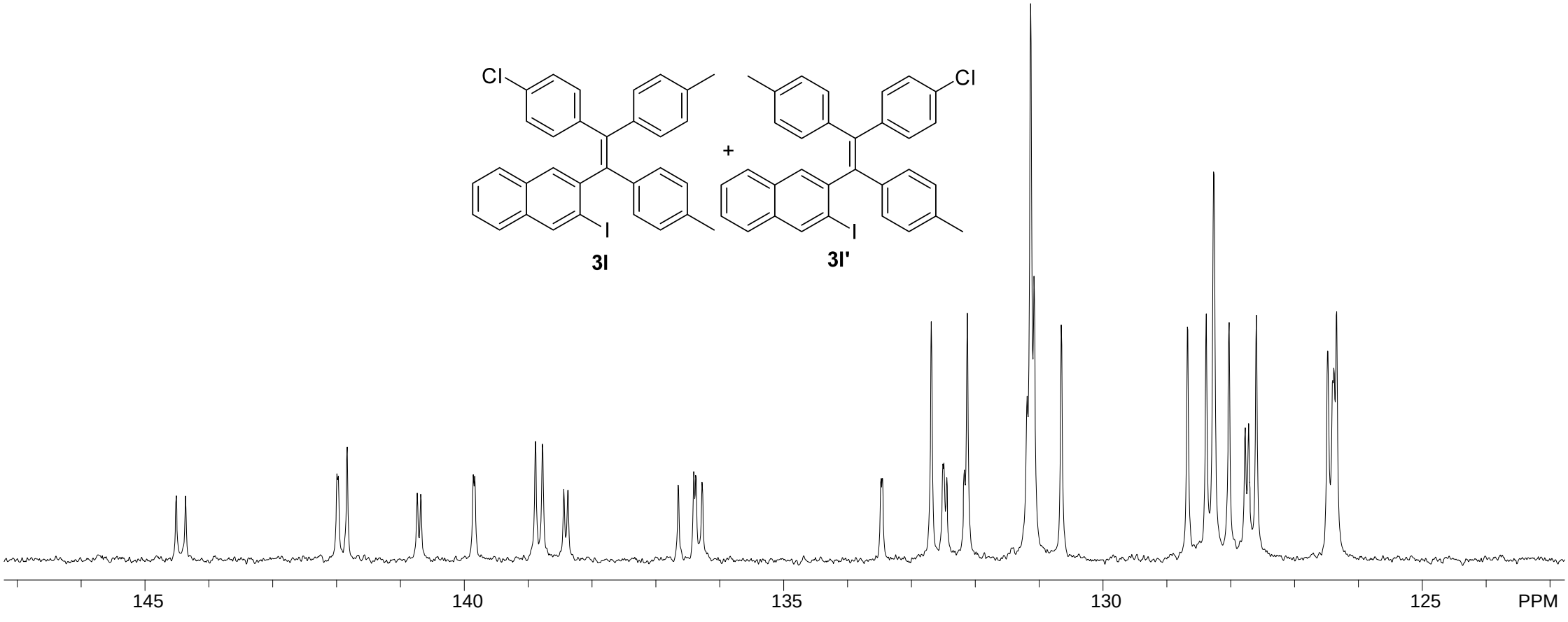
3l **3l'**



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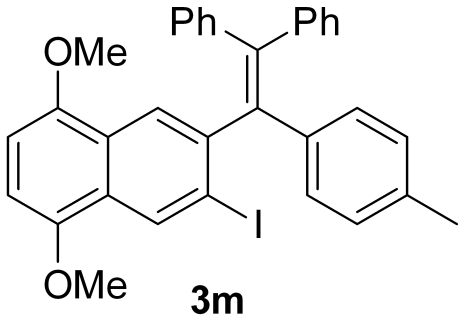

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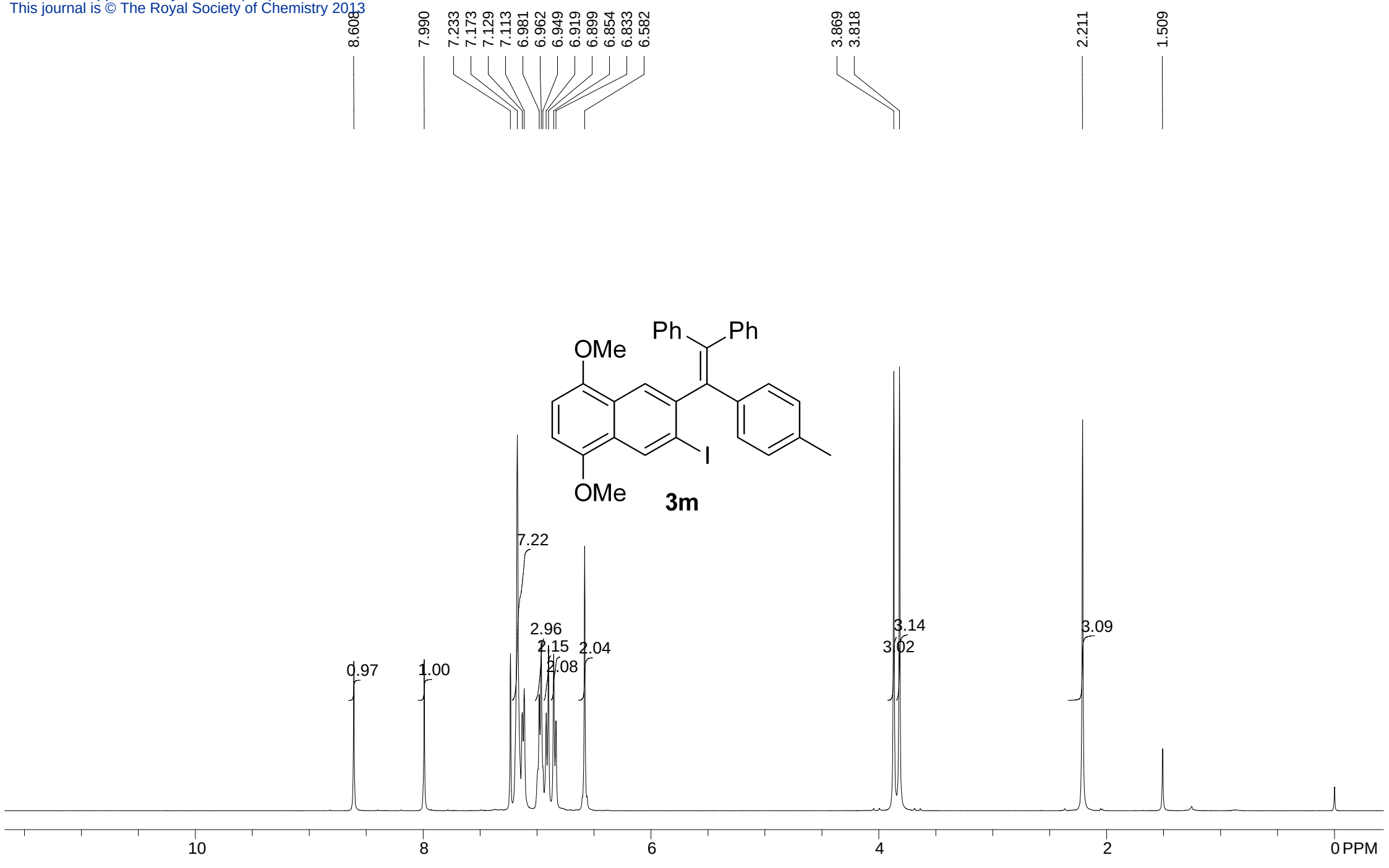

