SUPPLEMENTARY MATERIAL

for

Synthesis, Stereochemical and Photophysical Properties of Functionalized Thiahelicenes

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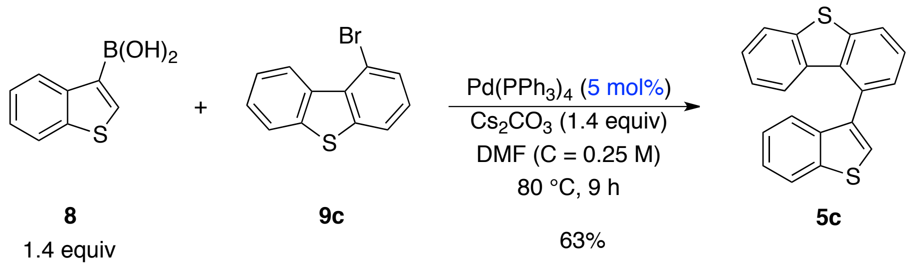
1. Synthesis of 5c through the Suzuki coupling using 5 mol% of $Pd(PPh_3)_4$



Scheme S1. Suzuki coupling between **8** and **9c** with 5 mol% of $Pd(PPh_3)_4$.

A degassed mixture of bromide **9c** (50 mg, 0.19 mmol), boronic acid **8** (46 mg, 0.26 mmol), $Pd(PPh_3)_4$ (11 mg, 0.0095 mmol) and Cs_2CO_3 (85 mg, 0.26 mmol) in dry DMF (1 mL) was stirred at 80 °C under nitrogen. After 9 h, the mixture was cooled to room temperature, diluted with CH_2Cl_2 and added to water. The aqueous phase was extracted with CH_2Cl_2 (3 × 5 mL) and the collected organic phases were washed with water (3 × 5 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude was purified by column chromatography on silica gel with hexane as the eluent to afford **5c** as a colorless solid (40 mg, 63%). The ^1H NMR data of this compound were in agreement with those of compound **5c** prepared using 10% of $Pd(PPh_3)_4$, Scheme 1. The bromide **9c** was also recovered (25%).

2. Characterization

5a. The crude reaction product obtained from the Pd-catalyzed Suzuki reaction of **8** with **9a** (Scheme 1) was purified by column chromatography on silica gel with a mixture of hexane and CH_2Cl_2 (95:5) as eluent to afford **5a** (441 mg, 94%) as a colorless solid: mp 121–123 °C. IR (neat): $\tilde{\nu}$ = 2924, 1579, 1464, 1424, 1150, 1019, 785, 759, 721 cm^{-1}. HRMS-EI: calcd for $C_{21}H_{15}NS$ $[M]^+$: 313.0925, found: 313.0925. For the ^1H and ^{13}C NMR data, see Table S1.

5b. The crude reaction product obtained from the Pd-catalyzed Suzuki reaction of **8** with **9b** (Scheme 1) was purified by column chromatography on silica gel using hexane as eluent to afford **5b** (423 mg, 93%) as a colorless solid: mp 122–123 °C. IR (neat): $\tilde{\nu}$ = 3100, 3046, 2916, 2847, 1599, 1579, 1444, 1424, 1411, 1342, 1243, 1219, 1105, 1064, 1019, 839, 814, 794, 761, 741, 721, 549 cm^{-1}. HRMS-EI: calcd for $C_{20}H_{12}OS$ $[M]^+$: 300.0609, found: 300.0596. For the ^1H and ^{13}C NMR data, see Table S2.

5c. The crude reaction product obtained from the Pd-catalyzed Suzuki reaction of **8** with **9c** (Scheme 1) was purified by column chromatography on silica gel using hexane as eluent to afford **5c** (436 mg, 92%) as a colorless solid: mp 101–103 °C. IR (neat): $\tilde{\nu}$ = 3105, 3055, 2916, 2842, 1572, 1444, 1428, 1309, 1150, 1055, 957, 843, 778, 753, 732, 688, 622 cm^{-1}. HRMS-EI: calcd for $C_{20}H_{12}S_2$ $[M]^+$: 316.0380, found: 316.0390. For the ^{1}H and ^{13}C NMR data, see Table S3.

6. The crude reaction product obtained from the Pd-catalyzed Suzuki reaction of **8** with **10** (Scheme 1) was purified by column chromatography on silica gel with a mixture of hexane and CH_2Cl_2 (95:5) as eluent to afford **6** (475 mg, 95%) as a colorless solid: mp 160–162 °C. IR (neat): $\tilde{v}$ = 3092, 1424, 1178, 843, 761, 749, 729, 709 cm^{-1}. HRMS-EI: calcd for $C_{24}H_{14}S$ $[M]^+$: 334.0816, found: 334.0815. For the ^{1}H and ^{13}C NMR data, see Table S4.

7. The crude reaction product obtained from the Pd-catalyzed Suzuki reaction of **8** with **11** (Scheme 1) was purified by column chromatography on silica gel with a mixture of hexane and CH_2Cl_2 (95:5) as eluent to afford **7** (658 mg, 98%) as a colorless solid: mp 243–244 °C. IR (neat): $\tilde{v}$ = 3092, 2924, 2851, 1444, 1411, 1338, 1280, 831, 802, 782, 766, 745, 729, 647 cm^{-1}. HRMS-EI: calcd for $C_{33}H_{20}S$ $[M]^+$: 448.1286, found: 448.1277. For the ^{1}H and ^{13}C NMR data, see Table S5.

12a. The crude reaction product obtained from the iodination of **5a** (Scheme 2) was washed with pentane and diethyl ether to afford **12a** (578 mg, 88%) as a colorless solid: mp 162–163 °C. IR (neat): $\tilde{v}$ = 1579, 1464, 1416, 1320, 1283, 1150, 924, 785, 760, 724 cm^{-1}. HRMS-EI: calcd for $C_{21}H_{14}SNI$ $[M]^+$: 438.9892, found: 438.9888. For the ^{1}H and ^{13}C NMR data, see Table S6.

12b. The crude reaction product obtained from the iodination of **5b** (Scheme 2) was washed with pentane and diethyl ether to afford **12b** (535 mg, 84%) as a colorless solid: mp 131–132 °C. IR (neat): $\tilde{v}$ = 3056, 1575, 1469, 1444, 1411, 1326, 1260, 1199, 1183, 1028, 942, 847, 798, 778, 758, 741, 725, 709, 623, 517 cm^{-1}. HRMS-EI: calcd for $C_{20}H_{11}SOI$ $[M]^+$: 425.9575, found: 425.9574. For the ^{1}H and ^{13}C NMR data, see Table S7.

12c. The crude reaction product obtained from the iodination of **5c** (Scheme 2) was washed with pentane and diethyl ether to afford **12c** (608 mg, 92%) as a colorless solid: mp 141–143 °C. IR (neat): $\tilde{v}$ = 3052, 1436, 1420, 1399, 1297, 1203, 1150, 1060, 904, 791, 762, 733, 647, 532 cm^{-1}. HRMS-EI: calcd for $C_{20}H_{11}SI$ $[M]^+$: 441.9347, found: 441.9341. For the ^{1}H and ^{13}C NMR data, see Table S8.

13. The crude reaction product obtained from the iodination of **6** (Scheme 2) was washed with pentane and diethyl ether to afford **13** (633 mg, 92%) as a colorless solid: mp 210–213 °C. IR (neat): $\tilde{v}$ = 3039, 1421, 1180, 848, 760, 723, 681, 638 cm^{-1}. HRMS-EI: calcd for $C_{24}H_{14}SI$ $[M]^+$: 459.9783, found: 459.9783. For the ^{1}H and ^{13}C NMR data, see Table S9.

14. The crude reaction product obtained from the iodination of **7** (Scheme 2) was washed with pentane and diethyl ether to afford **14** (740 mg, 86%) as a colorless solid: mp 296–298 °C. IR (neat): $\tilde{v}$ = 3059, 1477, 1440, 1415, 1146, 778, 738, 725, 700, 627, 603 cm^{-1}. HRMS-EI: calcd for $C_{33}H_{19}SI$ [M]$^+$: 574.0252, found: 574.0252. For the ^{1}H and ^{13}C NMR data, see Table S10.

1aa. The crude reaction product obtained from the Pd-catalyzed annulation of alkyne **15a** with **12a** (Scheme 3) was purified by column chromatography on silica gel with a mixture of hexane and CH_2Cl_2 (95:5) as eluent to afford **1aa** (38 mg, 79%) as a yellow solid: mp 289–290 °C. IR (neat): ṽ = 3052, 2921, 1583, 1471, 1154, 1022, 983, 786, 763, 747, 734, 704, 695 cm^{-1}. HRMS-EI: calcd for $C_{35}H_{23}NS$ [M]$^+$: 489.1551, found: 489.1533. For the ^{1}H and ^{13}C NMR data, see Table S11.

1ab. The crude reaction product obtained from the Pd-catalyzed annulation of alkyne **15b** with **12a** (Scheme 3) was purified by column chromatography on silica gel with a mixture of hexane and CH_2Cl_2 (90:10) as eluent to afford **1ab** (8 mg, 16%) as a yellow solid: mp 275–278 °C. IR (neat): ṽ = 2959, 2922, 2851, 1581, 1470, 1319, 1261, 1152, 1020, 784, 744, 696, 635 cm^{-1}. HRMS-EI: calcd for $C_{31}H_{19}S_3N$ [M]$^+$: 501.0679, found: 501.0691. For the ^{1}H and ^{13}C NMR data, see Table S12.

1ac. The crude reaction product obtained from the Pd-catalyzed annulation of alkyne **15c** with **12a** (Scheme 3) was purified by column chromatography on silica gel with a mixture of hexane and CH_2Cl_2 (90:10) as eluent to afford **1ac** (14 mg, 31%) as a pale-yellow solid: mp 279–280 °C. IR (neat): ṽ = 3016, 2961, 2924, 2860, 1584, 1365, 1348, 1064, 1038, 983, 746, 735, 718, 702 cm^{-1}. HRMS-EI: calcd for $C_{31}H_{23}SN$ [M]$^+$: 441.1551, found: 441.1535. For the ^{1}H and ^{13}C NMR data, see Table S13.

1ba. The crude reaction product obtained from the Pd-catalyzed annulation of alkyne **15a** with **12b** (Scheme 3) was purified by column chromatography on silica gel using hexane as eluent to afford **1ba** (31 mg, 65%) as a yellow solid: mp 275–276 °C. IR (neat): ṽ = 3059, 1591, 1485, 1453, 1375, 1329, 1211, 1035, 802, 761, 749, 732, 696, 548 cm^{-1}. HRMS-EI: calcd for $C_{34}H_{20}SO$ [M]$^+$: 476.1235, found: 476.1204. For the ^{1}H and ^{13}C NMR data, see Table S14.

1bb. The crude reaction product obtained from the Pd-catalyzed annulation of alkyne **15b** with **12b** (Scheme 3) was purified by column chromatography on silica gel with a mixture of hexane and CH_2Cl_2 (95:5) as eluent to afford **1bb** (17 mg, 35%) as a yellow solid: mp 273 °C (dec). IR (neat): ṽ = 1588, 1497, 1448, 1321, 1256, 843, 786, 749, 692 cm^{-1}. HRMS-EI: calcd for $C_{30}H_{16}OS$ [M]$^+$: 488.0363, found: 488.0342. For the ^{1}H and ^{13}C NMR data, see Table S15.

1ca. The crude reaction product obtained from the Pd-catalyzed annulation of alkyne **15a** with **12c** (Scheme 3) was purified by column chromatography on silica gel with a mixture of hexane and CH_2Cl_2 (90:10) as eluent to afford **1ca** (30 mg, 61%) as a pale pink solid: mp 274–275 °C. IR (neat): ṽ = 3046, 3026, 1595, 1566, 1542, 1477, 1431, 1199, 995, 949, 814, 781, 753, 725, 696, 643, 603, 541 cm^{-1}. HRMS-EI: calcd for $C_{34}H_{20}S_2$ [M]$^+$: 492.1006, found: 492.1011. For the ^{1}H and ^{13}C NMR data, see Table S16.

1cb. The crude reaction product obtained from the Pd-catalyzed annulation of alkyne **15b** with **12c** (Scheme 3) was purified by column chromatography on silica gel with a mixture of hexane and CH_2Cl_2 (95:5) as eluent to afford **1cb** (23 mg, 46%) as a yellow solid: mp 289 °C (dec). IR (neat): $\tilde{\nu}$ = 1433, 1250, 1155, 1024, 943, 847, 784, 736, 696 cm^{-1}. HRMS-EI: calcd for $C_{30}H_{16}S_4$ $[M]^+$: 504.0135, found: 504.0126. For the ^1H and ^{13}C NMR data, see Table S17.

3. The crude reaction product obtained from the Pd-catalyzed annulation of alkyne **15a** with **13** (Scheme 3) was purified by column chromatography on silica gel with a mixture of hexane and CH_2Cl_2 (90:10) as eluent to afford **3** (36 mg, 71%) as a yellow solid: mp 339 °C (dec). IR (neat): $\tilde{\nu}$ = 3049, 1438, 1246, 1177, 1124, 880, 838, 801, 750, 699 cm^{-1}. HRMS-EI: calcd for $C_{38}H_{22}S$ $[M]^+$: 510.1442, found: 510.1448. For the ^1H and ^{13}C NMR data, see Table S18.

4. The crude reaction product obtained from the Pd-catalyzed annulation of alkyne **15a** with **14** (Scheme 3) was purified by column chromatography on silica gel with a mixture of hexane and CH_2Cl_2 (95:5) as eluent to afford **4** (48 mg, 77%) as a colorless solid: mp 239–240 °C. IR (neat): $\tilde{\nu}$ = 3056, 3019, 1596, 1486, 1440, 1019, 904, 738, 721, 692, 643, 532 cm^{-1}. HRMS-LDI: calcd for $C_{47}H_{28}S$ $[M]^+$: 624.1911, found: 624.1914. For the ^1H and ^{13}C NMR data, see Table S19.

17a. The crude reaction product obtained from the Pd-catalyzed Suzuki reaction of **16** with **12a** (Scheme 4) was purified by column chromatography on silica gel with a mixture of hexane and AcOEt (97:3) as eluent to afford **17a** (115 mg, 74%) as a colorless solid: mp 159–160 °C. IR (neat): $\tilde{\nu}$ = 1583, 1467, 1424, 1320, 1283, 1229, 1149, 944, 758, 744, 735, 694 cm^{-1}. HRMS-EI: calcd for $C_{27}H_{19}SN$ $[M]^+$: 389.1238, found: 389.1222. For the ^1H and ^{13}C NMR data, see Table S20.

17b. The crude reaction product obtained from the Pd-catalyzed Suzuki reaction of **16** with **12b** (Scheme 4) was purified by column chromatography on silica gel with a mixture of hexane and CH_2Cl_2 (90:10) as eluent to afford **17b** (143 mg, 95%) as a colorless solid: mp 150–151 °C. IR (neat): $\tilde{\nu}$ = 3056, 2953, 2921, 1596, 1579, 1444, 1428, 1244, 1224, 1191, 1105, 1068, 1019, 957, 835, 815, 786, 758, 738, 725, 692, 619, 512 cm^{-1}. HRMS-EI: calcd for $C_{26}H_{16}SO$ $[M]^+$: 376.0922, found: 376.0911. For the ^1H and ^{13}C NMR data, see Table S21.

17c. The crude reaction product obtained from the Pd-catalyzed Suzuki reaction of **16** with **12c** (Scheme 4) was purified by column chromatography on silica gel with a mixture of hexane and CH_2Cl_2 (90:10) as eluent to afford **17c** (147 mg, 94%) as a colorless solid: mp 81–82 °C. IR (neat): $\tilde{\nu}$ = 3056, 3019, 1431, 1305, 1227, 1154, 1064, 1028, 904, 786, 758, 725, 688, 627, 606 cm^{-1}. HRMS-EI: calcd for $C_{26}H_{16}S_2$ $[M]^+$: 392.0693, found: 392.0727. For the ^1H and ^{13}C NMR data, see Table S22.

18. The crude reaction product obtained from the Pd-catalyzed Suzuki reaction of **16** with **13** (Scheme 4) was purified by column chromatography on silica gel with a mixture of hexane and CH_2Cl_2 (95:5) as eluent to afford **18** (128 mg, 78%) as a yellow solid: mp 165–168 °C. IR (neat): $\tilde{v}$ = 3035, 1431, 903, 753, 737, 724, 710, 692, 679, 623 cm^{-1}. HRMS-EI: calcd for $C_{30}H_{18}S$ [M]$^+$: 410.1129, found: 410.1132. For the ^{1}H and ^{13}C NMR data, see Table S23.

19. The crude reaction product obtained from the Pd-catalyzed Suzuki reaction of **16** with **14** (Scheme 4) was purified by column chromatography on silica gel with a mixture of hexane and CH_2Cl_2 (90:10) as eluent to afford **19** (176 mg, 84%) as a colorless solid: mp 223–224 °C. IR (neat): $\tilde{v}$ = 3052, 3014, 2961, 1444, 1408, 1260, 1019, 904, 798, 741, 721, 683, 656, 614, 549 cm^{-1}. HRMS-EI: calcd for $C_{39}H_{24}S$ [M]$^+$: 524.1599, found: 524.1597. For the ^{1}H and ^{13}C NMR data, see Table S24.

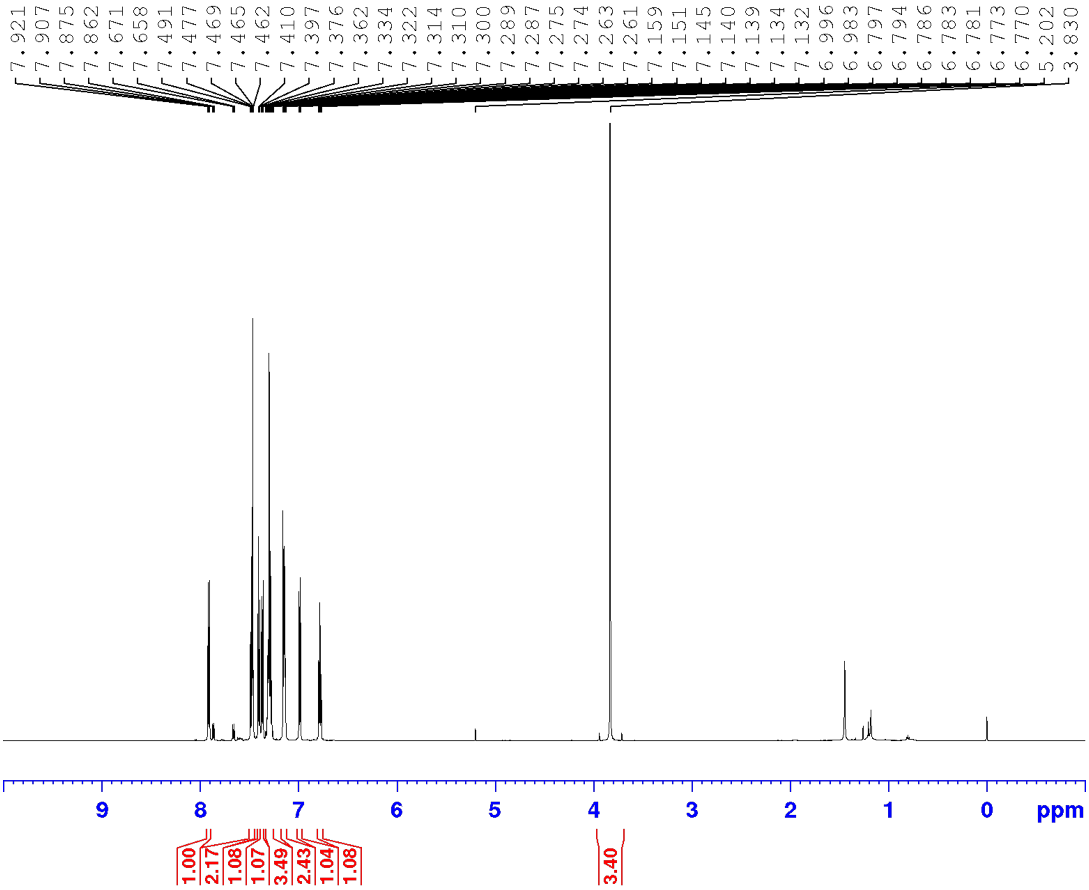
2a. The crude reaction product obtained from photocyclization of **17a** (Scheme 5) was purified by column chromatography on silica gel with a mixture of hexane and AcOEt (97:3) as eluent to afford **2a** (26 mg, 42%) as a yellow solid: mp 272–273 °C. IR (neat): $\tilde{v}$ = 1579, 1473, 1445, 1236, 963, 788, 744, 733 cm^{-1}. HRMS-EI: calcd for $C_{27}H_{17}SN$ [M]$^+$: 387.1081, found: 387.1076. For the ^{1}H and ^{13}C NMR data, see Table S25.

2b. The crude reaction product obtained from photocyclization of **17b** (Scheme 5) was purified by column chromatography on silica gel with a mixture of hexane and AcOEt (98:2) as eluent to afford **2b** (25 mg, 42%) as a colorless solid: mp 202–203 °C. IR (neat): $\tilde{v}$ = 3043, 1510, 1444, 1399, 1232, 1211, 1105, 1068, 1032, 966, 929, 811, 786, 745, 721, 610 cm^{-1}. HRMS-EI: calcd for $C_{26}H_{14}SO$ [M]$^+$: 374.0765, found: 374.0764. For the ^{1}H and ^{13}C NMR data, see Table S26.

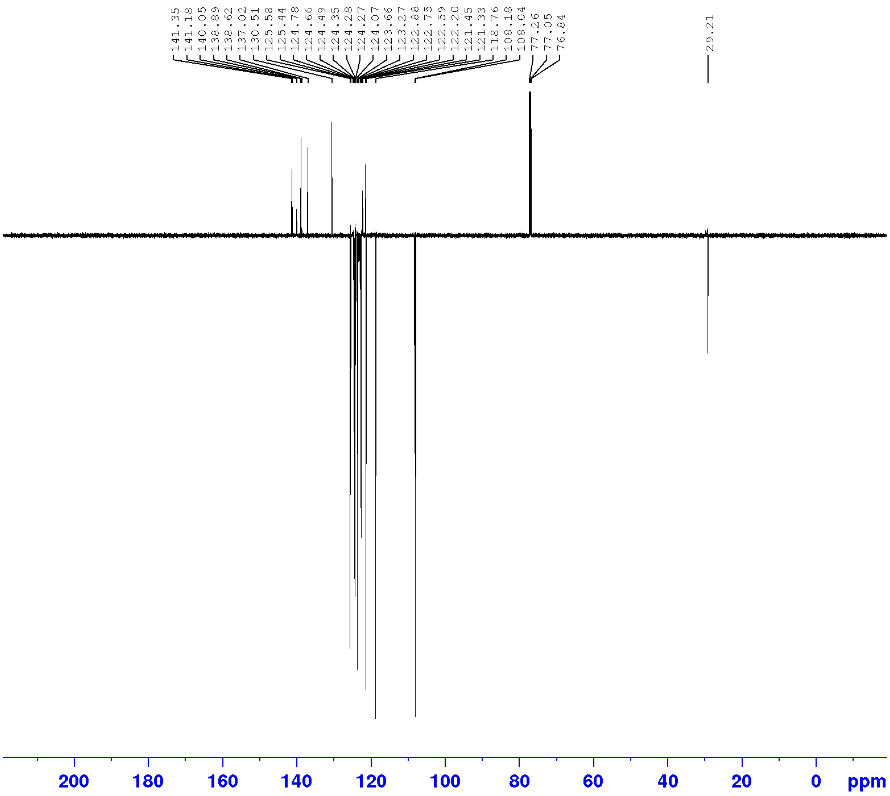
2c. The crude reaction product obtained from photocyclization of **17c** (Scheme 5) was purified by column chromatography on silica gel with a mixture of hexane and AcOEt (95:5) as eluent to afford **2c** (20 mg, 33%) as a colorless solid: mp 225–226 °C. IR (neat): $\tilde{v}$ = 2961, 2921, 2851, 1710, 1440, 1252, 1072, 1011, 855, 782, 749, 725, 700, 606 cm^{-1}. HRMS-EI: calcd for $C_{26}H_{14}S_2$ [M]$^+$: 390.0537, found: 390.0541. For the ^{1}H and ^{13}C NMR data, see Table S27.

3. ^{1}H and ^{13}C NMR spectra

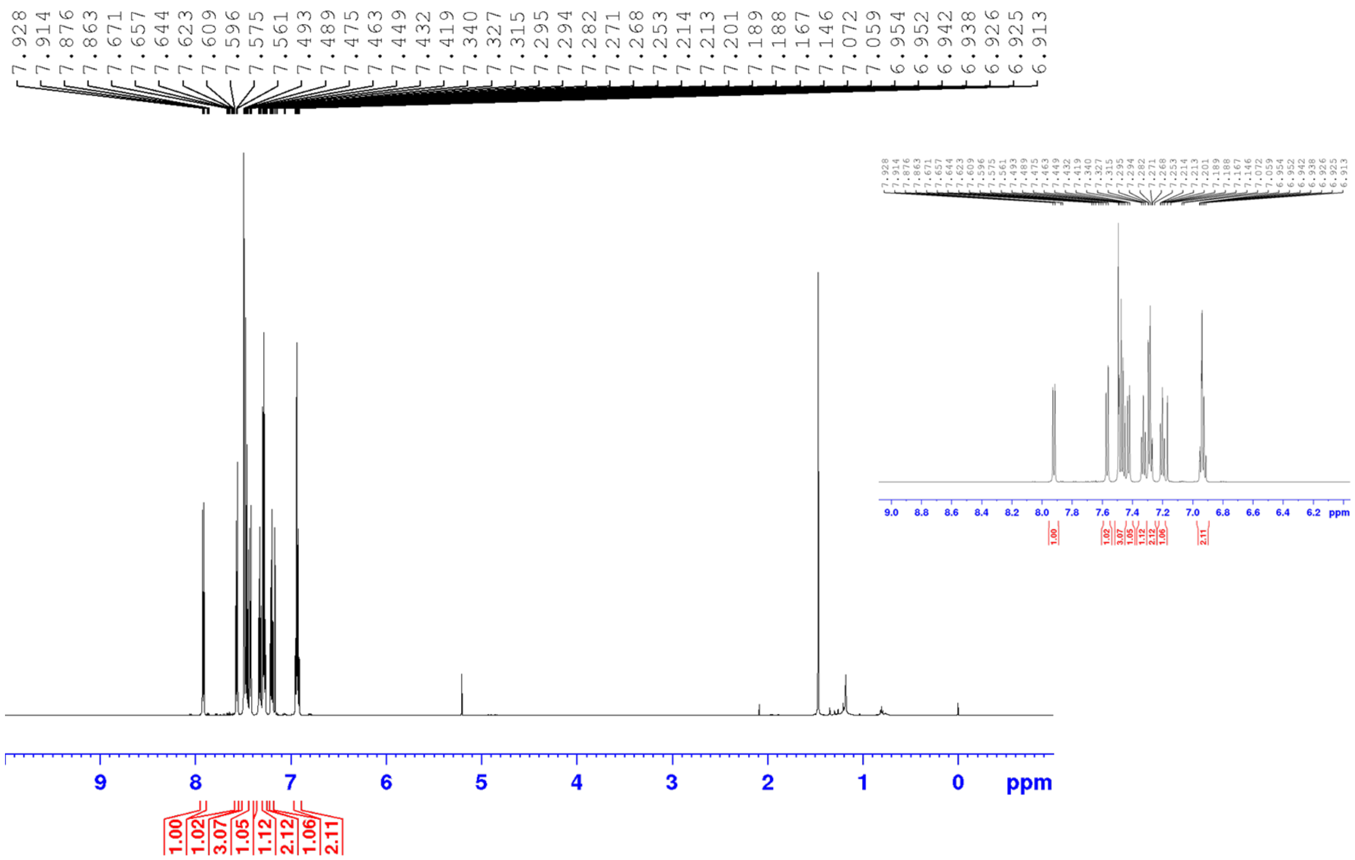
^{1}H NMR (600.33 MHz, $CDCl_3$) of compound **5a**.



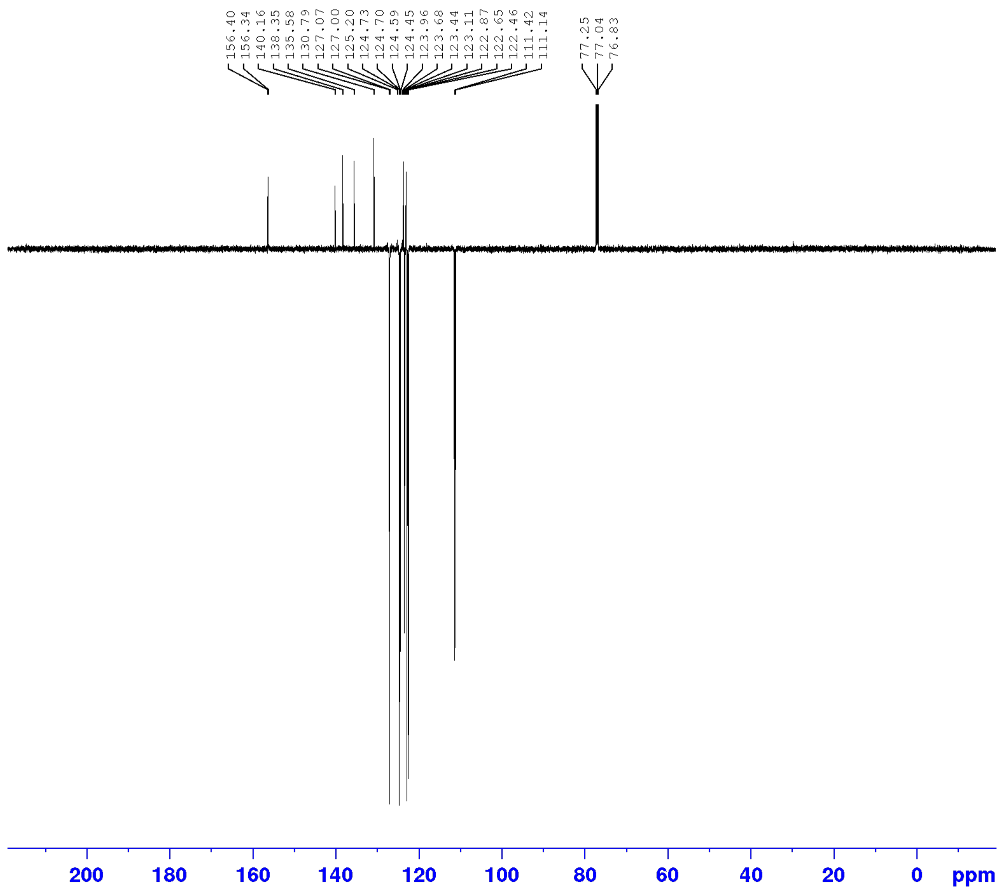
^{13}C NMR (150.95 MHz, $CDCl_3$) of compound **5a**.



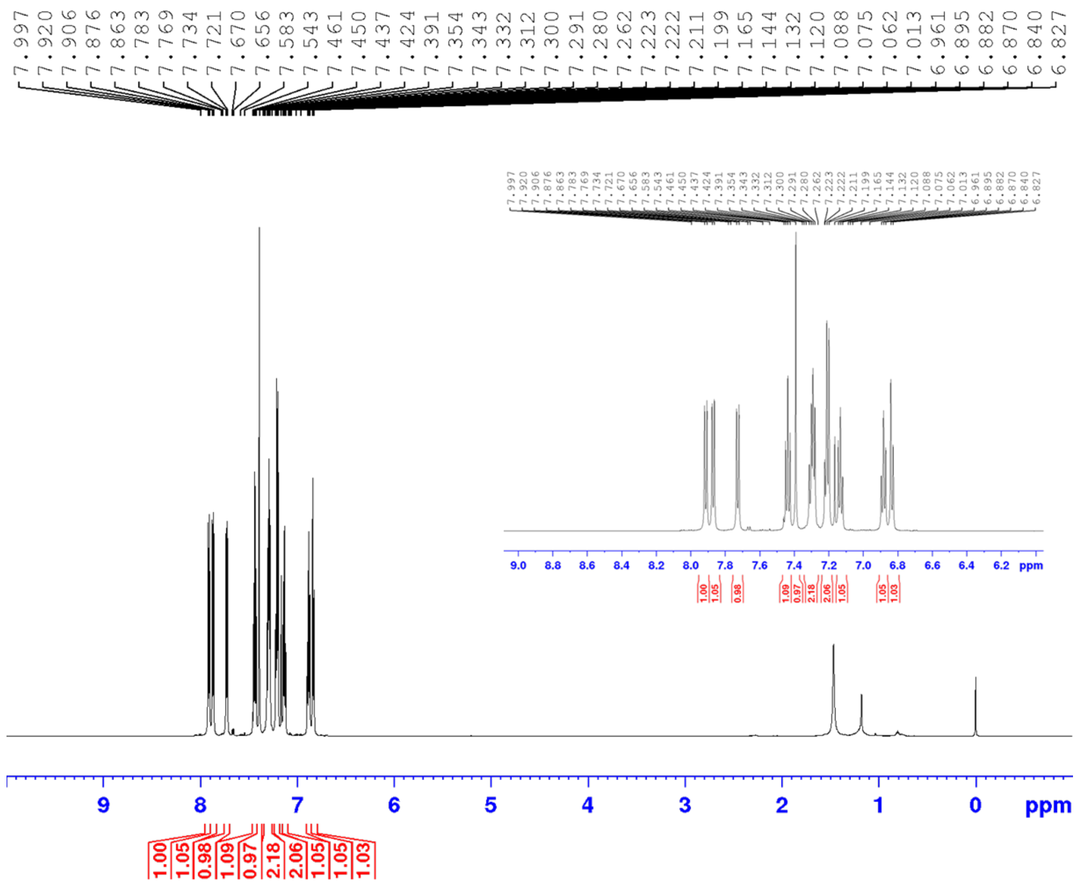
[1]H NMR (600.33 MHz, $CDCl_3$) of compound **5b**.



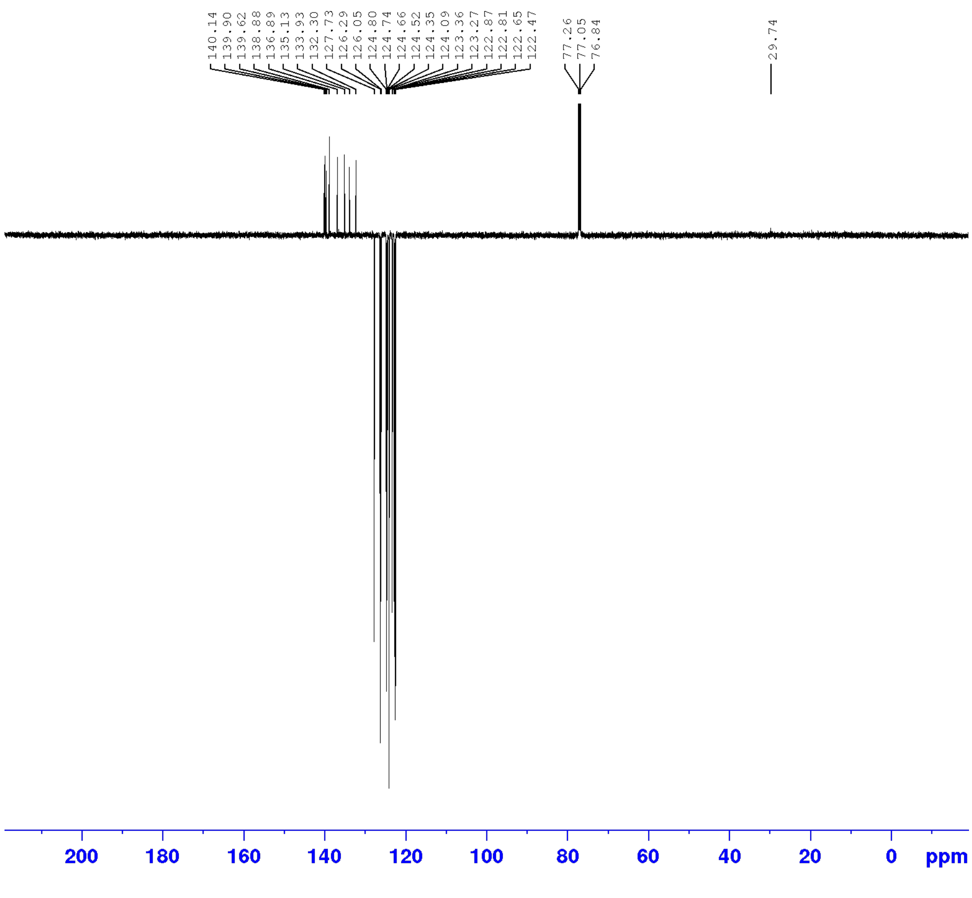
[13]C NMR (150.95 MHz, $CDCl_3$) of compound **5b**.



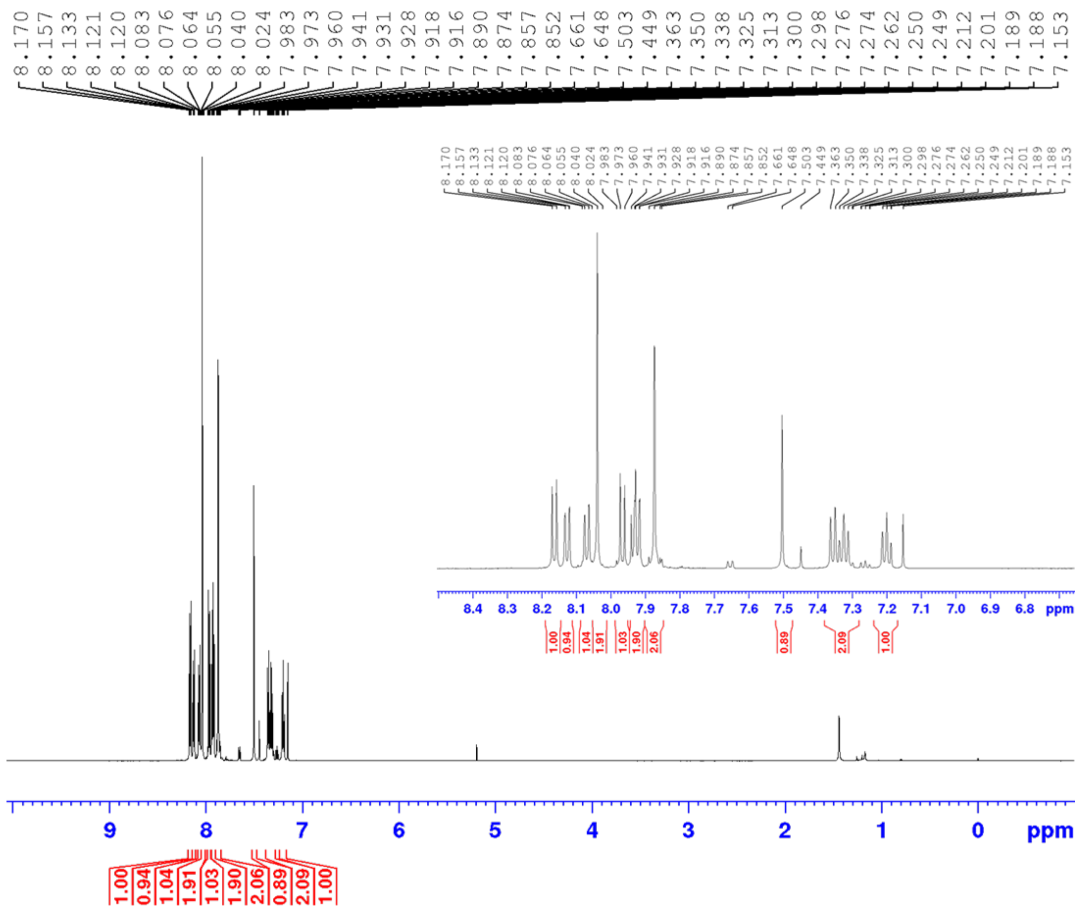
[1]H NMR (600.33 MHz, $CDCl_3$) of compound **5c**.



