Regioselective Asao-Yamamoto Benzannulations of Diaryl Acetylenes

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Supplementary Information

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A. Materials. All reagents were purchased from commercial sources and used without further purification. CH_2Cl_2, and PhMe were purchased from commercial sources and purified using a custom-built alumina-column based solvent purification system. Other solvents were purchased from commercial sources and used without further purification. Compound **10** was purchased from Sigma-Aldrich and used without further purification. Compounds **1**, **1-$^{13}C_2$**, **12**, **13**, and **13-$^{13}C_2$** were synthesized according to previously described procedures.[1,2]

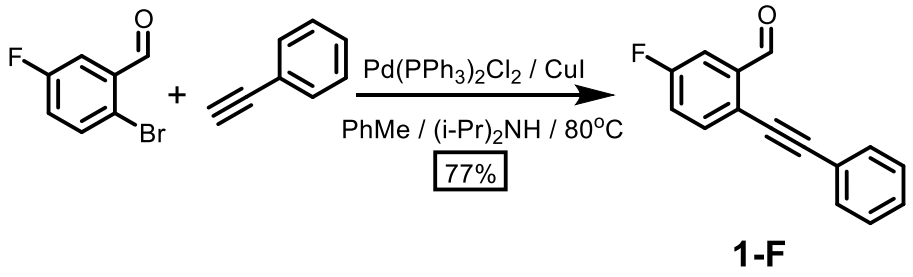
Instrumentation. Infrared spectra were recorded on a Thermo Nicolet iS10 with a diamond ATR attachment and are uncorrected.

Gas chromatography/electron impact mass spectrometry was performed on an Agilent 6890N Network GC System with a JEOL JMS-GCmate II Mass Spectrometer (magnetic sector). DART MS was performed on an Exactive Plus Orbitrap Mass Spectrometer with a DART SVP ion source from Ion Sense.

NMR spectra were recorded on a Varian 400 MHz, a Varian 500 MHz, a Varian 600 MHz or a Bruker ARX 300 MHz spectrometer using a standard ^{1}H/X Z-PFG probe at ambient temperature with a 20 Hz sample spin rate.

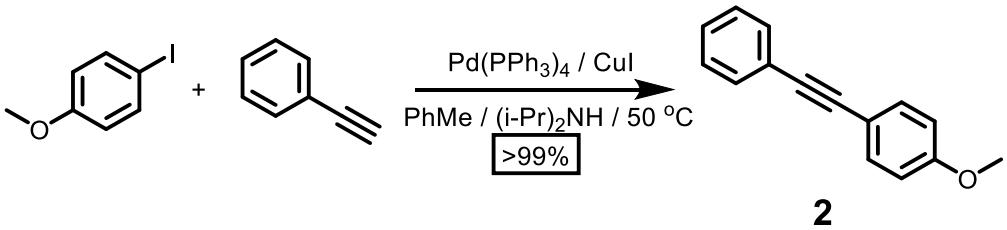
B. Synthetic Procedures

Scheme S1. Synthesis of **1-F**.



Synthesis of 1-F: 2-Bromo-5-fluorobenzaldehyde (1.000 g, 4.926 mmol), $Pd(PPh_3)_2Cl_2$ (0.069 g, 0.099 mmol) and CuI (0.038 g, 0.197 mmol) were added to a 3-neck round bottomed flask equipped with a condenser. The flask was evacuated and backfilled with N_2. In a separate flask, a solution of phenylacetylene (1.006 g, 9.852 mol) in DIPA (12 mL) was sparged with N_2 for 15 min. This solution and dry PhMe (25 mL) were added to the 3-neck flask, and the reaction was heated to 80 ºC. After stirring for 3 h, the mixture was cooled to rt, passed through a pad of celite, and the solvent was removed. Purification of the crude mixture by flash chromatography (SiO_2, 1% *v*/*v* EtOAc/hexanes to 4% *v*/*v* EtOAc/hexanes) provided **1-F** (0.849 g, 77% yield) as an off-white solid. **1-F:** ^{1}H NMR (400 MHz, $CDCl_3$) 10.60 (d, J = 3.2 Hz, 1H), 7.69 – 7.60 (m, 2H), 7.59 – 7.52 (m, 2H), 7.44 – 7.35 (m, 3H), 7.30 (ddd, J = 8.5, 7.8, 2.8 Hz, 1H).. ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.65, 162.53 (d, J_{CF} = 252 Hz), 137.90 (d, J_{CF} = 7 Hz), 137.40 (d, J_{CF} = 8 Hz), 131.78, 129.32, 128.71, 123.16 (d, J_{CF} = 3 Hz), 122.25, 121.55 (d, J_{CF} = 23 Hz), 113.87 (d, J_{CF} = 23 Hz), 96.16 (d, J_{CF} = 2 Hz), 83.95. IR (solid, ATR) 3079, 2845, 2750, 2213, 1720, 1688, 1603, 1594, 1576, 1494, 1479, 1444, 1418, 1392, 1312, 1290, 1266, 1207, 1146, 1207, 1137, 1070, 1024, 997, 964, 917, 875, 829, 751, 685 cm^{-1}. HRMS (EI, *m/z*): calcd for $[C_{15}H_9FO+H]^+$ 225.07157, found 225.07086.

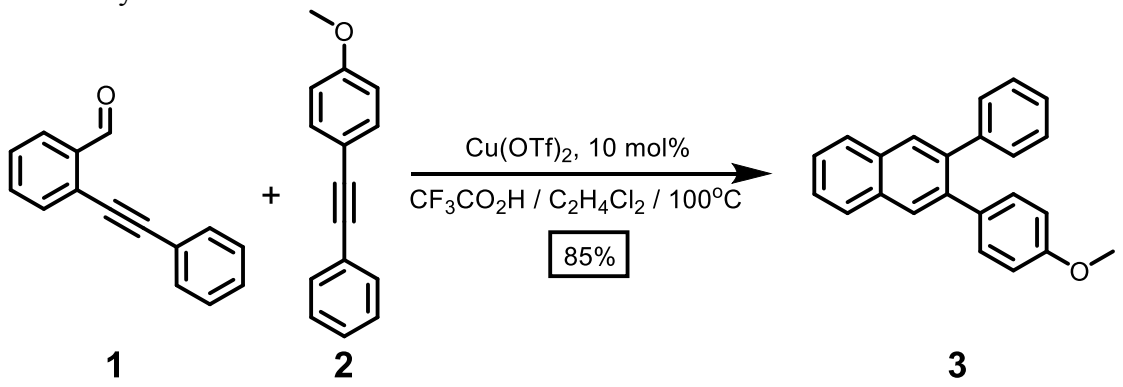
Scheme S2. Synthesis of **2**.



Synthesis of 2: A solution of phenylacetylene (218 mg, 2.136 mmol) and 4-iodoanisole (250 mg, 1.068 mmol) in DIPA (5 mL) was sparged with N_2 for 20 min. This solution was transferred using a cannula into a flask containing $Pd(PPh_3)_4$ (37 mg, 0.032 mmol) and CuI (20 mg, 0.107 mmol) suspended in PhMe (4 mL) under N_2. The mixture was heated to 50 °C and stirred for 1 h. The reaction mixture was cooled to rt and diluted with Et_2O (50 mL). The organic solution was washed with aqueous HCl (1M, 50 mL), and brine (2 x 50 mL). The organic phase was dried ($MgSO_4$), filtered, and the solvent was removed. The crude product was purified by flash

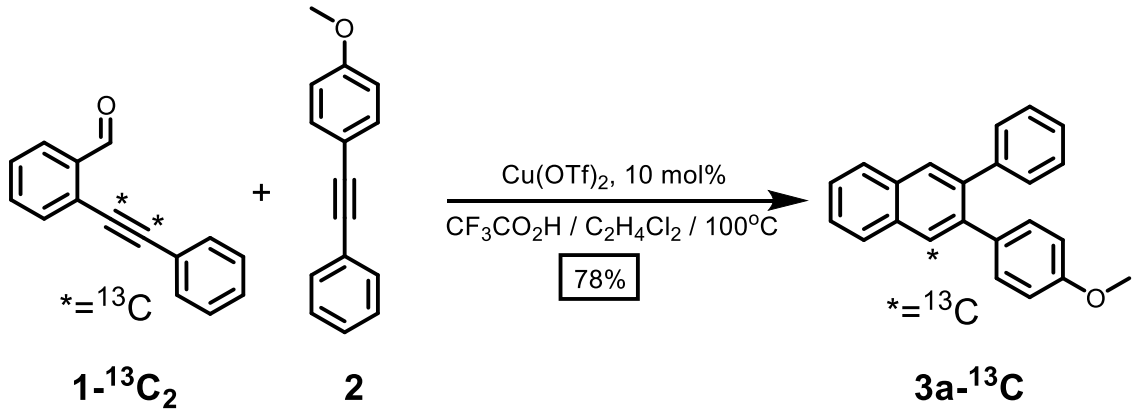
chromatography (SiO_2, 1:4 *v/v* $CHCl_3$:hexanes) to provide **2** (0.2314g, >99% yield) as a white powder **2:** δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.38 – 7.29 (m, 3H), 6.93 – 6.84 (d, *J* = 8.5 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.76, 133.19, 131.58, 128.44, 128.06, 123.74, 115.53, 114.14, 89.51, 88.21, 55.44. IR (solid, ATR) 3053, 2936, 2837, 2535, 2214, 1604, 1593, 1567, 1507, 1456, 1439, 1315, 1287, 1246, 1174, 1137, 1107, 1069, 1025, 835, 779, 752, 689 cm^{-1}. HRMS (EI, *m/z*): calcd for $[C_{15}H_{13}O+H]^+$ 209.09609, found 209.09552.

Scheme S3. Synthesis of **3**.



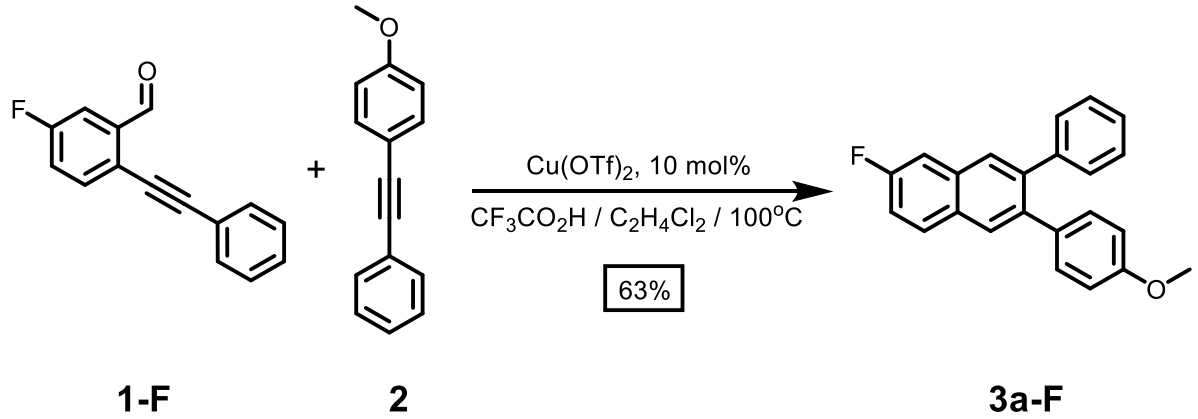
Synthesis of 3 and representative benzannulation procedure: Alkyne **2** (18 mg, 0.087 mmol) and benzaldehyde **1** (30 mg, 0.145 mmol) were dissolved in 1,2-dichloroethane (1.5 mL) under N_2. $Cu(OTf)_2$ (5 mg, 0.015 mmol) and CF_3CO_2H (12 µL, 0.160 mmol) were added in quick succession. The solution was heated to 100 °C for 15 min, after which it was cooled to rt and poured into a saturated aqueous $NaHCO_3$ solution (25 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 25 mL), and the combined organic layers were dried ($MgSO_4$) and filtered. The solvent was evaporated to provide the crude mixture, which was purified by chromatography (SiO_2, 4% *v/v* EtOAc/hexanes) to provide **3** (23 mg, 85% yield) as a colorless, viscous oil. **3:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 – 7.83 (m, 2H), 7.87 (s, 1H), 7.86 (s, 1H), 7.53 – 7.45 (m, 2H), 7.24 (m, 5H), 7.13 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.53, 141.76, 139.31, 138.83, 133.96, 132.92, 132.68, 131.19, 130.13, 129.59, 129.32, 128.03, 127.83, 127.75, 126.62, 126.37, 126.24, 113.48, 55.33. IR (solid, ATR) 3054, 2922, 2850, 1711, 1609, 1515, 1489, 1457, 1436, 1360, 1288, 1245, 1220, 1177, 1032, 1023, 960, 892, 832, 763, 735, 700 cm^{-1}. HRMS (EI, *m/z*): calcd for $[C_{23}H_{18}O]^+$ 310.13631, found 310.13460.

Scheme S4. Synthesis of **3a-^{13}C**.



Synthesis of 3a-^{13}C: 3a-^{13}C was synthesized using a similar procedure to that used to prepare **3.** Alkyne **2** (18 mg, 0.087 mmol), benzaldehyde **1-^{13}C$_2$** (30 mg, 0.145 mmol), 1,2-dichloroethane (1.5 mL), $Cu(OTf)_2$ (5 mg, 0.015 mmol) and CF_3CO_2H (12 µL, 0.160 mmol) were used. Chromatography (SiO_2, 1:4 *v*/*v* $CHCl_3$:hexanes) provided **3a-^{13}C** (21 mg, 78% yield) as a colorless, viscous oil. **3a-^{13}C:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.83 (m, 2H), 7.87 (s, 1H), 7.86 (d, J_{CH} = 158 Hz, 1H), 7.53 – 7.45 (m, 2H), 7.24 (m, 5H), 7.13 (d, J = 8.7 Hz, 2H), 6.78 (d, J = 8.7 Hz, 2H), 3.79 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 129.30 (one ^{13}C-enriched carbon signal). IR (solid, ATR) 3052, 2925, 2833, 1608, 1513, 1488, 1454, 1434, 1331, 1287, 1244, 1176, 1074, 1032, 1023, 957, 887, 830, 802, 781, 772, 762, 747, 735, 714, 700 cm^{-1}. HRMS (EI, *m/z*): calcd for $[C_{22}{}^{13}CH_{18}O]^+$ 311.13857, found 311.13758.

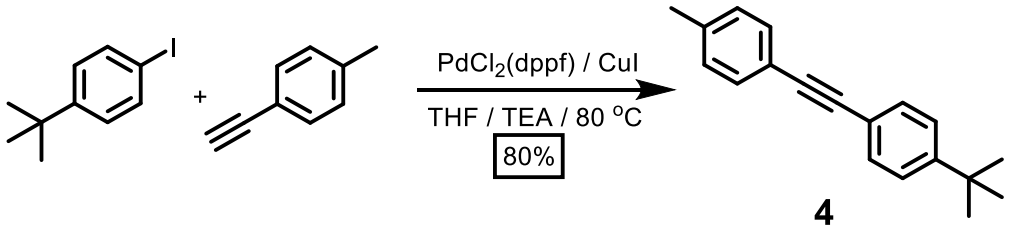
Scheme S5. Synthesis of **3a-F**.



Synthesis of 3a-F: 3a-F was synthesized using a similar procedure to that used to prepare **3.** Alkyne **2** (22 mg, 0.107 mmol), benzaldehyde **1-F** (30 mg, 0.134 mmol), 1,2-dichloroethane (1.5 mL), $Cu(OTf)_2$ (5 mg, 0.013 mmol) and CF_3CO_2H (11 µL, 0.147 mmol) were used. Chromatography (SiO_2, 1:2 *v*/*v* $CHCl_3$:hexanes) provided **3a-F** (22 mg, 63% yield) as a colorless, viscous oil. **3a-F:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.82 (m, 1H), 7.84 (s, 1H), 7.80 (s, 1H), 7.47 (dd, J = 9.8, 2.5 Hz, 1H), 7.31 – 7.18 (m, 6H), 7.11 (d, J = 8.4 Hz, 2H), 6.78

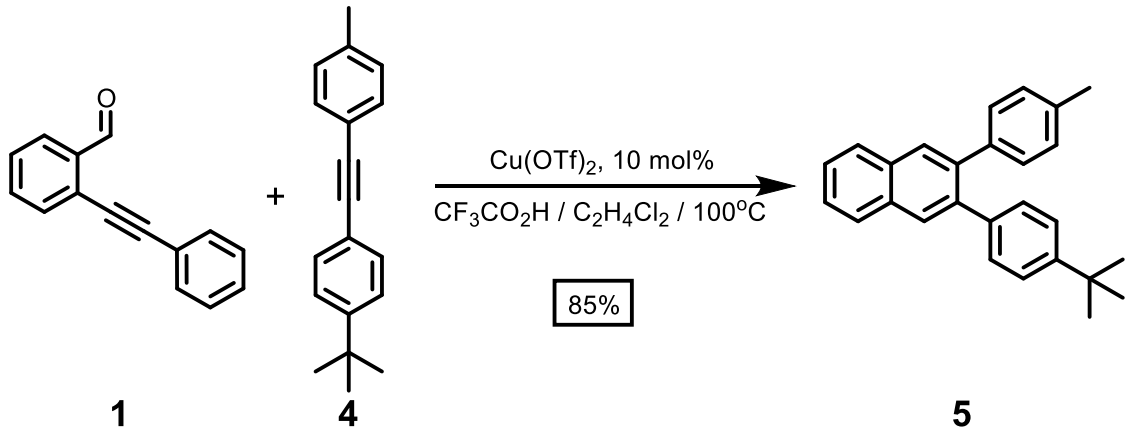
(d, J = 8.4 Hz, 2H), 3.79 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.96 (d, J_{CF} = 246 Hz), 158.56, 141.39, 140.37, 138.19 (d, J_{CF} = 3 Hz), 133.64, 133.33 (d, J_{CF} = 9 Hz), 131.13, 130.18 (d, J_{CF} = 9 Hz), 130.05, 129.93, 129.28 (d, J_{CF} = 8 Hz), 128.90 (d, J_{CF} = 6 Hz), 128.09, 126.83, 116.77 (d, J_{CF} = 26 Hz), 113.51, 110.79 (d, J_{CF} = 21 Hz), 55.34. IR (solid, ATR) 3056, 2930, 2835, 1636, 1607, 1570, 1514, 1490, 1461, 1440, 1408, 1386, 1347, 1283, 1244, 1218, 1190, 1175, 1143, 1119, 1074, 1046, 1033, 1022, 973, 947, 897, 835, 807,787, 777, 760, 736, 715, 700, cm^{-1}. HRMS (EI, *m/z*): calcd for $[C_{23}H_{17}FO]^+$ 328.12579, found 328.12487.

Scheme S6. Synthesis of **4**.



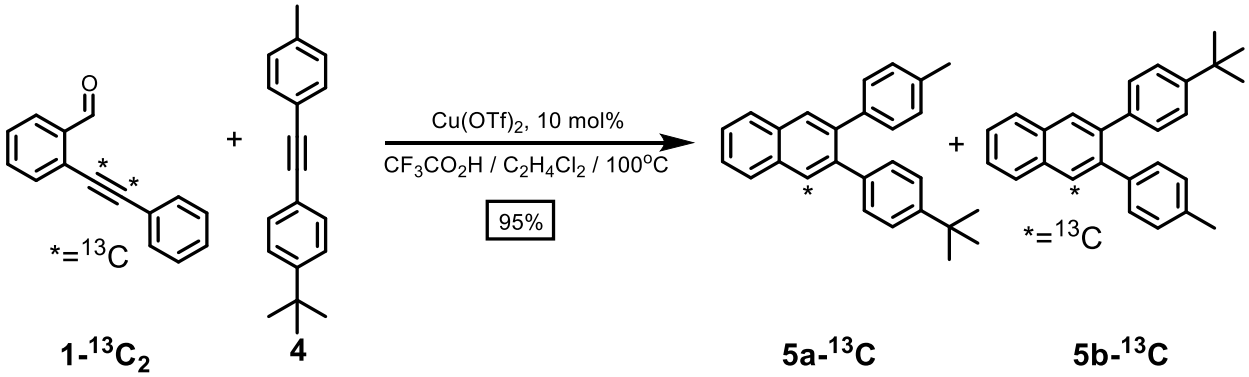
Synthesis of 4: $PdCl_2$(dppf) (0.108 g, 0.154 mmol) and CuI (0.073 g, 0.0.384 mmol) were added to a Schlenk flask. 1-*tert*-Butyl-4-iodobenzene (2.000 g, 7.689 mmol) and 4-ethynyltoluene (0.893 g, 7.689 mmol) and THF (12.0 mL) were added under N_2 atmosphere. TEA (6.0 mL) was added and the mixture was subjected to 3 freeze-pump-thaw degassing cycles. The reaction was heated to 80 ºC for 20 h and then cooled to rt. It was passed through a pad of celite, and the solvent was removed. The crude product was washed with MeOH (100 mL) to provide **4** (1.522 g, 80% yield) as a white powder. **4:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 7.8 Hz, 2H), 7.36 (d, J = 8.5 Hz, 2H), 7.14 (d, J = 7.8 Hz, 2H), 2.36 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.28, 138.13, 131.42, 131.21, 129.04, 125.28, 120.36, 109.99, 88.83, 88.80 34.75, 31.17, 21.51. IR (solid, ATR) 2962, 2865, 2163, 1979, 1913, 1515, 1462, 1405, 1393, 1362, 1307, 1267, 1183, 1114, 1103, 1015, 832, 819, 737, 703 cm^{-1}. HRMS (EI, *m/z*): calcd for $[C_{19}H_{20}+H]^+$ 248.16487, found 248.16311.

Scheme S7. Synthesis of **5**.



Synthesis of 5: 5 was synthesized using a similar procedure to that used to prepare **3.** Alkyne **4** (19 mg, 0.076 mmol), benzaldehyde **1** (26 mg, 0.126 mmol), 1,2-dichloroethane (1.5 mL), $Cu(OTf)_2$ (5 mg, 0.013 mmol) and CF_3CO_2H (11 μL, 0.139 mmol) were used. Chromatography (SiO_2, 1:9 *v/v* $CHCl_3$:hexanes) provided **5** (24 mg, 85% yield) as a colorless, viscous oil. **5:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.91 – 7.85 (m, 2H), 7.88 (s, 1H), 7.52 – 7.48 (m, 2H), 7.29 (d, J = 8.3 Hz, 2H), 7.19 (d, J = 8.3 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 2.36 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.51, 139.23, 139.16, 138.74, 138.65, 136.20, 132.79, 132.78, 129.99, 129.70, 129.60, 129.52, 128.70, 127.78, 126.22, 124.91, 34.60, 31.53, 21.33. IR (solid, ATR) 3050, 2960, 2865, 1739, 1514, 1488, 1457, 1403, 1362, 1267, 1203, 1132, 1110, 1018, 851, 894, 886, 835, 820, 745, 706 cm^{-1}. HRMS (EI, *m/z*): calcd for $[C_{27}H_{26}+H]^+$ 351.21182, found 351.20945.

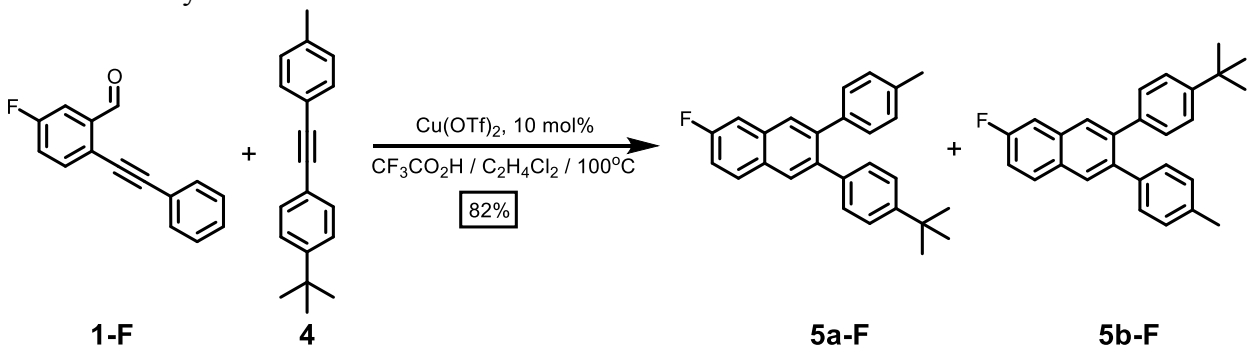
Scheme S8. Synthesis of **5a-^{13}C** and **5b-^{13}C**.



Synthesis of 5a-^{13}C and 5b-^{13}C: 5a-^{13}C and **5b-^{13}C** were synthesized using a similar procedure to that used to prepare **3.** Alkyne **4** (21 mg, 0.084 mmol), benzaldehyde **1-^{13}C$_2$** (25 mg, 0.120 mmol), 1,2-dichloroethane (1.5 mL), $Cu(OTf)_2$ (4 mg, 0.012 mmol) and CF_3CO_2H (10 μL, 0.132 mmol) were used. Chromatography (SiO_2, 1:9 *v/v* $CHCl_3$:hexanes) provided **5a-^{13}C** and **5b-^{13}C** (29 mg, 95% yield) as a colorless, viscous oil, that was an inseparable mixture. **5a-^{13}C** and **5b-^{13}C: ^{1}**H NMR (400 MHz, $CDCl_3$) **5a-^{13}C:** δ 7.90 (d, J_{CH} = 158.0 Hz, 1H), 7.91 – 7.85 (m, 2H),

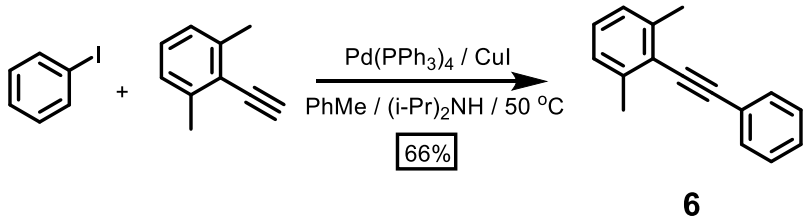
7.88 (s, 1H), 7.52 – 7.48 (m, 2H), 7.29 (d, J = 8.3 Hz, 2H), 7.19 (d, J = 8.3 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 2.36 (s, 3H), 1.34 (s, 9H). **5b-^{13}C:** δ 7.90 (s, 1H), 7.91 – 7.85 (m, 2H), 7.88 (d, J_{CH} = 158.0 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.29 (d, J = 8.3 Hz, 2H), 7.19 (d, J = 8.3 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 2.36 (s, 3H), 1.34 (s, 9H). **5a-^{13}C** and **5b-^{13}C:** ^{13}C NMR (75 MHz, $CDCl_3$) δ 129.60, 129.52 (two ^{13}C-enriched carbon signals) IR (solid, ATR) 3050, 2960, 2865, 1904, 1587, 1513, 1487, 1450, 1402, 1362, 1265, 1109, 1018, 950, 883, 834, 819, 738, 704 cm^{-1}. HRMS (EI, *m/z*): calcd for $[C_{26}{}^{13}CH_{26}+H]^+$ 352.21518, found 352.21293.

Scheme S9. Synthesis of **5a-F** and **5b-F**.



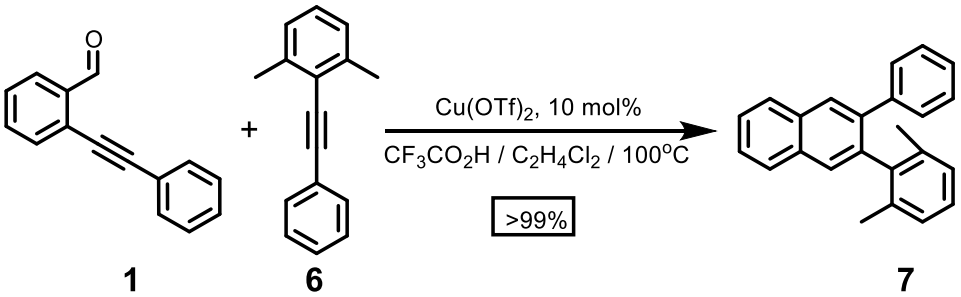
Synthesis of 5a-F and 5b-F: 5a-F and **5b-F** were synthesized using a similar procedure to that used to prepare **3.** Alkyne **4** (89 mg, 0.357 mmol), benzaldehyde **1-F** (100 mg, 0.446 mmol), 1,2-dichloroethane (5.0 mL), $Cu(OTf)_2$ (16 mg, 0.045 mmol) and CF_3CO_2H (38 μL, 0.491 mmol) were used. Chromatography (SiO_2, 2.5% *v/v* EtOAc/hexanes) provided **5a-F** and **5b-F** (107 mg, 82% yield) as a colorless, viscous oil, which was an inseparable mixture. **5a-F** and **5b-F:** ^{1}H NMR (500 MHz, $CDCl_3$) **5a-F:** δ 7.85 (s, 1H), 7.84 – 7.80 (m, 1H), 7.78 (s, 1H), 7.45 (dt, J = 10.0, 1.9 Hz, 1H), 7.31 – 7.20 (m, 3H), 7.14 (d, J = 8.3 Hz, 2H), 7.11 (d, J = 8.3 Hz, 2H), 7.04 (d, J = 8.4 Hz, 2H), 2.33 (s, 3H), 1.31 (s, 9H). **5b-F:** δ 7.84 – 7.80 (m, 1H), 7.83 (s, 1H), 7.80 (s, 1H), 7.45 (dt, J = 10.0, 1.9 Hz, 1H), 7.31 – 7.20 (m, 3H), 7.14 (d, J = 8.3 Hz, 2H), 7.11 (d, J = 8.3 Hz, 2H), 7.04 (d, J = 8.4 Hz, 2H), 2.33 (s, 3H), 1.31 (s, 9H). **5a-F** and **5b-F:** ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.98 (d, J_{CF} = 246 Hz), 160.97 (d, J_{CF} = 246 Hz), 149.75, 149.61, 140.31, 140.24, 138.55 (d, J_{CF} = 7 Hz), 138.54 (d, J_{CF} = 7 Hz), 138.45, 138.38, 138.37, 138.30, 136.45, 136.29, 133.45 (d, J_{CF} = 9 Hz), 133.44 (d, J_{CF} = 9 Hz), 130.24, 130.17, 129.93, 129.80, 129.65, 129.53, 129.45, 128.91 (d, J_{CF} = 5 Hz), 128.83 (d, J_{CF} = 5 Hz), 128.76, 128.74, 124.96, 116.60 (d, J_{CF} = 25 Hz), 116.59 (d, J_{CF} = 25 Hz), 110.73 (d, J_{CF} = 20 Hz), 110.72 (d, J_{CF} = 20 Hz), 34.62, 34.60, 31.51, 31.50, 21.32, 21.31. IR (solid, ATR) 2962, 2867, 1905, 1635, 1599, 1512, 1492, 1459, 1422, 1399, 1362, 1346, 1265, 1219, 1190, 1144, 1119, 1110, 1046, 1015, 973, 948, 898, 836, 820, 762, 736, 703 cm^{-1}. HRMS (EI, *m/z*): calcd for $[C_{27}H_{25}F]^+$ 368.19348, found 368.19249.

Scheme S10. Synthesis of **6**.



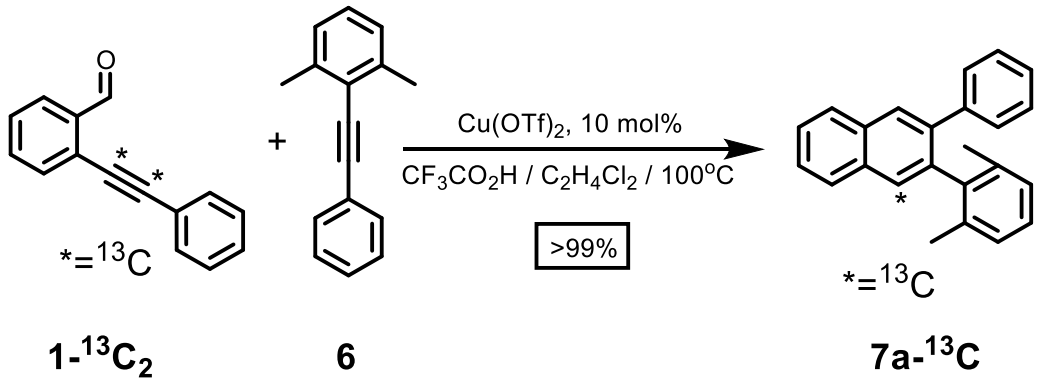
Synthesis of 6: A solution of 2-ethynyl-1,3-dimethylbenzene (100 mg, 0.768 mmol) and iodobenzene (313 mg, 1.536 mmol) in DIPA (2 mL) was sparged with nitrogen for 20 min. The solution was transferred using a cannula to a flask containing $Pd(PPh_3)_4$ (44 mg, 0.038 mmol) and CuI (15 mg, 0.077 mmol) suspended in PhMe (4 mL) under N_2 atmosphere. The mixture was heated to 50 °C and stirred for 1 h. It was cooled to rt and added to a separatory funnel containing 50 mL Et_2O. It was extracted with aqueous 1 M HCl (50 mL), and brine (2 x 50 mL). The organic phase was dried ($MgSO_4$), filtered and the solvent was removed. The crude product was purified by flash chromatography (SiO_2, hexanes) to provide **6** (0.105g, 66% yield) as a clear oil. **6:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.1 Hz, 2H), 7.36 (m, 3H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 2H), 2.52 (s, 6H). 13C NMR (75 MHz, $CDCl_3$) δ 140.40, 131.53, 128.50, 128.23, 127.91, 126.83, 123.97, 123.10, 97.97, 87.26, 21.28. IR (solid, ATR) 3061, 2916, 1596, 1570, 1489, 1466, 1441, 1376, 1300, 1164, 1085, 1068, 1026, 911, 768, 753, 731, 688 cm^{-1}. HRMS (EI, *m/z*): calcd for $[C_{16}H_{14}+H]^+$ 207.11792, found 207.11644.

Scheme S11. Synthesis of **7**.



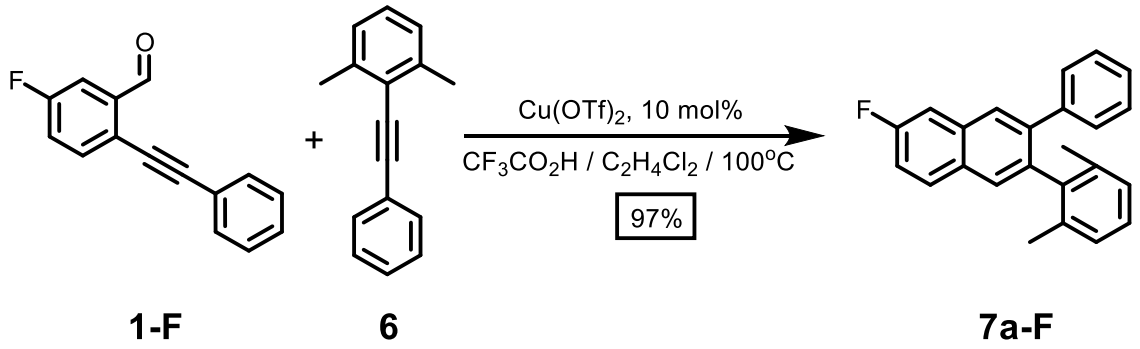
Synthesis of 7: **7** was synthesized using a similar procedure to that used to prepare **3**. Alkyne6 (18 mg, 0.087 mmol), benzaldehyde **1** (30 mg, 0.145 mmol), 1,2-dichloroethane (1.5 mL), $Cu(OTf)_2$ (5 mg, 0.015 mmol) and CF_3CO_2H (12 µL, 0.160 mmol) were used. Chromatography (SiO_2, 1:9 *v/v* $CHCl_3$:hexanes) provided **7** (28 mg, >99% yield) as a colorless oil. **7:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.98 – 7.93 (m, 1H), 7.91 – 7.85 (m, 1H), 7.70 (s, 1H), 7.59 – 7.51 (m, 2H), 7.22 (s, 5H), 7.13 (t, *J* = 8.1, 1H), 7.03 (d, *J* = 8.1 Hz, 2H), 2.00 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.22, 140.77, 139.73, 137.72, 136.43, 132.99, 132.83, 129.22, 129.18, 127.98, 127.78, 127.76, 127.68, 127.29, 127.19, 126.83, 126.21, 126.20, 21.11. IR (solid, ATR) 3053, 2919, 1599, 1488, 1462, 1442, 1376, 1327, 1264, 1164, 1131, 1099, 1075, 1022, 958, 915, 890, 765, 746, 717, 697, 668 cm^{-1}. HRMS (EI, *m/z*): calcd for $[C_{24}H_{20}]^+$ 308.15595, found 308.15514.

Scheme S12. Synthesis of **7a-^{13}C**.



Synthesis of 7a-^{13}C: 7a-^{13}C was synthesized using a similar procedure to that used to prepare **3.** Alkyne **6** (21 mg, 0.102 mmol), benzaldehyde **1-^{13}C$_2$** (30 mg, 0.145 mmol), 1,2-dichloroethane (1.5 mL), $Cu(OTf)_2$ (5 mg, 0.015 mmol) and CF_3CO_2H (12 μL, 0.160 mmol) were used. Chromatography (SiO_2, 1:9 *v*/*v* $CHCl_3$:hexanes) provided **7a-^{13}C** (35 mg, >99% yield) as a colorless, viscous oil. **7a-^{13}C:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.98 – 7.93 (m, 1H), 7.91 – 7.85 (m, 1H), 7.70 (d, J_{CH} = 158.0 Hz, 1H), 7.59 – 7.51 (m, 2H), 7.22 (s, 5H), 7.13 (t, J = 8.1, 1H), 7.03 (d, J = 8.1 Hz, 2H), 2.00 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 129.22 (one ^{13}C-enriched carbon signal). IR (solid, ATR) 3052, 2920, 1580, 1488, 1463, 1441, 1376, 1272, 1191, 1163, 1131, 1075, 1022, 955, 914, 887, 796, 764, 746, 717, 698 cm^{-1}. HRMS (EI, *m/z*): calcd for $[C_{23}{}^{13}CH_{20}]^+$ 309.16040, found 309.15851.

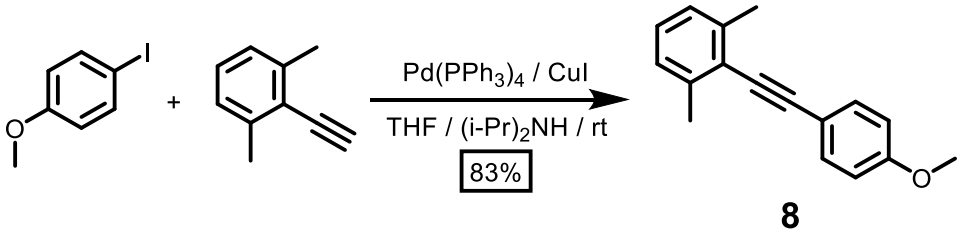
Scheme S13. Synthesis of **7a-F**.



Synthesis of 7a-F: 7a-F was synthesized using a similar procedure to that used to prepare **3**. Alkyne **6** (21 mg, 0.103 mmol), benzaldehyde **1-F** (29 mg, 0.129 mmol), 1,2-dichloroethane (1.5 mL), $Cu(OTf)_2$ (5 mg, 0.013 mmol) and CF_3CO_2H (11 μL, 0.142 mmol) were used. Chromatography (SiO_2, 1:9 *v*/*v* $CHCl_3$:hexanes) provided **7a-F** (33 mg, 97% yield) as a colorless, viscous oil. **7a-F:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.85 (dd, J = 9.0, 5.6 Hz, 1H), 7.68 (s, 1H), 7.55 (dd, J = 9.8, 2.6 Hz, 1H), 7.31 (td, J = 8.7, 2.6 Hz, 1H), 7.21 (m, 5H), 7.12 (t, J = 7.6 Hz, 1H), 7.02 (d, J = 7.6 Hz, 2H), 1.98 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.98 (d, J_{CF} = 246 Hz), 140.87, 140.79, 140.47, 137.02 (d, J_{CF} = 3 Hz), 136.43, 133.02 (d, J_{CF} = 10 Hz), 130.10 (d, J_{CF} = 9 Hz), 129.84, 129.20, 129.13, 128.20 (d, J_{CF} = 5 Hz), 127.82, 127.34,

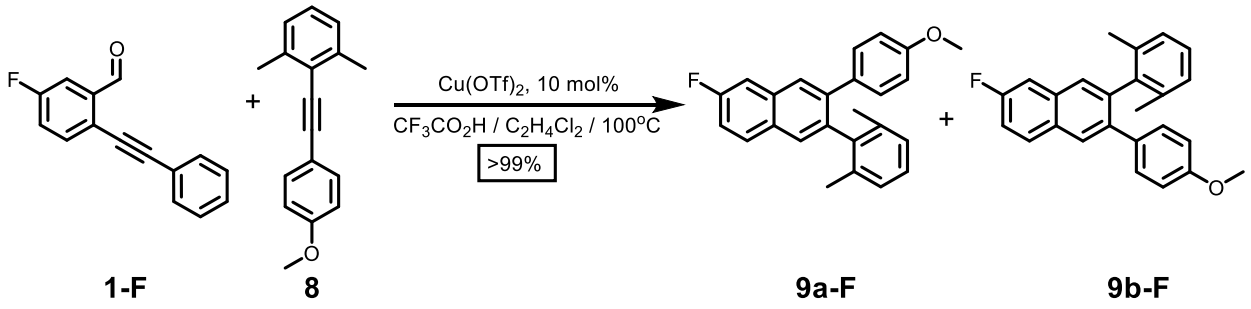
127.28, 127.04, 116.63 (d, J_{CF} = 26 Hz), 110.89 (d, J_{CF} = 21 Hz), 21.09. IR (solid, ATR) 3057, 2918, 1636, 1602, 1571, 1489, 1462, 1442, 1377, 1347, 1265, 1218, 1185, 1144, 1120, 1074, 1020, 972, 945, 896, 849, 806, 763, 748, 740, 713, 697 cm^{-1}. HRMS (EI, *m/z*): calcd for $[C_{24}H_{19}F]^+$ 326.14653, found 326.14555.

Scheme S14. Synthesis of **8**.



Synthesis of 8: A solution of 2-ethynyl-1,3-dimethylbenzene (50 mg, 0.768 mmol) and 4-iodoanisole (180 mg, 1.536 mmol) in DIPA (2 mL) was sparged with nitrogen for 20 min. The above solution was transferred using a cannula to a flask containing $Pd(PPh_3)_4$ (44 mg, 0.038 mmol) and CuI (15 mg, 0.077 mmol) suspended in THF (4 mL) under N_2 atmosphere. The mixture was heated to 50 °C and stirred for 2 h. It was cooled to rt and added to a separatory funnel containing 50 mL Et_2O. It was extracted with aqueous 1 M HCl (50 mL), and brine (2 x 50 mL). The organic phase was dried ($MgSO_4$), filtered and the solvent was removed. The crude product was purified by flash chromatography (SiO_2, hexanes) to provide **8** (76 mg, 83% yield) as colorless needles. **8:** ^{1}H NMR (599 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.9 Hz, 2H), 7.11(dd, *J* = 8.5, 6.3 Hz, 1H), 7.06 (d, *J* = 7.4 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 3.84 (s, 3H), 2.50 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.66, 140.16, 132.95, 127.56, 126.78, 123.42, 116.15, 114.15, 97.96, 85.94, 55.48, 21.29. IR (solid, ATR) 3068, 3003, 2967, 2914, 2838, 2733, 2533, 2208, 2035, 1930, 1891, 1602, 1568, 1508, 1465, 1441, 1377, 1301, 1285, 1244, 1181, 1172, 1142, 1105, 1087, 1025, 988, 918, 832, 808, 790, 768, 731, 713 cm^{-1}. HRMS (EI, *m/z*): calcd for $[C_{17}H_{16}O+H]^+$ 237.12739, found 237.12670.

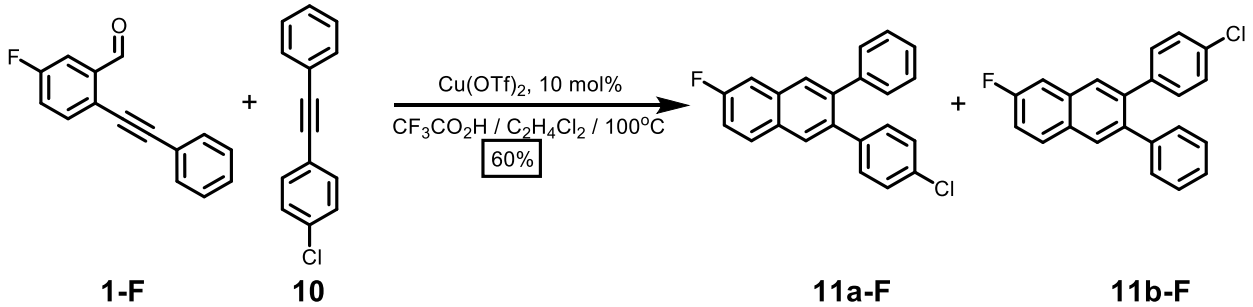
Scheme S15. Synthesis of **9a-F** and **9b-F**.



Synthesis of 9a-F and 9b-F: 9a-F and **9b-F** were synthesized using a similar procedure to that used to prepare **3.** Alkyne **8** (24 mg, 0.100 mmol), benzaldehyde **1-F** (30 mg, 0.134 mmol), 1,2-dichloroethane (1.5 mL), $Cu(OTf)_2$ (5 mg, 0.013 mmol) and CF_3CO_2H (11 μL, 0.147 mmol) were used. Chromatography (SiO_2, 4% *v/v* EtOAc/hexanes) provided **9a-F** and **9b-F** (39 mg,

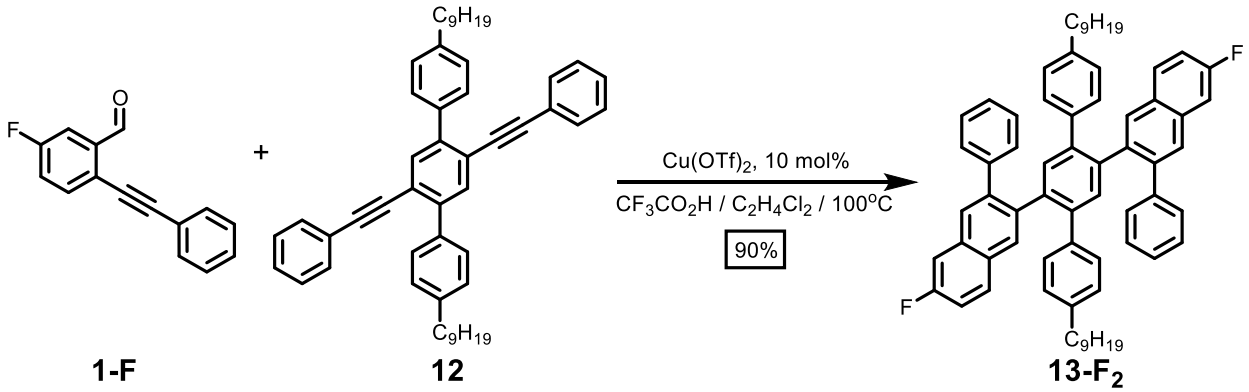
>99% yield) as a colorless viscous oil, which was an inseparable mixture. **9a-F** and **9b-F:** ^{1}H NMR (599 MHz, $CDCl_3$) **9a-F:** 7.86 (s, 1H) 7.82 (dd, J = 8.9, 5.6 Hz, 1H), 7.64 (s, 1H), 7.52 (dd, J = 9.9, 2.5 Hz, 1H), 7.33 – 7.27 (m, 1H), 7.16 – 7.07 (m, 3H), 7.02 (d, J = 7.6 Hz, 2H), 6.74 (d, J = 8.5 Hz, 2H) 3.76 (s, 3H), 1.97 (s, 6H). **9b-F:** δ 7.93 – 7.88 (m, 1H), 7.91 (s, 1H), 7.59 (s, 1H), 7.45 (dd, J = 9.8, 2.6 Hz, 1H), 7.33 – 7.27 (m, 1H), 7.16 – 7.07 (m, 3H), 7.02 (d, J = 7.6 Hz, 2H), 6.74 (d, J = 8.5 Hz, 2H) 3.76 (s, 3H), 1.97 (s, 6H). **9a-F** and **9b-F:** ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.97 (d, J_{CF} = 246 Hz), 160.89 (d, J_{CF} = 246 Hz), 158.73, 158.62, 140.67, 140.63, 140.39, 138.98, 138.67 (d, J_{CF} = 3 Hz), 137.10 (d, J_{CF} = 3 Hz), 136.43, 136.29, 133.73 (d, J_{CF} = 9 Hz), 133.38, 133.29 (d, J_{CF} = 9 Hz), 130.28 (d, J_{CF} = 9 Hz), 130.23, 130.20, 130.10, 130.06 (d, J_{CF} = 9 Hz), 129.66, 129.18, 128.78, 128.53 (d, J_{CF} = 5 Hz), 128.13 (d, J_{CF} = 5 Hz), 127.39, 127.27, 127.23, 116.57 (d, J_{CF} = 25 Hz), 116.40 (d, J_{CF} = 26 Hz), 113.33, 113.32, 110.77 (d, J_{CF} = 20 Hz), 110.62 (d, J_{CF} = 20 Hz), 55.24, 21.06, 21.03. IR (solid, ATR) 2919, 2835, 1635, 1608, 1515, 1494, 1462, 1441, 1377, 1343, 1283, 1246, 1215, 1177, 1143, 1119, 1041, 1026, 972, 946, 898, 833, 807, 771, 736, 710, 668 cm^{-1}. HRMS (EI, *m/z*): calcd for $[C_{25}H_{21}FO]^+$ 356.15595, found 356.15631.

Scheme S16. Synthesis of **11a-F** and **11b-F**.



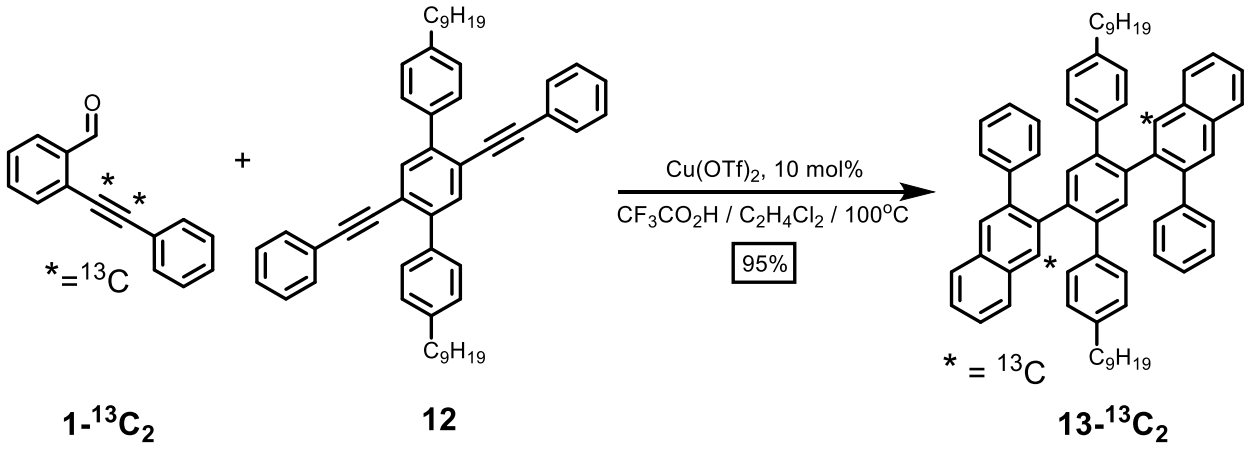
Synthesis of 11a-F and 11b-F: 11a-F and **11b-F** were synthesized using a similar procedure to that used to prepare **3.** 1-Chloro-4-(phenylethynyl)benzene (19 mg, 0.089 mmol), benzaldehyde **1-F** (25 mg, 0.111 mmol), 1,2-dichloroethane (1.5 mL), $Cu(OTf)_2$ (4 mg, 0.011 mmol) and CF_3CO_2H (9 µL, 0.123 mmol) were used. Chromatography (SiO_2, hexanes) provided **11a-F** and **11b-F** (18 mg, 60% yield) as a colorless viscous oil, which was an inseparable mixture. 37% of 1-Chloro-4-(phenylethynyl)benzene was recovered unreacted. **11a-F** and **11b-F:** ^{1}H NMR (599 MHz, $CDCl_3$) **11a-F:** δ 7.88 – 7.84 (m, 1H), 7.84 (s, 1H), 7.81 (s, 1H), 7.48 (dd, J = 9.8, 2.5 Hz, 1H), 7.32 – 7.23 (m, 4H), 7.23 – 7.16 (m, 4H), 7.15 – 7.10 (m, 2H). **11b-F:** δ 7.88 – 7.84 (m, 1H), 7.87 (s, 1H), 7.78 (s, 1H), 7.48 (dd, J = 9.8, 2.5 Hz, 1H), 7.32 – 7.23 (m, 4H), 7.23 – 7.16 (m, 4H), 7.15 – 7.10 (m, 2H). **11a-F** and **11b-F:**^{13}C NMR (126 MHz, $CDCl_3$) δ 161.04 (d, J_{CF} = 247 Hz), 160.99 (d, J_{CF} = 247 Hz), 140.80, 140.74, 139.95, 139.61, 139.54, 138.87, 138.24 (d, J_{CF} = 3 Hz), 137.16 (d, J_{CF} = 3 Hz), 133.51 (d, J_{CF} = 9 Hz), 133.34 (d, J_{CF} = 9 Hz), 132.89, 132.75, 131.18, 131.17, 130.20 (d, J_{CF} = 9 Hz), 130.17 (d, J_{CF} = 9 Hz), 129.91, 129.89, 129.81, 129.66, 129.54 (d, J_{CF} = 1 Hz), 129.32 (d, J_{CF} = 1 Hz), 128.92 (d, J_{CF} = 5 Hz), 128.69 (d, J_{CF} = 5 Hz), 128.14, 128.13, 128.08, 126.93, 126.80, 116.94 (d, J_{CF} = 25 Hz), 116.88 (d, J_{CF} = 25 Hz), 110.74 (d, J_{CF} = 21 Hz), 110.71 (d, J_{CF} = 21 Hz). IR (solid, ATR) 3059, 2920, 2849, 1637, 1601, 1491, 1443, 1418, 1396, 1348, 1220, 1190, 1144, 1120, 1093, 1013, 973, 947, 899, 834, 768, 735, 707, 699 cm^{-1}. HRMS (EI, *m/z*): calcd for $[C_{22}H_{14}ClF]^+$ 332.07626, found 332.07520.

Scheme S17. Synthesis of **13-F$_2$**.



Synthesis of 13-F$_2$: 13-F$_2$ was synthesized using a similar procedure to that used to prepare **3.** Dialkyne **12** (30 mg, 0.045 mmol), benzaldehyde **1-F** (33 mg, 0.147 mmol), 1,2-dichloroethane (1.5 mL), $Cu(OTf)_2$ (4 mg, 0.011 mmol) and CF_3CO_2H (9 μL, 0.123 mmol) were used. Chromatography (SiO_2, 2% *v*/*v* EtOAc:hexanes) provided **13-F$_2$** (37 mg, 90% yield) as a colorless, viscous oil. **13-F$_2$:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (s, 2H), 7.82 (dd, J = 9.0, 5.6 Hz, 2H), 7.57 (s, 2H), 7.47 – 7.41 (m, 4H), 7.30 – 7.23 (m, 2H), 7.19 (t, J = 7.3 Hz, 2H), 7.12 (t, J = 7.6 Hz, 4H), 6.76 (d, J = 7.8 Hz, 4H), 6.72 (d, J = 7.3 Hz, 4H), 6.51 (d, J = 7.8 Hz, 4H), 2.50 (td, J = 7.3, 2.5 Hz, 4H), 1.66 – 1.50 (m, 4H), 1.43 – 1.17 (m, 24H), 0.90 (t, J = 6.7 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.48 (d, J_{CF} = 247 Hz), 141.02, 140.69, 140.61, 140.05, 138.96, 138.28 (d, J_{CF} = 3 Hz), 137.60, 133.82, 133.71 (d, J_{CF} = 9 Hz), 130.51, 130.14 (d, J_{CF} = 9 Hz), 129.88, 129.32, 128.95, 128.21 (d, J_{CF} = 5 Hz), 127.90, 127.52, 126.39, 116.60 (d, J_{CF} = 26 Hz), 110.87 (d, J_{CF} = 20 Hz), 35.65, 32.07, 31.82, 29.81, 29.72, 29.53, 29.45, 22.86, 14.30. IR (solid, ATR) 2924, 2853, 1635, 1602, 1491, 1464, 1443, 1417, 1349, 1262, 1215, 1186, 1144, 1119, 1015, 949, 895, 805, 750, 697, 668 cm^{-1}. HRMS (EI, *m/z*): calcd for $[C_{68}H_{68}F_2+H]^+$ 923.53619, found 923.53201.