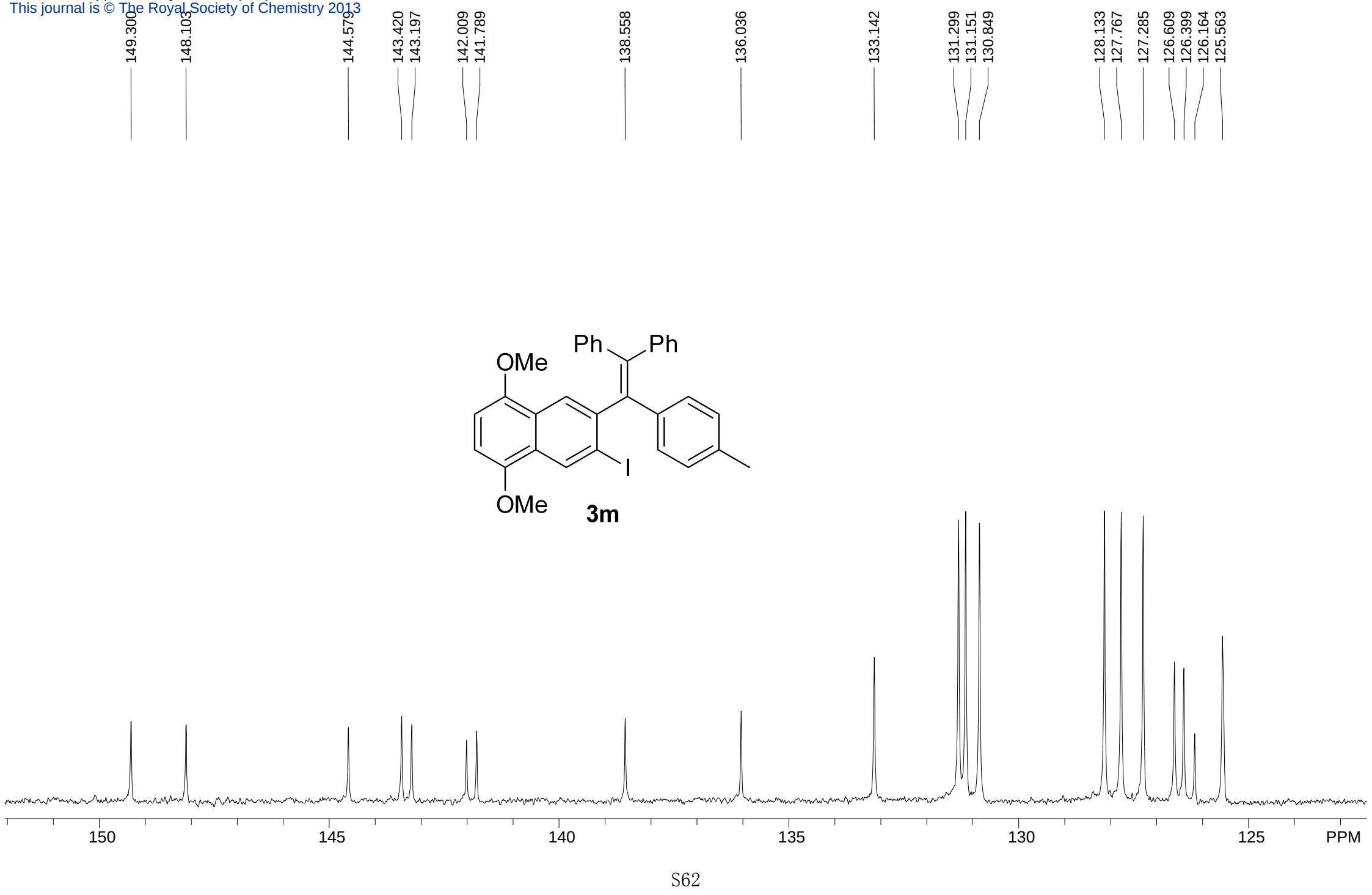

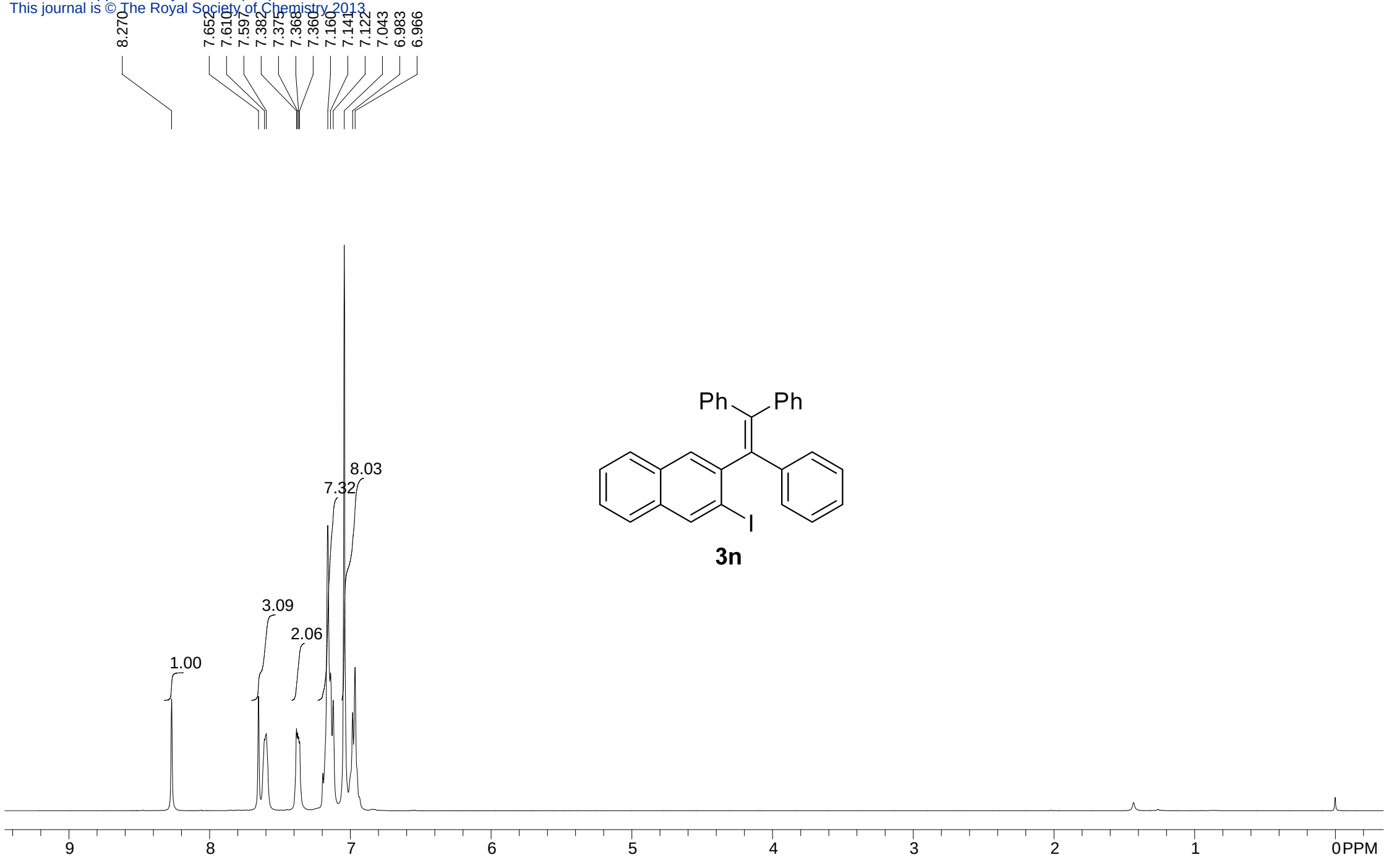

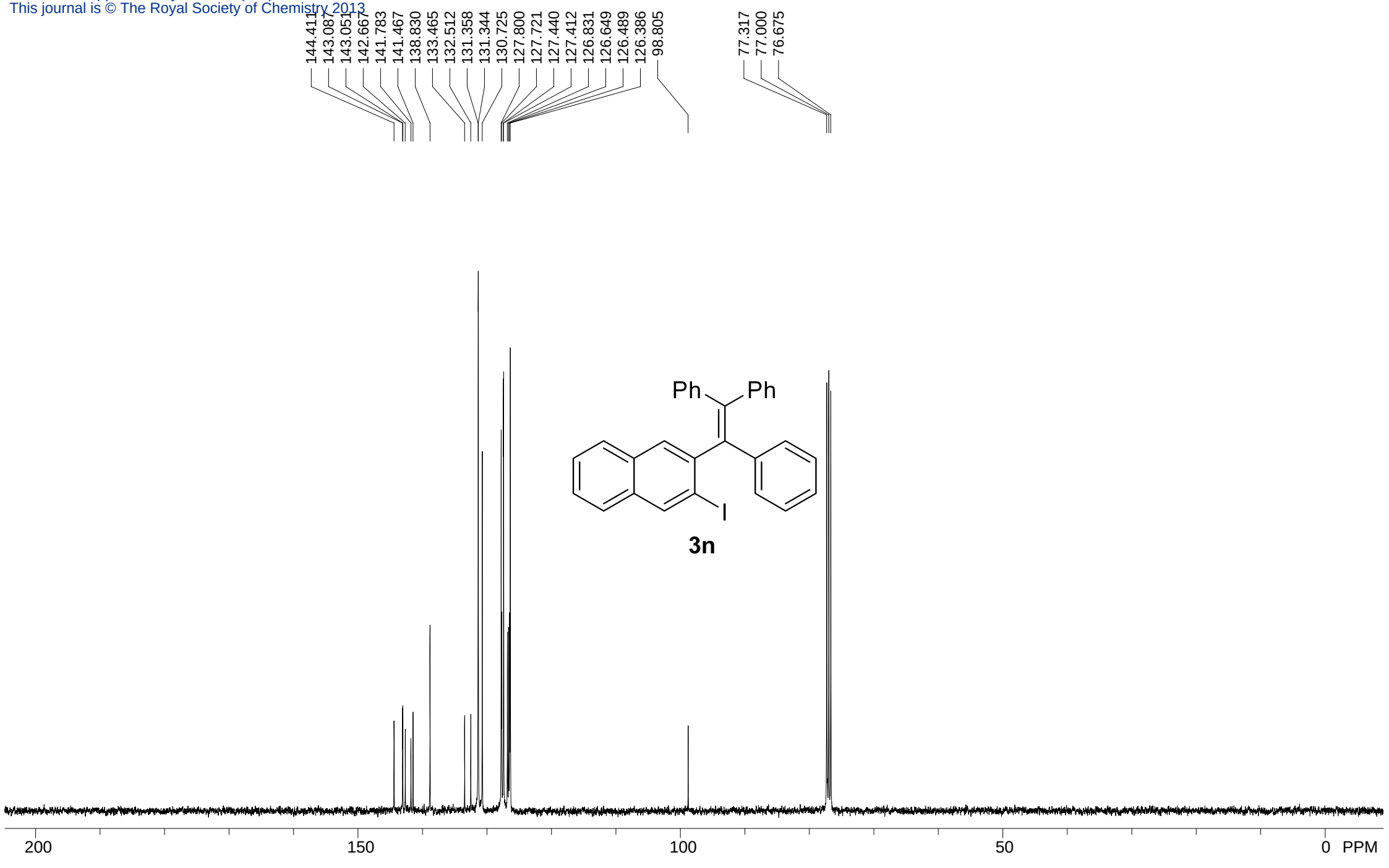

