Supplementary information

A single pot synthesis of 4-hydroxybenzophenones via acid-catalyzed alkoxylation followed by DDQ assisted oxo-demethoxylation of *p*-quinone methides

Jasbir Kaur Mahey,[ab] Chunilal B. Pawara,[ab] Sumit B. Kamble[ab]*

[a]Department of Salt and Marine Chemicals, CSIR-Central Salt and Marine Chemicals Research Institute, Gijubhai Badekha Marg, Waghavadi road Bhavnagar, Gujarat-364002, India. sbkamble@csmcri.res.in

[b]Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, Uttar Pradesh, India.

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General information

Unless others noted, a flame-dried clean glass apparatus was used to carry out all the reactions under a closed atmosphere. A.R. grade alcohols and dry toluene purchased from Finar chemicals, DDQ, Amberlyst-15, and aldehydes procured from Alfa Aser and other reagents obtained from TCI. All the *p*-QMs were synthesized using different aldehydes according to the reported procedure.[55] Aluminum TLC plates coated with silica gel 60 F_{254} purchased from Merck and used in TLC chromatography (10-35% ethyl acetate in hexane mobile phase) after 4 cm X 2 cm uniform cutting. The crude reaction mixture was purified to separate the compounds over column chromatography using 10-20 % ethyl acetate in hexane packed with 200-400 mesh flash silica. Final products were characterized using ^{1}H-NMR and ^{13}C-NMR in D_6-DMSO (0.01% TMS, as reference std.) as a solvent on 500 MHz/600 MHz JEOL NMR instruments. FT-IR was carried out at room temperature in ATR (PIKE make) mode on the PerkinElmer frontier instrument. BRUKER SMART APEX (CCD) diffractometer used to analyze the single-crystal structure of the compound **1a** at room temperature. LC-MS was carried out on the Agilent 1290 infinity-2 in methanol as a solvent at room temperature. GENESYS 10S UV-Vis, 190-1100 nm instrument used for UV-Visible spectroscopic study at room temperature. EPR of the reaction mixtures carried out on Magnettech MS-5000 EPR spectrometer instrument having magnetic field range of 30 to 650 mT with a field resolution of 0.03 μT.

General procedures

1. General procedure for the synthesis of 3,5-di-tert-butyl-4-hydroxyphenyl(Ar)methanone (3,5-DtBu-4HBP) (Compound 1)

Amberlyst-15 (10 wt.%) was added to the solution of *p*-QMs (1 mmol) in methanol (10 mL) taken in 25 mL RBF. Then the mixture was stirred at room temperature until the alkoxylation intermediate 8 formed, confirmed by TLC. Consecutively DDQ (1.1 mmol) was added, and the solution was stirred continually until complete consumption of the intermediate. Amberlyst-15 was filtered to separate from the reaction mixture and washed with 10 mL methanol. The crude solid obtained from filtrate after recovery methanol on a rota evaporator was purified using column chromatography on silica gel (200-420 mesh) over ethyl acetate in hexane (0-5 %) mobile phase to obtain desired products 3,5-di-tert-butyl-4-HBP (**1**). The DDHQ remained in the column separated using 100% ethyl acetate for the recycling study. The purified products were characterized using NMR, FT-IR and Mass spectroscopy.

2. Procedure for the dealkylation of 3,5-di-tert-butyl-4-HBP (compound 1*)* to 4-HBP (Compound 9)

Compound **1** (1 mmol) was treated with $AlCl_3$ (5 mmol) in dry toluene (10 mL) and stirred the reaction mixture for 30 Min. at 120 ^{o}C in a 25 mL RBF under nitrogen. After completion of the reaction monitored by the TLC (50% EA in hexane), the mixture was cooled to room temperature. Further, the toluene was recovered using a rota evaporator, and the remaining residue was extracted using ethyl acetate and water

to remove the unreacted $AlCl_3$ and water-soluble impurities. Ethyl acetate was recovered on a rota evaporator, and crude was washed with 5 mL heptane and decanted to remove non-polar impurities and get a pure dealkylated product with 70-80% yield. The obtained dealkylated products were analyzed using NMR spectroscopy (^1H & ^{13}C) and compared with the reported compounds.[1,2]