Scheme S18. Synthesis of **13-$^{13}C_2$**.



Synthesis of 13-$^{13}C_2$: 13-$^{13}C_2$ was synthesized using a similar procedure to that used to prepare **3.** Dialkyne **12** (50 mg, 0.073 mmol), benzaldehyde **1-$^{13}C_2$** (90 mg, 0.439 mmol), 1,2-dichloroethane (1.3 mL), $Cu(OTf)_2$ (9 mg, 0.026 mmol) and CF_3CO_2H (28 μL, 0.439 mmol) were used. Chromatography (SiO_2, 2% *v*/*v* EtOAc:hexanes) provided **13-$^{13}C_2$** (62 mg, 95% yield) as a colorless, viscous oil. **13-$^{13}C_2$:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J_{CH} = 159.17 Hz, 2H), 7.87 (m, 4H), 7.67 (s, 2H), 7.52 (m, J = 3.64 Hz, 6H), 7.20-7.13 (m, 4H), 6.78-6.77 (m, 8H), 6.57-6.55 (d, J = 8.35 Hz, 4H) 2.52 (t, J = 7.6 Hz, 4H), 1.61 (t, J = 7.2 Hz, 4H), 1.33 (m, br, 24H), 0.93 (t, J = 6.7 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 130.58 (s). MS: (*m*/*z* MALDI-TOF, TCNQ) calcd for $[C_{66}H_{70}{}^{13}C_2]^+$ 888.5477, found 888.5207.

C. NMR Spectra

Figure S1. ^{1}H NMR of **1-F** (400 MHz, $CDCl_3$, 298 K).

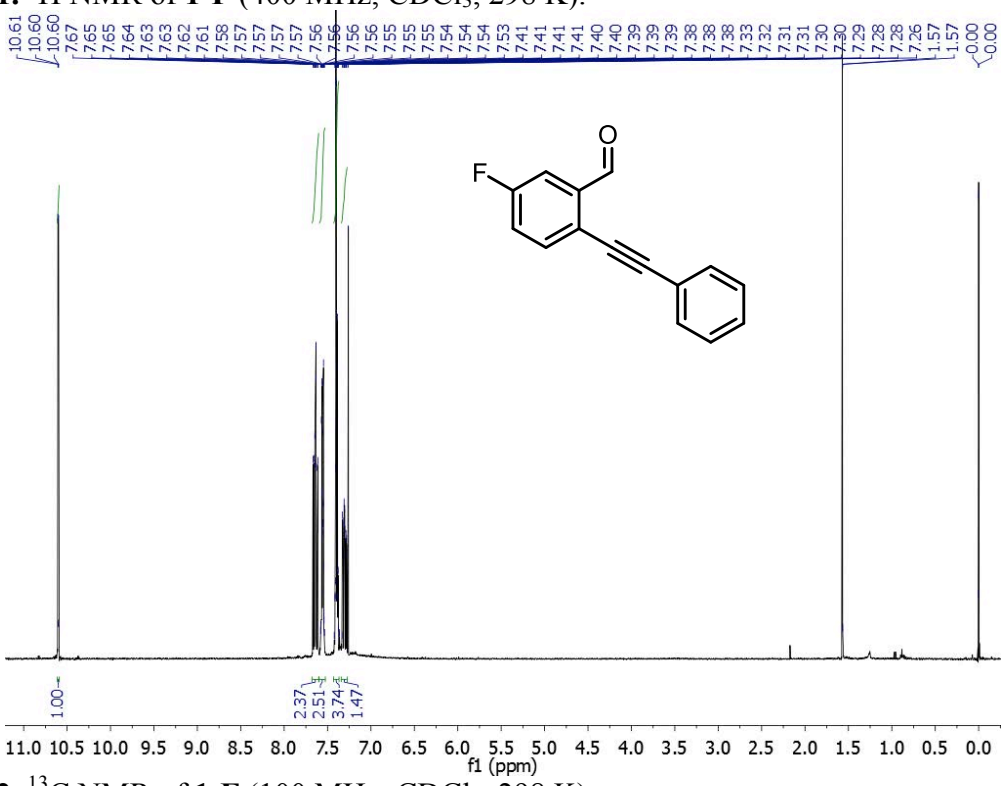


Figure S2. ^{13}C NMR of **1-F** (100 MHz, $CDCl_3$, 298 K).

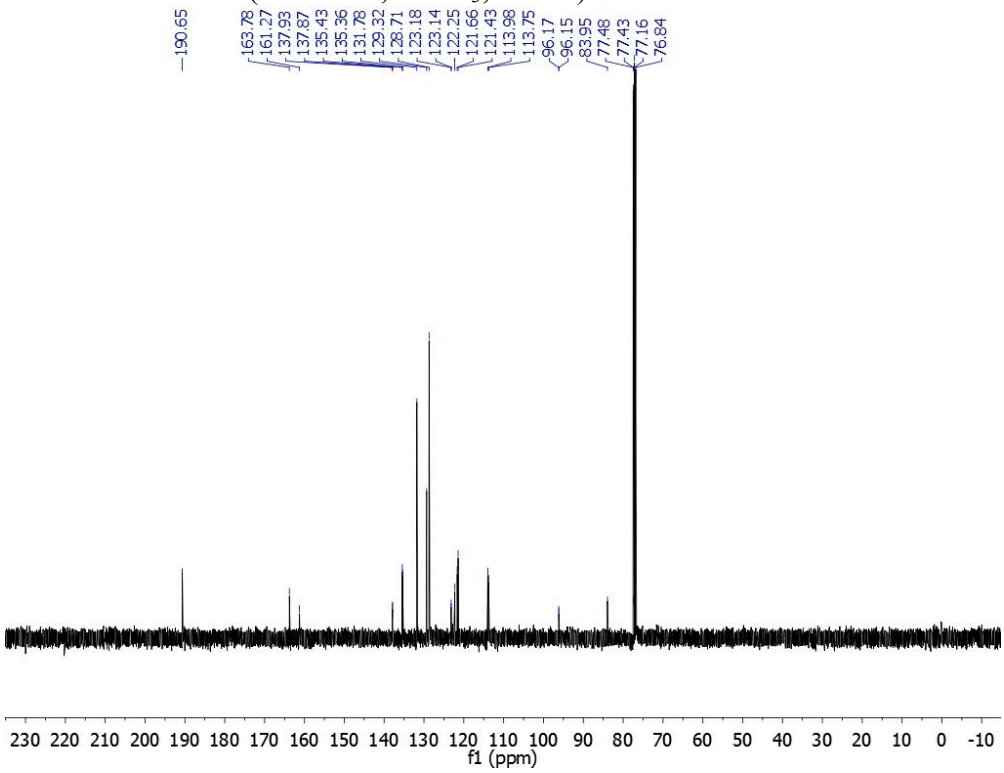


Figure S3. ^{1}H NMR of **2** (500 MHz, $CDCl_3$, 298 K).

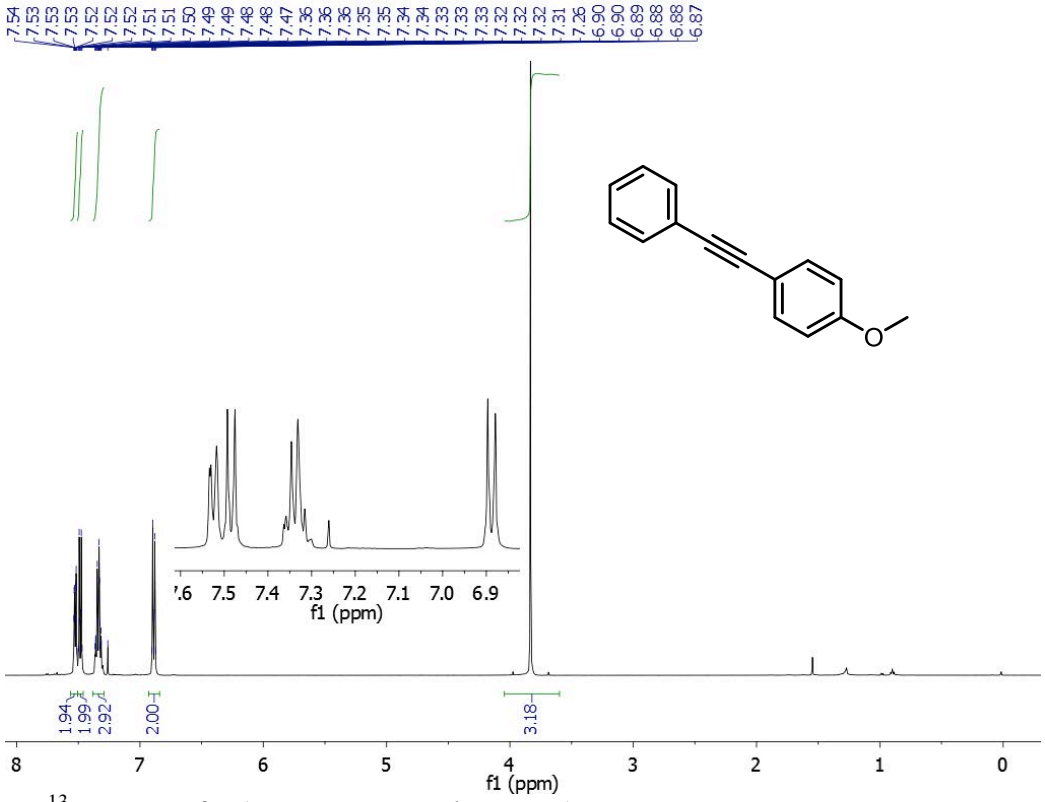


Figure S4. ^{13}C NMR of **2** (125 MHz, $CDCl_3$, 298 K).

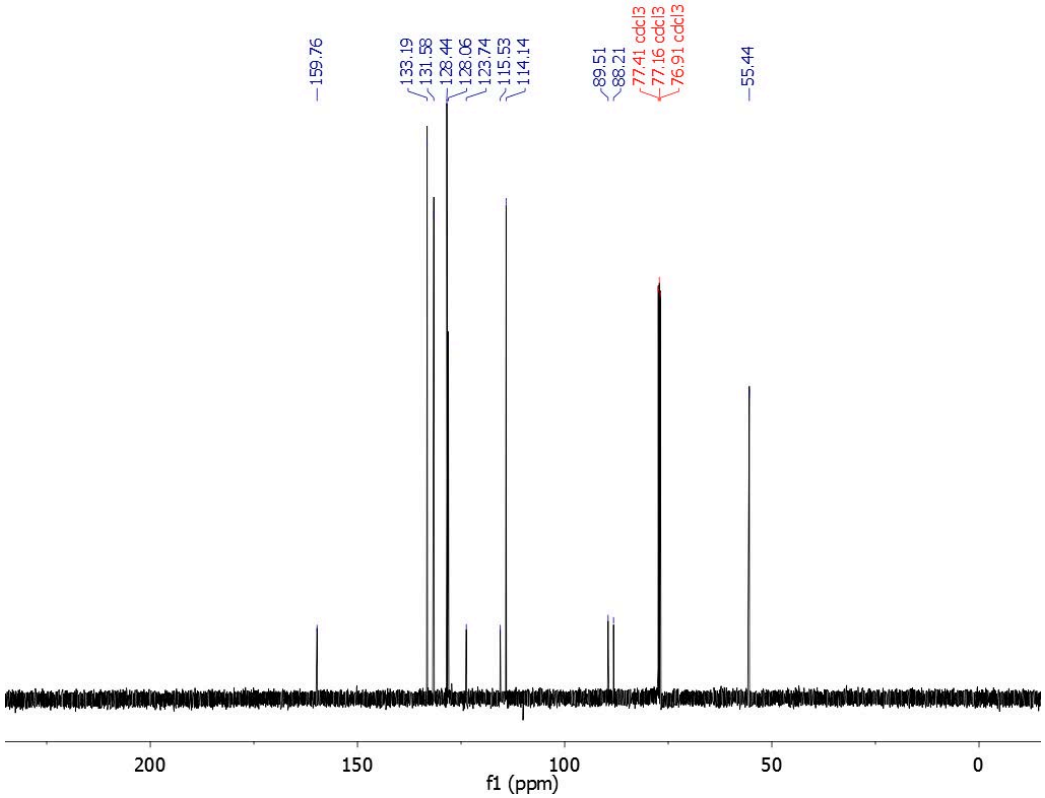


Figure S5. ^{1}H NMR of **3** (500 MHz, $CDCl_3$, 298 K).

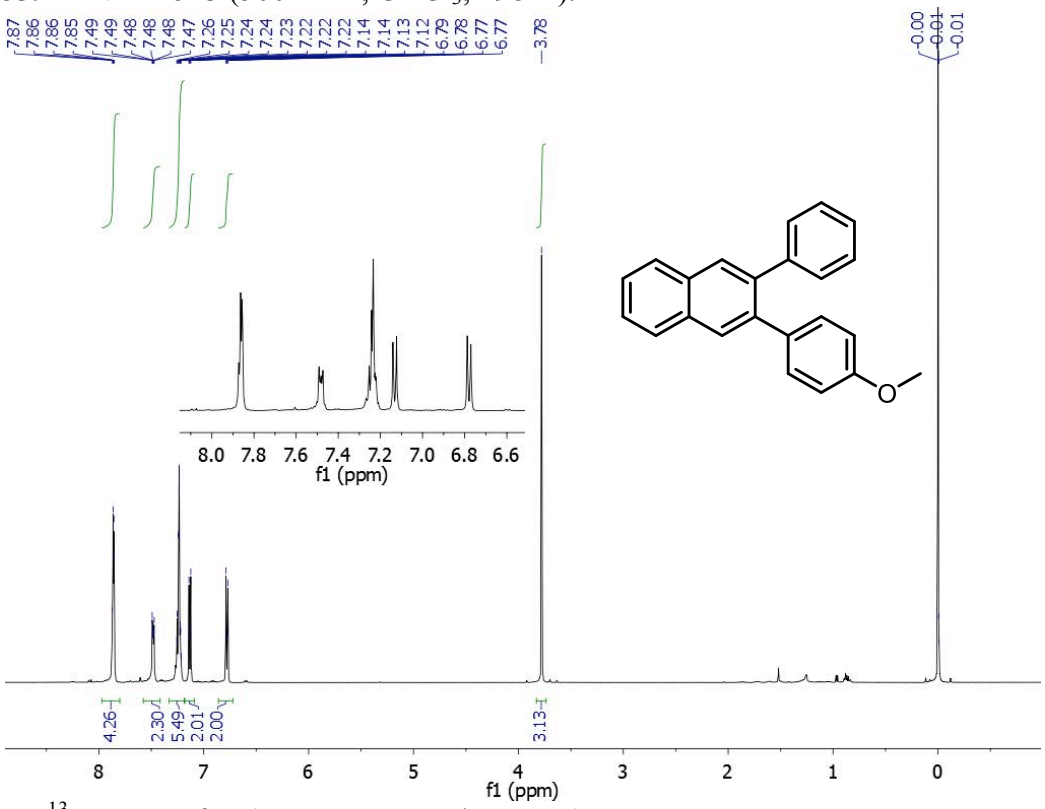


Figure S6. ^{13}C NMR of **3** (125 MHz, $CDCl_3$, 298 K).

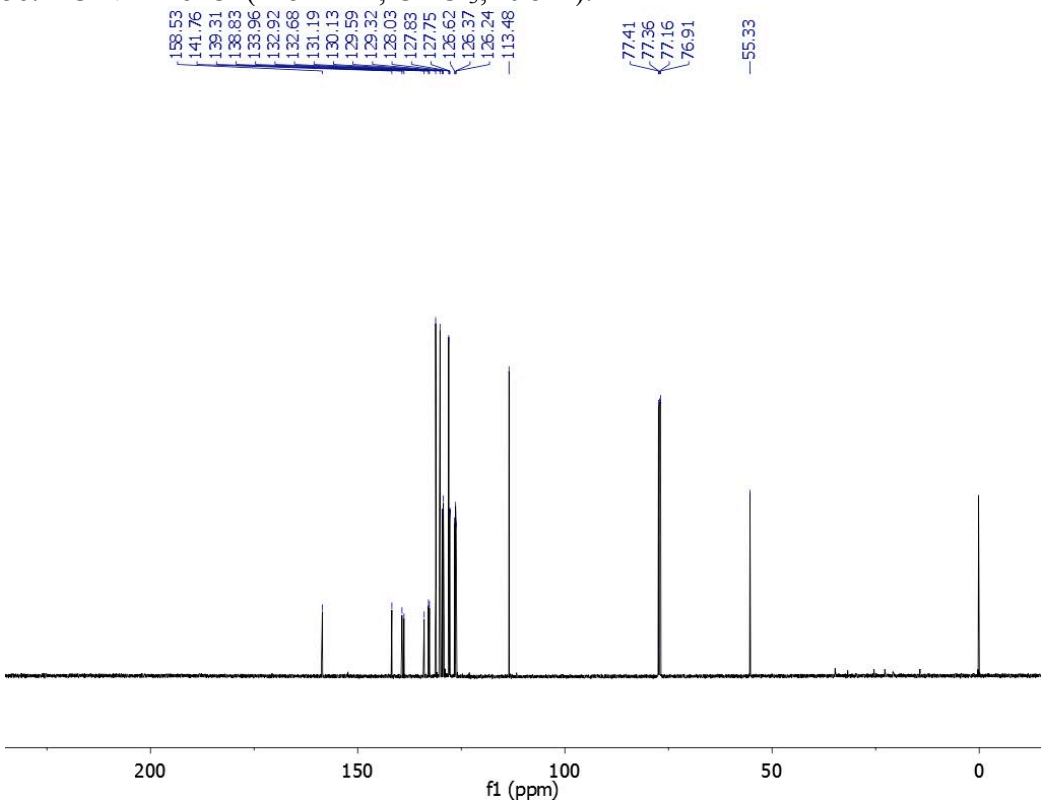


Figure S7. ^{1}H NMR of **3a-^{13}C** (400 MHz, $CDCl_3$, 298 K).

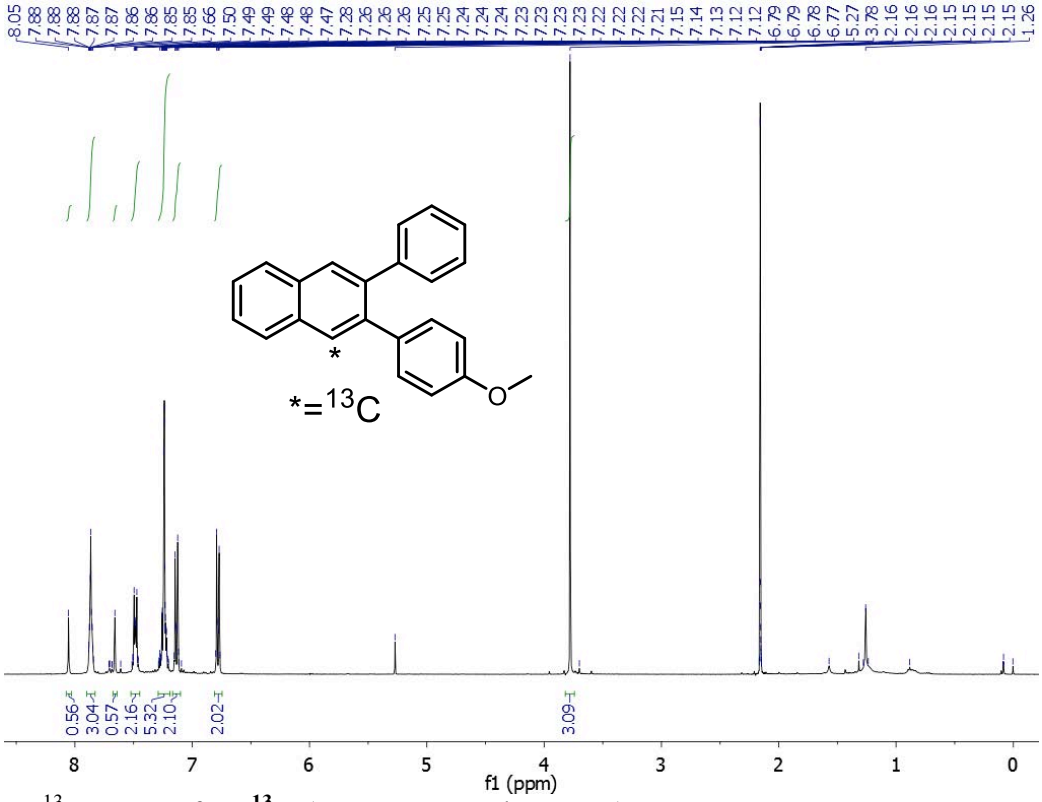


Figure S8. ^{13}C NMR of **3a-^{13}C** (75 MHz, $CDCl_3$, 298 K).

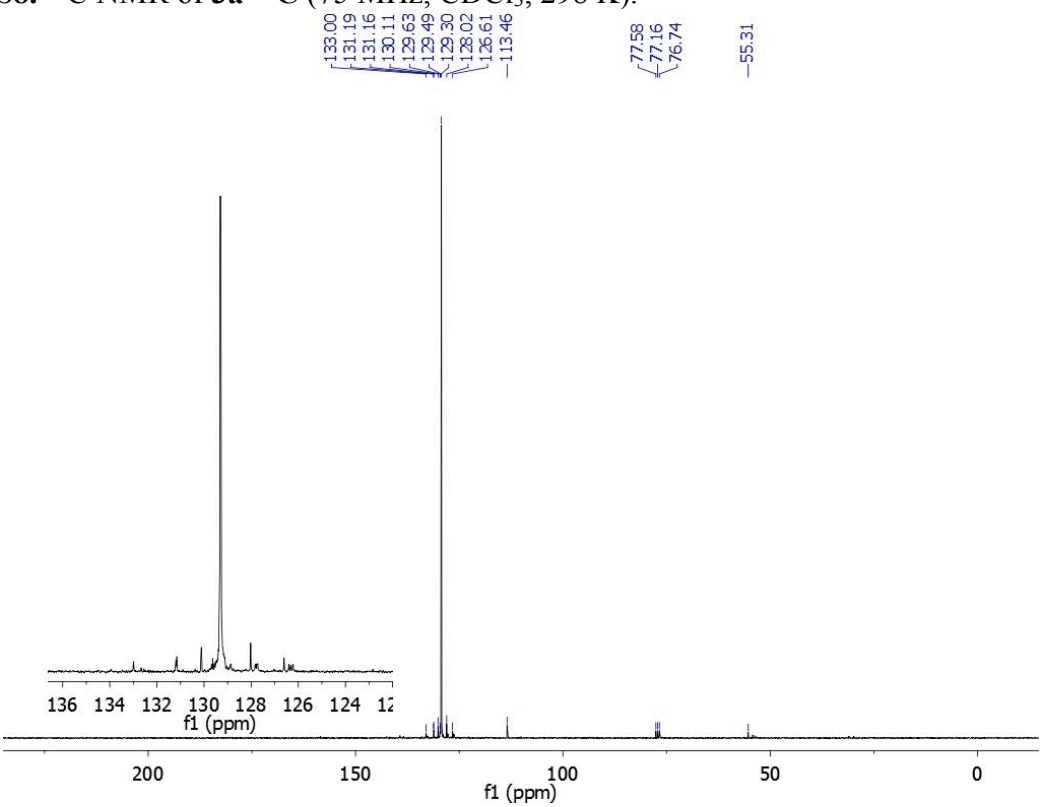


Figure S9. ^{1}H NMR of **3a-F** (500 MHz, $CDCl_3$, 298 K).

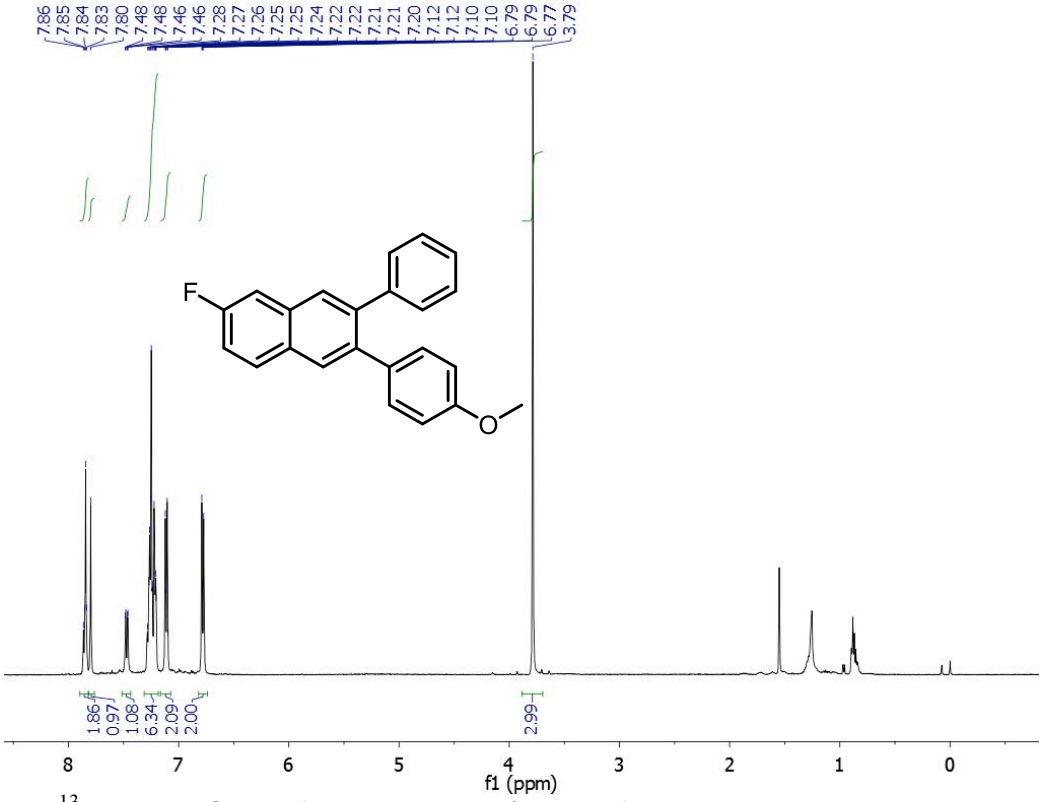


Figure S10. ^{13}C NMR of **3a-F** (125 MHz, $CDCl_3$, 298 K).

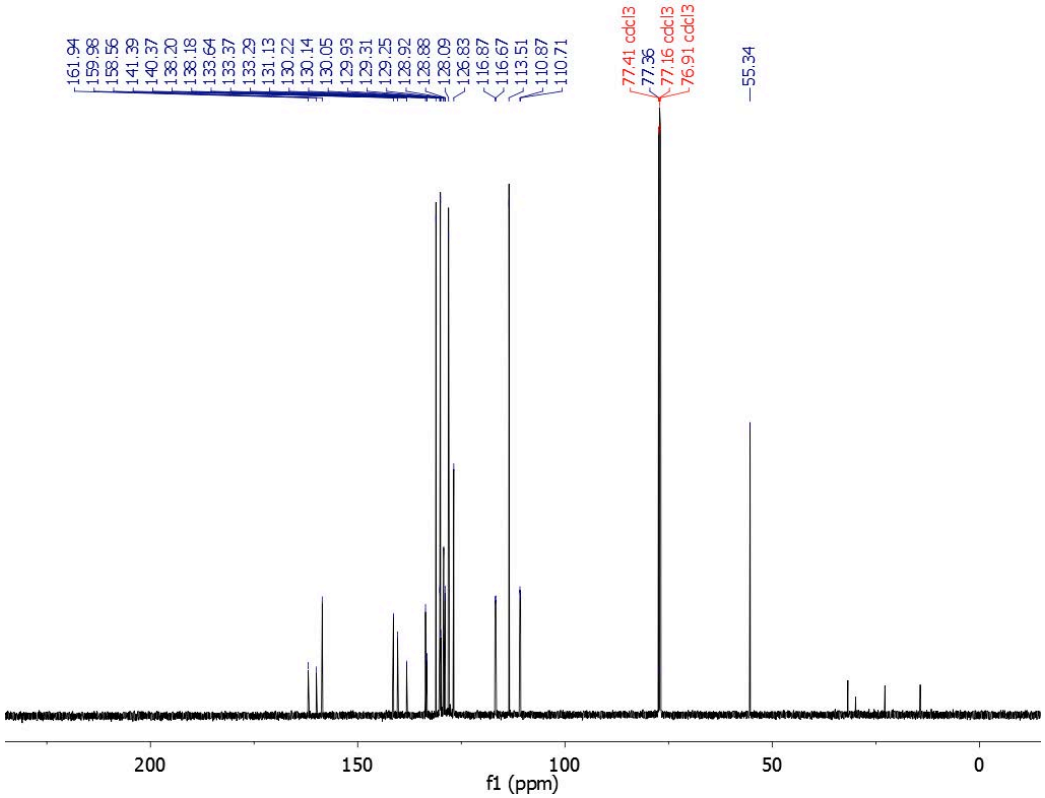


Figure S11. ^{1}H NMR of **4** (400 MHz, $CDCl_3$, 298 K).

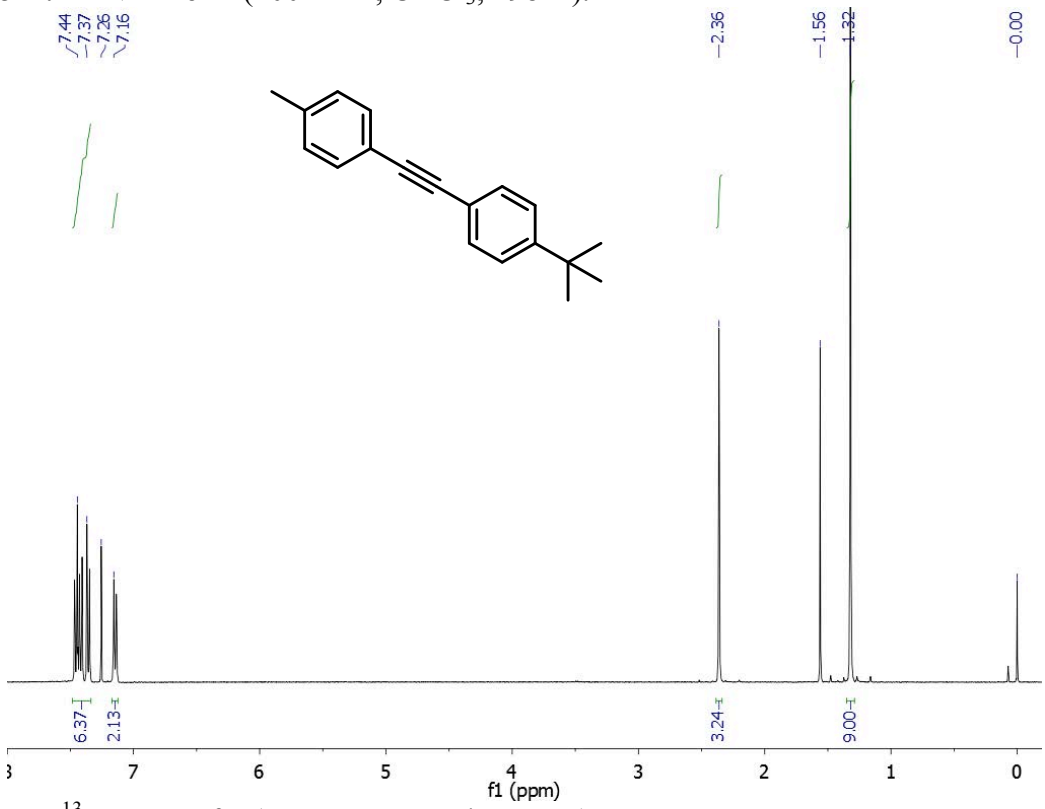


Figure S12. ^{13}C NMR of **4** (100 MHz, $CDCl_3$, 298 K).

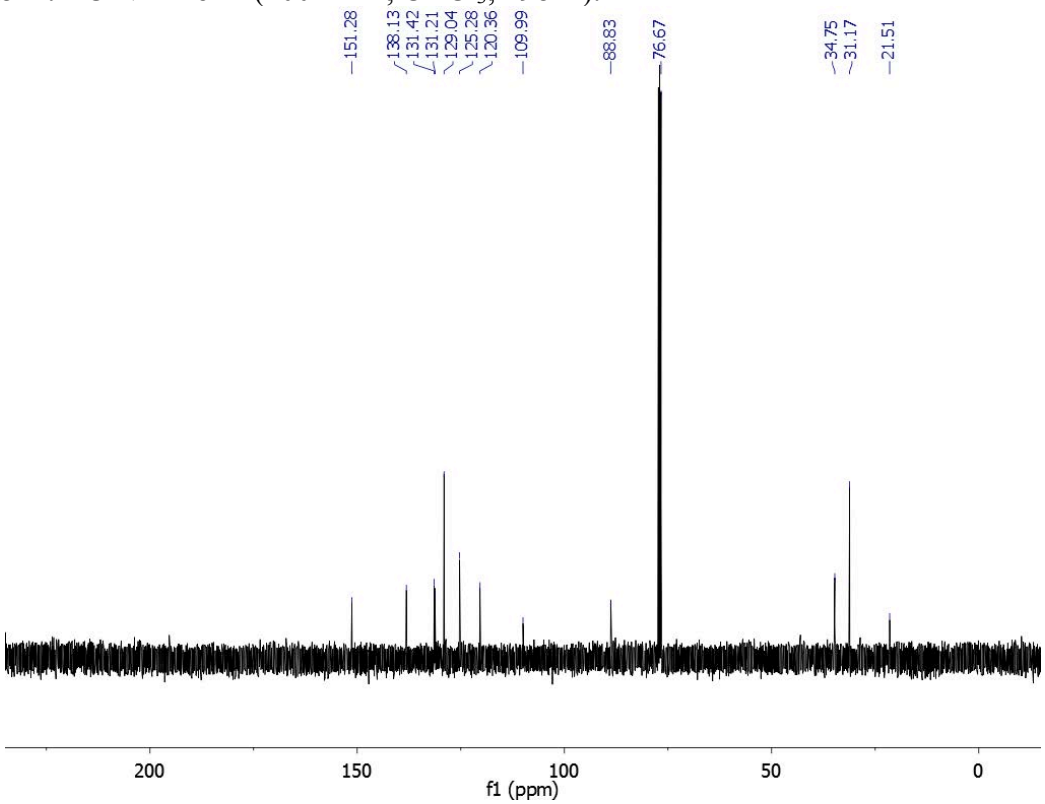


Figure S13. ^{1}H NMR of **5** (500 MHz, $CDCl_3$, 298 K).

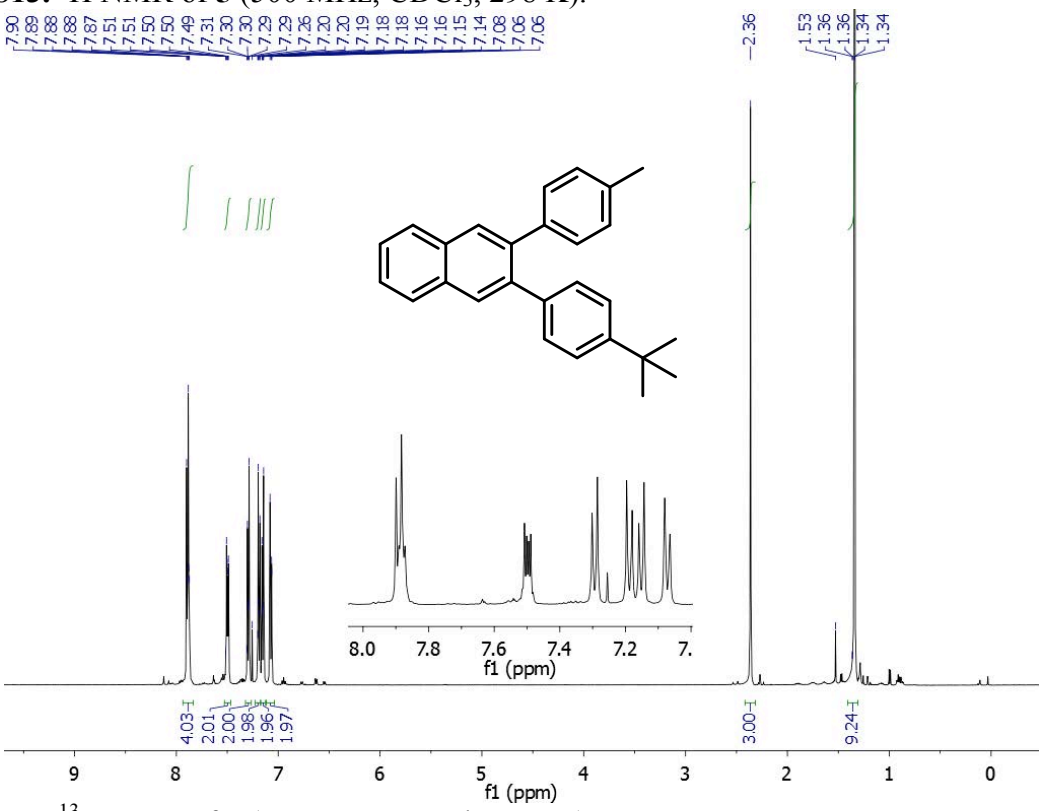


Figure S14. ^{13}C NMR of **5** (125 MHz, $CDCl_3$, 298 K).

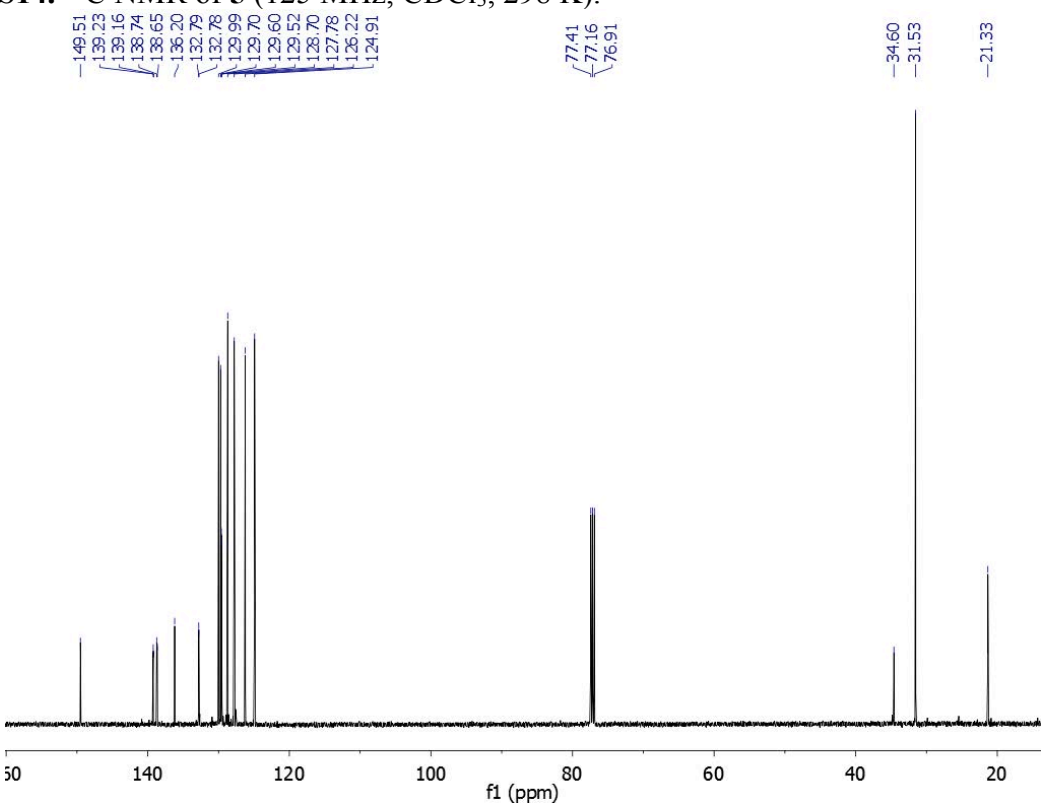


Figure S15. ^{1}H NMR of **5a-^{13}C** and **5b-^{13}C** (400 MHz, $CDCl_3$, 298 K).

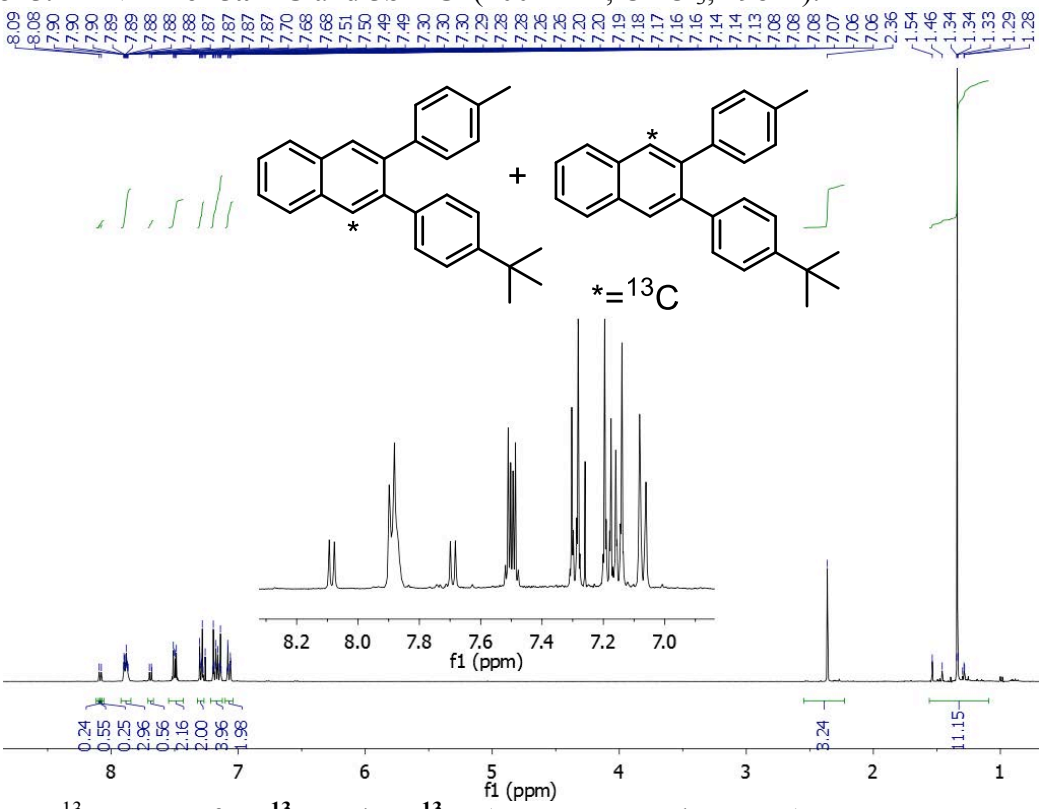


Figure S16. ^{13}C NMR of **5a-^{13}C** and **5b-^{13}C** (75 MHz, $CDCl_3$, 298 K).

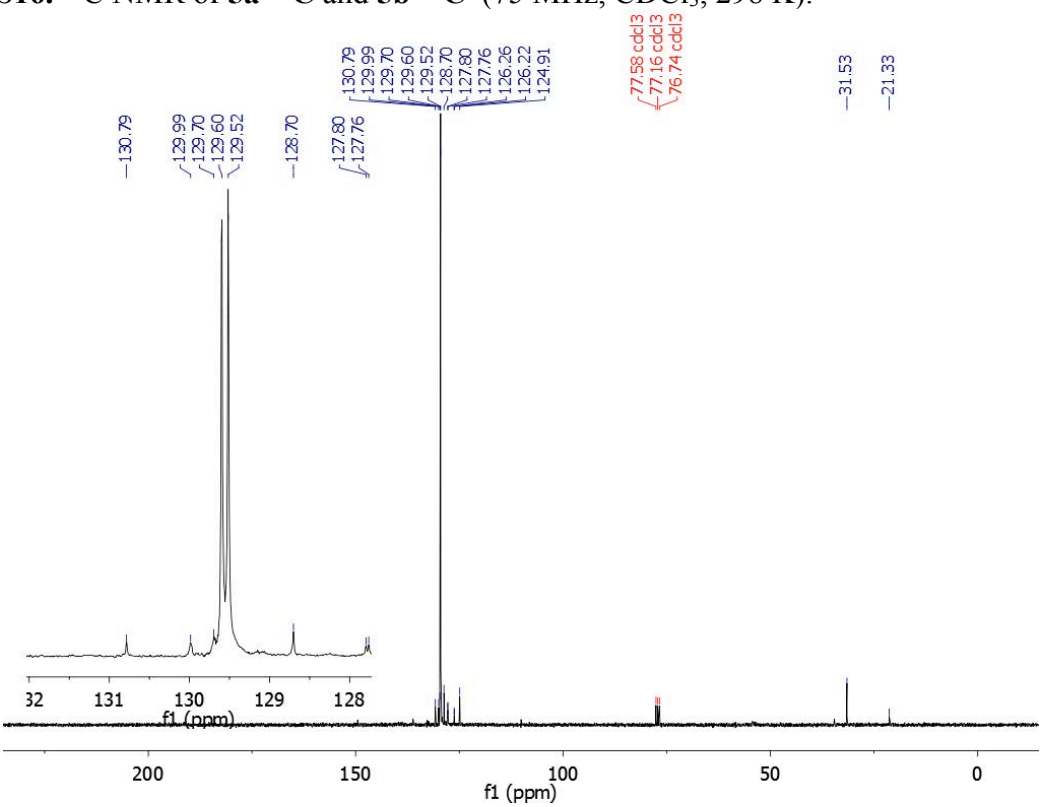


Figure S17. ^{1}H NMR of **5a-F** and **5 d-F** (500 MHz, $CDCl_3$, 298 K).

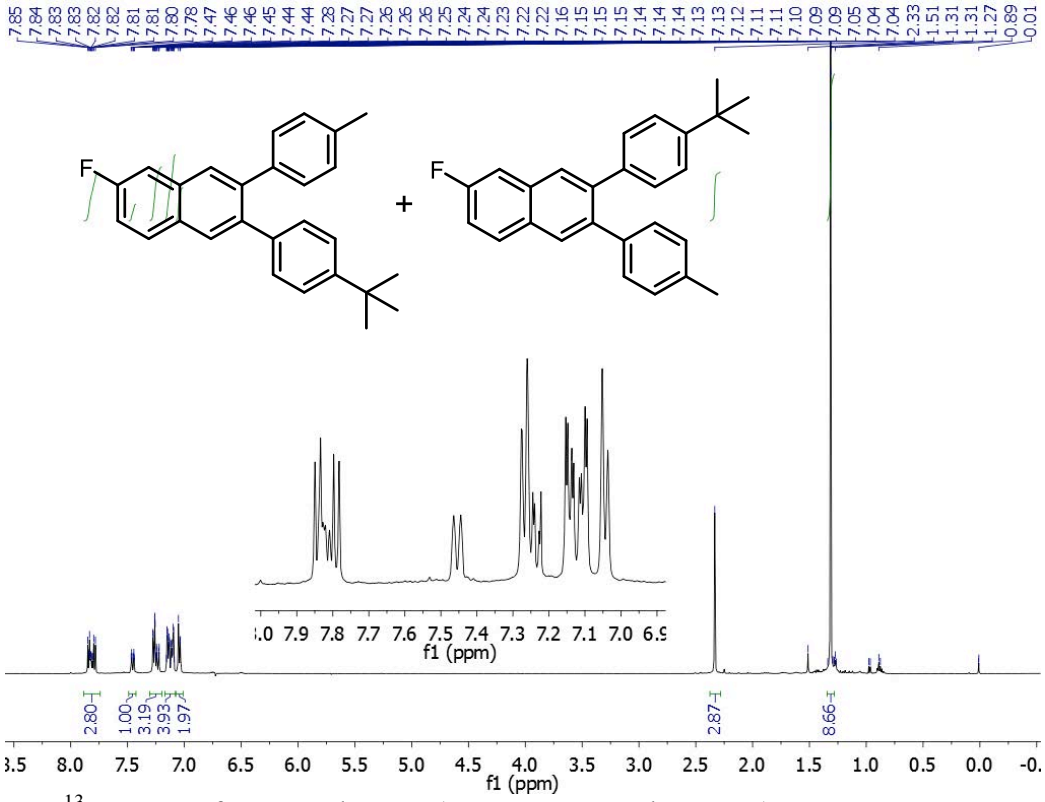


Figure S18. ^{13}C NMR of **5a-F** and **5 d-F** (125 MHz, $CDCl_3$, 298 K).

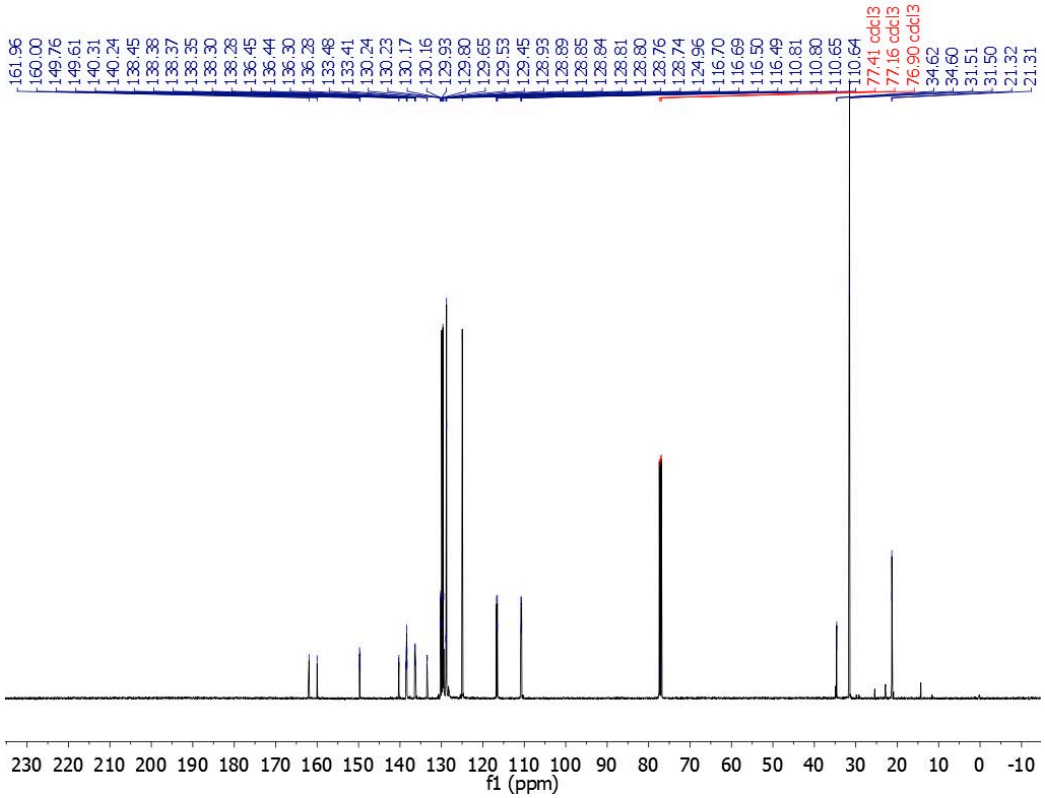


Figure S19. ^{1}H NMR of **6** (500 MHz, $CDCl_3$, 298 K).

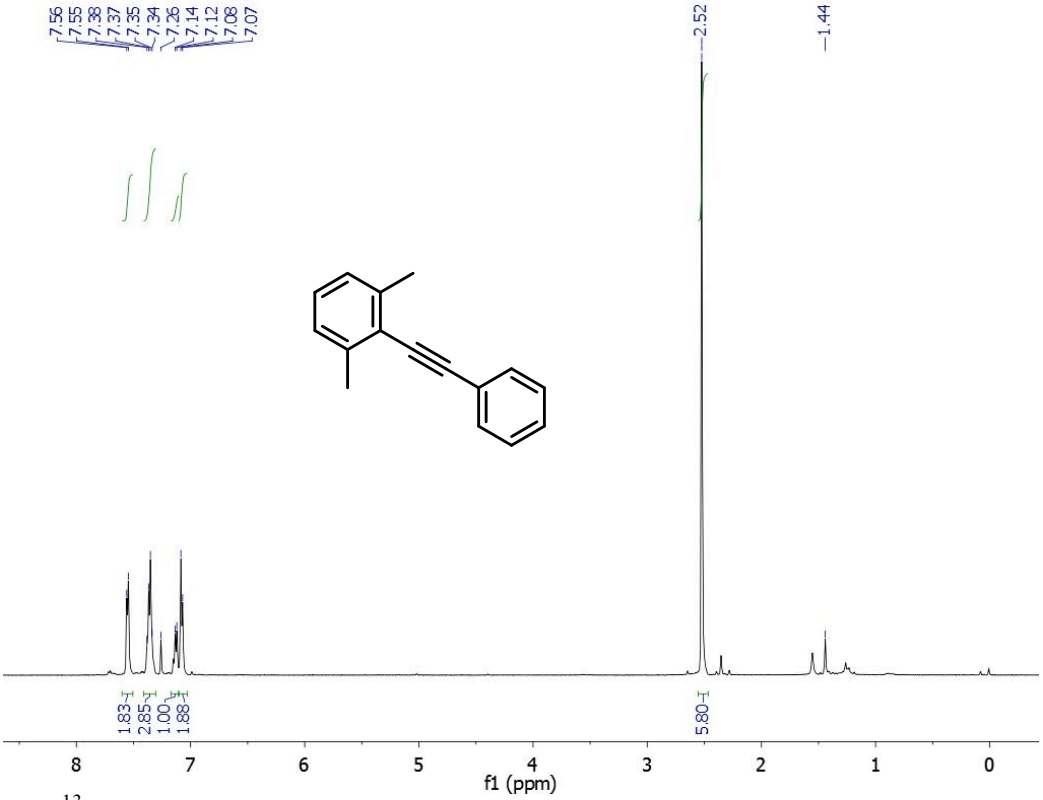


Figure S20. ^{13}C NMR of **6** (125 MHz, $CDCl_3$, 298 K).

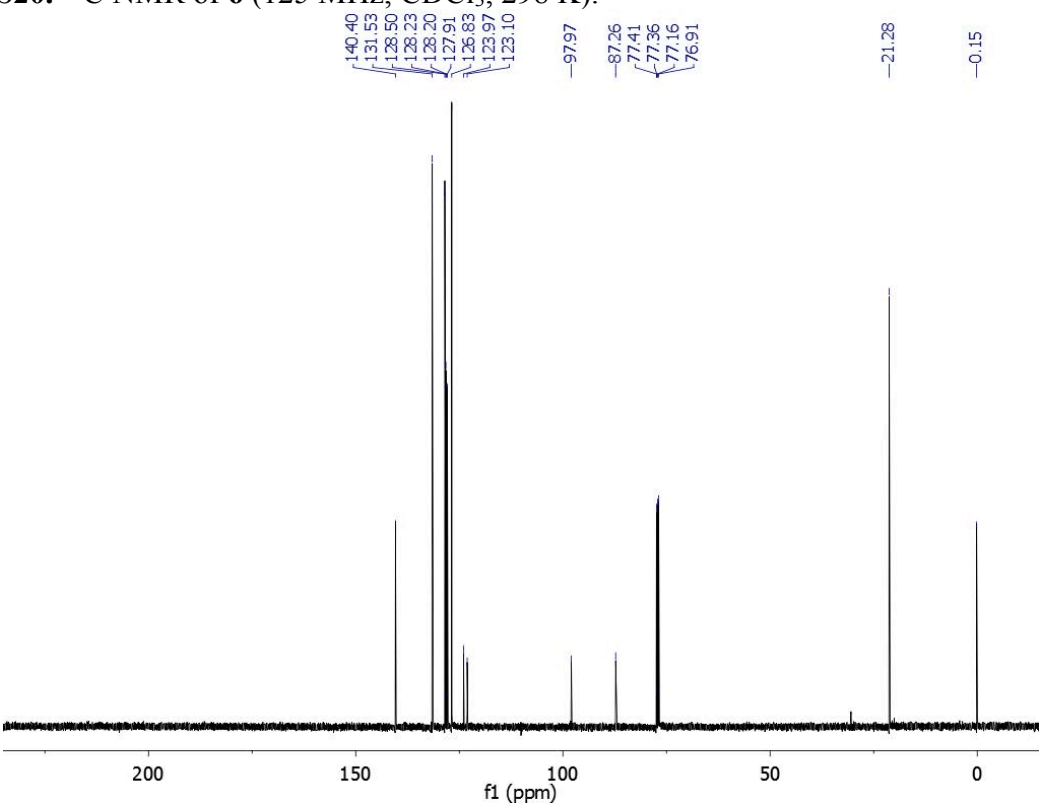


Figure S21. ^{1}H NMR of **7** (500 MHz, $CDCl_3$, 298 K).