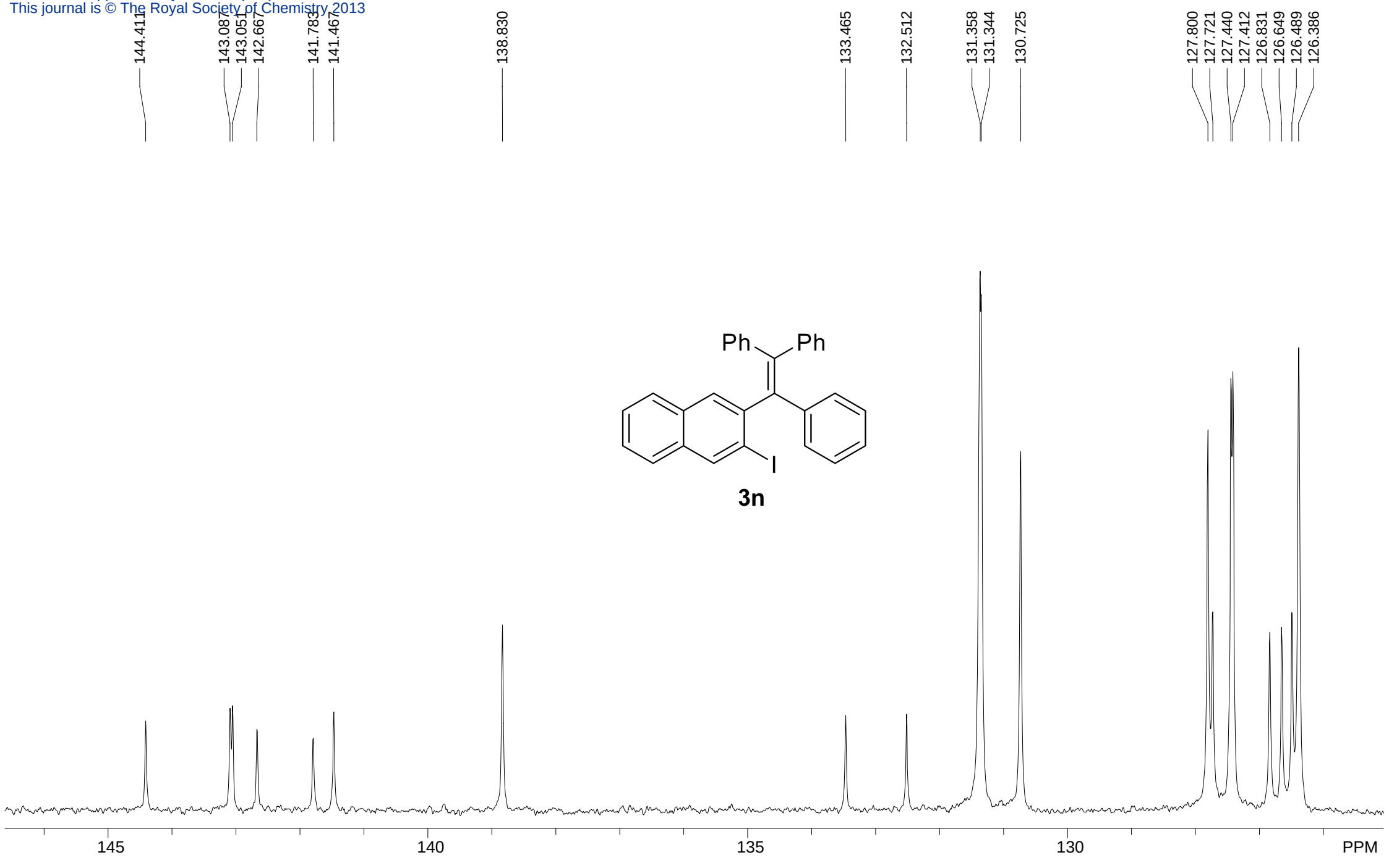

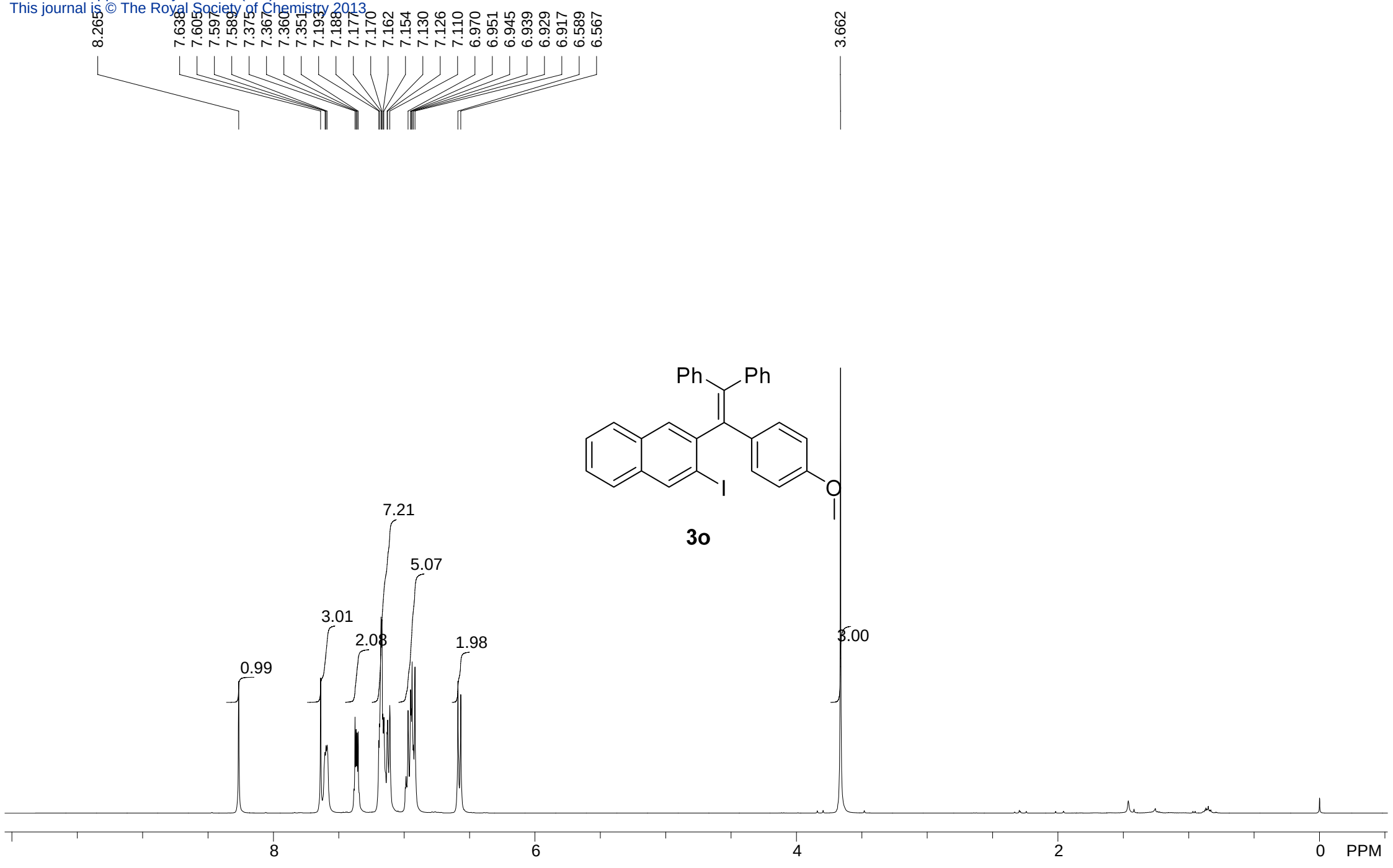