[13]C NMR (150.95 MHz, $CDCl_3$) of compound **5c**.



^{1}H NMR (600.33 MHz, $CDCl_3$) of compound **6**.



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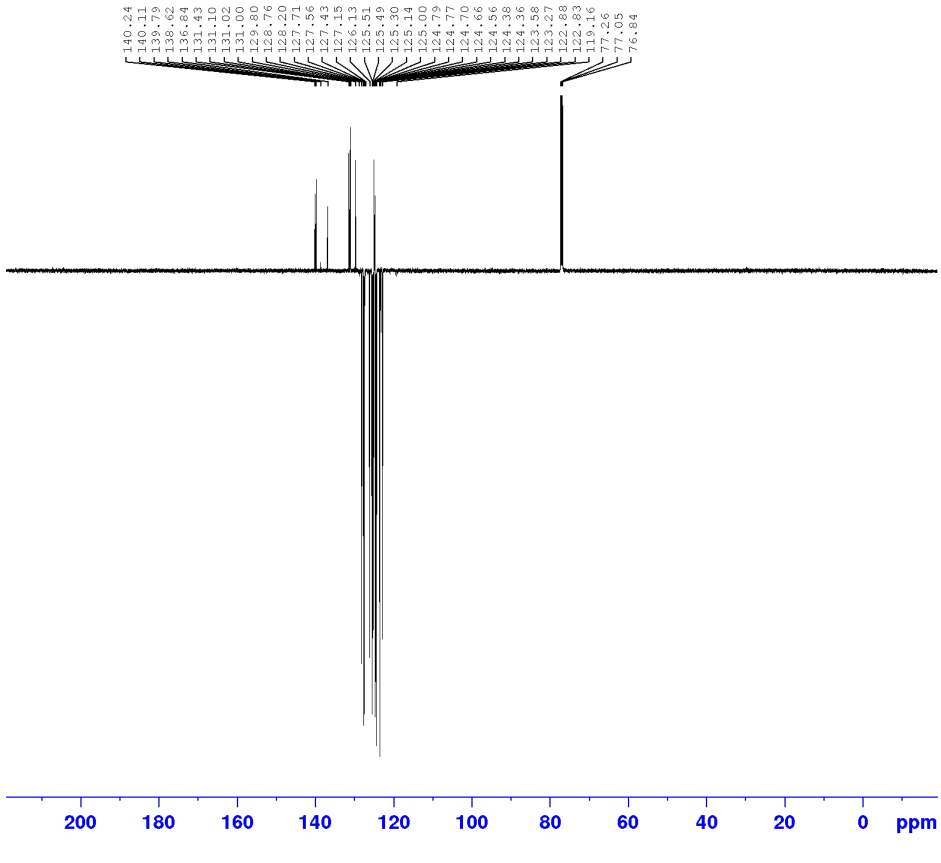
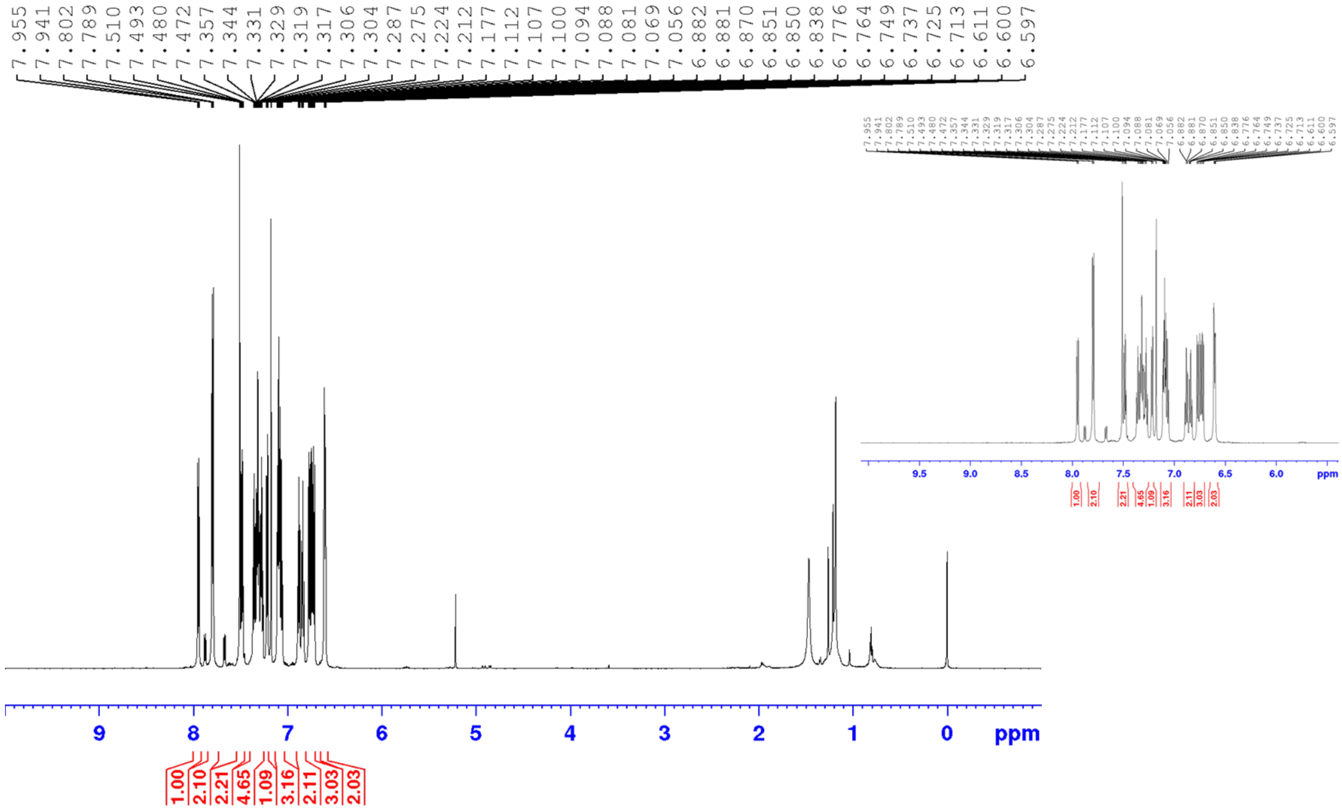
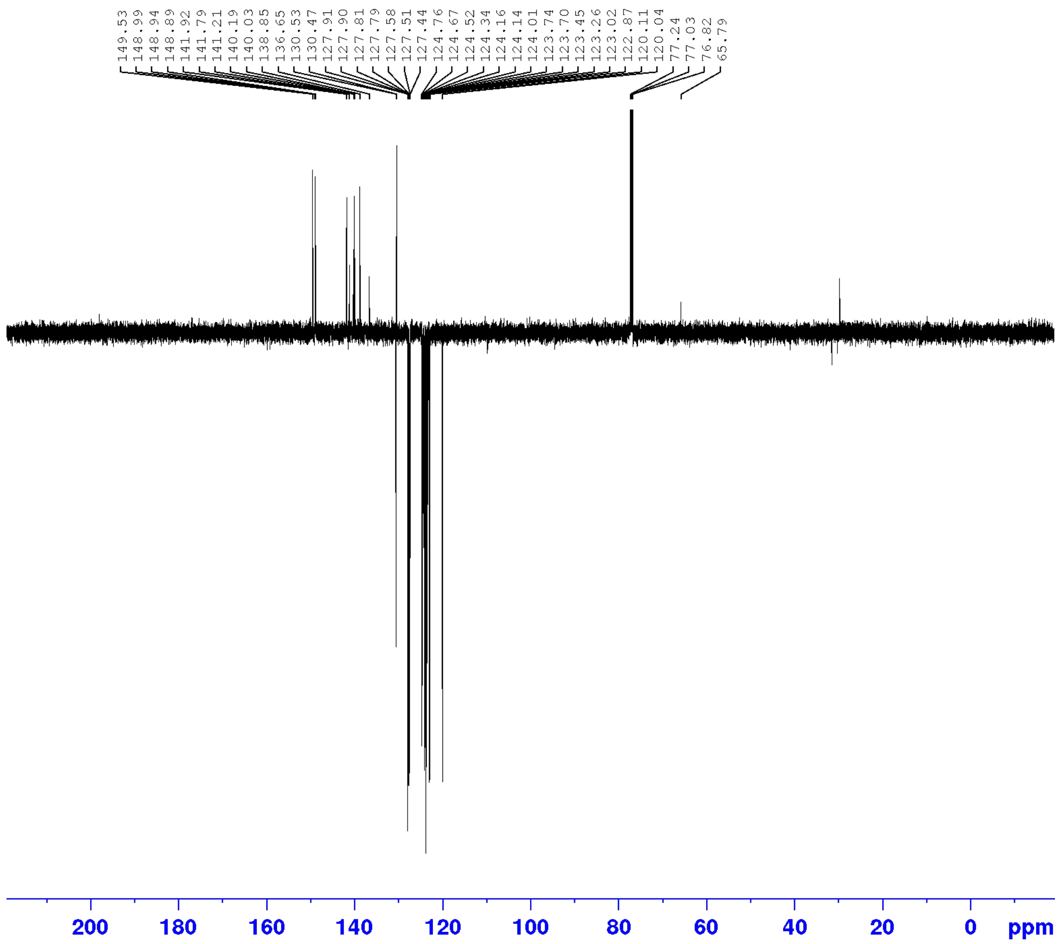


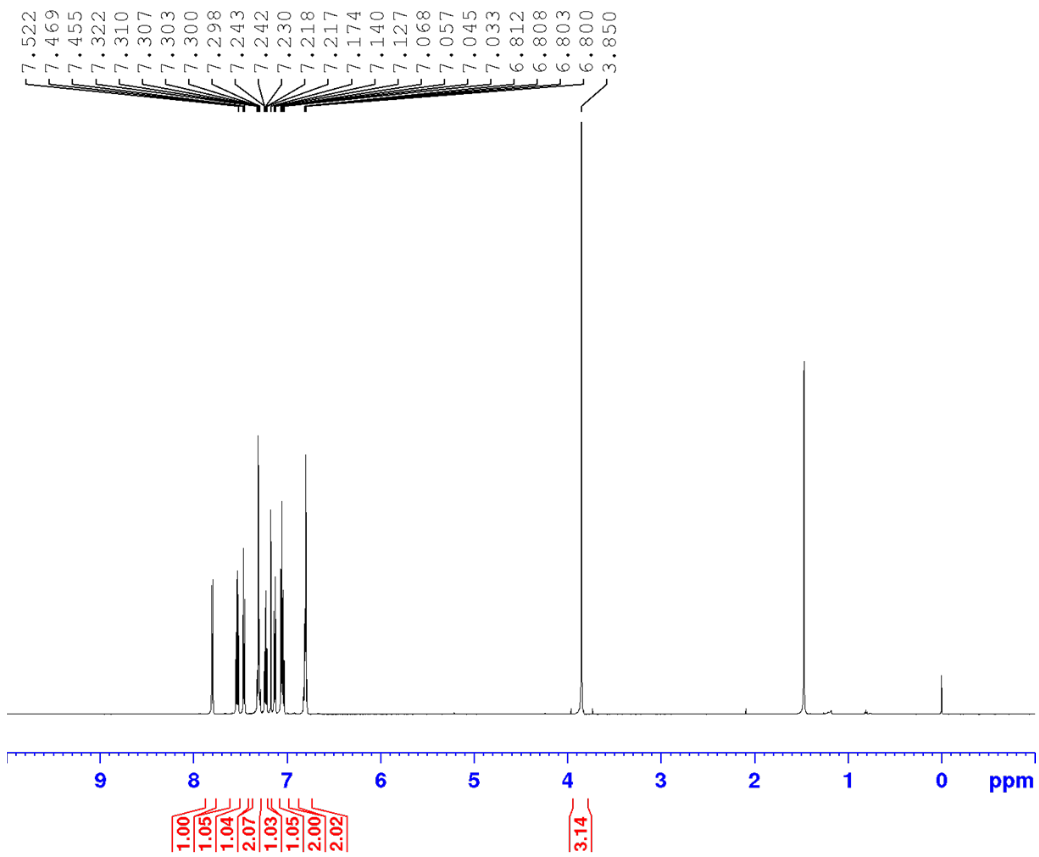
^{1}H NMR (600.33 MHz, $CDCl_3$) of compound **7**.



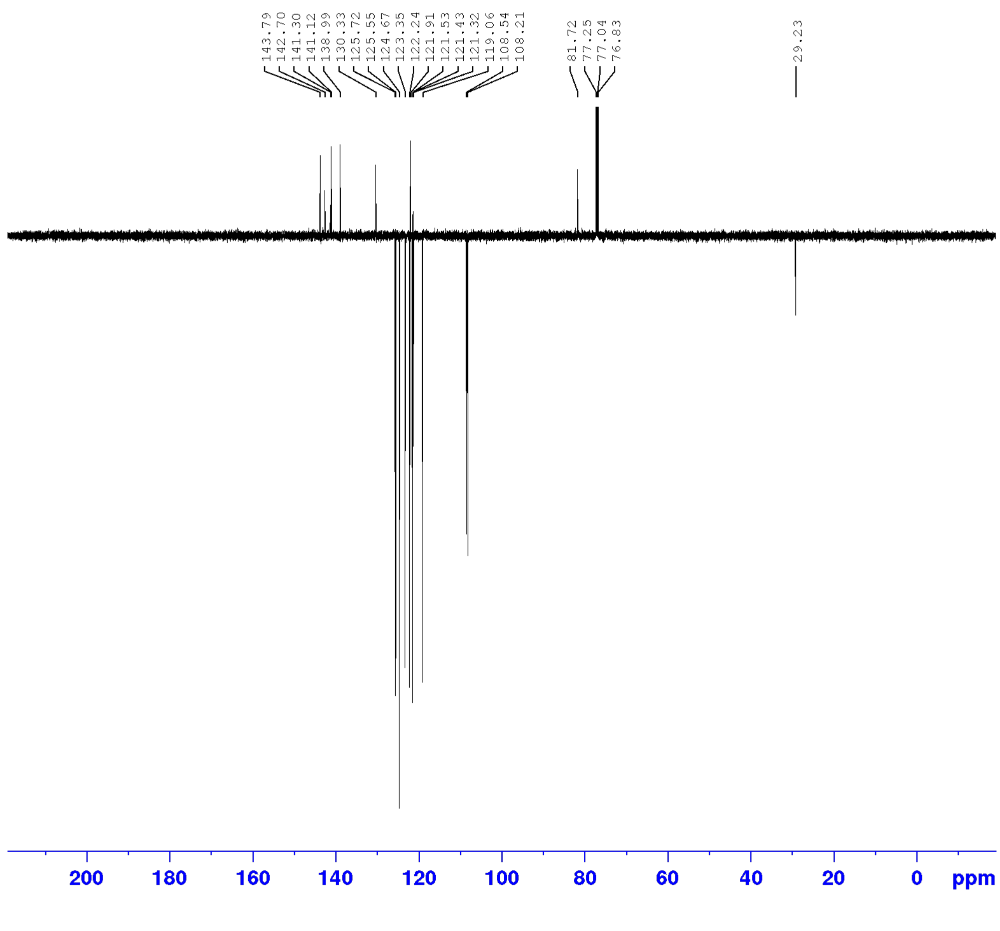
^{13}C NMR (150.95 MHz, $CDCl_3$) of compound **7**.



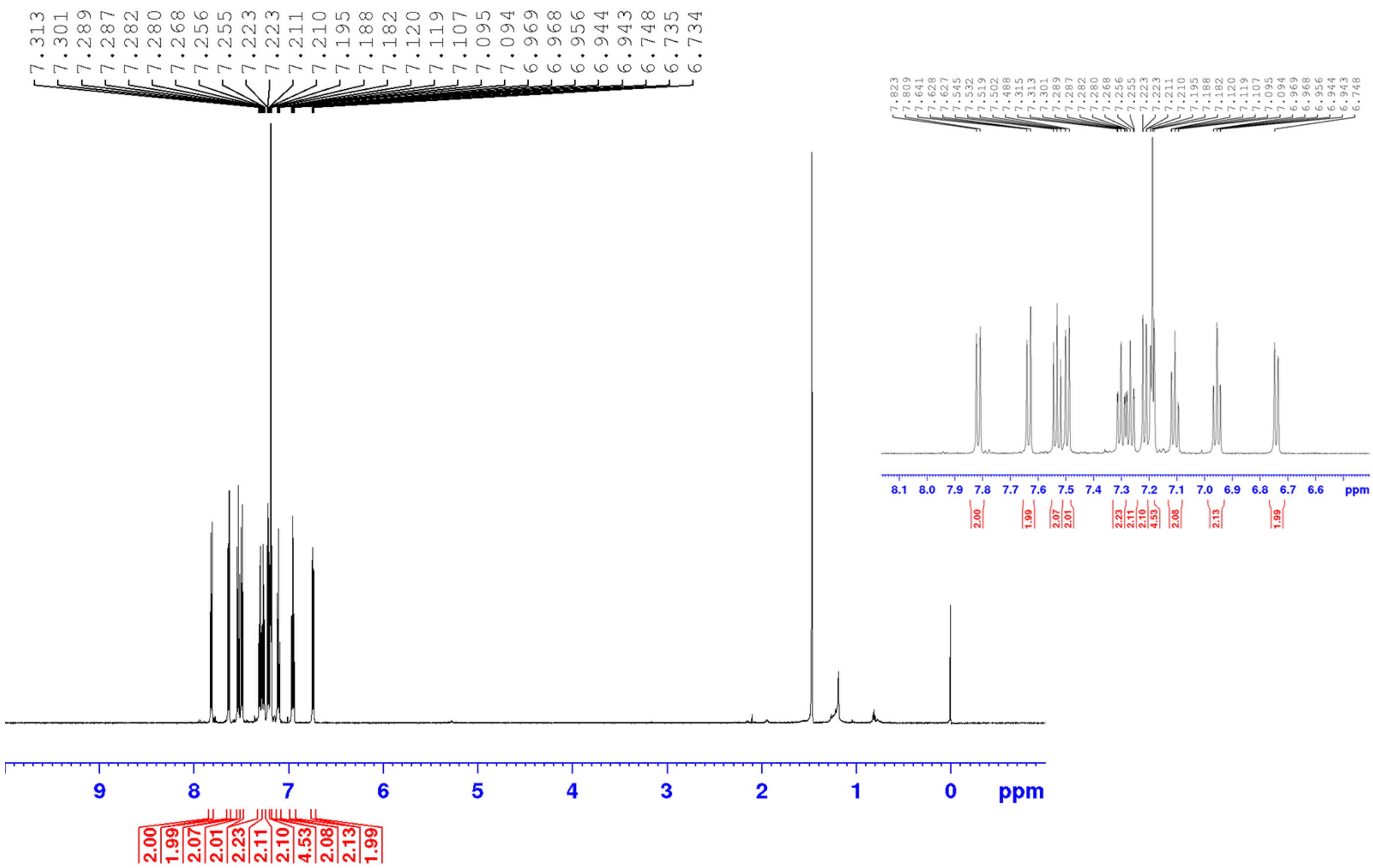
[1]H NMR (600.33 MHz, $CDCl_3$) of compound **12a**.



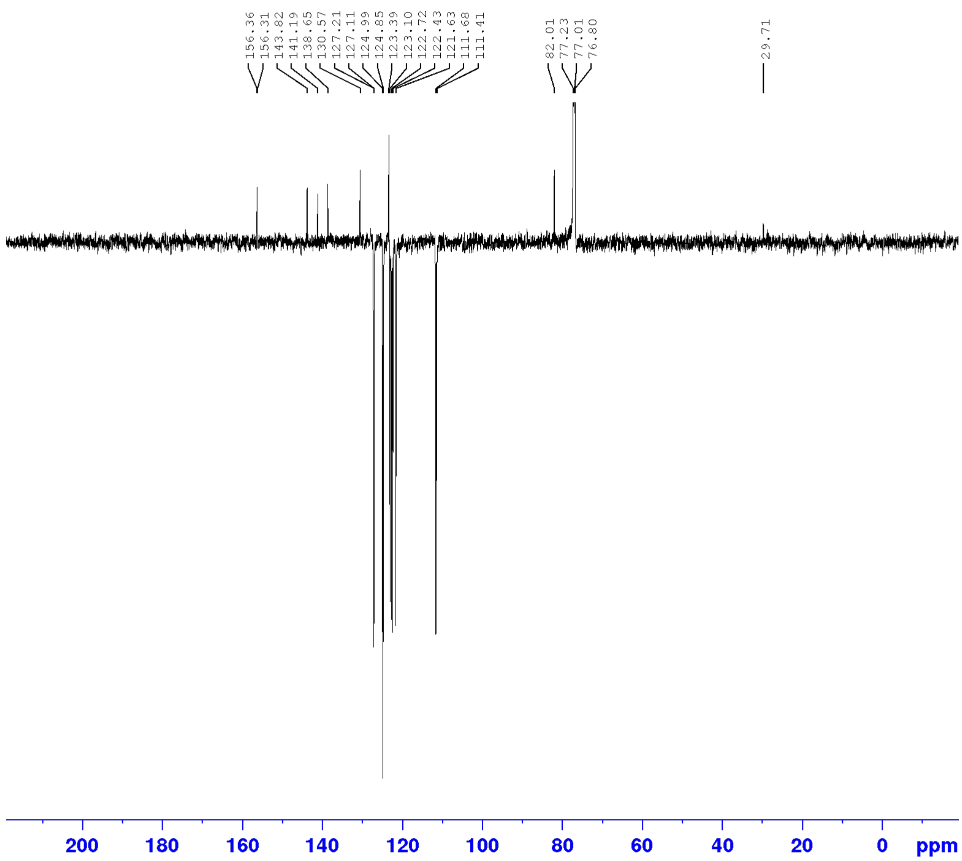
[13]C NMR (150.95 MHz, $CDCl_3$) of compound **12a**.



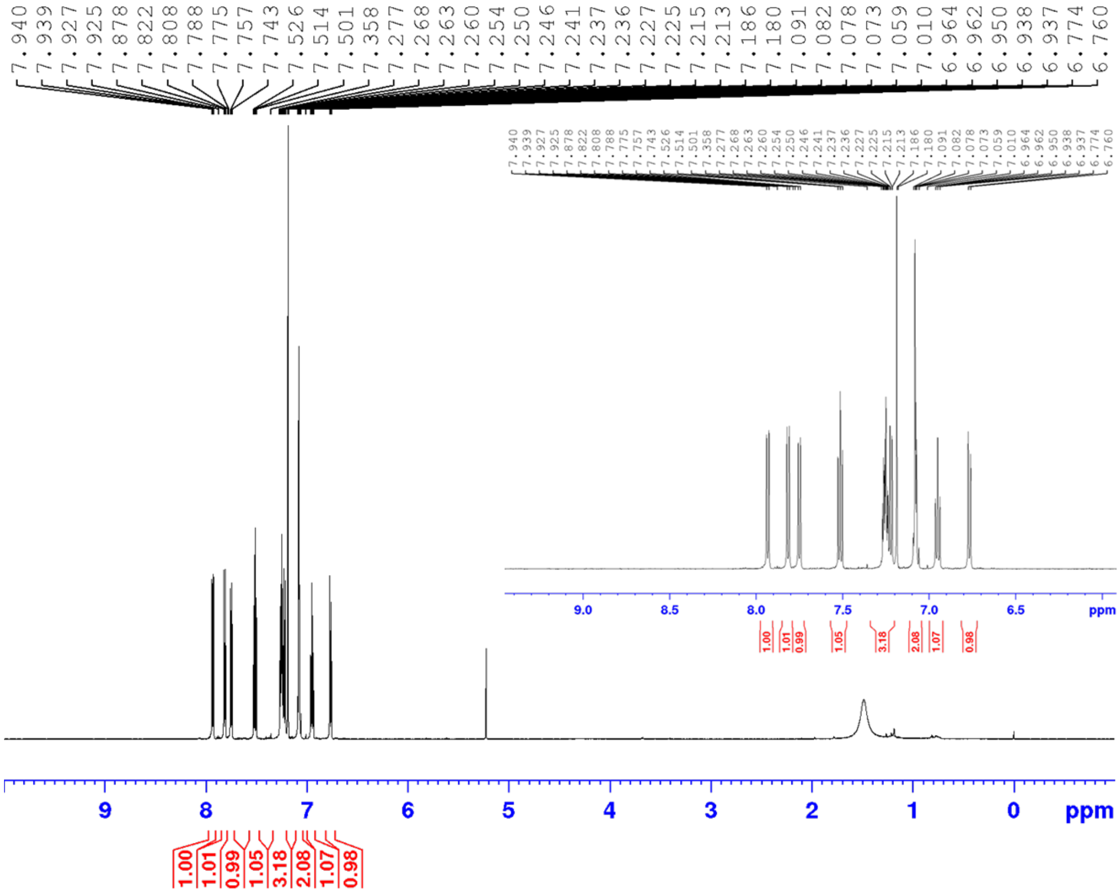
[1]H NMR (600.33 MHz, $CDCl_3$) of compound **12b**.



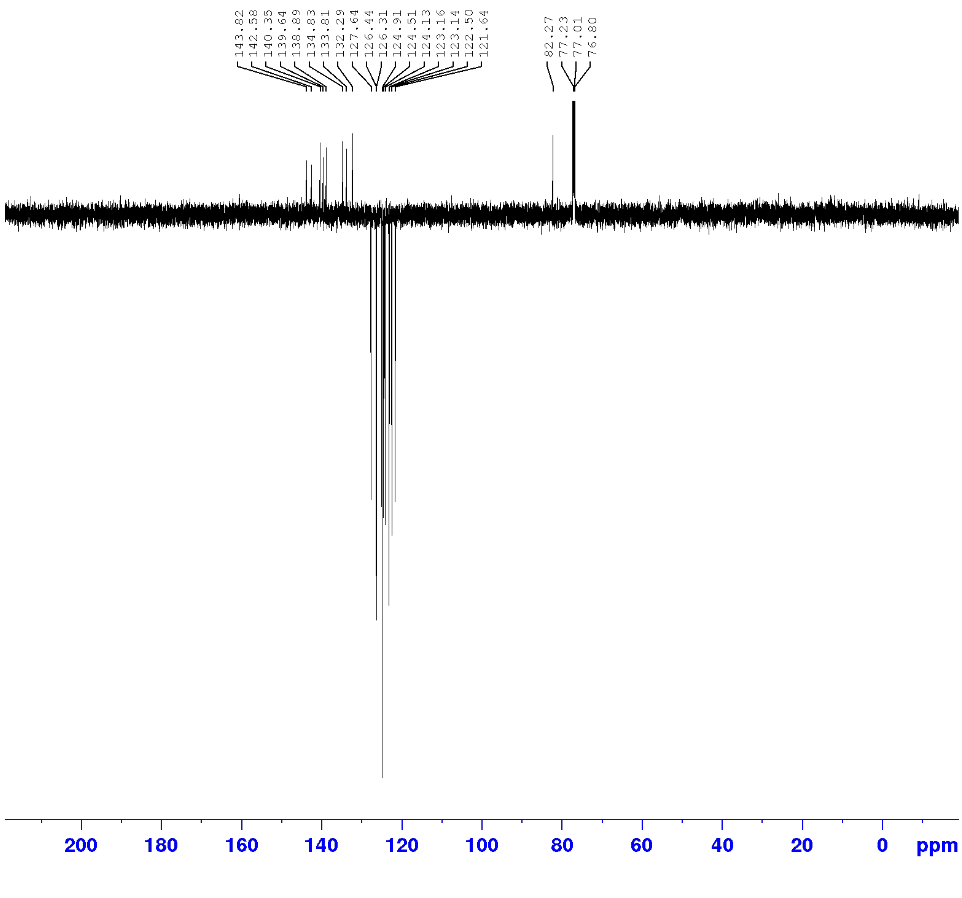
[13]C NMR (150.95 MHz, $CDCl_3$) of compound **12b**.



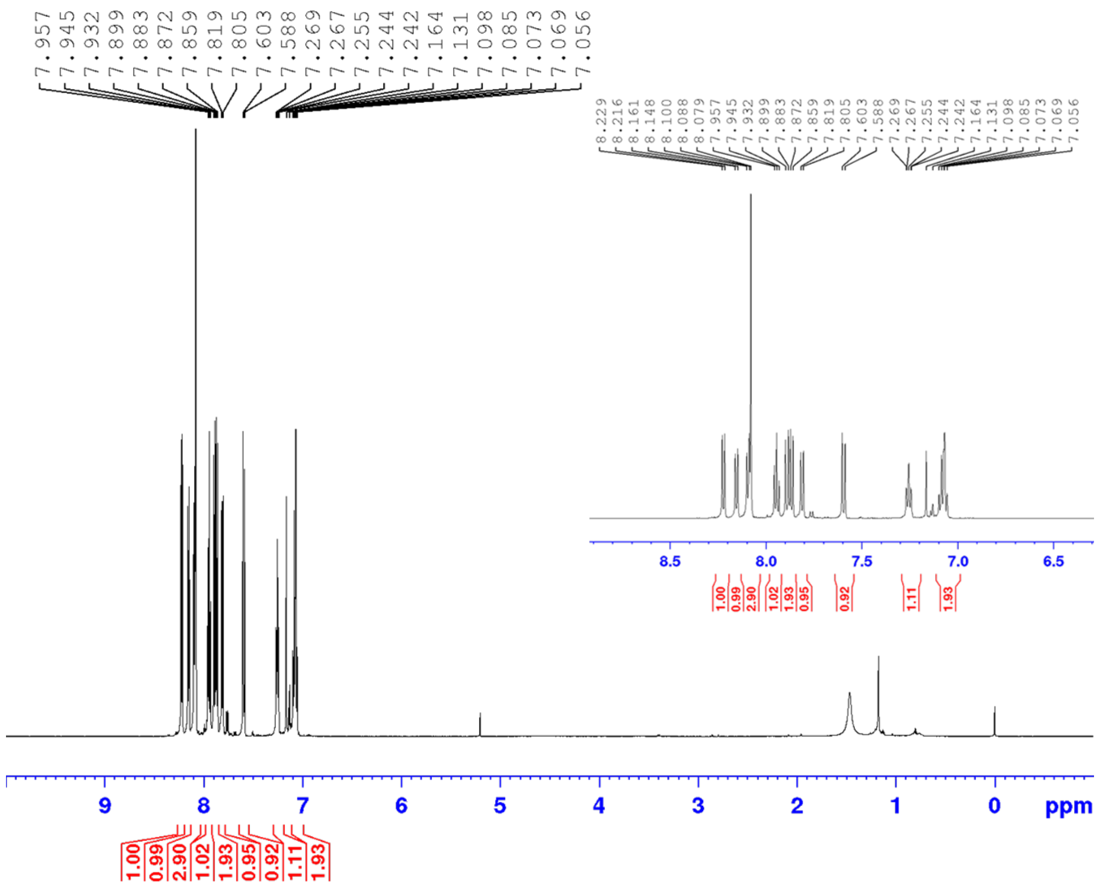
[1]H NMR (600.33 MHz, $CDCl_3$) of compound **12c**.



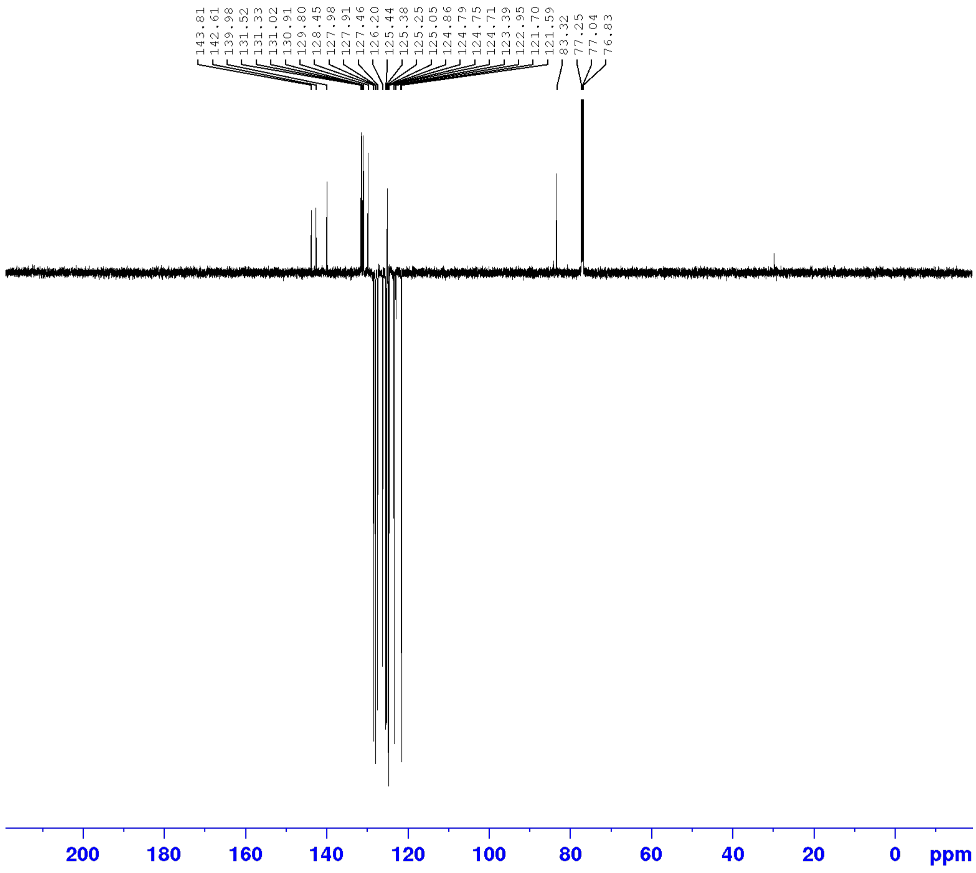
[13]C NMR (150.95 MHz, $CDCl_3$) of compound **12c**.



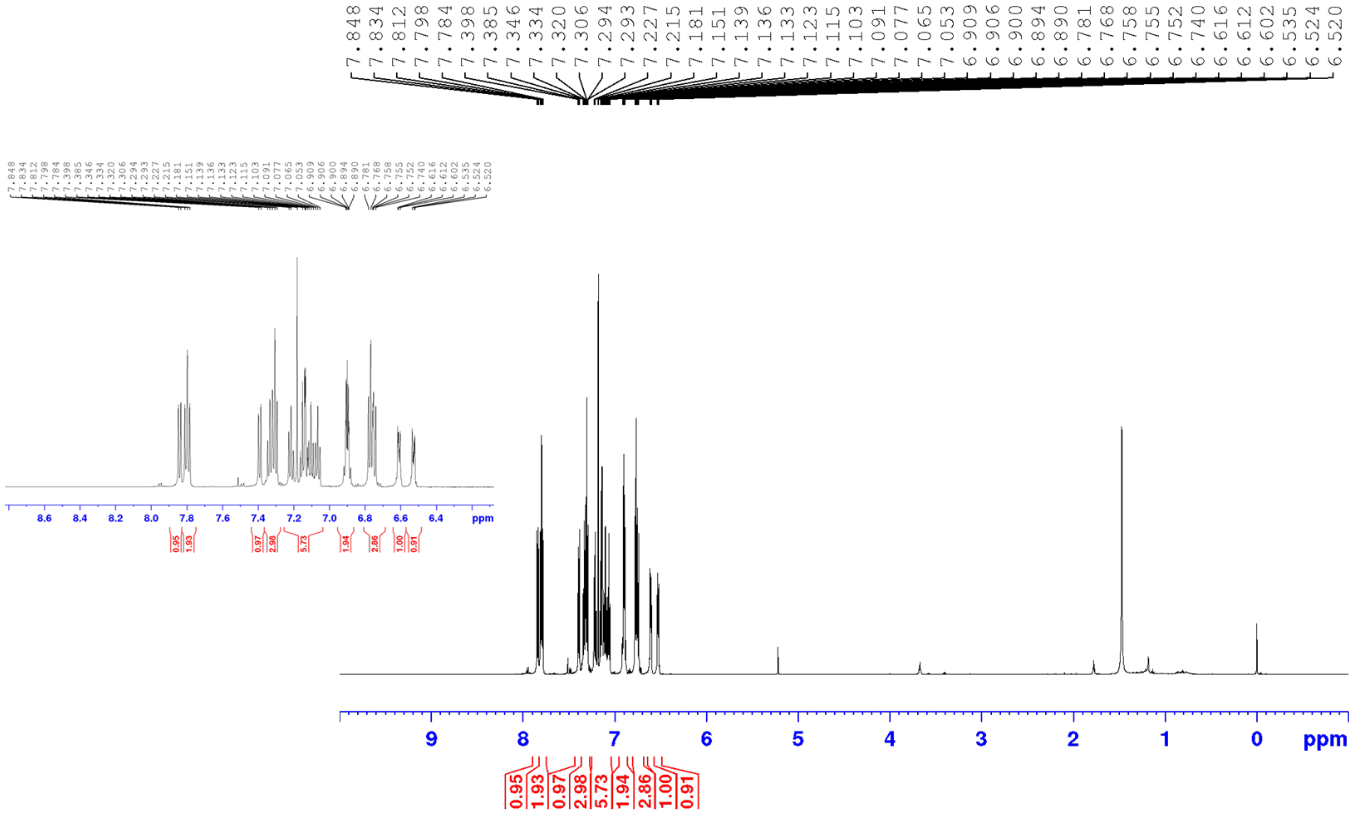
[1]H NMR (600.33 MHz, $CDCl_3$) of compound **13**.



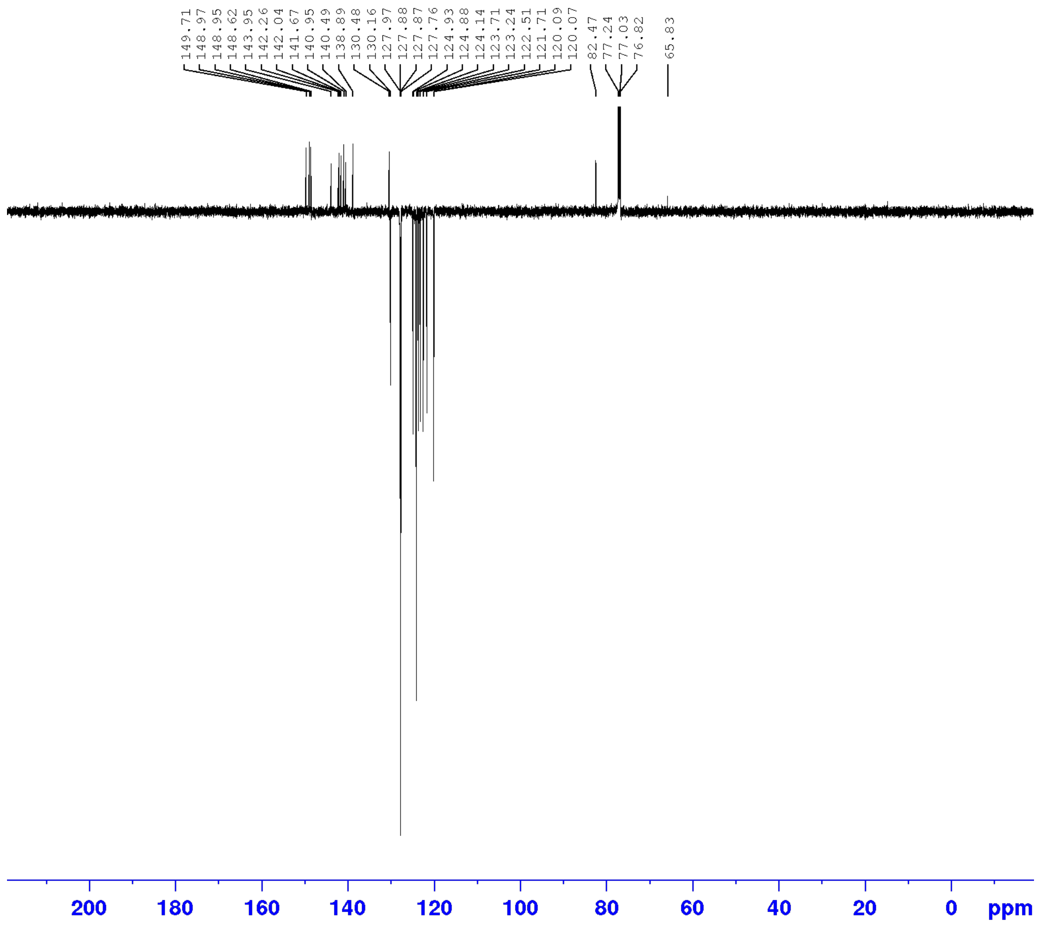
[13]C NMR (150.95 MHz, $CDCl_3$) of compound **13**.