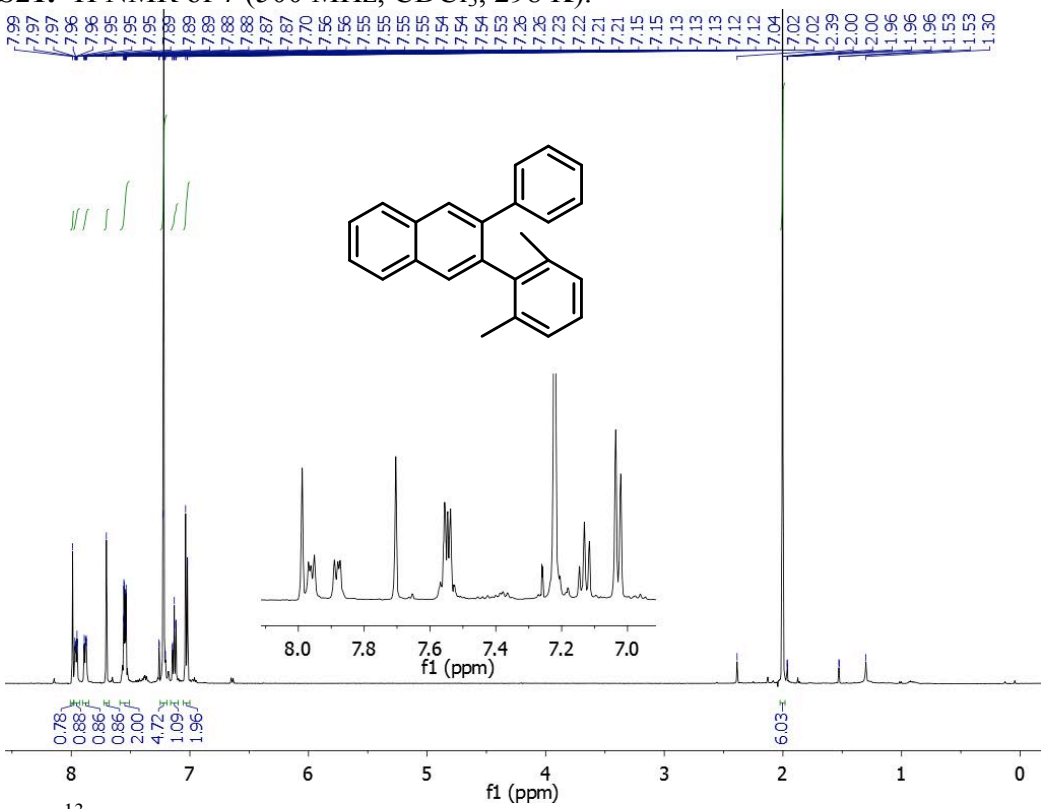


Figure S22. ^{13}C NMR of **7** (125 MHz, $CDCl_3$, 298 K).

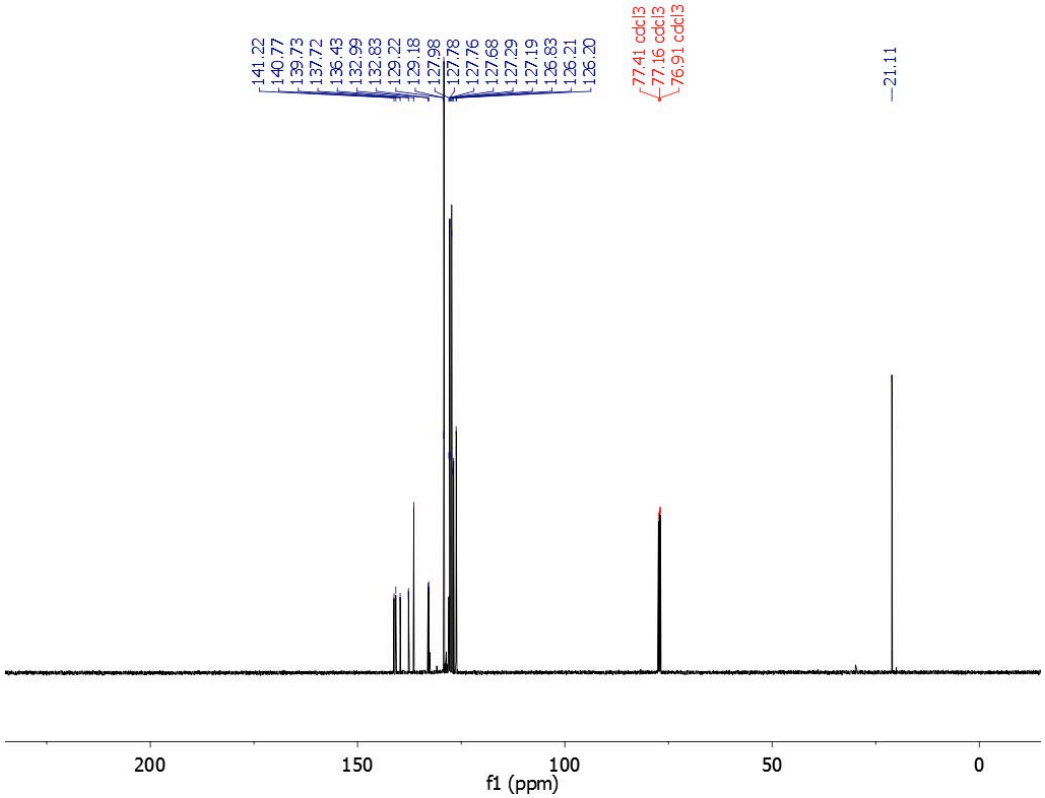


Figure S23. ^{1}H NMR of **7a-^{13}C** (400 MHz, $CDCl_3$, 298 K).

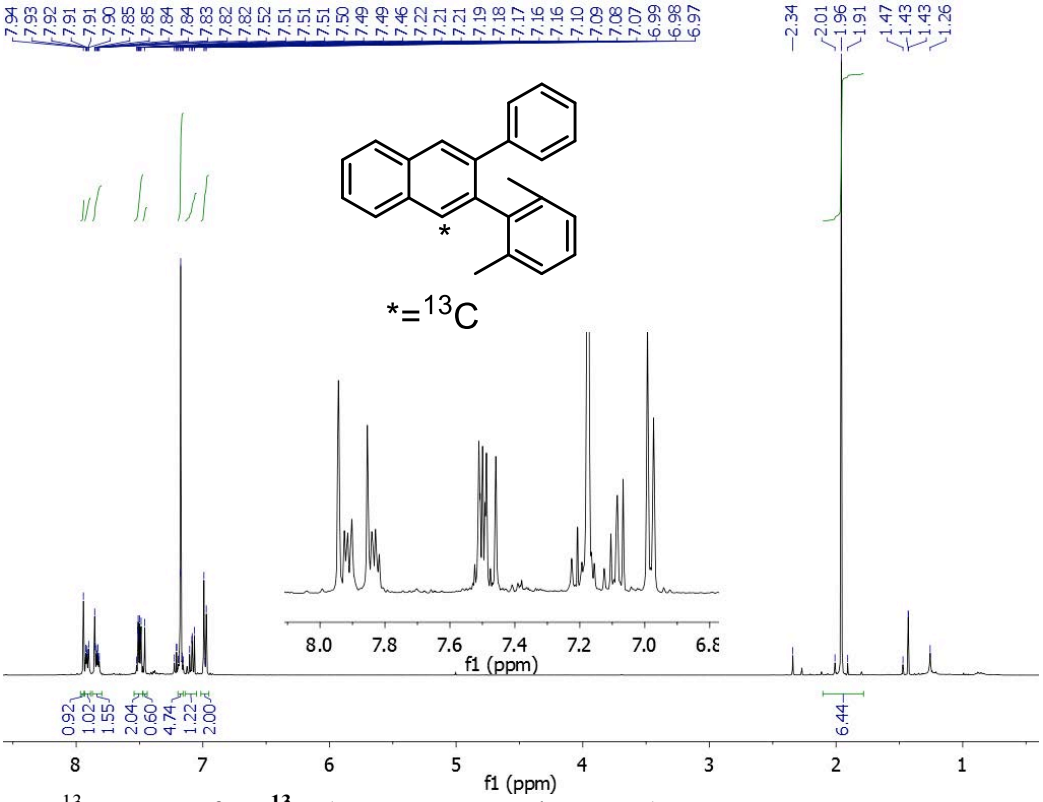


Figure S24. ^{13}C NMR of **7a-^{13}C** (125 MHz, $CDCl_3$, 298 K).

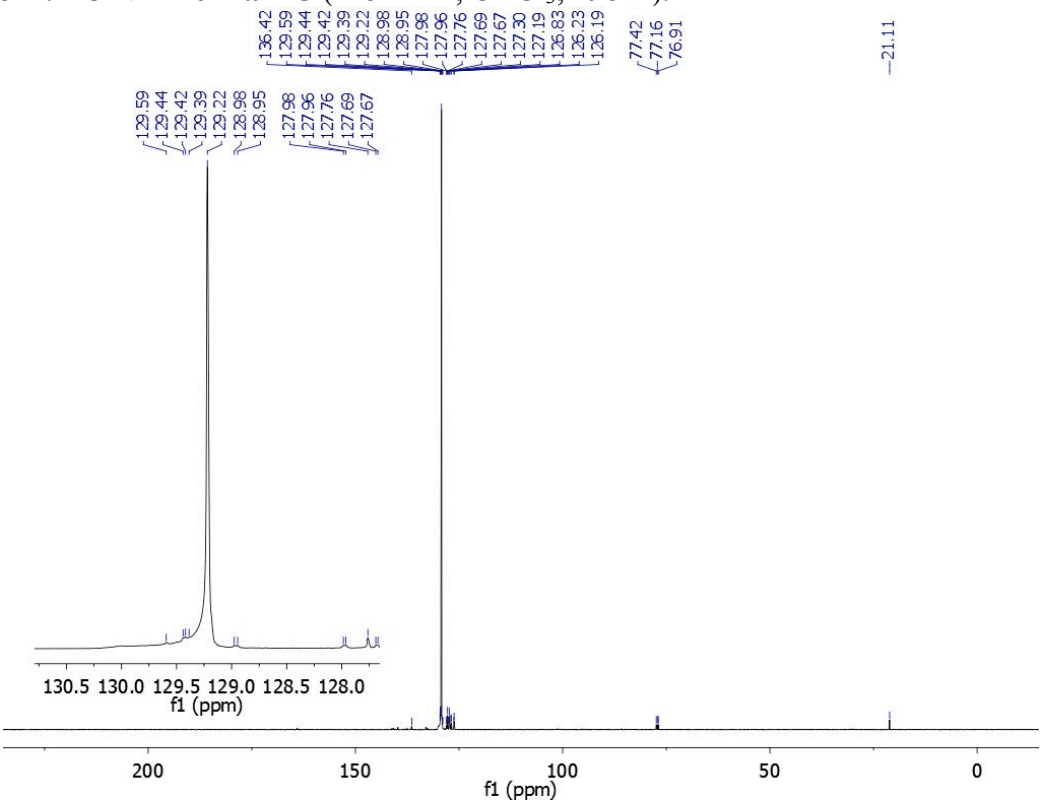


Figure S25. ^{1}H NMR of **7a-F** (500 MHz, $CDCl_3$, 298 K).

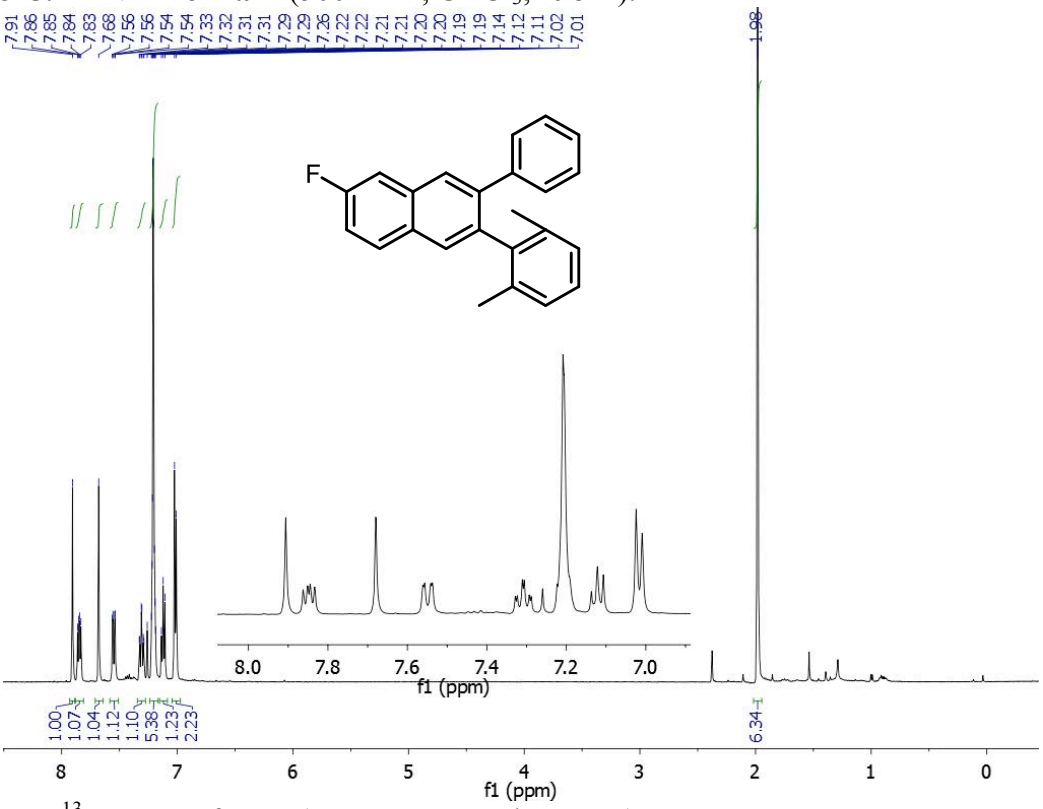


Figure S26. ^{13}C NMR of **7a-F** (125 MHz, $CDCl_3$, 298 K).

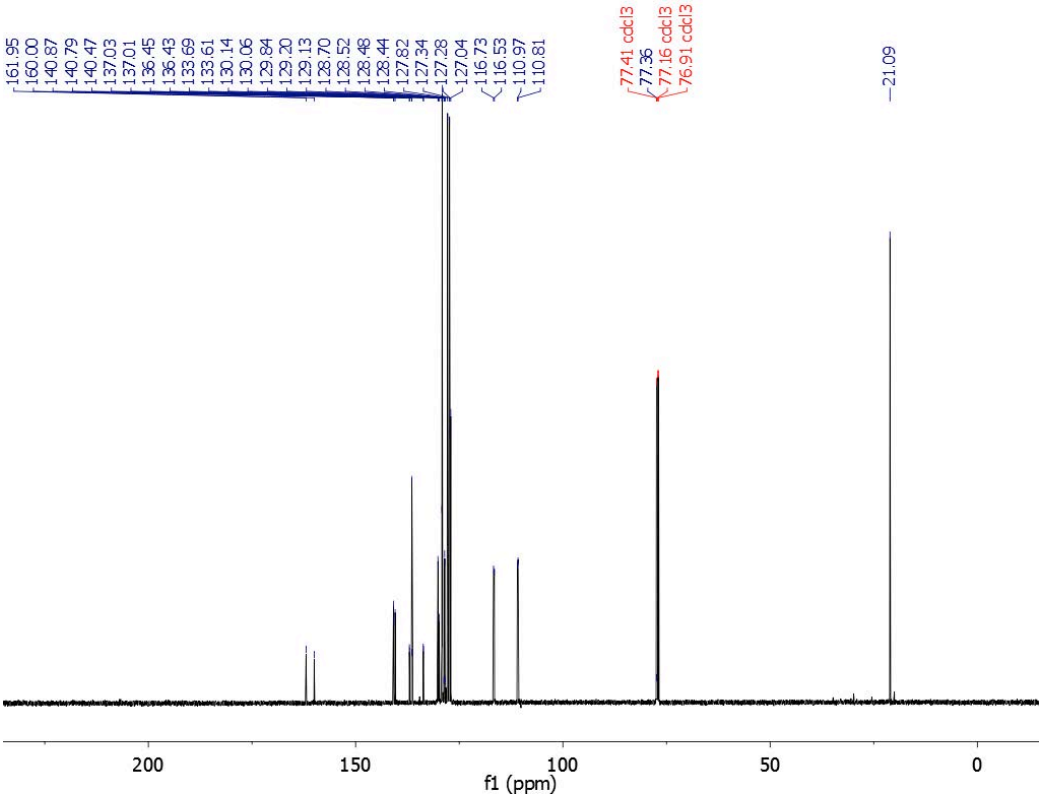


Figure S27. ^{1}H NMR of **8** (600 MHz, $CDCl_3$, 298 K).

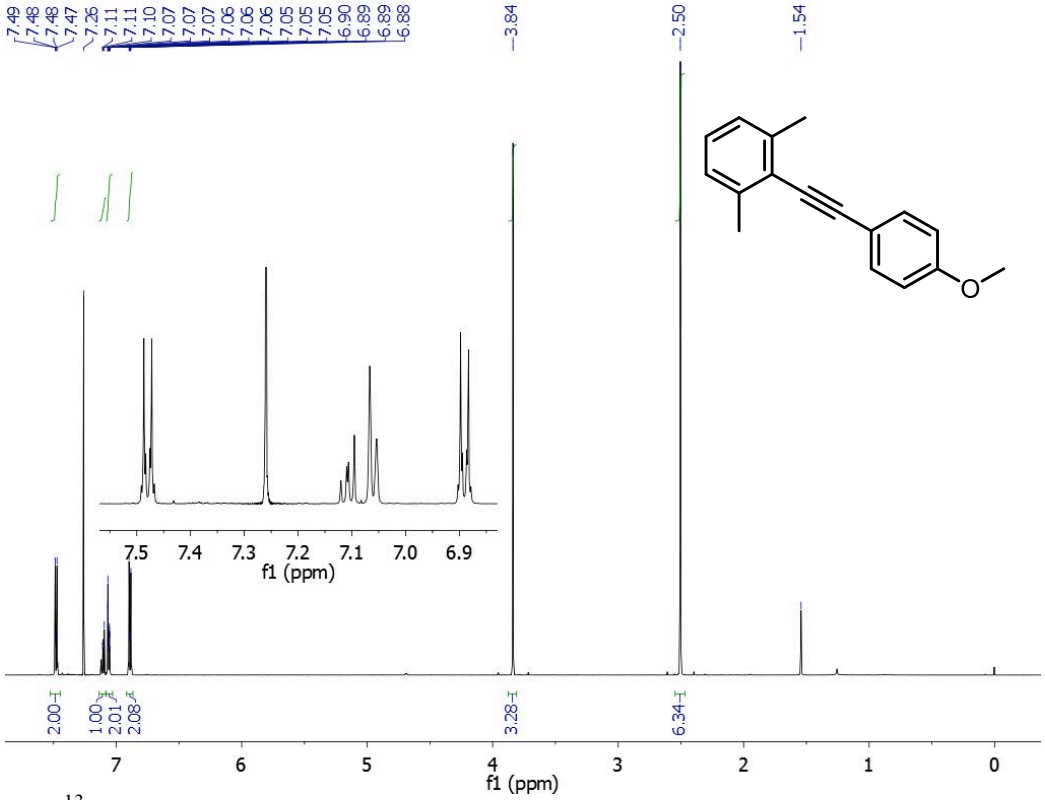


Figure S28. ^{13}C NMR of **8** (125 MHz, $CDCl_3$, 298 K).

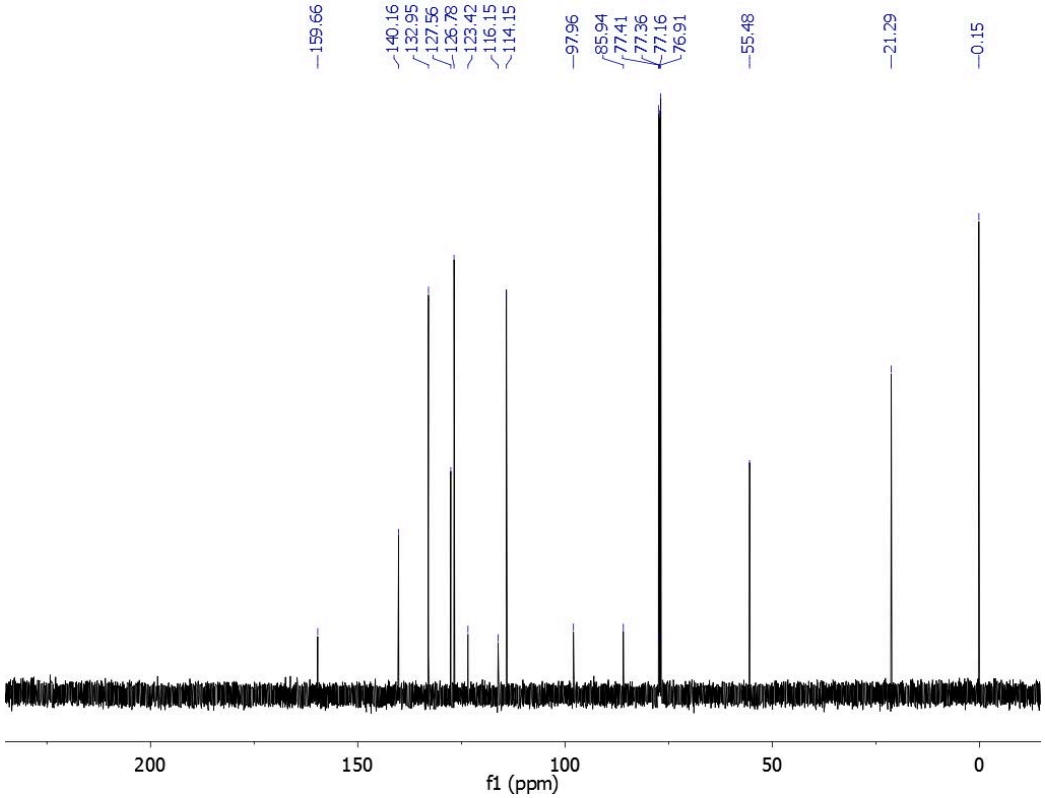


Figure S29. ^{1}H NMR of **9a-F** and **9b-F** (600 MHz, $CDCl_3$, 298 K).

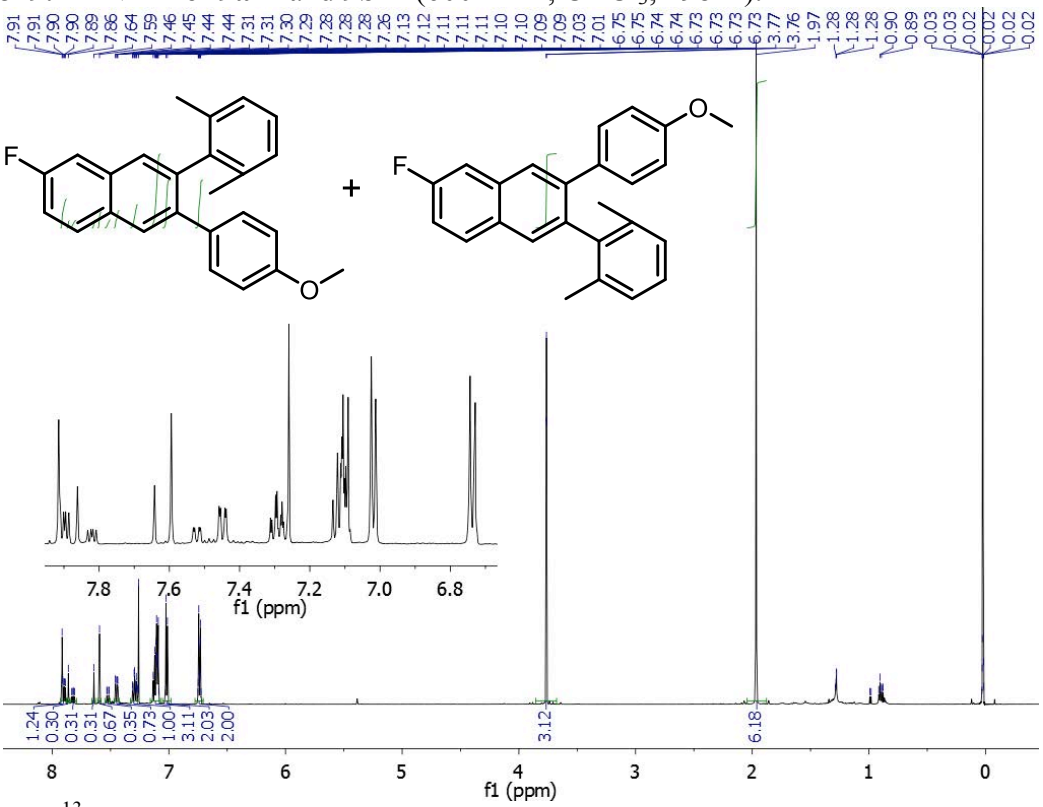


Figure S30. ^{13}C NMR of **9a-F** and **9b-F** (150 MHz, $CDCl_3$, 298 K).

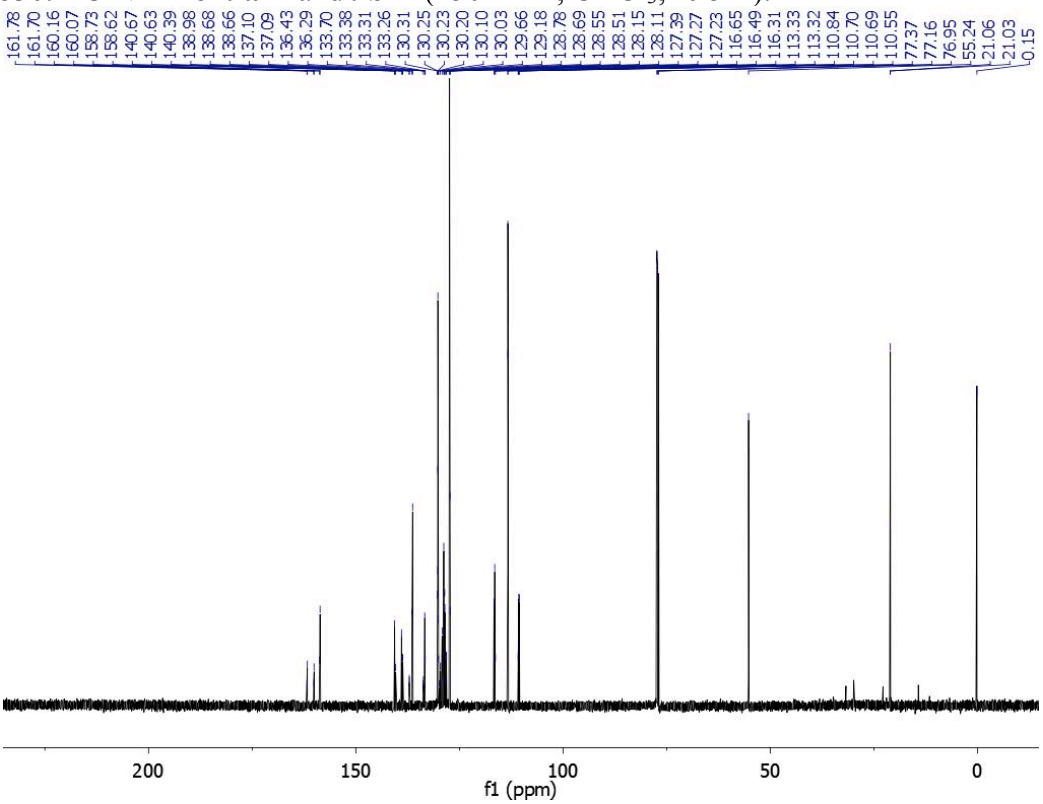


Figure S31. ^{1}H NMR of **11a-F** and **11b-F** (600 MHz, $CDCl_3$, 298 K).

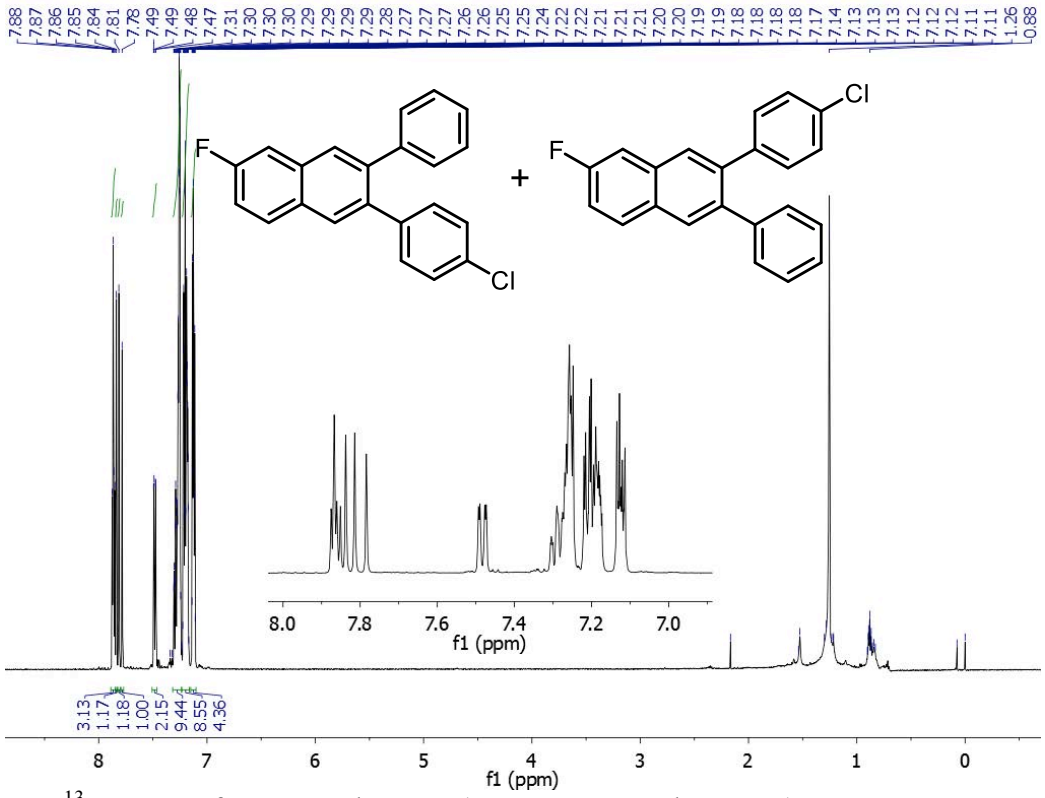


Figure S32. ^{13}C NMR of **11a-F** and **11b-F** (125 MHz, $CDCl_3$, 298 K).

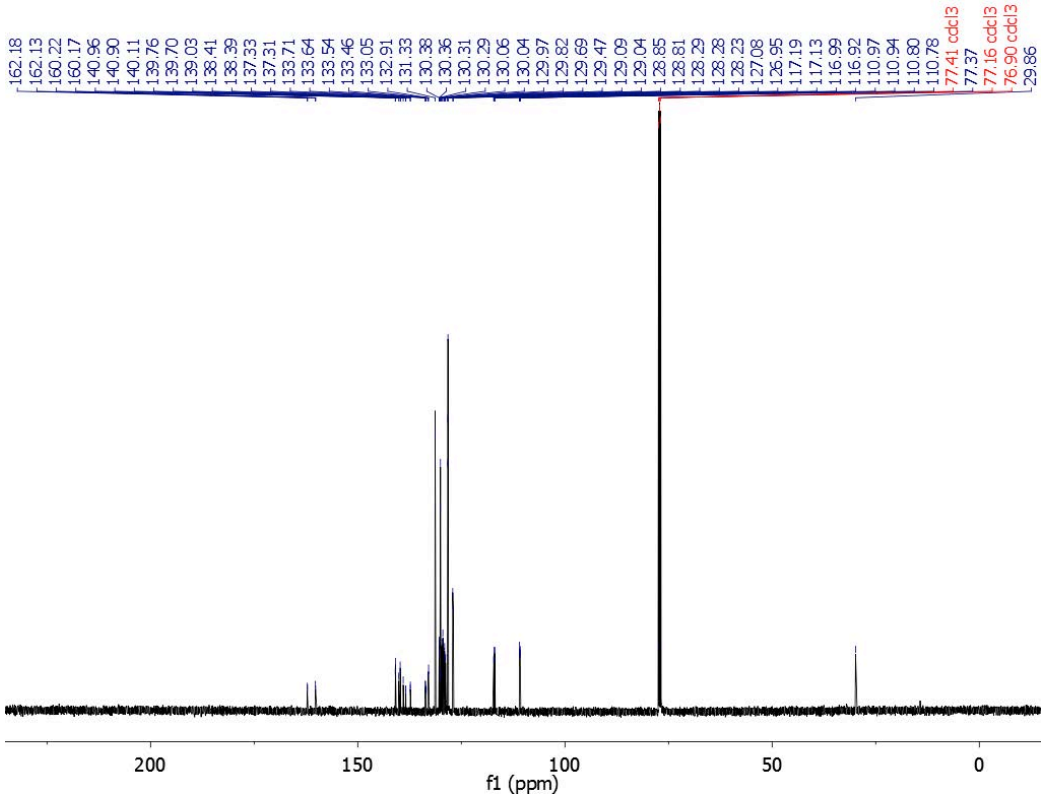


Figure S33. ^{1}H NMR of **13-F$_2$** (500 MHz, $CDCl_3$, 298 K).

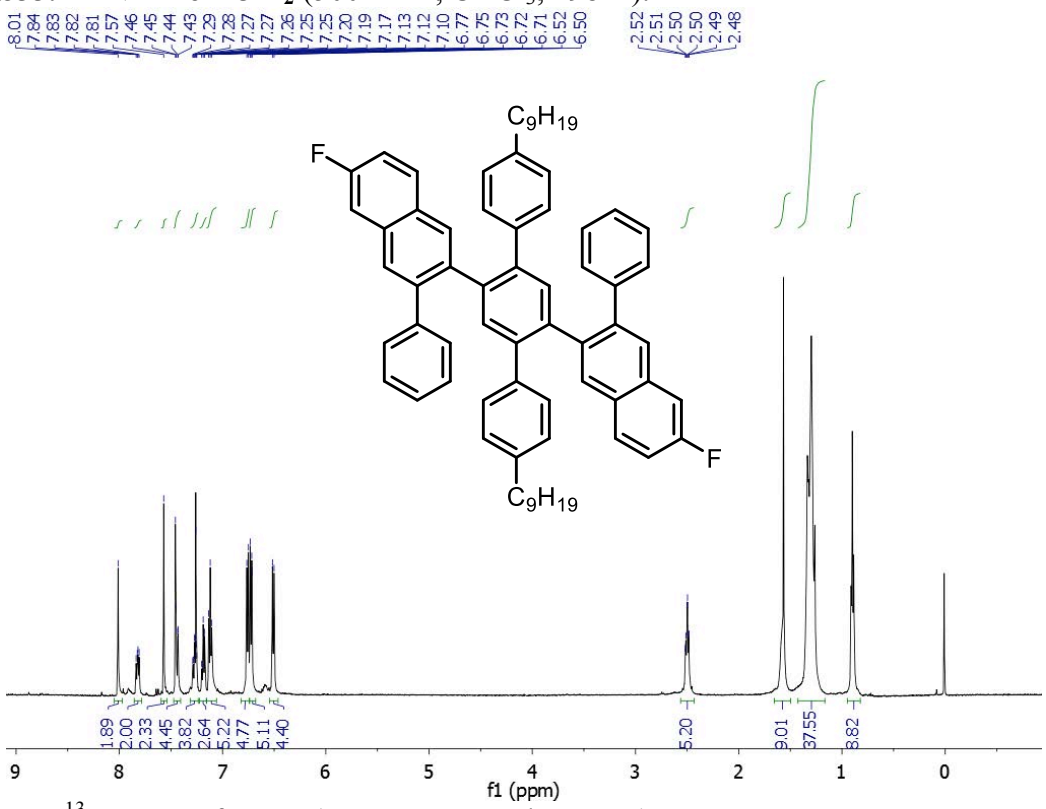


Figure S34. ^{13}C NMR of **13-F$_2$** (125 MHz, $CDCl_3$, 298 K).

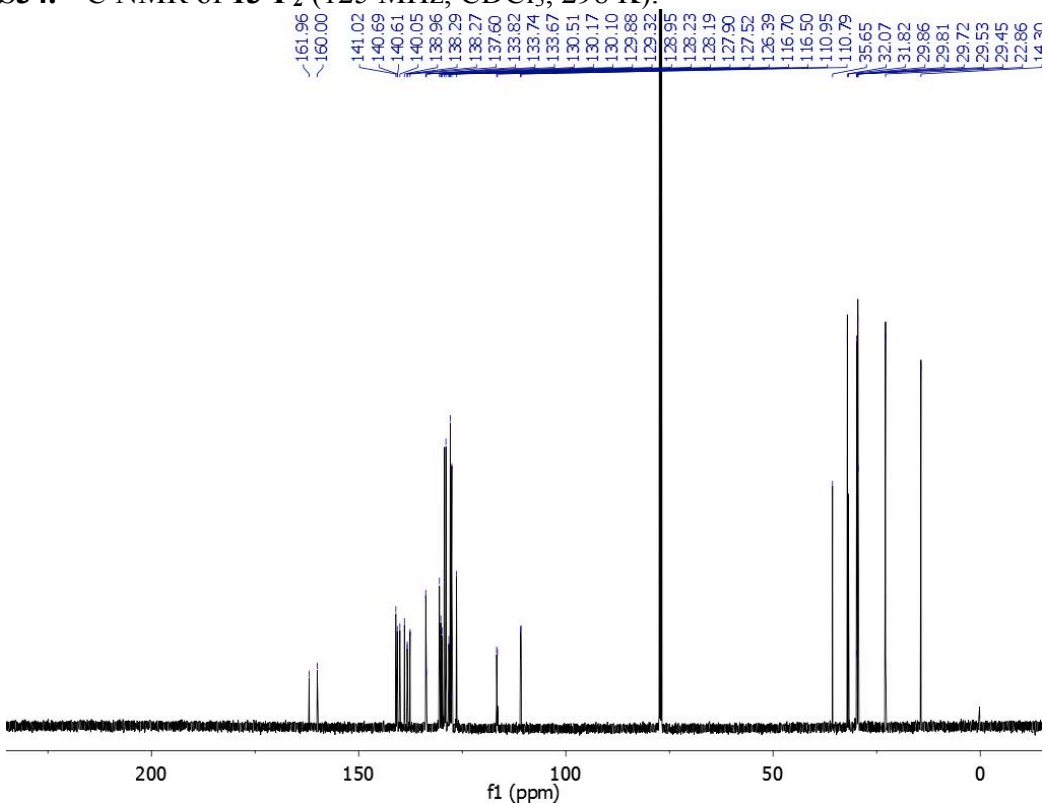


Figure S35. ^{1}H NMR of **13-^{13}C$_2$** (500 MHz, $CDCl_3$, 298 K).

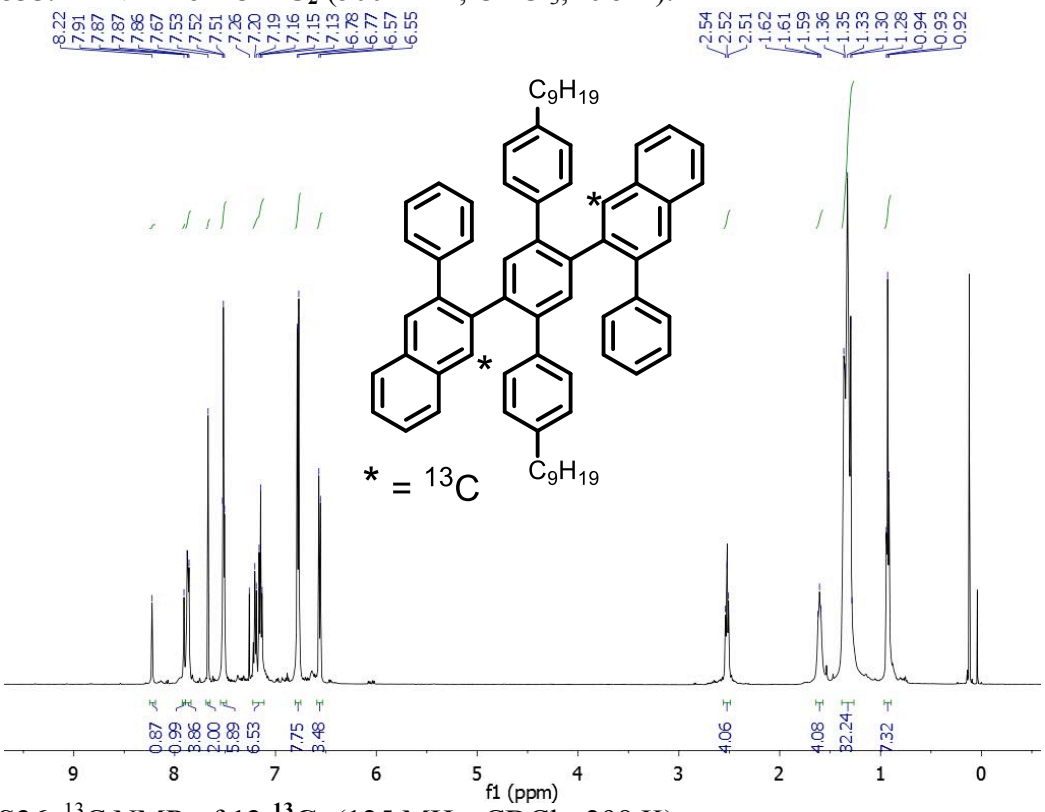
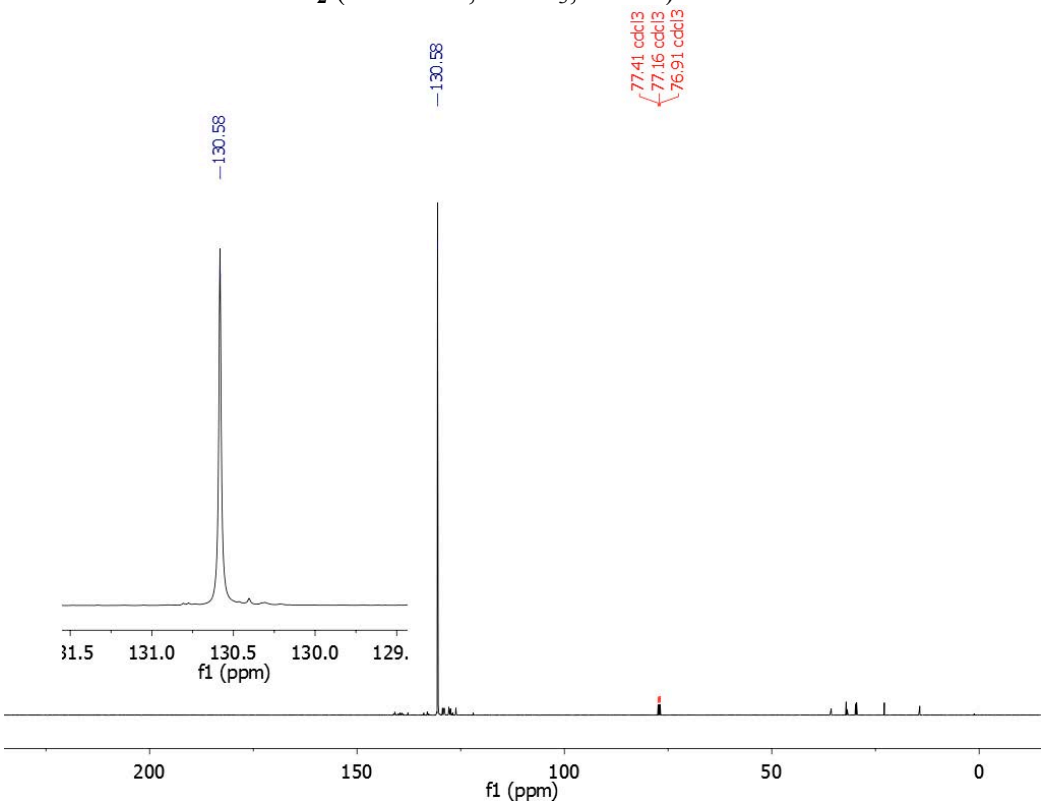


Figure S36. ^{13}C NMR of **13-^{13}C$_2$** (125 MHz, $CDCl_3$, 298 K).



D. 2D NMR Spectra Assignments

Peak assignments for compound **3:**

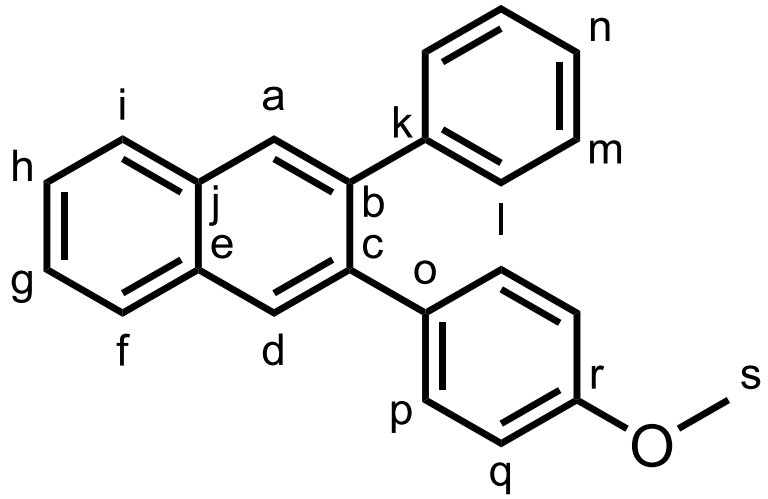


Figure S37. Full COSY spectrum of **3** (500 MHz, 500 MHz, $CDCl_3$, 298 K).

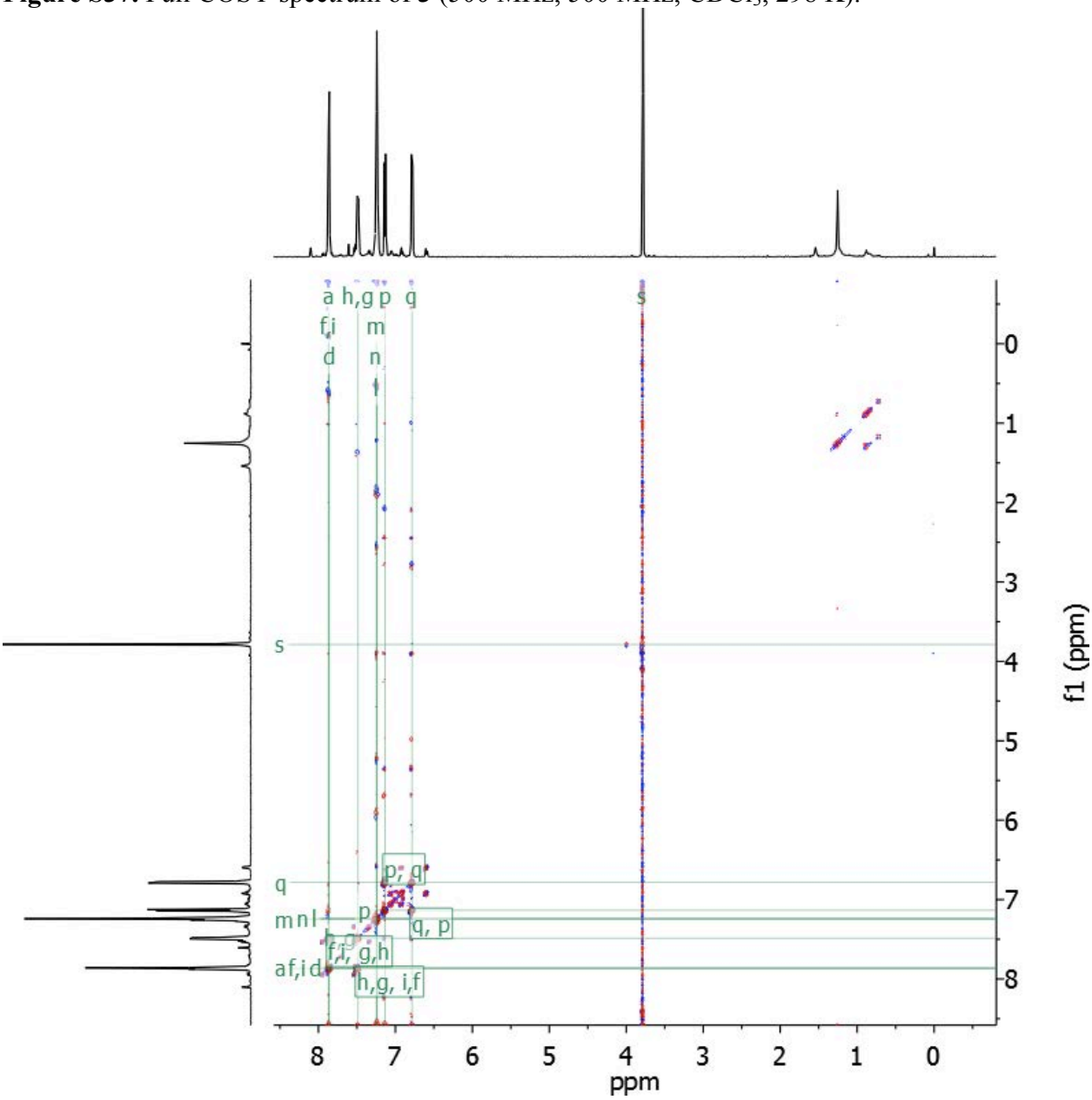


Figure S38. Partial COSY spectrum of **3** showing the aromatic region (500 MHz, 500 MHz, $CDCl_3$, 298 K).

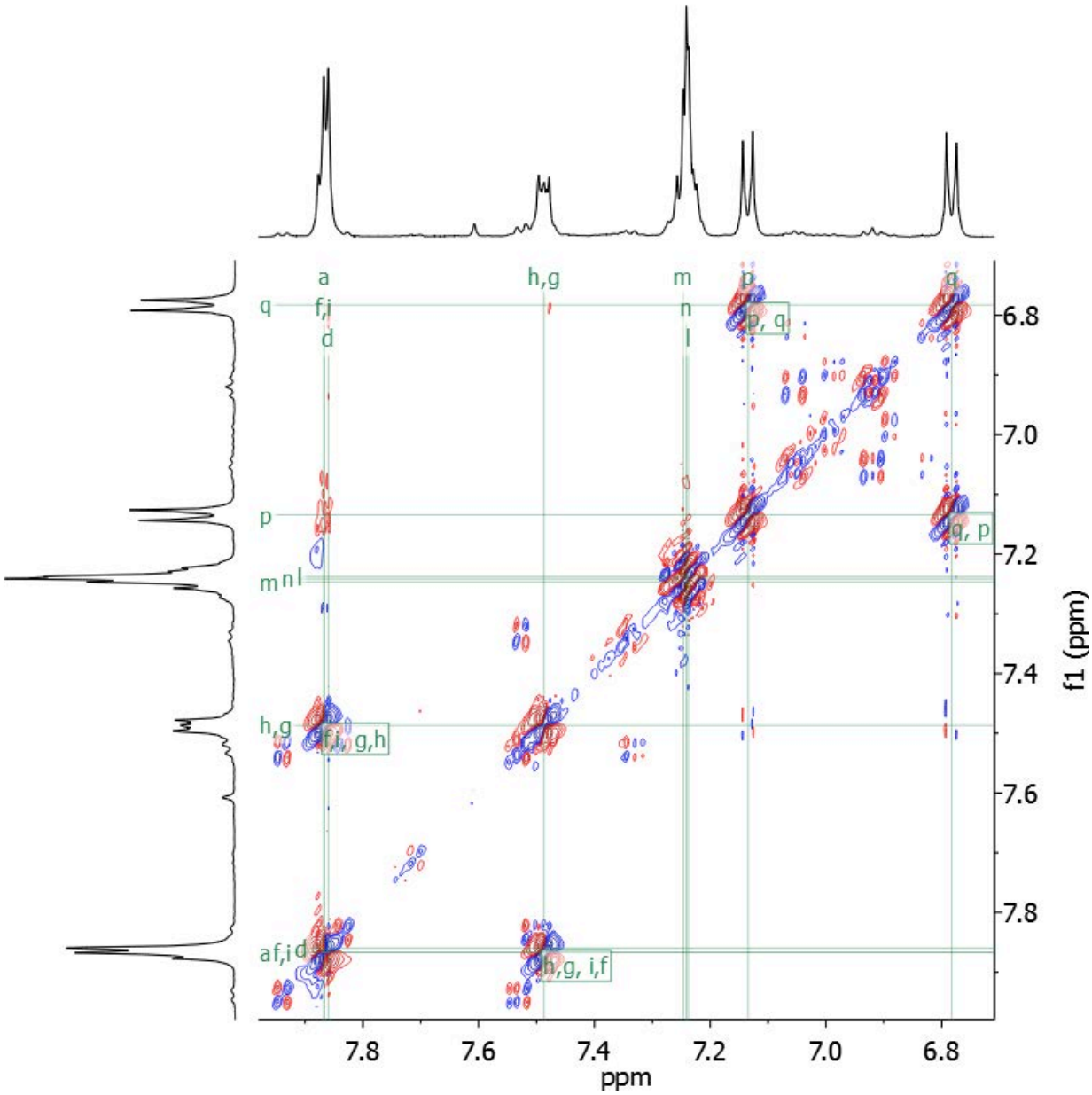


Figure S39. Full NOESY spectrum of **3** (500 MHz, 500 MHz, $CDCl_3$, 298 K).

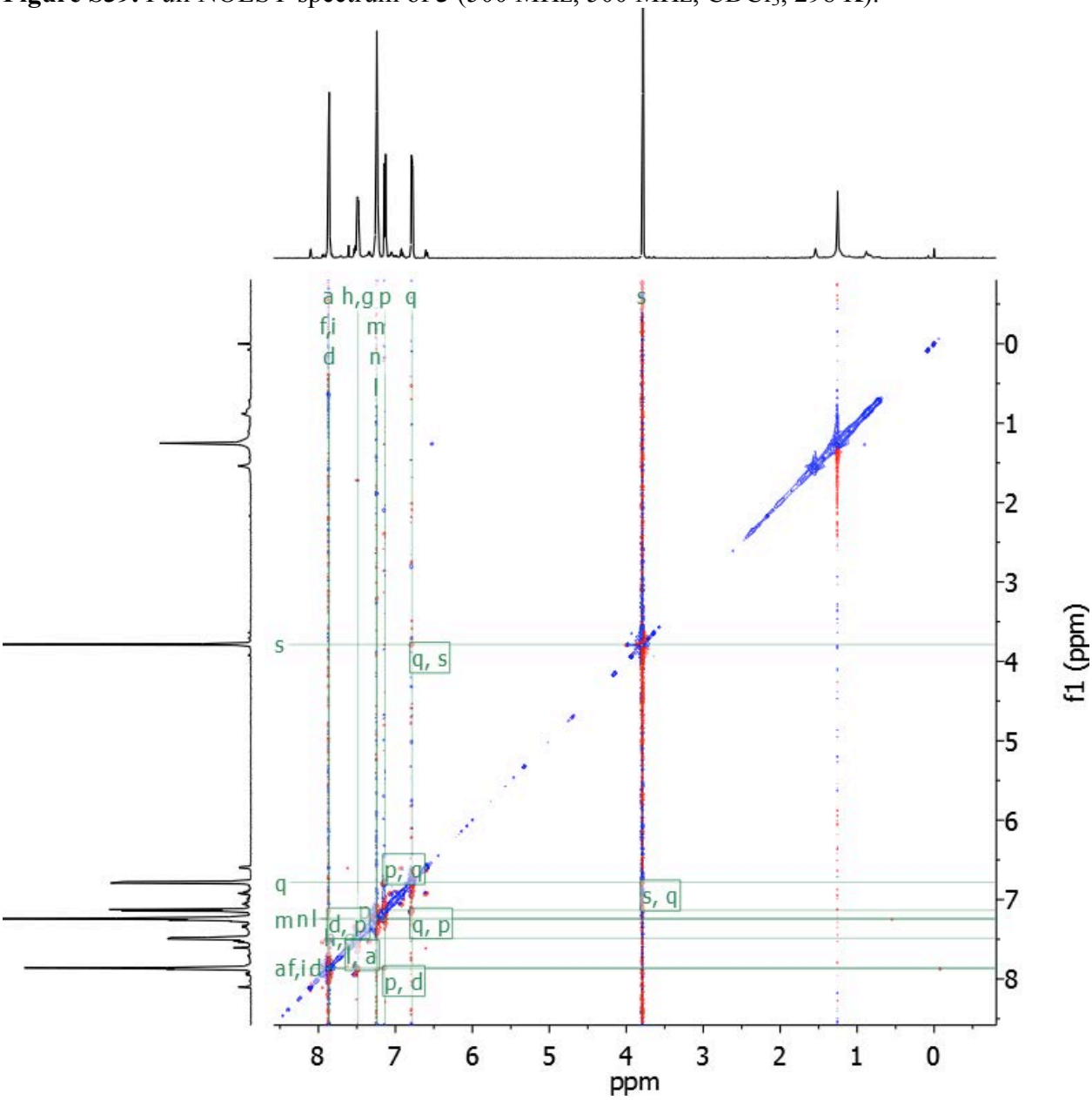


Figure S40. Partial NOESY spectrum of **3** showing the aromatic region (500 MHz, 500 MHz, $CDCl_3$, 298 K).