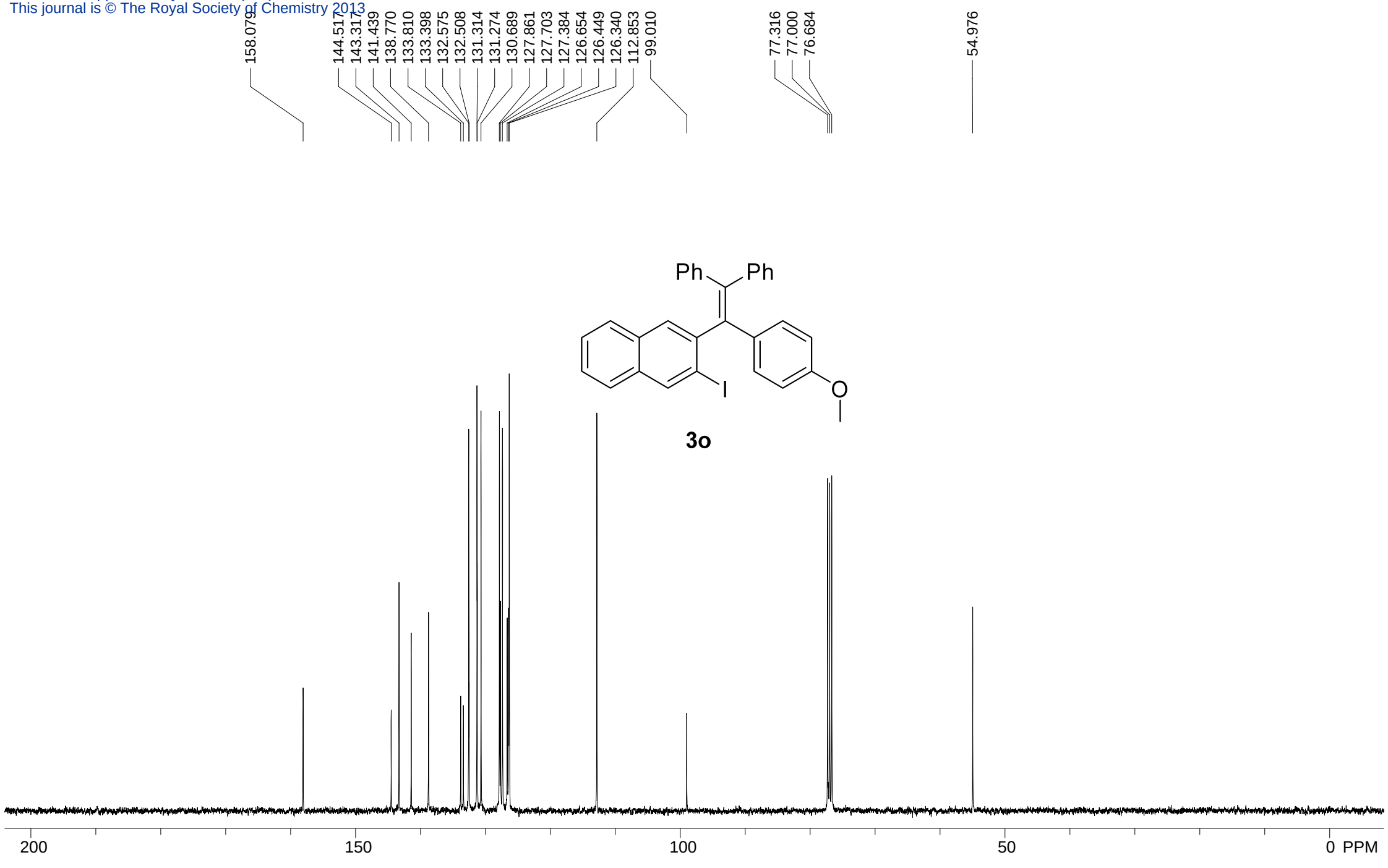

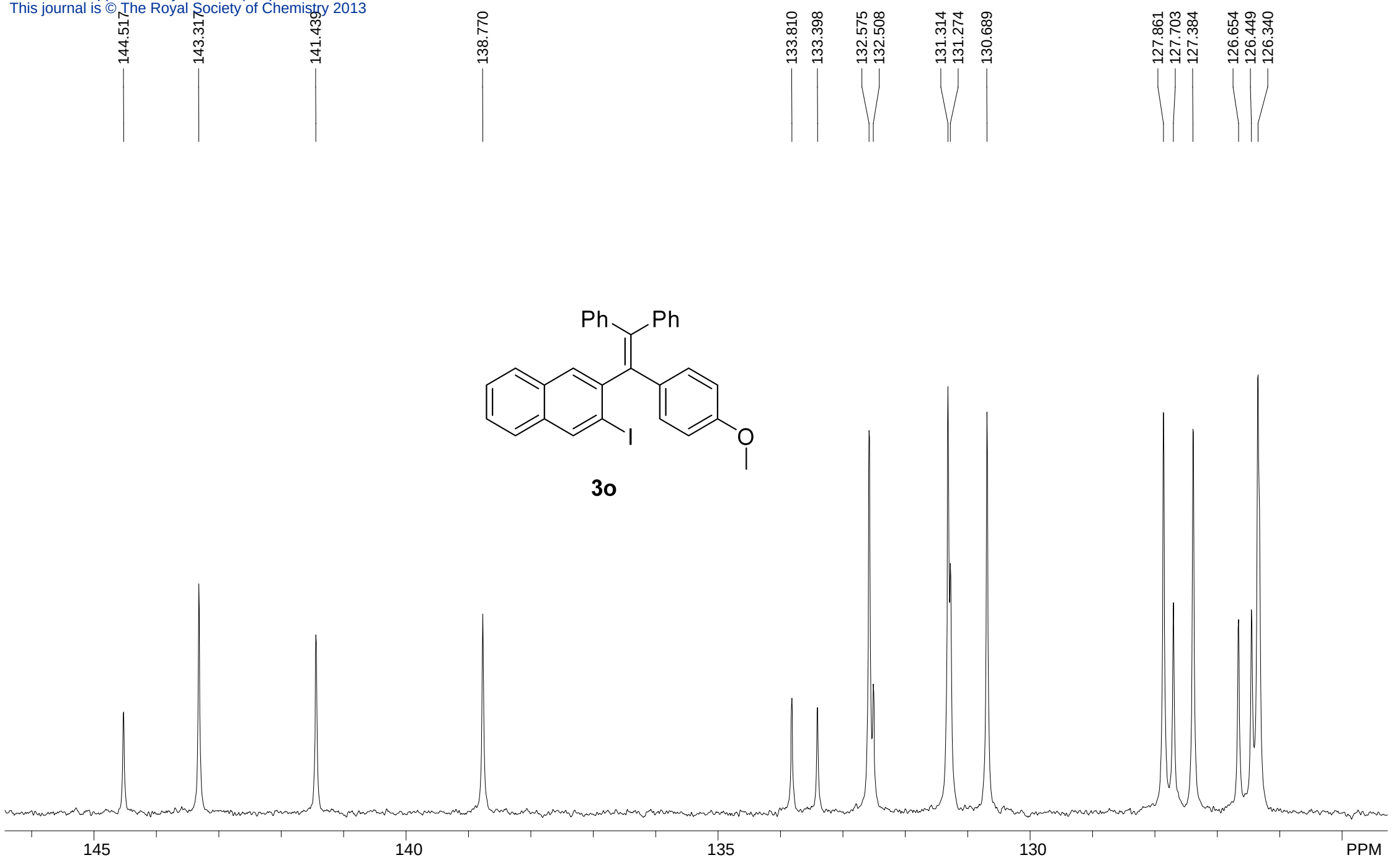

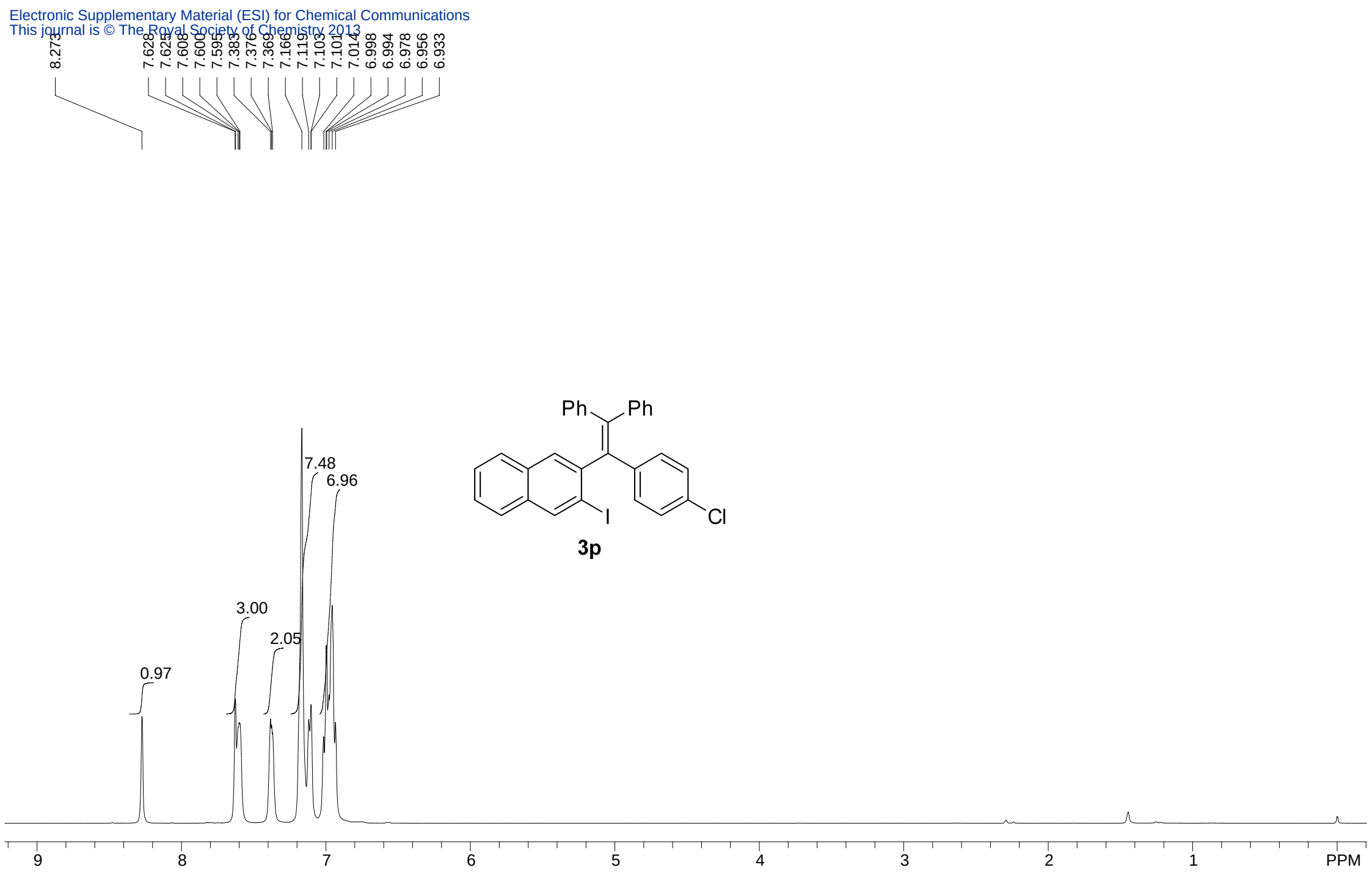