3. Gram scale synthesis of compound 1a using *p*-QMs (7a) as starting material

Amberlyst-15 (0.1 g, 10 wt.%) was added to the solution of *p*-QMs **7a** (1 g, 3.04 mmol) in 50 mL of methanol taken in 100 mL RBF. Then the mixture was stirred at room temperature for 1 h to complete alkoxylation. Then constantly stirred the solution for 1 h after adding the DDQ (0.759 g, 3.34 mmol) to obtain the desired 1a product by oxo-demethoxylation. The reaction mixture was then filtered to remove the Amberlyst-15 and washed with 25 mL methanol. The filtrate was evaporated on a rota evaporator to recover methanol and solid crude was purified using column chromatography on silica gel (200-420 mesh) using ethyl acetate in hexane (0-5 %) to obtain desired products 3,5-di-tert-butyl-4-HBP (**1**) with 97% yield (1.02 g).[3]

4. Direct gram-scale synthesis of compound 1a using 4-chlorobenzaldehyde (10a) as a starting material

Initially, 1 gm of 4-chlorobenzaldehyde (10a) was converted into p-QMs **7a** using the reported procedure in the two necks 250 mL RBF fitted with Dean-Stark apparatus in toluene, piperidine and acetic anhydride. After the formation of **7a** monitored by TLC, toluene was recovered by evaporation and extracted the reaction crude in ethyl acetate and water. The **7a** contained crude from recovered ethyl acetate further used for directly synthesizing compound **1a** using our developed protocol. Accordingly, Amberlyst-15 (0.1 g, 10 wt.%) was added, and the reaction mixture was stirred for 1 h at room temperature to form an intermediate **8a**. DDQ (0.759 g, 3.34 mmol) was added and stirred the reaction mixture for 1h till the completion of the reaction. Amberlyst-15 was filtered, and the methanol was removed to get the crude solid. The crude was purified using column chromatography on silica gel (200-420 mesh) to obtain the 0.786 g (75%) of the compound of the desired 4-HBP (**1a**).

Reference

1. A. Sagadevan, V. P. Charpe, A. Ragupathi and K. C. Hwang, *J. Am. Chem. Soc.*, 2017, **139**, 2896-2899.
2. S. Sultan, M. U. S. Bhat, M. A. Rizvi and B. A. Shah, *J. Org. Chem.*, 2019, **84**, 8948–8958.
3. J. Li, K. Wang, J. Wu, H. Zhang, Y. Chen, Q. Liu, J. Xu and W. Yi, *European J. Org. Chem.*, 2022, **2022**, e202200158.

5. Direct gram-scale synthesis of compound 9a using 10a as starting material

The crude obtained before column purification after following above-mentioned procedure of gram-scale synthesis using **10a**, majorly constituted with 1a, was further subjected to the gram-scale dealkylation. For this, $AlCl_3$ (5 eq. to **10a**) was added in 50 mL toluene and stirred the reaction mixture for 30 Min. at

120 °C in a 100 mL RBF under nitrogen. After the reaction completion, monitored by the TLC (50% EA in hexane), the mixture was cooled to room temperature. Toluene was recovered using a rota evaporator, and the remaining residue was extracted using ethyl acetate and water to remove the unreacted $AlCl_3$ and water-soluble impurities. Ethyl acetate was recovered on a rota evaporator, and crude was washed and decanted with 20 mL heptane to remove non-polar impurities and get a pure dealkylated product **9a** with a 69% yield (0.366 g).