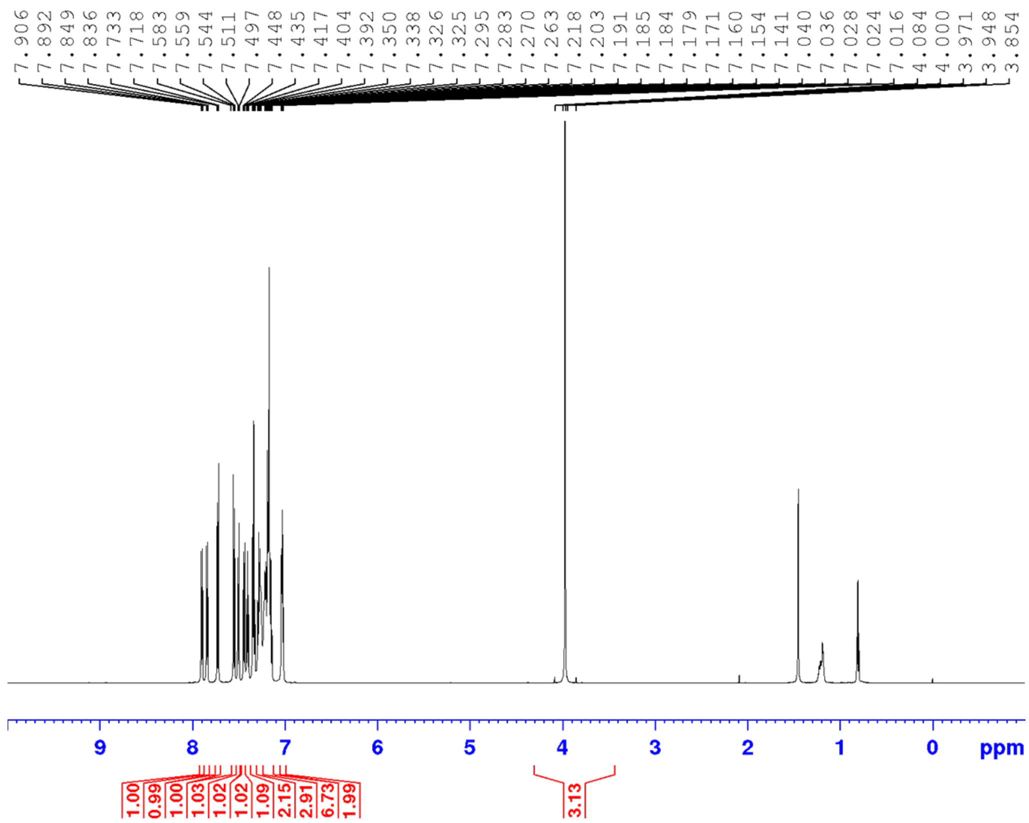
^{1}H NMR (600.33 MHz, $CDCl_3$) of compound **14**.



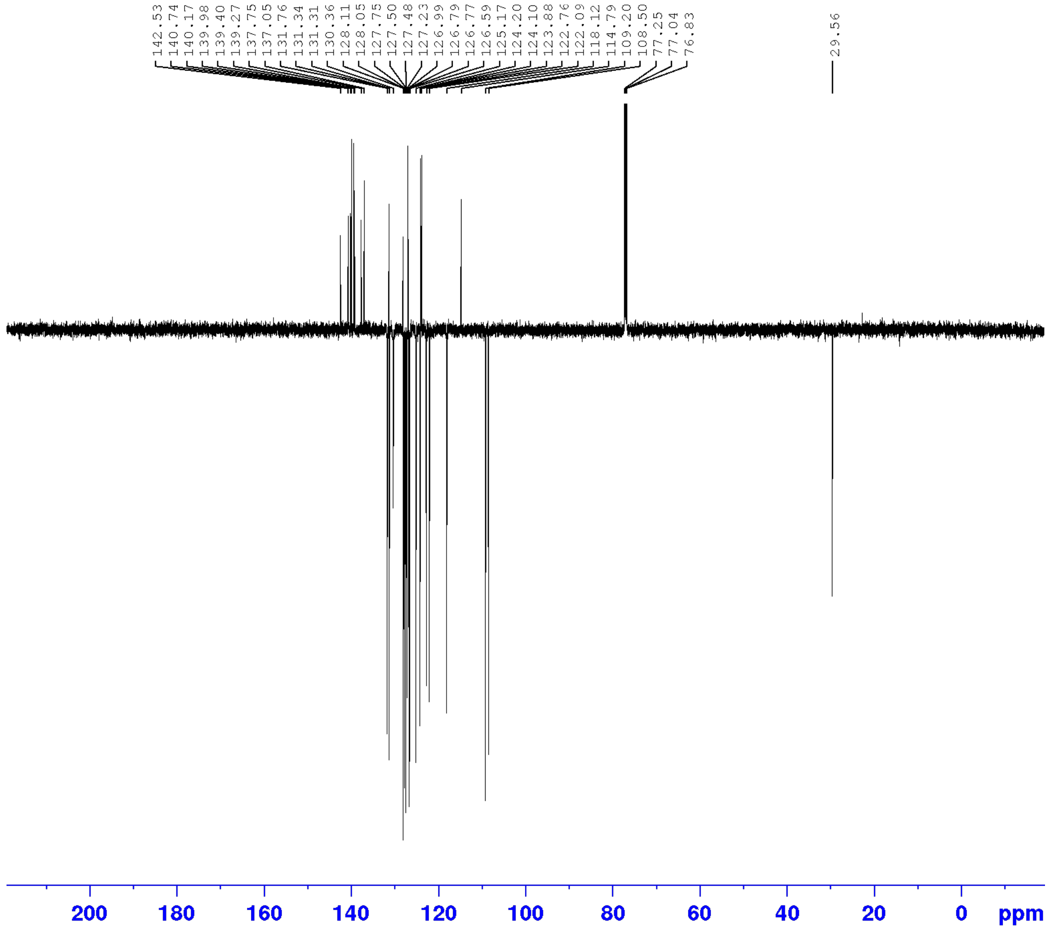
^{13}C NMR (150.95 MHz, $CDCl_3$) of compound **14**.



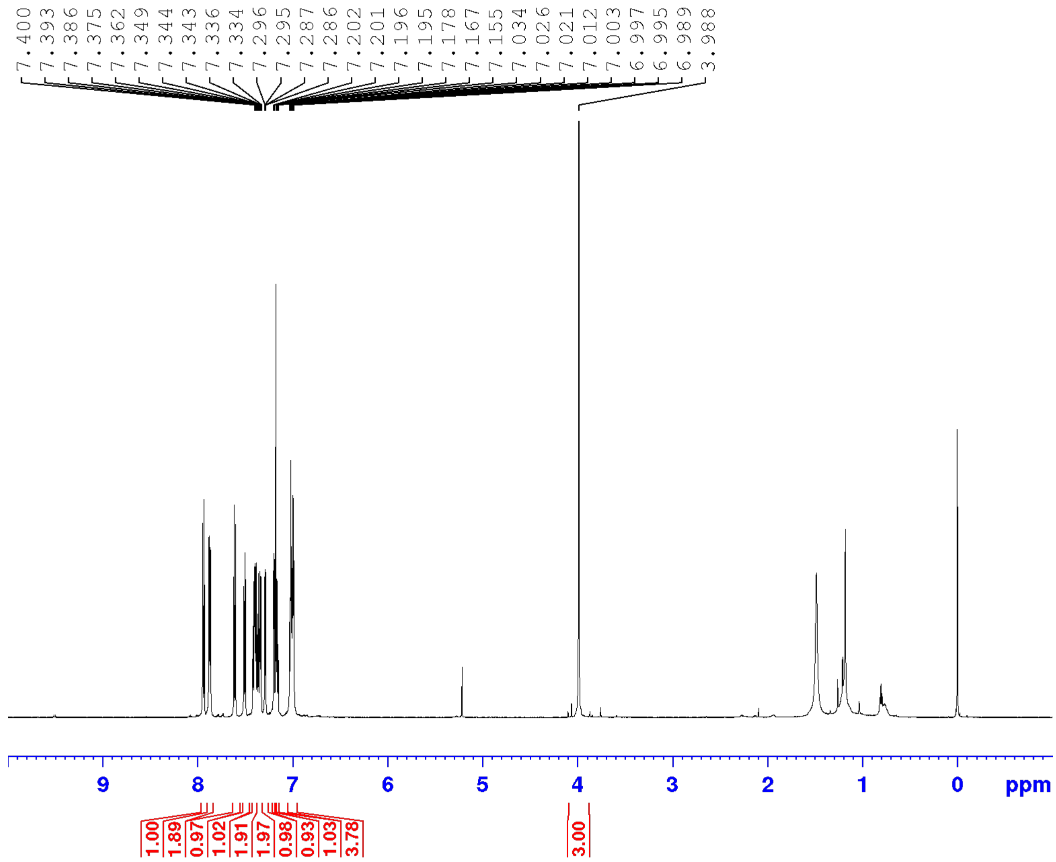
^{1}H NMR (600.33 MHz, $CDCl_3$) of compound **1aa**.



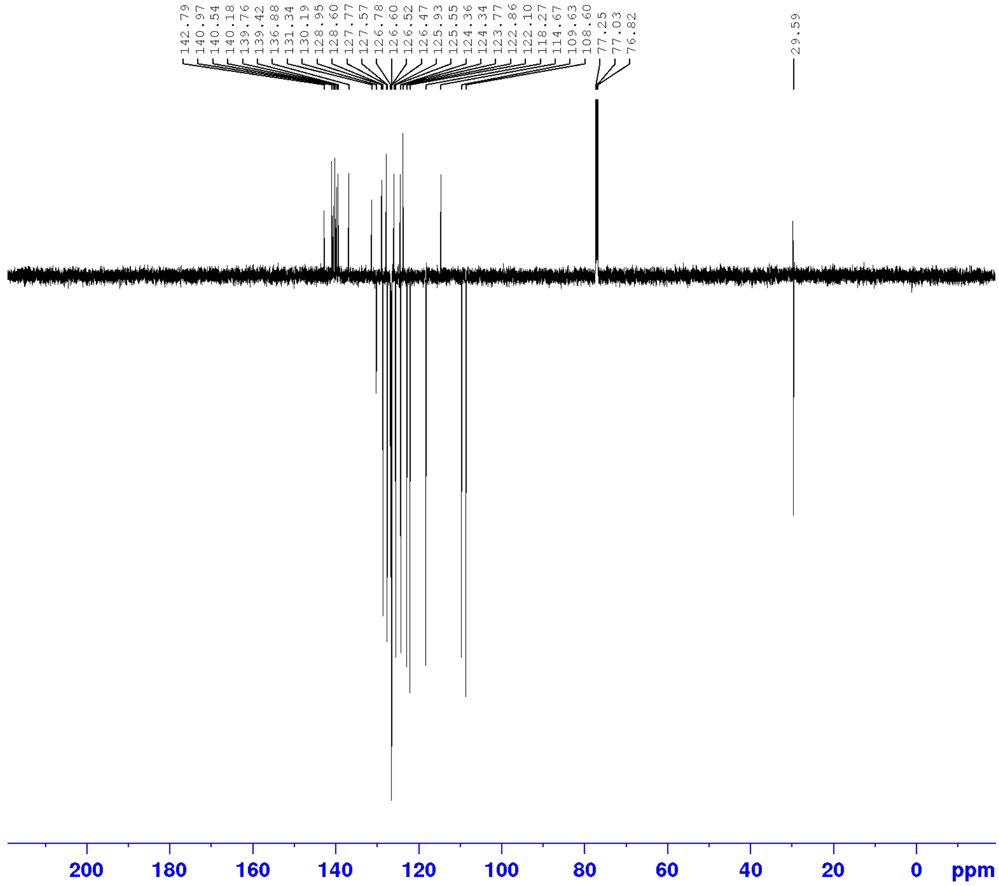
^{13}C NMR (150.95 MHz, $CDCl_3$) of compound **1aa**.



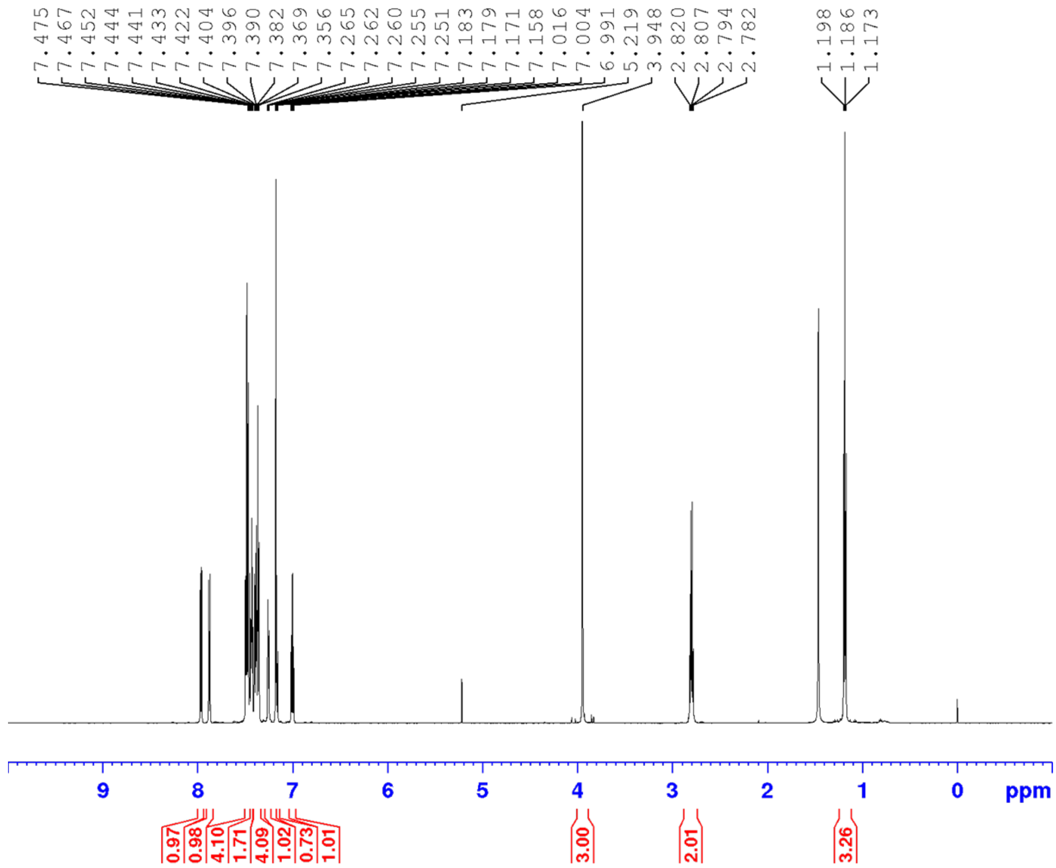
^{1}H NMR (600.33 MHz, $CDCl_3$) of compound **1ab**.



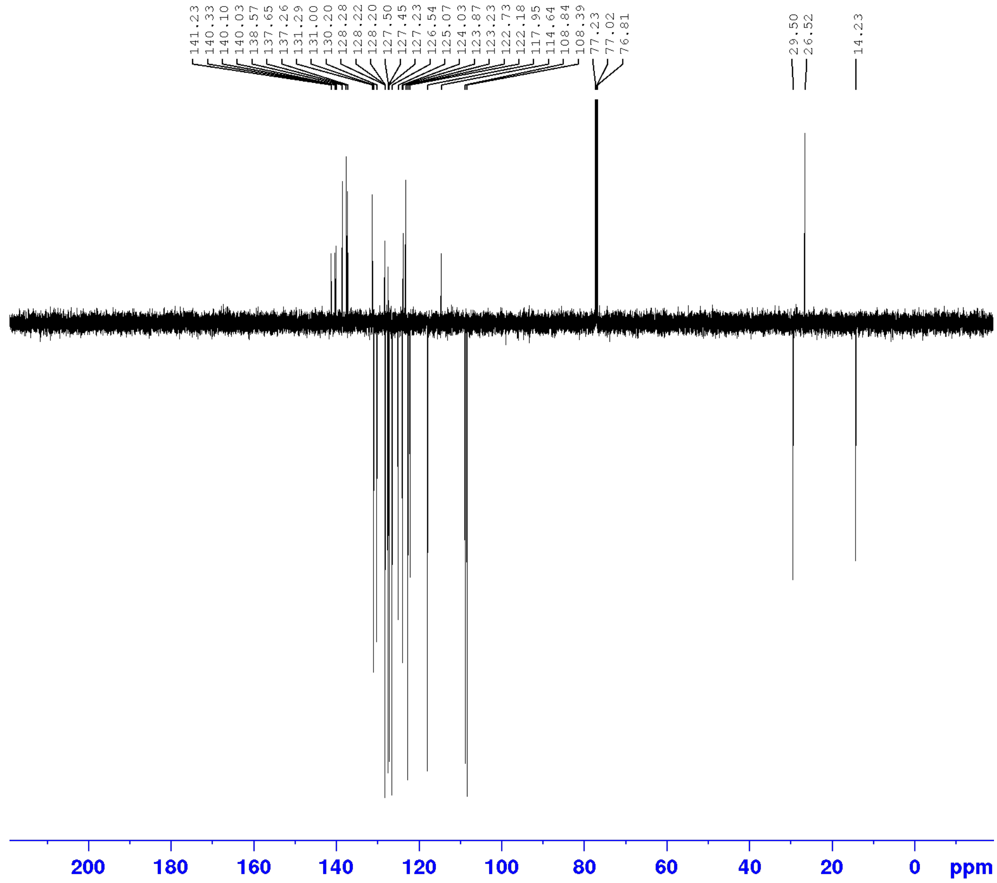
^{13}C NMR (150.95 MHz, $CDCl_3$) of compound **1ab**.



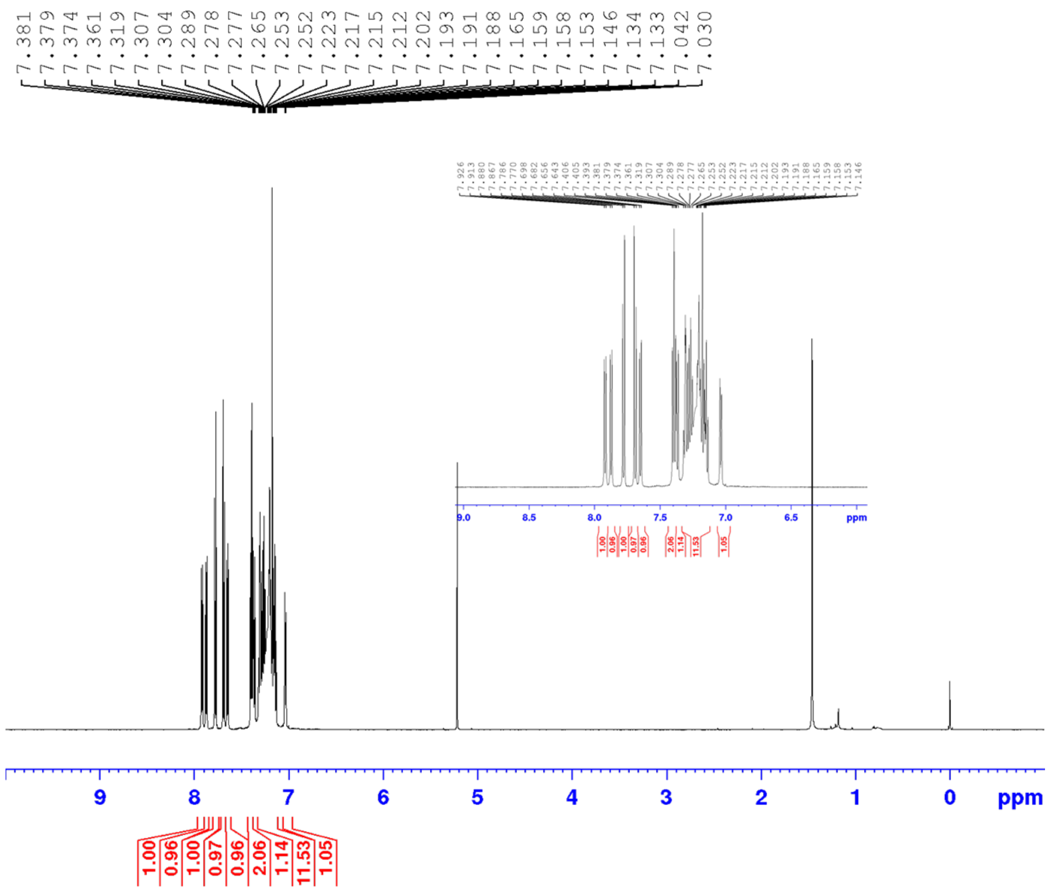
^{1}H NMR (600.33 MHz, $CDCl_3$) of compound **1ac**.



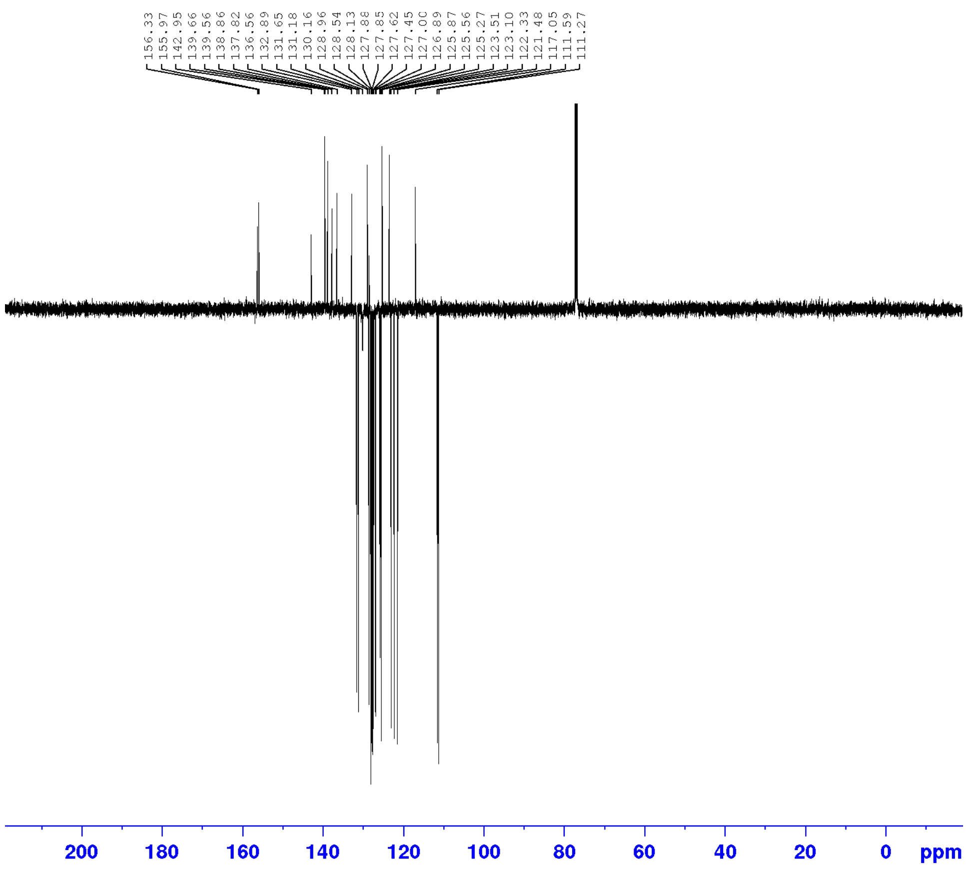
^{13}C NMR (150.95 MHz, $CDCl_3$) of compound **1ac**.



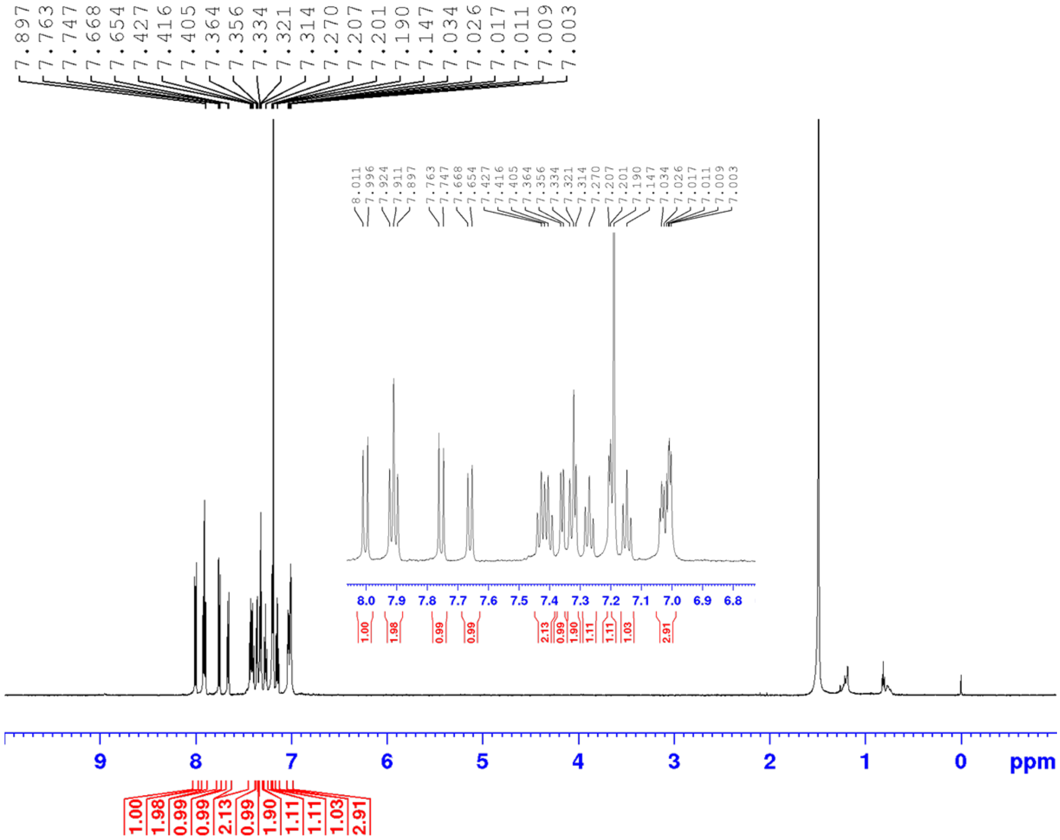
[1]H NMR (600.33 MHz, $CDCl_3$) of compound **1ba**.



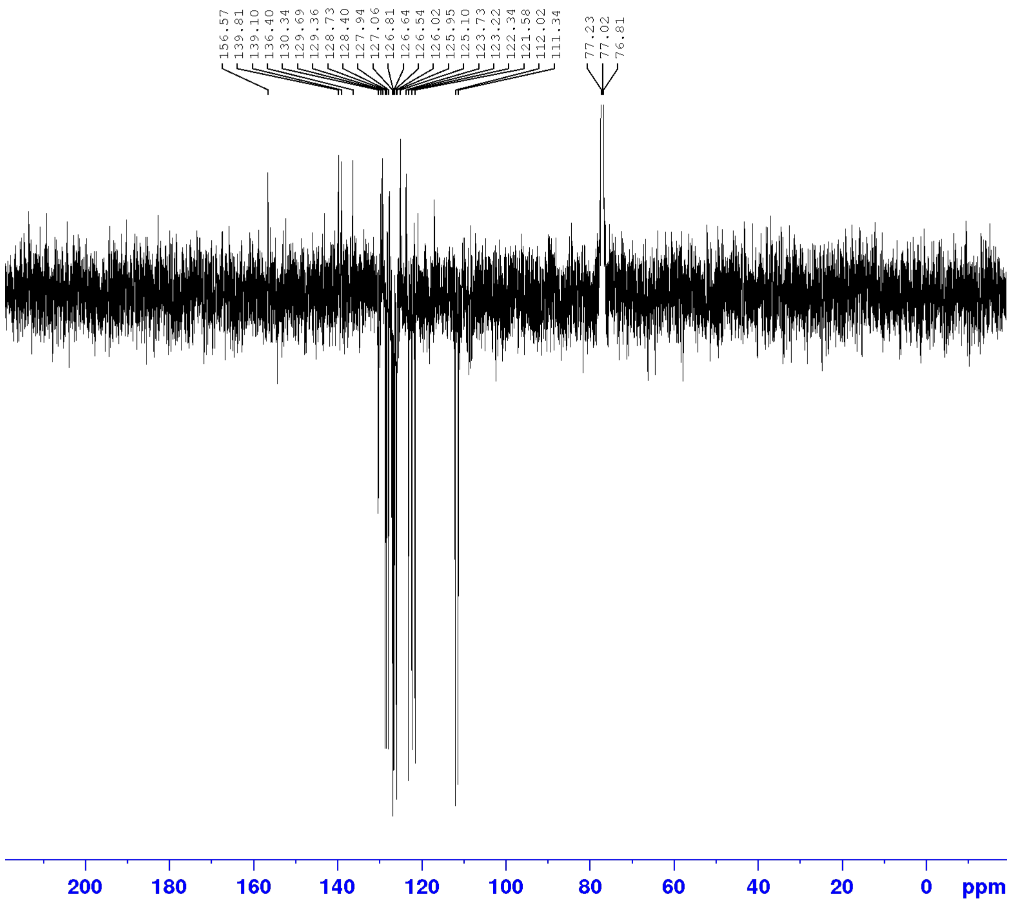
[13]C NMR (150.95 MHz, $CDCl_3$) of compound **1ba**.



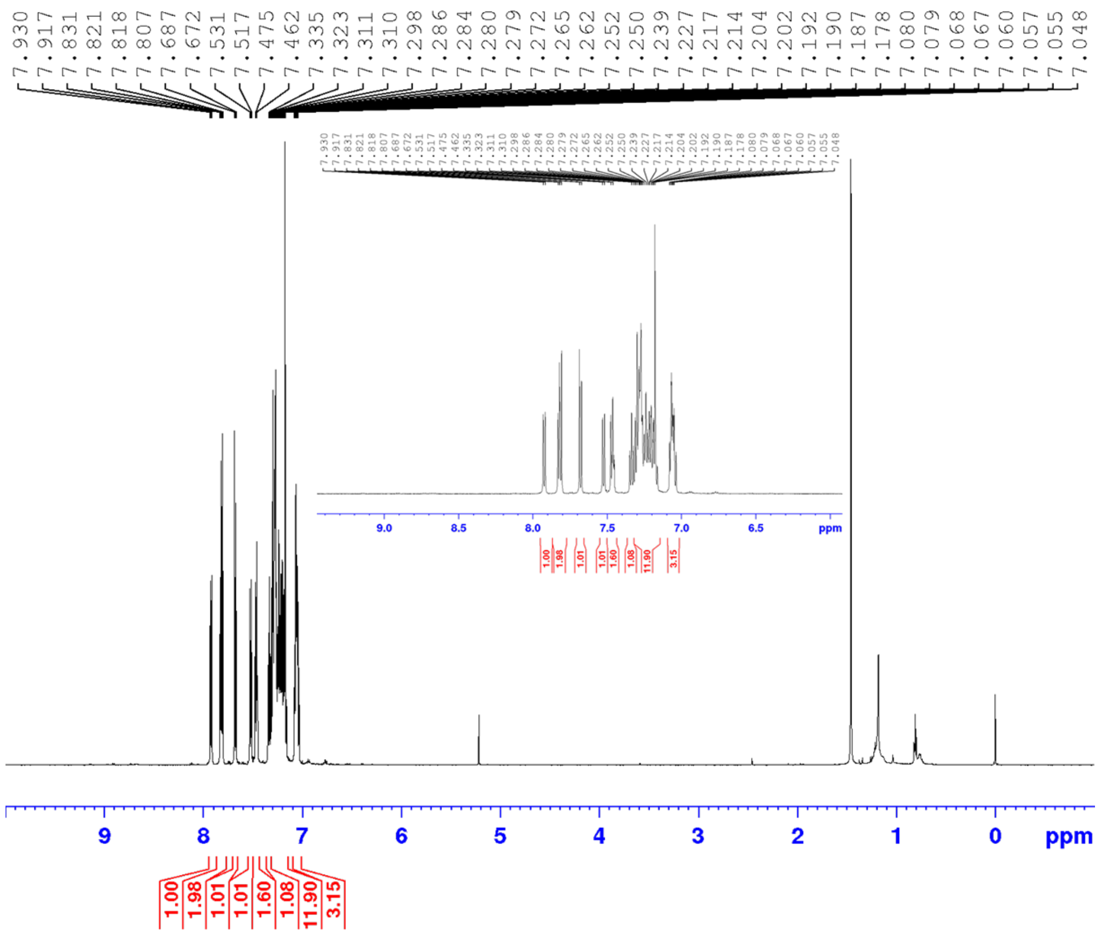
^{1}H NMR (600.33 MHz, $CDCl_3$) of compound **1bb**.



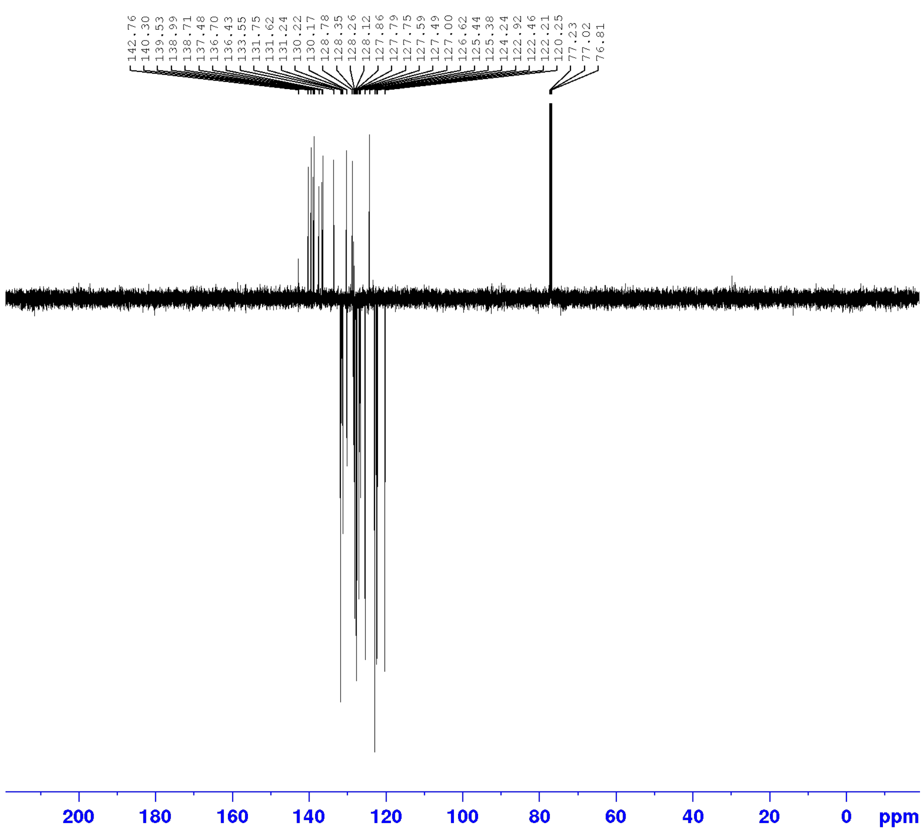
^{13}C NMR (150.95 MHz, $CDCl_3$) of compound **1bb**.



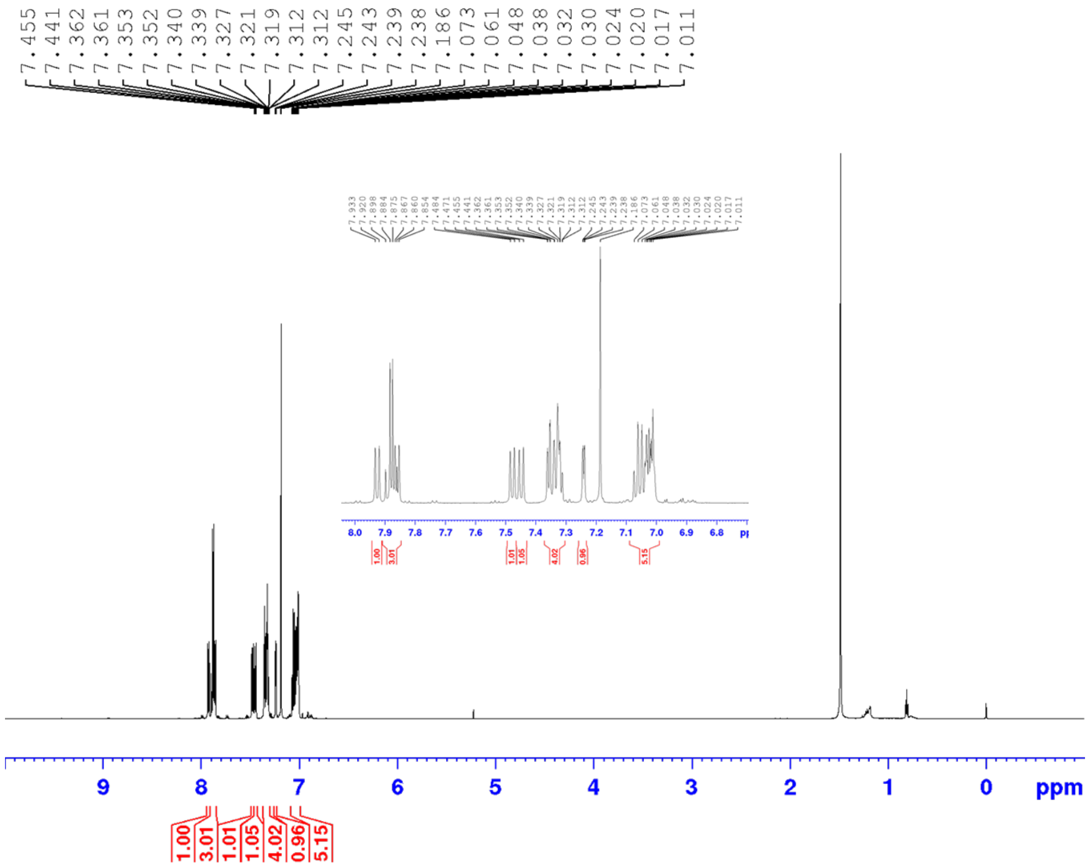
^{1}H NMR (600.33 MHz, $CDCl_3$) of compound **1ca**.