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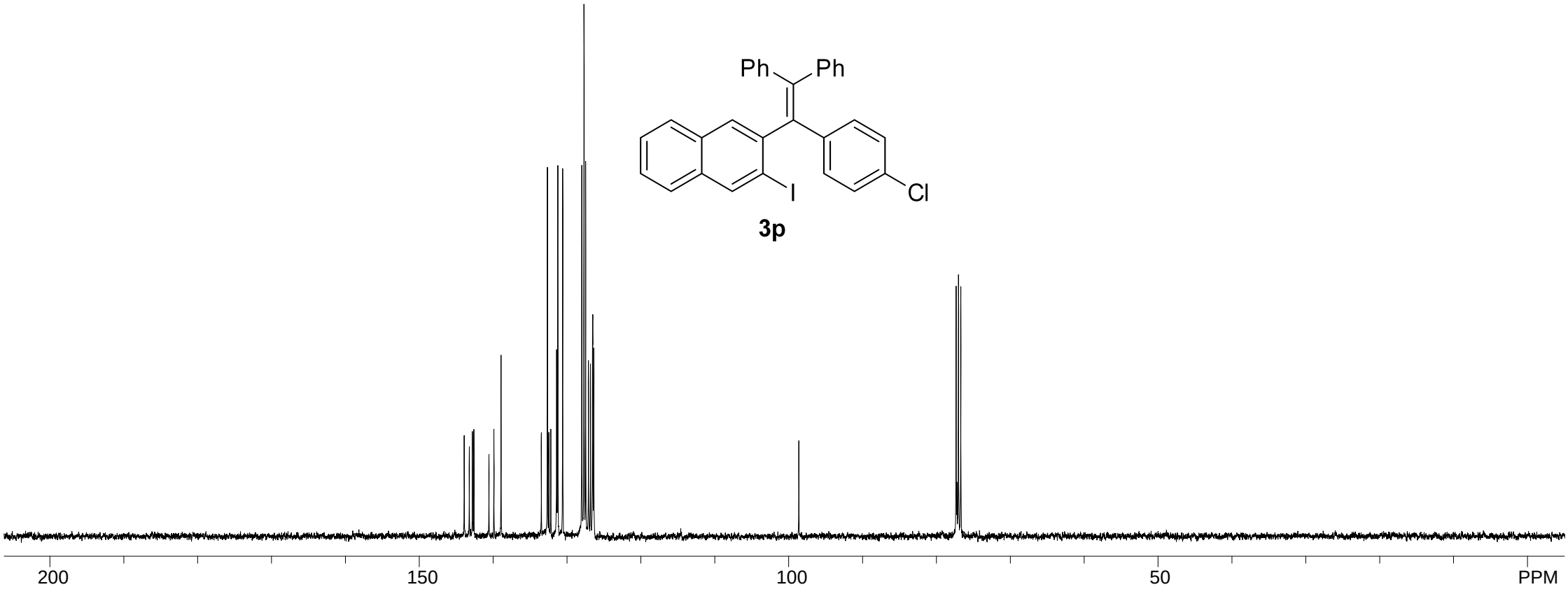