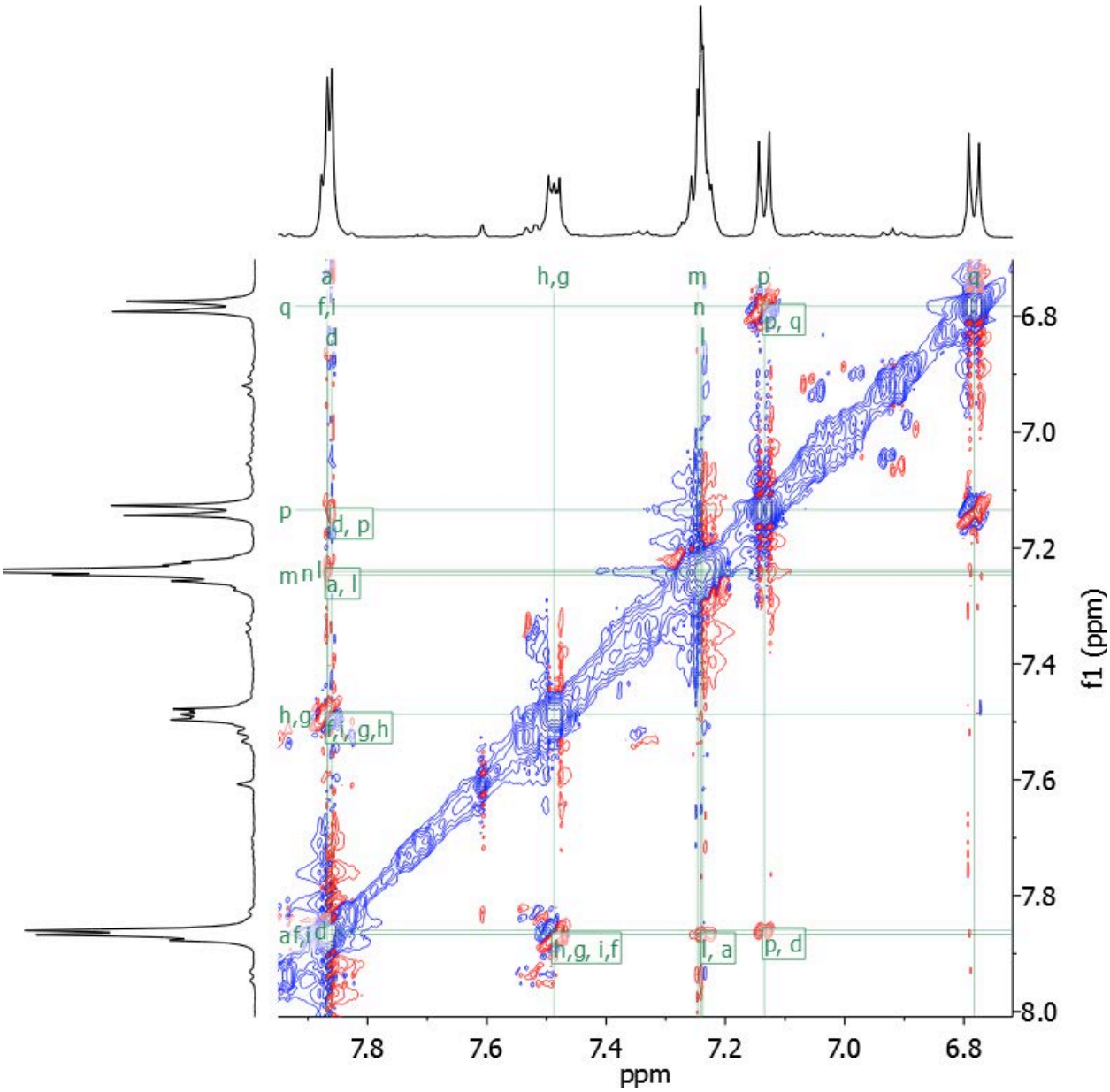


Figure S41. Full HSQC spectrum of **3** (500 MHz, 125 MHz, $CDCl_3$, 298 K).

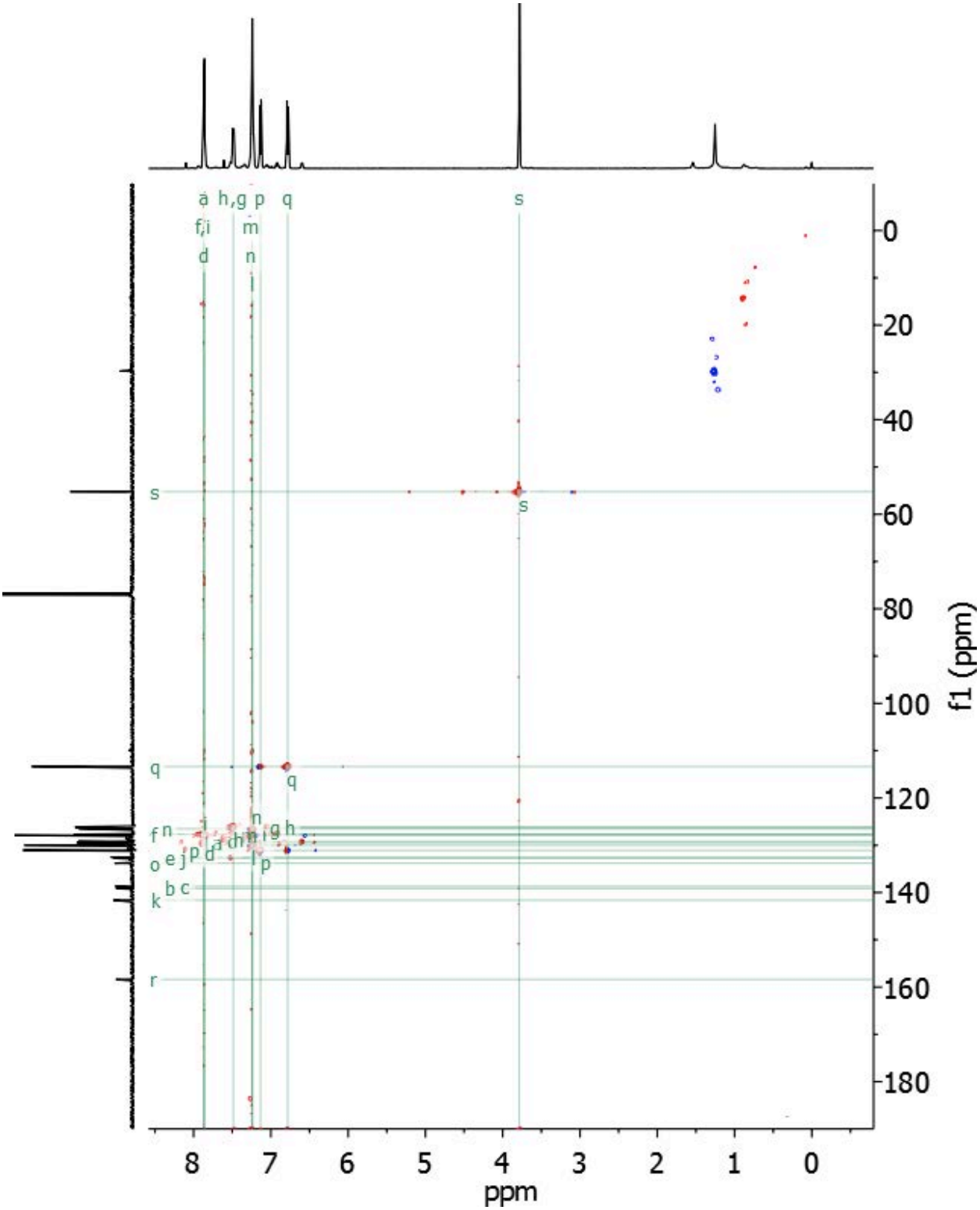


Figure S42. Partial HSQC spectrum of **3** showing the aromatic region (500 MHz, 125 MHz, $CDCl_3$, 298 K).

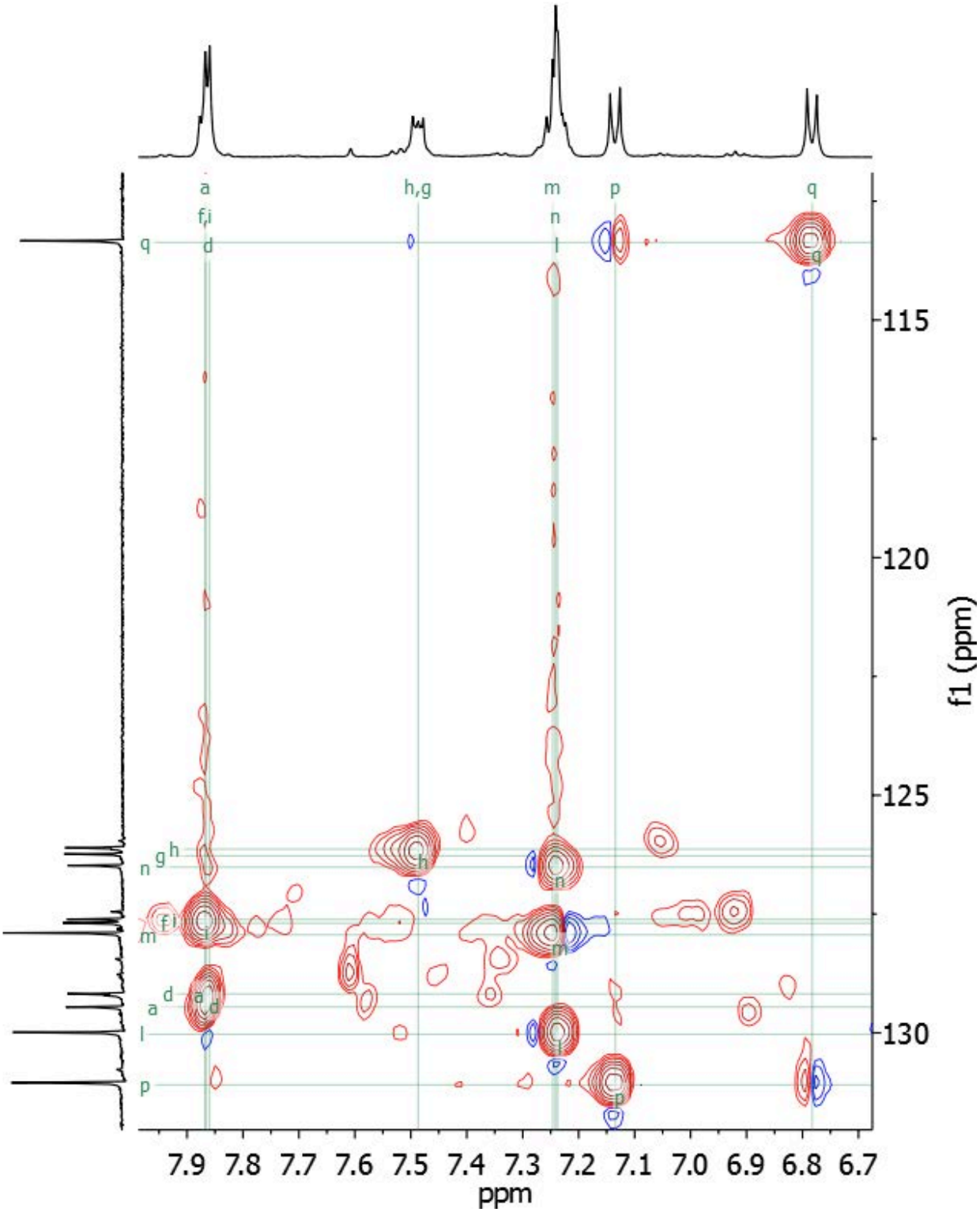


Figure S43. Full HMBC spectrum of **3** (500 MHz, 125 MHz, $CDCl_3$, 298 K).

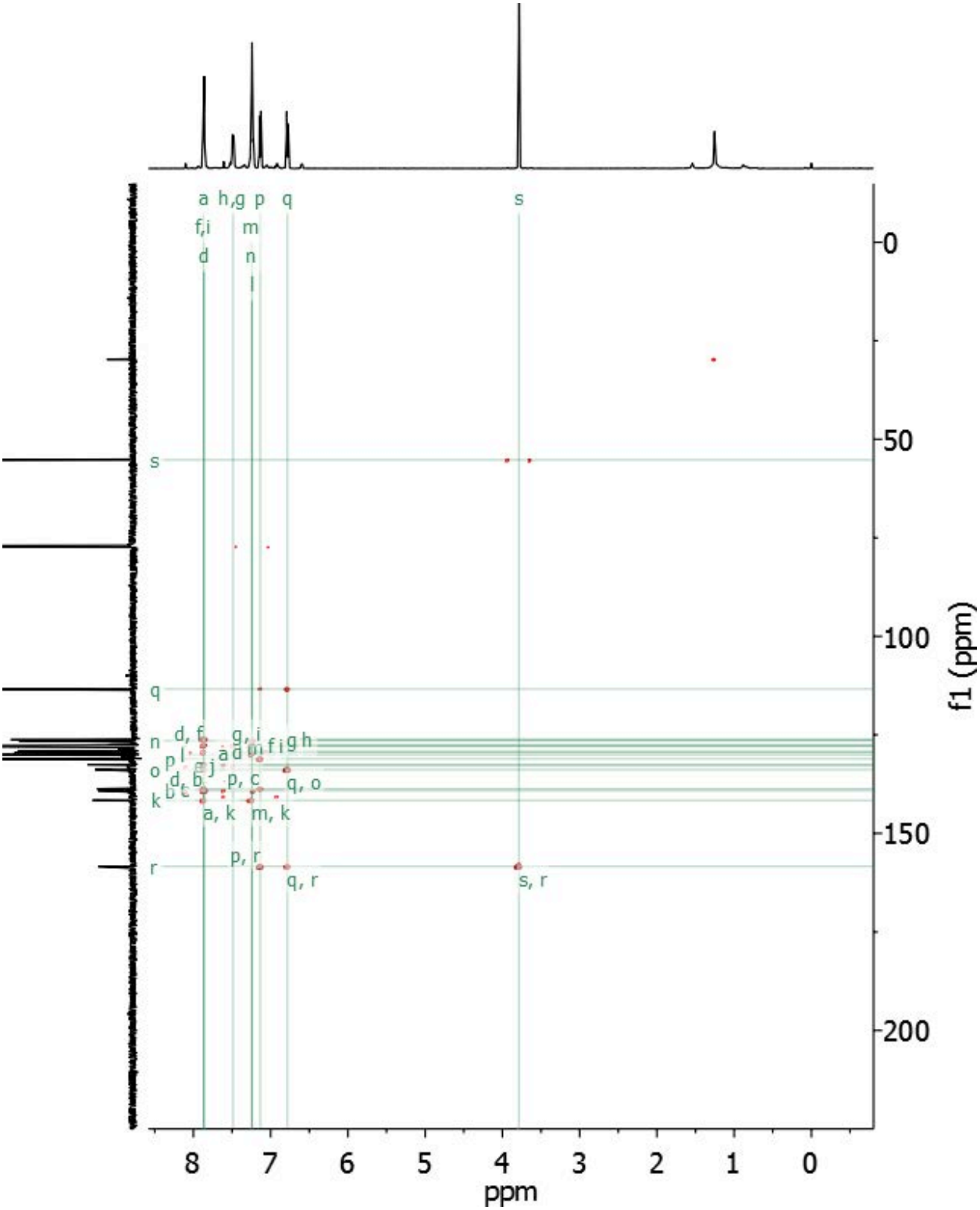
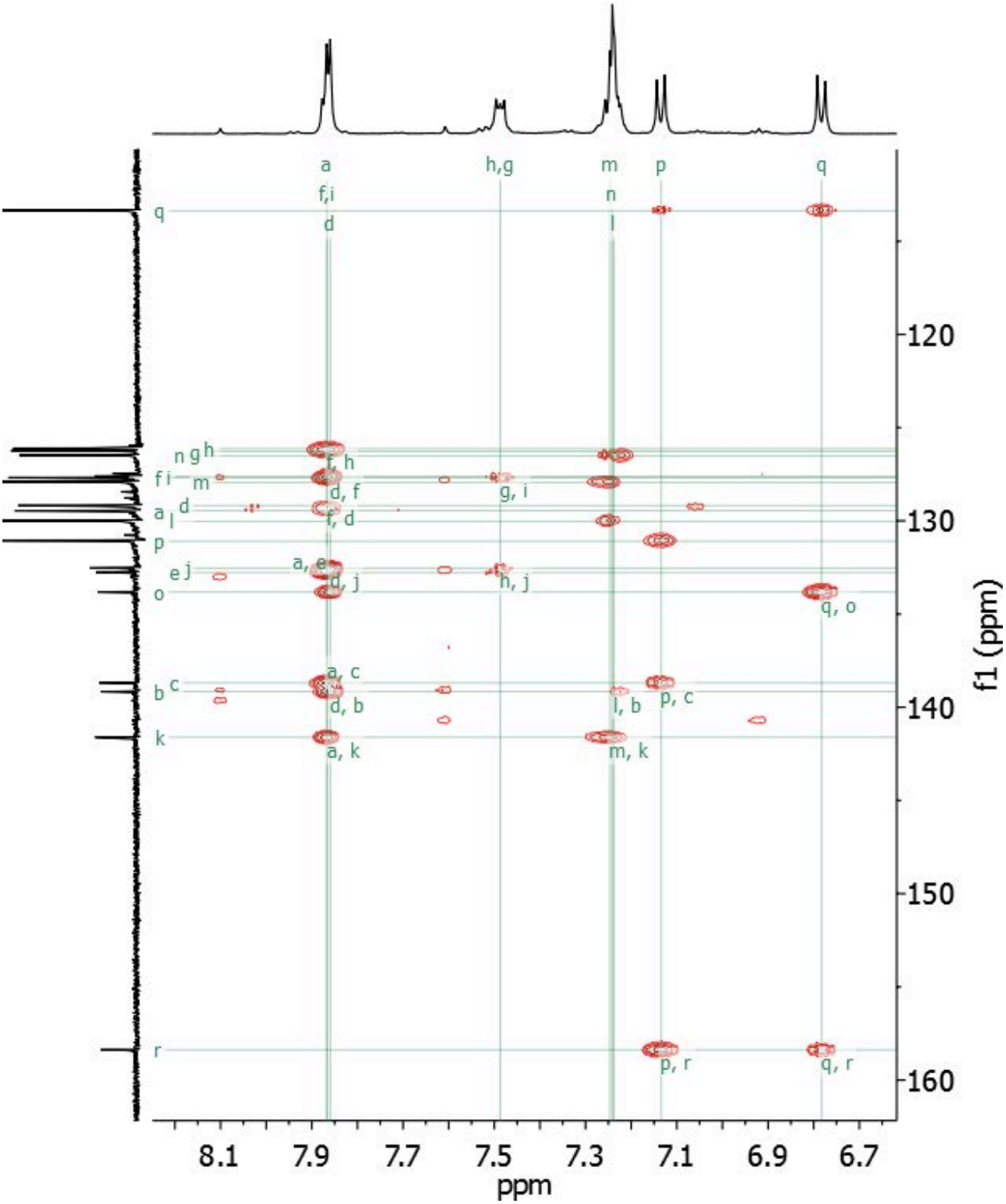


Figure S44. Partial HMBC spectrum of **3** showing the aromatic region (500 MHz, 125 MHz, $CDCl_3$, 298 K).



Peak assignments for compound **3a-F:**

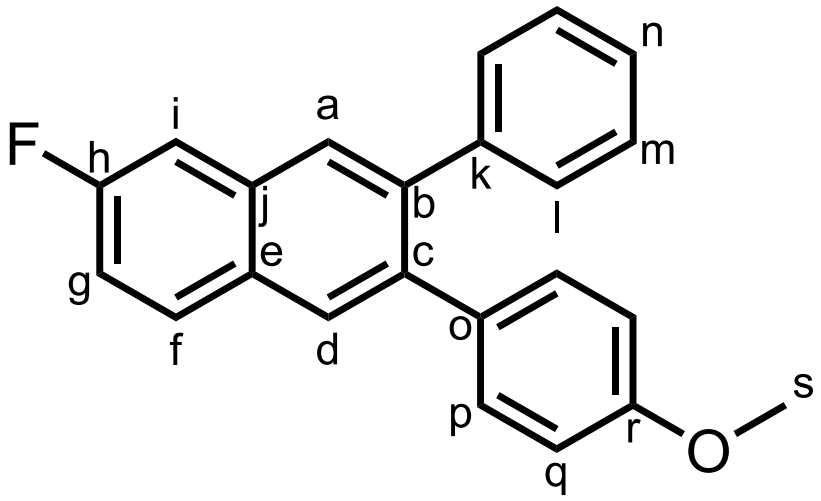


Figure S45. Full COSY spectrum of **3a-F** (500 MHz, 500 MHz, $CDCl_3$, 298 K).

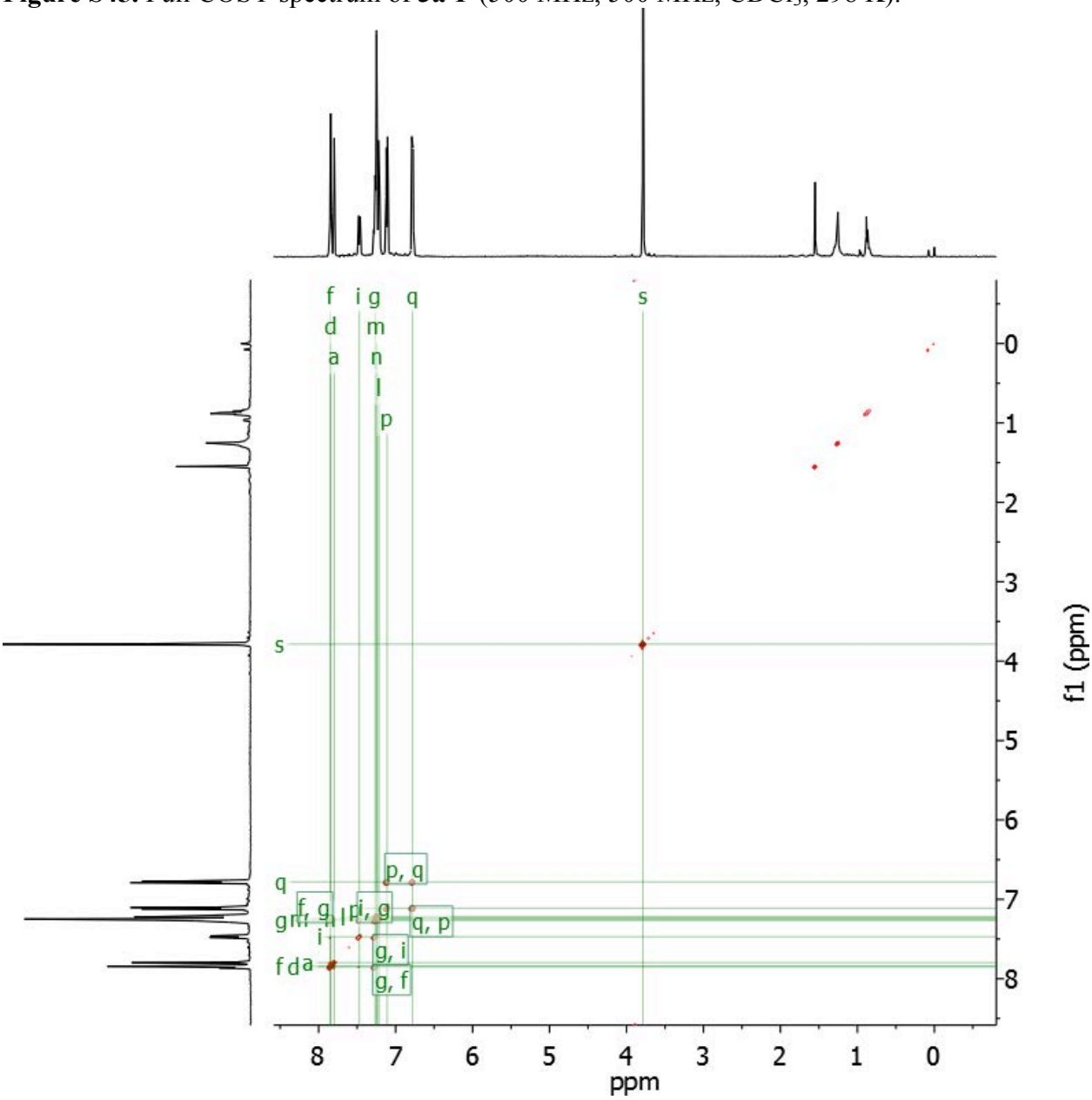


Figure S46. Partial COSY spectrum of **3a-F** showing the aromatic region (500 MHz, 500 MHz, $CDCl_3$, 298 K).

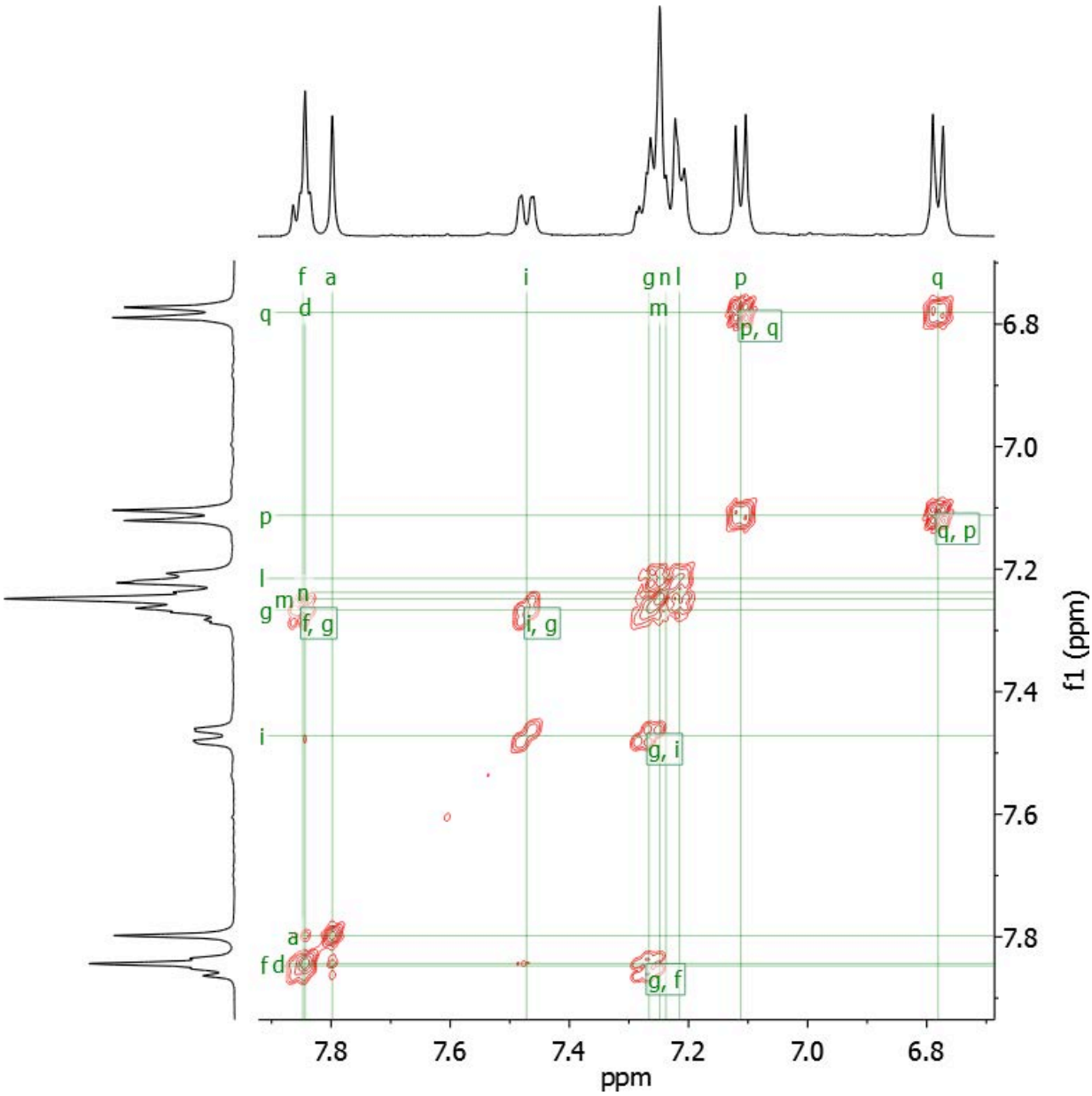


Figure S47. Full NOESY spectrum of **3a-F** (500 MHz, 500 MHz, $CDCl_3$, 298 K).

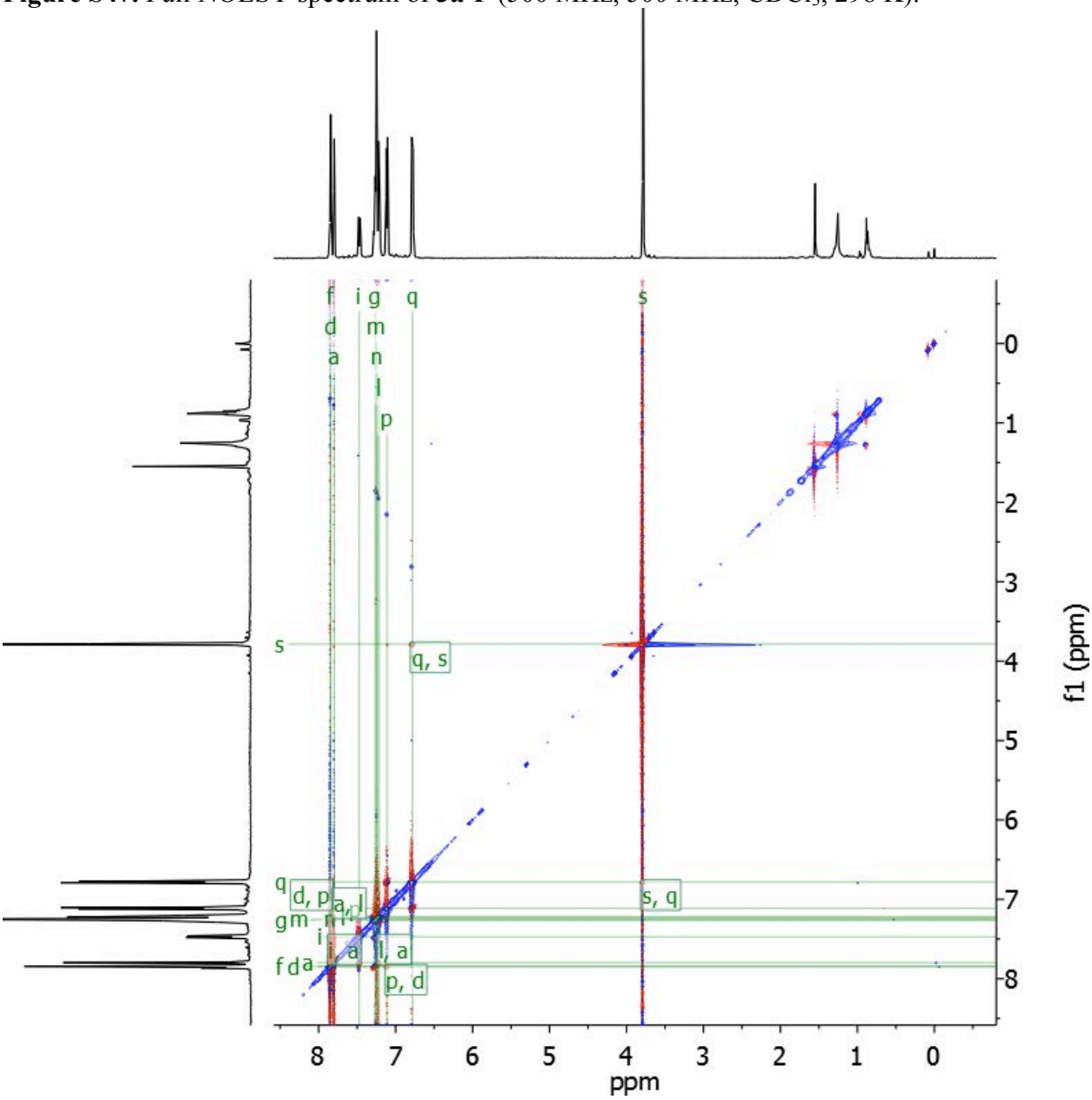


Figure S48. Partial NOESY spectrum of **3a-F** showing the aromatic region (500 MHz, 500 MHz, $CDCl_3$, 298 K).

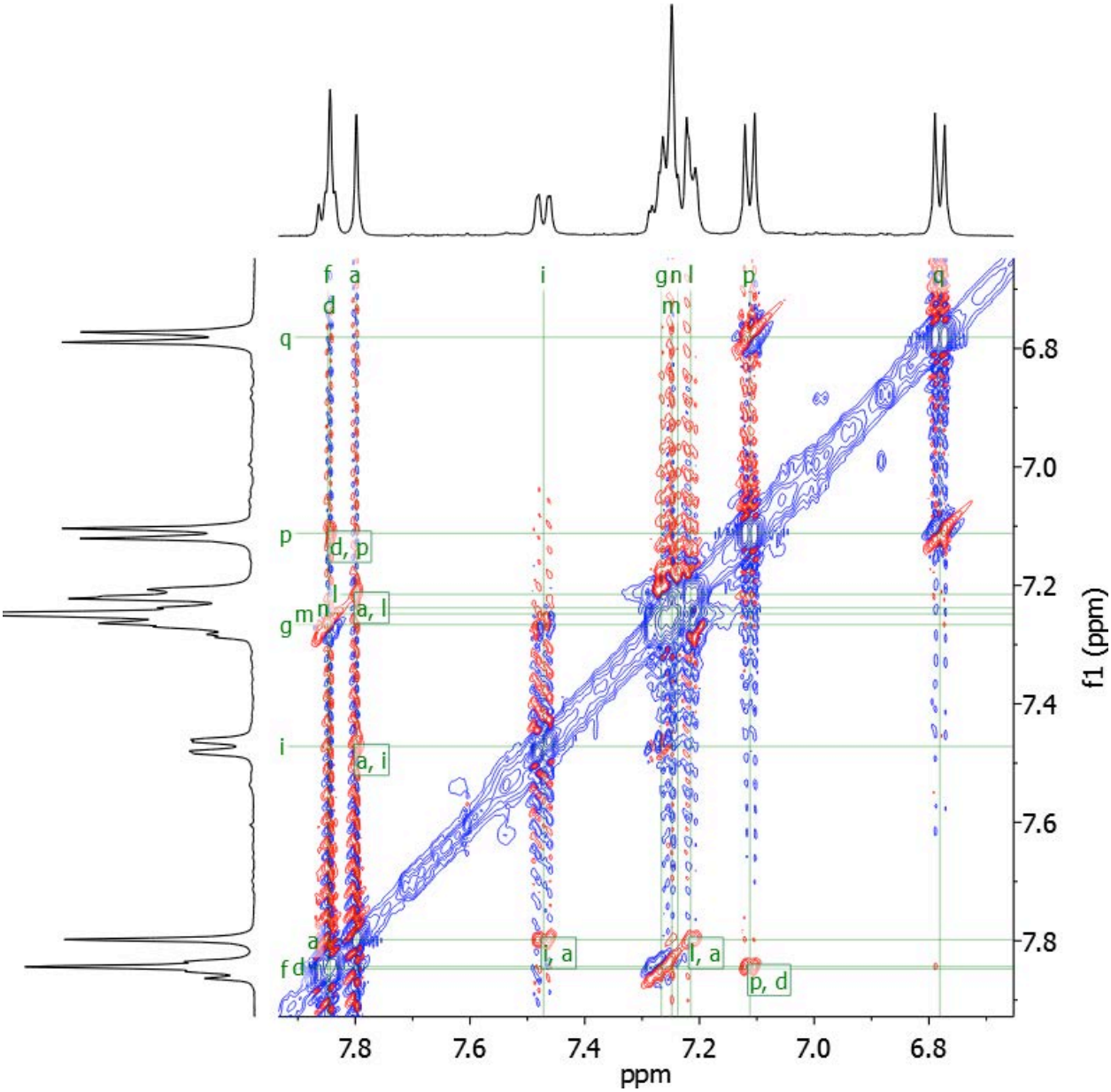


Figure S49. Full HSQC spectrum of **3a-F** (500 MHz, 125 MHz, $CDCl_3$, 298 K).

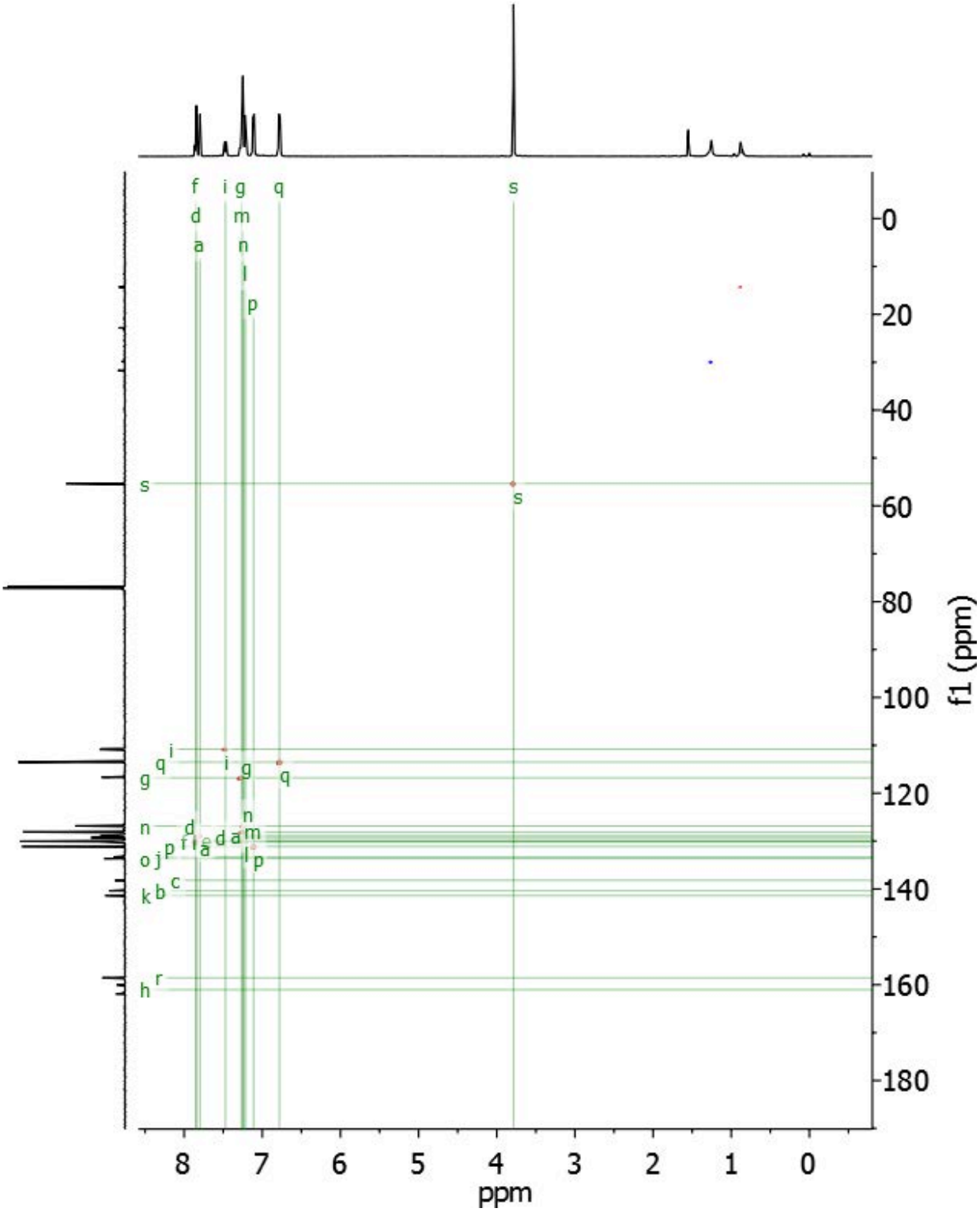


Figure S50. Partial HSQC spectrum of **3a-F** showing the aromatic region (500 MHz, 125 MHz, $CDCl_3$, 298 K).

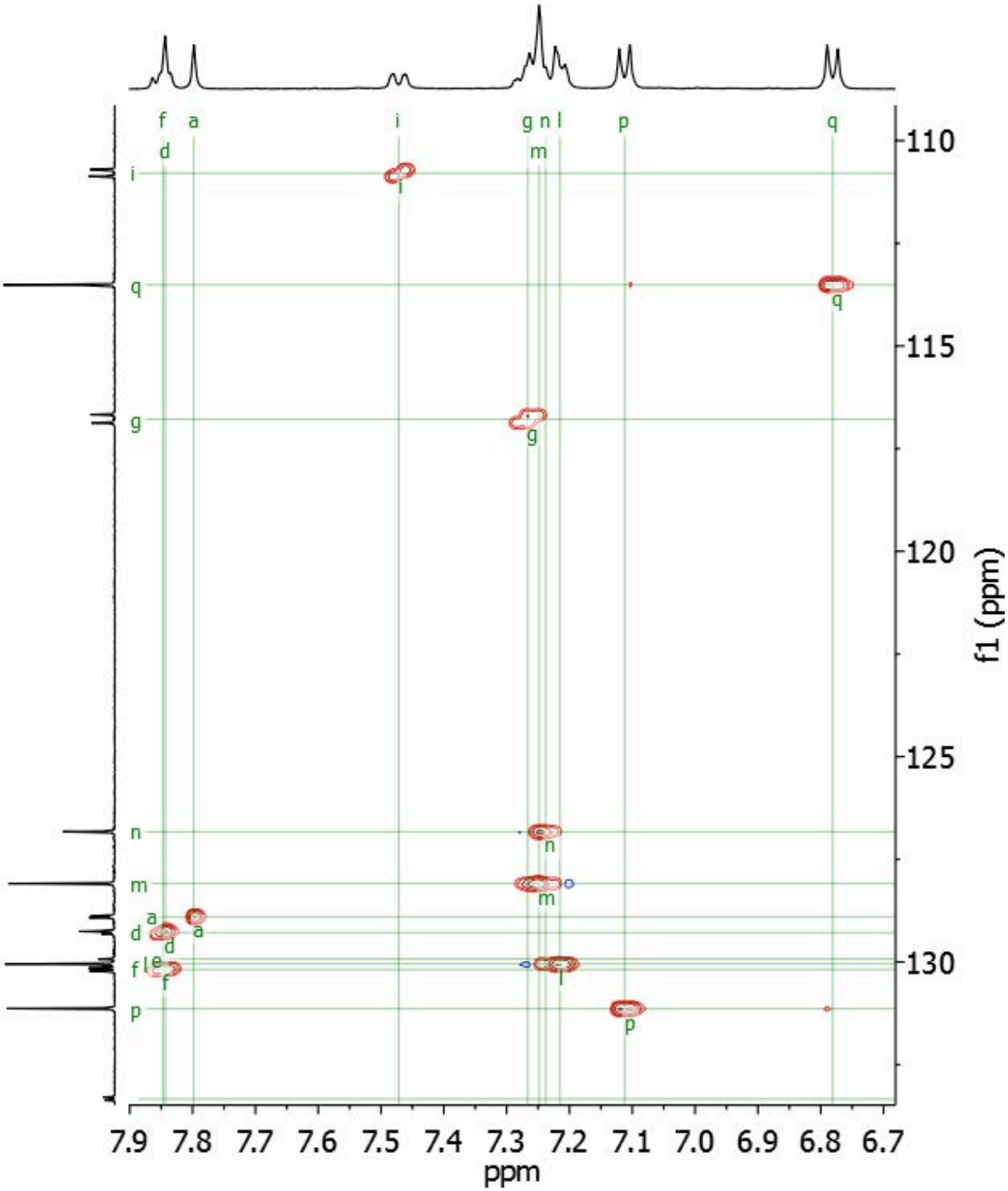


Figure S51. Full HMBC spectrum of **3a-F** (500 MHz, 125 MHz, $CDCl_3$, 298 K).

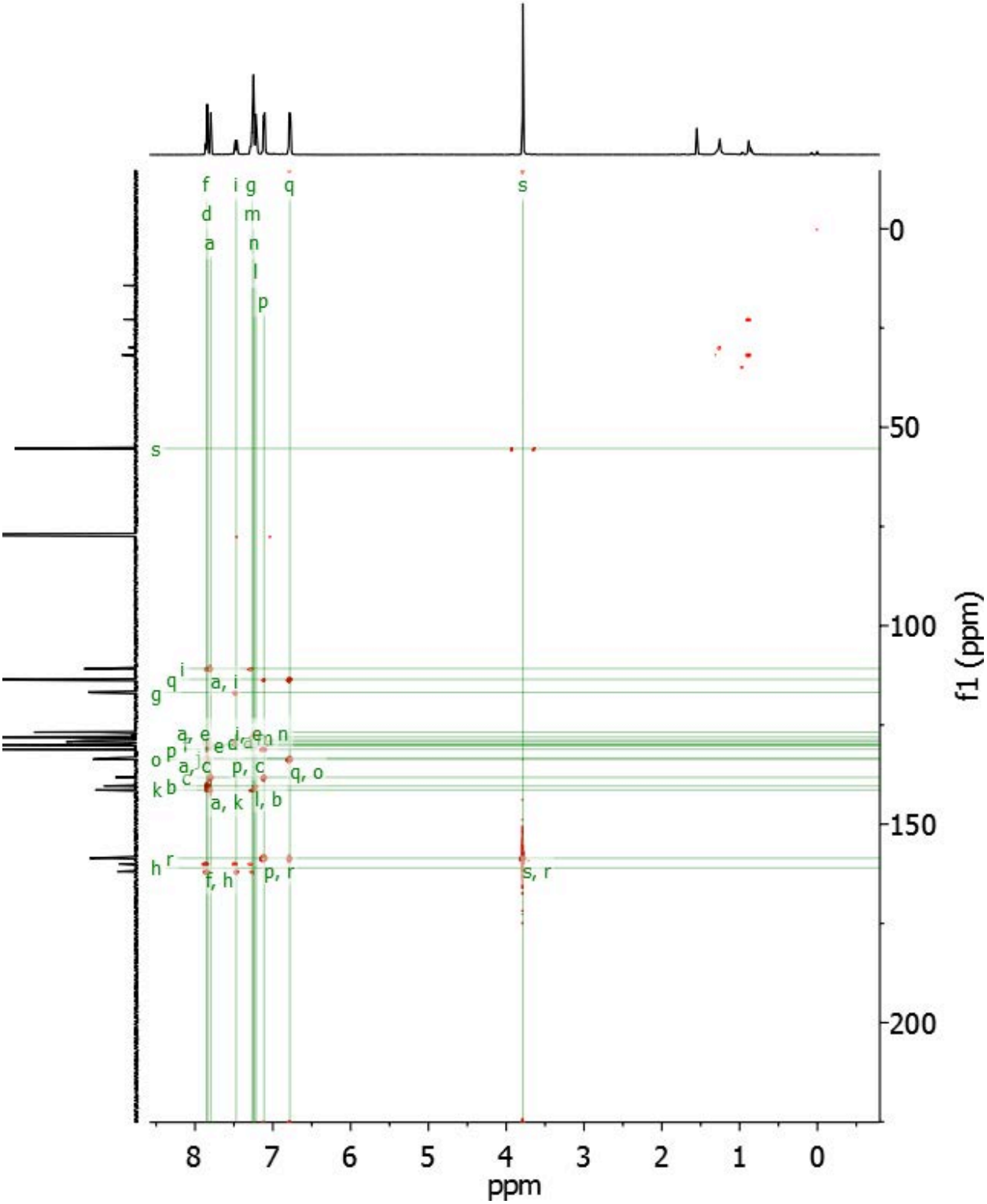
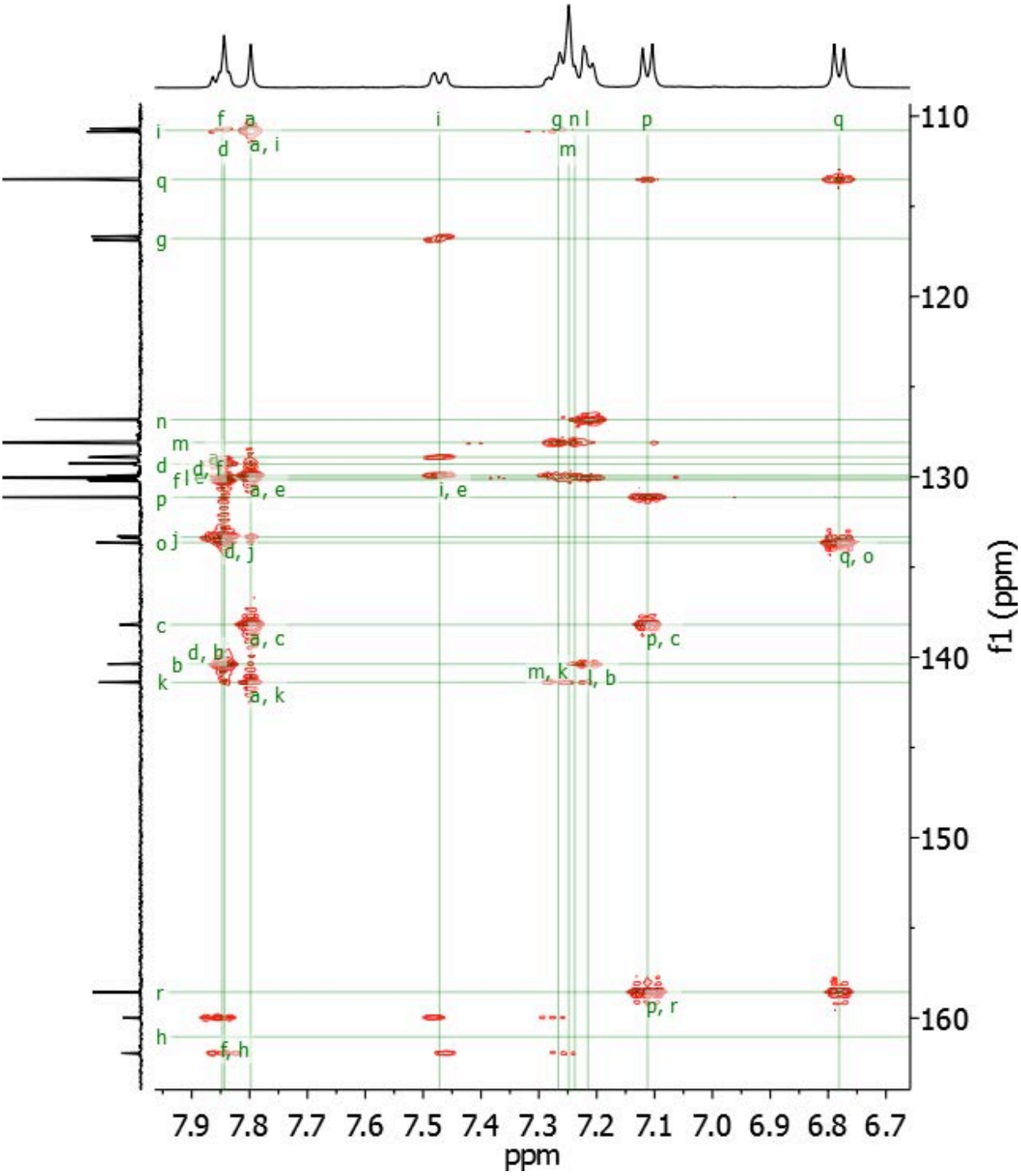


Figure S52. Partial HMBC spectrum of **3a-F** showing the aromatic region (500 MHz, 125 MHz, $CDCl_3$, 298 K).



Peak assignments for compound **5:**

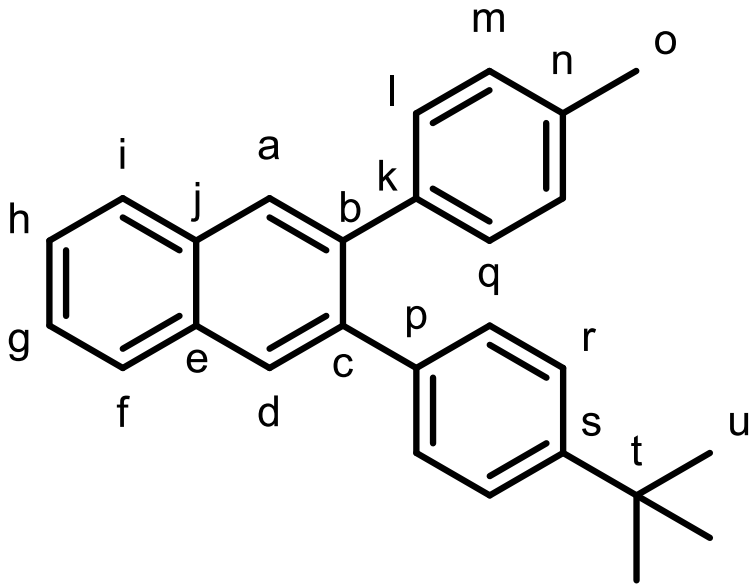


Figure S53. Full COSY spectrum of **5** (500 MHz, 500 MHz, $CDCl_3$, 298 K).

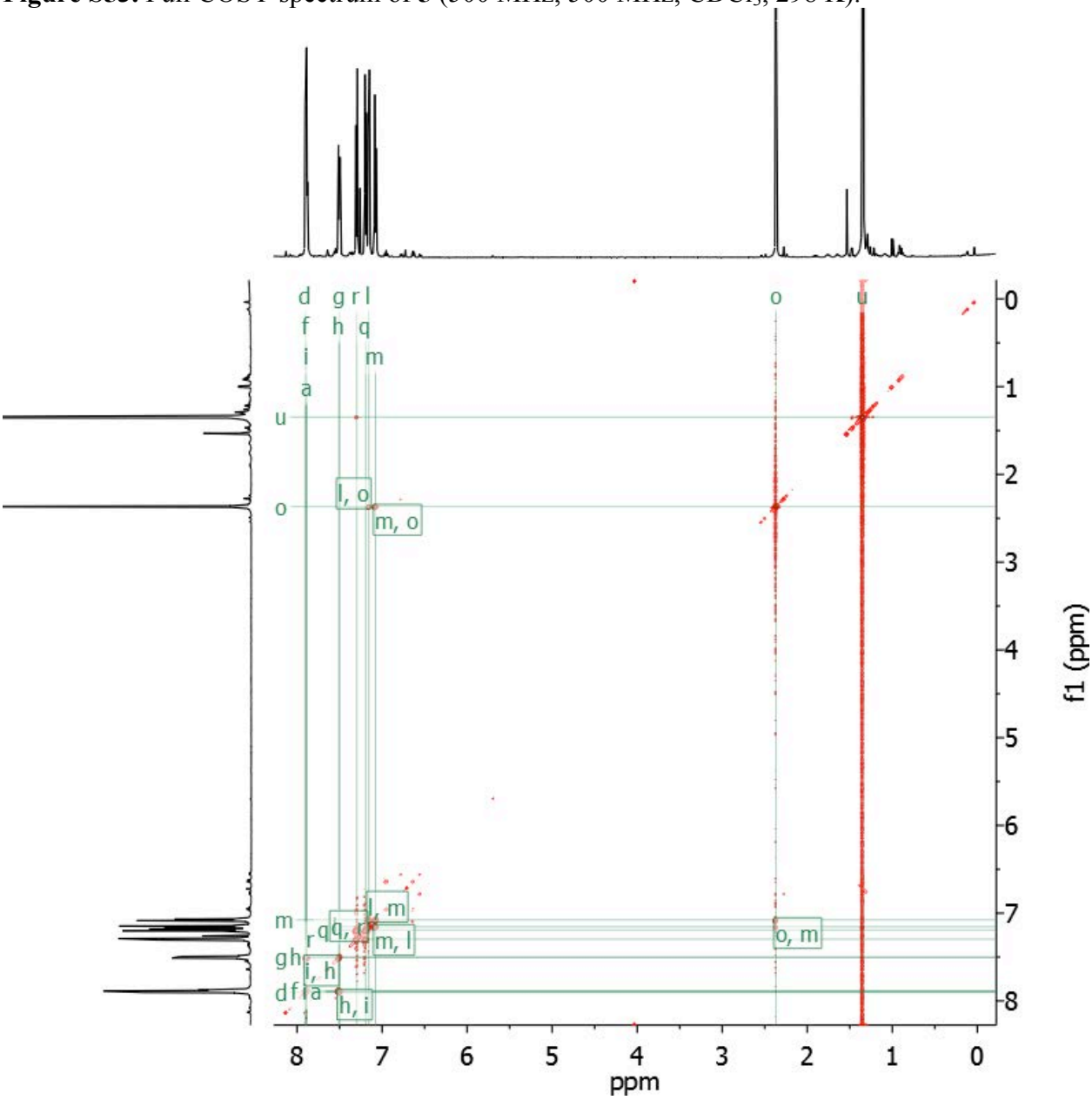


Figure S54. Partial COSY spectrum of **5** showing the aromatic region (500 MHz, 500 MHz, $CDCl_3$, 298 K).