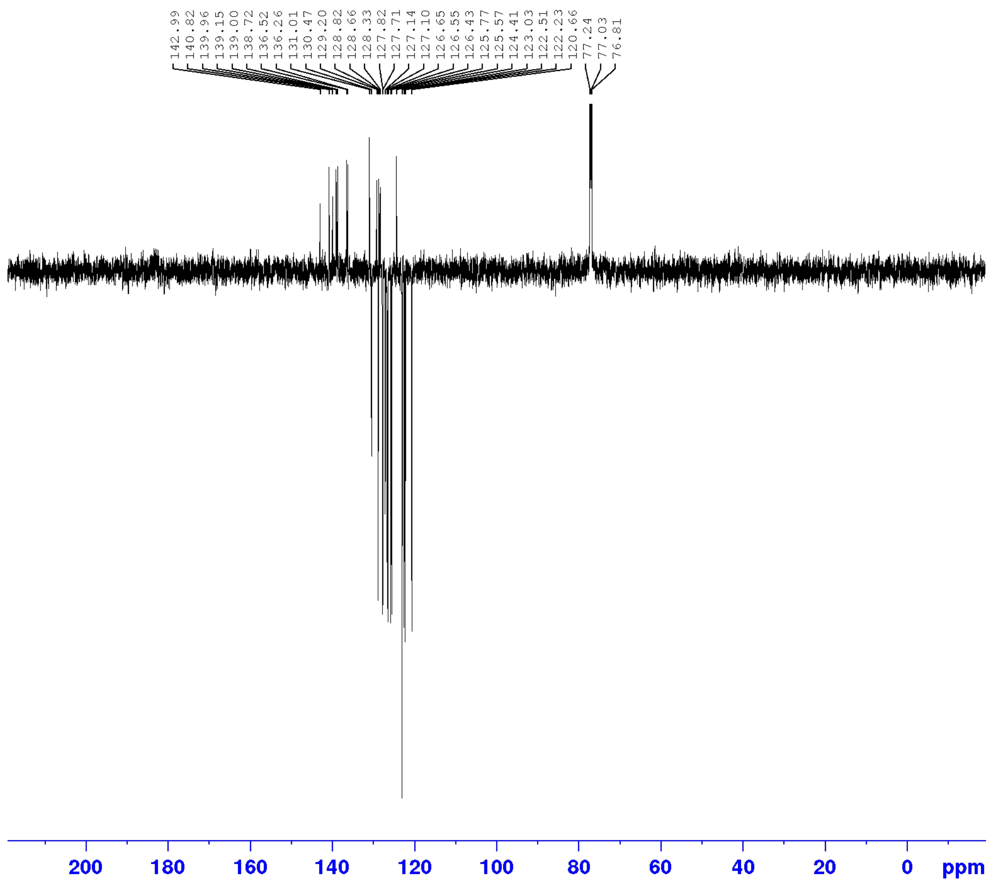
^{13}C NMR (150.95 MHz, $CDCl_3$) of compound **1ca**.



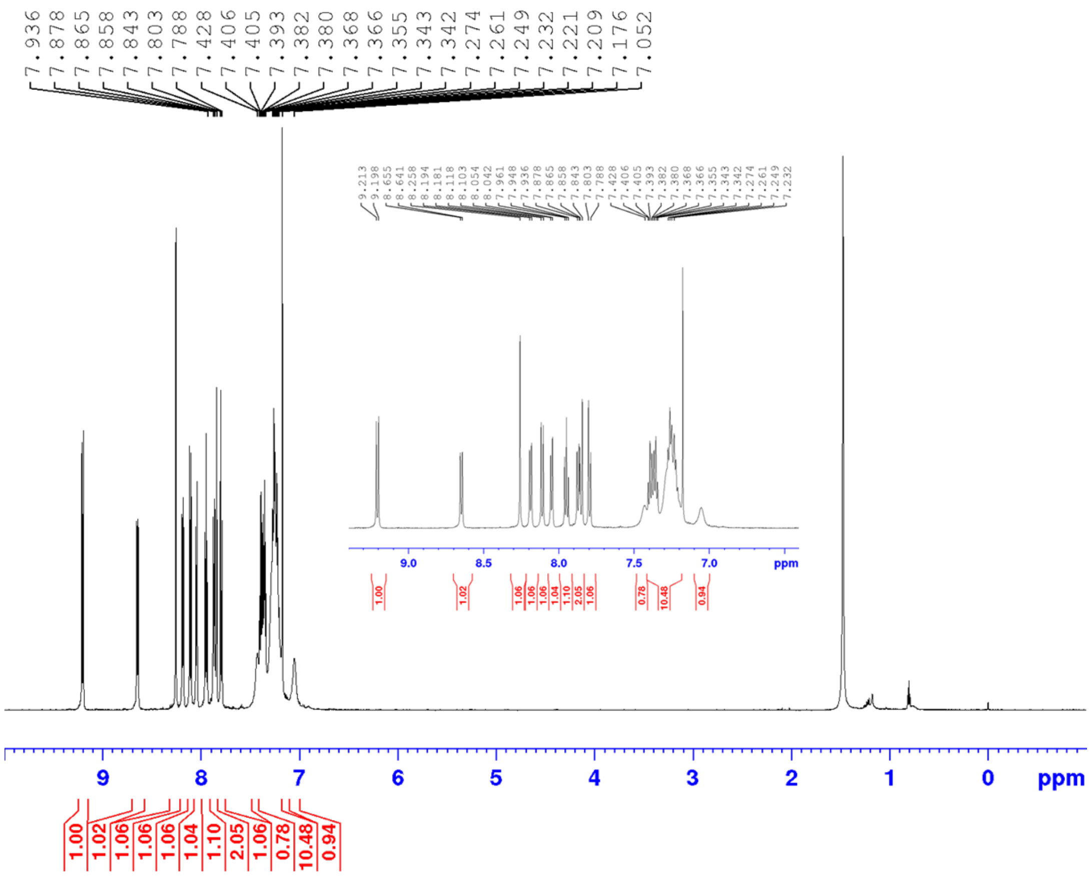
^{1}H NMR (600.33 MHz, $CDCl_3$) of compound **1cb**.



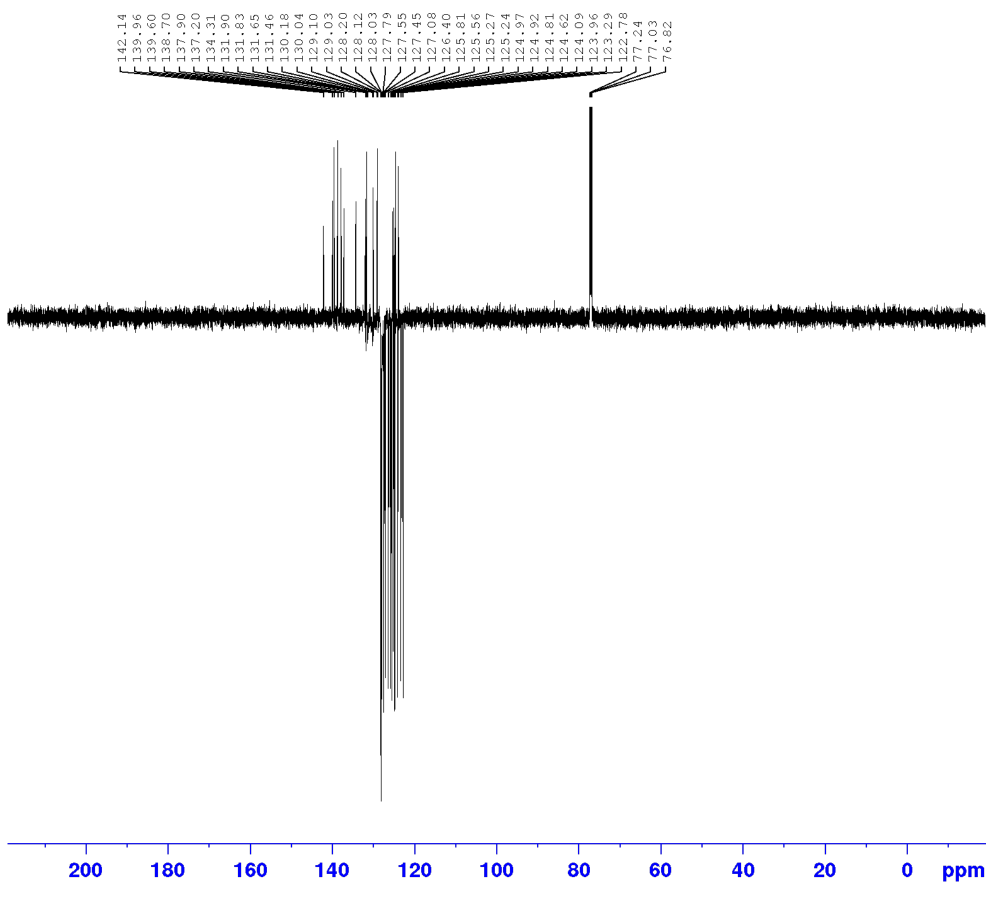
^{13}C NMR (150.95 MHz, $CDCl_3$) of compound **1cb**.



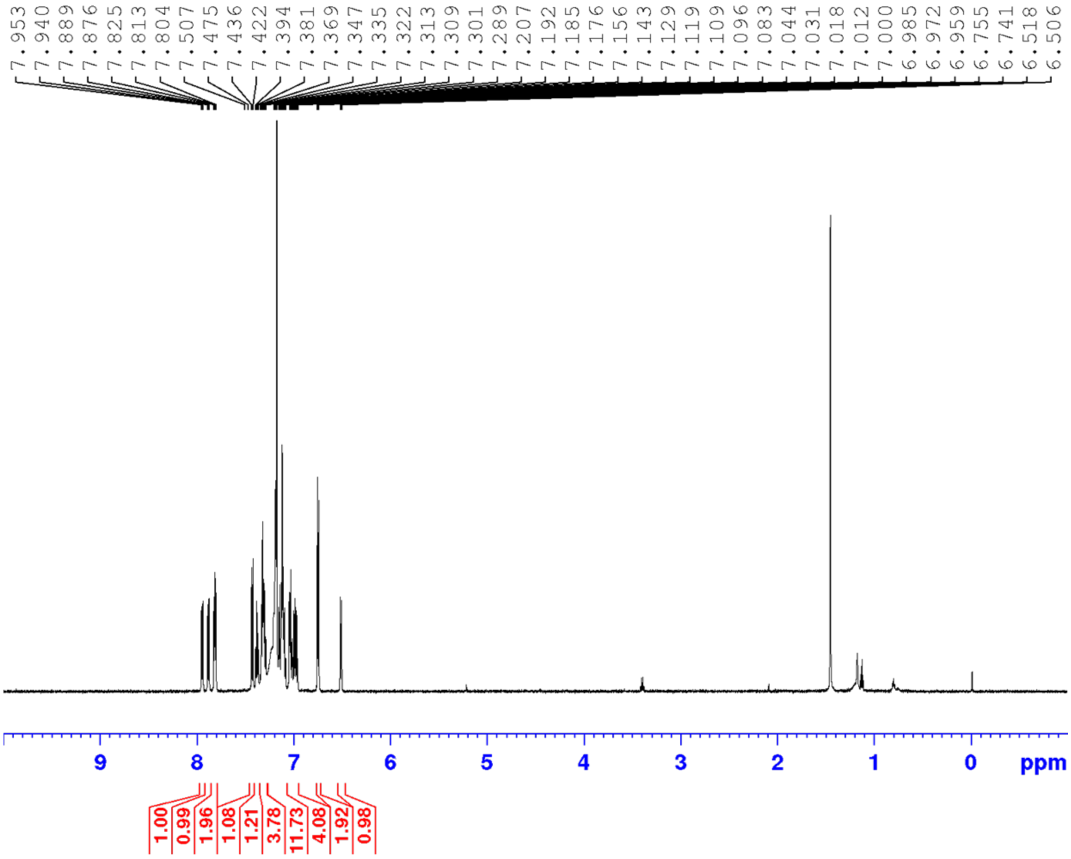
^{1}H NMR (600.33 MHz, $CDCl_3$) of compound **3**.



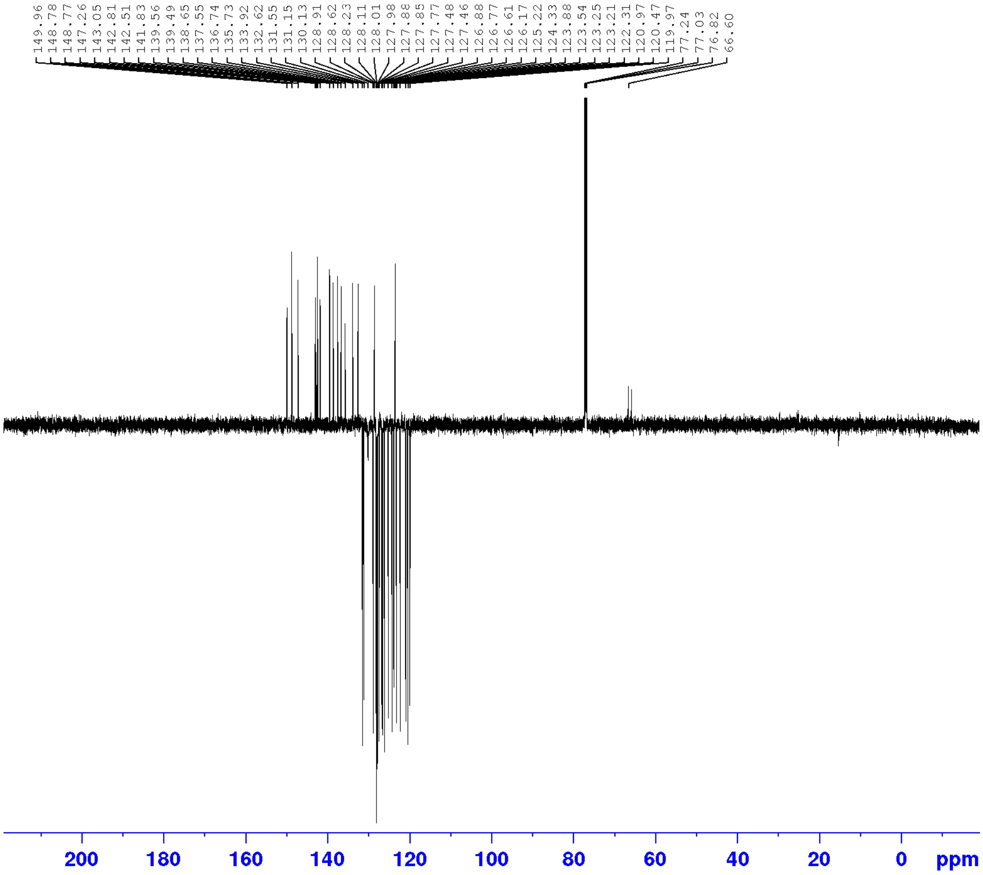
^{13}C NMR (150.95 MHz, $CDCl_3$) of compound **3**.



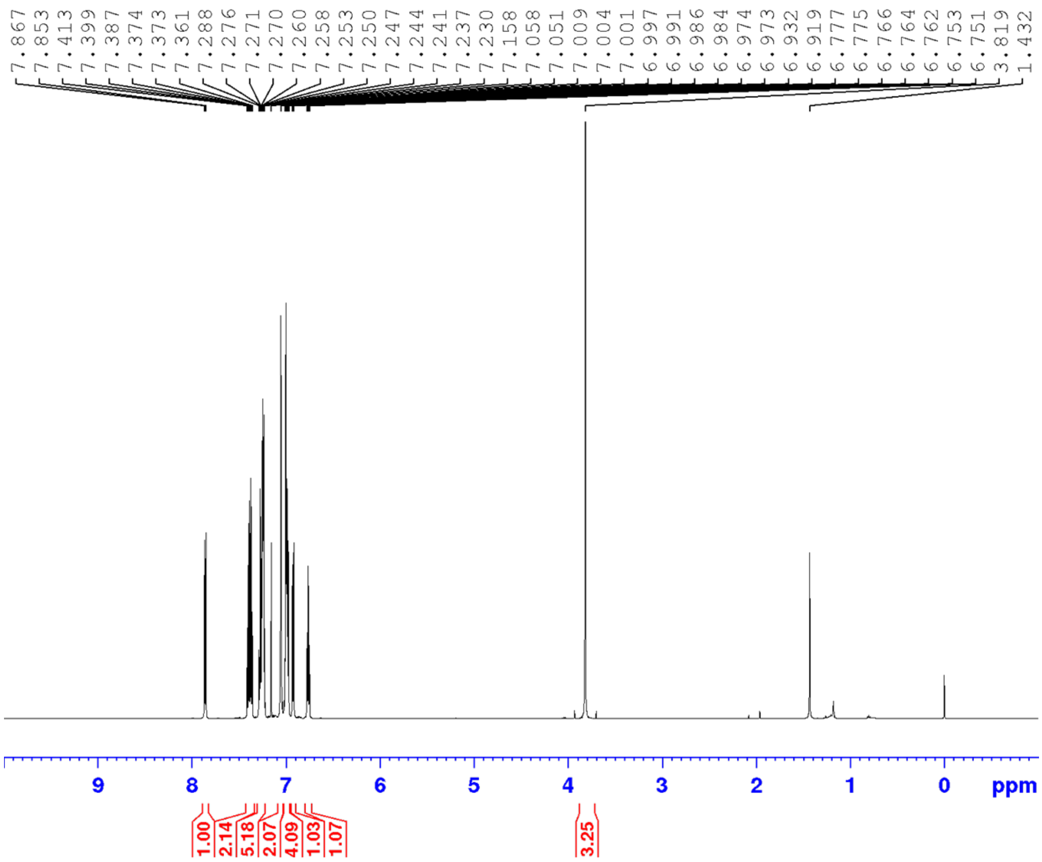
^{1}H NMR (600.33 MHz, $CDCl_3$) of compound **4**.



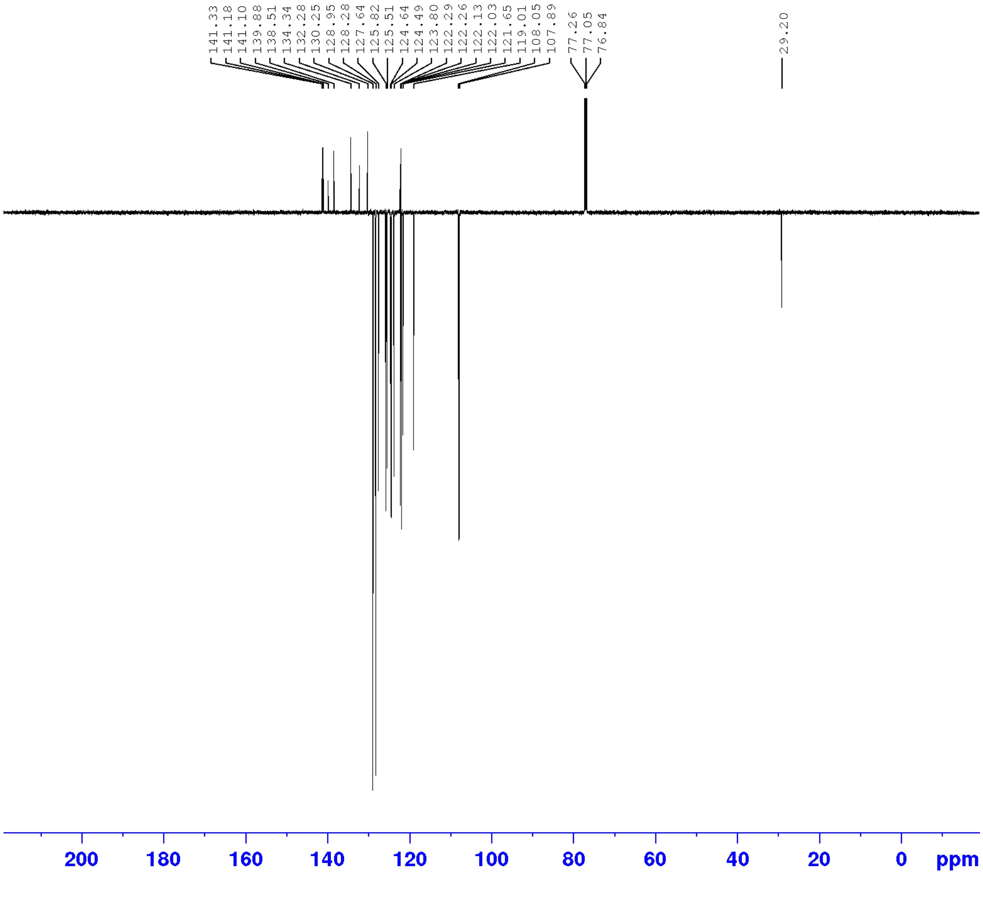
^{13}C NMR (150.95 MHz, $CDCl_3$) of compound **4**.



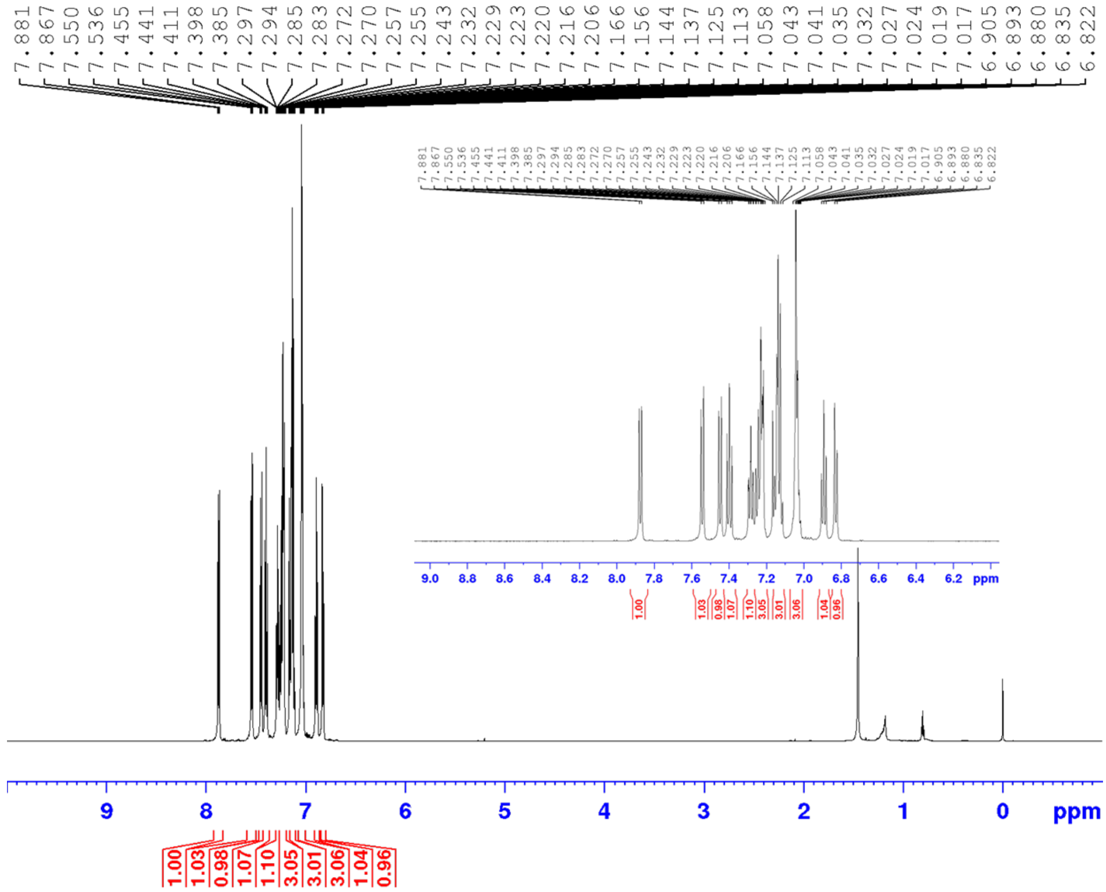
^{1}H NMR (600.33 MHz, $CDCl_3$) of compound **17a**.



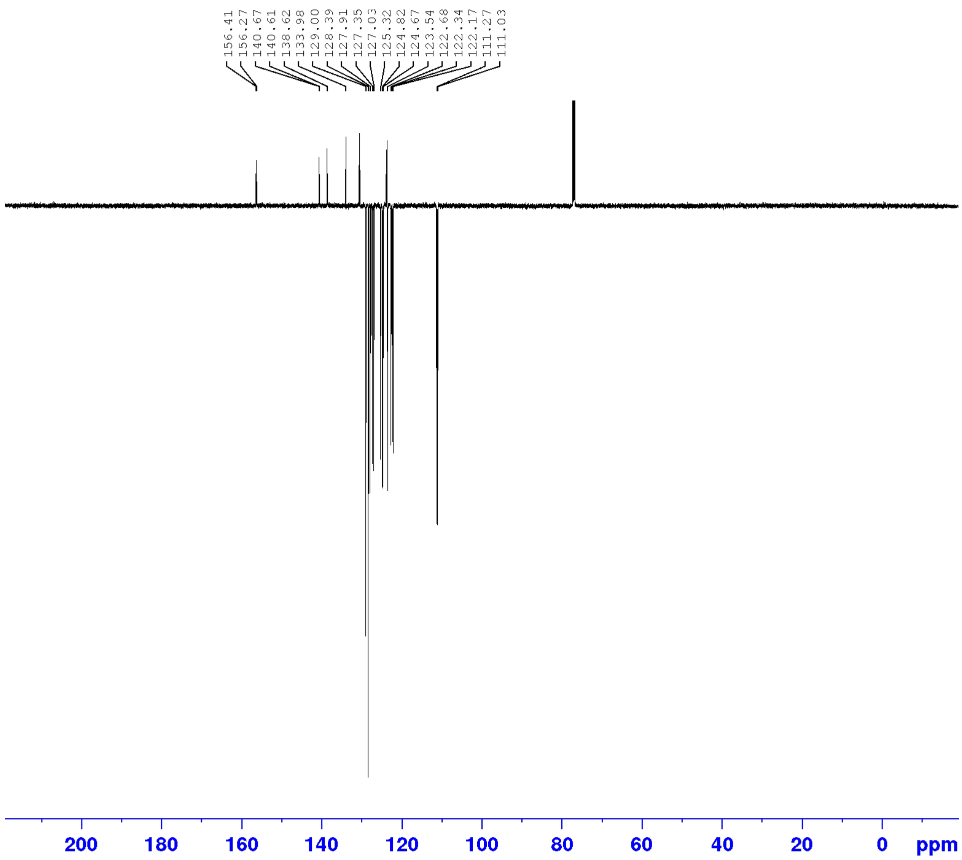
^{13}C NMR (150.95 MHz, $CDCl_3$) of compound **17a**.



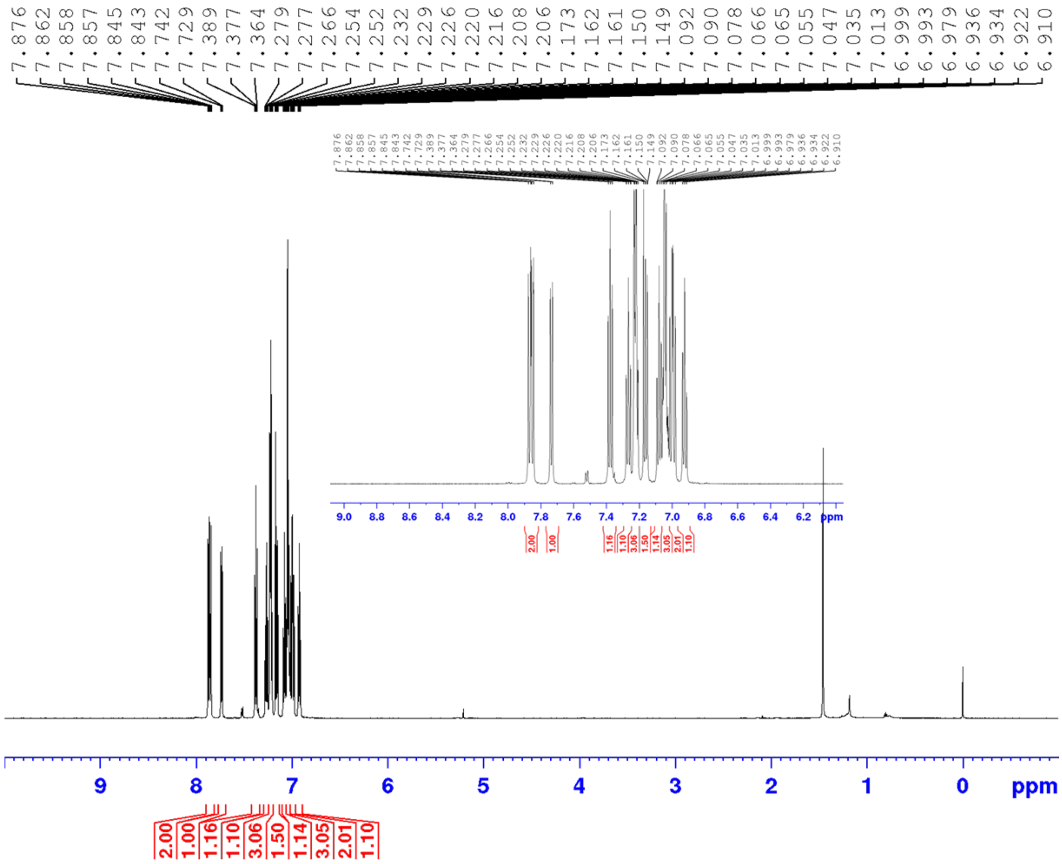
[1]H NMR (600.33 MHz, $CDCl_3$) of compound **17b**.



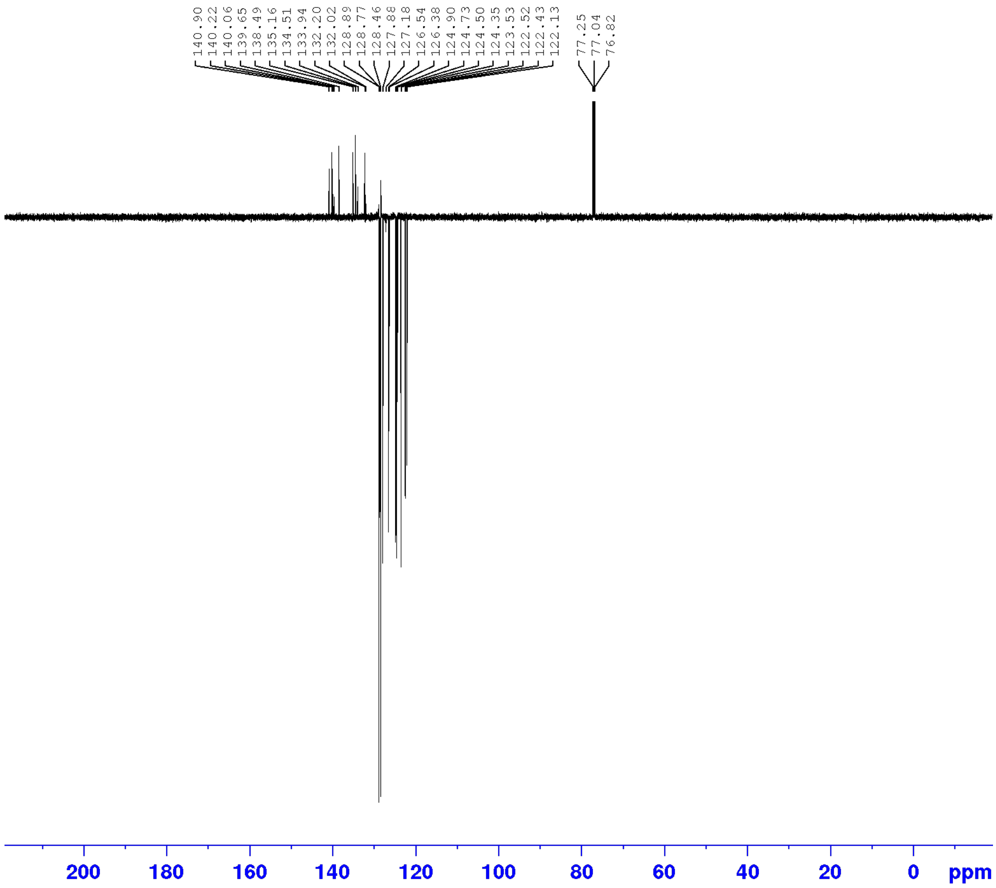
[13]C NMR (150.95 MHz, $CDCl_3$) of compound **17b**.



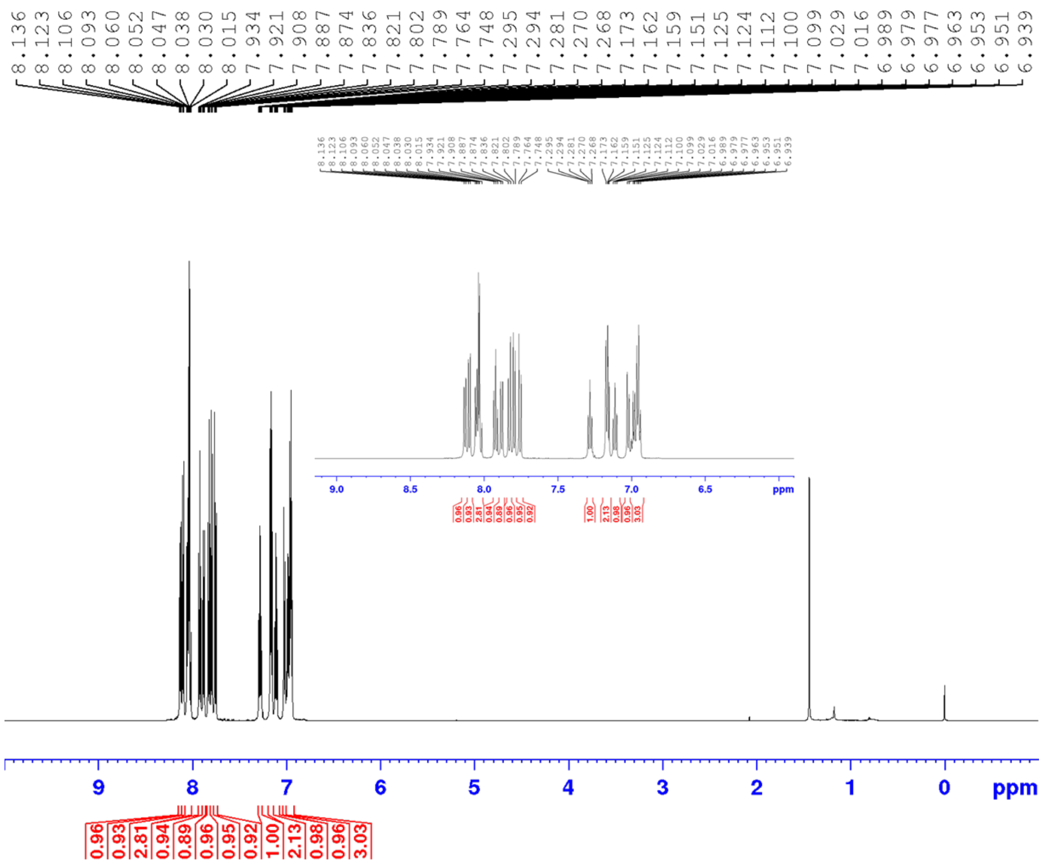
[1]H NMR (600.33 MHz, $CDCl_3$) of compound **17c**.



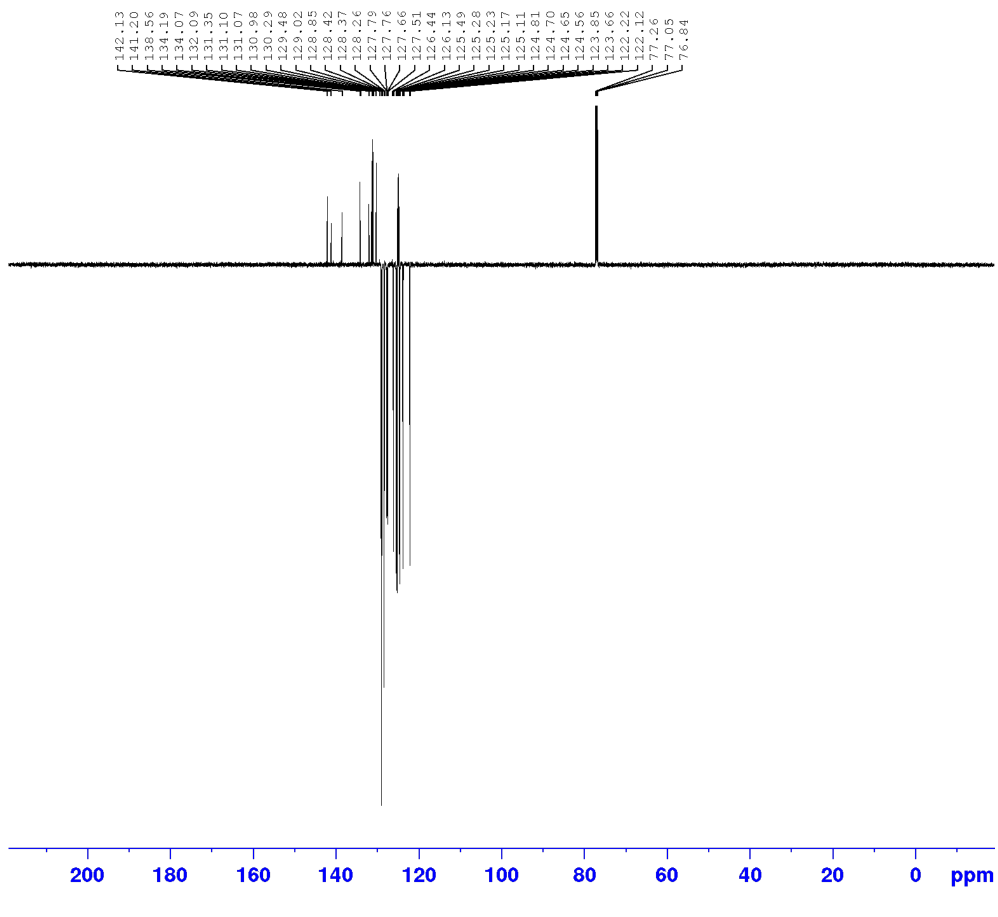
[13]C NMR (150.95 MHz, $CDCl_3$) of compound **17c**.