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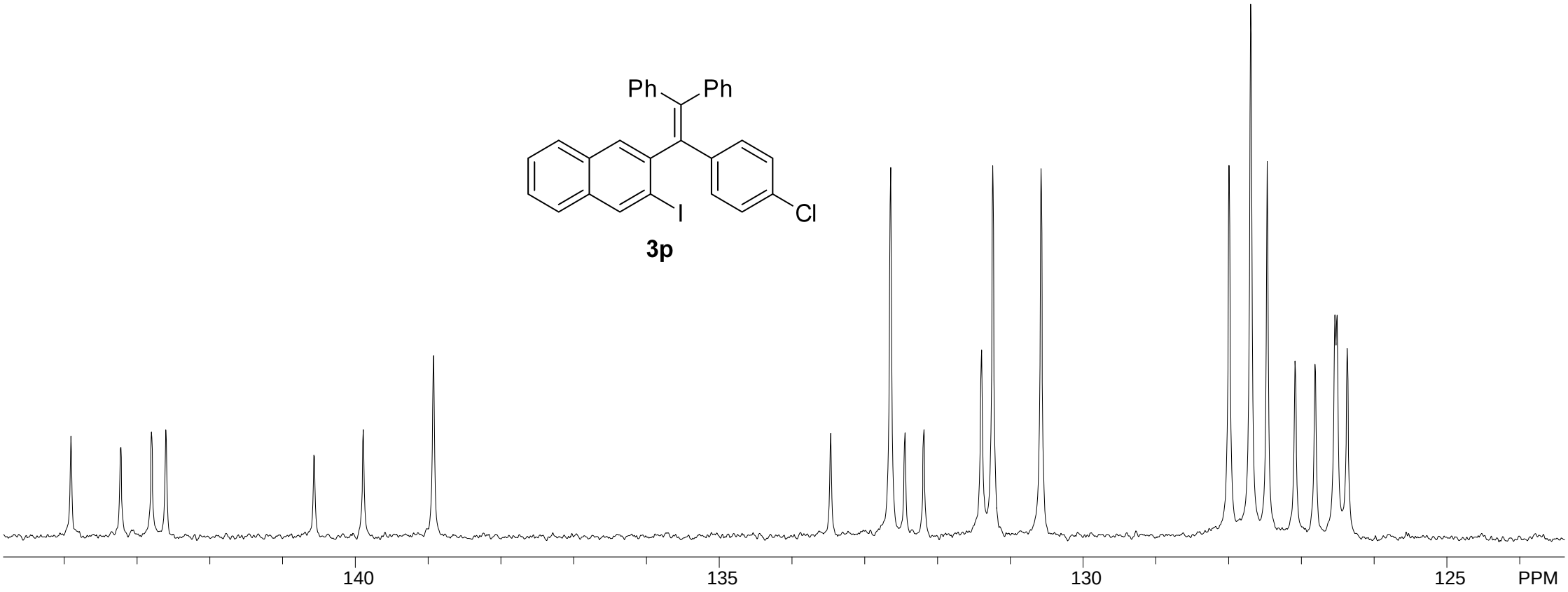