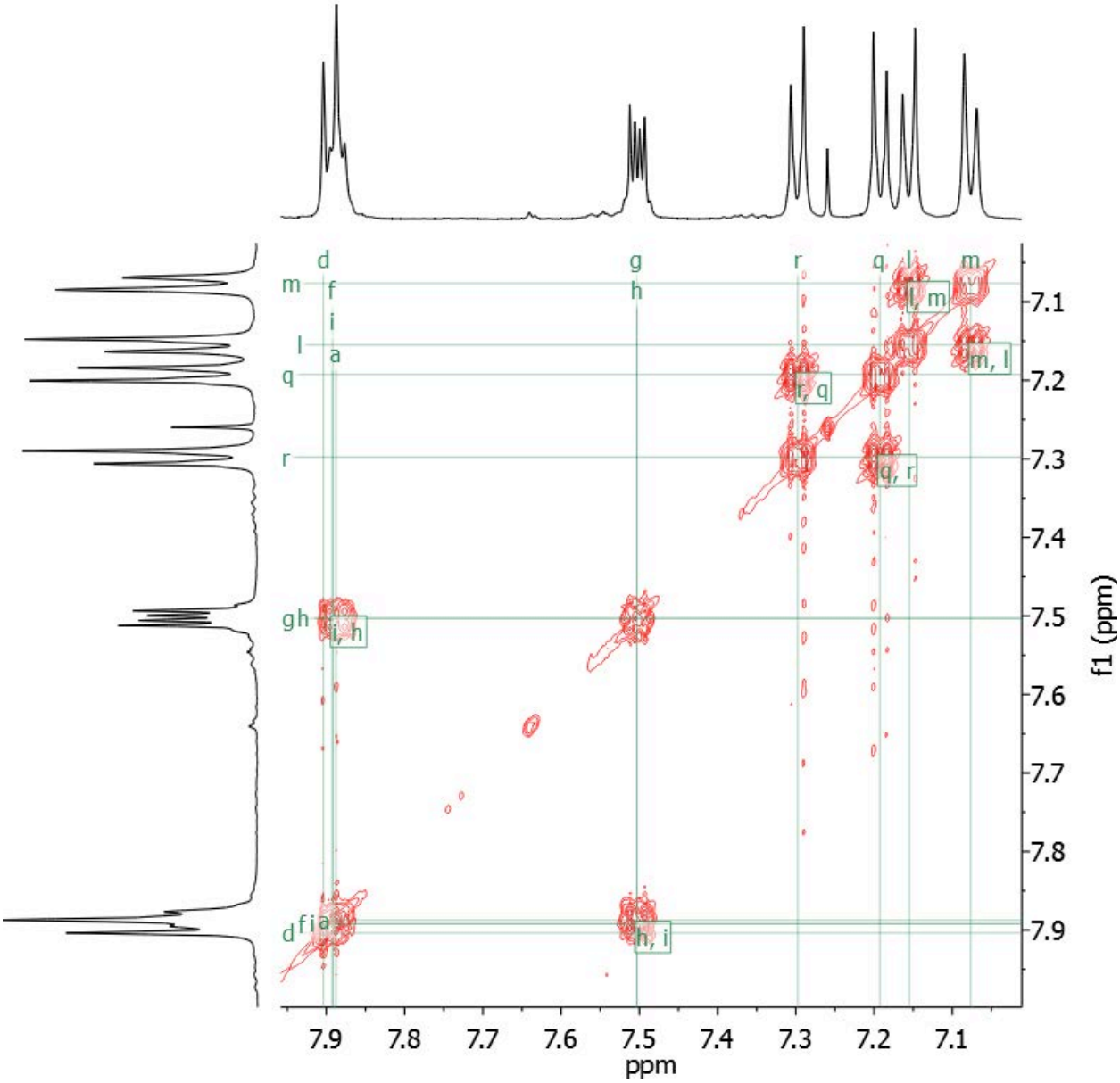


Figure S55. Full NOESY spectrum of **5** (500 MHz, 500 MHz, $CDCl_3$, 298 K).

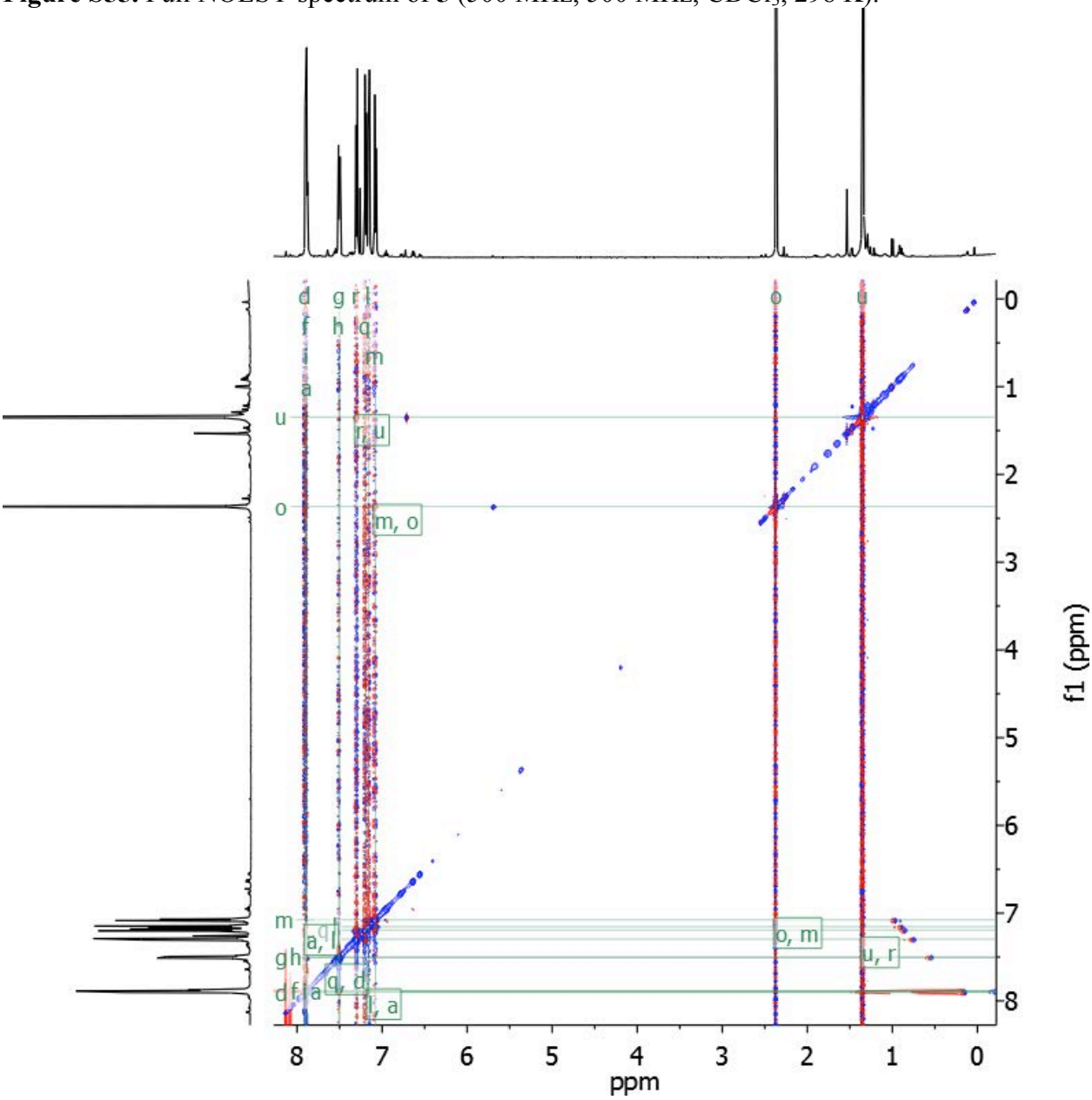


Figure S56. Partial NOESY spectrum of **5** showing the aromatic region (500 MHz, 500 MHz, $CDCl_3$, 298 K).

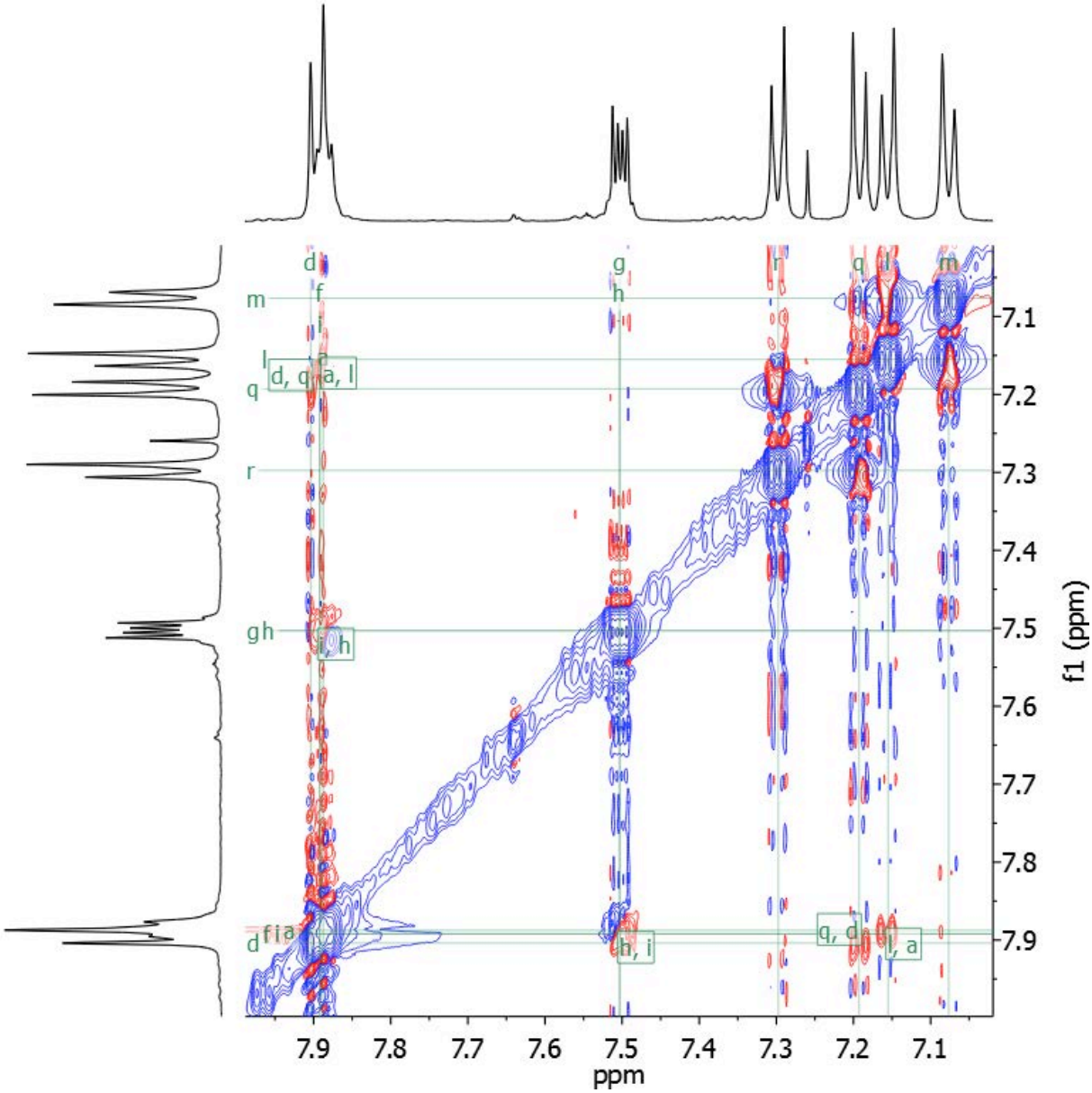


Figure S57. Full HSQC spectrum of **5** (500 MHz, 125 MHz, $CDCl_3$, 298 K).

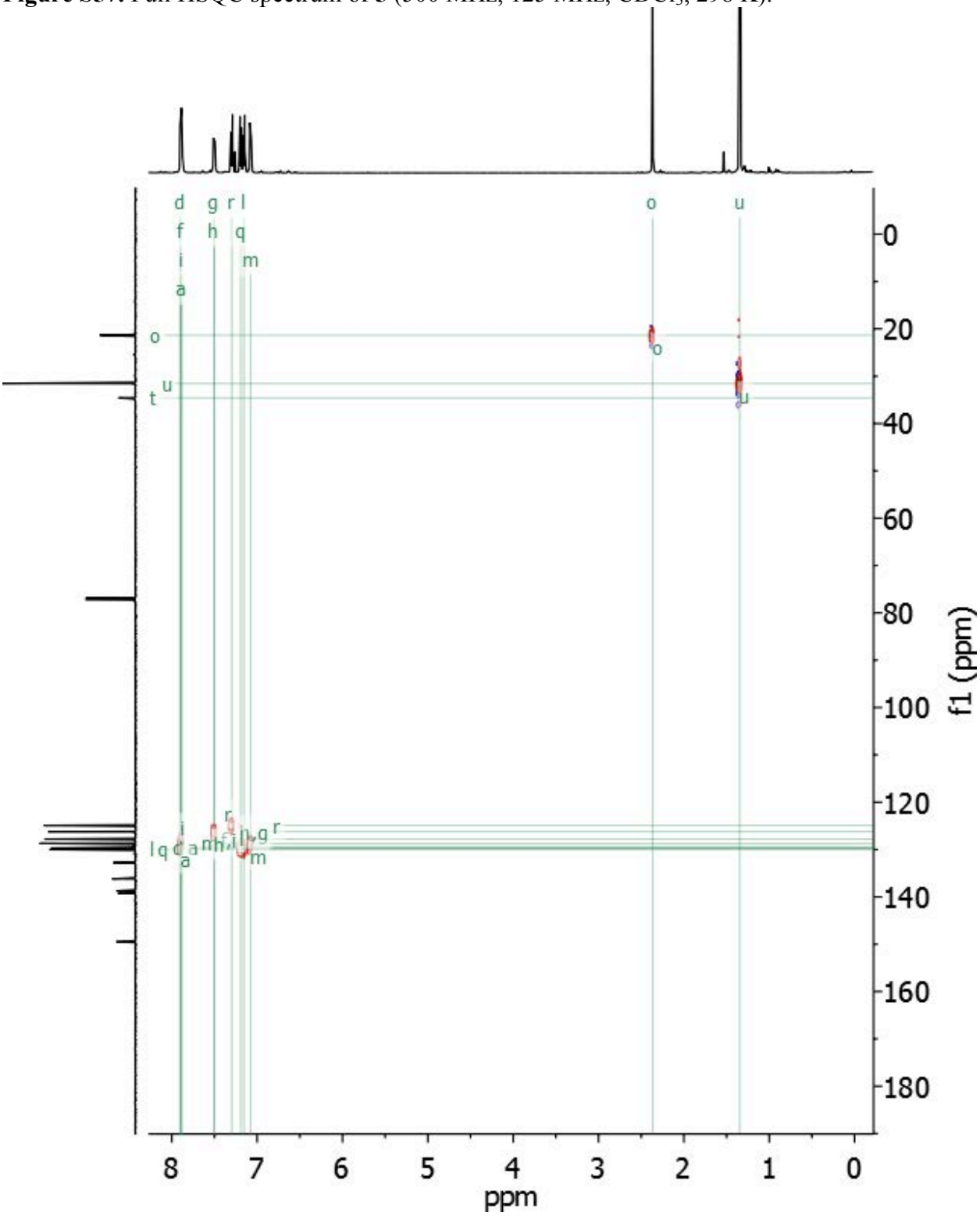
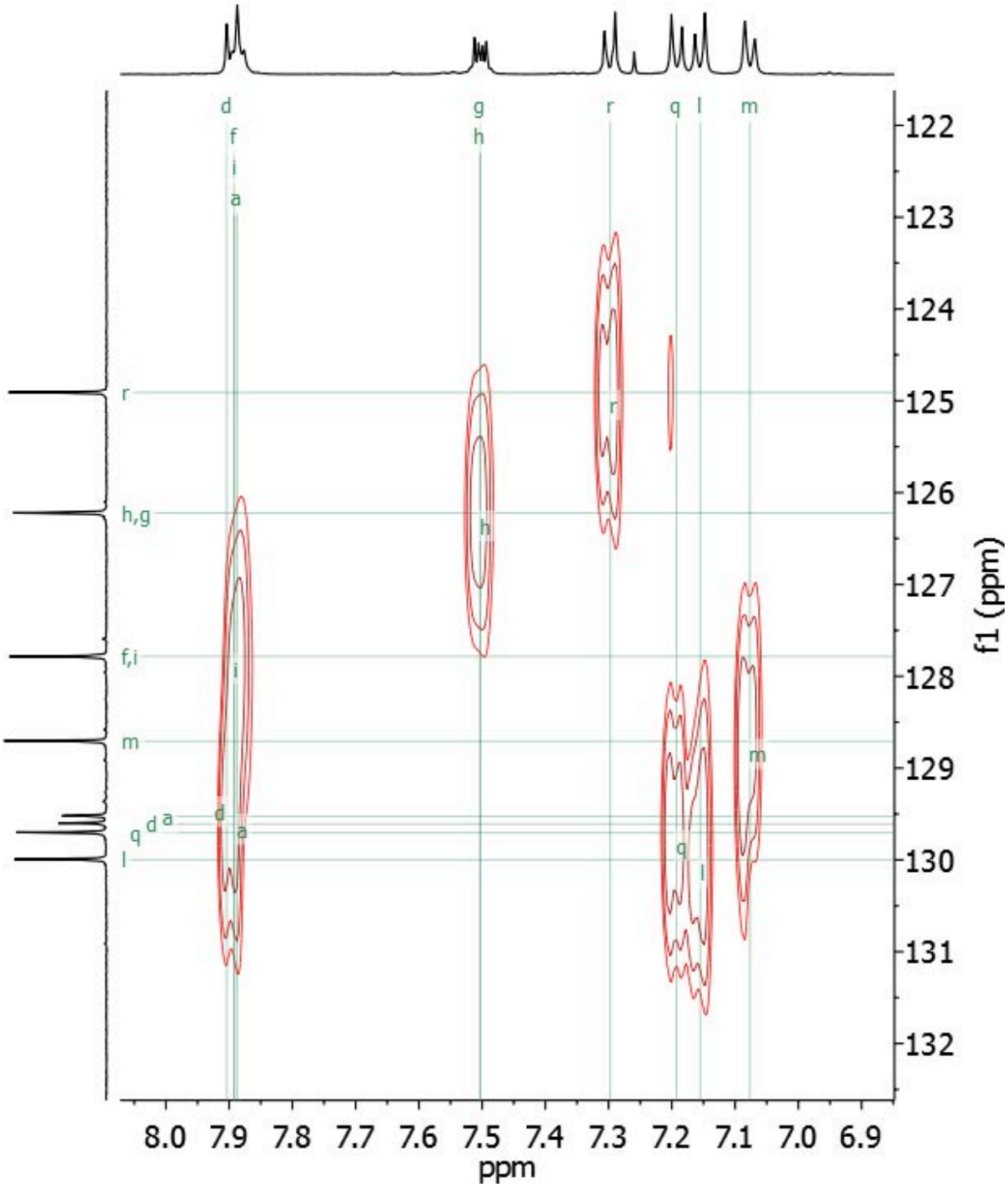
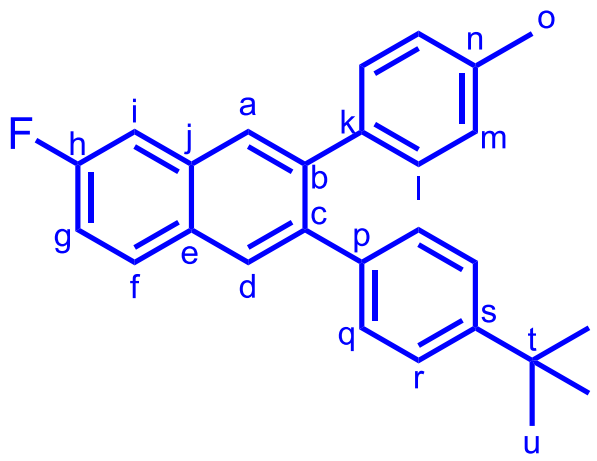


Figure S58. Partial HSQC spectrum of **5** showing the aromatic region (500 MHz, 125 MHz, $CDCl_3$, 298 K).



Peak assignments for compounds **5a-F** (blue) and **5b-F** (green):



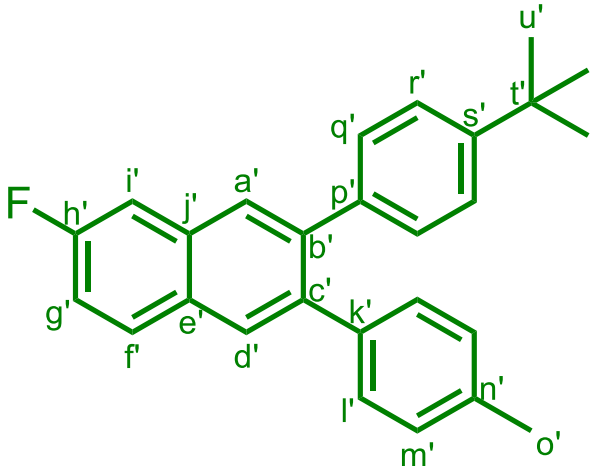


Figure S59. Full COSY spectrum of **5a-F** (blue) and **5b-F** (green) (500 MHz, 500 MHz, $CDCl_3$, 298 K).

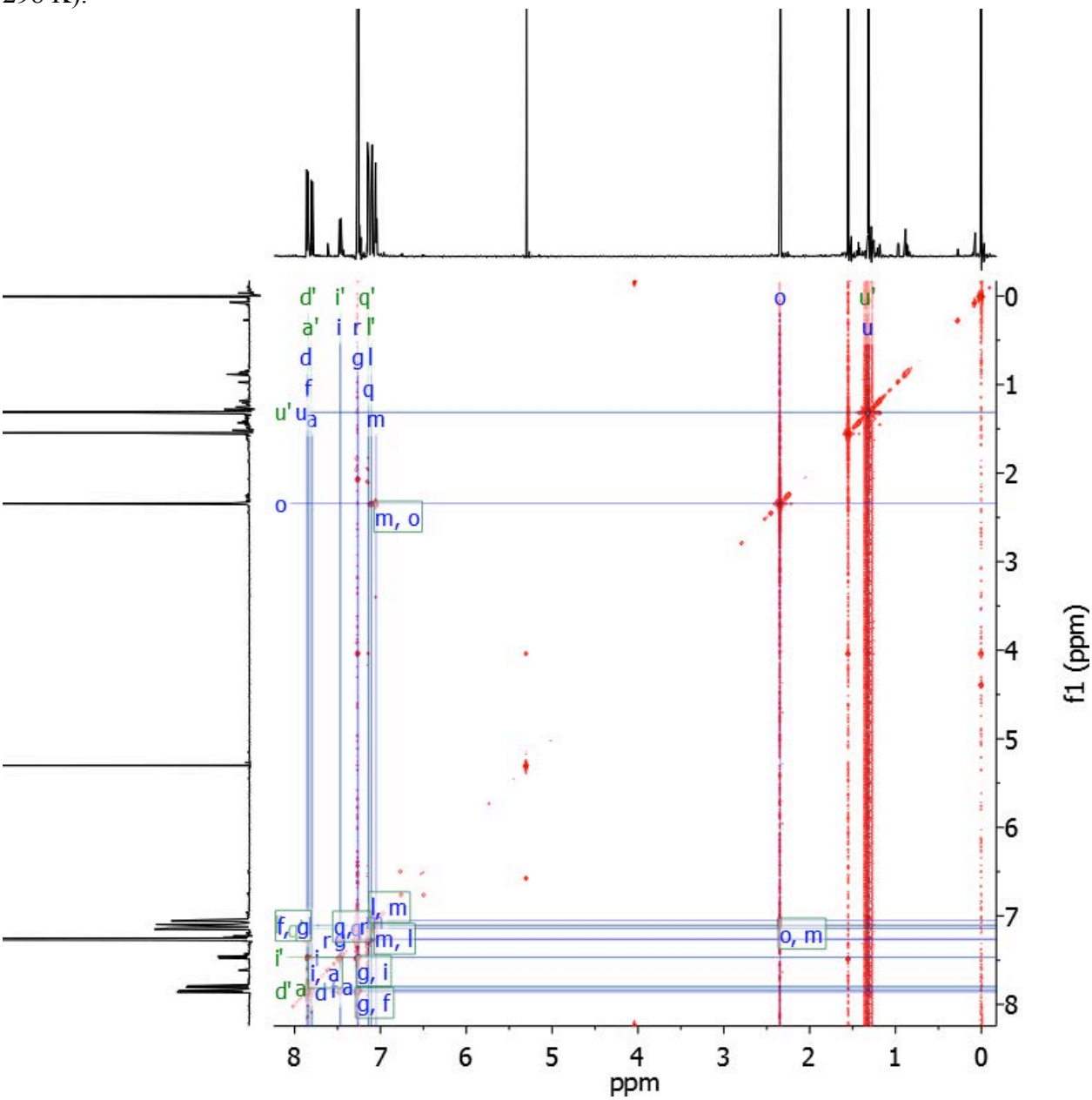


Figure S60. Partial COSY spectrum of **5a-F** (blue) and **5b-F** (green) showing the aromatic region (600 MHz, 600 MHz, $CDCl_3$, 298 K).

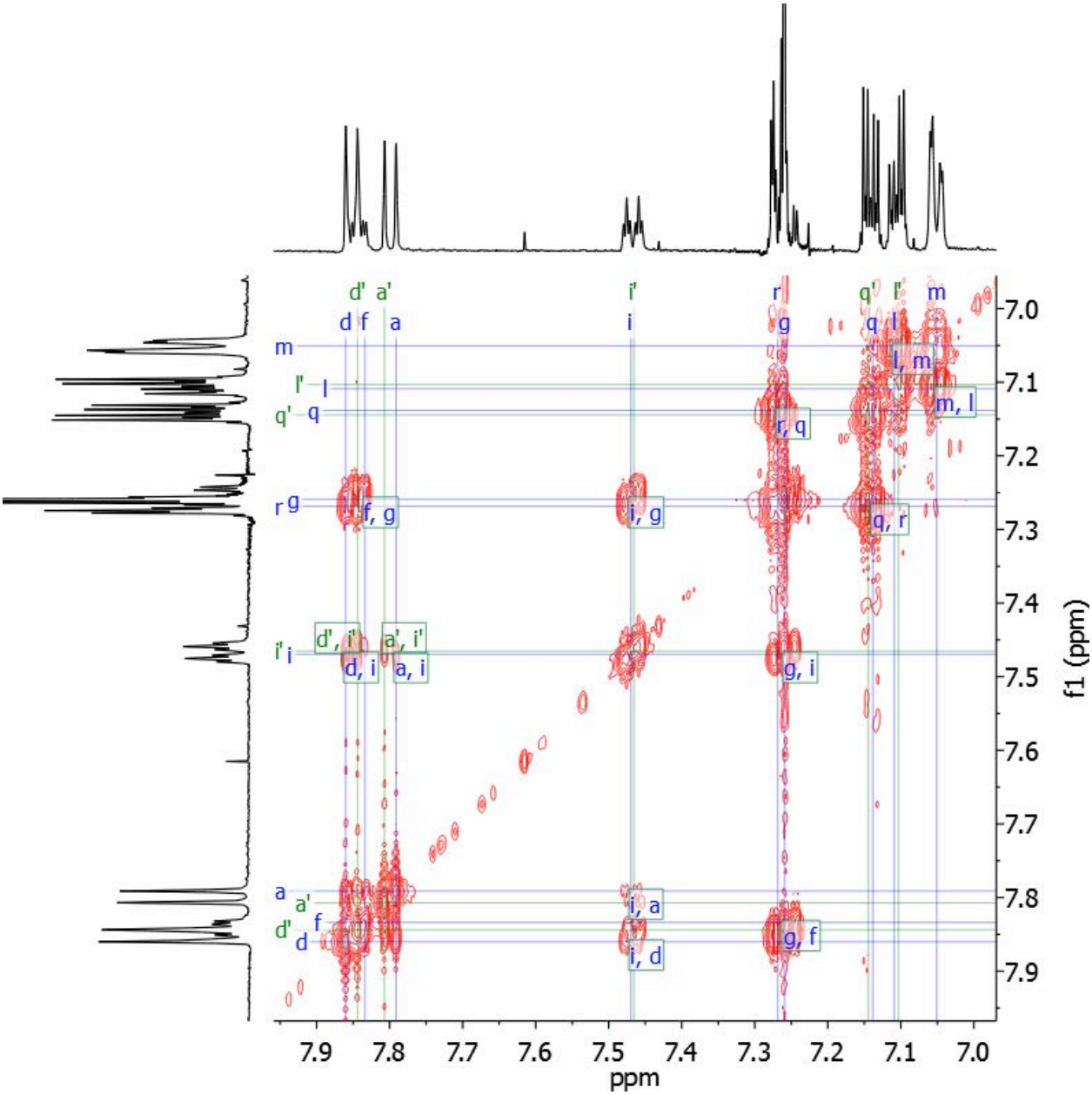


Figure S61. Full NOESY spectrum of **5a-F** (blue) and **5b-F** (green) (600 MHz, 600 MHz, $CDCl_3$, 298 K).

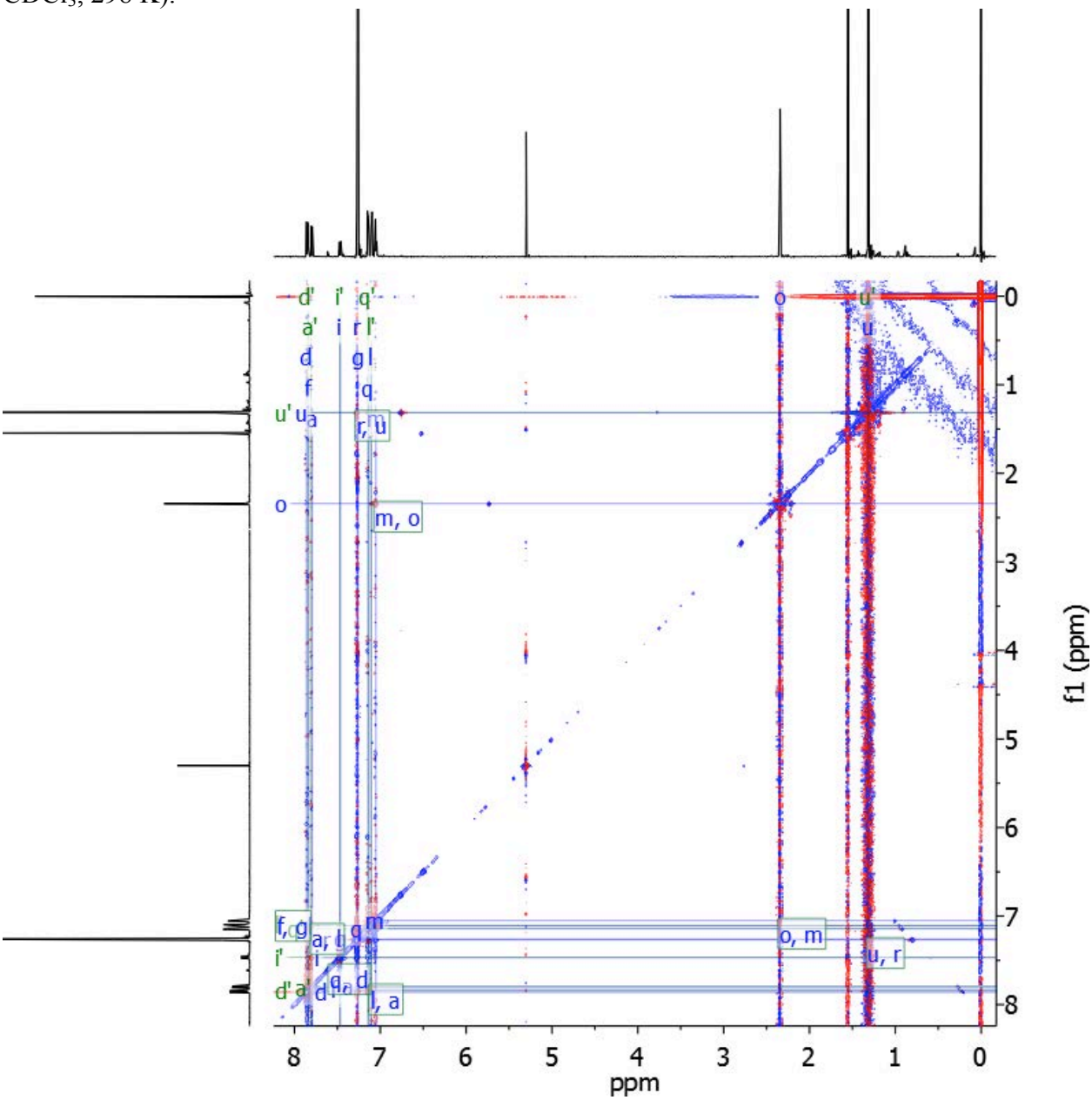


Figure S62. Partial NOESY spectrum of **5a-F** (blue) and **5b-F** (green) showing the aromatic region (600 MHz, 600 MHz, $CDCl_3$, 298 K).

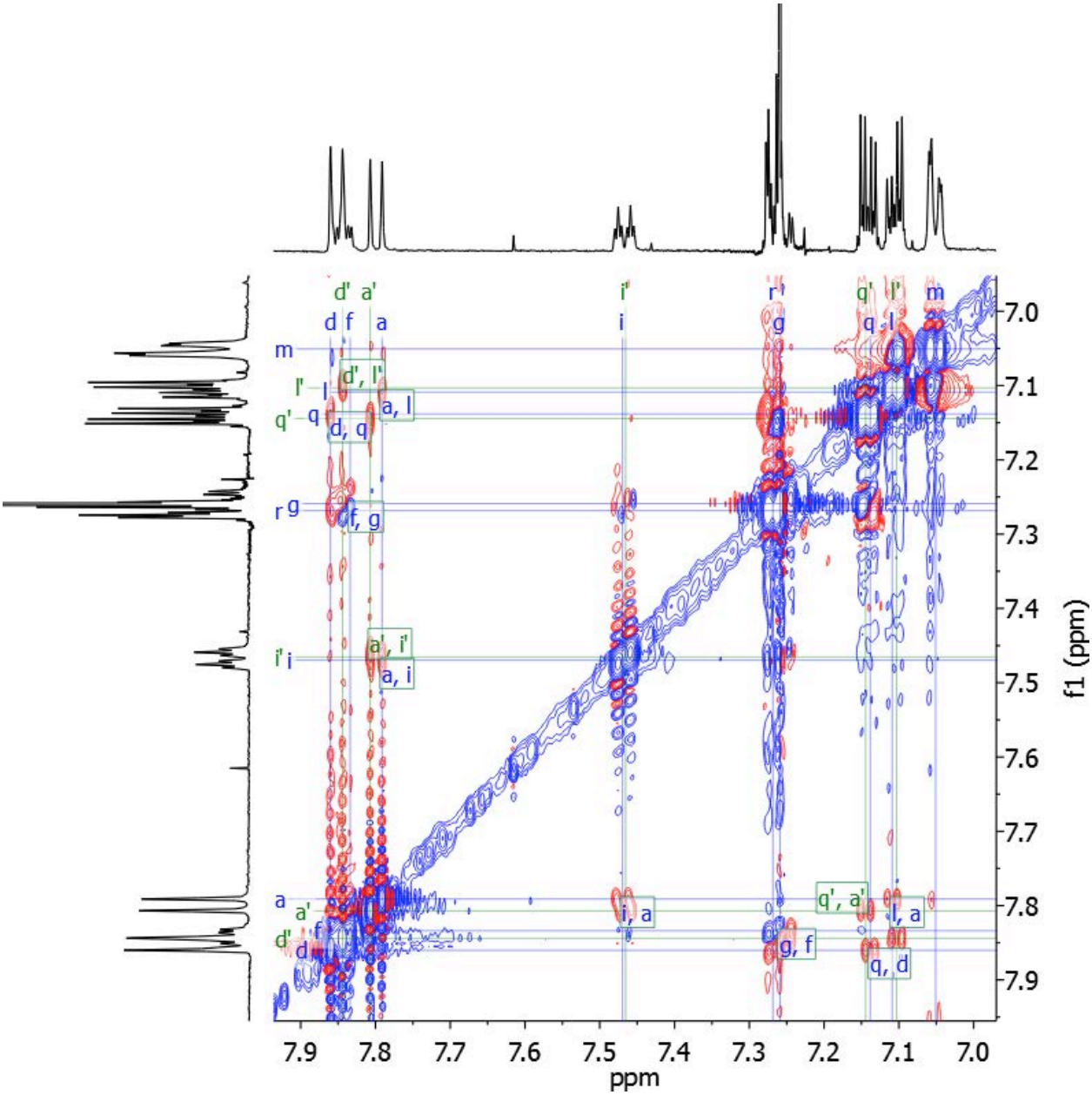


Figure S63. Full HSQC spectrum of **5a-F** (blue) and **5b-F** (green) (500 MHz, 125 MHz, $CDCl_3$, 298 K).

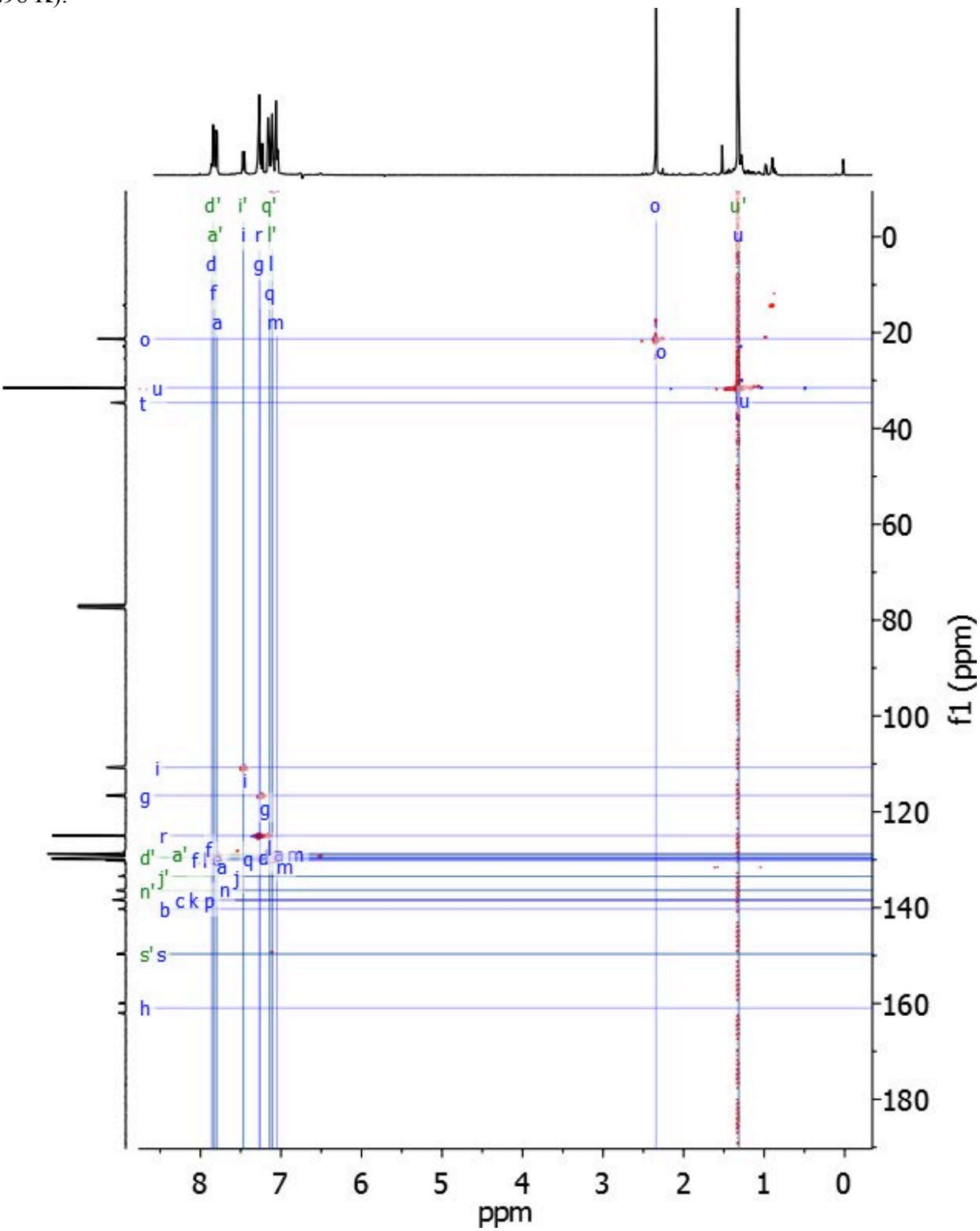


Figure S64. Partial HSQC spectrum of **5a-F** (blue) and **5b-F** (green) showing the aromatic region (500 MHz, 125 MHz, $CDCl_3$, 298 K).

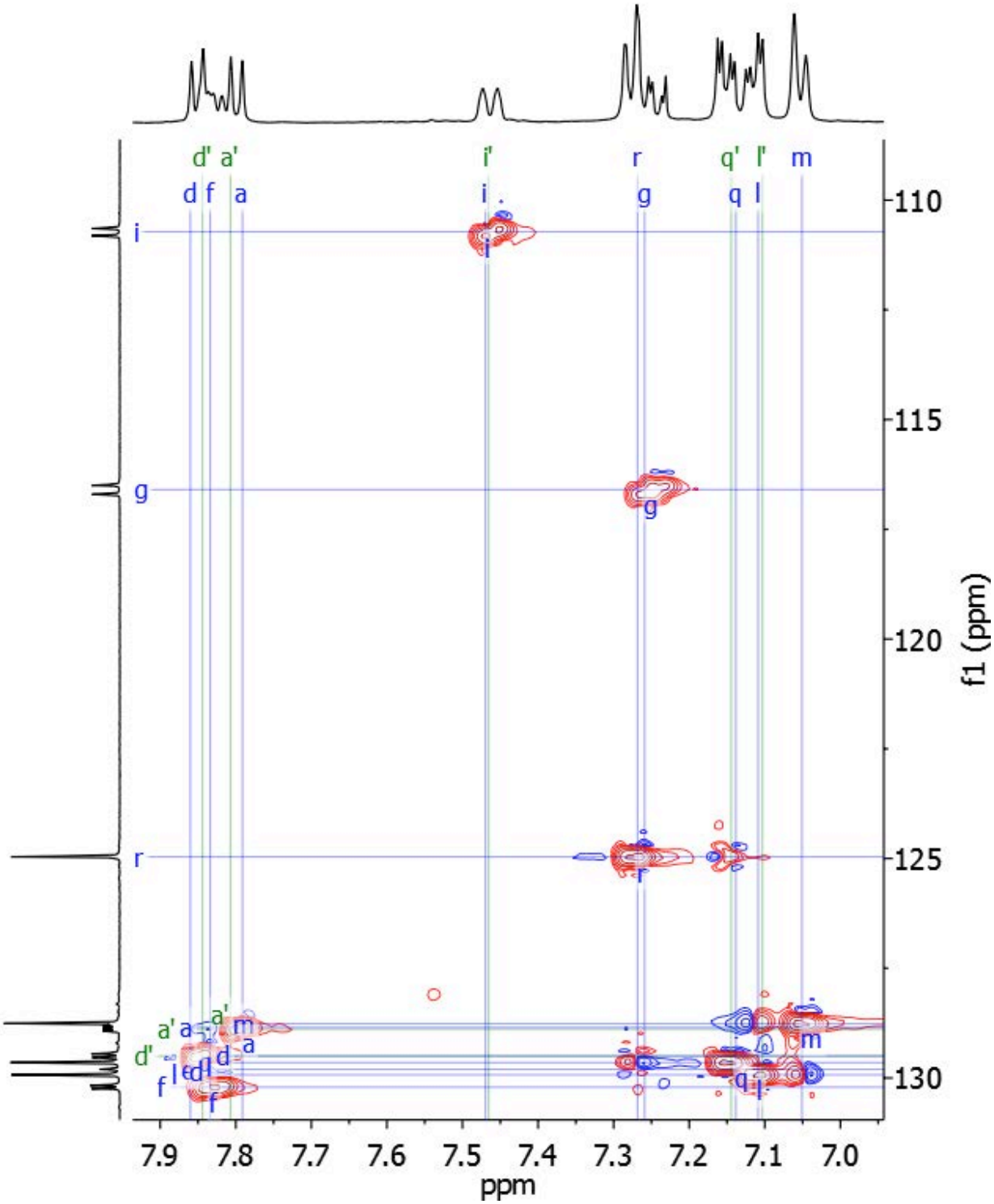


Figure S65. Full HMBC spectrum of **5a-F** (blue) and **5b-F** (green) (500 MHz, 125 MHz, $CDCl_3$, 298 K).

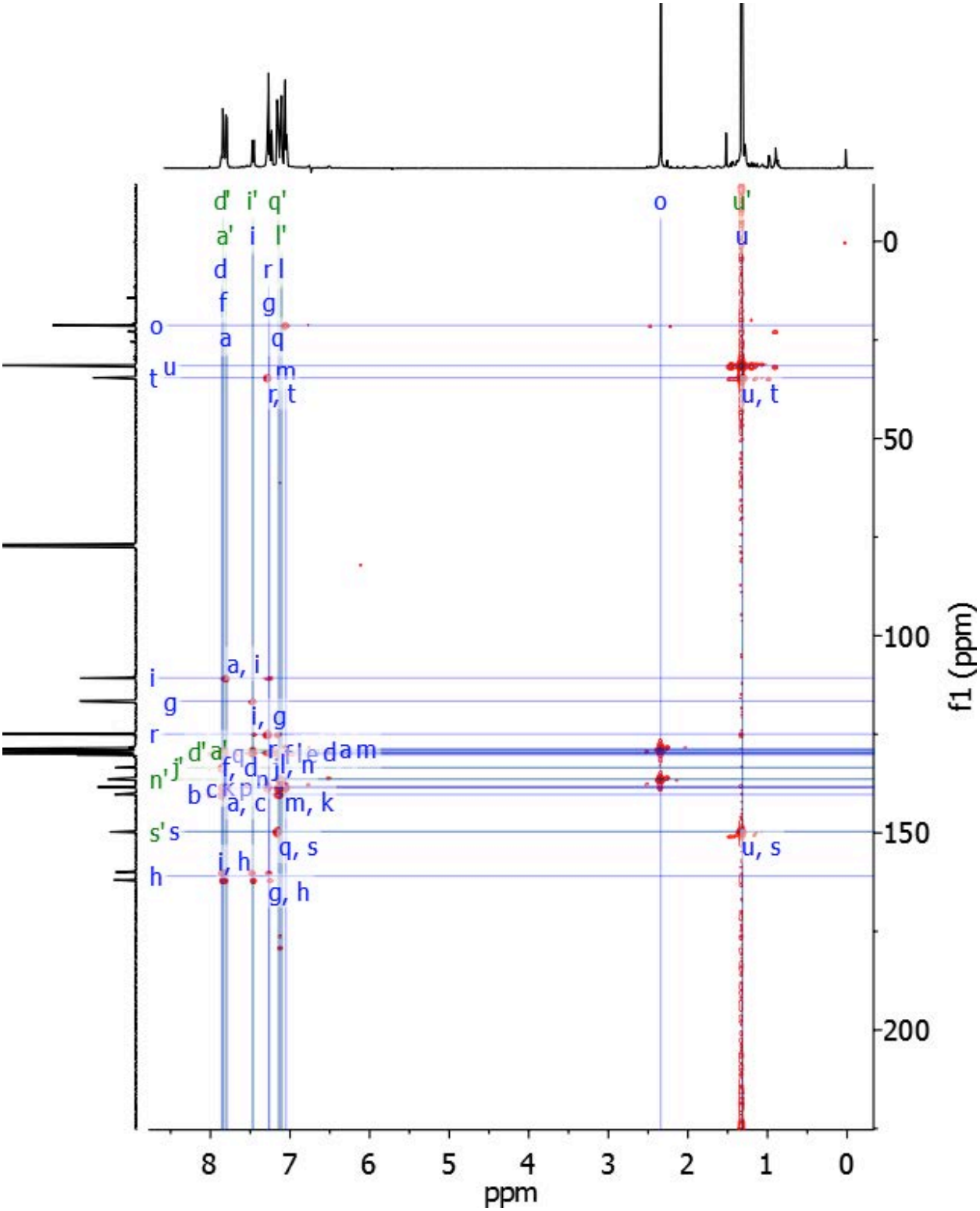
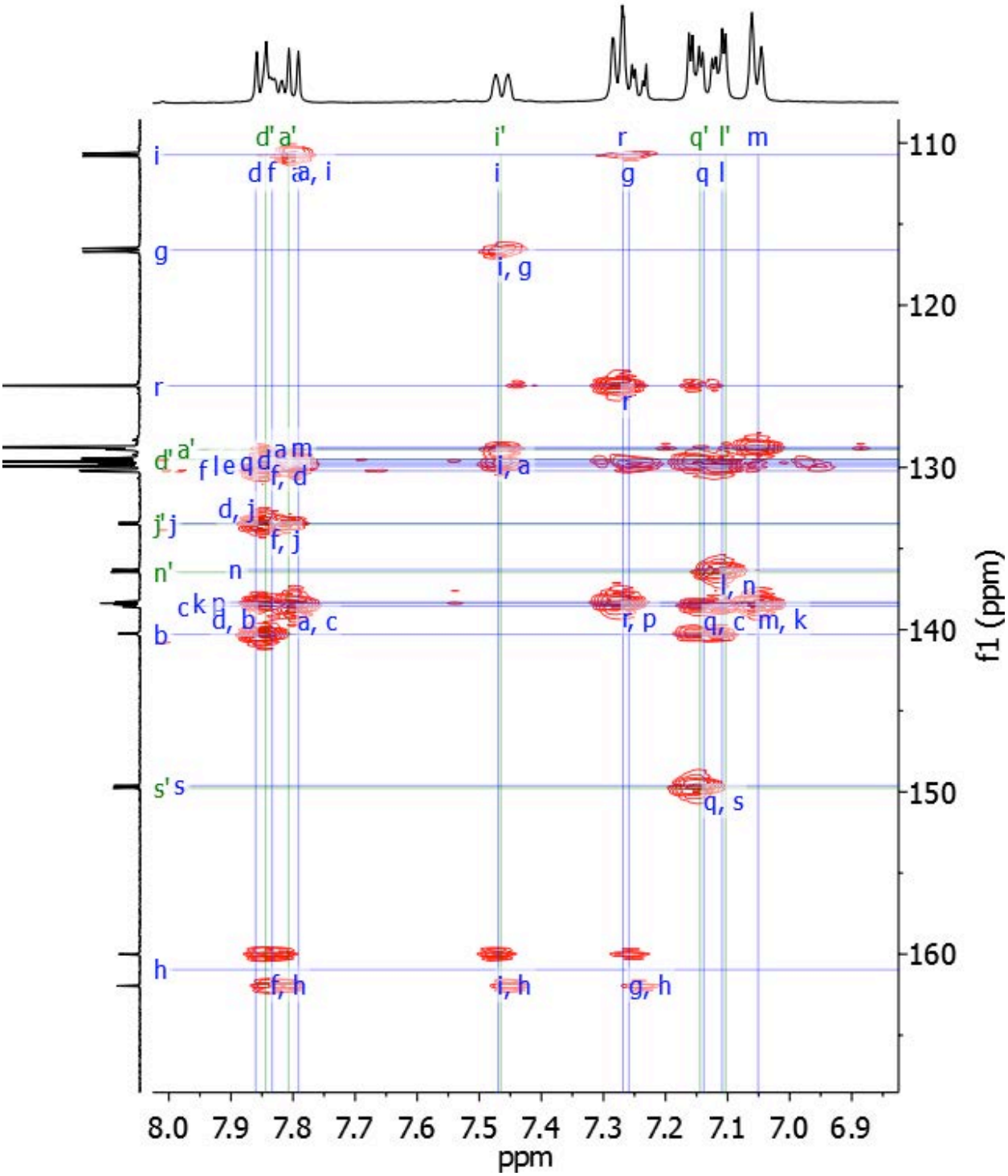


Figure S66. Partial HMBC spectrum of **5a-F** (blue) and **5b-F** (green) showing the aromatic region (500 MHz, 125 MHz, $CDCl_3$, 298 K).



Peak assignments for compound **7:**

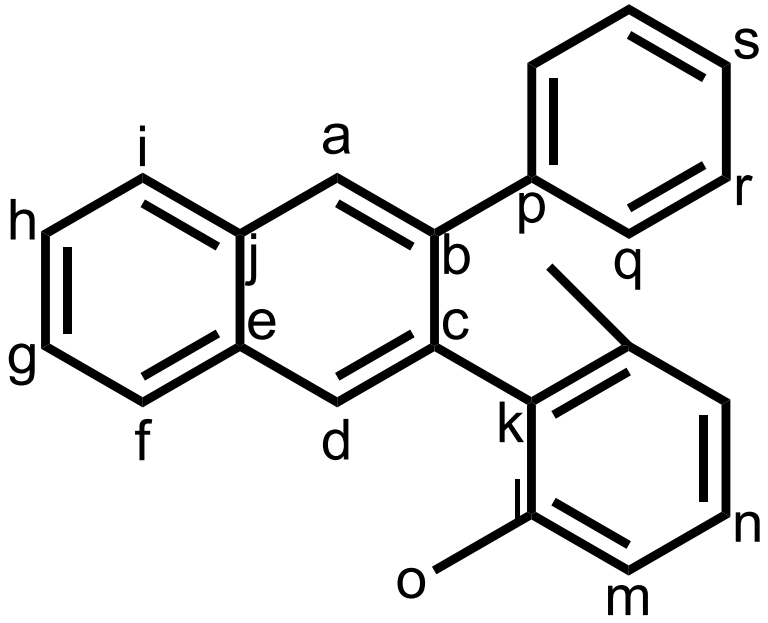


Figure S67. Full COSY spectrum of **7** (500 MHz, 500 MHz, $CDCl_3$, 298 K).