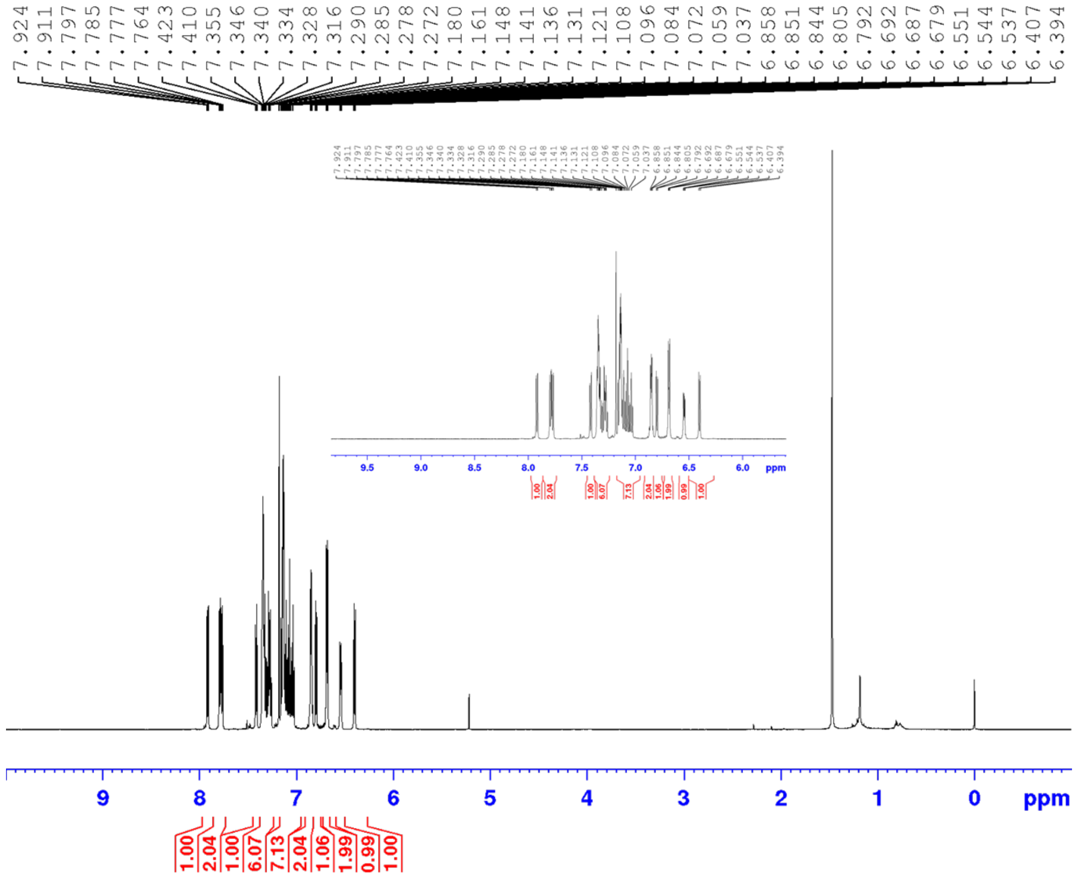
^{1}H NMR (600.33 MHz, $CDCl_3$) of compound **18**.



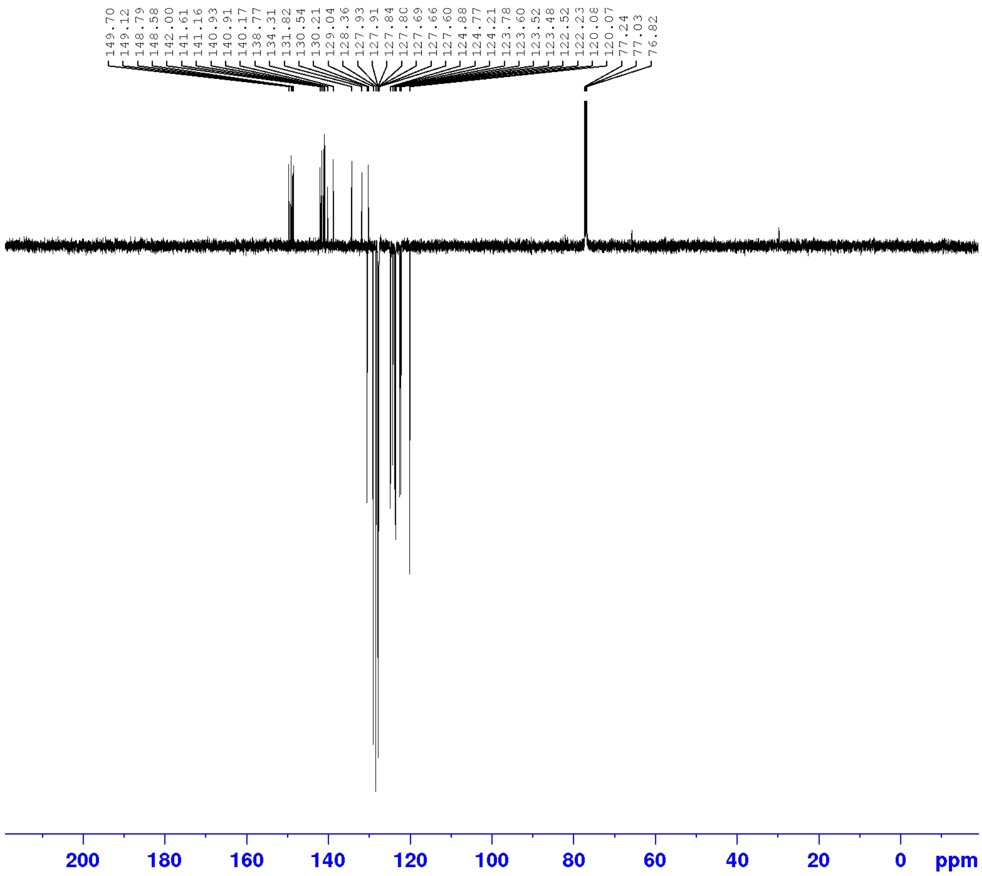
^{13}C NMR (150.95 MHz, $CDCl_3$) of compound **18**.



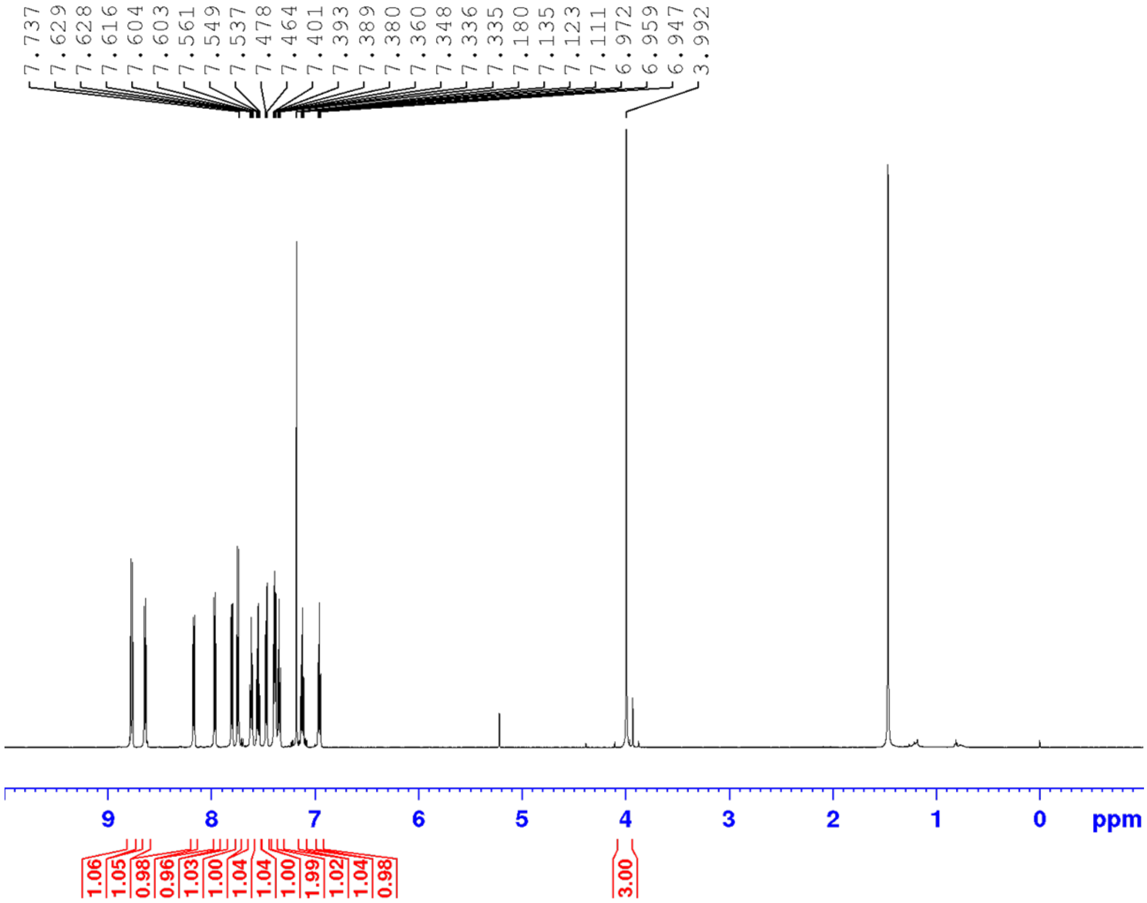
^{1}H NMR (600.33 MHz, $CDCl_3$) of compound **19**.



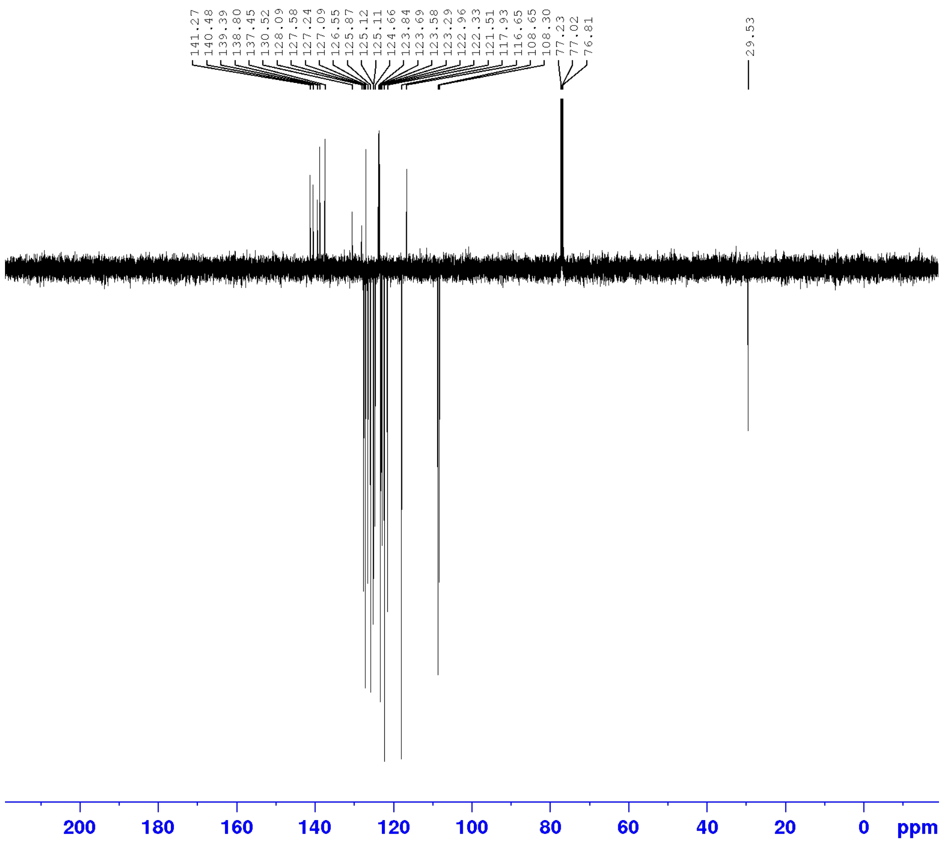
^{13}C NMR (150.95 MHz, $CDCl_3$) of compound **19**.



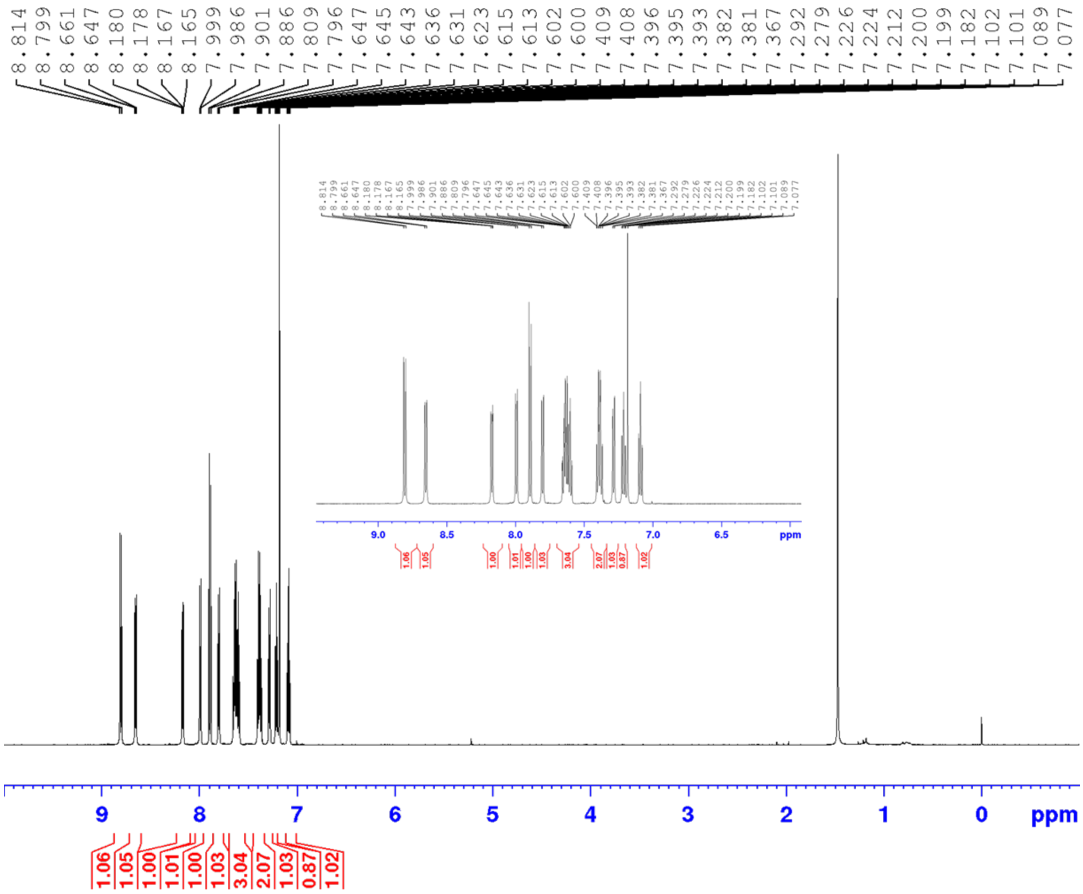
^{1}H NMR (600.33 MHz, $CDCl_3$) of compound **2a**.



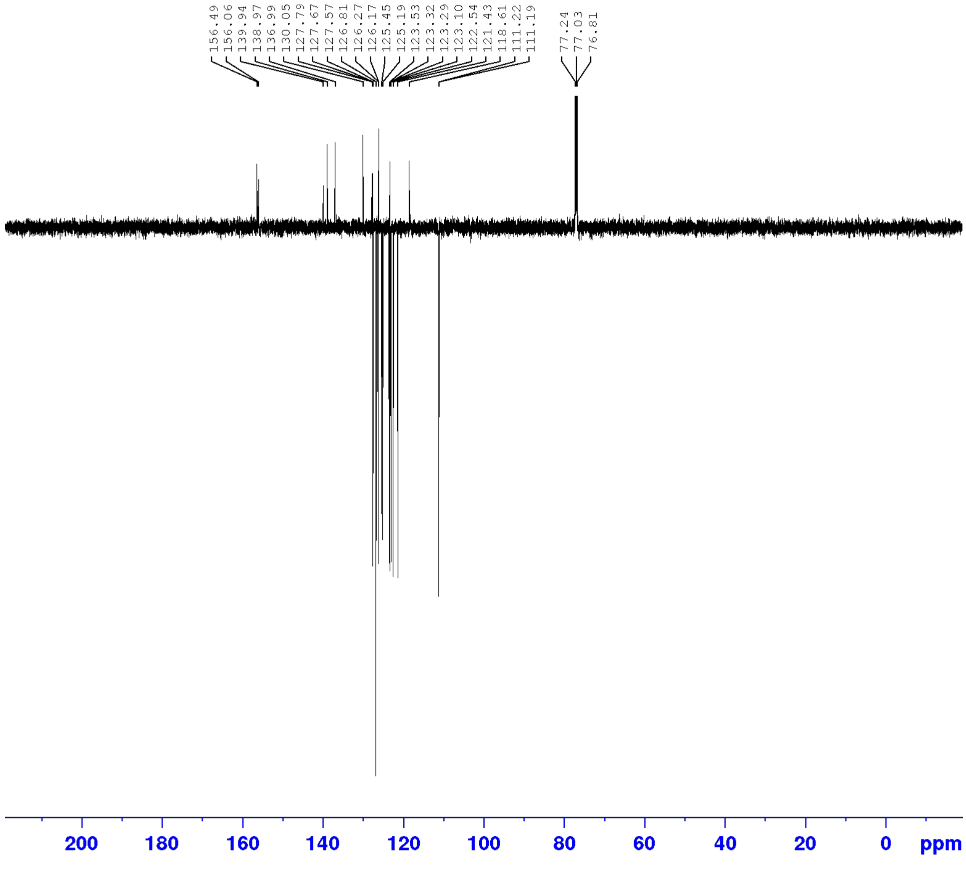
^{13}C NMR (150.95 MHz, $CDCl_3$) of compound **2a**.



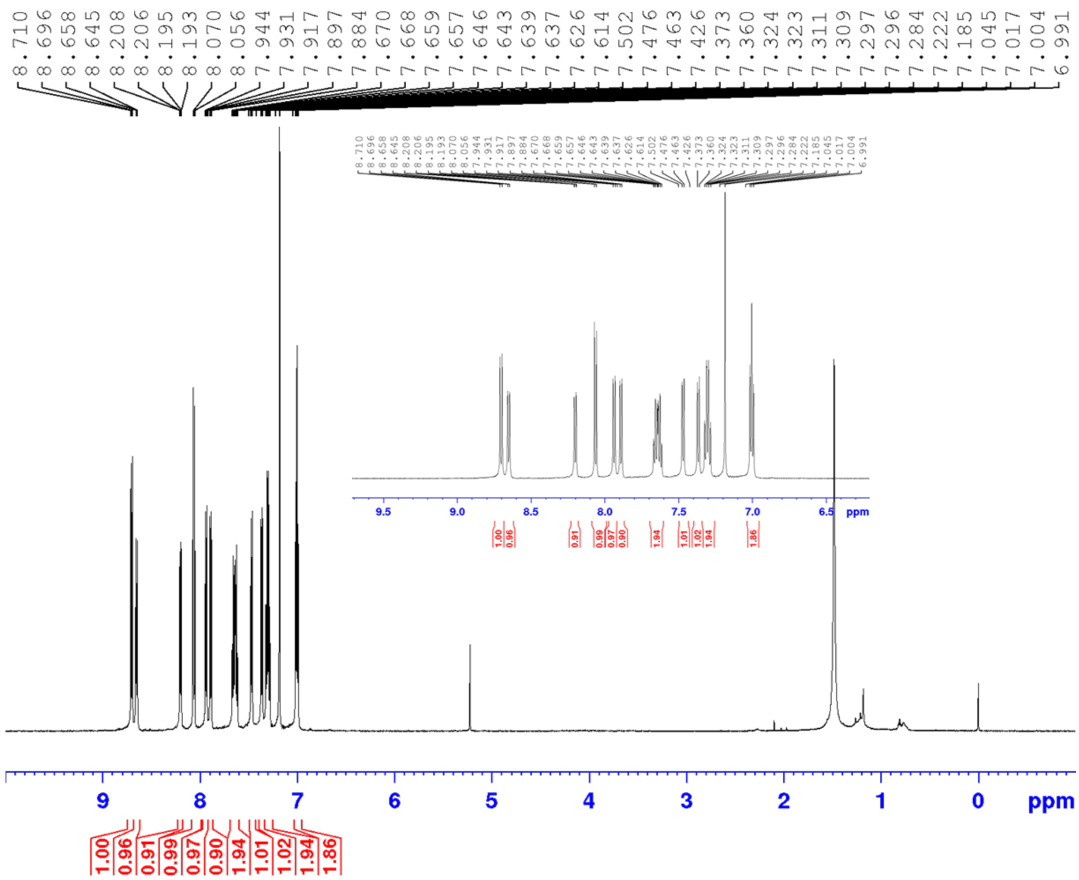
[1]H NMR (600.33 MHz, $CDCl_3$) of compound **2b**.



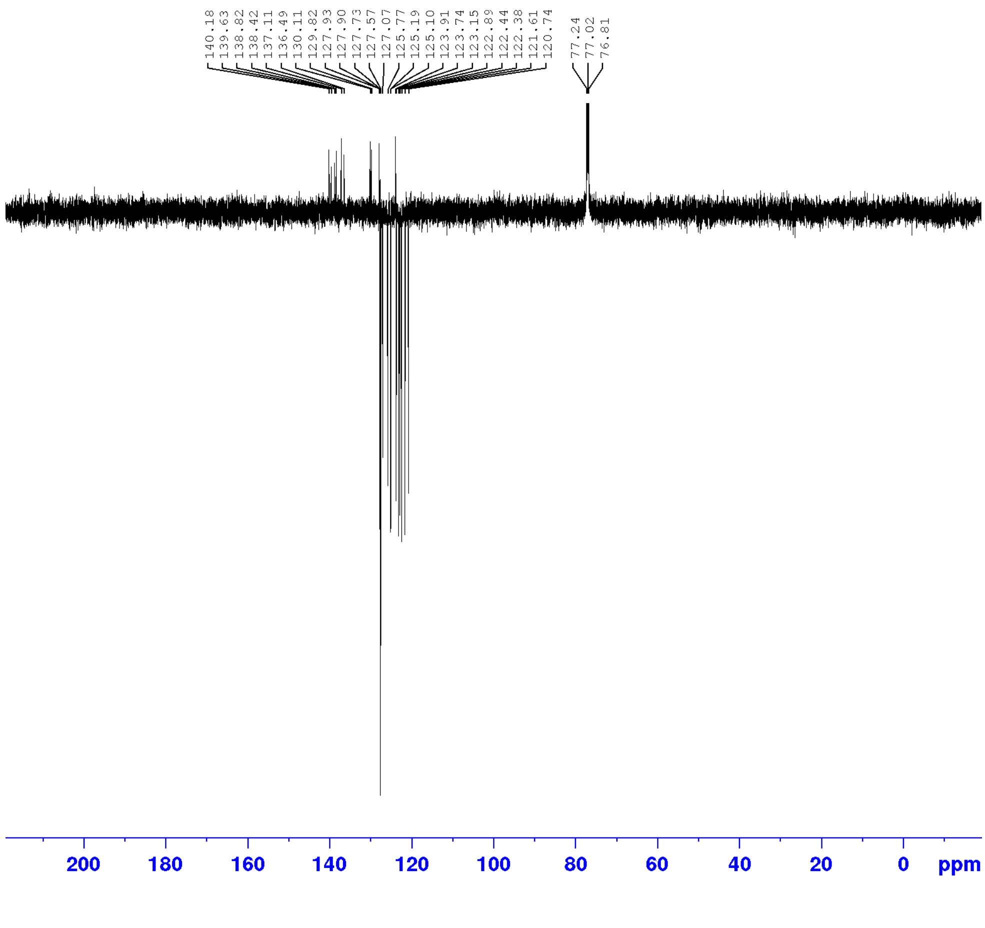
[13]C NMR (150.95 MHz, $CDCl_3$) of compound **2b**.



^{1}H NMR (600.33 MHz, $CDCl_3$) of compound **2c**.

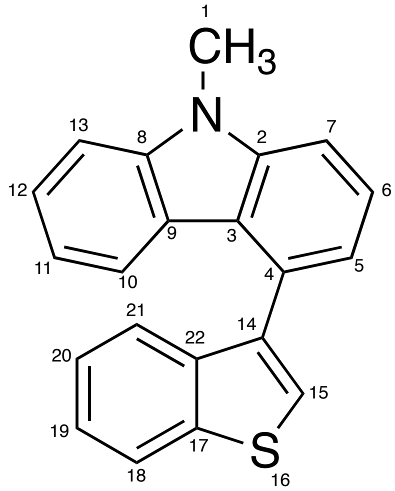


^{13}C NMR (150.95 MHz, $CDCl_3$) of compound **2c**.



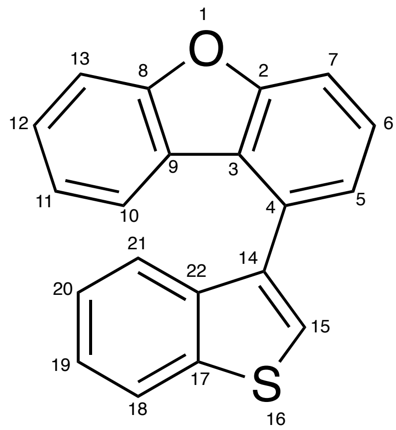
4. NMR assignment

Table S1. ^{1}H and ^{13}C NMR assignment of compound **5a**.



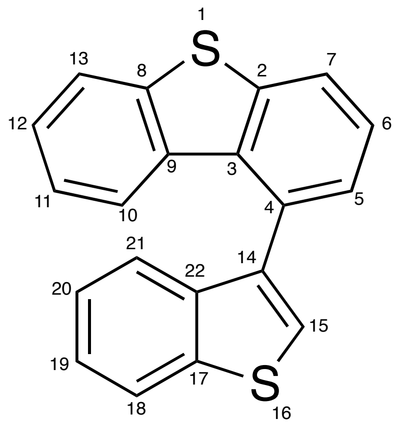
Atom	^{1}H (ppm)	*J* (Hz)	^{13}C (ppm)
1- CH_3	3.83	s	29.3
2	-	-	141.4
3	-	-	121.5
4	-	-	130.6
5	7.14	m	121.1
6	7.48	m	125.3
7	7.4	d, 7.8	108.0
8	-	-	141.2
9	-	-	122.1
10	6.99	d, 7.8	122.5
11	7.29	m	124.4
12	6.78	dt, 7.8, 1.89	118.7
13	7.30	m	108.2
14	-	-	137.0
15	7.47	s	124.1
17	-	-	140.0
18	7.91	d, 8.1	122.7
19	7.15	m	124.1
20	7.29	m	125.5
21	7.37	d, 8.1	123.9
22	-	-	138.8

Table S2. ^{1}H and ^{13}C NMR assignment of compound **5b**.



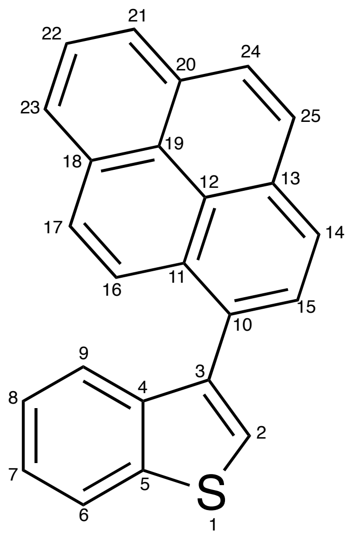
Atom	^{1}H (ppm)	*J* (Hz)	^{13}C (ppm)
2	-	-	156.4
	-	-	123.1
4	-	-	130.8
5	6.92	m	122.4
6	7.28	m	127.1
7	7.48	d, 7.9 (m)	111.4
8	-	-	156.3
9	-	-	123.8
10	6.94	m	122.4
11	7.28	t, 8.1 (m)	124.5
12	7.46	m	127.1
13	7.57	d, 8.1	111.1
14	-	-	135.5
15	7.49	s	124.5
17	-	-	140.2
18	7.42	d, 7.8	123.3
19	7.2	t, 7.8	124.3
20	7.33	t, 7.8	124.6
21	7.92	d, 7.8	122.9
22	-	-	138.3

Table S3. ^{1}H and ^{13}C NMR assignment of compound **5c**.



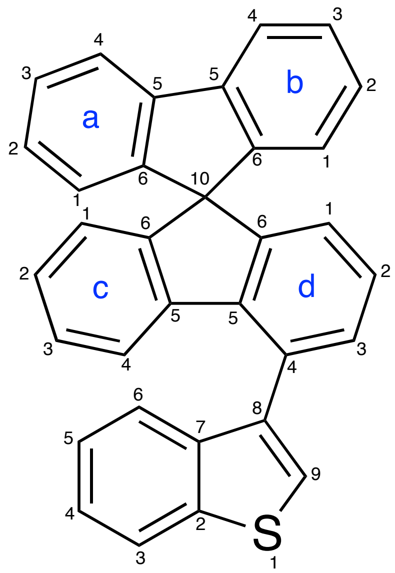
Atom	^{1}H (ppm)	*J* (Hz)	^{13}C (ppm)
2	-	-	140.2
3	-	-	133.9
4	-	-	132.3
5	7.28	m	127.7
6	7.44	t, 8	126.0
7	7.87	d, 8	122.6
8	-	-	139.9
9	-	-	138.9
10	7.21	m	123.2
11	7.13	t, 8	124.3
12	7.3	m	124.7
13	7.91	d, 8	122.8
14	-	-	137.0
15	7.39	s	124.0
17	-	-	139.6
18	7.73	d, 7.8	122.4
19	7.21	m	126.2
20	6.88	t, 7.8	124.1
21	6.83	d, 7.8	124.7
22	-	-	135.2

Table S4. ^{1}H and ^{13}C NMR assignment of compound **6**.



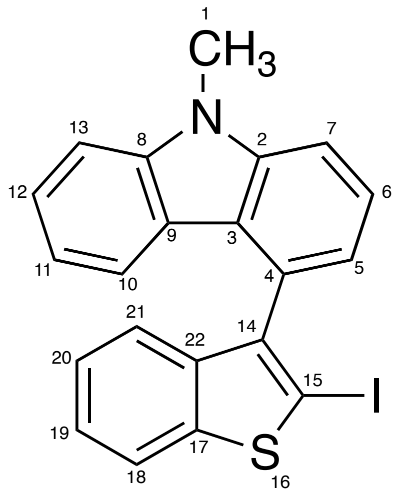
Atom	^{1}H (ppm)	*J* (Hz)	^{13}C (ppm)
2	7.50	s	125.5
3	-	-	136.9
4	-	-	139.8
5	-	-	140.1
6	7.92	m	122.8
7	7.32	t, 8.1	124.5
8	7.20	t, 8.1	124.4
9	7.35	d, 8.1	123.5
10	-	-	125.0
11	-	-	129.8
12	-	-	131.4
13	-	-	131.1
14	8.16	d, 7.8	124.8
15	7.96	d, 7.8	128.1
16	8.04	m	127.5
17	8.04	m	127.5
18	-	-	130.9
19	-	-	124.8
20	-	-	131.0
21	8.07	d, 7.8	125.1
22	7.93	m	126.1
23	8.13	d, 7.8	125.3
24	7.87	m	127.4
25	7.87	m	125.5

Table S5. ^{1}H and ^{13}C NMR assignment of compound **7**.



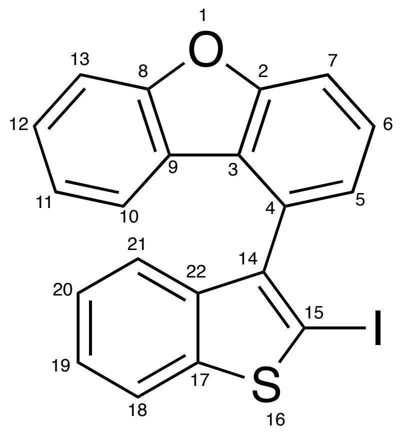
Atom	^{1}H (ppm)	*J* (Hz)	^{13}C (ppm)
a1 b1	6.72 6.74	d, 7.6 d, 7.6	123.6 123.9
a2 b2	7.09	m	127.6
a3 b3	7.32	t, 7.6	127.5
a4 b4	7.79	d, 7.6	119.9
a5 b5	-	-	141.9
a6 b6	-	-	149.0
c1	6.60	m	123.0
c2	6.84	t, 7.6	127.4
c3	6.88	t, 7.6	127.6
c4	6.60	m	123.0
c5	-	-	141.2
c6	-	-	149.6
d1	6.77	d, 7.6	124.0
d2	7.08	m	127.6
d3	7.22	d, 7.6	130.3
d4	-	-	130.6
d5	-	-	141.8
d6	-	-	149.7
10	-	-	65.7
2	-	-	140.0
3	7.85	d, 8.0	122.6
4	7.36	t, 8.0	124.6
5	7.27	t, 8.0	124.3
6	7.49	d, 8.0	123.5
7	-	-	138.9
8	-	-	140.2
9	7.51	s	123.8

Table S6. ^{1}H and ^{13}C NMR assignment of compound **12a**.



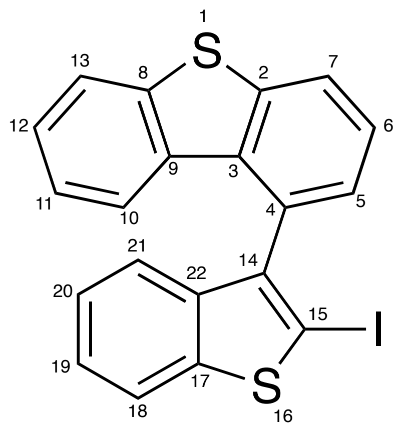
Atom	^{1}H (ppm)	*J* (Hz)	^{13}C (ppm)
1	3.85	s	29.2
2	-	-	141.3
3	-	-	121.9
4	-	-	130.3
5	7.06	d, 8.0	121.1
6	7.54	t, 8.0	125.4
7	7.46	d, 8.0	108.3
8	-	-	141.1
9	-	-	122.2
10	7.31	m	125.7
11	6.8	m	119.1
12	6.8	m	122.4
13	7.31	m	108.1
14	-	-	142.8
15	-	-	81.9
17	-	-	143.9
18	7.80	d, 8.1	121.6
19	7.23	t, 8.1	124.6
20	7.04	t, 8.1	124.6
21	7.13	d, 8.1	123.3
22	-	-	139.1

Table S7. ^{1}H and ^{13}C NMR assignment of compound **12b**.



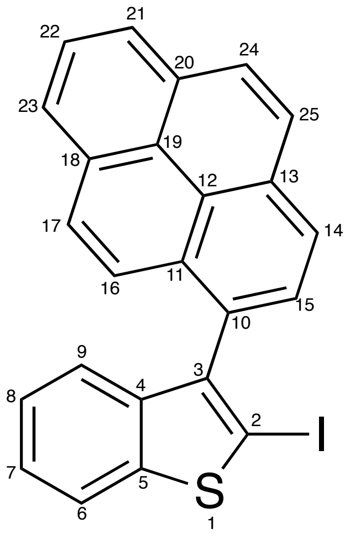
Atom	^{1}H (ppm)	*J* (Hz)	^{13}C (ppm)
2	-	-	156.3
3	-	-	123.5
4	-	-	130.6
5	7.22	d, 7.8	124.9
6	7.53	t, 7.8	126.9
7	7.63	d, 7.8	111.6
8	-	-	156.4
9	-	-	123.5
10	6.74	d, 8.0	122.3
11	6.95	t, 8.0	122.8
12	7.3	t, 8.0	127.1
13	7.5	d, 8.0	111.3
14	-	-	141.1
15	-	-	82.0
17	-	-	143.9
18	7.81	d, 8.1	121.6
19	7.27	t, 8.1	123.9
20	7.11	t, 8.1	124.4
21	7.18	d, 8.1	123.0
22	-	-	138.9

Table S8. ^{1}H and ^{13}C NMR assignment of compound **12c**.



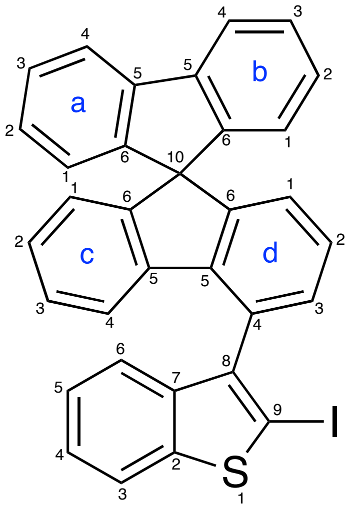
Atom	^{1}H (ppm)	*J* (Hz)	^{13}C (ppm)
2	-	-	140.3
3	-	-	133.9
4	-	-	132.3
5	7.22	d, 8.1	127.6
6	7.51	t, 8.1	126.1
7	7.93	d, 8.1	123.2
8	-	-	142.7
9	-	-	134.7
10	6.76	d, 8.2	124.1
11	6.95	t, 8.2	124.4
12	7.25	m	126.3
13	7.75	d, 8.2	122.4
14	-	-	138.9
15	-	-	82.3
17	-	-	143.8
18	7.82	d, 8.0	121.4
19	7.25	m	125.0
20	7.07	m	123.2
21	7.07	m	124.9
22	-	-	139.7

Table S9. ^{1}H and ^{13}C NMR assignment of compound **13**.



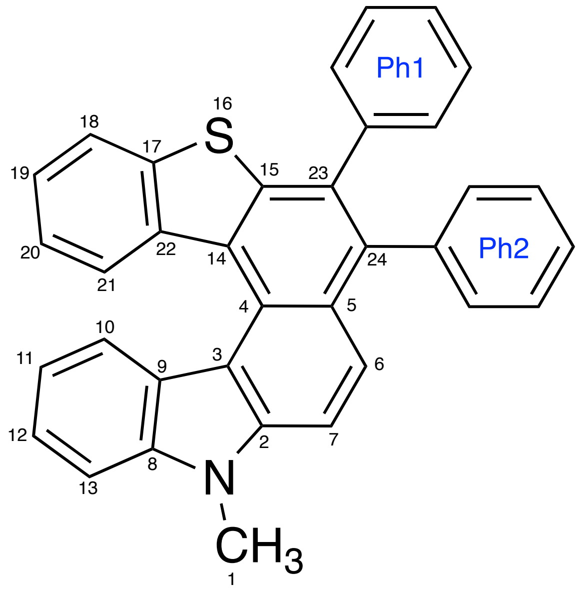
Atom	^{1}H (ppm)	*J* (Hz)	^{13}C (ppm)
2	-	-	83.3
3	-	-	142.6
4	-	-	140.0
5	-	-	143.9
6	7.82	d, 8.1	121.6
7	7.26	t, 8.1	124.7
8	7.09	m	124.7
9	7.07	m	123.3
10	-	-	125.0
11	-	-	129.8
12	-	-	130.9
13	-	-	131.5
14	8.22	d, 7.8	124.7
15	7.86	d, 7.8	128.4
16	7.59	d, 8.9	125.3
17	7.89	d, 8.9	127.8
18	-	-	131.0
19	-	-	131.3
20	-	-	131.5
21	8.09	m	125.5
22	7.95	t, 7.8	126.2
23	8.16	d, 7.8	125.4
24	8.08	m	127.6
25	8.08	m	127.6

Table S10. ^1H and ^{13}C NMR assignment of compound **14**.



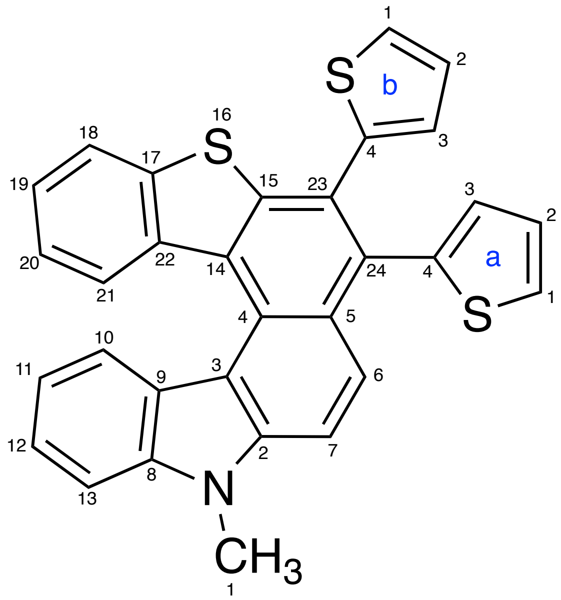
Atom	^1H (ppm)	*J* (Hz)	^{13}C (ppm)
a1 b1	6.76	m	124.3
a2 b2	7.10 7.15	t, 7.6 m	127.6 127.6
a3 b3	7.32	t, 7.6	127.7
a4 b4	7.8	m	119.8
a5 b5	-	-	140.6 140.9
a6 b6	-	-	148.9
c1	6.53	m	122.4
c2	6.90	m	127.6
c3	6.90	m	127.6
c4	6.60	m	123.6
c5	-	-	142.0
c6	-	-	149.0
d1	6.77	m	124.0
d2	7.07	t, 7.6	127.7
d3	7.13	m	130.2
d4	-	-	130.6
d5	-	-	141.7
d6	-	-	149.7
10	-	-	65.8
2	-	-	142.3
3	7.84	d, 8.0	121.6
4	7.31	m	124.9
5	7.22	t, 8.0	124.7
6	7.39	d, 8.0	123.1
7	-	-	138.9
8	-	-	143.9
9	-	-	82.5

Table S11. ^{1}H and ^{13}C NMR assignment of compound **1aa**.