6. Recycling experiment procedure of the Amberlyst-15 and DDQ

After completion of the fresh reaction using 1 mmol of **7a** according to the standard developed procedure, Amberlyst-15 was filtered, washed with methanol and dried at 70°C for the next recycle run. The separation of **1a** from the crude on the column chromatography later provided the DDHQ, which then oxidized to DDQ with the slow addition of 70% aq. HNO_3 (3 mL). A yellow precipitate of DDQ was then filtered and washed with cold distilled water, and the yellow solid was dried at 70 °C for 2 h. The recovered Amberlyst-15 and DDQ were consequently used for the first recycle run with fresh **7a** and recovered methanol to get **1a**. Repeated the above procedure for the subsequent recycling runs up to five recycling experiments.

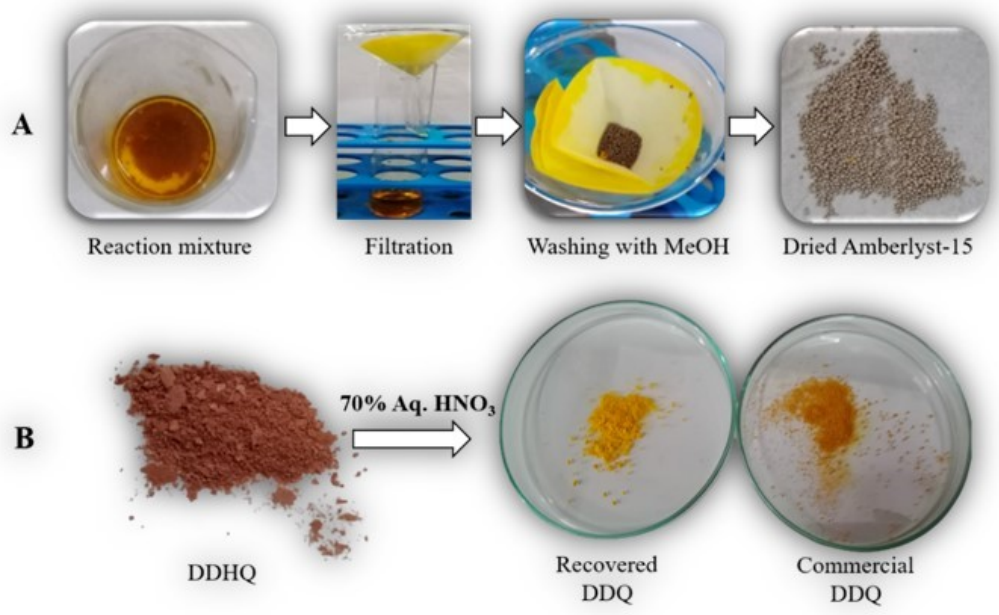


Figure S1. Separation of the Amberlyst-15 and DDQ for recycling experiments.