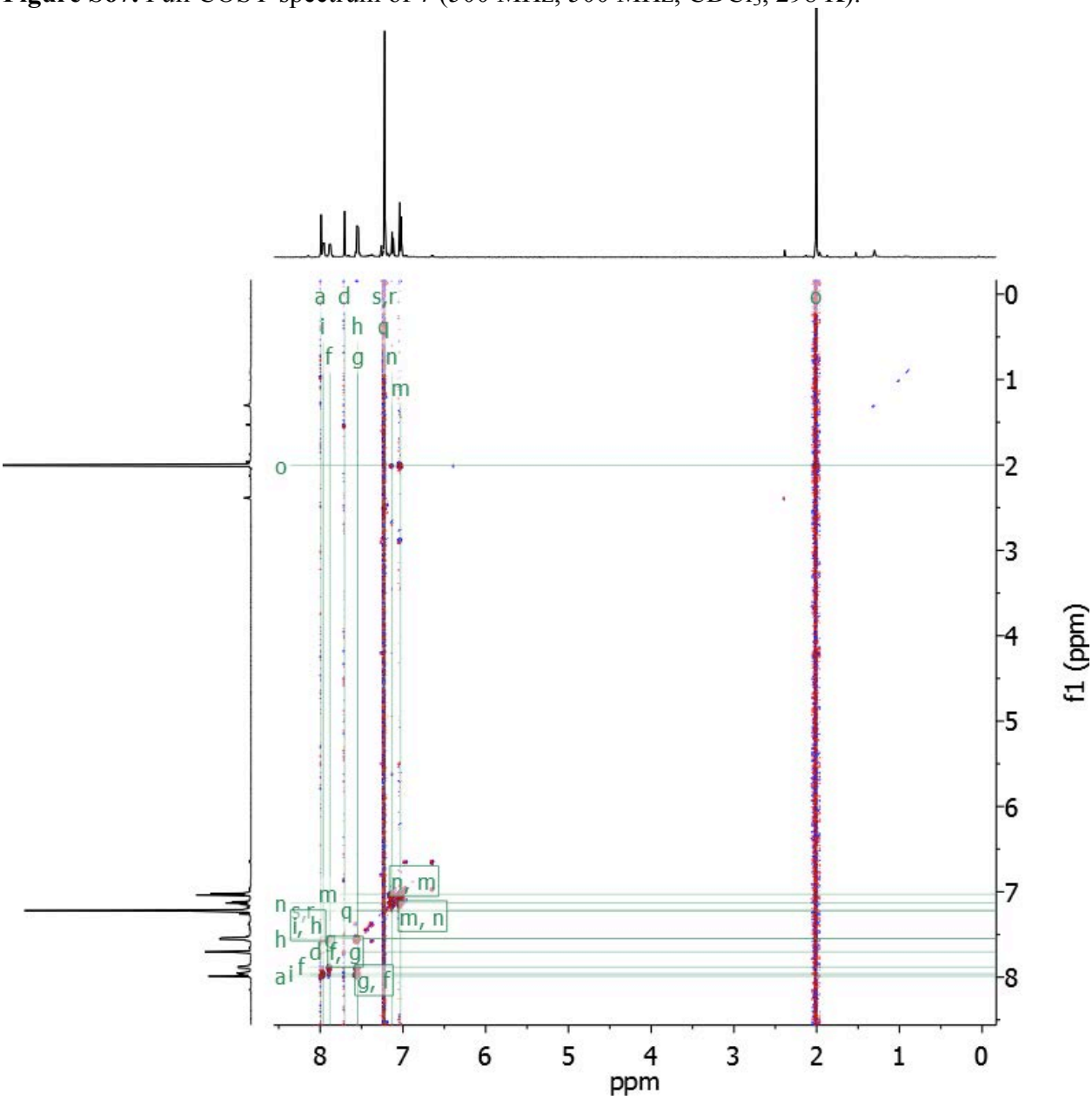


Figure S68. Partial COSY spectrum of **7** showing the aromatic region (500 MHz, 500 MHz, $CDCl_3$, 298 K).

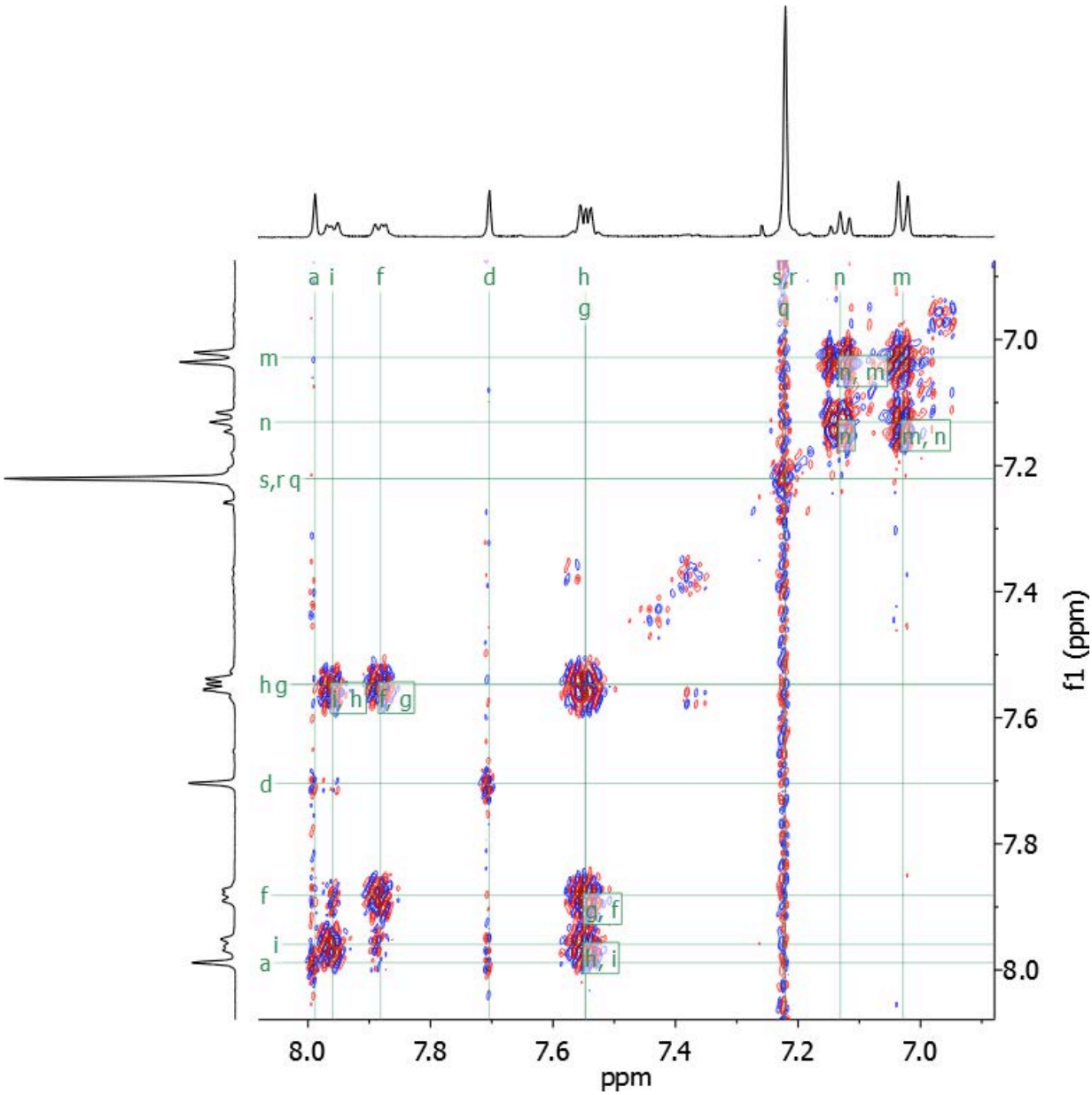


Figure S69. Full ROESY spectrum of **7** (500 MHz, 500 MHz, $CDCl_3$, 298 K).

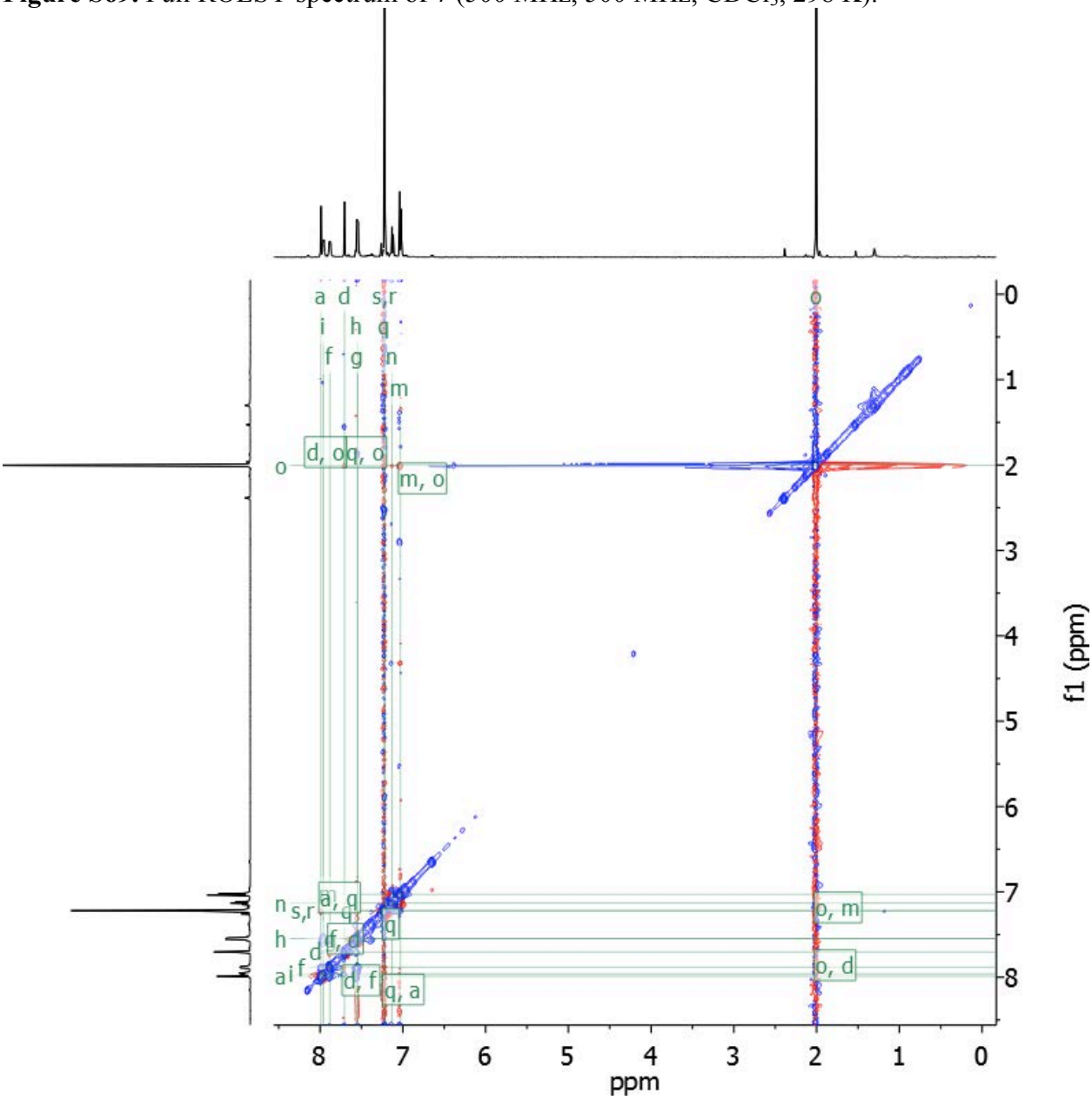


Figure S70. Partial ROESY spectrum of **7** showing the aromatic region (500 MHz, 500 MHz, $CDCl_3$, 298 K).

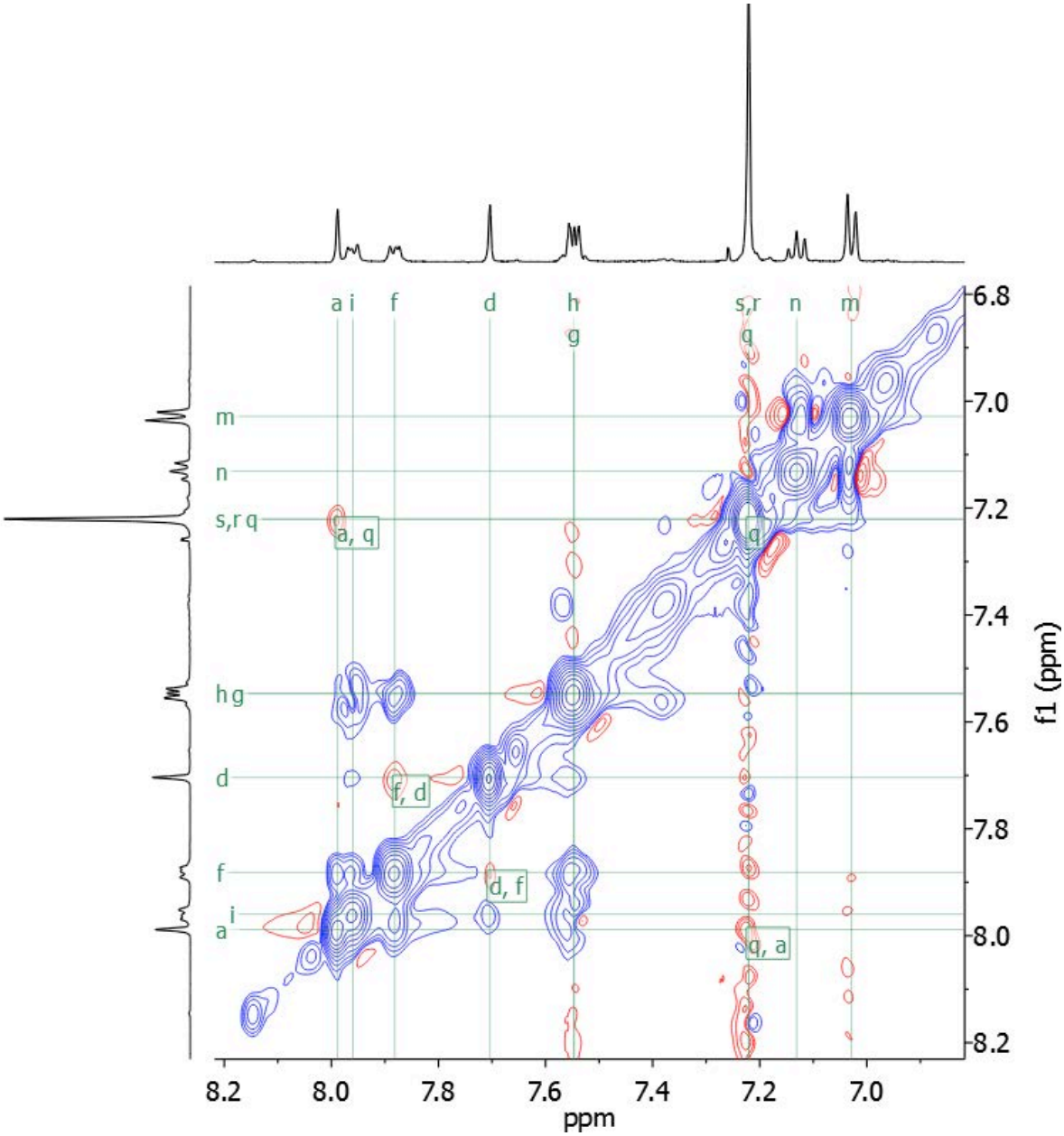


Figure S71. Full HSQC spectrum of **7** (500 MHz, 125 MHz, $CDCl_3$, 298 K).

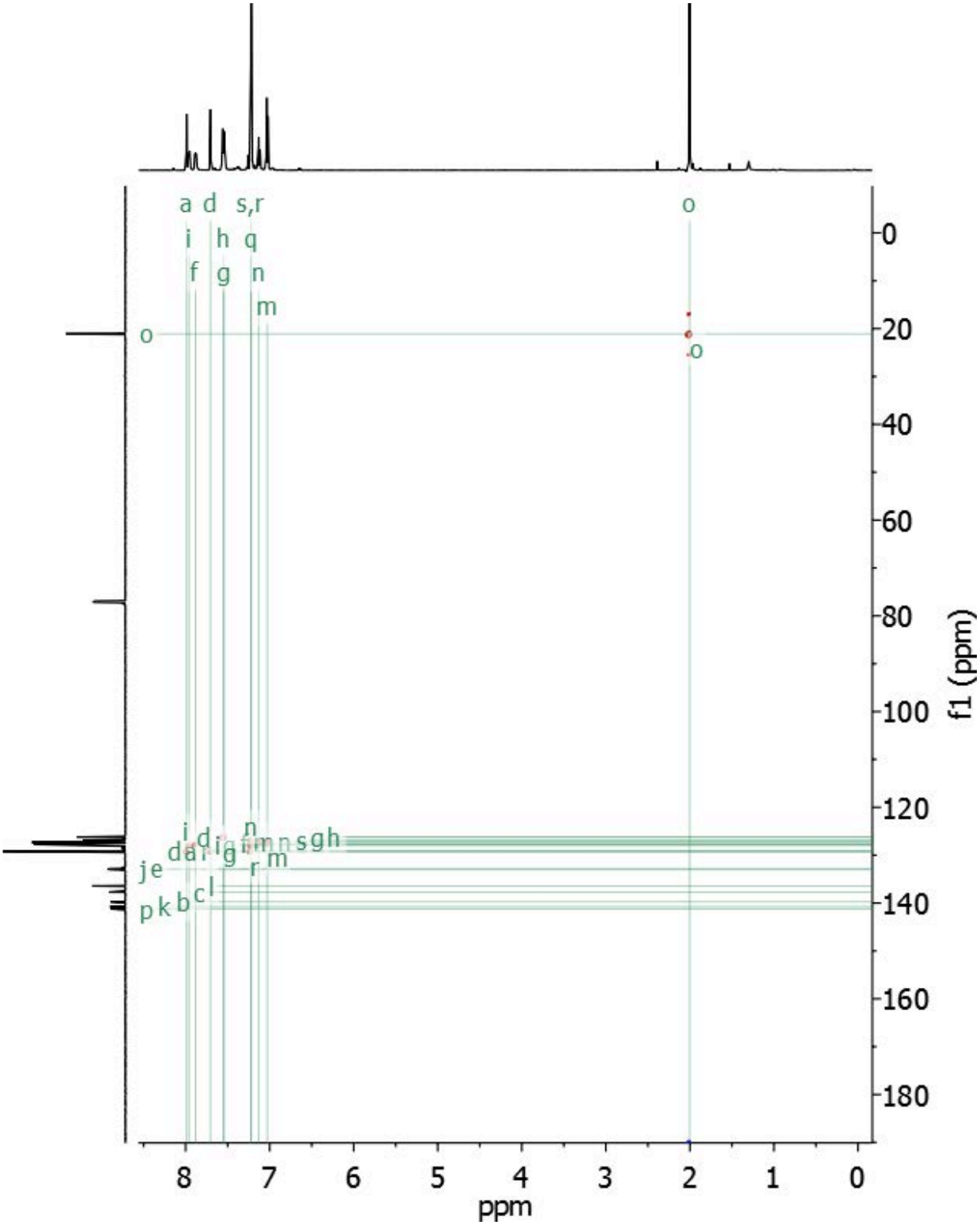


Figure S72. Partial HSQC spectrum of **7** showing the aromatic region (500 MHz, 125 MHz, $CDCl_3$, 298 K).

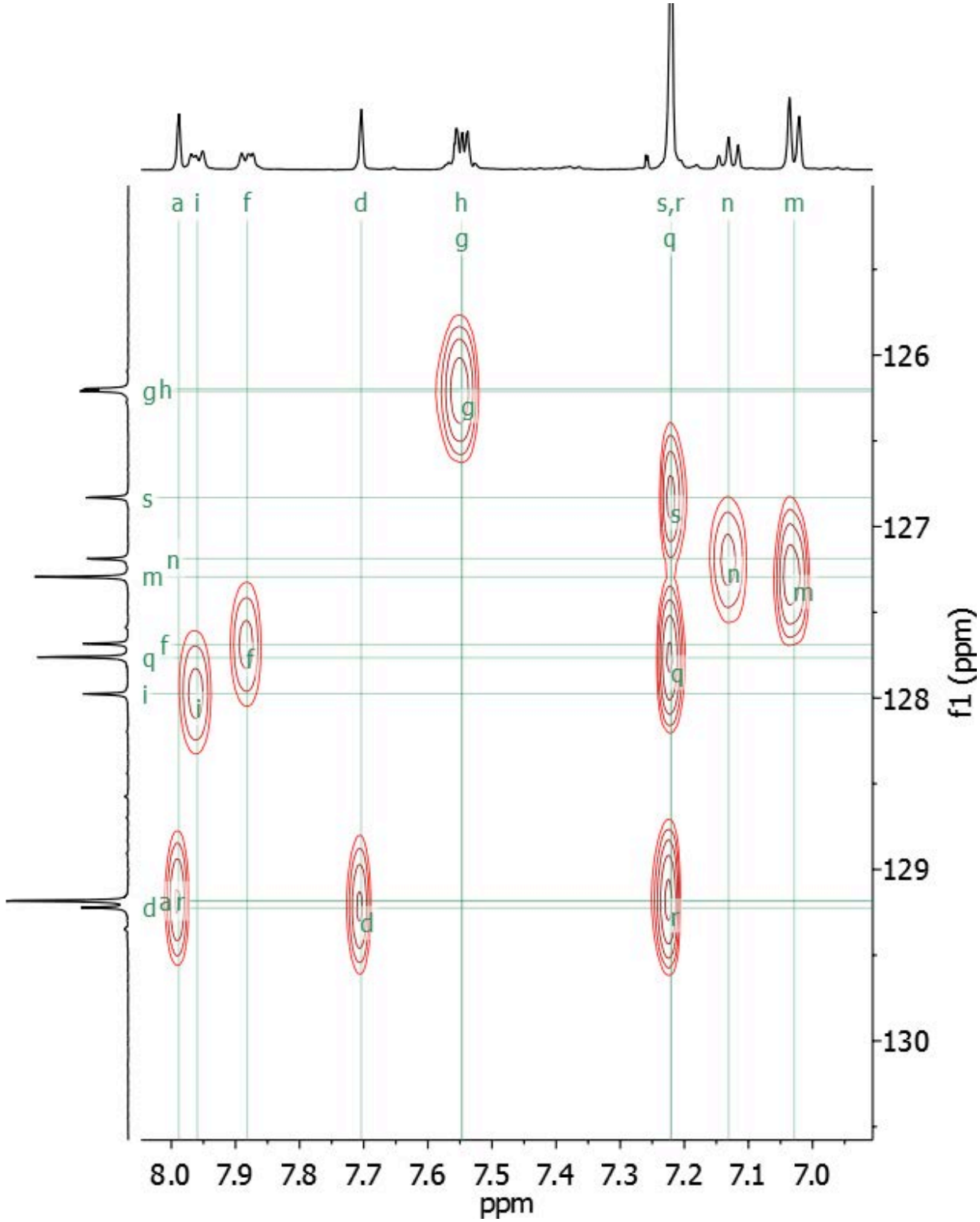


Figure S73. Full HMBC spectrum of **7** (500 MHz, 125 MHz, $CDCl_3$, 298 K).

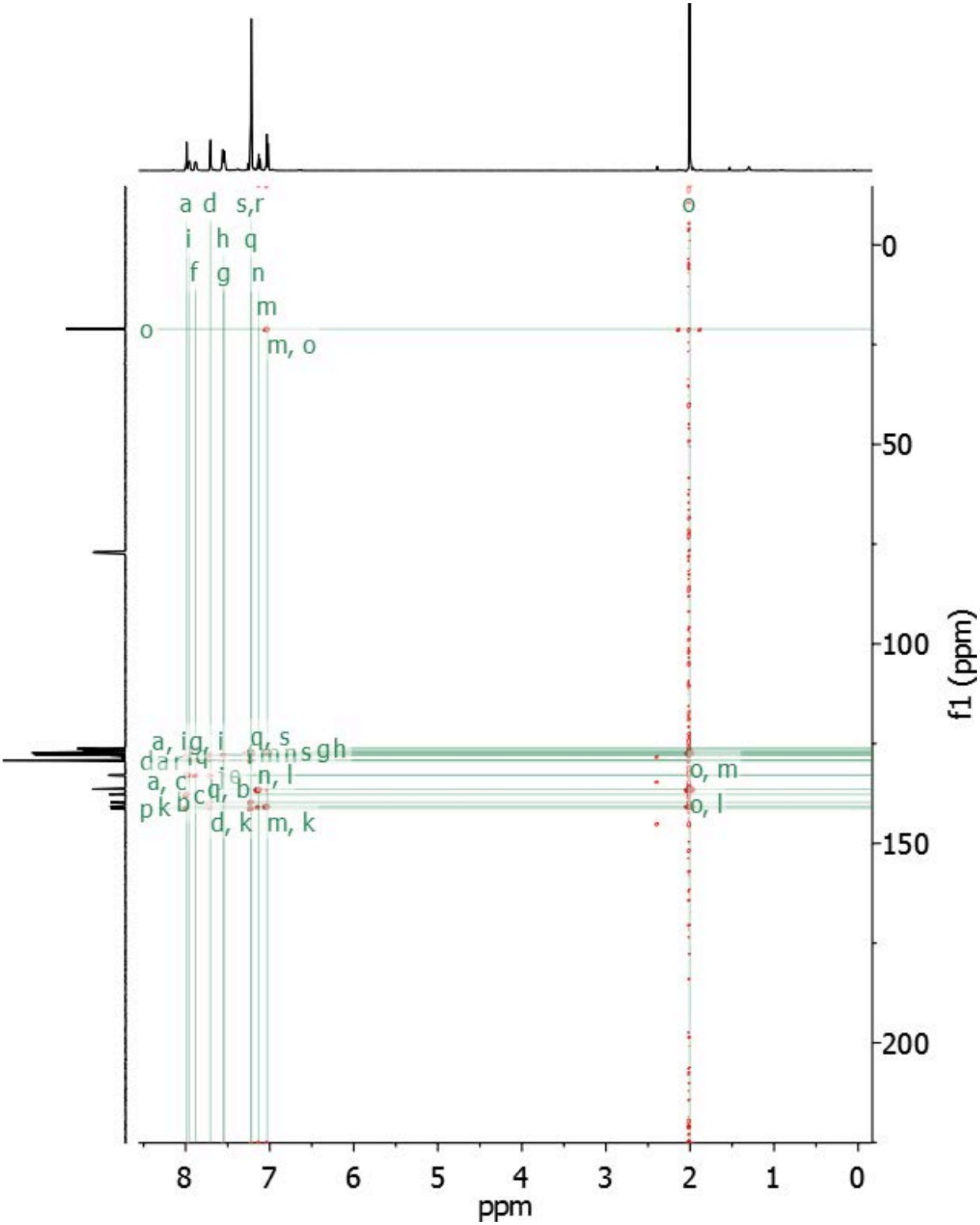
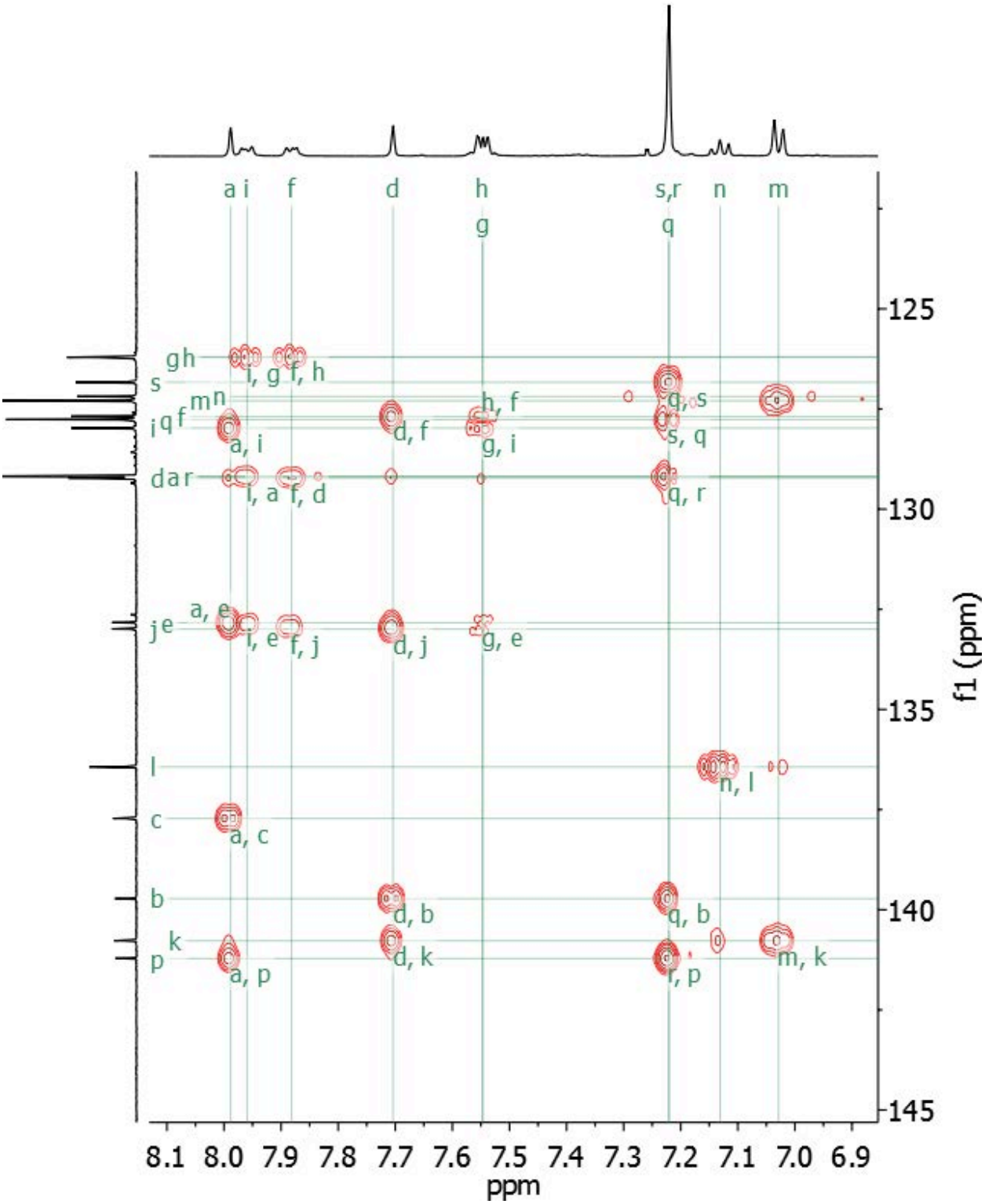


Figure S74. Partial HMBC spectrum of **7** showing the aromatic region (500 MHz, 125 MHz, $CDCl_3$, 298 K).



Peak assignments for compound **7a-F:**

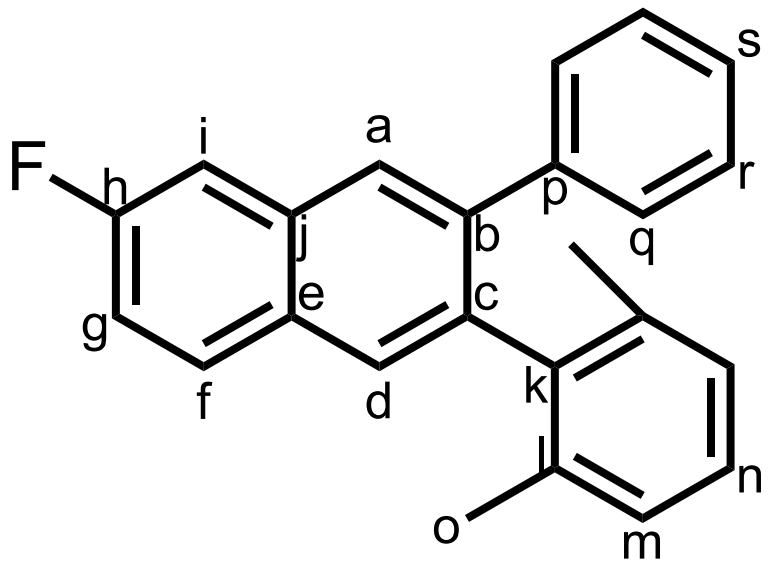


Figure S75. Full COSY spectrum of **7a-F** (500 MHz, 500 MHz, $CDCl_3$, 298 K).

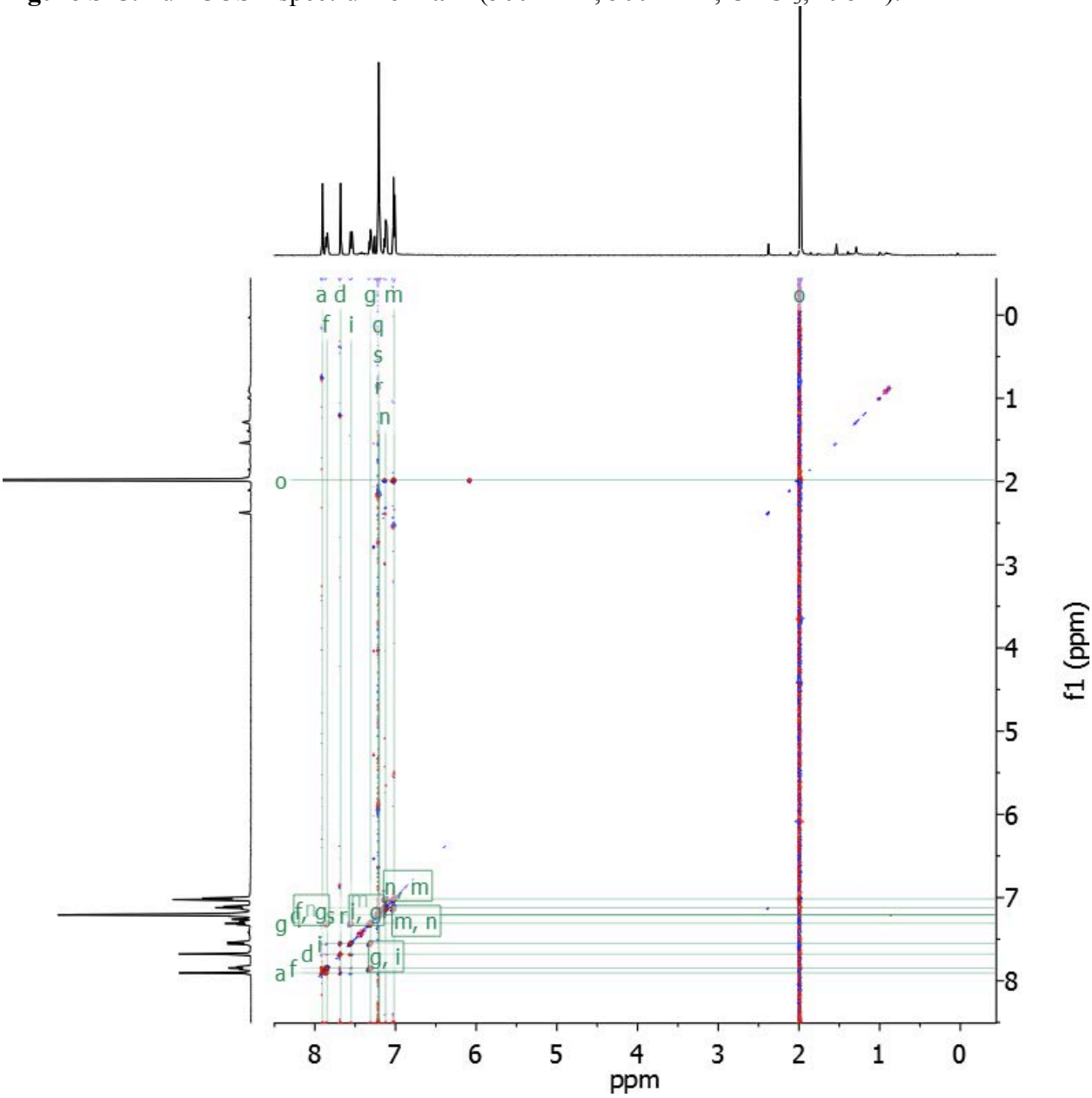


Figure S76. Partial COSY spectrum of **7a-F** showing the aromatic region (500 MHz, 500 MHz, $CDCl_3$, 298 K).

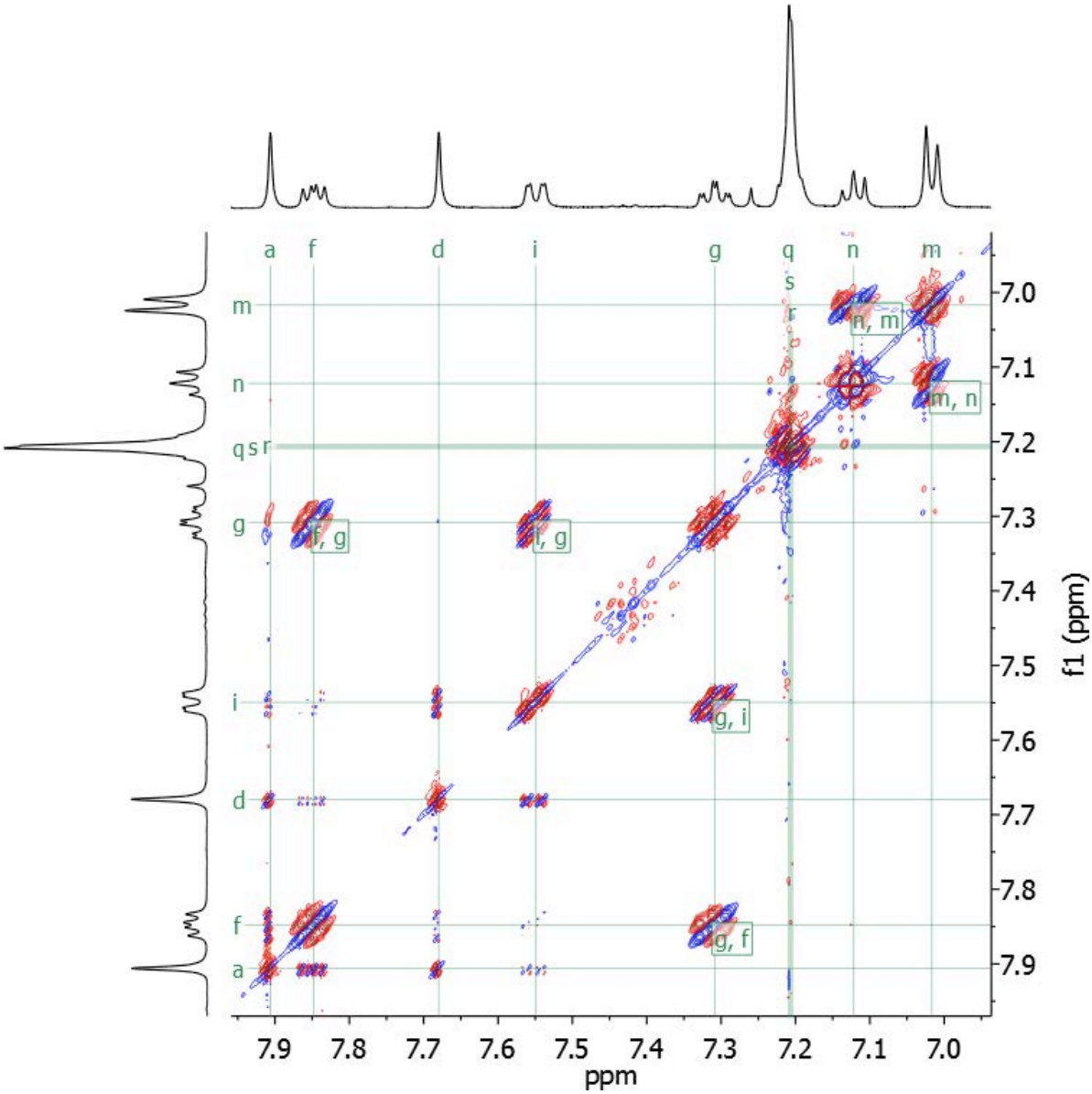


Figure S77. Full ROESY spectrum of **7a-F** (500 MHz, 500 MHz, $CDCl_3$, 298 K).

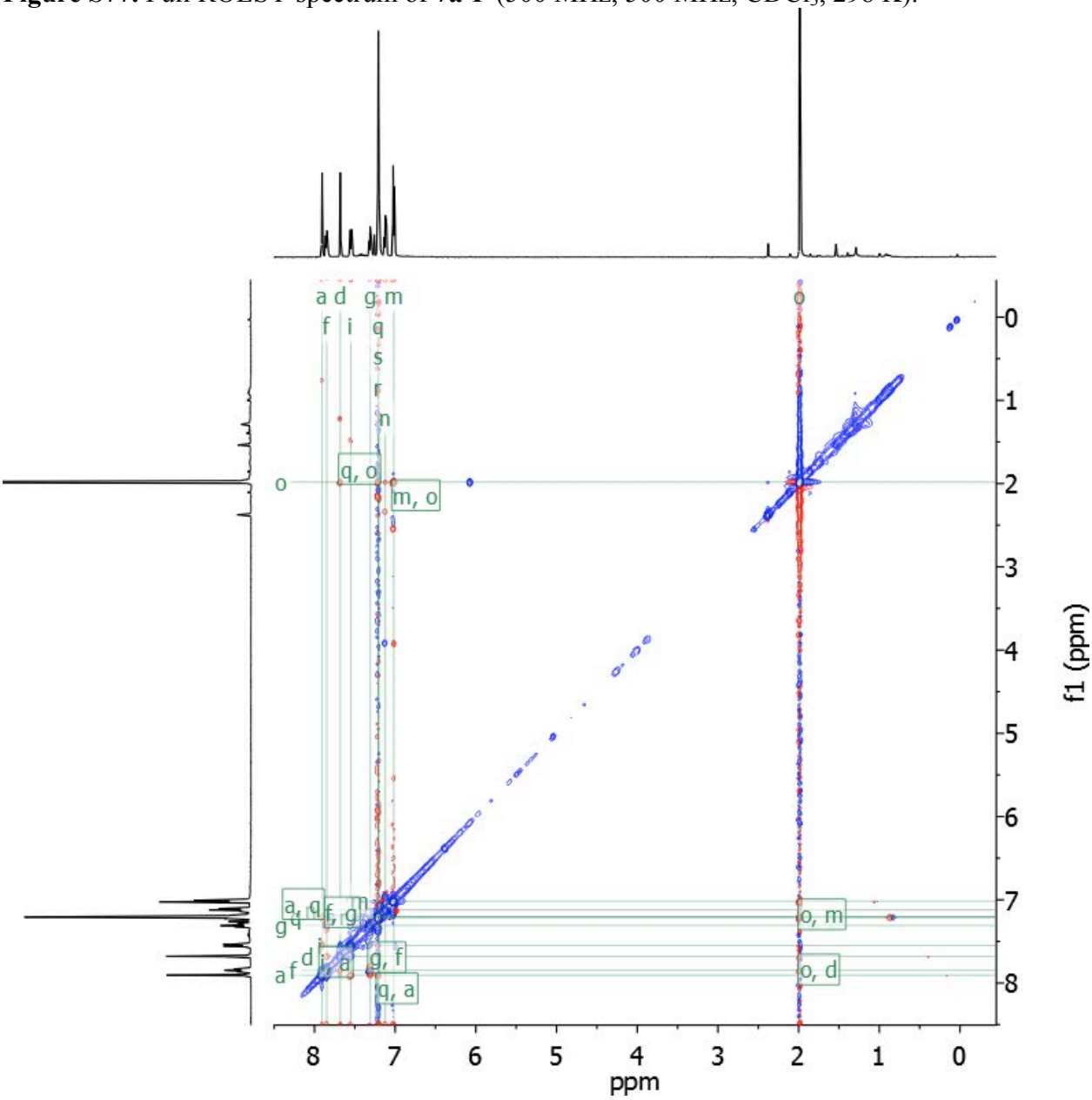


Figure S78. Partial ROESY spectrum of **7a-F** showing the aromatic region (500 MHz, 500 MHz, $CDCl_3$, 298 K).

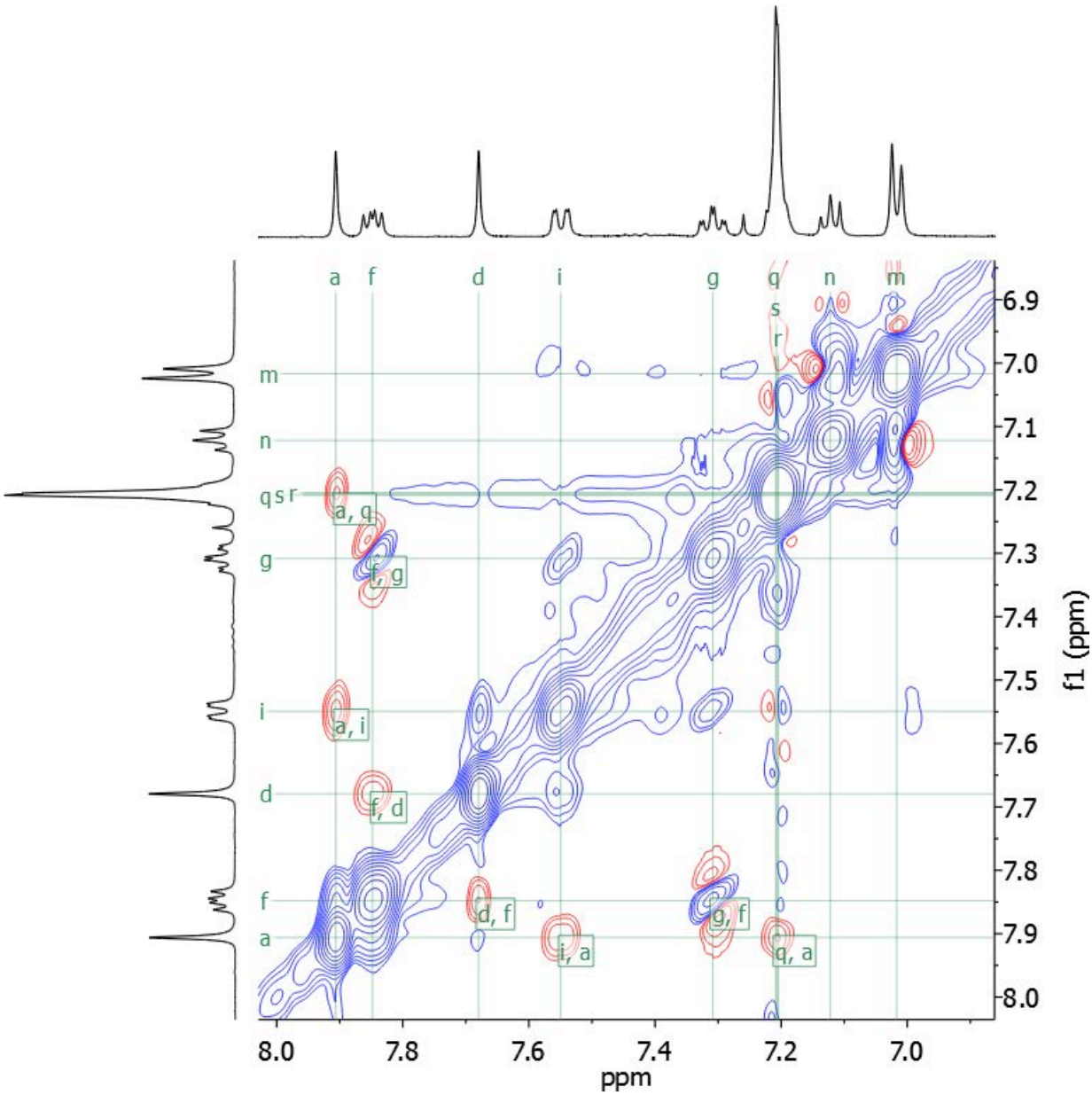


Figure S79. Full HSQC spectrum of **7a-F** (500 MHz, 125 MHz, $CDCl_3$, 298 K).

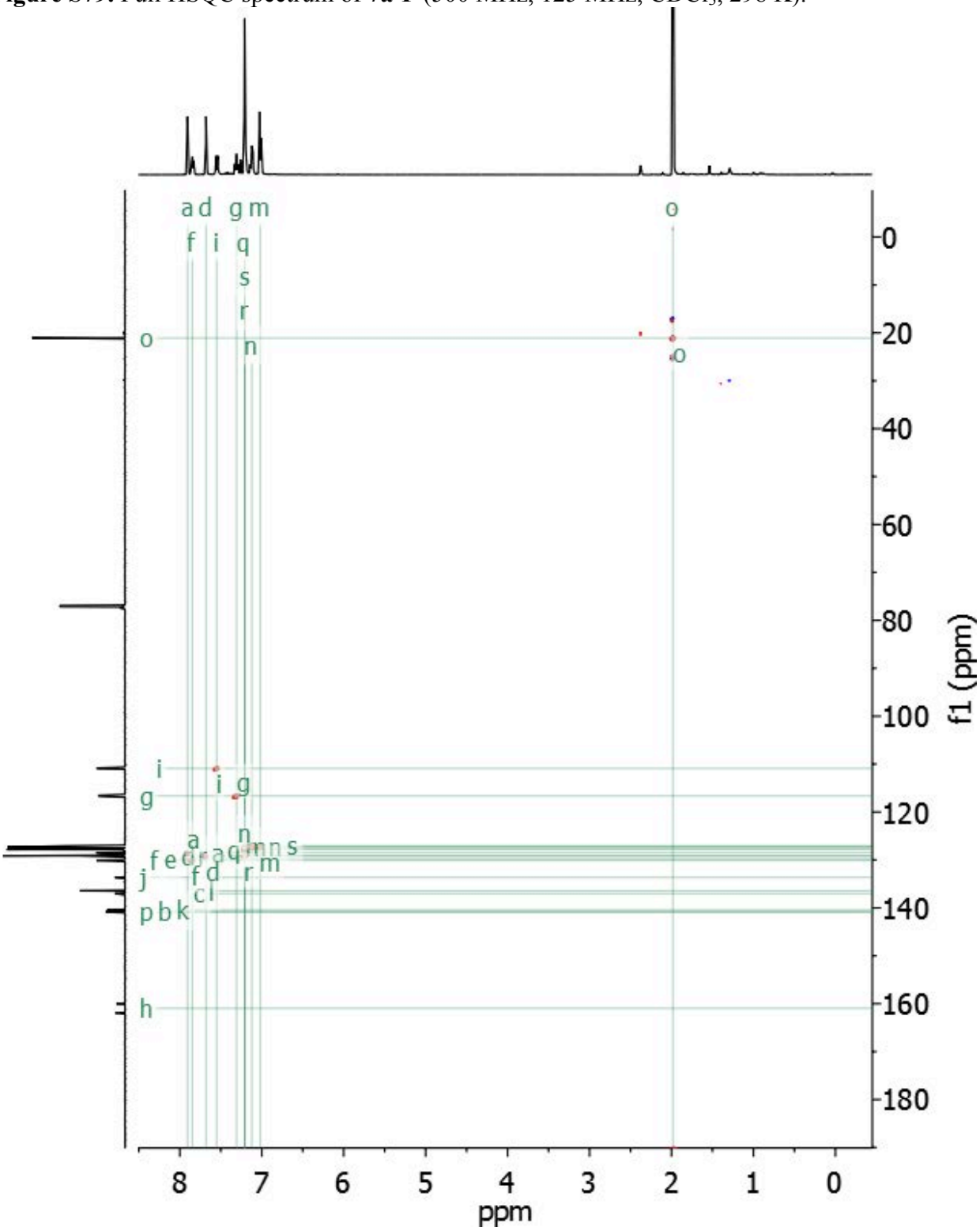


Figure S80. Partial HSQC spectrum of **7a-F** showing the aromatic region (500 MHz, 125 MHz, $CDCl_3$, 298 K).

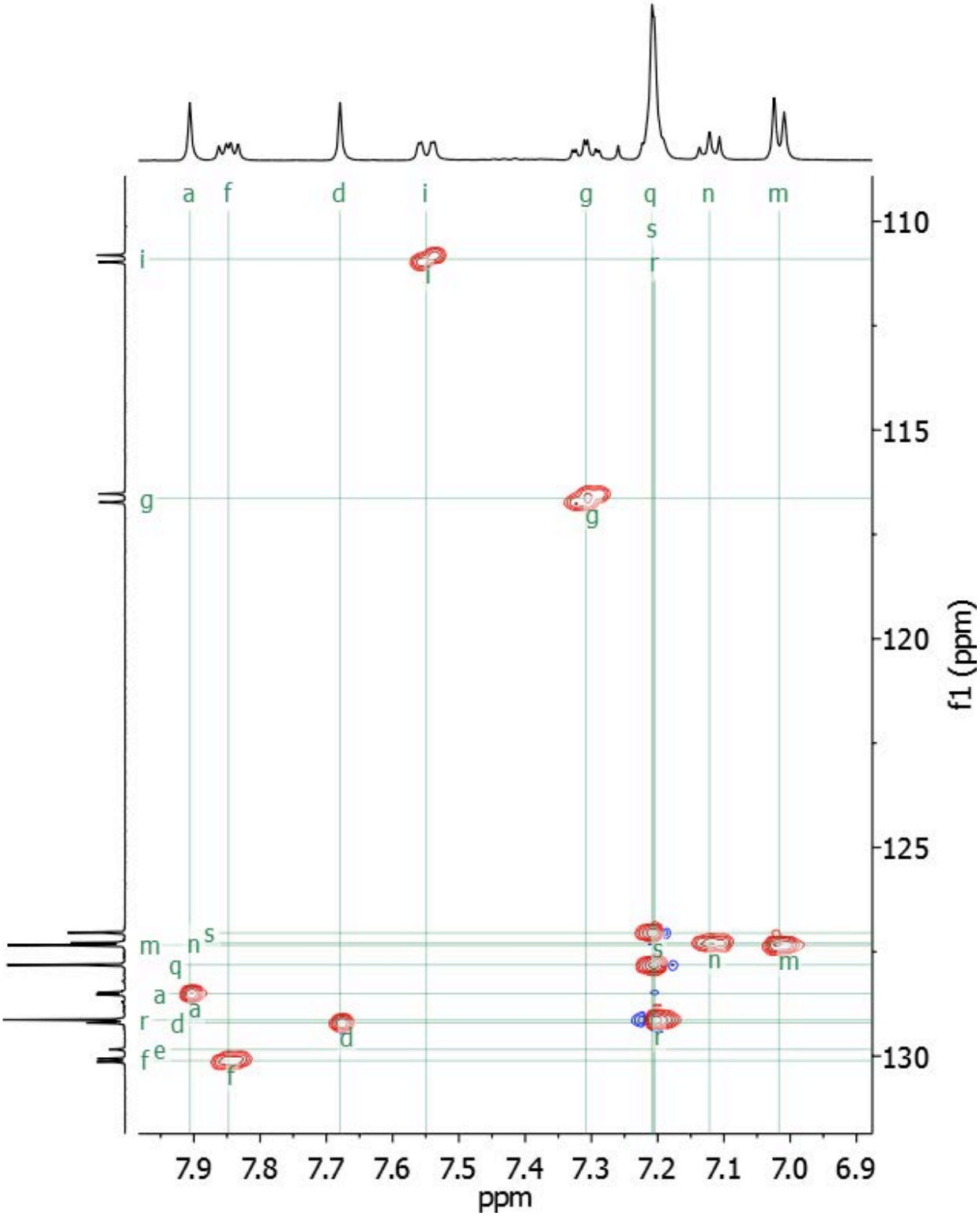


Figure S81. Full HMBC spectrum of **7a-F** (500 MHz, 125 MHz, $CDCl_3$, 298 K).