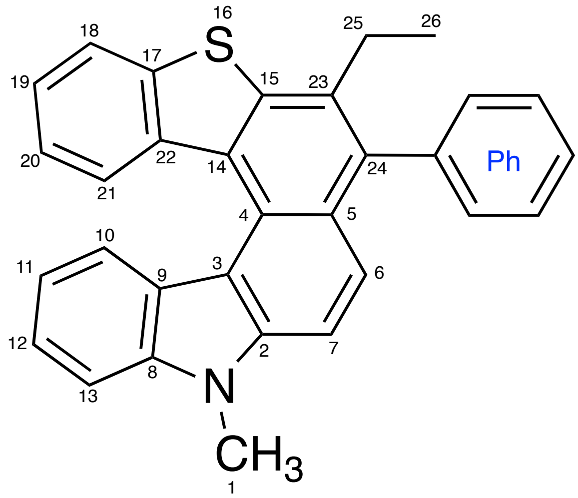
Atom	^{1}H (ppm)	*J* (Hz)	^{13}C (ppm)
1	3.97	s	29.7
2	-	-	140.7
3	-	-	126.9
4	-	-	124.8
5	-	-	114.8
6	7.73	d, 9.1	126.7
7	7.55	d, 9.1	109.2
8	-	-	140.2
9	-	-	123.8
10	7.44	d, 8.1	126.6
11	7.02	m	118.1
12	7.39	t, 8.1	124.2
13	7.50	d, 8.1	108.4
14	-	-	127.0
15	-	-	142.5
17	-	-	139.5
18	7.84	d, 8.1	122.0
19	7.34	m	125.1
20	7.17	m	122.6
21	7.9	d, 8.1	127.5
22	-	-	137.06
23	-	-	131.4
24	-	-	128.1
Ph1 e Ph2	7.01 7.34 7.19 7.22 7.28 7.26	m	131.7 131.2 126.9 128.0 127.3 130.3 139.3 140.0

Table S12. ^{1}H and ^{13}C NMR assignment of compound **1ab**.



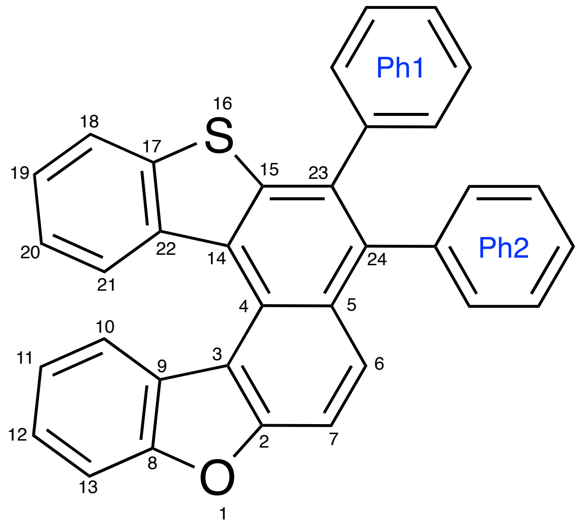
Atom	^{1}H (ppm)	*J* (Hz)	^{13}C (ppm)
1	3.99	s	29.5
2	-	-	141.1
3	-	-	124.3
4	-	-	127.7
5	-	-	114.6
6	7.94	d, 9.1	126.5
7	7.61	d, 9.1	109.6
8	-	-	139.8
9	-	-	123.7
10	7.34	m	126.6
11	7.03	m	118.1
12	7.39	m	126.5
13	7.51	m	108.6
14	-	-	128.9
15	-	-	142.9
17	-	-	139.4
18	7.88	m	122.0
19	7.37	m	125.4
20	7.17	m	122.8
21	7.87	m	127.5
22	-	-	136.9
23	-	-	125.9
24	-	-	131.3
1a and 1b	7.29 7.41	d, 5.3 m	126.4 124.1
2a and 2b	7.20 6.99	m m	128.6 130.2
3a and 3b	7.01	m	126.6
4a and 4b	-	-	140.5 140.3

Table S13. ^{1}H and ^{13}C NMR assignment of compound **1ac**.



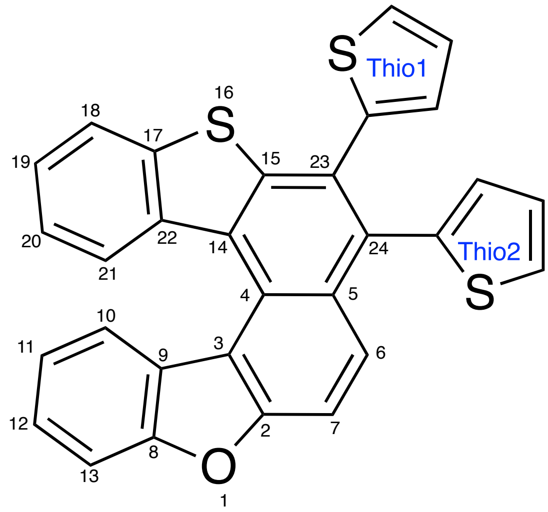
Atom	^{1}H (ppm)	*J* (Hz)	^{13}C (ppm)
1	3.95	s	29.4
2	-	-	140.1
3	-	-	128.4
4	-	-	127.6
5	-	-	114.6
6	7.40	m	126.5
7	7.48	m	108.5
8	-	-	140.0
9	-	-	123.2
10	7.87	d, 8.0	127.4
11	7.17	t, 8.0	122.6
12	7.37	m	130.2
13	7.48	m	108.5
14	-	-	138.6
15	-	-	141.2
17	-	-	140.3
18	7.94	d, 8.1	121.9
19	7.39	m	123.9
20	6.99	t, 8.1	117.8
21	7.38	m	124.8
22	-	-	137.3
23	-	-	131.3
24	-	-	123.9
25	2.8	q, 7.3	26.5
26	1.19	t, 7.3	14.3
Ph	7.26 7.43 7.46	m m m	130.9 127.7 126.6 137.6

Table S14. ^{1}H and ^{13}C NMR assignment of compound **1ba**.



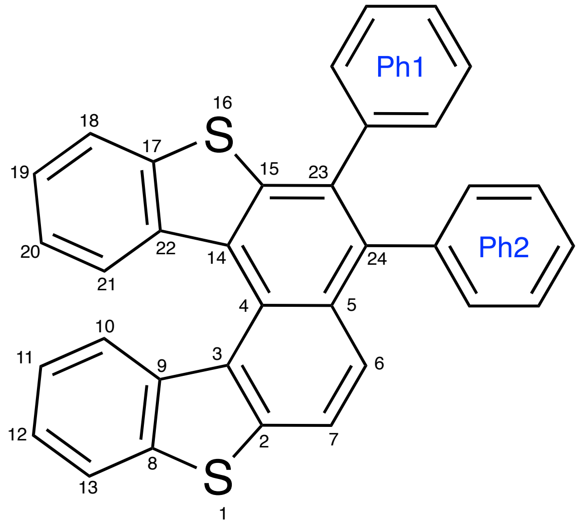
Atom	^{1}H (ppm)	*J* (Hz)	^{13}C (ppm)
2	-	-	156.3
3	-	-	138.0
4	-	-	137.9
5	-	-	129.1
6	7.68	d, 8.7	111.5
7	7.78	d, 8.7	128.4
8	-	-	155.9
9	-	-	138.9
10	7.03	d, 8.0	131.5
11	7.16	m	121.6
7.3	7.39	t, 8.0	125.5
13	7.65	d, 8.0	111.1
14	-	-	139.5
15	-	-	143.0
17	-	-	139.7
18	7.92	d, 8.0	127.9
19	7.26	m	123.1
20	7.39	t, 8.0	125.5
21	7.87	d, 8.0	122.1
22	-	-	136.6
23	-	-	132.9
24	-	-	128.5
Ph1 and Ph2	7.31-7.16	m	131.1-127.2 125.2, 123.5

Table S15. ^{1}H and ^{13}C NMR assignment of compound **1bb**.



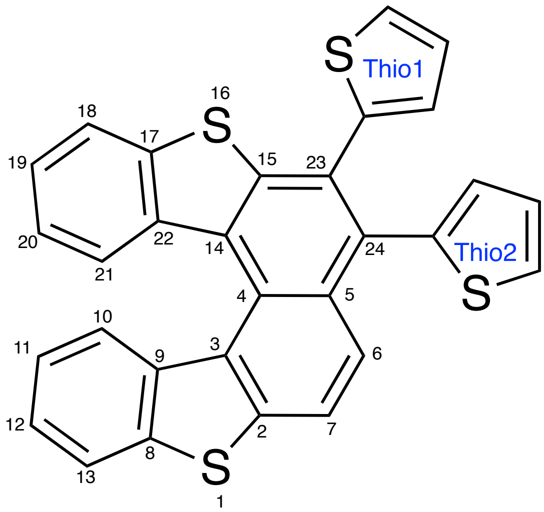
Atom	^{1}H (ppm)	*J* (Hz)	^{13}C (ppm)
2	-	-	156.9
3	-	-	130.0
4	-	-	131.6
5	-	-	129.7
6	8.00	d, 8.9	128.3
7	7.76	d, 8.9	112.1
8	-	-	155.6
9	-	-	125.0
10	7.33	m	126.6
11	7.14	t, 8.0	121.4
12	7.40	m	125.7
13	7.66	d, 8.0	111.3
14	-	-	139.4
15	-	-	143.2
17	-	-	140.2
18	7.91	m	122.2
19	7.43	m	125.7
20	7.28	t, 8.0	123.0
21	7.9	m	127.6
22	-	-	136.6
23	-	-	127.8
24	-	-	128.2
Thio 1 and Thio 2	7.36-7.32 7.2-7.0 7.02	m	126.6 130.3-128.6 126.4 140.0

Table S16. ^{1}H and ^{13}C NMR assignment of compound **1ca**.



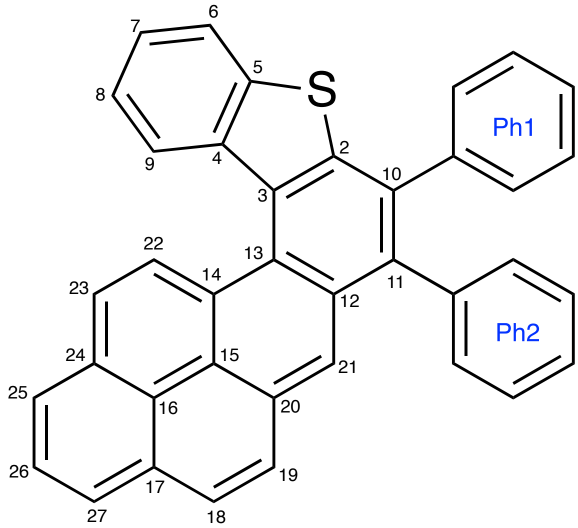
Atom	^{1}H (ppm)	*J* (Hz)	^{13}C (ppm)
2	-	-	140.4
3	-	-	133.6
4	-	-	137.5
5	-	-	124.2
6	7.81	d, 8.7	120.2
7	7.68	d, 8.7	126.6
8	-	-	139.0
9	-	-	136.7
10	7.47	d, 8.1	128.8
11	7.06	m	122.9
7.3	7.3	m	125.3
13	7.83	d, 8.1	122.2
14	-	-	139.6
15	-	-	142.8
17	-	-	138.7
18	7.92	d, 8.2	122.5
19	7.34	t, 8.2	125.3
20	7.06	m	122.9
21	7.52	d, 8.2	127.9
22	-	-	136.4
23	-	-	128.3
24	-	-	128.7
Ph1 and Ph2	7.18-7.03	m	127.9 – 127.1 130.3

Table S17. ^{1}H and ^{13}C NMR assignment of compound **1cb**.



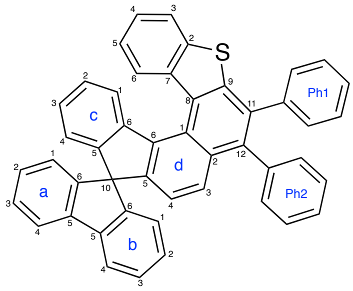
Atom	^{1}H (ppm)	*J* (Hz)	^{13}C (ppm)
2	-	-	140.8
3	-	-	131.1
4	-	-	124.4
5	-	-	129.2
6	7.89	d, 8.9	126.5
7	7.87	m	120.6
8	-	-	139.05
9	-	-	136.3
10	7.45	d, 8.1	127.7
11	7.05	m	126.5
12	7.33	m	127.0
13	7.86	m	122.0
14	-	-	139.1
15	-	-	143.0
17	-	-	138.7
18	7.92	d, 8.1	122.6
19	7.03	m	126.6
20	7.31	m	125.6
21	7.48	d, 8.1	127.7
22	-	-	136.5
23	-	-	128.3
24	-	-	128.7
Thio 1 and Thio 2	7.24 7.06 7.01	m	128.5 122.9 130.2 139.9

Table S18. ^{1}H and ^{13}C NMR assignment of compound **3**.



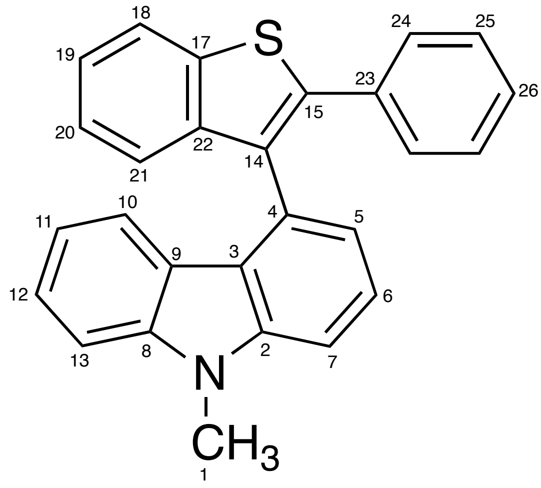
Atom	^{1}H (ppm)	*J* (Hz)	^{13}C (ppm)
2	-	-	142.3
3	-	-	138.7
4	-	-	137.9
5	-	-	140.0
6	7.87	d, 8.0	122.5
7	7.39	t, 8.0	125.7
8	7.36	t, 8.0	123.0
9	8.65	d, 8.0	125.6
10	-	-	130.0
11	-	-	124.0
12	-	-	134.4
13	-	-	137.2
14	-	-	129.06
15	-	-	129.1
16	-	-	124.9
17	-	-	131.9
18	7.85	d, 9.0	127.4
19	7.8	d, 9.0	128.1
20	-	-	125.2
21	8.26	s	124.0
22	9.21	d, 9.1	127.8
23	8.11	d, 9.1	124.8
24	-	-	131.6
25	8.18	d, 7.8	125.0
26	7.95	t, 7.8	126.3
27	8.05	d, 7.8	124,9
Ph1 and Ph2	7.44, 7.28-7.23	m	131.3, 131.6, 130.2 128.0, 127.6, 124.7

Table S19. ^{1}H and ^{13}C NMR assignment of compound **4**.



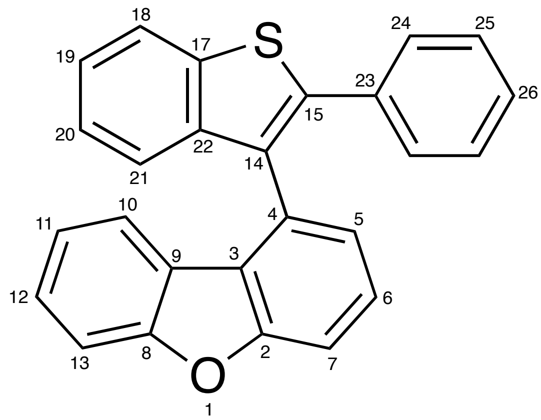
Atom	^{1}H (ppm)	*J* (Hz)	^{13}C (ppm)
a1 b1	7.11 6.52	m d, 7.8	123.6 124.7
a2 b2	7.12 7.03	m m	131.2 131.4
a3 b3	7.32	m	127.9
a4 b4	7.82	d, 7.8	120.2
a5 b5	-	-	141.9 142.5
a6 b6	-	-	147.2 148.7
c1	6.76	m	123.1
c2	7.03	m	127.8
c3	6.99	m	126.5
c4	7.16	m	126.5
c5	-	-	142.8
c6	-	-	148.7
d1	6.76	m	121.0
d2	7.44	d, 8.5	128.2
d3	-	-	132.6
d4	-	-	135.7
d5	-	-	143.1
d6	-	-	150.2
10	-	-	66.5
2	-	-	139.6
3	7.88	d, 7.8	122.2
4	7.38	t, 7.8	125.2
5	7.32	m	123.2
6	7.95	d, 7.8	128.7
7	-	-	136.8
8	-	-	138.7
9	-	-	139.5
11	-	-	137.6
12	-	-	133.9
Ph1 and Ph2	7.24-7.1	m	126.5-128 128.7 123.5

Table S20. ^{1}H and ^{13}C NMR assignment of compound **17a**.



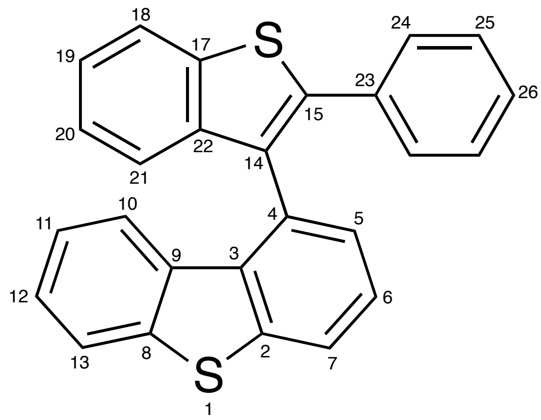
Atom	^{1}H (ppm)	*J* (Hz)	^{13}C (ppm)
1- CH_3	3.82	s	29.2
2	-	-	141.2
3	-	-	122.1
4	-	-	130.3
5	6.98	m	121.5
6	7.4	t, 8.0	125.7
7	7.36	d, 8.0	107.8
8	-	-	141.3
9	-	-	122.3
10	6.93	d, 7.8	122.3
11	7.25	m	124.5
12	6.76	dt, 7.8, 1.6	119.6
13	7.28	m	107.9
14	-	-	134.3
15	-	-	141.1
17	-	-	139.9
18	7.85	d, 8.0	122.0
19	7.26	m	125.4
20	7.00	m	127.4
21	7.24	m	128.9
22	-	-	138.5
23	-	-	132.3
24	7.05	m	123.9
25	7.25	m	129.0
26	6.99	m	128.1

Table S21. ^{1}H and ^{13}C NMR assignment of compound **17b**.



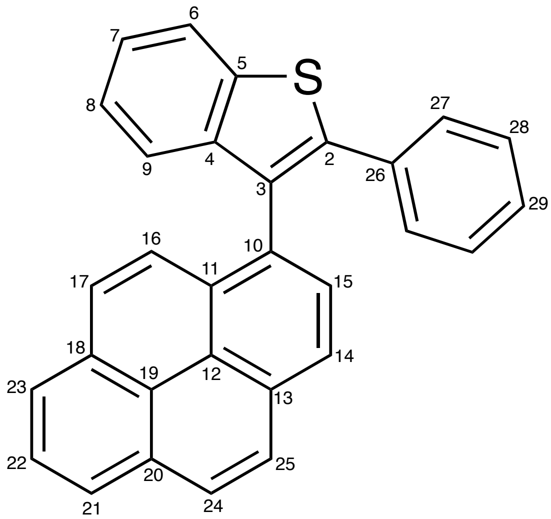
Atom	^{1}H (ppm)	*J* (Hz)	^{13}C (ppm)
2	-	-	156.3
3	-	-	123.7
4	-	-	130.7
5	7.12	m	124.8
6	7.4	t, 8.1	127.3
7	7.54	d, 8.1	110.9
8	-	-	156.4
9	-	-	123.9
10	6.83	d, 7.5	122.2
11	6.88	t, 7.5	122.6
12	7.24	m	127.1
13	7.45	d, 8.3	111.2
14	-	-	130.5
15	-	-	138.8
17	-	-	140.7
18	7.87	d, 8.0	122.1
19	7.28	dt, 8.0,1.6	124.8
20	7.12	m	124.8
21	7.15	m	123.6
22	-	-	140.6
23	-	-	134.2
24	7.22	m	129.0
25 26	7.04	m	128.2

Table S22. ^{1}H and ^{13}C NMR assignment of compound **17c**.



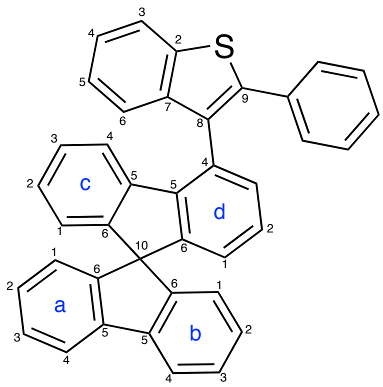
Atom	^{1}H (ppm)	*J* (Hz)	^{13}C (ppm)
2	-	-	140.3
3	-	-	134.5
4	-	-	132.3
5	7.15	dd, 7.8,0.85	127.9
6	7.37	t, 7.8	126.5
7	7.85	dd, 7.8,0.85	122.5
8	-	-	138.5
9	-	-	140.9
10	6.98	d, 8.0	123.5
11	7.07	dt, 8.0, 0.8	124.7
12	7.25	dt, 8.0,1.0	124.9
13	7.87	d, 8.0	122.2
14	-	-	139.7
15	-	-	134.0
17	-	-	140.1
18	7.73	d, 8.0	122.4
19	7.21	m	126.4
20	6.92	dt, 8.0, 0.85	124.4
21	7.00	d, 8.0	124.3
22	-	-	135.2
23	-	-	132.0
24	7.22	m	128.8
25	7.04	m	128.5
26	7.04	m	128.5

Table S23. ^{1}H and ^{13}C NMR assignment of compound **18**.



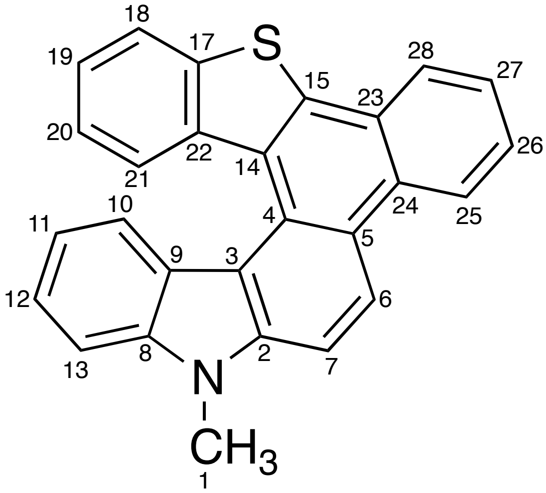
Atom	^{1}H (ppm)	*J* (Hz)	^{13}C (ppm)
2	-	-	141.2
3	-	-	124.8
4	-	-	138.6
5	-	-	142.1
6	7.88	d, 8.1	122.1
7	7.28	t, 8.1	124.6
8	7.11	t, 8.1	124.5
9	7.03	d, 8.1	123.8
10	-	-	125.1
11	-	-	130.3
12	-	-	130.9
13	-	-	132.1
14	8.1	d, 7.8	125.2
15	7.79	d, 7.8	128.8
16	7.76	d, 8.9	125.5
17	7.83	d, 8.9	127.8
18	-	-	131.1
19	-	-	131.07
20	-	-	131.4
21	8.05	d, 7.8	125.1
22	7.92	t, 7.8	126.1
23	8.13	d, 7.8	125.2
24	8.03	m	127.4
25	8.03	m	127.4
26	-	-	132.1
27	7.17	m	128.8
28	6.96	m	128.2
29	6.98	m	127.9

Table S24. ^{1}H and ^{13}C NMR assignment of compound **19**.



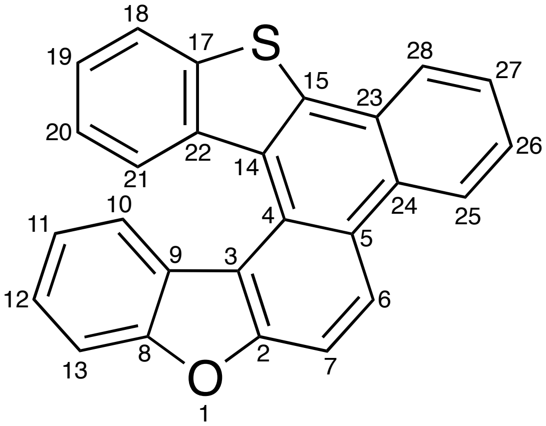
Atom	^{1}H (ppm)	*J* (Hz)	^{13}C (ppm)
a1 b1	6.79 6.40	d, 7.8 d, 7.8	124.1 123.7
a2 b2	7.10 7.05	t, 7.8 t, 7.8	127.7 127.6
a3 b3	7.33 7.29	m m	127.8 127.6
a4 b4	7.79 7.77	d, 7.8 d, 7.8	119.9 119.9
a5 b5	-	-	142.0 141.6
a6 b6	-	-	148.8 148.6
c1	6.54	m	123.1
c2	6.85	m	127.6
c3	6.85	m	127.6
c4	6.68	m	122.6
c5	-	-	140.9
c6	-	-	149.1
d1	6.68	m	123.4
d2	7.07	t, 7.8	127.8
d3	7.15	m	130.5
d4	-	-	130.2
d5	-	-	141.1
d6	-	-	149.7
10	-	-	65.8
2	-	-	140.9
3	7.91	d, 8.1	122.1
4	7.35	m	124.7
5	7.28	m	124.6
6	7.42	d, 8.1	123.5
7	-	-	138.8
8	-	-	140.1
9	-	-	131.8
Ph (*o*-) Ph (*m*-, *p*-)	7.34 7.13	m m	129.0 127.8 134.4

Table S25. ^1H and ^{13}C NMR assignment of compound **2a**.



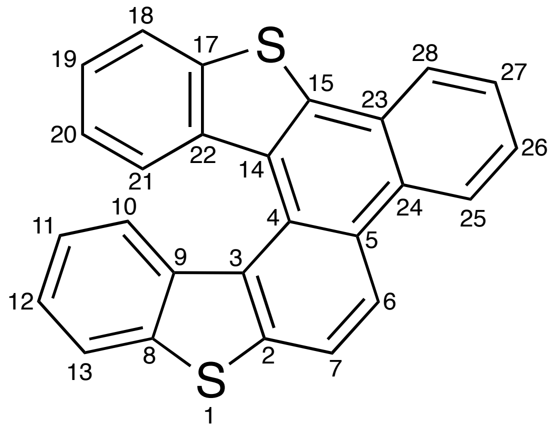
Atom	^1H (ppm)	*J* (Hz)	^{13}C (ppm)
1	3.99	s	29.5
2	-	-	141.4
3	-	-	123.9
4	-	-	123.4
5	-	-	116.5
6	8.77	d, 9.1	121.6
7	7.74	d, 9.1	108.5
8	-	-	140.4
9	-	-	123.9
10	7.37	m	126.6
11	6.95	t, 8.1	117.9
12	7.39	m	124.6
13	7.47	d, 8.1	108.2
14	-	-	127.9
15	-	-	139.5
17	-	-	138.8
18	7.97	d, 7.9	122.0
19	7.34	t, 7.9	125.0
20	7.11	t, 7.9	122.9
21	7.80	d, 7.9	127.5
22	-	-	137.6
23	-	-	127.2
24	-	-	130.6
25	8.64	d, 8.1	123.1
26	7.61	t, 8.1	127.2
27	7.56	t, 8.1	125.7
28	8.17	d, 8.1	125.0

Table S26. ^{1}H and ^{13}C NMR assignment of compound **2b**.



Atom	^{1}H (ppm)	*J* (Hz)	^{13}C (ppm)
2	-	-	156.6
3	-	-	127.6
4	-	-	126.2
5	-	-	118.6
6	8.81	d, 9.0	111.5
7	7.9	d, 9.0	123.0
8	-	-	156.1
9	-	-	127.0
10	7.28	d, 7.8	126.5
11	7.09	t, 7.8	121.4
12	7.38	m	126.3
13	7.63	m	111.1
14	-	-	136.9
15	-	-	140.1
17	-	-	138.9
18	7.99	d, 7.9	122.6
19	7.39	m	125.7
20	7.21	t, 7.9	123.2
21	7.80	d, 7.9	127.4
22	-	-	136.9
23	-	-	123.3
24	-	-	130.1
25	8.60	d, 8.1	123.3
26	7.65	m	127.1
27	7.60	m	126.5
28	8.17	dd, 8.1,1.0	125.1

Table S27. ^{1}H and ^{13}C NMR assignment of compound **2c**.



Atom	^{1}H (ppm)	*J* (Hz)	^{13}C (ppm)
2	-	-	140.3
3	-	-	130.1
4	-	-	129.9
5	-	-	127.6
6	8.70	d, 9.0	121.9
7	8.06	d, 9.0	120.6
8	-	-	138.4
9	-	-	137.7
10	7.37	d, 8.0	127.5
11	7.00	m	122.9
12	7.31	m	125.4
13	7.94	d, 8.0	122.4
14	-	-	127.9
15	-	-	139.6
17	-	-	138.9
18	7.88	d, 8.0	122.3
19	7.30	m	125.1
20	7.01	m	122.9
21	7.47	d, 8.0	127.6
22	-	-	136.5
23	-	-	123.9
24	-	-	127.9
25	8.66	d, 8.0	123.7
26	7.65	m	127.4
27	7.62	m	127.1
28	8.20	d, 8.0	125.1

5. X-Ray crystallography of 1ac and 3

The crystallographic data for the compounds **1ac** and **3** were obtained by mounting a well-formed single crystal on a glass fiber and transferring it to a APEX II Bruker CCD diffractometer. The APEX 3 program package[1] was used to obtain the unit-cell geometrical parameters and for the data collection (30s/frame scan time for a sphere of diffraction data). The raw frame data were processed using SAINT[1] and SADABS[2] to obtain the data file of the reflections. The structures were solved using SHELXT[3] (Intrinsic Phasing method in the APEX 3 program). The refinement of the structures (based on F^2 by full-matrix least-squares techniques) was carried out using the SHELXTL-2014/7 program[3] in the WinGX suite v.2014.1.[4] The hydrogen atoms were introduced in the refinement in defined geometry and refined "riding" on the corresponding carbon atoms.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. CCDC 2152004-2152005. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223 336033; e-mail, deposit@ccdc. cam.ac.uk).

6. HPLC analyses

Table S28. HPLC analyses data

compound	K'1[a]	α[b]	eluent	Column temperature (°C)	CD sign at 280 nm
1aa	1.125	1.74	Hexane/CH_2Cl_2 80/20	20	+
2a	1.21	2.00	Hexane/CH_2Cl_2 80/20	20	**+**
2b	1.67	1.36	Hexane/CH_2Cl_2 80/20	20	**+**
2c	0.66	1.12	Hexane/CH_2Cl_2 80/20	20	**+**
3	0.77	1.00	Hexane/CH_2Cl_2 80/20	20	No signal

[a] retention factor, defined as $(t_1-t_0)/t_0$ where t_1 is the elution time of the 1st eluted enantiomer and t_0 is the retention time of a non-retained probe solute

[b] enantioselectivity factor, defined as k'2/k'1

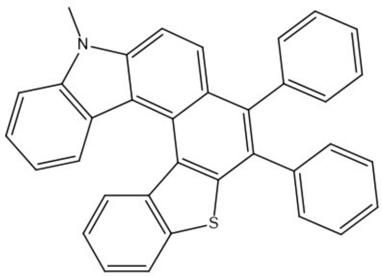
[1] Bruker. APEX3 and SAINT; Bruker AXS Inc.: Madison, WI,USA, 2015.

[2] Krause, L.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D. Comparison of Silver and Molybdenum Microfocus X-Ray Sources for Single-Crystal Structure Determination. *J. Appl. Crystallogr.* **2015**, *48*, 3−10.

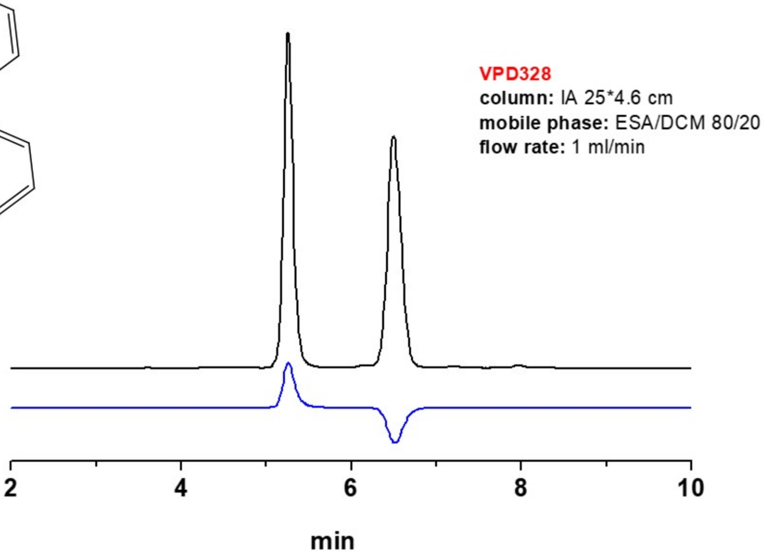
[3] Sheldrick, G. M. SHELXT − Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr., Sect. A: Found. Adv.* **2015**, *71*, 3−8.

[4] Farrugia, L. J. WinGX and ORTEP for Windows: An Update. *J. Appl. Crystallogr.* **2012**, *45*, 849−854.

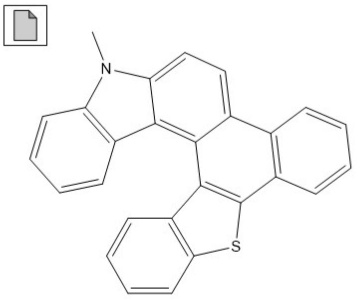
HPLC chromatogram of (±)-**1aa**



Compound: **1aa**

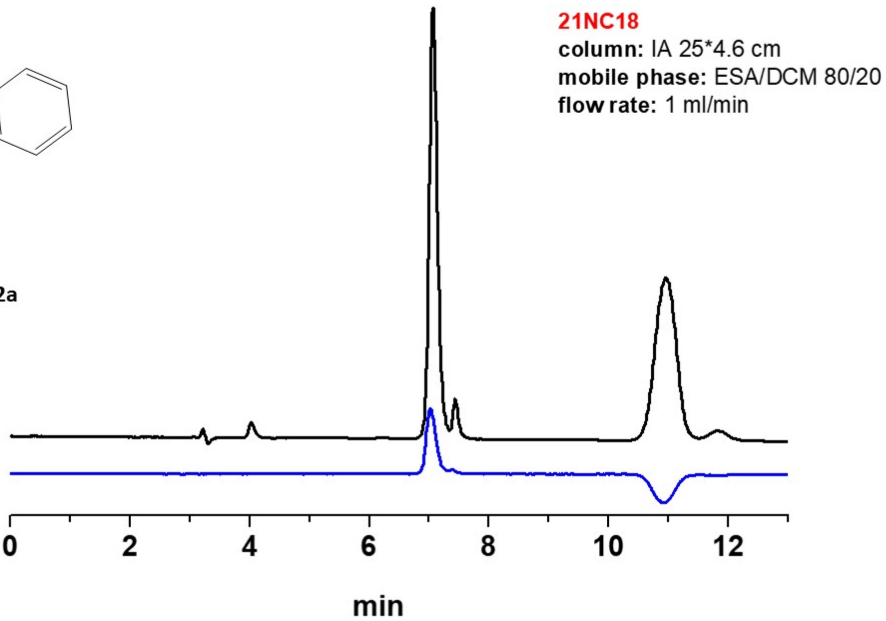


HPLC chromatogram of (±)-**2a**

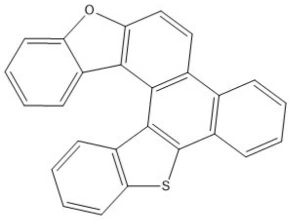


Compound: **2a**

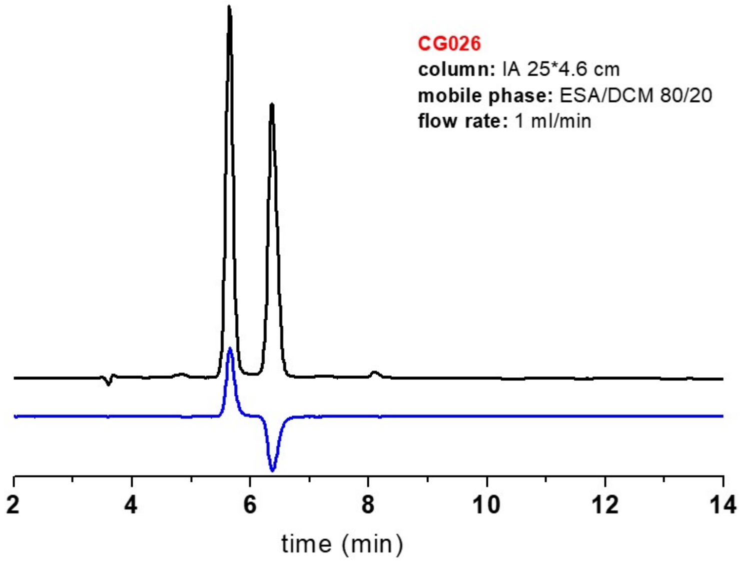
k’ = 1,21
k’’ = 2,43
α = 2,01



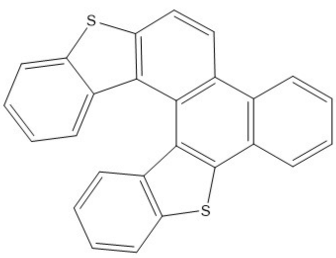
HPLC chromatogram of (±)-**2b**



Compound: **2b**

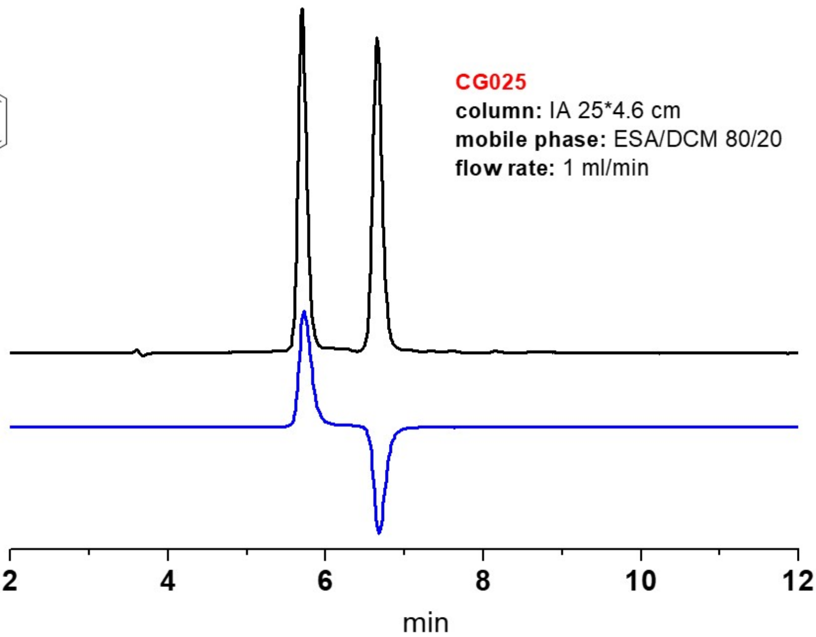


HPLC chromatogram of (±)-**2c**

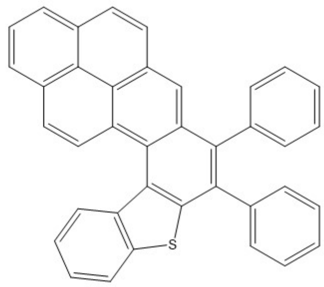


2c

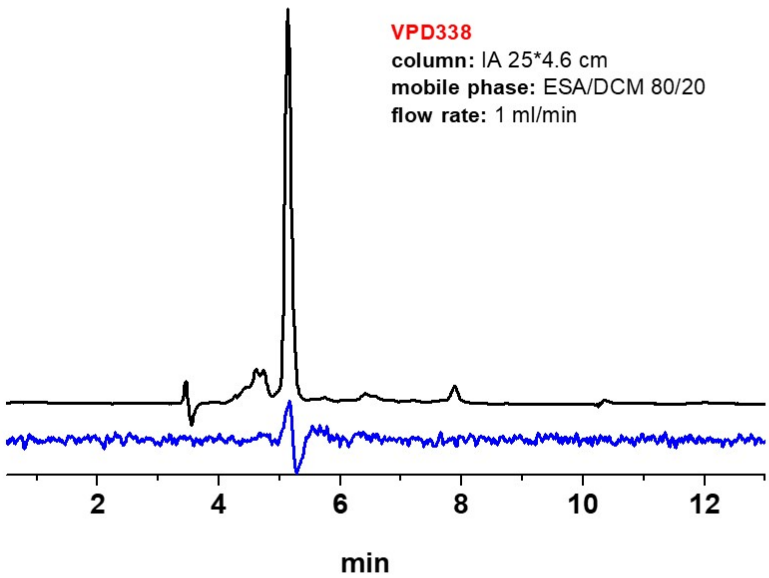
Compound: **2c**



HPLC chromatogram of (±)-**3**



Compound: **3**



7. DFT calculations of racemization barriers and absolute configuration assignment of 2a

DFT calculations have been conducted to optimize the structure of compounds **1aa**, **1ba**, **1ca**, **2a**, **2b**, **2c** and **3**. With the aim of determining the transition states, relaxed scans have been performed at M06-2X/6-31+g(d,p) level by varying the τ dihedral angle defined below. For compounds with phenyl pendants also the ϕ angle varies during the interconversion run; for this reason, we report the lowest energy path obtained by varying both angles τ and ϕ: this permits one to identify the correct TS state, which is characterized by just one imaginary frequency. The plots of energy values versus τ are reported in the text.