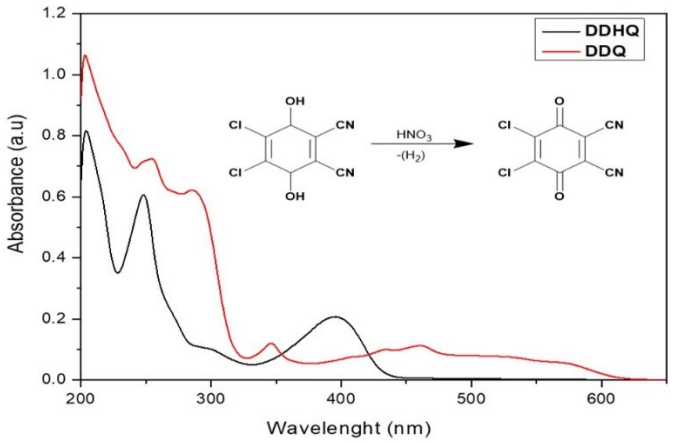


Figure S2. UV-Vis spectra of the recovered DDHQ and DDQ

EPR study of the reaction mixture

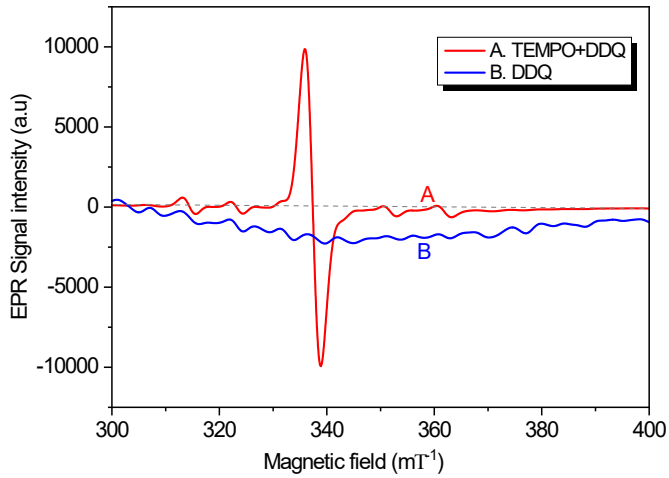


Figure S3. EPR study of the reaction mixture with A) TEMPO + DDQ and B) DDQ.

UV-Visible spectroscopic study of the reaction mixture

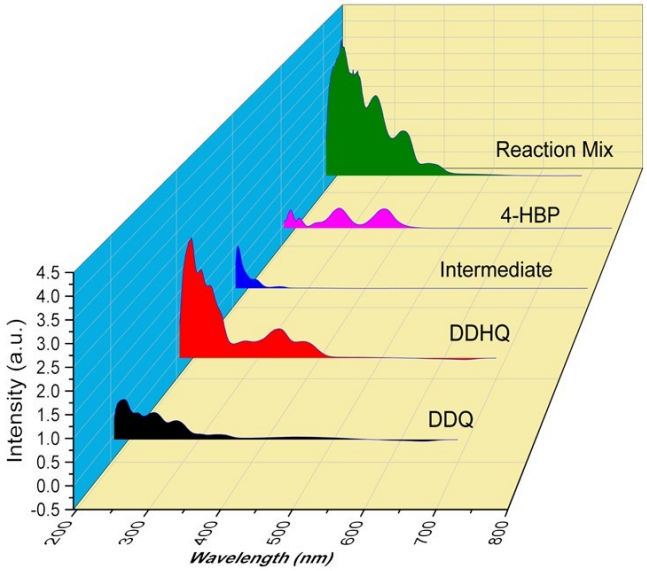


Figure S4. UV-Visible study of the reaction mixture and individual components of the reaction.

GC-MS spectra of intermediate (8a)