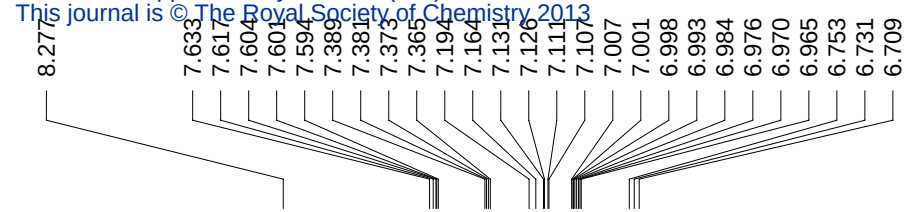

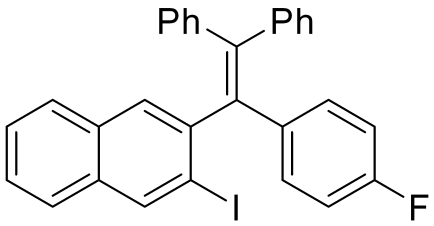

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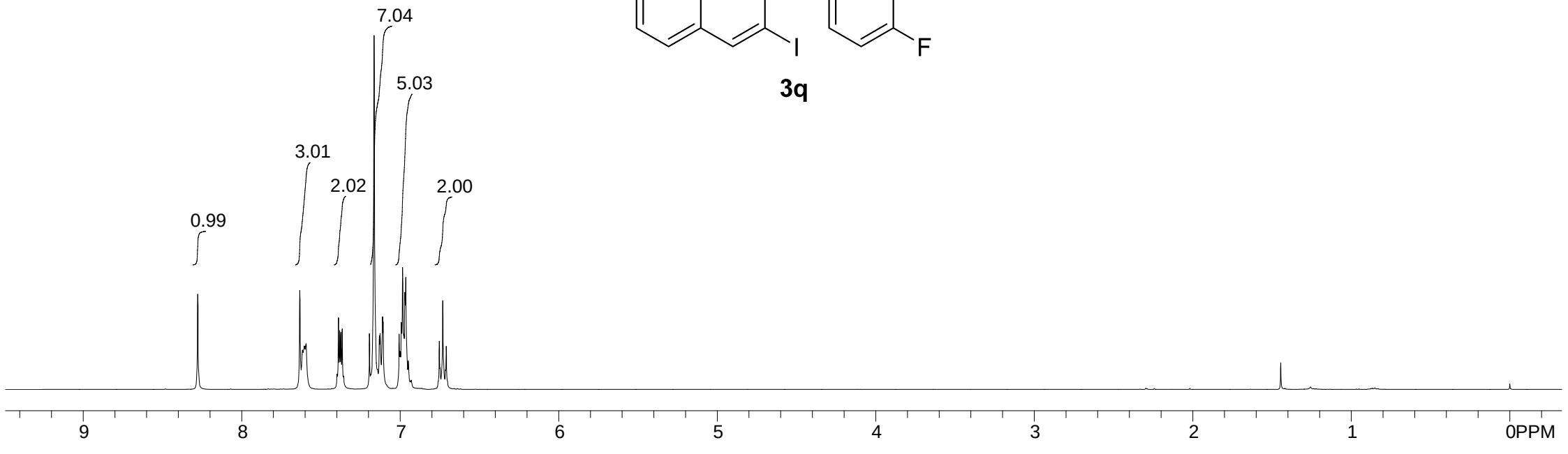

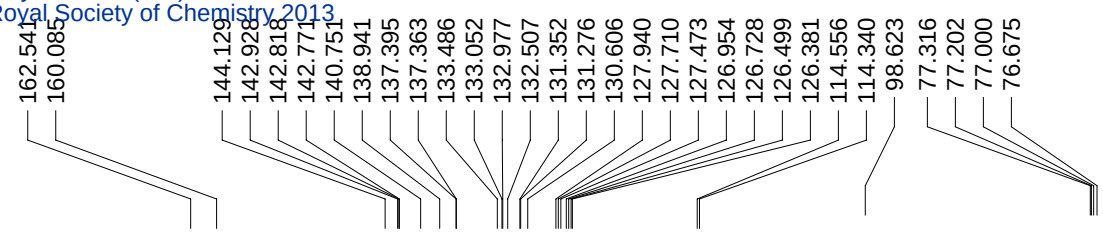

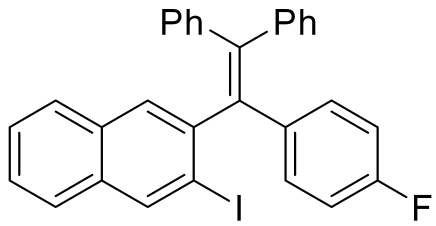

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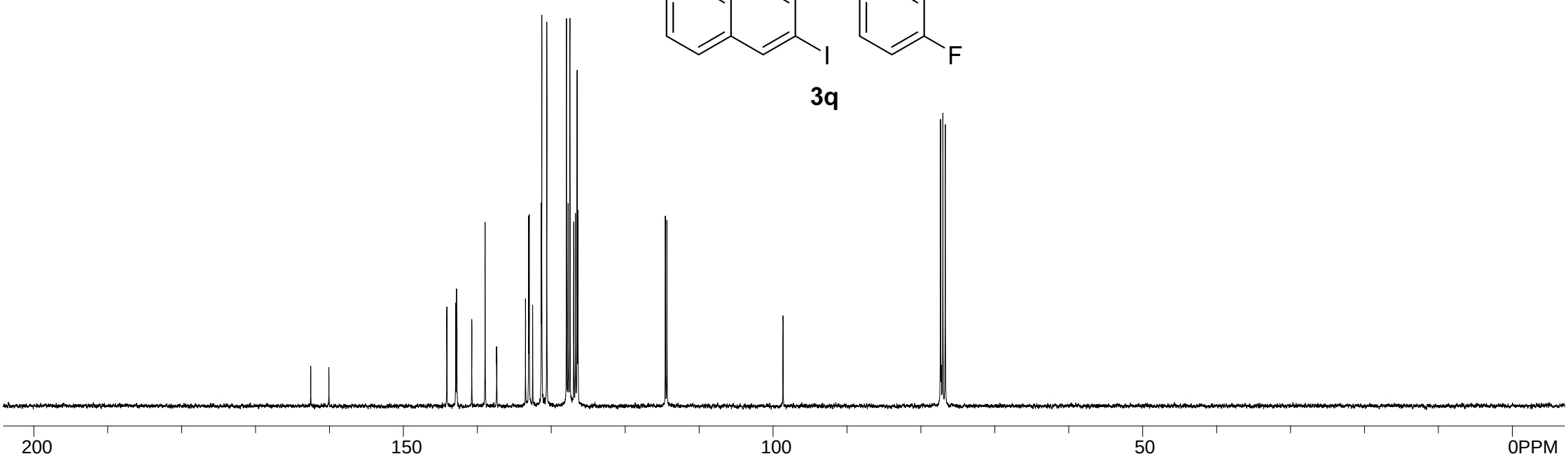

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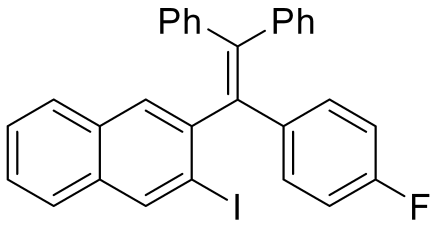

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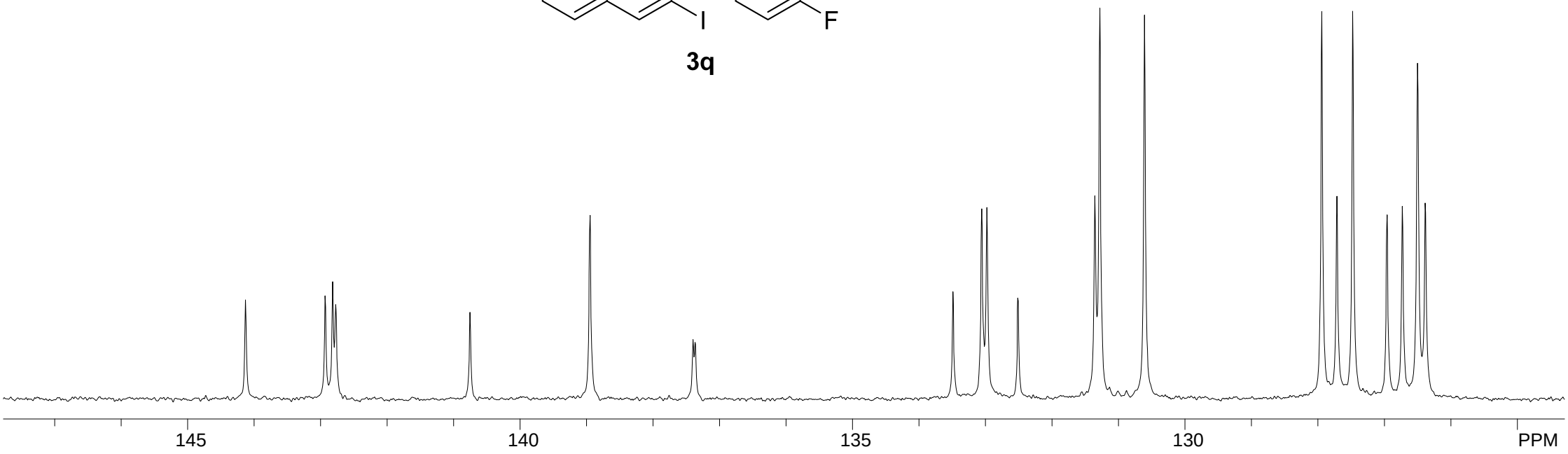