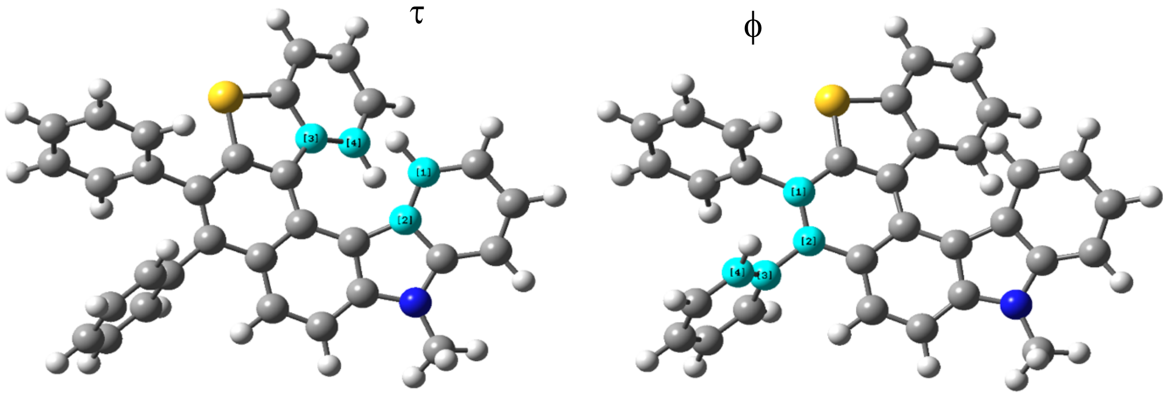


Figure S1. Definition of τ and ϕ dihedral angles (see Figure 3, text)

The minimum energy state and the transition state have been determined at M06-2X/cc-ptvz level to obtain the barrier values reported in the text.

For compound **3** the optimized stable structure can be compared with the X-ray structure; similar geometrical parameters are obtained, in particular: the dihedral angle between the mean planes of the two components is 29.66° according to theory, and the C–C inner core bonds are longer than 1.40 Å, as expected from X-ray data.

To assign the absolute configuration we considered compound **2a** optimized in its *P* configuration and for it we performed TD-DFT calculation of the UV and ECD spectra.

The comparison presented here of M06-2X/cc-ptvz and M06/cc-ptvz calculated spectra has been made by assigning 0.2 eV bandwidth Gaussian shape bands to calculated transitions. Also calculations at CAM-B3LYP level with Becke-Johnson damping Grimme's dispersion (GD3B)[5] (not shown) confirm the M06-2X result. All calculations have been conducted with Gaussian16 package.[6]

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[5] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comp. Chem.* **2011**, *32*, 1456-1465.

[6] M. J. Frisch, G.W. Trucks, H.B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta Jr, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 16 Revision B.0.1., Gaussian Inc. Wallingford CT, **2016**.

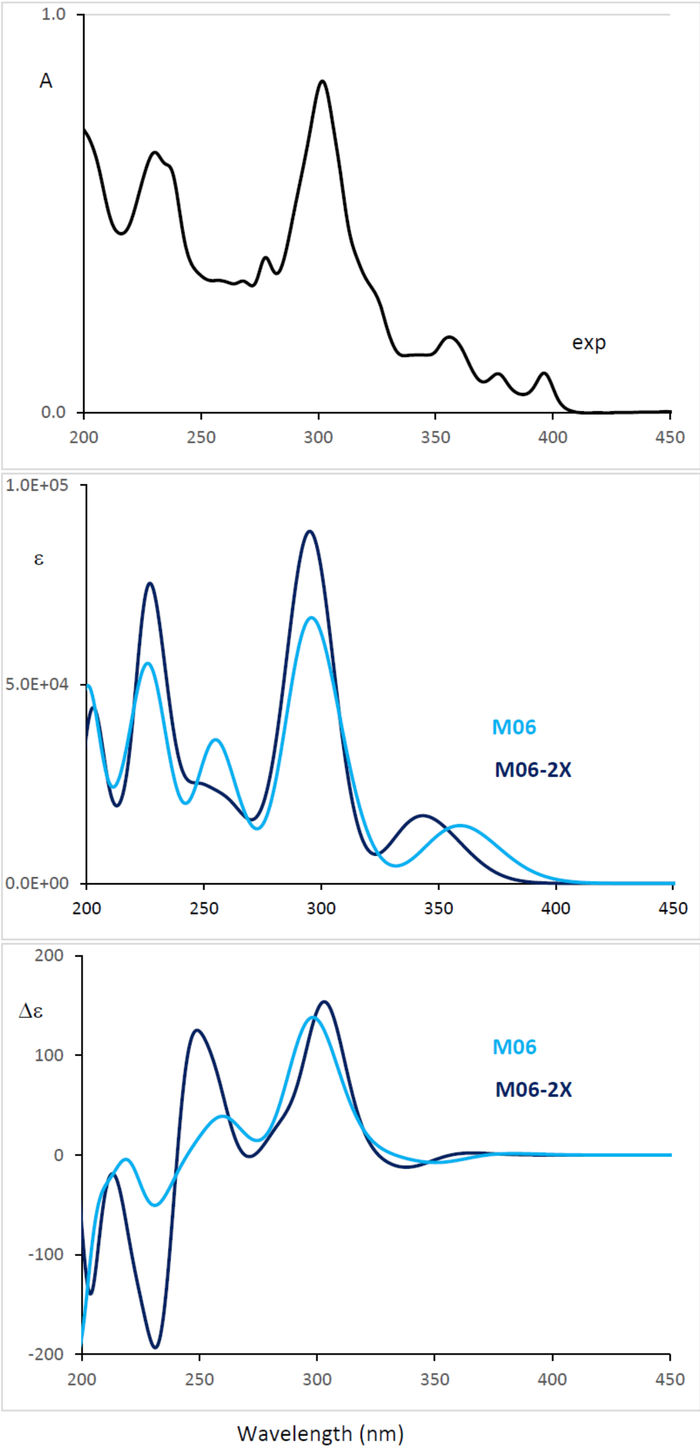


Figure S2. (top) experimental absorption spectrum of **2a**, (middle) calculated absorption spectra and (bottom) calculated CD spectra at M06-2X/cc-pvtz and M06/cc-pvtz level for the *P* structure of **2a.** Wavelength shift of +25 nm has been applied to the first calculation, no shift to the second.

8. Absorption and emission spectra of spirobifluorene, pyrene, dibenzothiophene and dibenzofuran series

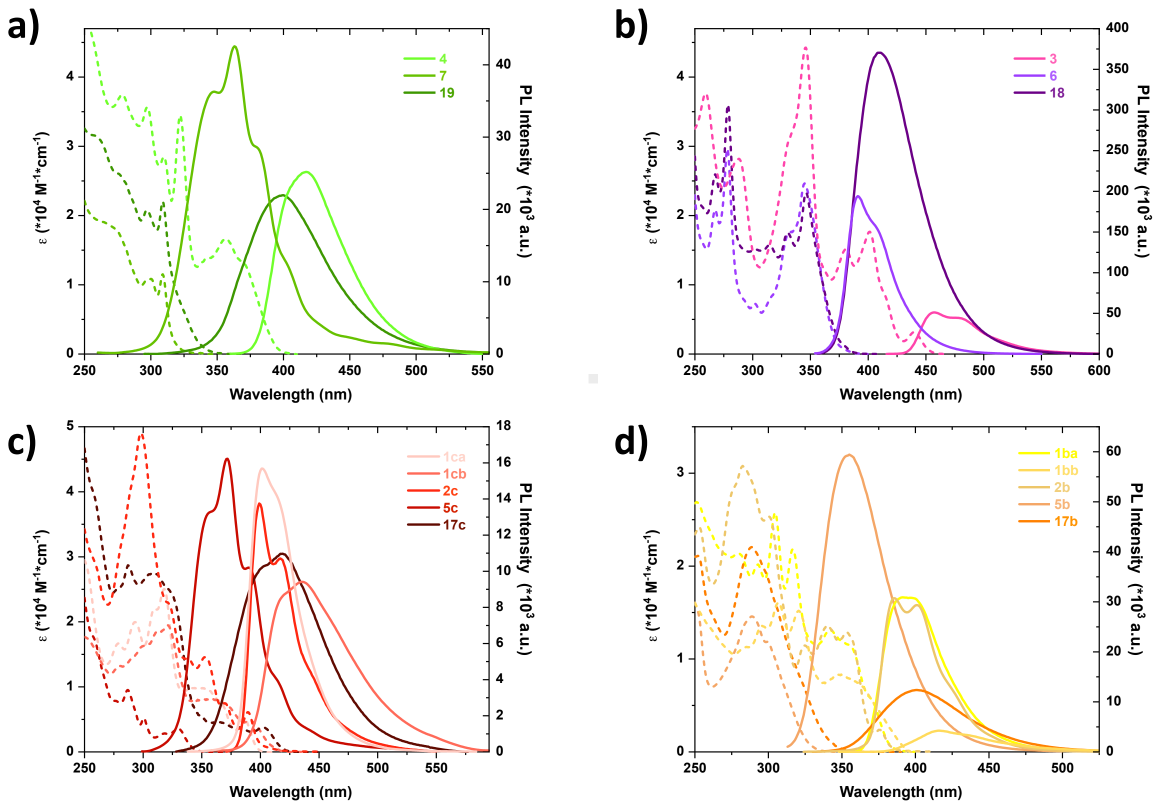
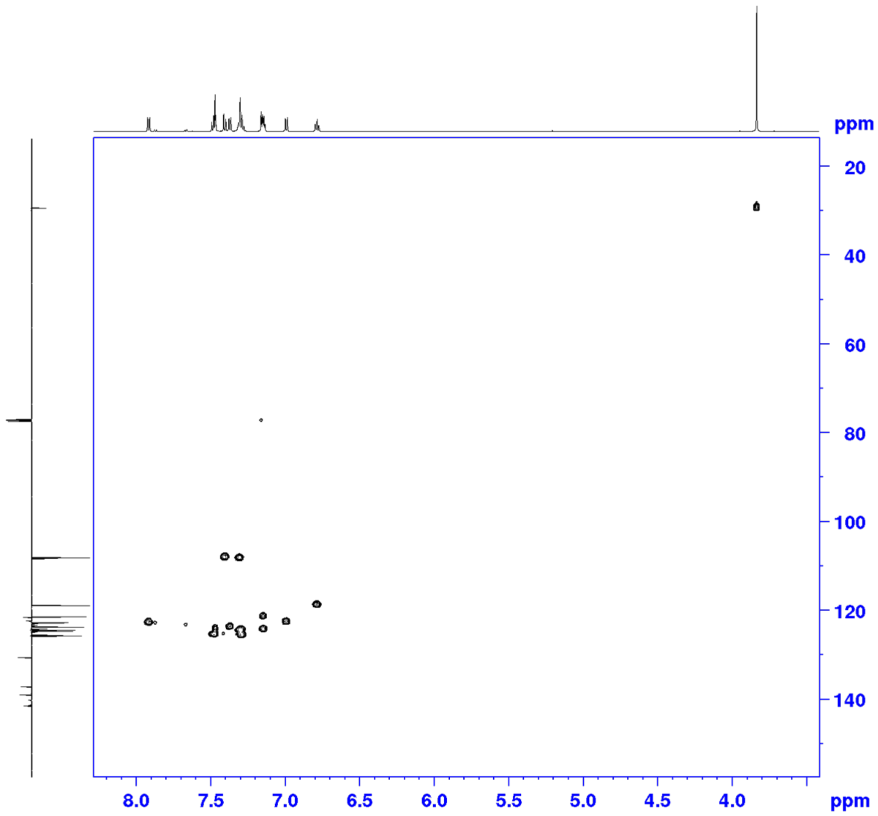
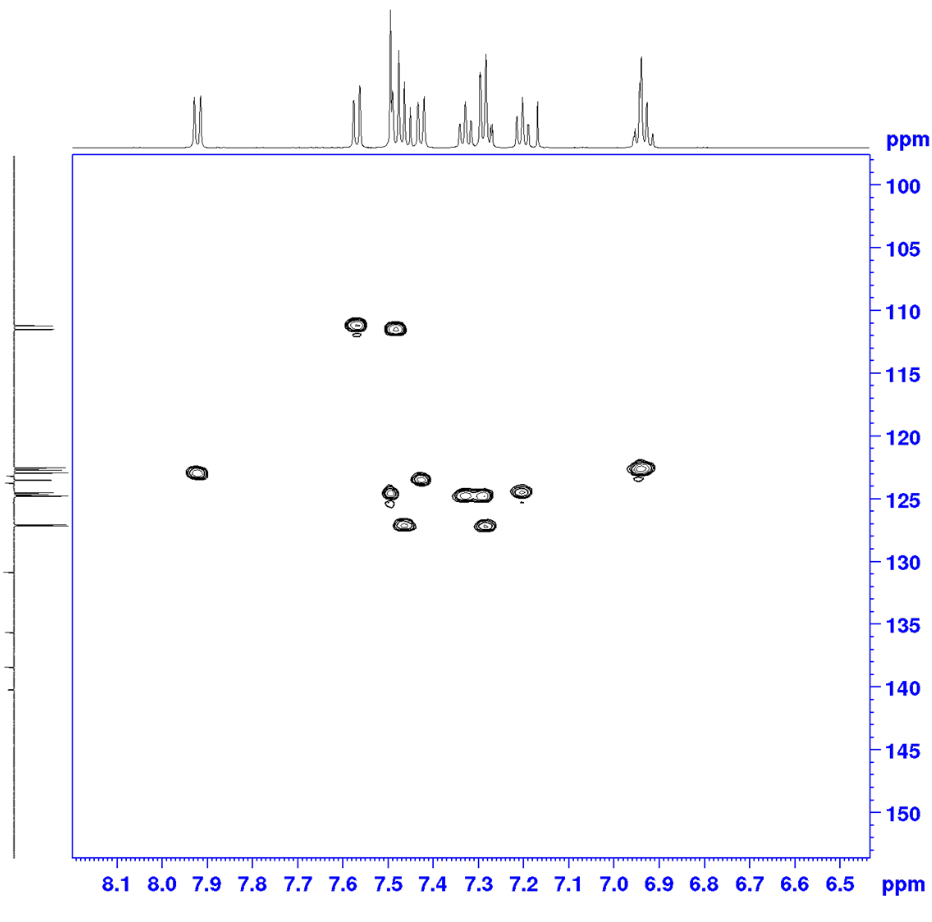


Figure S3. Absorption (dashed) and emission (solid) spectra in CH_2Cl_2 of the different series: a) spirobifluorene, b) pyrene c) dibenzothiophene d) dibenzofuran. Emission spectra were normalized to 0.1 intensity at excitation wavelength.

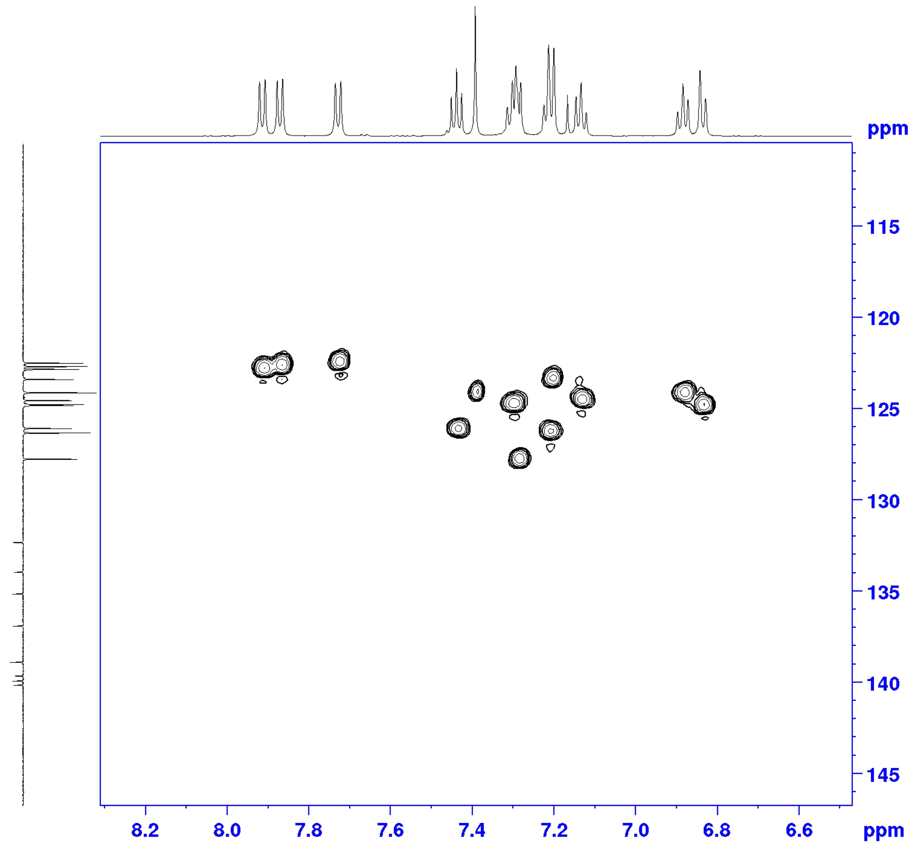
^{1}H-^{13}C HSQC spectra of compound **5a**.



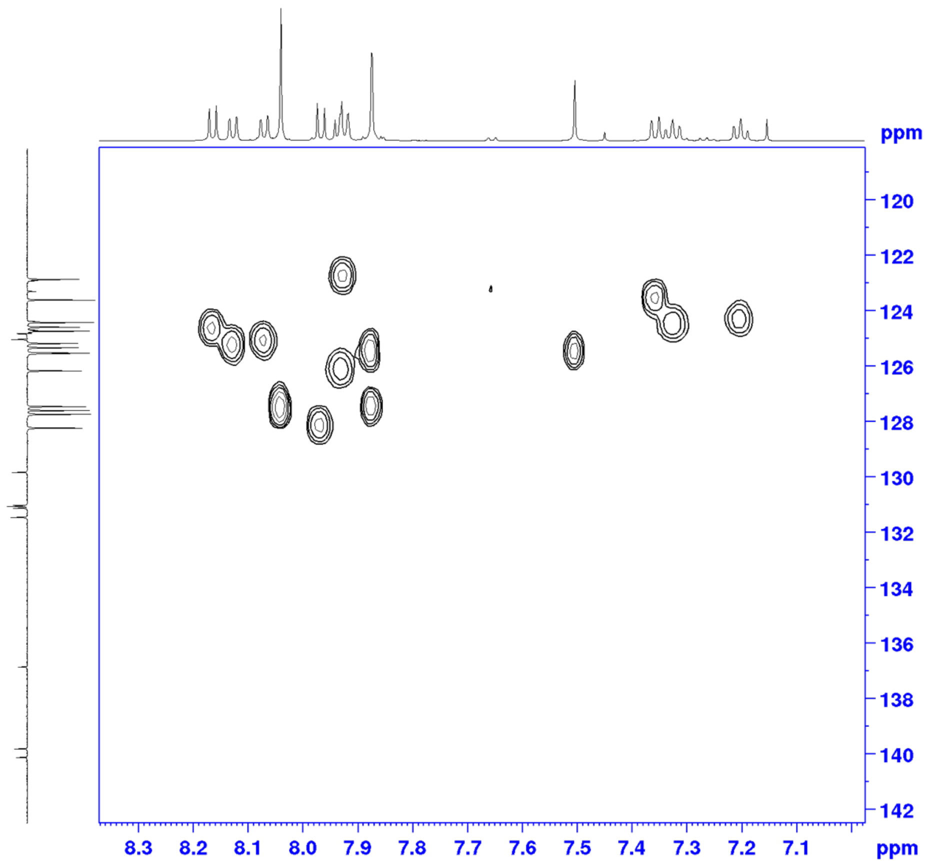
^{1}H-^{13}C HSQC spectra of compound **5b**.



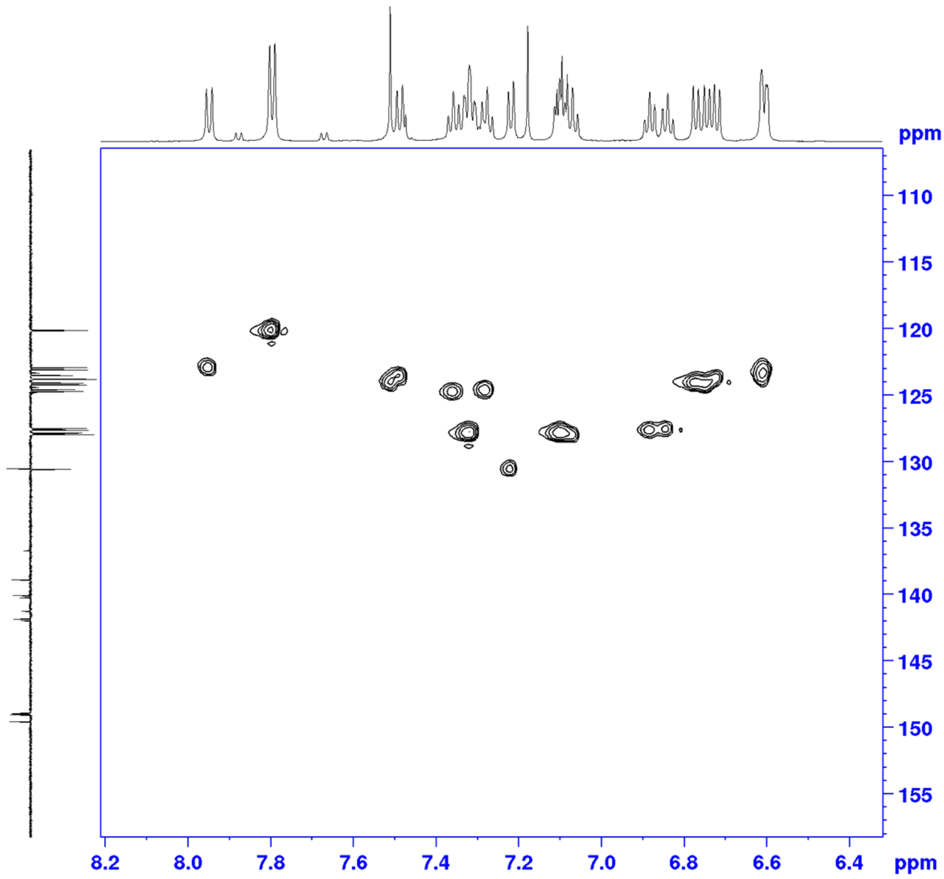
^1H-^{13}C HSQC spectra of compound **5c**.



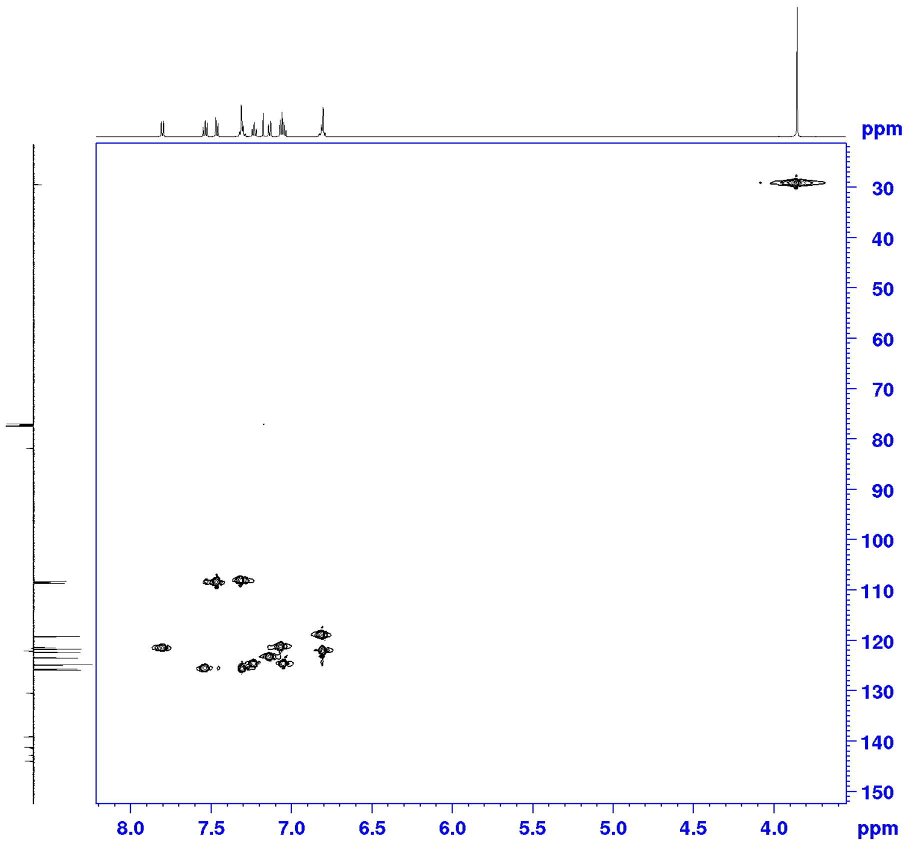
^1H-^{13}C HSQC spectra of compound **6**.



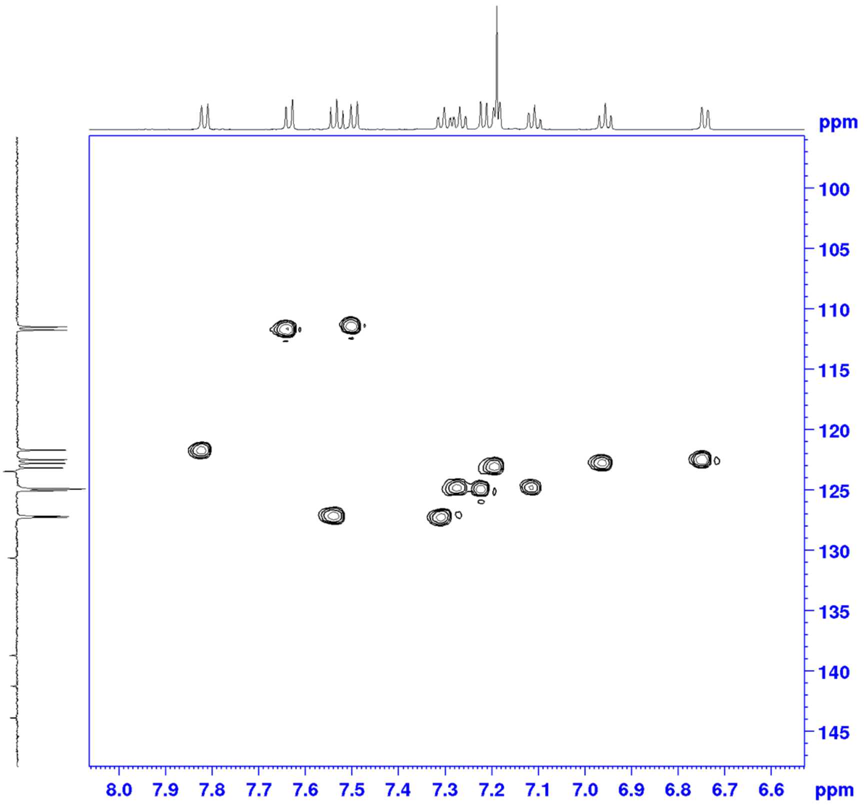
^{1}H-^{13}C HSQC spectra of compound **7**.



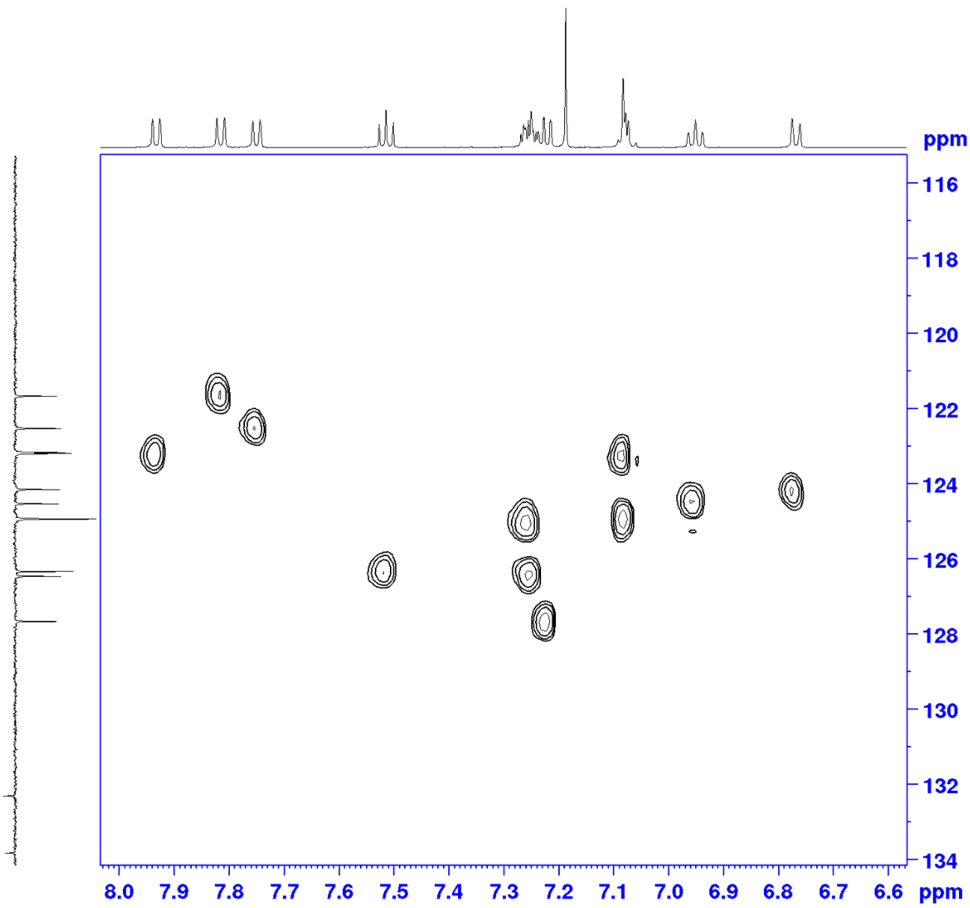
^{1}H-^{13}C HSQC spectra of compound **12a**.



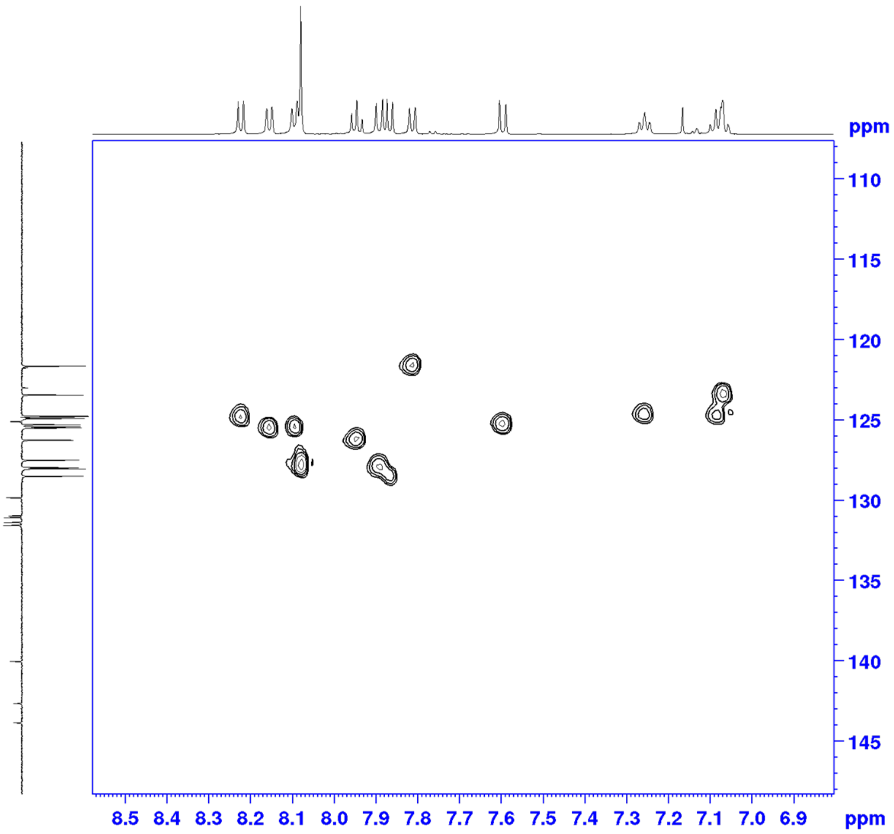
[1]H-[13]C HSQC spectra of compound **12b**.



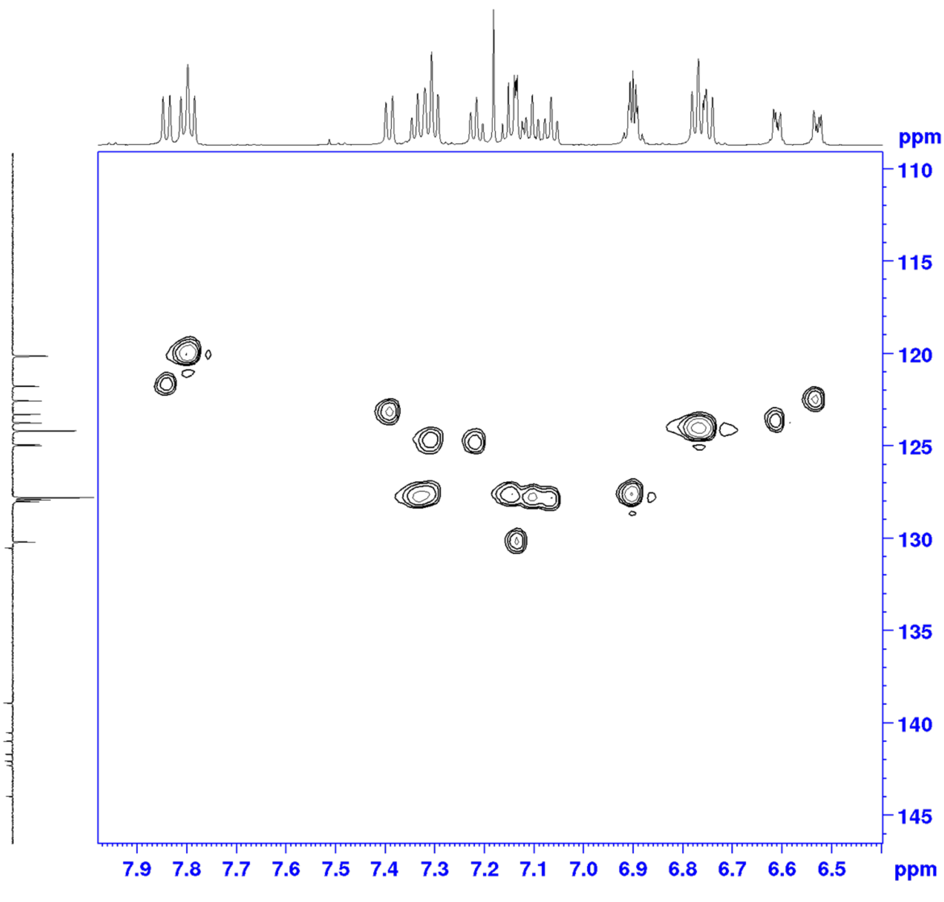
[1]H-[13]C HSQC spectra of compound **12c**.



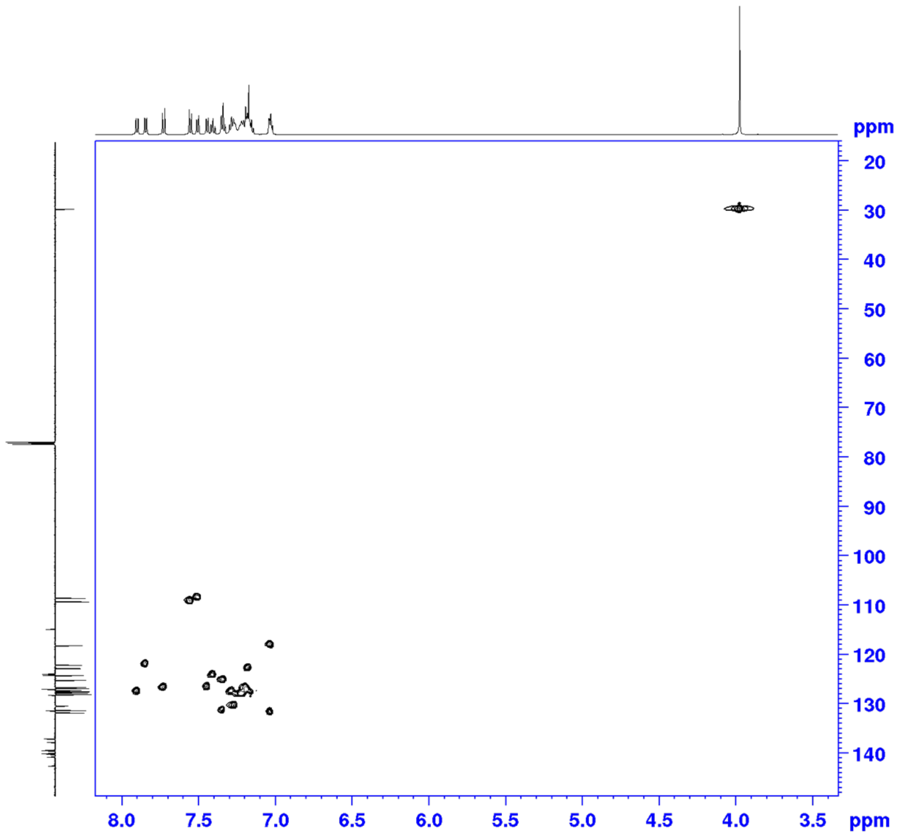
^{1}H-^{13}C HSQC spectra of compound **13**.