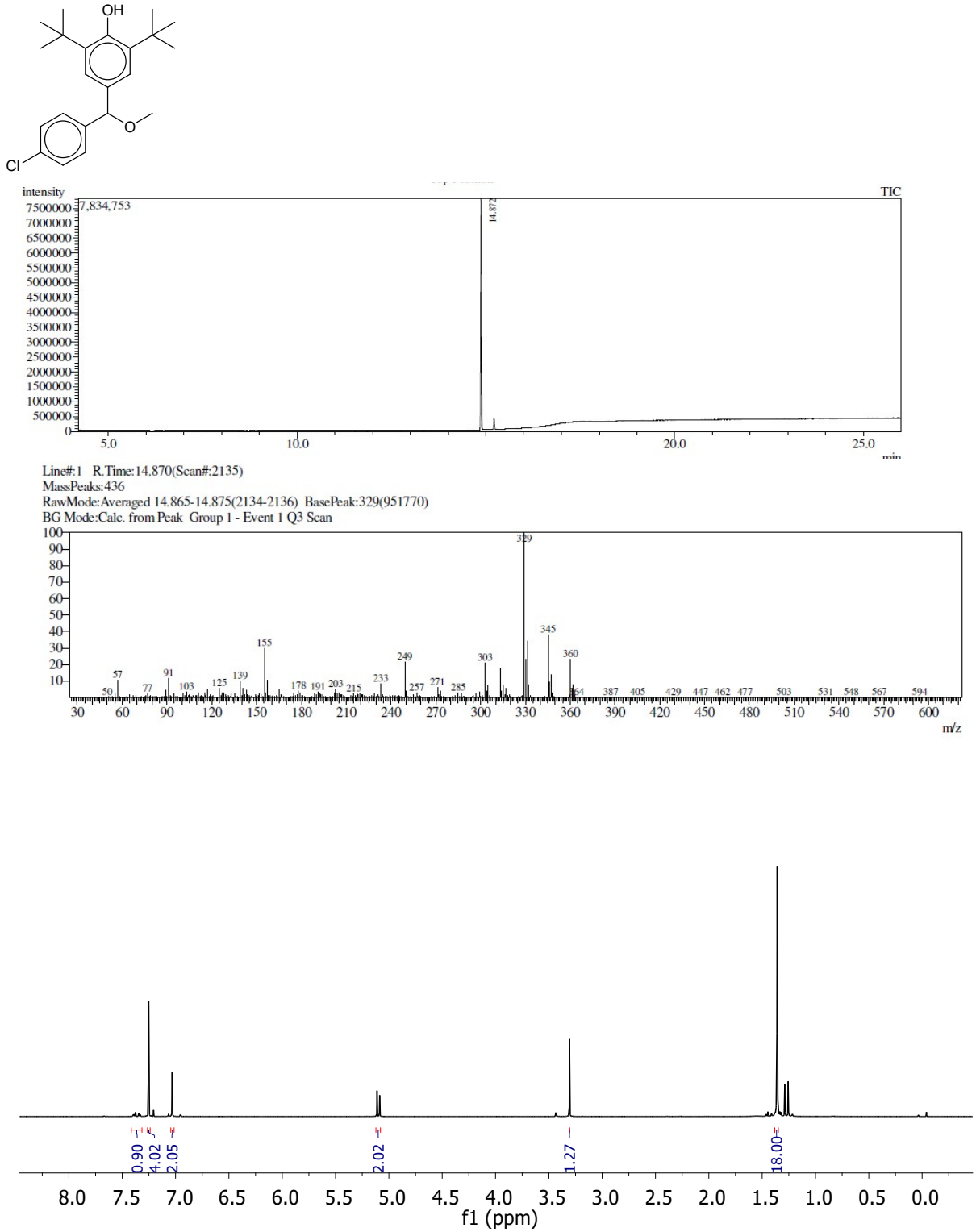


Figure S5. ^{1}H-NMR spectra of compound **8a**

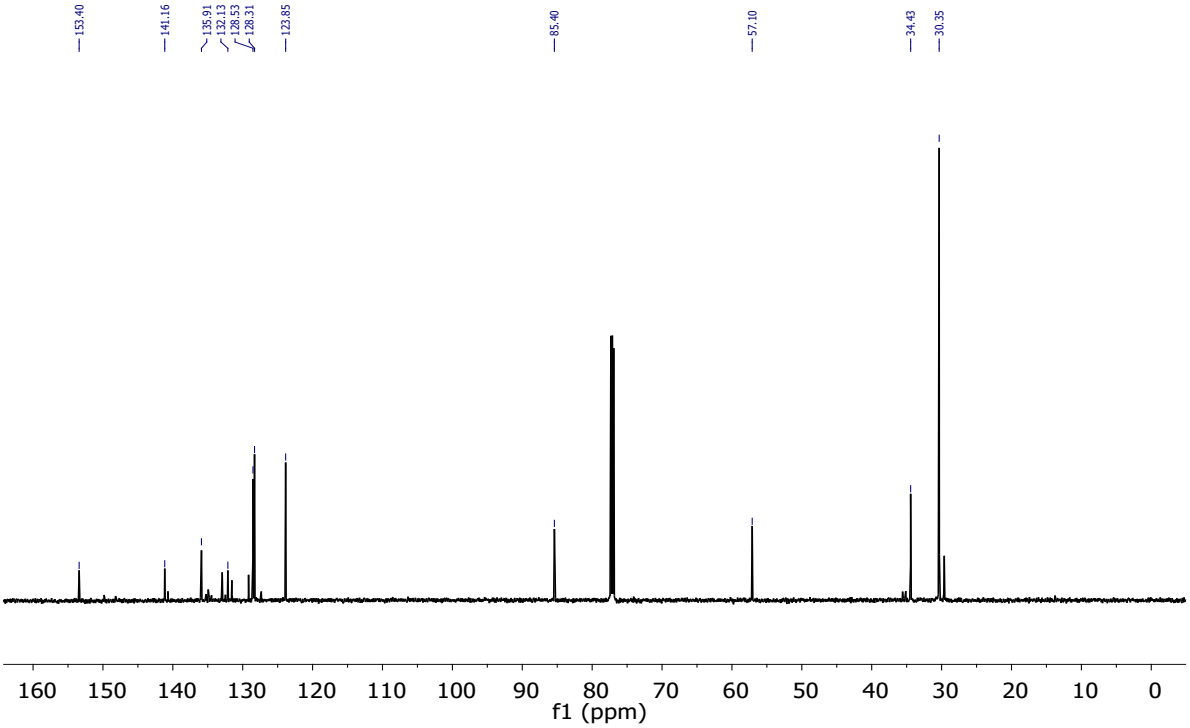


Figure S6. ^{13}C-NMR spectra of compound **8a**