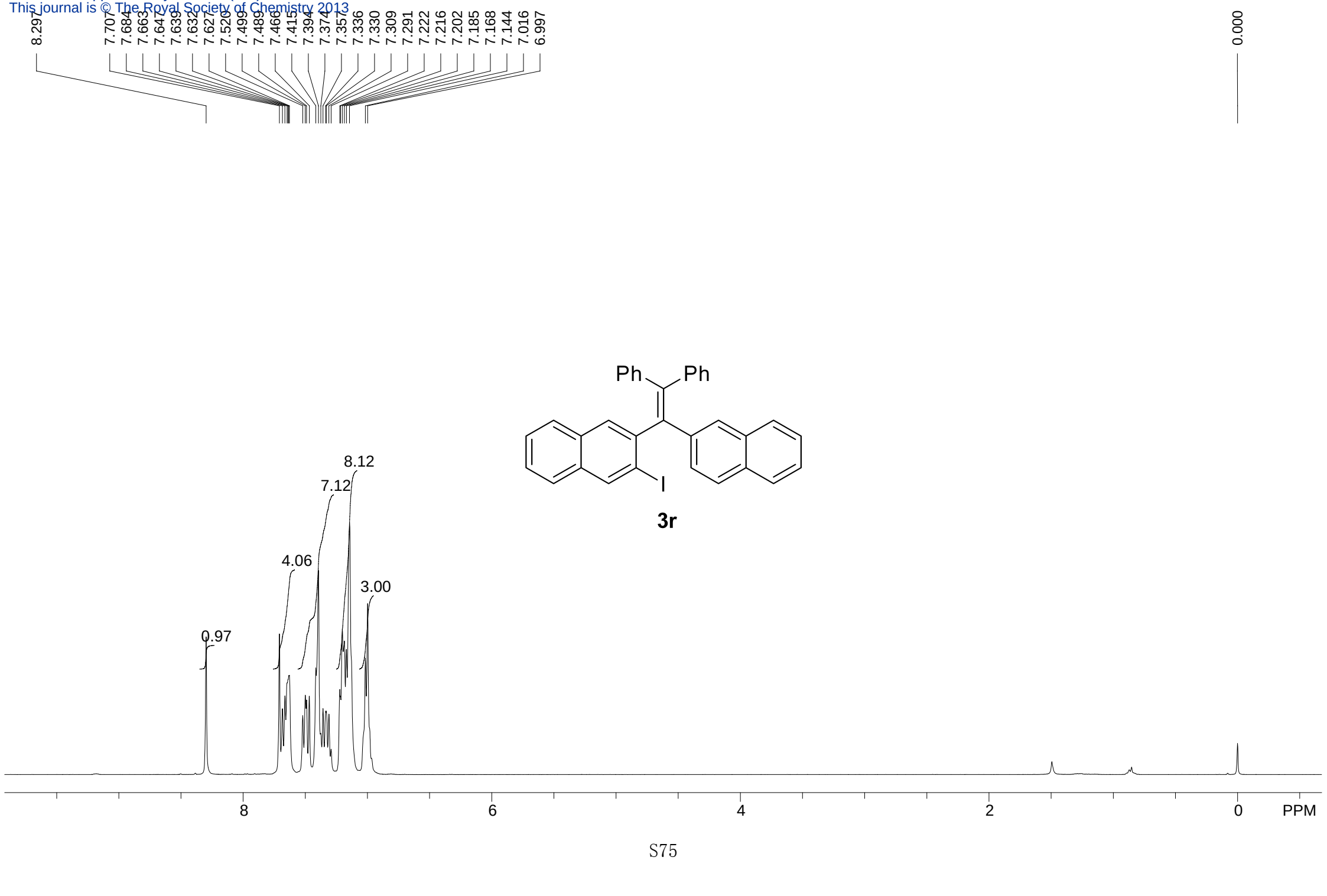

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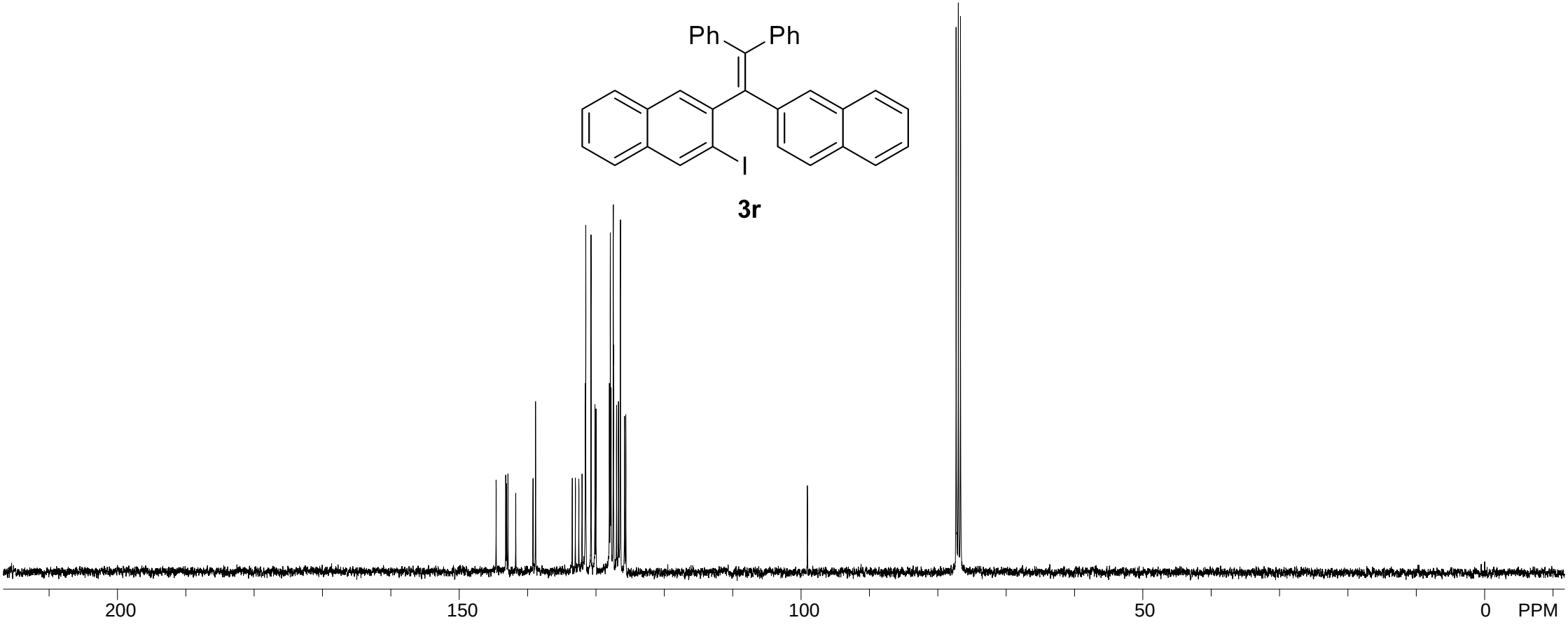
77.000
76.677

3r



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143.064
142.870
141.733
139.200
138.832
133.460
133.011
132.503
132.031
131.555
131.490
130.710
130.139
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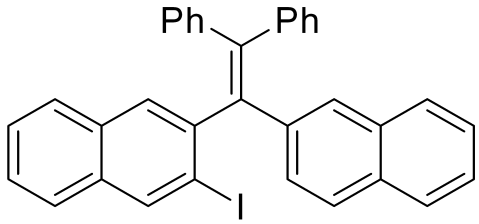
125.626



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