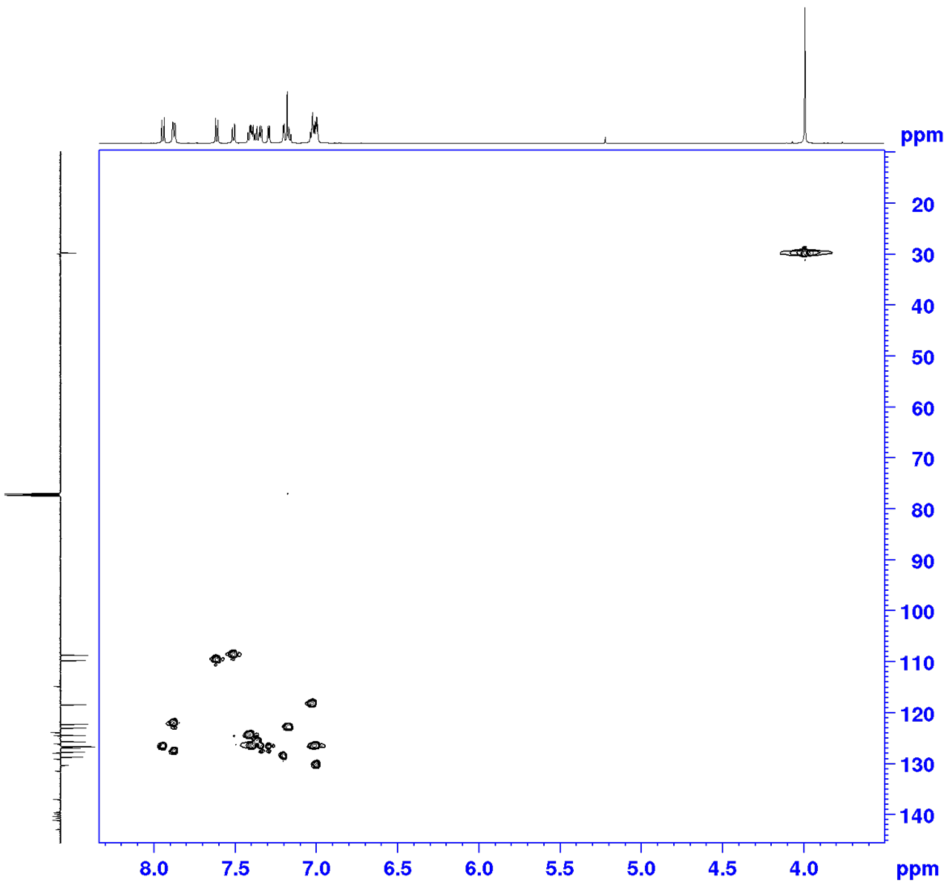
^{1}H-^{13}C HSQC spectra of compound **14**.



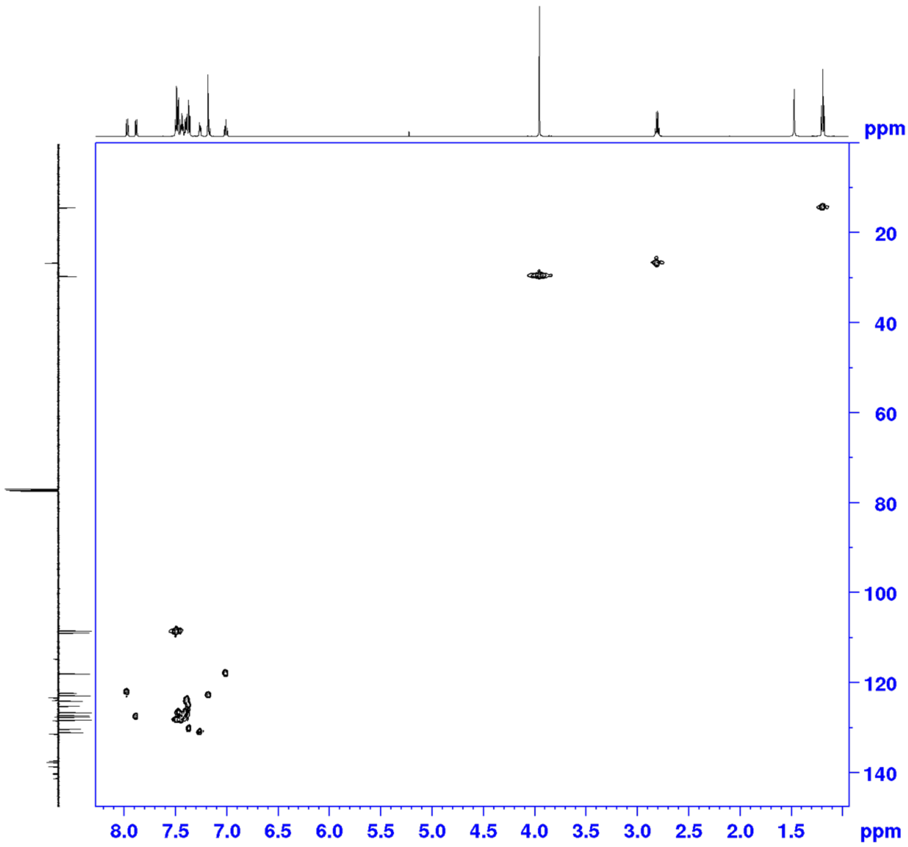
^{1}H-^{13}C HSQC spectra of compound **1aa**.



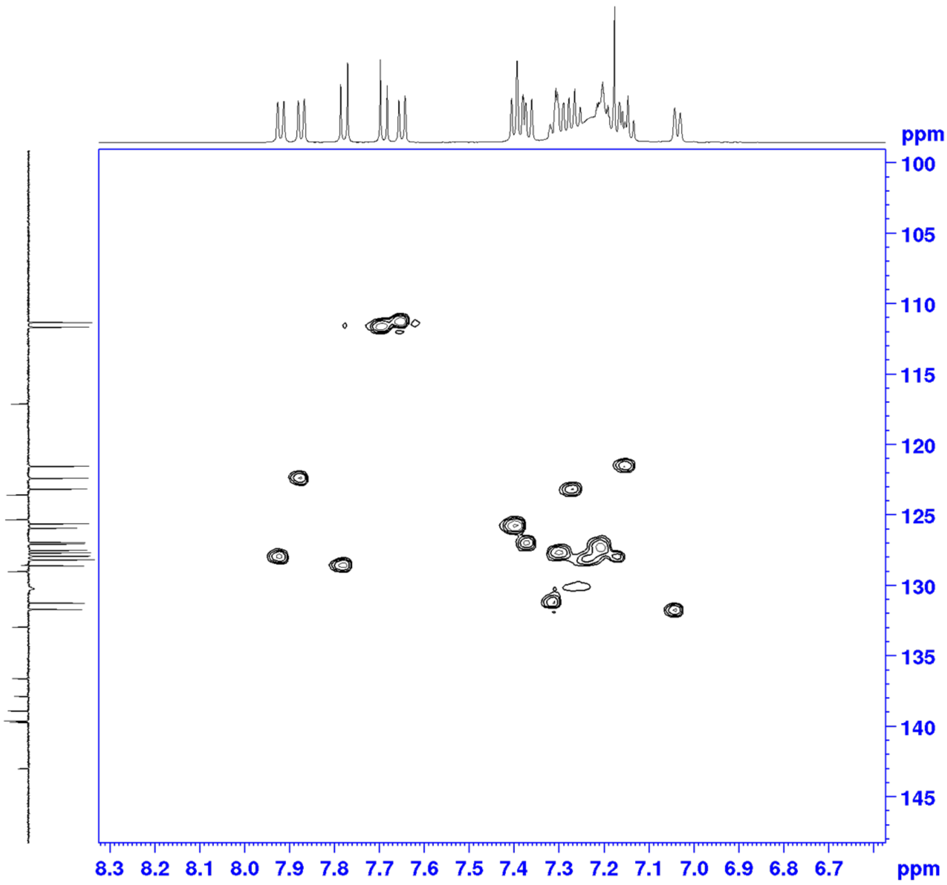
^{1}H-^{13}C HSQC spectra of compound **1ab**.



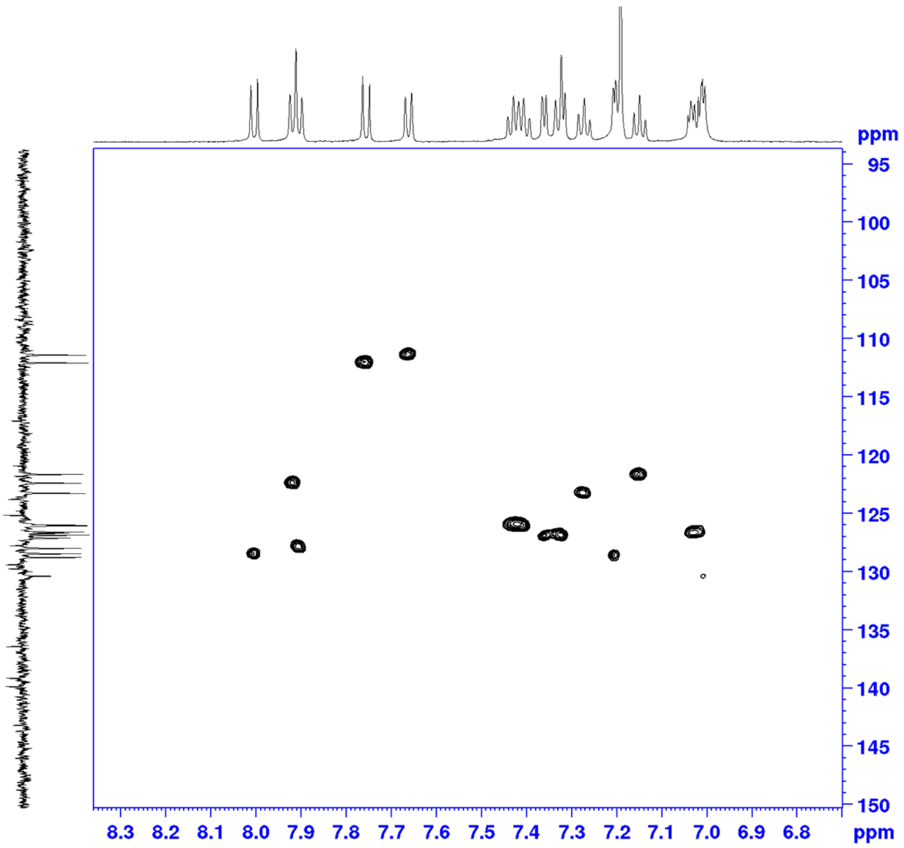
^{1}H-^{13}C HSQC spectra of compound **1ac**.



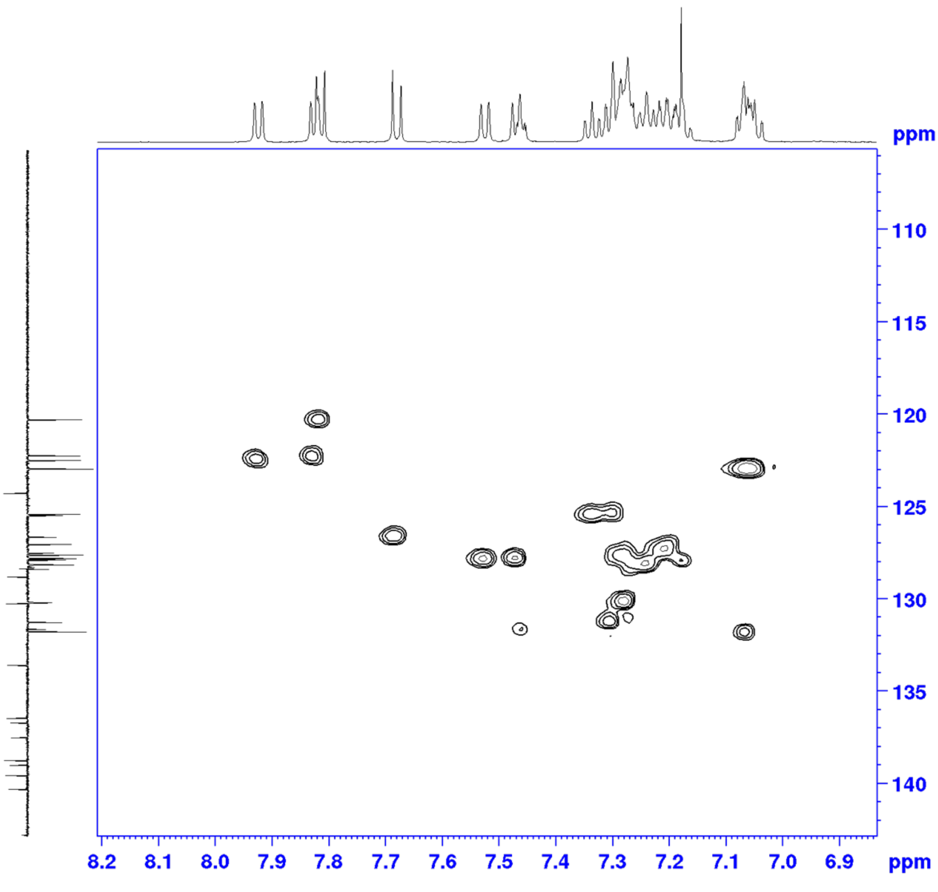
^{1}H-^{13}C HSQC spectra of compound **1ba**.



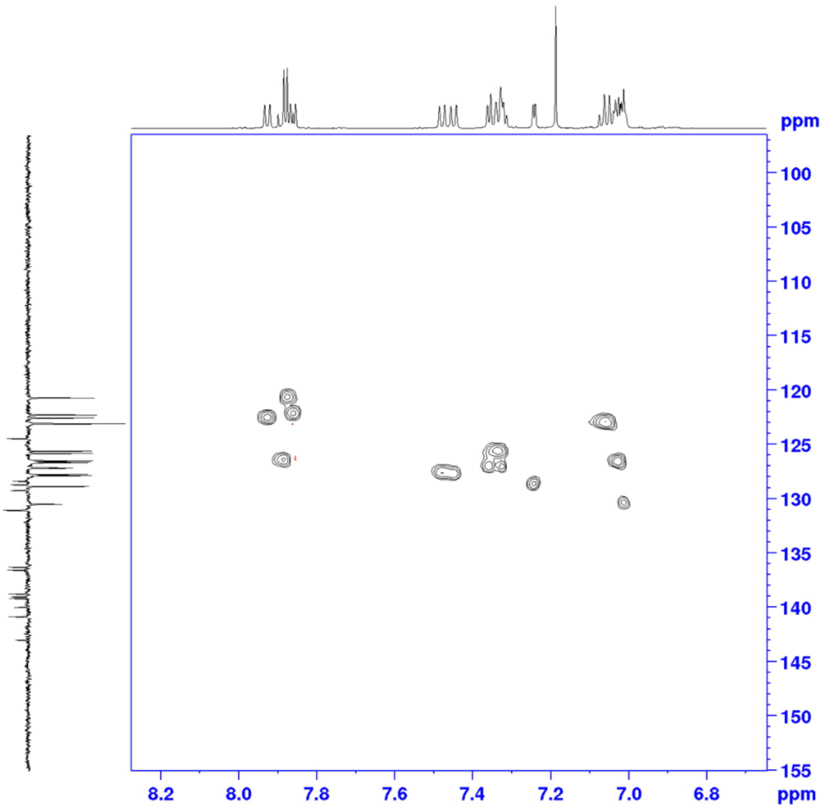
^{1}H-^{13}C HSQC spectra of compound **1bb**.



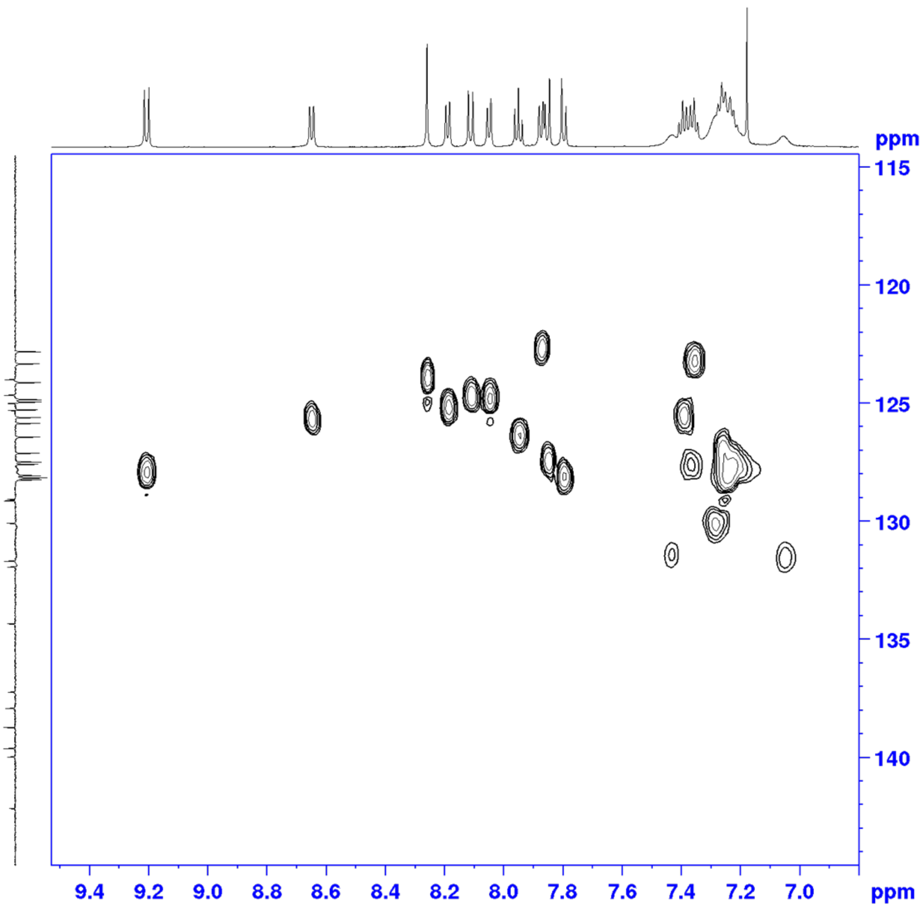
^{1}H-^{13}C HSQC spectra of compound **1ca**.



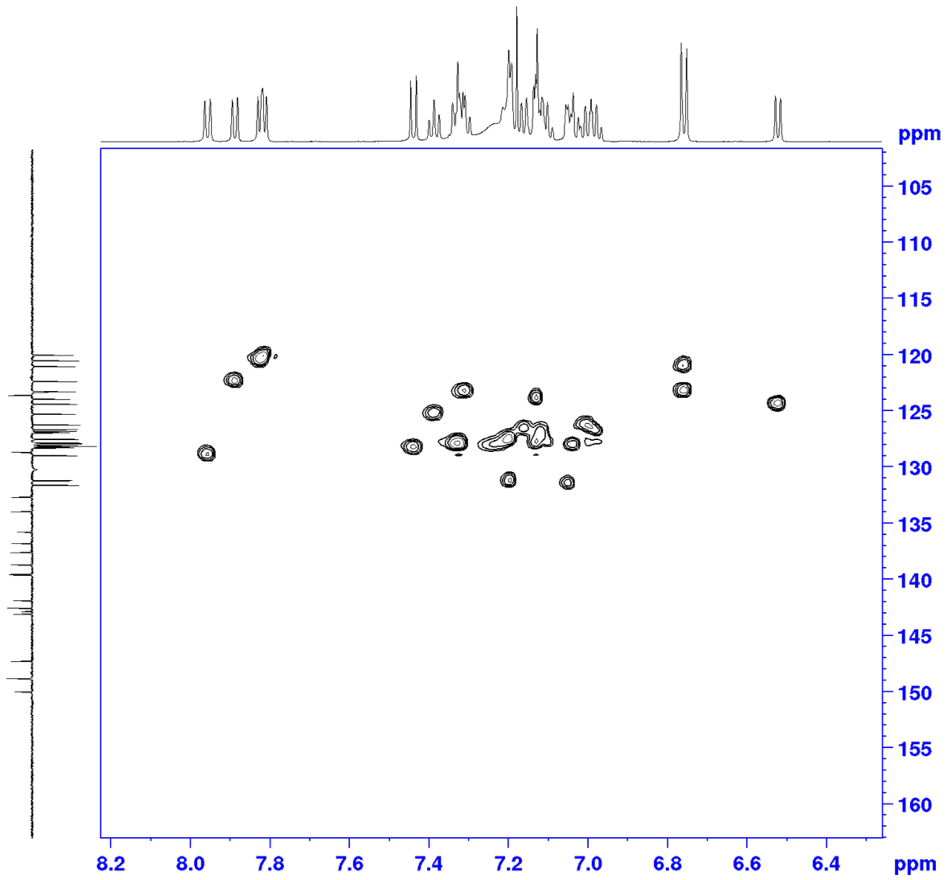
^{1}H-^{13}C HSQC spectra of compound **1cb**.



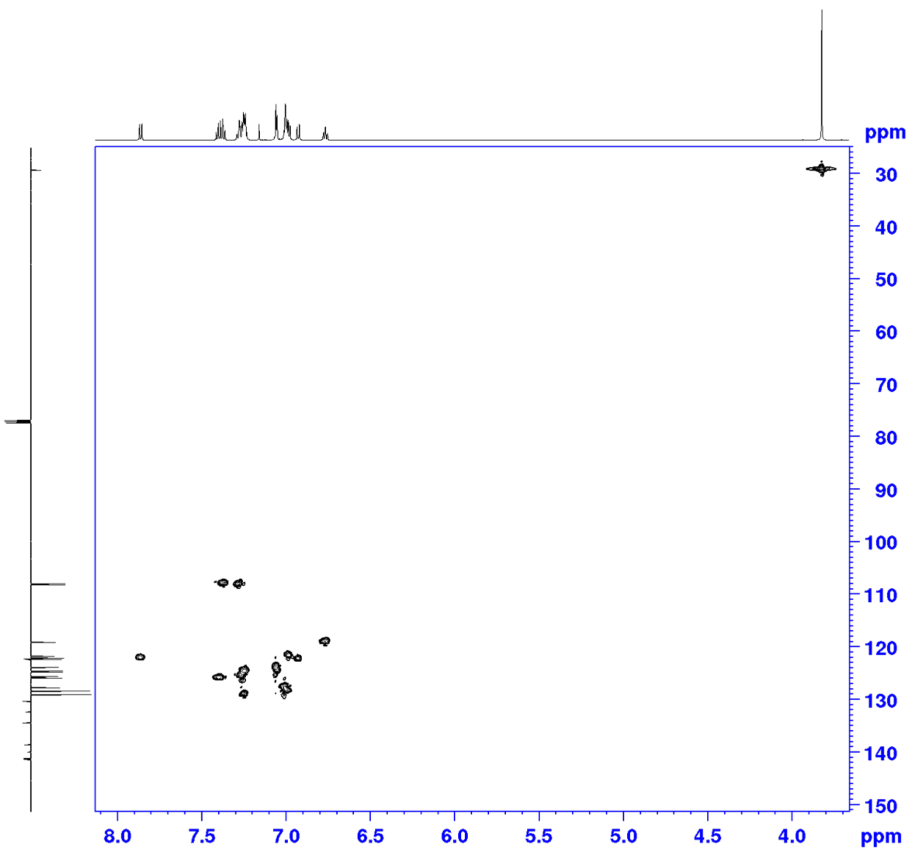
^{1}H-^{13}C HSQC spectra of compound **3**.



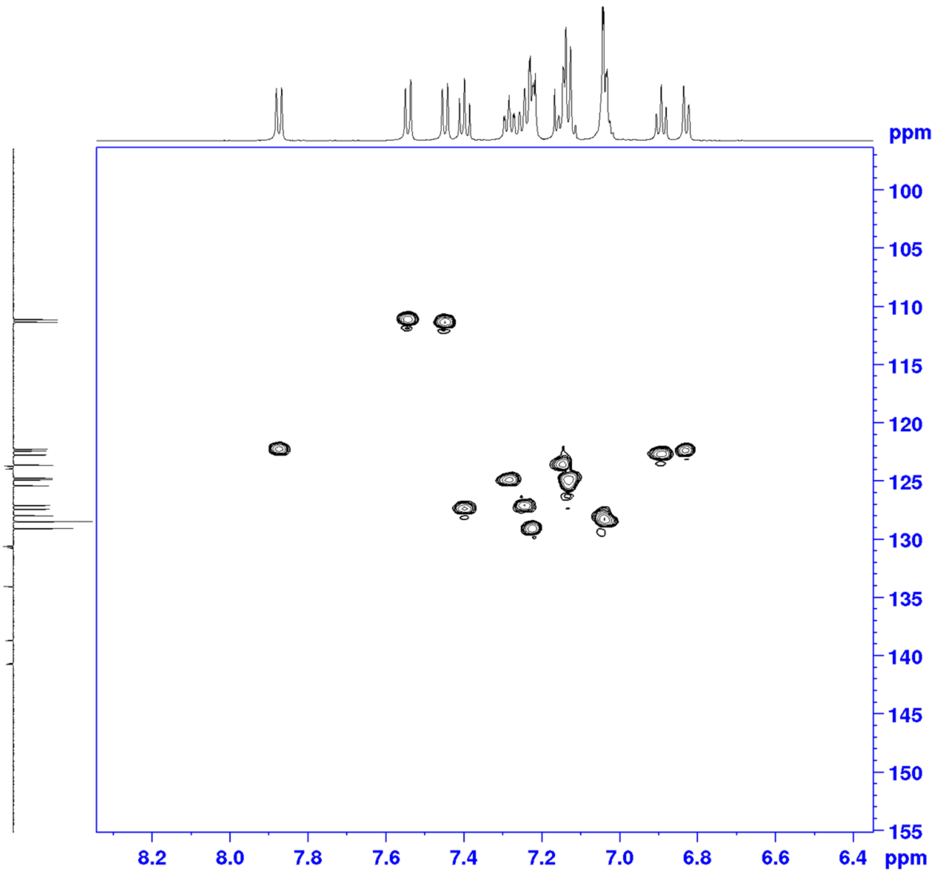
^{1}H-^{13}C HSQC spectra of compound **4**.



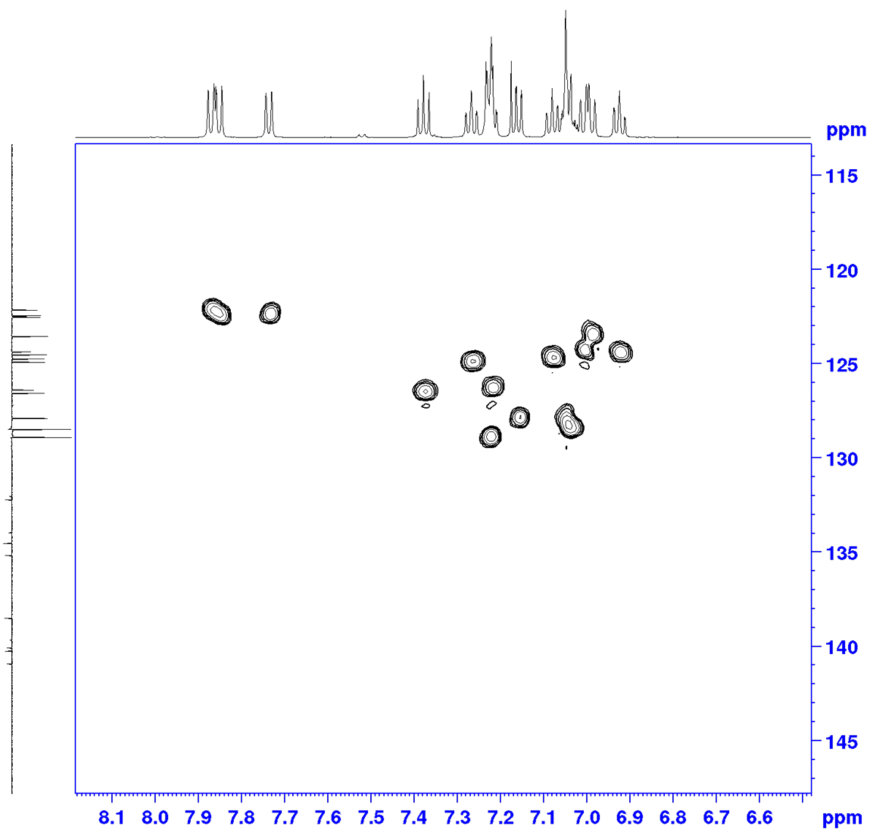
^{1}H-^{13}C HSQC spectra of compound **17a**.



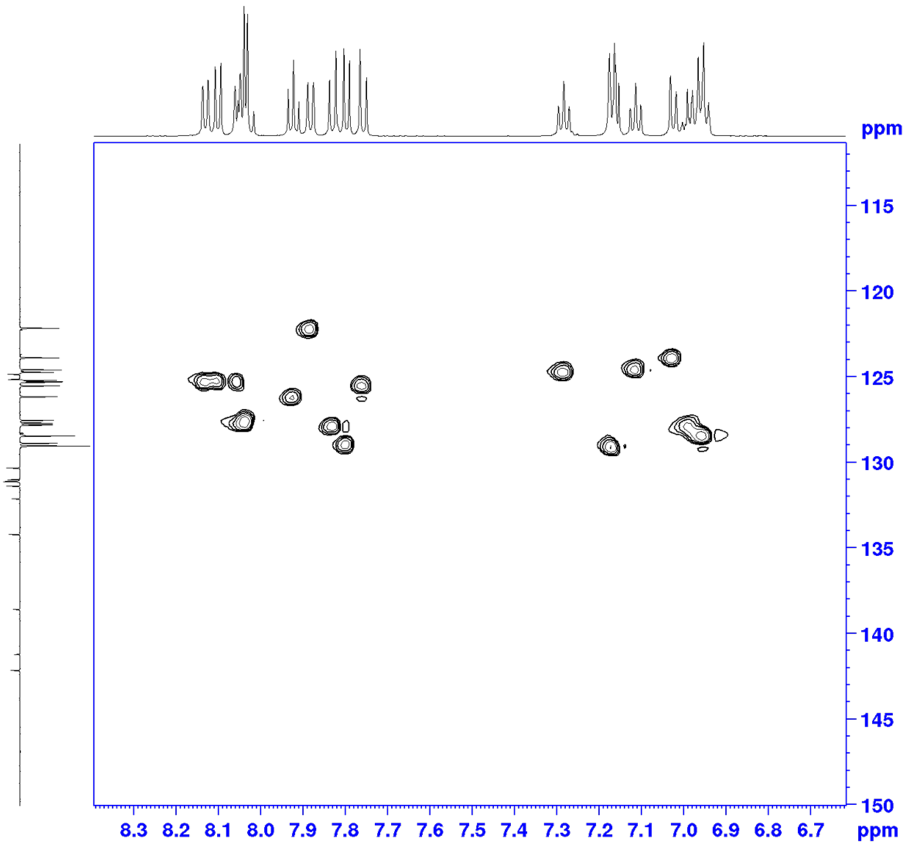
^{1}H-^{13}C HSQC spectra of compound **17b**.



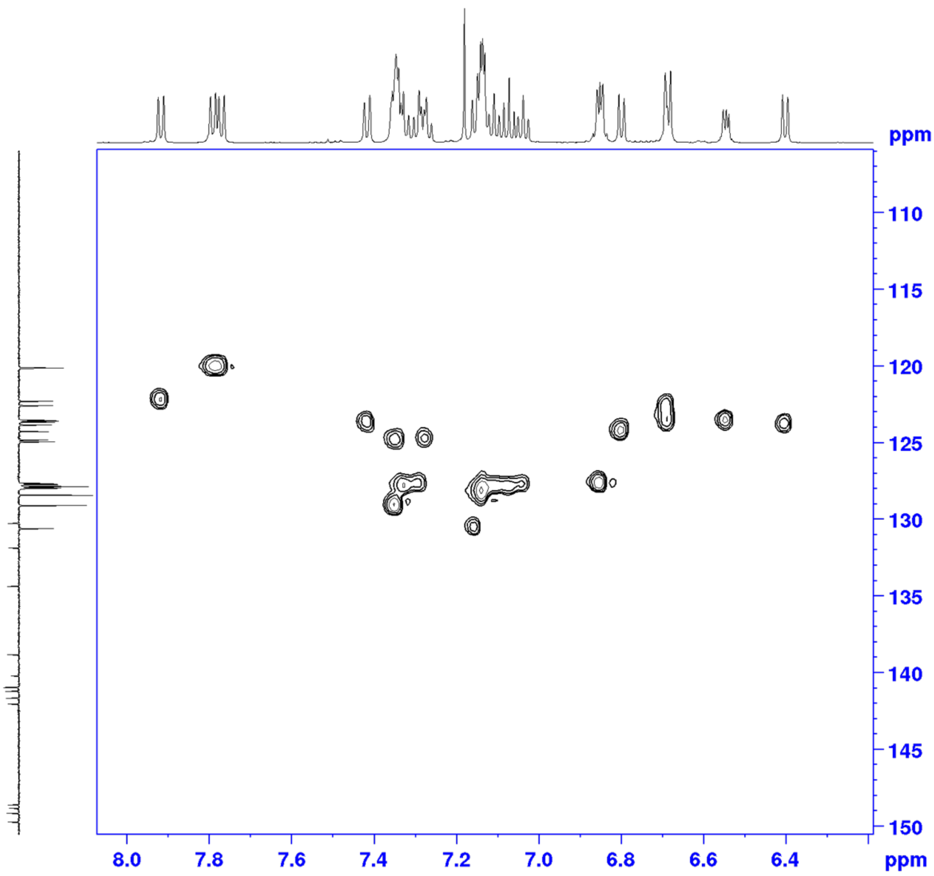
^{1}H-^{13}C HSQC spectra of compound **17c**.



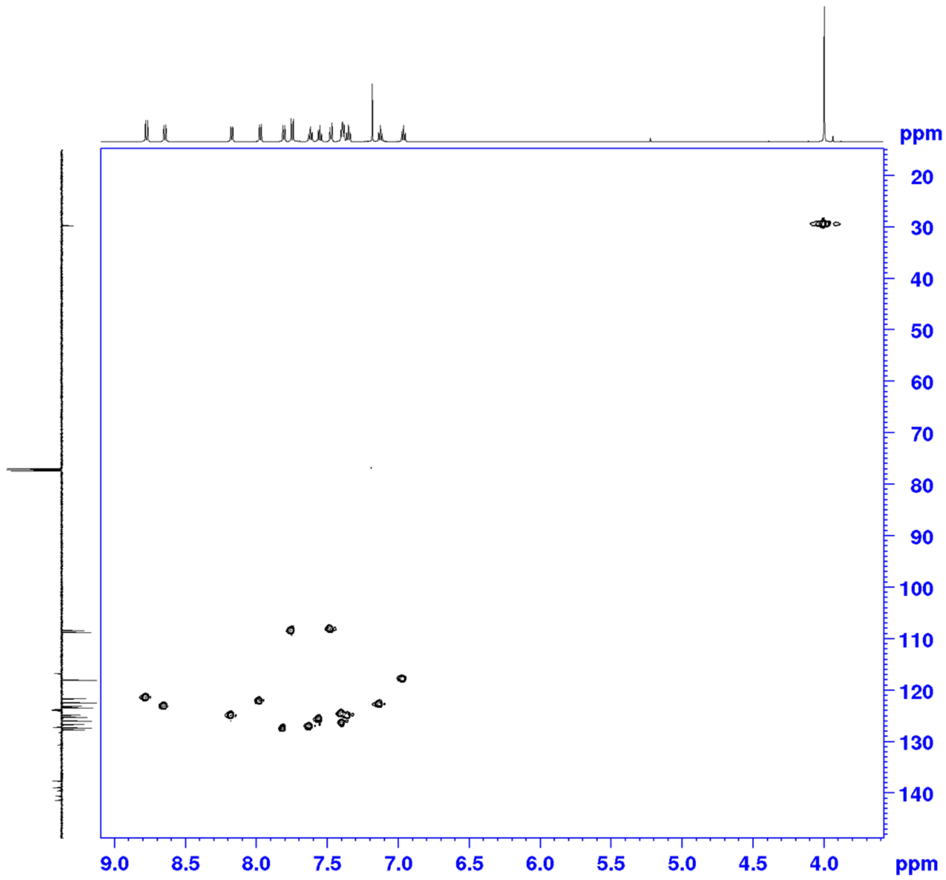
^{1}H-^{13}C HSQC spectra of compound **18**.



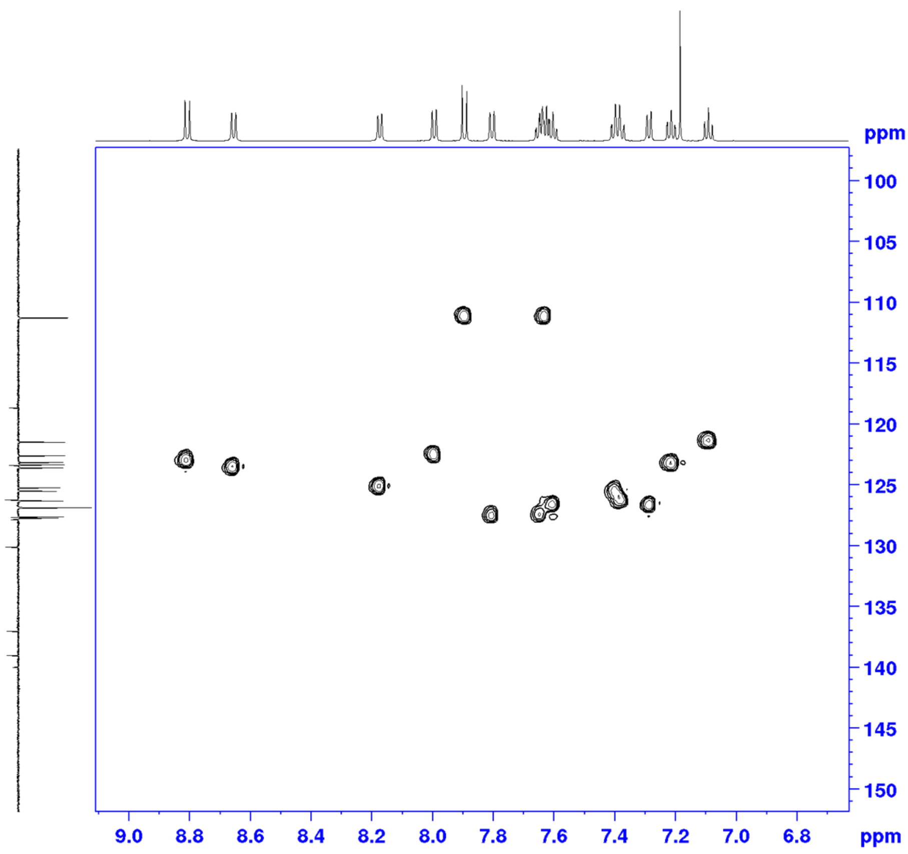
^{1}H-^{13}C HSQC spectra of compound **19**.



^{1}H-^{13}C HSQC spectra of compound **2a**.



^{1}H-^{13}C HSQC spectra of compound **2b**.



^{1}H-^{13}C HSQC spectra of compound **2c**.