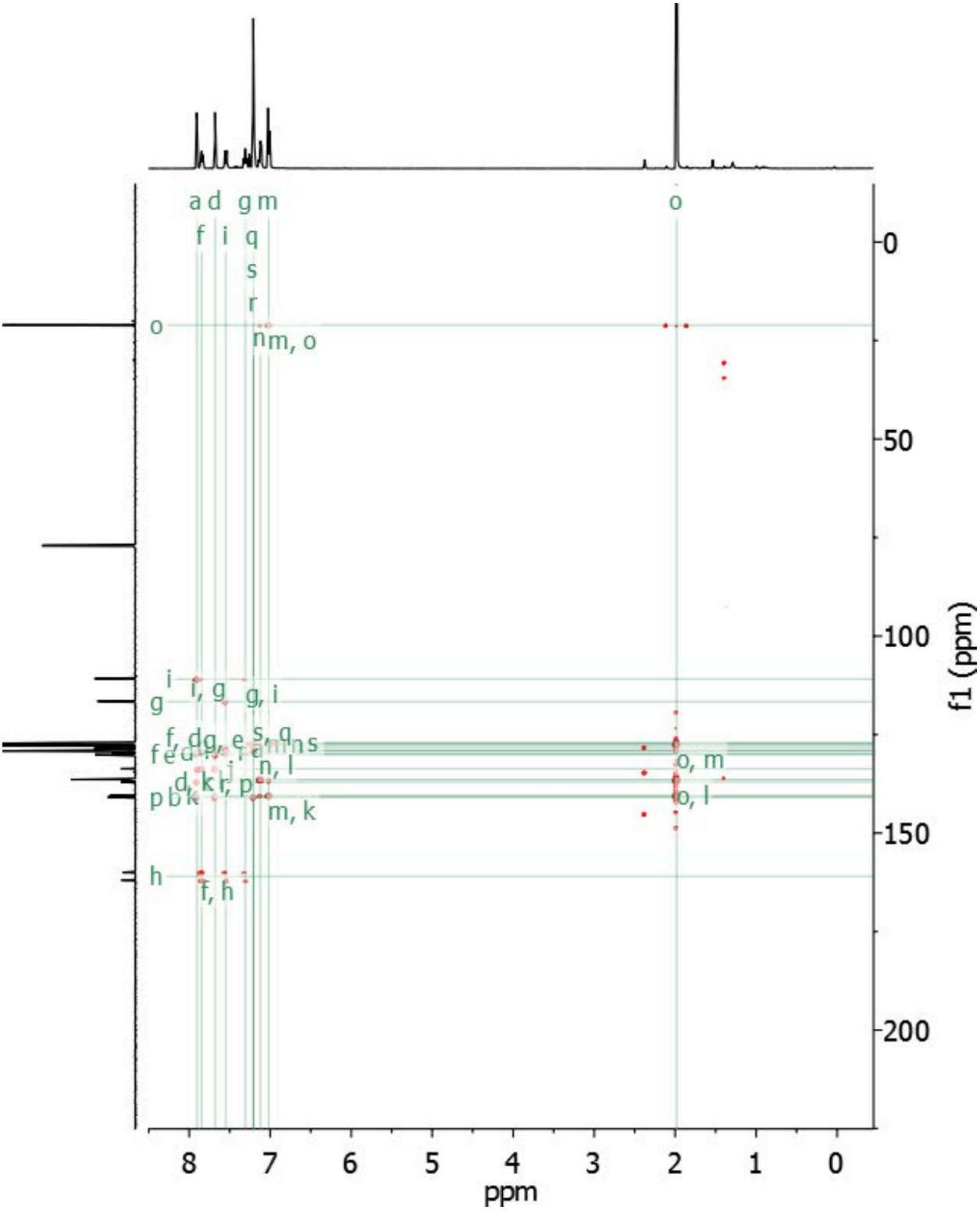
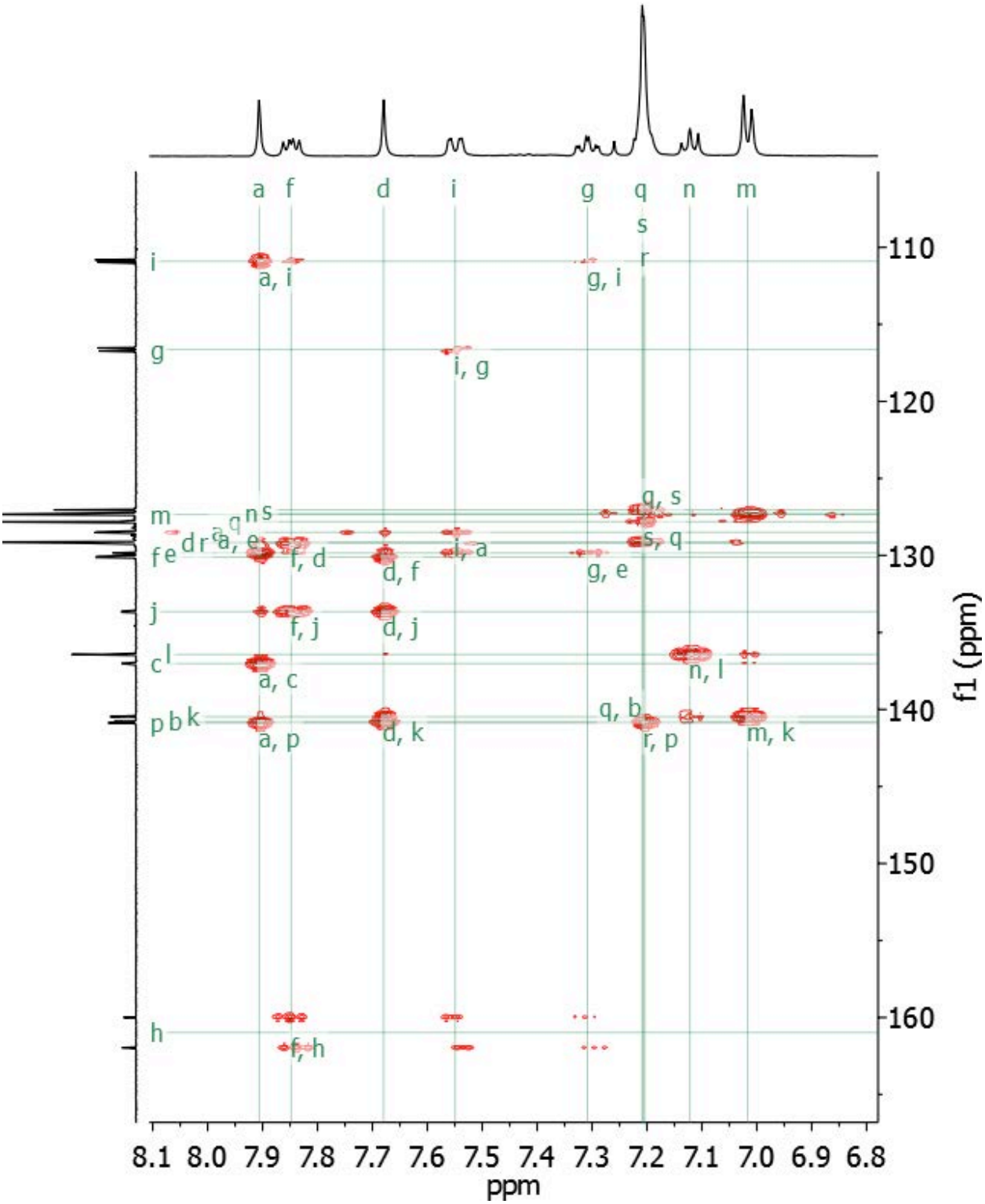


Figure S82. Partial HMBC spectrum of **7a-F** showing the aromatic region (500 MHz, 125 MHz, $CDCl_3$, 298 K).



Peak assignments for compounds **9a-F** (green) and **9b-F** (blue):

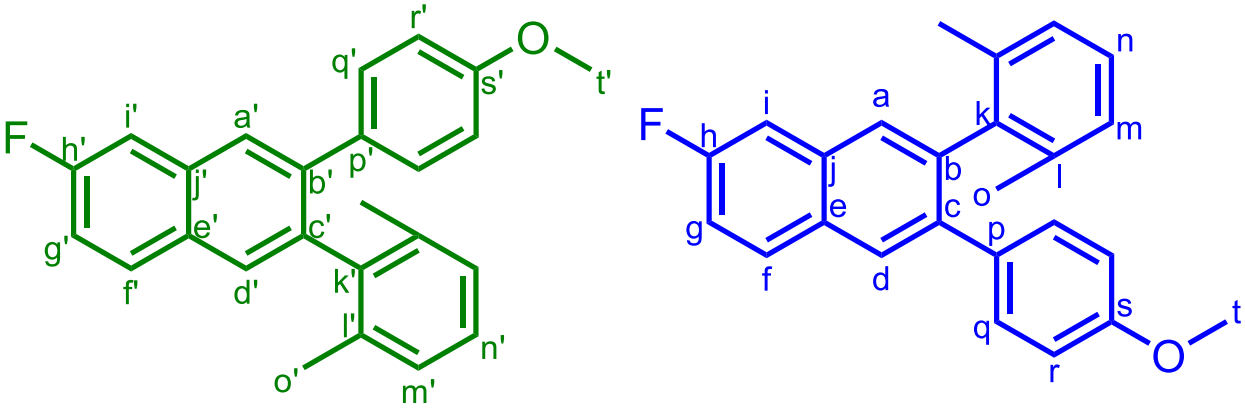


Figure S83. Full COSY spectrum of **9a-F** (green) and **9b-F** (blue) (500 MHz, 500 MHz, $CDCl_3$, 298 K).

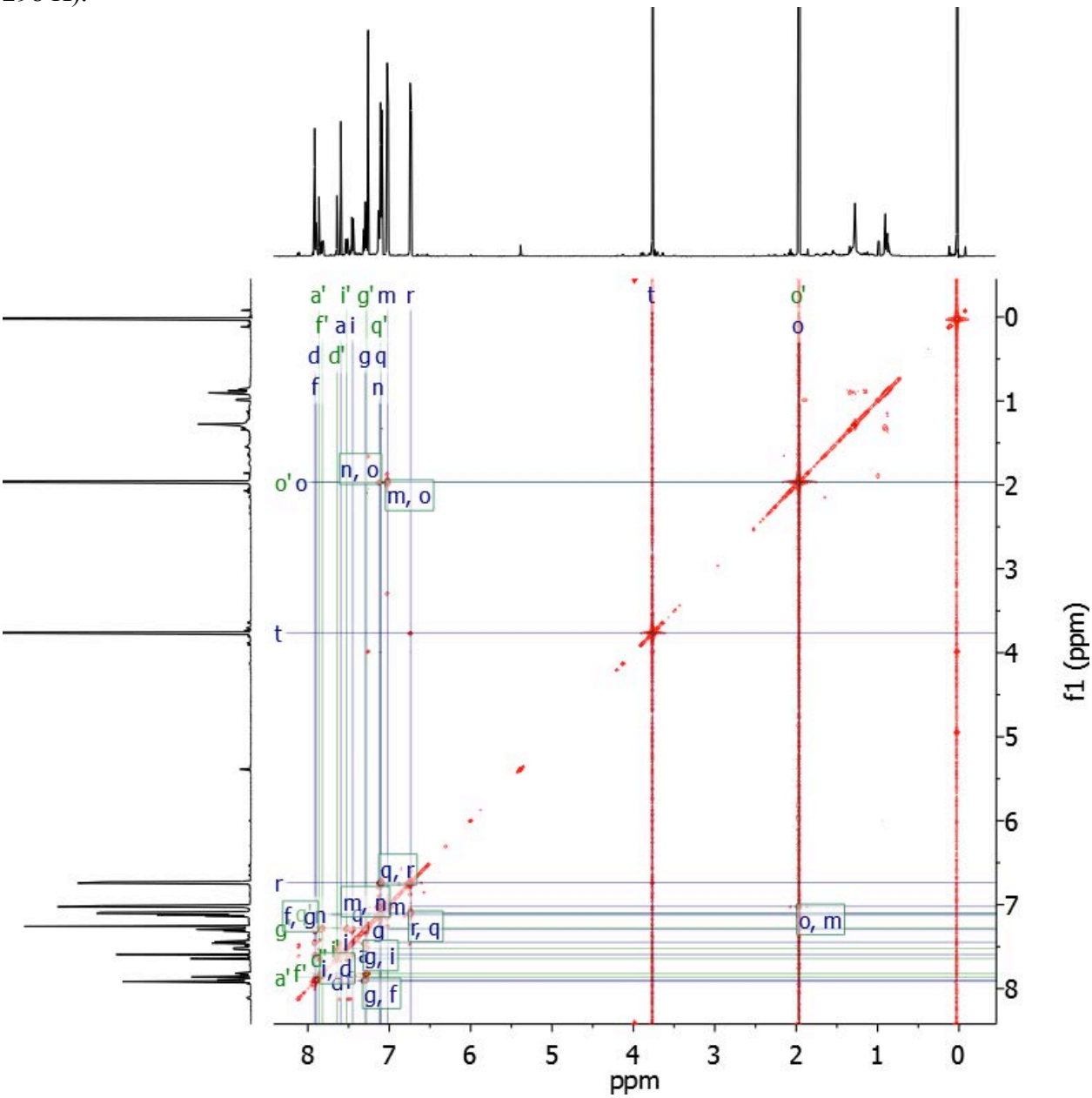


Figure S84. Partial COSY spectrum of **9a-F** (green) and **9b-F** (blue) showing the aromatic region (600 MHz, 600 MHz, $CDCl_3$, 298 K).

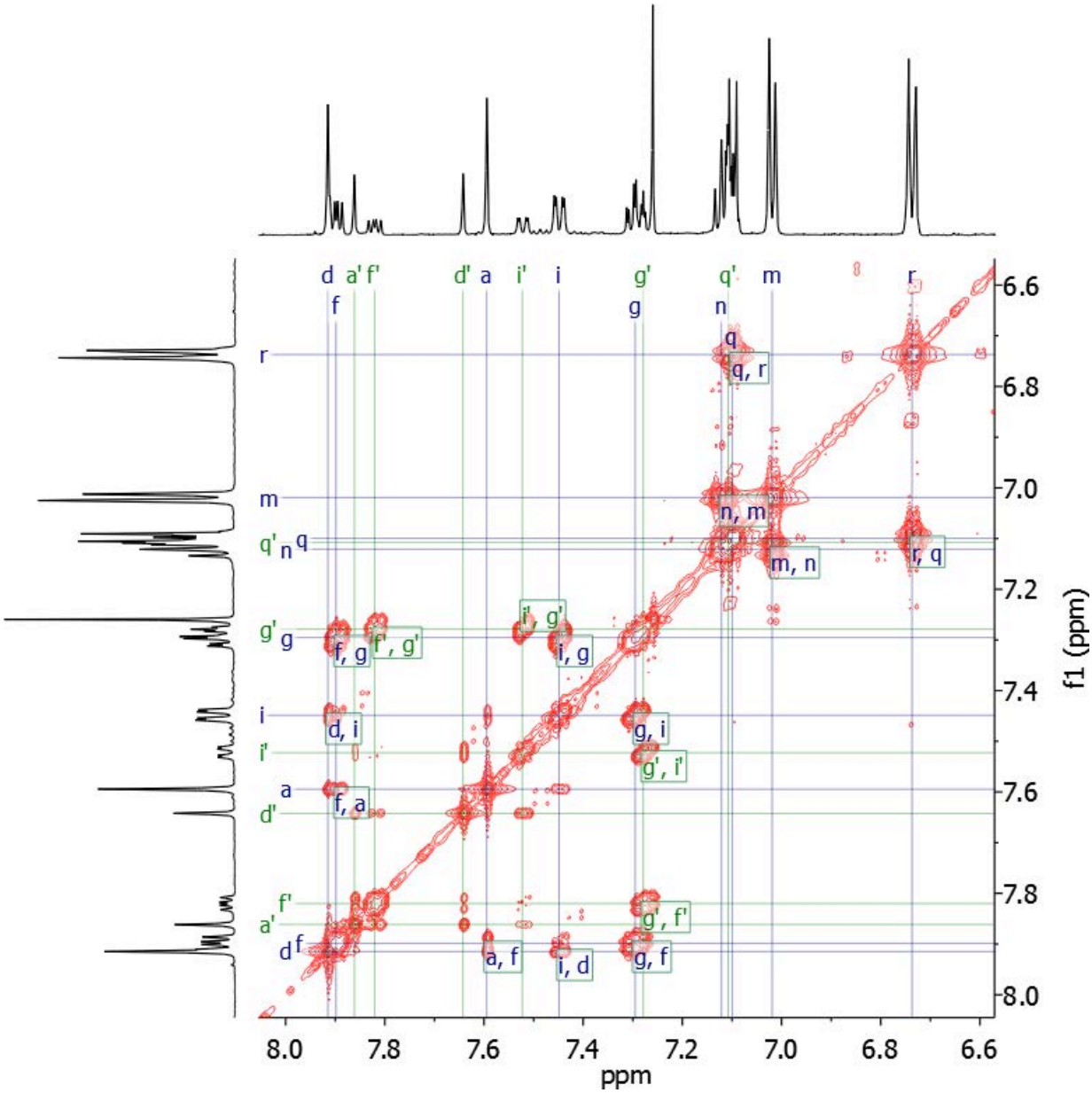


Figure S85. Full ROESY spectrum of **9a-F** (green) and **9b-F** (blue) (600 MHz, 600 MHz, $CDCl_3$, 298 K).

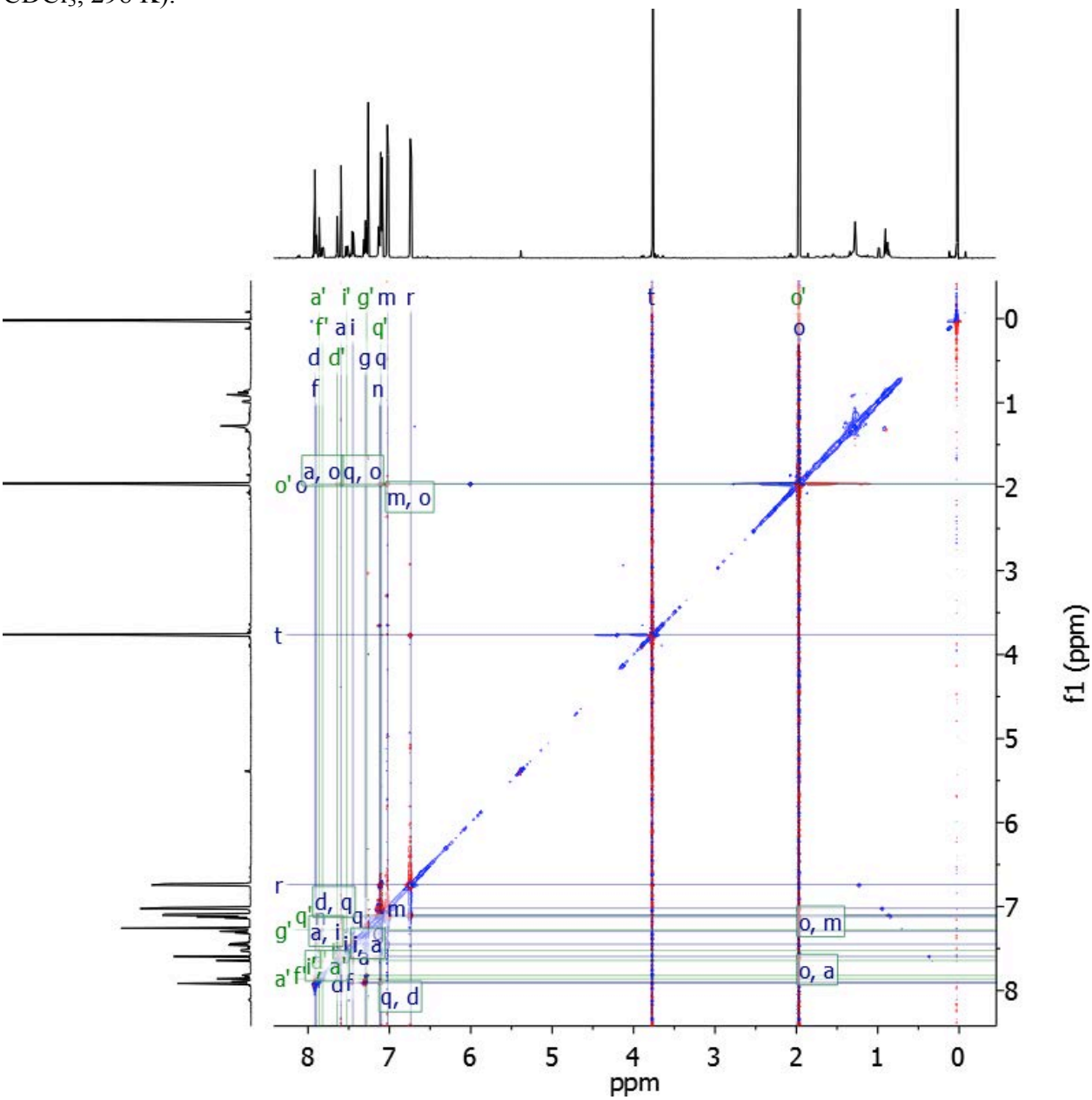


Figure S86. Partial ROESY spectrum of **9a-F** (green) and **9b-F** (blue) showing the aromatic region (600 MHz, 600 MHz, $CDCl_3$, 298 K).

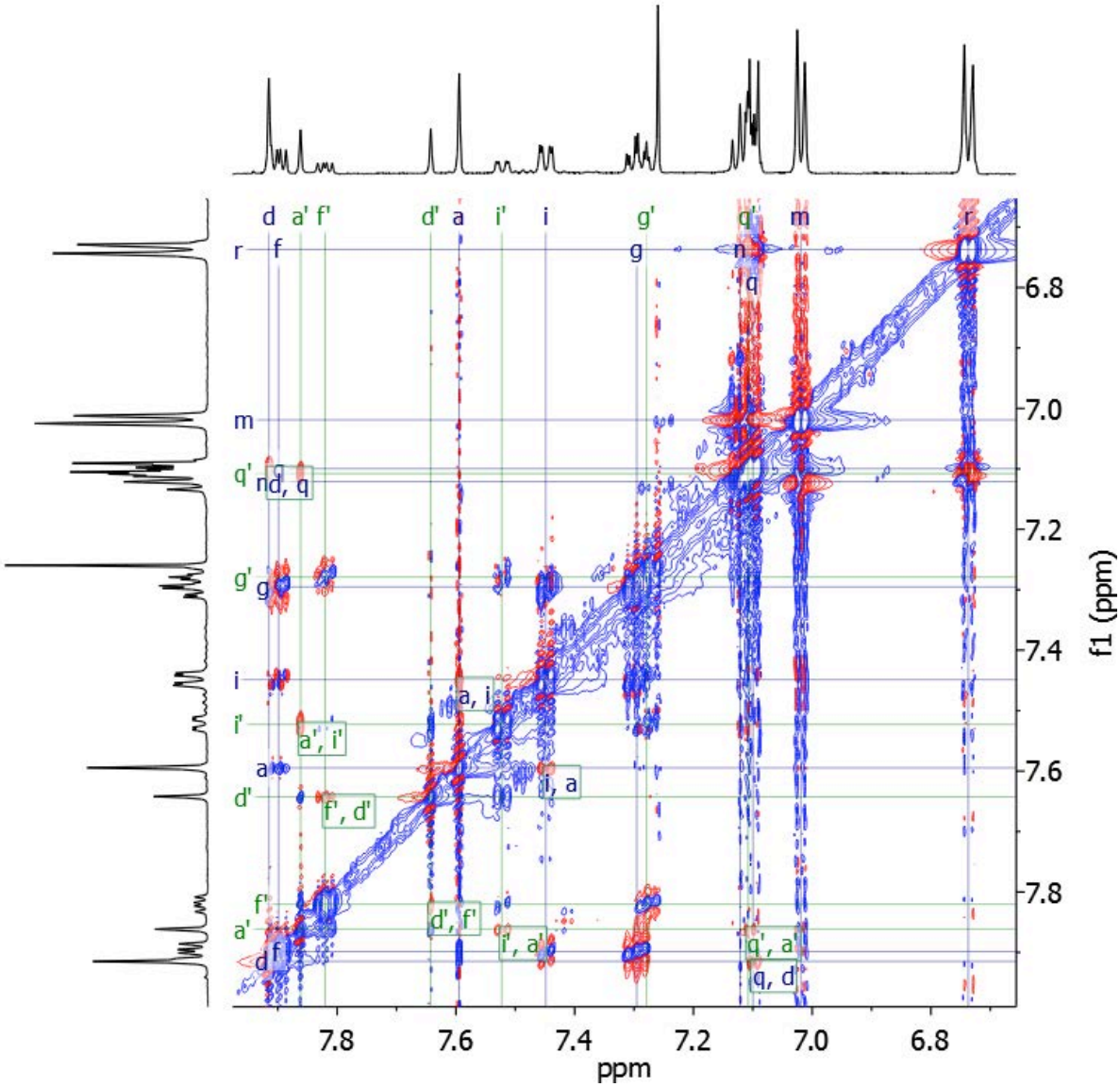


Figure S87. Full HSQC spectrum of **9a-F** (green) and **9b-F** (blue) (600 MHz, 150 MHz, $CDCl_3$, 298 K).

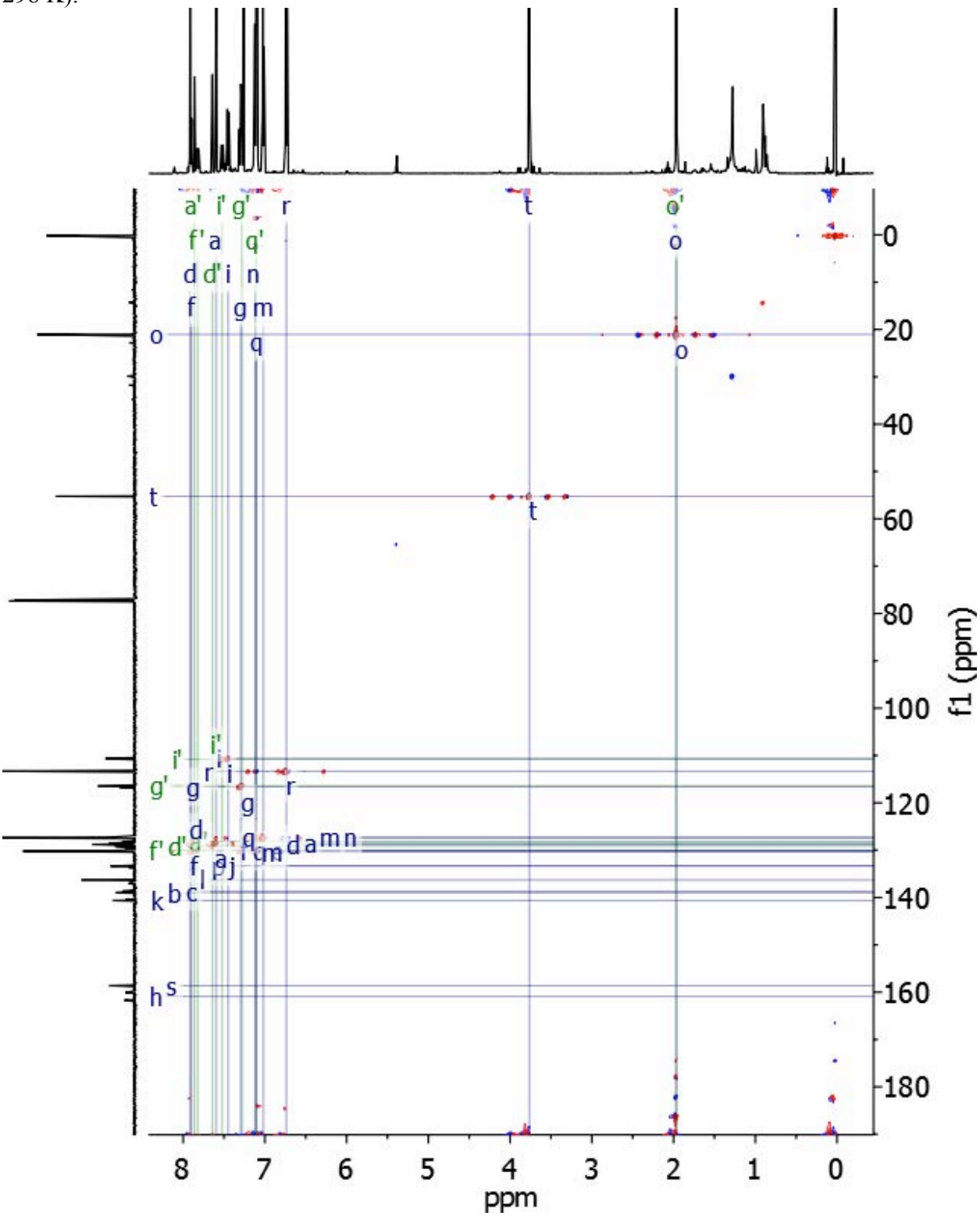


Figure S88. Partial HSQC spectrum of **9a-F** (green) and **9b-F** (blue) showing the aromatic region (600 MHz, 150 MHz, $CDCl_3$, 298 K).

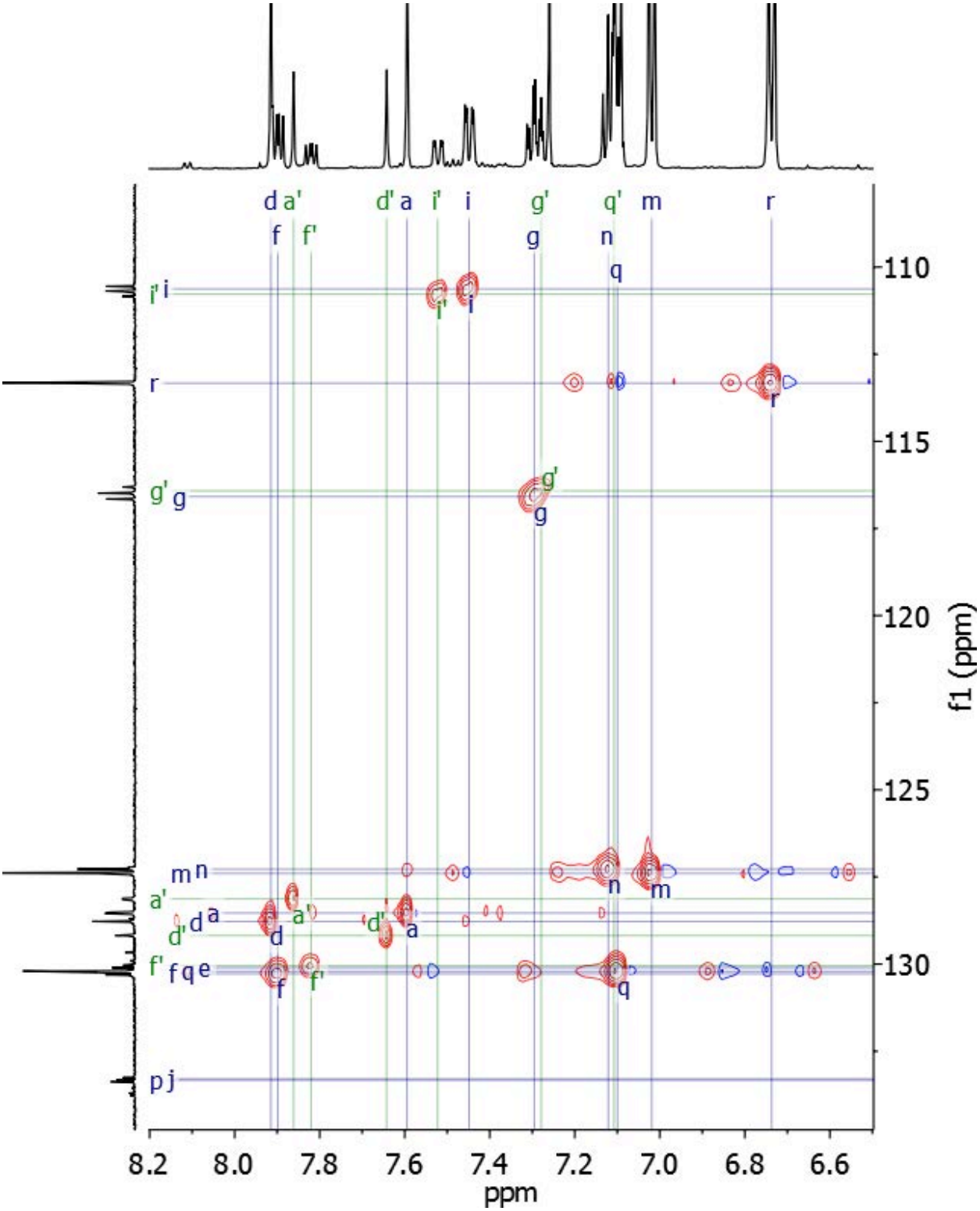


Figure S89. Full HMBC spectrum of **9a-F** (green) and **9b-F** (blue) (600 MHz, 150 MHz, $CDCl_3$, 298 K).

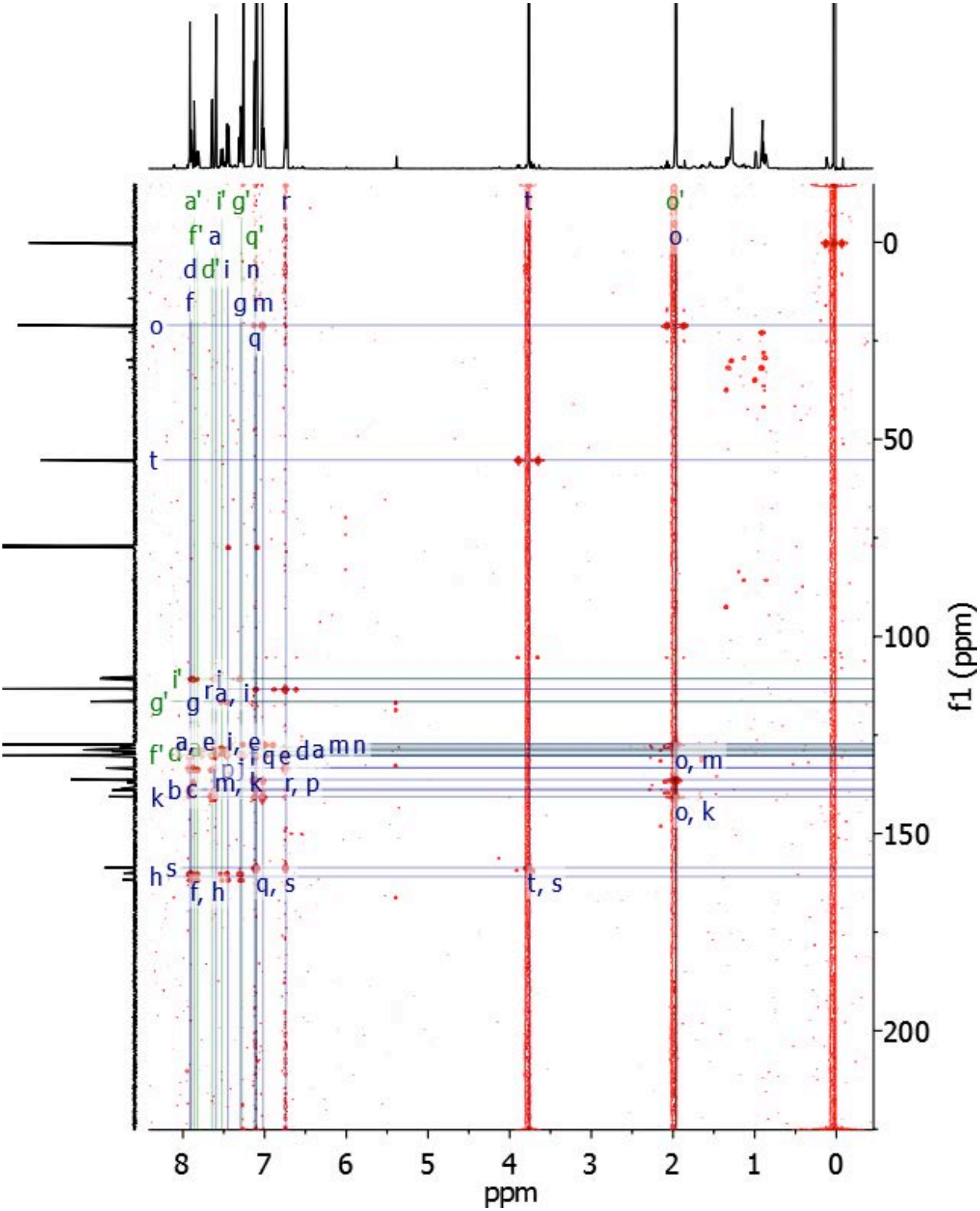
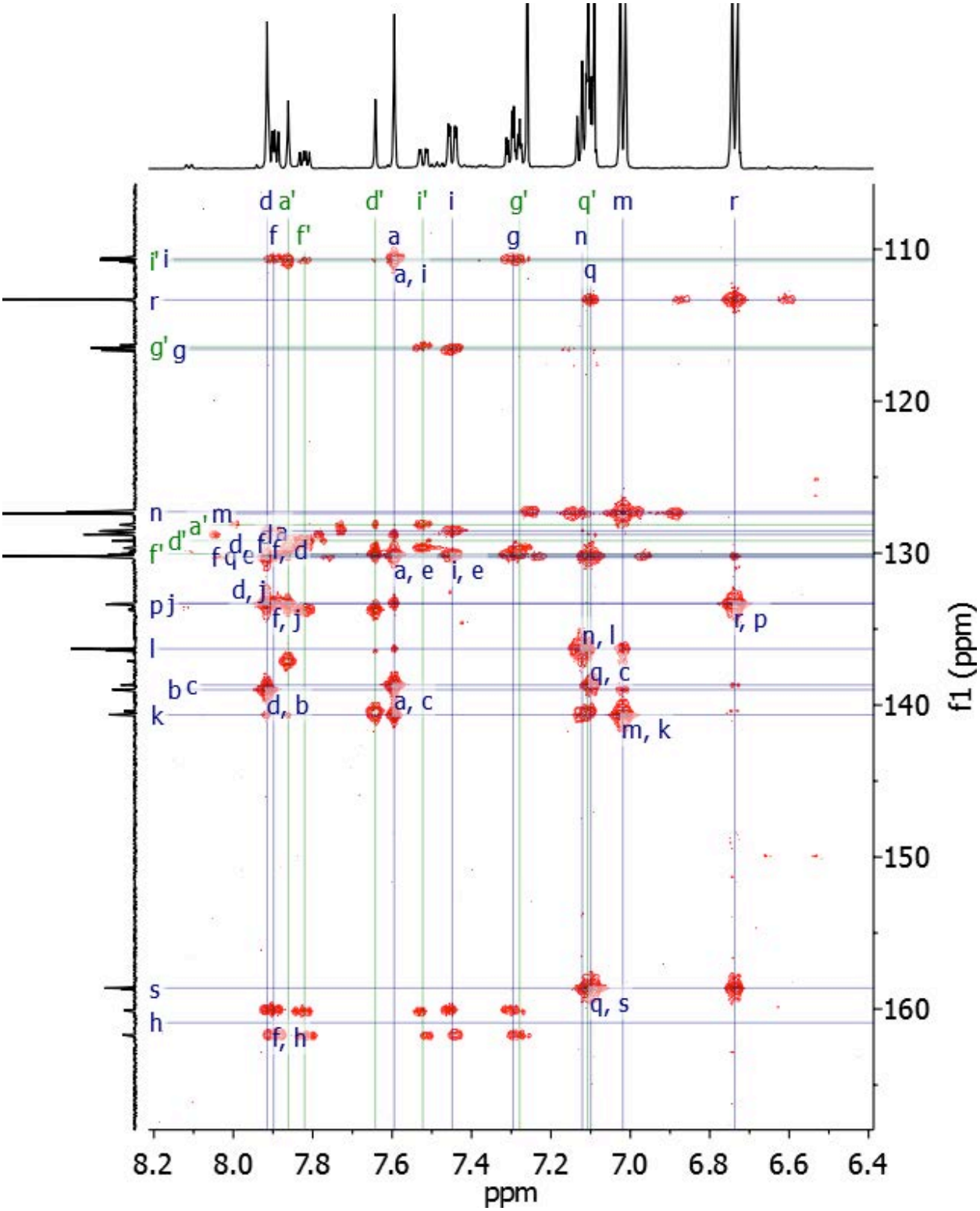
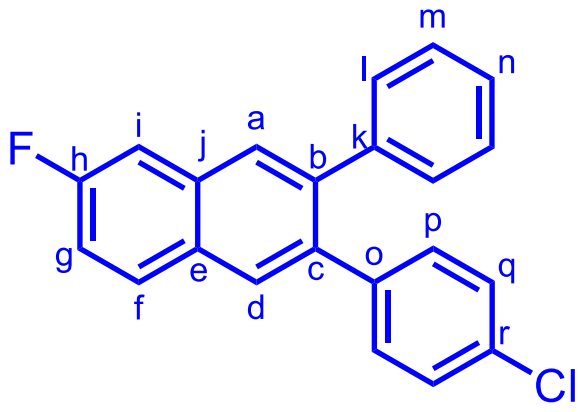


Figure S90. Partial HMBC spectrum of **9a-F** (green) and **9b-F** (blue) showing the aromatic region (600 MHz, 150 MHz, $CDCl_3$, 298 K).



Peak assignments for compounds **11a-F** (blue) and **11b-F** (green):



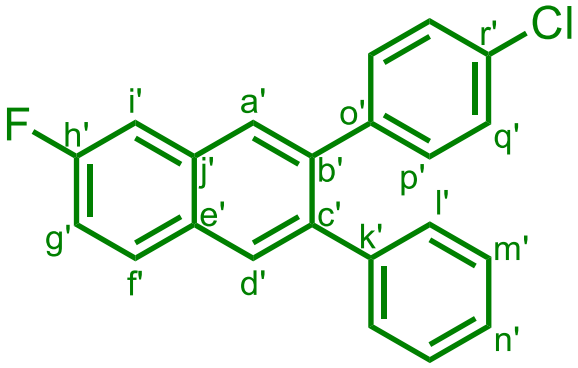


Figure S91. COSY spectrum of **11a-F** (blue) and **11b-F** (green) (600 MHz, 600 MHz, $CDCl_3$, 298 K).

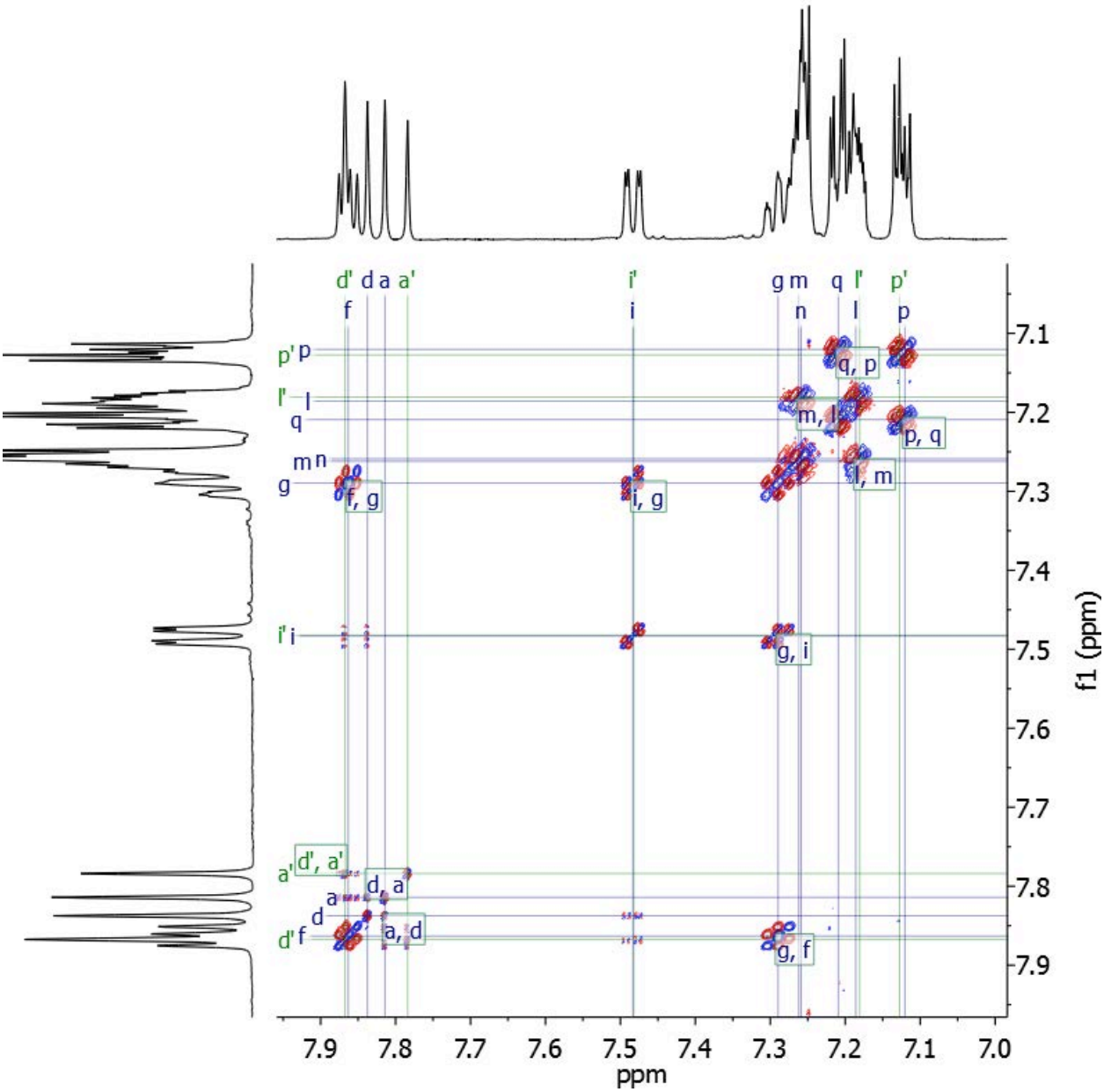


Figure S92. ROESY spectrum of **11a-F** (blue) and **11b-F** (green) (600 MHz, 600 MHz, $CDCl_3$, 298 K).

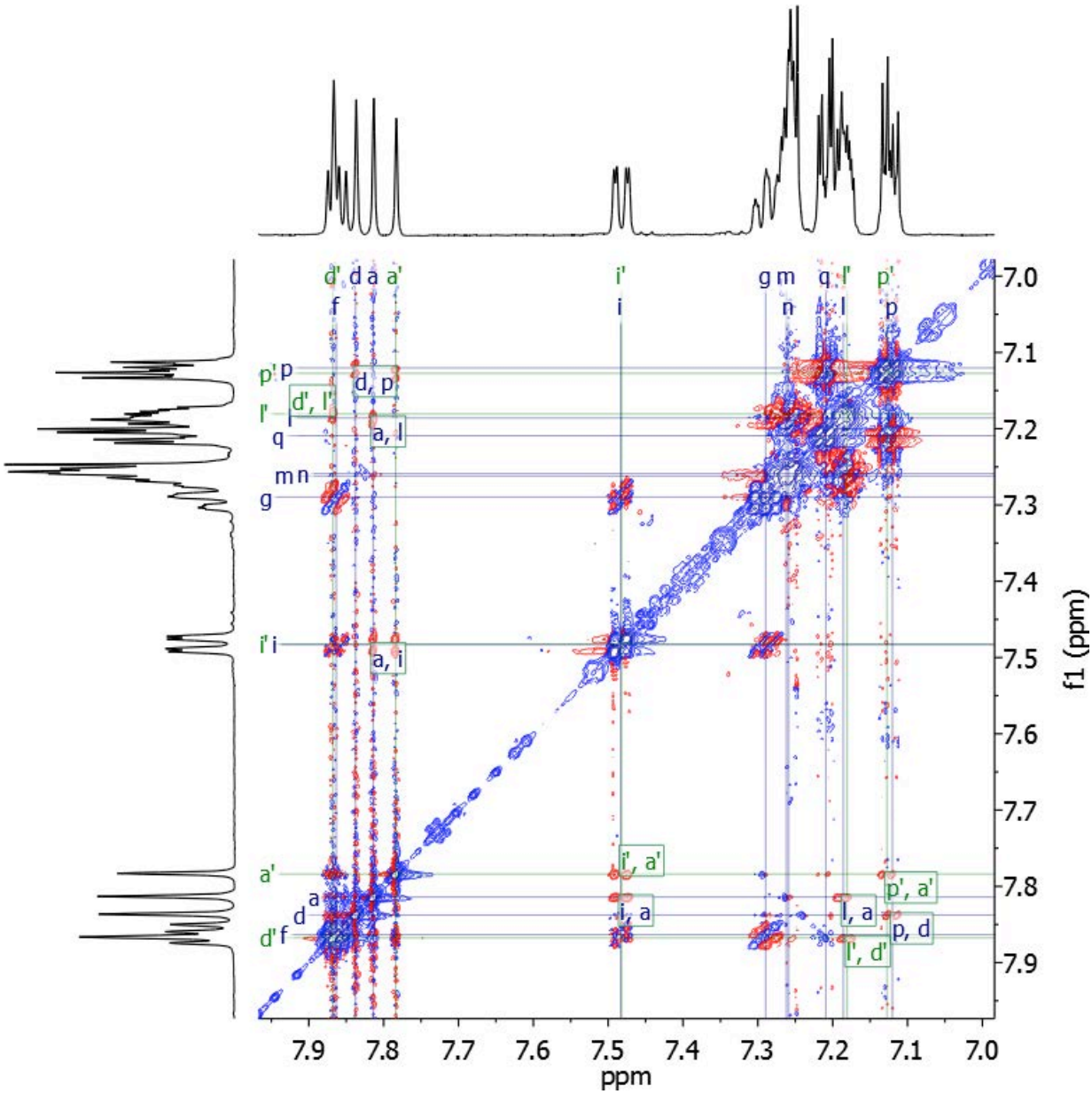


Figure S93. HSQC spectrum of **11a-F** (blue) and **11b-F** (green) (600 MHz, 150 MHz, $CDCl_3$, 298 K).

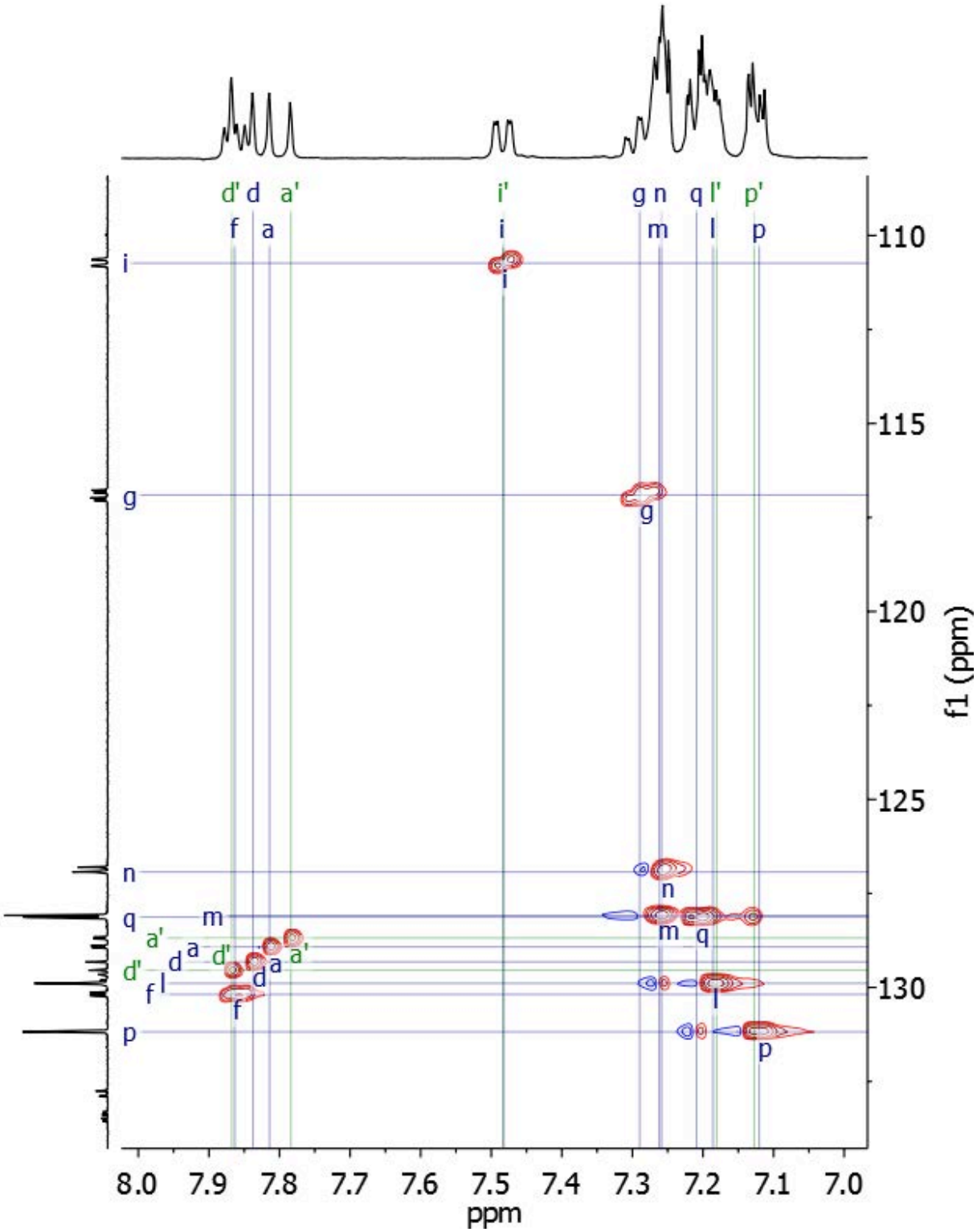
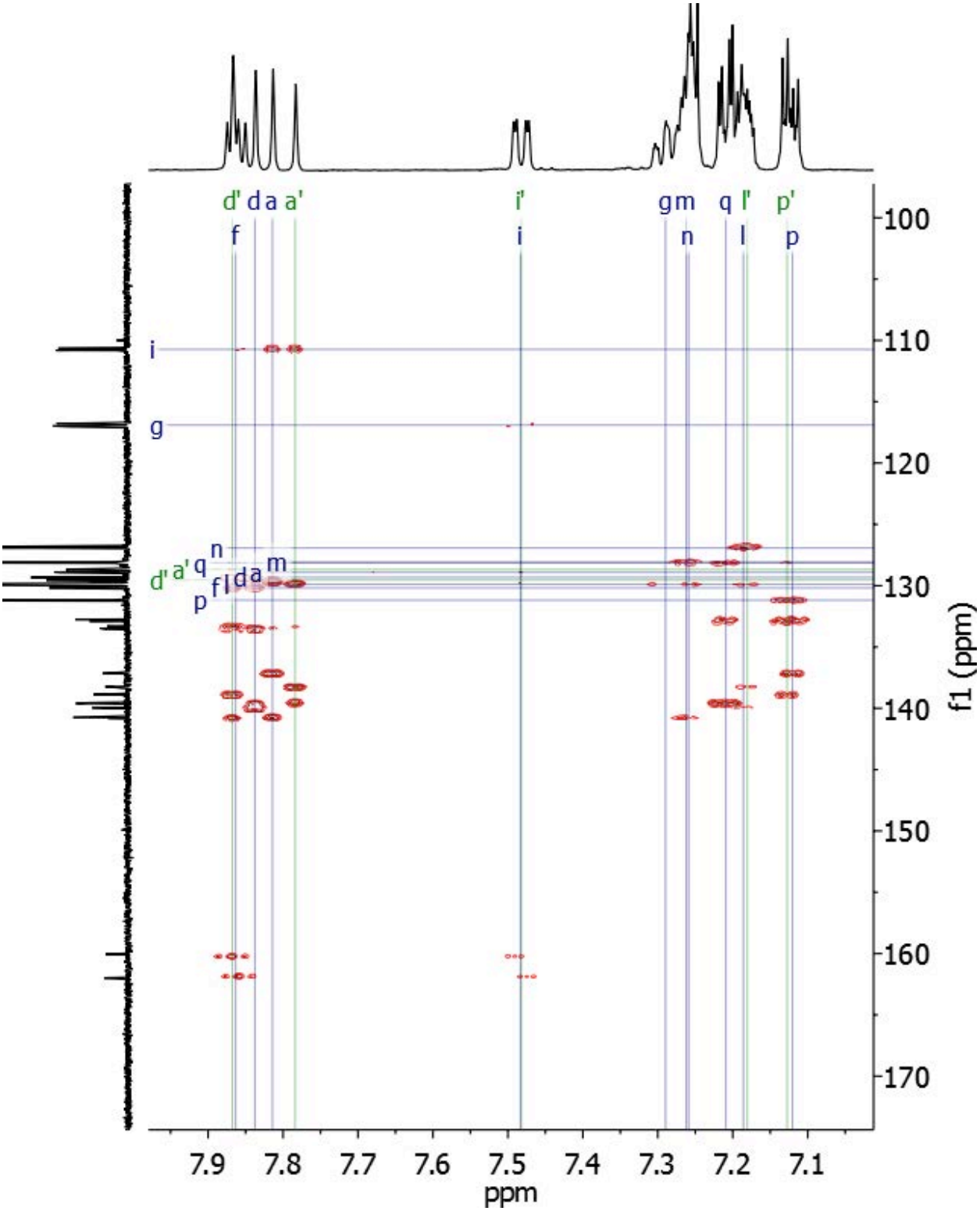


Figure S94. HMBC spectrum of **11a-F** (blue) and **11b-F** (green) (600 MHz, 150 MHz, $CDCl_3$, 298 K).



Peak assignments for compound **13-F_2:**

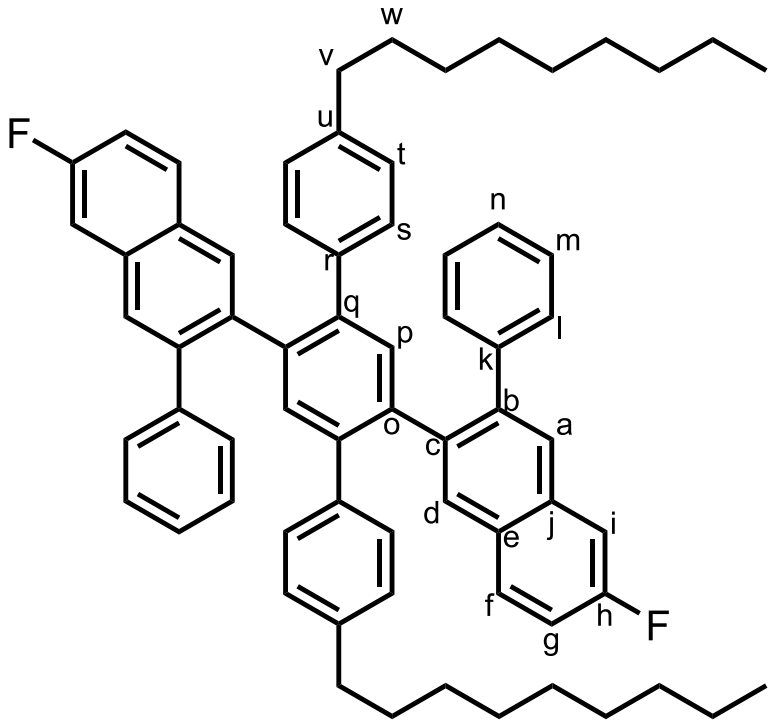


Figure S95. Full COSY spectrum of **13-F$_2$** (500 MHz, 500 MHz, $CDCl_3$, 298 K).

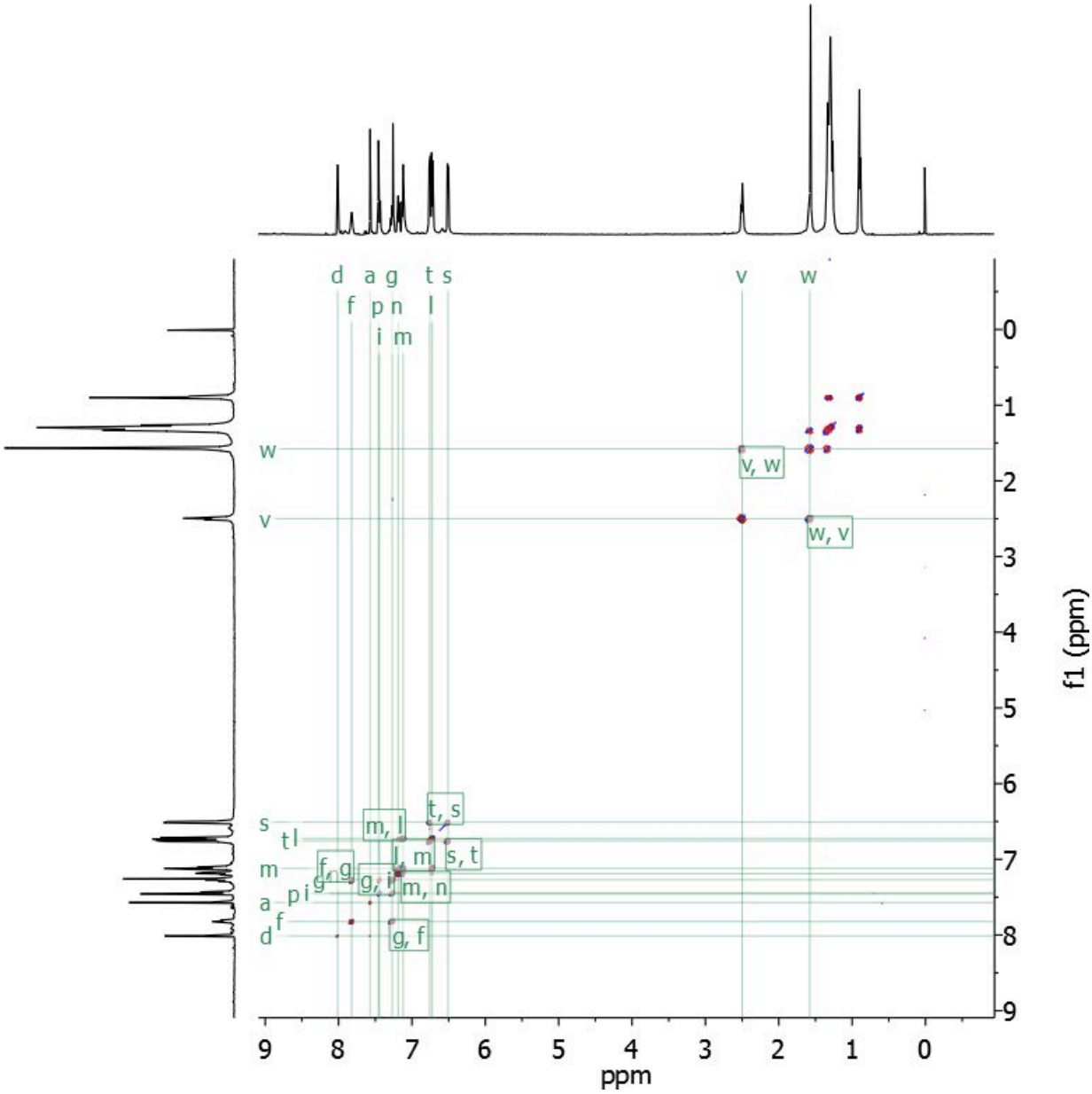


Figure S96. Partial COSY spectrum of **13-F$_2$** showing the aromatic region (500 MHz, 500 MHz, $CDCl_3$, 298 K).

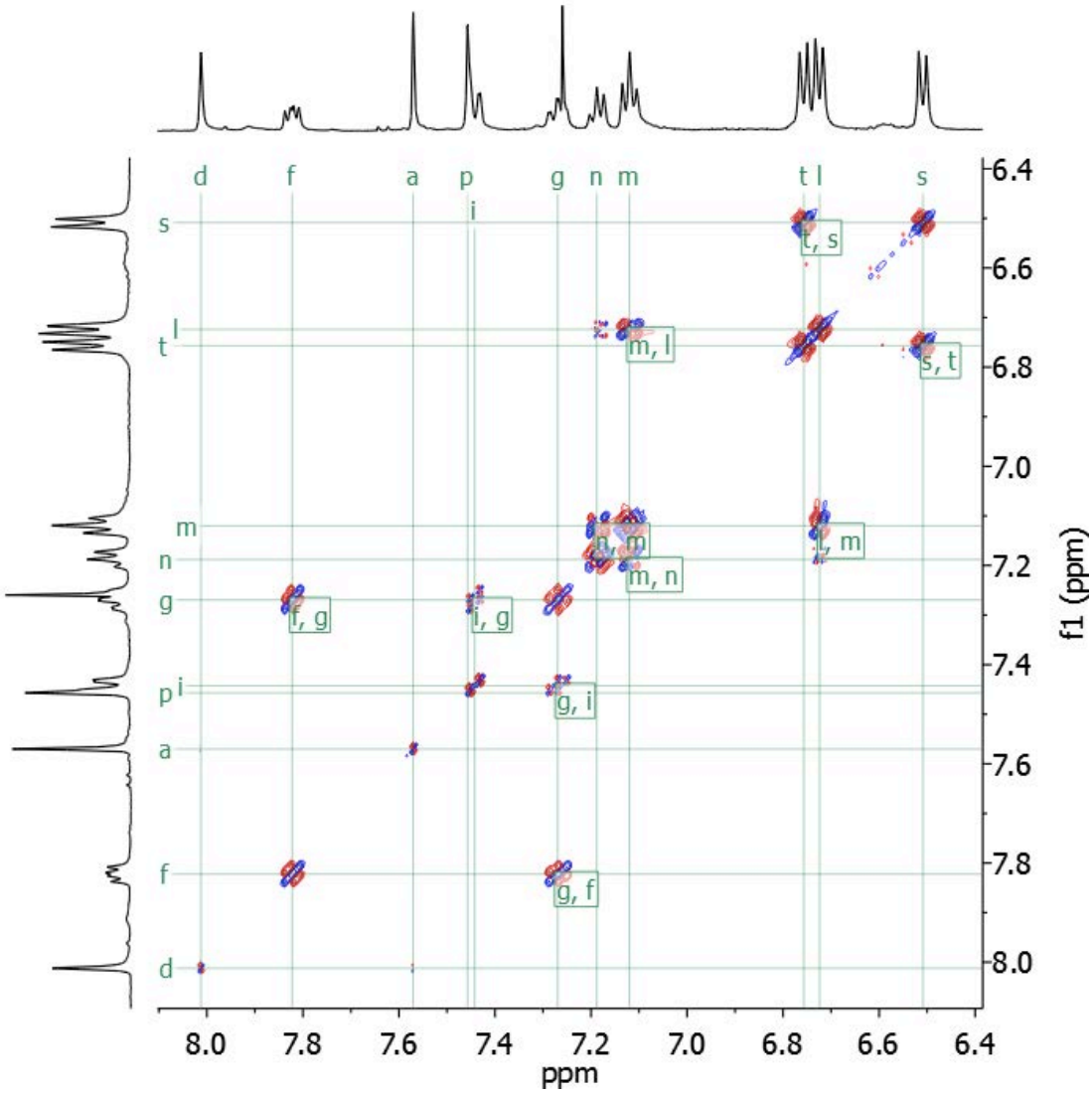


Figure S97. Full ROESY spectrum of **13-F$_2$** (500 MHz, 500 MHz, $CDCl_3$, 298 K).

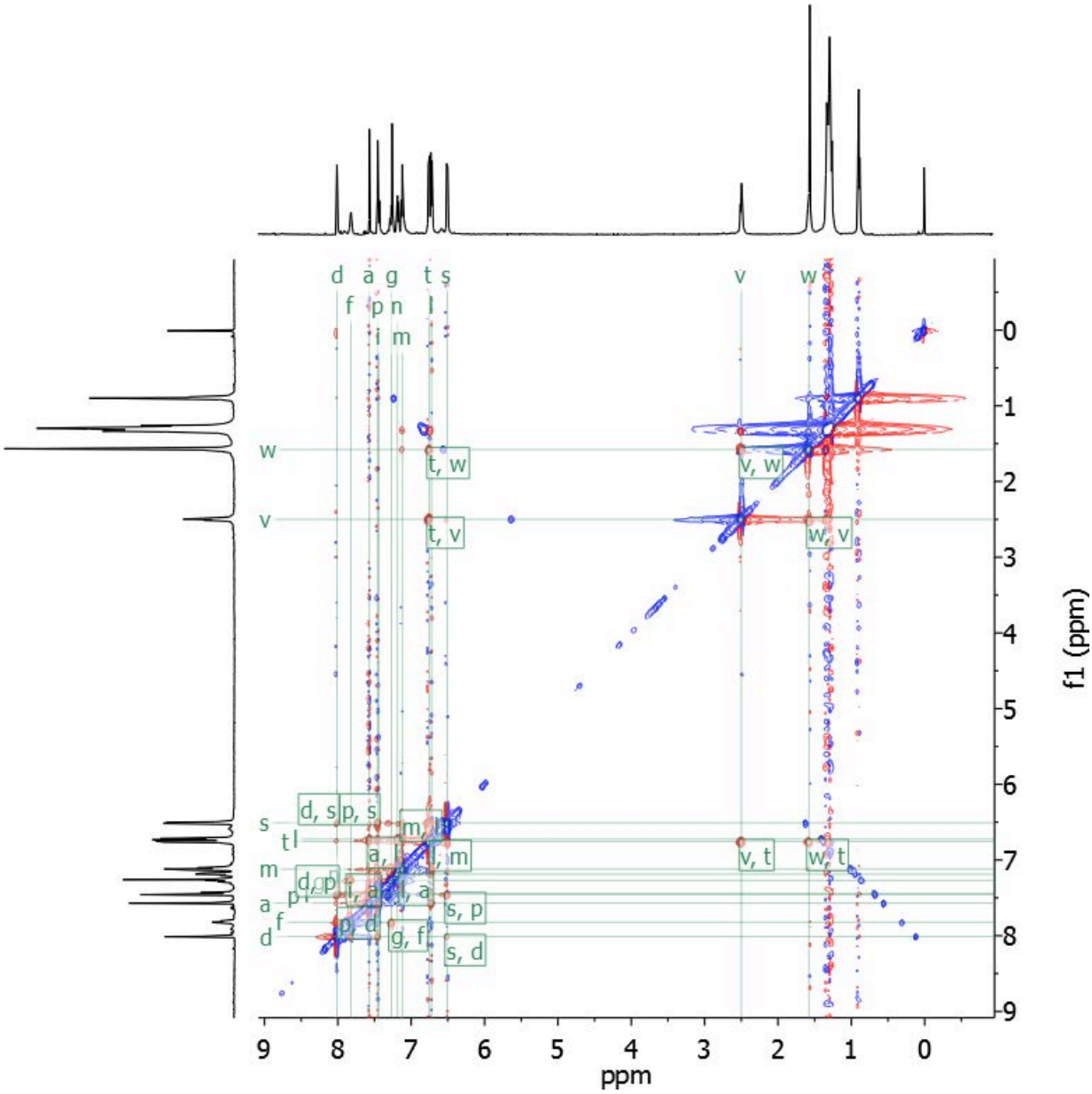


Figure S98. Partial ROESY spectrum of **13-F$_2$** showing the aromatic region (500 MHz, 500 MHz, $CDCl_3$, 298 K).

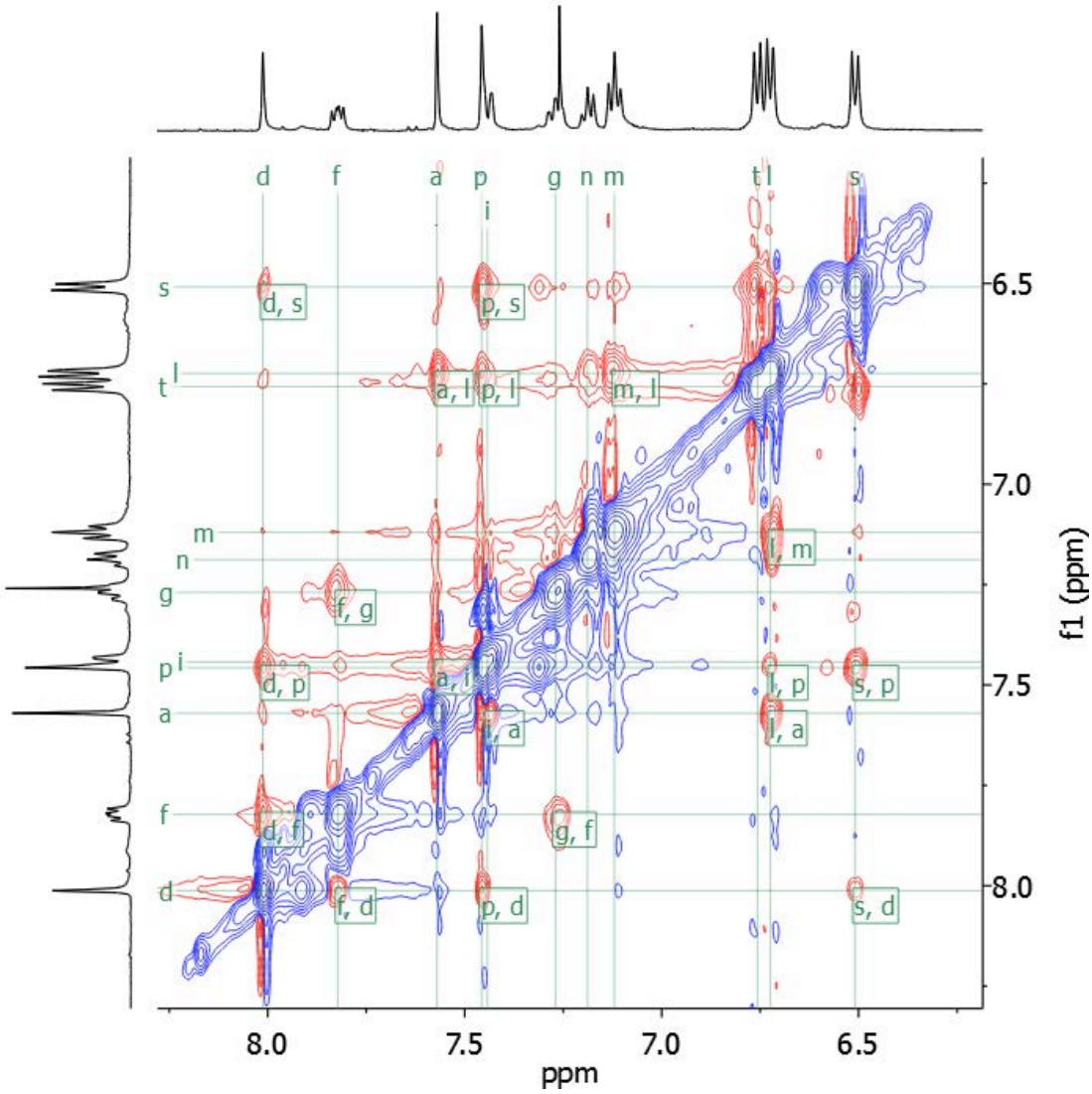


Figure S99. Full HSQC spectrum of **13-F$_2$** (500 MHz, 125 MHz, $CDCl_3$, 298 K).

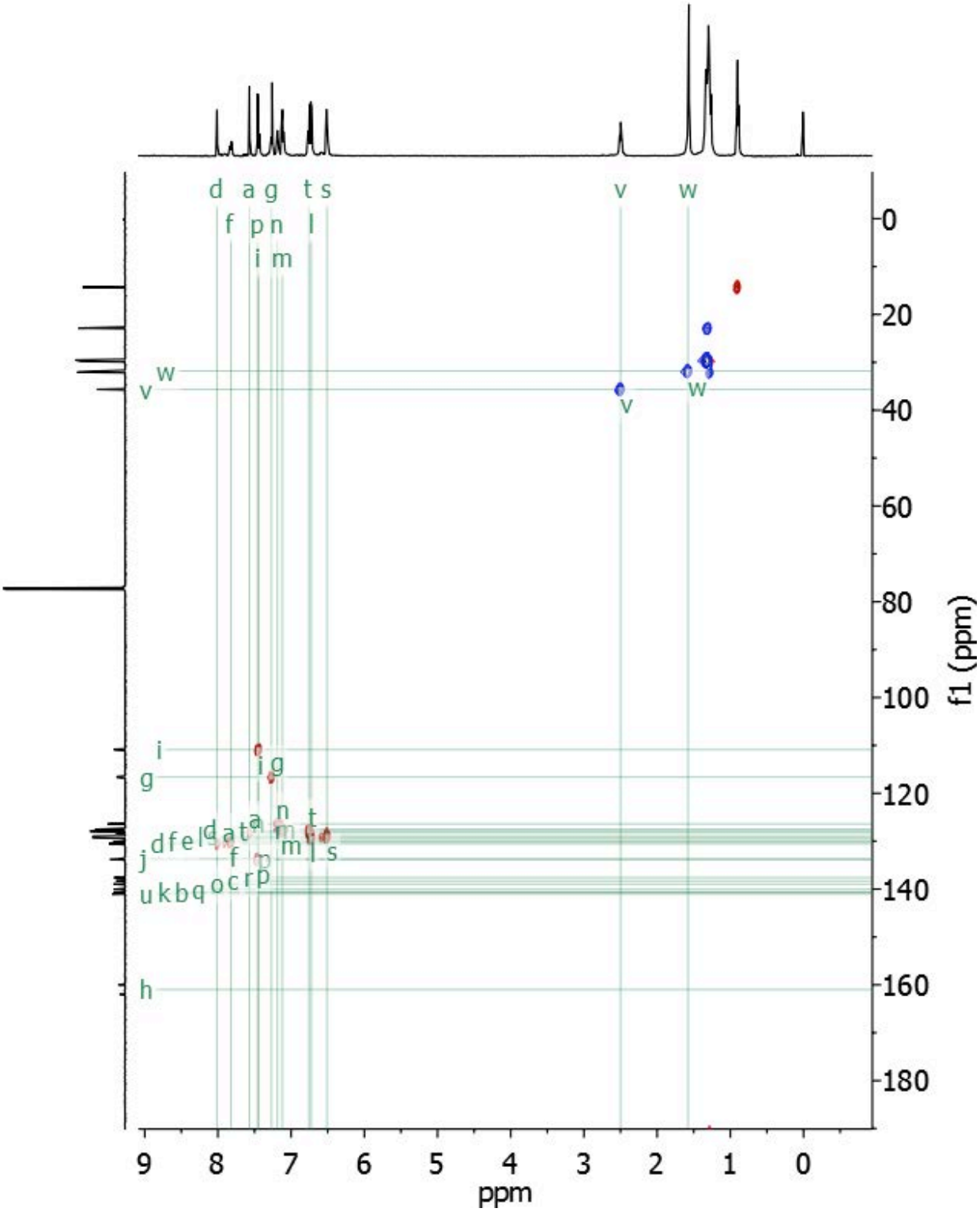


Figure S100. Partial HSQC spectrum of **13-F$_2$** showing the aromatic region (500 MHz, 125 MHz, $CDCl_3$, 298 K).

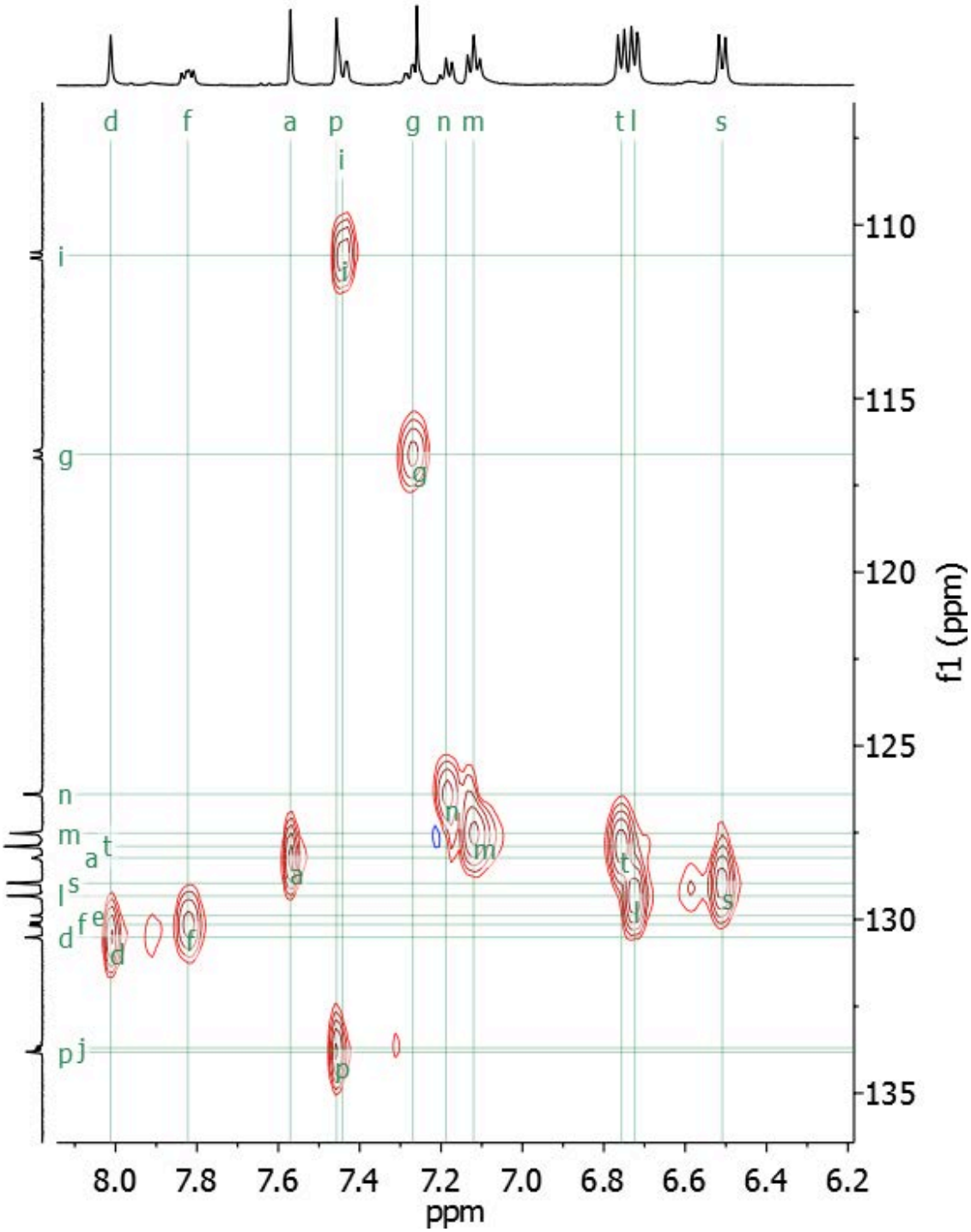


Figure S101. Full HMBC spectrum of **13-F$_2$** (500 MHz, 125 MHz, $CDCl_3$, 298 K).

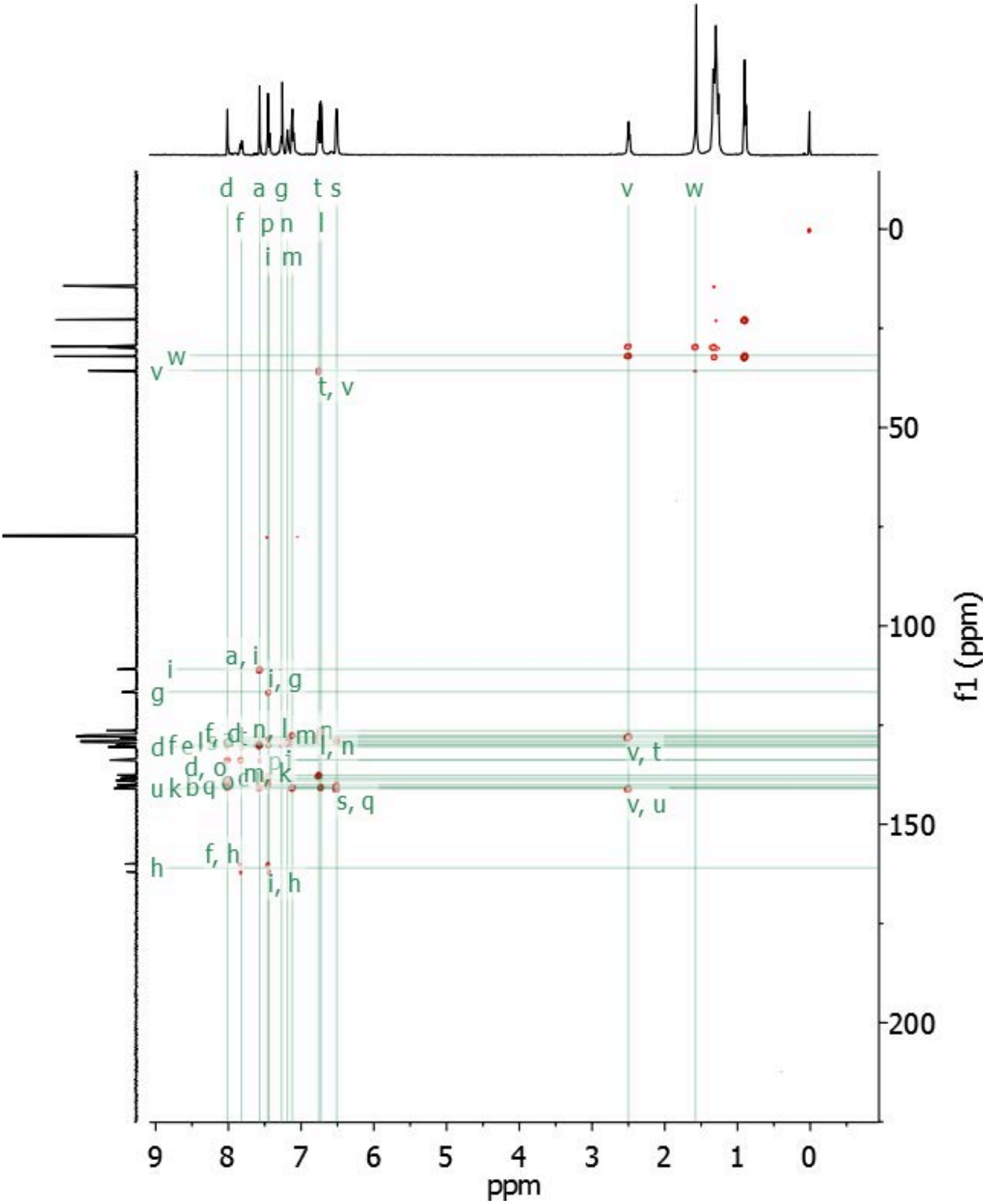
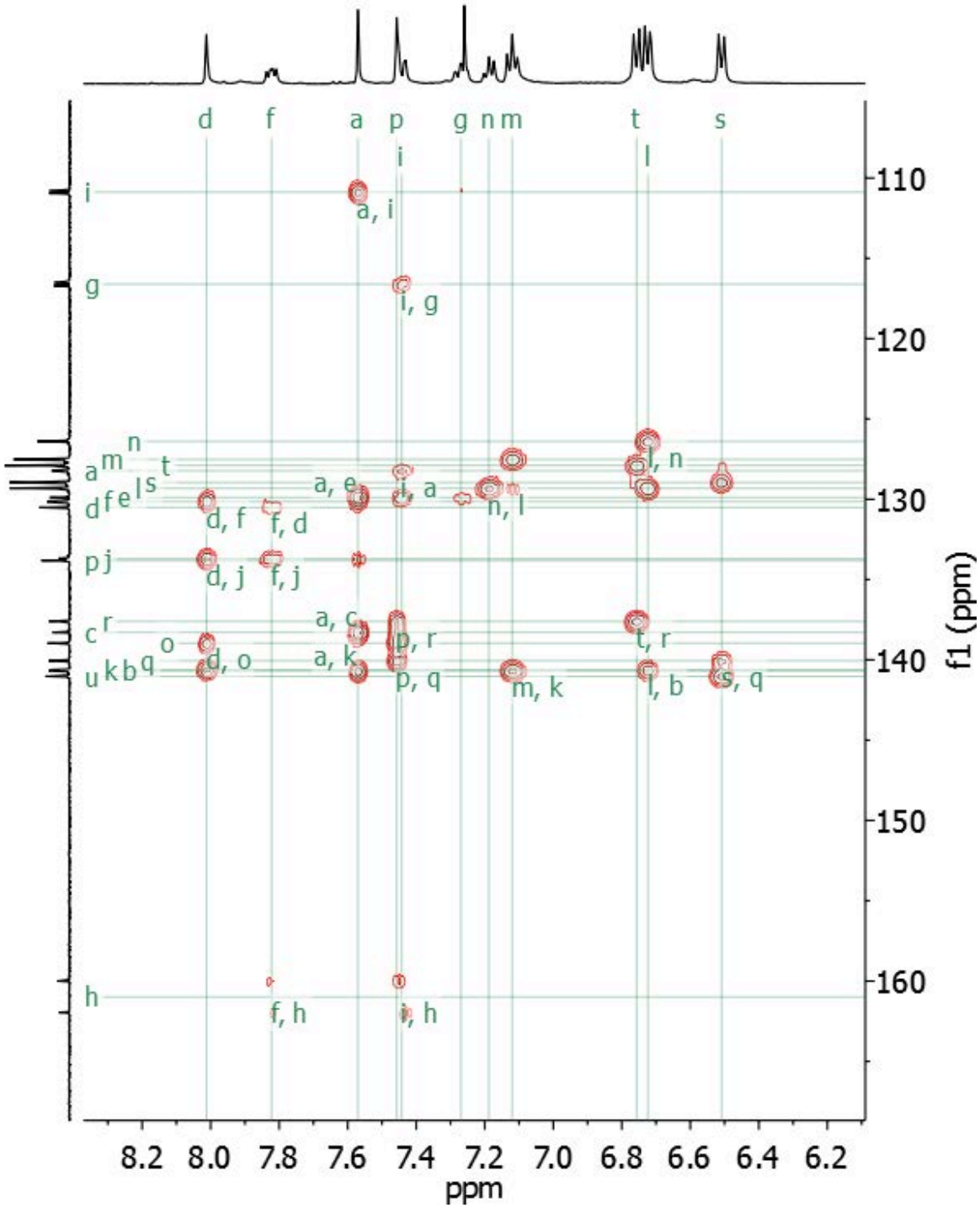


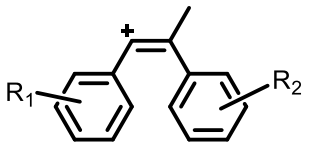
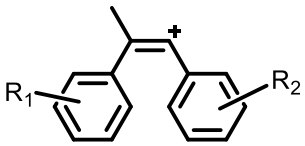
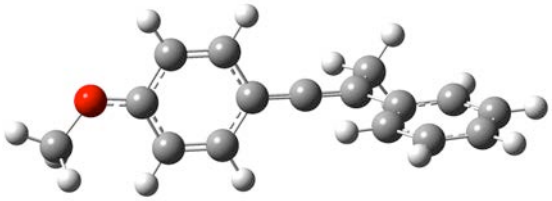
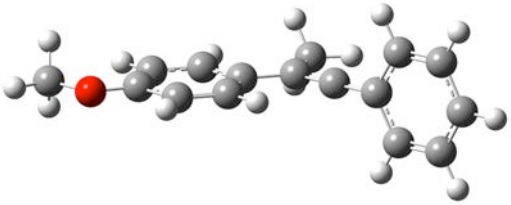
Figure S102. Partial HMBC spectrum of **13-F$_2$** showing the aromatic region (500 MHz, 125 MHz, $CDCl_3$, 298 K).

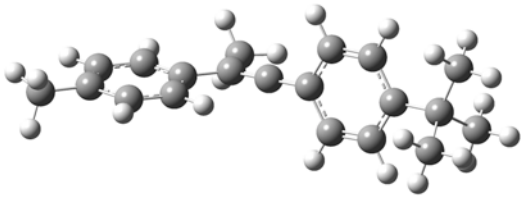
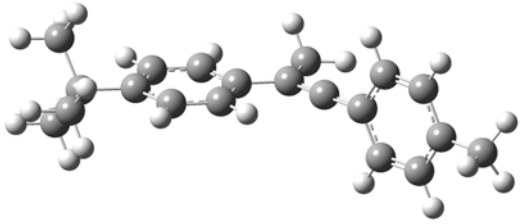
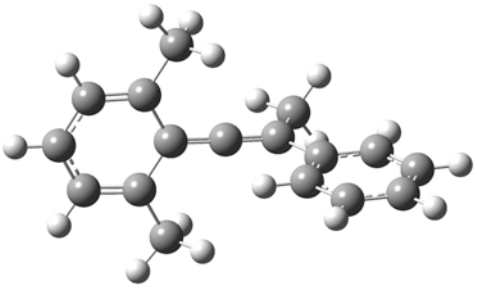
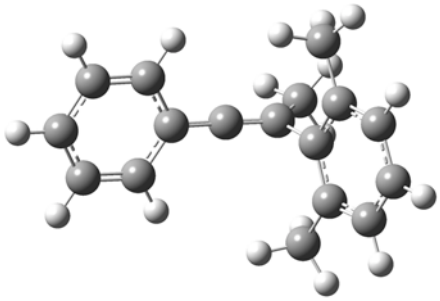
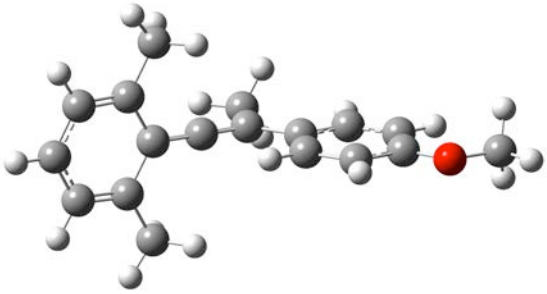
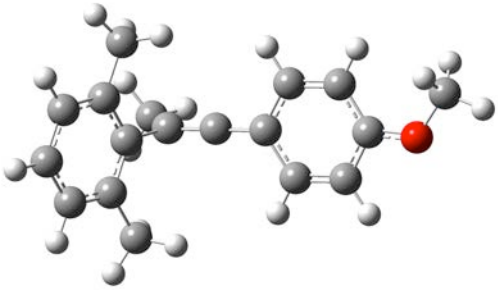


E. DFT Calculations

DFT calculations were performed using the Gaussian 09 program, Revision A.02.[3] Geometries were optimized in the gas phase using the B3LYP functional and 6-31g(d) basis set on all atoms and confirmed as stationary states using frequency calculations. We calculated the relative energies of carbocations formed at the two alkyne carbons of each substrate. These calculations indicate the relative abilities of each aromatic ring to stabilize a developing positive charge, which are predictive of the observed regioselectivity. For each pair of regioisomers, the less stable carbocation's energy was set to 0.0 kcal/mol and the more stable regioisomer is provided relative to this value.

Table S1. Calculated relative energies of carbocations **3a′- 13a′** and **3b′- 13b′**

Isomer 1	**Isomer 2**
	
 R_1 = *p*-MeO, R_2 = H -9.2 kcal/mol **3a′**	 R_1 = *p*-MeO, R_2 = H 0.0 kcal/mol **3b′**

 R_1 = *p*-(*t*Bu), R_2 = *p*-Me -1.0 kcal/mol **5a′**	 R_1 = *p*-(*t*Bu), R_2 = *p*-Me 0.0 kcal/mol **5b′**
 R_1 = 2,6-$(Me)_2$, R_2 = H -6.7 kcal/mol **7a′**	 R_1 = 2,6-$(Me)_2$, R_2 = H 0.0 kcal/mol **7b′**
 R_1 = 2,6-$(Me)_2$, R_2 = *p*-OMe 0.0 kcal/mol **8a′**	 R_1 = 2,6-$(Me)_2$, R_2 = *p*-OMe -1.3 kcal/mol **8b′**

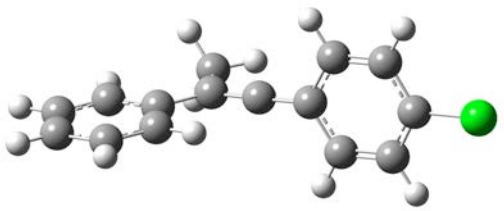
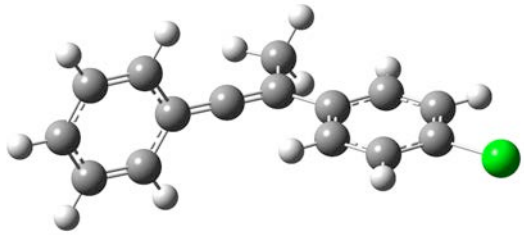
 R_1 = *p*-Cl, R_2 = H -1.1 kcal/mol **10a′**	 R_1 = *p*-Cl, R_2 = H 0.0 kcal/mol **10b′**

Table S2. Cartesian coordinates of DFT computed geometries

3a′

C	4.05633100	0.65432000	-0.08954300
C	2.73473100	0.18476800	-0.05090400
C	2.50306300	-1.20090600	0.02665800
C	3.56796900	-2.09233100	0.06618700
C	4.88271200	-1.61622100	0.02810100
C	5.12219500	-0.24482900	-0.04986200
H	4.26513400	1.71670100	-0.14928700
H	1.48467800	-1.58060100	0.05306000
H	3.37554900	-3.15931500	0.12538500
H	5.71454500	-2.31341600	0.05833700
H	6.14005300	0.13162100	-0.08018800
C	1.59964500	1.14318500	-0.09025700
C	0.34589200	0.78952500	-0.00994400
C	-0.96763700	0.47042100	0.07911000
C	-1.73523100	0.18255900	-1.10619200
C	-1.63567000	0.41113000	1.35886600
C	-3.06587800	-0.13596500	-1.02826600
H	-1.23658500	0.22374800	-2.06927800
C	-2.96100800	0.09370100	1.43634100
H	-1.06318300	0.62476000	2.25544600
C	-3.69743800	-0.18289600	0.24696700
H	-3.62826300	-0.34900800	-1.92902800

H	-3.48708500	0.04360100	2.38348000
C	1.85844500	2.64363400	-0.22987200
H	2.45293100	2.99150000	0.62072200
H	2.41642900	2.83291000	-1.15216200
H	0.92979700	3.21684500	-0.26056500
O	-4.96792800	-0.47458400	0.43363100
C	-5.84297100	-0.77330100	-0.67747900
H	-5.49230200	-1.66317400	-1.20723600
H	-6.81420600	-0.96522800	-0.22521100
H	-5.90497400	0.08495700	-1.35198900

3b′

C	3.37755100	-0.19101200	1.23977100
C	2.72317700	0.11729700	0.00060100
C	3.37593800	-0.19219600	-1.23914900
C	4.62530400	-0.78123400	-1.22856400
C	5.24463500	-1.07153500	-0.00048300
C	4.62689000	-0.78009500	1.22812300
H	2.87387100	0.04604000	2.17122000
H	2.87104100	0.04396900	-2.17016500
H	5.12901000	-1.01978500	-2.15944800
H	6.22776900	-1.53442500	-0.00090100
H	5.13179600	-1.01779100	2.15857500
C	1.48239500	0.69535100	0.00111900
C	0.32452100	1.29532500	-0.00008900
C	-0.98611300	0.62237200	-0.00002400
C	-2.17454200	1.36670700	0.00009700
C	-1.07703000	-0.78764100	-0.00008000
C	-3.41781500	0.73972300	0.00015500
H	-2.14788800	2.45110100	0.00015000
C	-2.30239400	-1.41984000	-0.00000800
H	-0.17230300	-1.39106300	-0.00023900
C	-3.49268800	-0.66174400	0.00014300
H	-4.31535700	1.34616100	0.00020400
H	-2.37967100	-2.50189700	-0.00009000
C	0.42108400	2.82714300	-0.00131000
H	-0.07814000	3.21611200	0.89110500
H	1.45509600	3.17783300	-0.00166100
H	-0.07831000	3.21458900	-0.89429200
O	-4.63299400	-1.37357300	0.00014300

C	-5.88668300	-0.68582300	0.00027400
H	-5.99558700	-0.06641900	-0.89724100
H	-6.64735200	-1.46620000	0.00035000
H	-5.99539900	-0.06643900	0.89782500

5a′

C	1.39372000	0.51560600	1.23373000
C	0.69281600	0.66513900	-0.00923000
C	1.40590200	0.40591800	-1.22982700
C	2.72622500	0.02918500	-1.19016600
C	3.42239000	-0.11489600	0.04113600
C	2.71778700	0.13652100	1.24476800
H	3.24675800	-0.16101700	-2.12179900
H	3.22465200	0.03176100	2.19551400
C	-0.61586800	1.04104100	-0.02753200
C	-1.85435900	1.44728200	-0.04838100
C	-3.03148700	0.54659500	-0.02363500
C	-4.32694100	1.07331000	0.07489700
C	-2.87539500	-0.85072200	-0.09315700
C	-5.43147800	0.22380900	0.10481200
H	-4.48862700	2.14422600	0.13307800
C	-3.98141700	-1.68615100	-0.06308300
H	-1.88148500	-1.28415900	-0.17585300
C	-5.28453900	-1.16631300	0.03499600
H	-6.42608200	0.65374300	0.18411700
H	-3.83791300	-2.76213500	-0.11817500
C	-2.03937100	2.96657700	-0.09647500
H	-2.57048200	3.29447100	0.80237800
H	-1.08569700	3.49569800	-0.14709100
H	-2.63311400	3.22834800	-0.97751600
H	0.86186900	0.70691100	2.16033700
C	4.89068300	-0.52993900	0.02927800
H	0.88336400	0.51416800	-2.17486200
C	5.69680800	0.52250400	-0.78057500
H	6.75231200	0.23209000	-0.79033200
H	5.36394600	0.59512000	-1.82046500
H	5.62390100	1.51633900	-0.32632400
C	5.49520700	-0.63150100	1.44224400
H	4.98898100	-1.38513400	2.05570500
H	6.54454800	-0.93060400	1.36309400

H	5.47000400	0.32712300	1.97223300
C	5.00965800	-1.91576600	-0.66252600
H	6.06226000	-2.21657500	-0.67784700
H	4.44688500	-2.68216000	-0.11910100
H	4.65513600	-1.89867400	-1.69757800
C	-6.48084800	-2.08359100	0.04503300
H	-7.38694500	-1.55950400	0.36134200
H	-6.32493000	-2.93425900	0.71736200
H	-6.66629000	-2.49342900	-0.95606400

5b′

C	-1.90493900	1.77379200	0.00010100
C	-0.73766700	0.99443500	-0.00011000
C	-0.87075700	-0.40328700	-0.00026700
C	-2.12635100	-0.99858400	-0.00019600
C	-3.30461600	-0.23195800	0.00001500
C	-3.15544000	1.16570200	0.00013600
H	-2.18201400	-2.08070400	-0.00036600
H	-4.03424200	1.80249500	0.00023200
C	0.59698300	1.63658800	-0.00017600
C	1.73049800	0.99336600	0.00081900
C	2.94206900	0.36822300	0.00052100
C	3.59289100	0.03373900	1.23669400
C	3.59184500	0.03287700	-1.23598600
C	4.81773500	-0.59360500	1.22303400
H	3.10342600	0.28746700	2.17144300
C	4.81669700	-0.59446400	-1.22293100
H	3.10155900	0.28595900	-2.17048100
C	5.45133800	-0.92091700	-0.00010100
H	5.31109600	-0.84182300	2.15789400
H	5.30926100	-0.84334100	-2.15803700
C	0.72560500	3.16348700	-0.00105900
H	0.23393400	3.56420800	-0.89264500
H	0.23399600	3.56527600	0.89007700
H	1.76743900	3.49000100	-0.00127200
C	6.76976500	-1.63145600	-0.00042900
H	7.35773800	-1.39732600	0.89140400
H	6.59942700	-2.71826000	-0.00060300
H	7.35741800	-1.39703400	-0.89240400
C	-4.70839100	-0.85673100	0.00009600

C	-5.47163000	-0.39133500	1.26445400
H	-5.58251700	0.69731100	1.30163100
H	-6.47699200	-0.82666700	1.27406600
H	-4.95649200	-0.70964000	2.17770900
C	-4.66398000	-2.39654000	-0.00017100
H	-4.16101900	-2.79294000	-0.88966100
H	-4.16079700	-2.79325900	0.88905000
H	-5.68527500	-2.79063800	-0.00011300
C	-5.47203700	-0.39090100	-1.26383900
H	-6.47741000	-0.82621000	-1.27326900
H	-5.58292500	0.69775800	-1.30060800
H	-4.95721300	-0.70890100	-2.17738000
H	0.01443300	-1.03547100	-0.00050200
H	-1.85054100	2.85715400	0.00021300

7a′

C	2.30006200	-1.26551800	0.03842200
C	1.62312200	0.01661600	0.17610200
C	2.28964800	1.26137500	-0.18093600
C	3.58607100	1.18418800	-0.66117100
C	4.22543800	-0.05681800	-0.79175000
C	3.59590900	-1.26198000	-0.44931600
H	4.11362400	2.09065600	-0.94035300
H	5.24312400	-0.08561200	-1.17247400
H	4.13082000	-2.19878600	-0.56827000
C	0.34328500	0.05173000	0.62859600
C	-0.87512900	0.09202400	1.08997000
C	-2.08698600	0.01450500	0.23262400
C	-3.36390100	0.11303500	0.80537000
C	-1.97200100	-0.15730000	-1.15959400
C	-4.50092800	0.04223200	0.00013100
H	-3.48369500	0.24525700	1.87502300
C	-3.10782000	-0.22721100	-1.95684000
H	-0.98970900	-0.23892600	-1.61918500
C	-4.37754700	-0.12735700	-1.37841700
H	-5.48327300	0.11989100	0.45570400
H	-3.00563100	-0.36071000	-3.02952100
C	-1.00476200	0.22886000	2.60813900
H	-1.56887100	-0.62240100	3.00155100
H	-0.03163500	0.25996600	3.10265000

H	-1.54418200	1.15114300	2.84517700
C	1.61779100	-2.54673900	0.42284800
H	1.44395500	-2.58693600	1.50521300
H	0.64097400	-2.64637200	-0.06187600
H	2.22932200	-3.40909900	0.14894200
C	1.59601600	2.58403800	-0.02549000
H	0.61868200	2.58841900	-0.51932800
H	1.42148900	2.81174900	1.03332500
H	2.20016200	3.39031600	-0.44690700
H	-5.26475700	-0.18263100	-2.00179500

7b′

C	-1.98690200	-1.23900600	-0.21698800
C	-1.50751400	0.00000200	0.27169800
C	-1.98693000	1.23898900	-0.21696400
C	-3.00724400	1.21019900	-1.17070800
C	-3.51248000	-0.00001300	-1.64482100
C	-3.00720900	-1.21023000	-1.17071300
H	-3.40752200	2.14786600	-1.54526300
H	-4.30261300	-0.00003000	-2.38983500
H	-3.40747200	-2.14789400	-1.54529300
C	-0.48327100	0.00000900	1.39728300
C	0.69639700	-0.00005600	0.87819400
C	1.92605300	0.00001200	0.25891500
C	2.57428800	-1.23625400	-0.05014100
C	2.57423200	1.23629300	-0.05016700
C	3.81981600	-1.22540600	-0.65008700
H	2.07817100	-2.16908400	0.19626000
C	3.81976000	1.22545000	-0.65012200
H	2.07809600	2.16912700	0.19618500
C	4.43759600	0.00003000	-0.94856300
H	4.32092700	-2.15781300	-0.88820000
H	4.32083900	2.15786500	-0.88826600
C	-0.88103700	-0.00002300	2.85279700
H	-1.49609600	0.88196400	3.05986600
H	-1.49650300	-0.88177300	3.05968300
H	-0.01331300	-0.00027900	3.51582900
C	-1.43469300	-2.56362300	0.25585600
H	-0.44900800	-2.76686100	-0.18284200
H	-1.32062300	-2.60802900	1.34410400

H	-2.09417800	-3.38267100	-0.04165700
C	-1.43479000	2.56362300	0.25590700
H	-1.32065000	2.60795200	1.34415300
H	-0.44916000	2.76698700	-0.18286700
H	-2.09437000	3.38263600	-0.04149200
H	5.41703500	0.00004800	-1.41862000

8a′

C	-3.04044800	-0.22890600	-1.26672100
C	-2.40156200	0.09632100	0.00011600
C	-3.04177200	-0.22671400	1.26683600
C	-4.27593400	-0.85417900	1.22710500
C	-4.87997200	-1.16109400	-0.00008800
C	-4.27465200	-0.85630400	-1.22717800
H	-4.78106000	-1.11196200	2.15250700
H	-5.84879500	-1.65391500	-0.00016700
H	-4.77880700	-1.11569000	-2.15266200
C	-1.18362600	0.69985200	0.00024200
C	-0.03021800	1.31219600	-0.00086000
C	1.27850400	0.62844600	-0.00021100
C	2.47268200	1.36288100	-0.00118400
C	1.36163400	-0.78185100	0.00135300
C	3.71239700	0.72730300	-0.00067100
H	2.45390900	2.44745100	-0.00235800
C	2.58312200	-1.42314900	0.00187800
H	0.45312400	-1.37990600	0.00218800
C	3.77836900	-0.67400100	0.00085800
H	4.61385300	1.32802600	-0.00143800
H	2.65256300	-2.50580600	0.00308000
C	-0.10973900	2.84147000	-0.00262900
H	0.39320600	3.22948400	-0.89369400
H	-1.14116800	3.20024400	-0.00299500
H	0.39329600	3.23160400	0.88745900
O	4.91488200	-1.39440300	0.00147500
C	6.17172500	-0.71385900	0.00026400
H	6.28485400	-0.09376500	0.89693700
H	6.92854700	-1.49807500	0.00074900
H	6.28411800	-0.09557600	-0.89774900
C	-2.38629000	0.11423100	-2.57431300
H	-2.34244200	1.20117900	-2.71578200

H	-1.35685600	-0.25575300	-2.62073400
H	-2.94537300	-0.31048000	-3.41093100
C	-2.38894700	0.11869800	2.57449800
H	-1.35954600	-0.25117000	2.62258700
H	-2.34527100	1.20588600	2.71414300
H	-2.94885100	-0.30459800	3.41128400

8b′

C	2.73440400	1.32419200	-0.18180100
C	2.32891900	0.02119300	0.18174200
C	2.83878600	-1.12689100	-0.46331500
C	3.80251200	-0.94432500	-1.46004600
C	4.23073700	0.33210900	-1.81906400
C	3.69989400	1.45369700	-1.18492900
H	4.21873400	-1.81548200	-1.95805300
H	4.97937200	0.45332300	-2.59642600
H	4.03657800	2.44677700	-1.46889500
C	1.35254600	-0.15292300	1.32932900
C	0.10730200	-0.17111900	0.97613000
C	-1.18621800	-0.19190400	0.55561800
C	-1.94758200	1.02376900	0.47407500
C	-1.82962600	-1.42981400	0.19588900
C	-3.25567500	1.01372000	0.06020600
H	-1.46852300	1.95783900	0.74898300
C	-3.13210200	-1.44057800	-0.21663700
H	-1.26258300	-2.35249800	0.25969200
C	-3.86515900	-0.22169800	-0.29238500
H	-3.81503400	1.93949300	0.00521700
H	-3.63995300	-2.35811200	-0.49316800
C	1.85635100	-0.29012500	2.75155600
H	2.52629900	-1.15394600	2.81527500
H	2.44204100	0.59670400	3.01526200
H	1.04273800	-0.41146400	3.47032800
O	-5.11318900	-0.34462500	-0.70228200
C	-5.97634200	0.80609700	-0.82684100
H	-5.56850100	1.51029300	-1.55743100
H	-6.92570900	0.40831900	-1.18093500
H	-6.11059800	1.28755800	0.14586400
C	2.15551500	2.55972500	0.46965700
H	1.11434200	2.72707400	0.16449900

H	2.16603500	2.50210800	1.56378100
H	2.72357700	3.44803800	0.18191300
C	2.37055000	-2.52211000	-0.11635000
H	2.36965900	-2.70961700	0.96302100
H	1.35052900	-2.70632500	-0.47791600
H	3.01763300	-3.27117300	-0.57976600

10a′

C	-4.03946300	0.67901800	0.00015700
C	-2.72436900	0.19005000	-0.00004900
C	-2.50677600	-1.20038100	-0.00009000
C	-3.58218200	-2.07942500	0.00008900
C	-4.89101400	-1.58515500	0.00030600
C	-5.11528100	-0.20874200	0.00033200
H	-4.23553600	1.74547100	0.00019000
H	-1.49287900	-1.59319100	-0.00031200
H	-3.40306500	-3.15022500	0.00004400
H	-5.73108000	-2.27297900	0.00044400
H	-6.12874300	0.18022200	0.00048700
C	-1.57847800	1.13362600	-0.00024500
C	-0.32617600	0.77583900	0.00061300
C	0.99922300	0.45273600	0.00042200
C	1.70744100	0.27806400	1.23824600
C	1.70674400	0.27678500	-1.23762600
C	3.04355200	-0.05133700	1.23507500
H	1.17249000	0.40973600	2.17309100
C	3.04285800	-0.05259600	-1.23486100
H	1.17126600	0.40748200	-2.17230600
C	3.70716500	-0.21555800	0.00000800
H	3.59147000	-0.18592600	2.16106400
H	3.59026600	-0.18813300	-2.16101500
C	-1.81365600	2.64796500	-0.00121300
H	-2.38550100	2.92075800	-0.89333500
H	-2.38544400	2.92195100	0.89058000
H	-0.87829100	3.21104600	-0.00159300
Cl	5.37279500	-0.62656100	-0.00025500

10b′

C	-3.29510500	-0.23151800	-1.24077100
C	-2.65633200	0.12515200	-0.00482000

C	-3.28193600	-0.21747500	1.24187300
C	-4.48798400	-0.88949200	1.23997400
C	-5.09171200	-1.22827100	0.01569900
C	-4.50107800	-0.90333500	-1.21864000
H	-2.81389600	0.03468800	-2.17620500
H	-2.79084200	0.05912600	2.16910800
H	-4.97090100	-1.15549800	2.17439400
H	-6.04155300	-1.75609900	0.02376000
H	-4.99386900	-1.17976700	-2.14483700
C	-1.46021400	0.78416100	-0.01475600
C	-0.32919500	1.40879900	-0.01020500
C	0.99528900	0.74615900	-0.00688200
C	2.16931200	1.51480400	0.01201400
C	1.10076200	-0.65731400	-0.02183500
C	3.41882700	0.90026600	0.01645100
H	2.12632000	2.59809400	0.02376300
C	2.34125700	-1.27739400	-0.01759900
H	0.20575000	-1.27389600	-0.03812500
C	3.50072400	-0.49280200	0.00168600
H	4.32315700	1.49828600	0.03111700
H	2.41834600	-2.35891800	-0.02959300
C	-0.44012100	2.93704800	-0.01122300
H	0.06202500	3.33195600	-0.89956800
H	-1.47817600	3.27532000	-0.01969700
H	0.04705300	3.33198800	0.88544900
Cl	5.05950700	-1.26576500	0.00674400

F. References to Supporting Information

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