FT-IR spectra of compound 1a

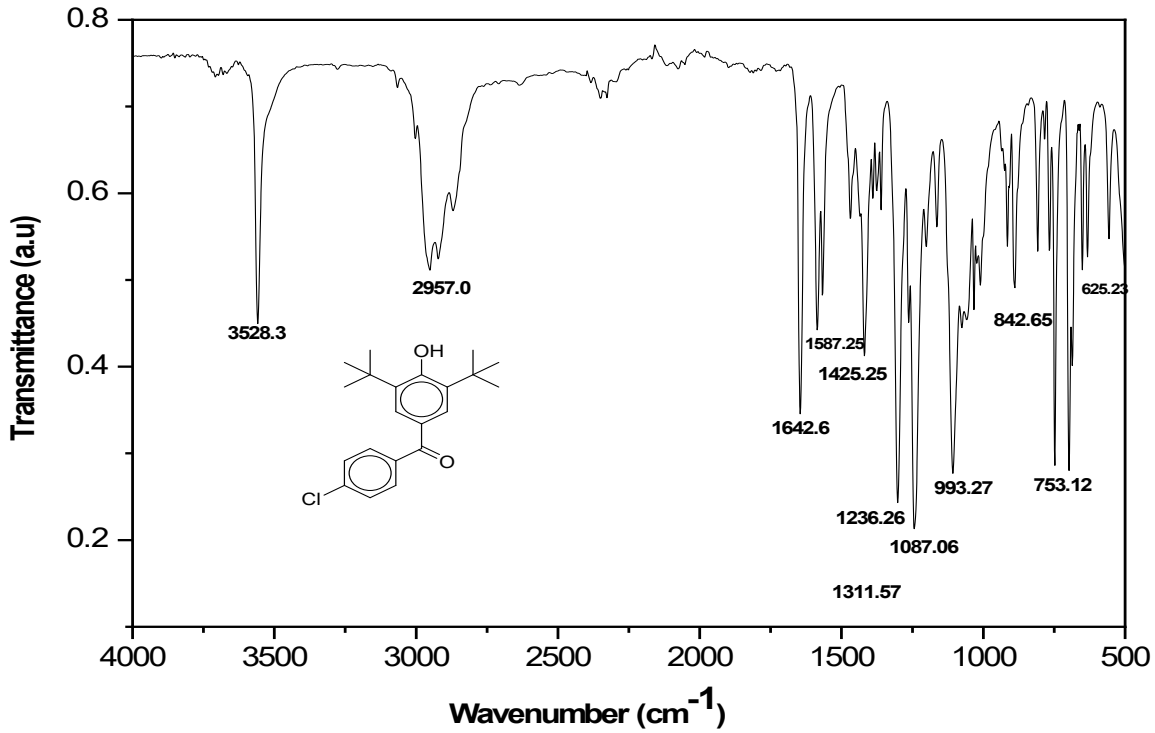


Figure S7: FT-IR spectra of compound **1a**

LC-MS spectra of compound 1a

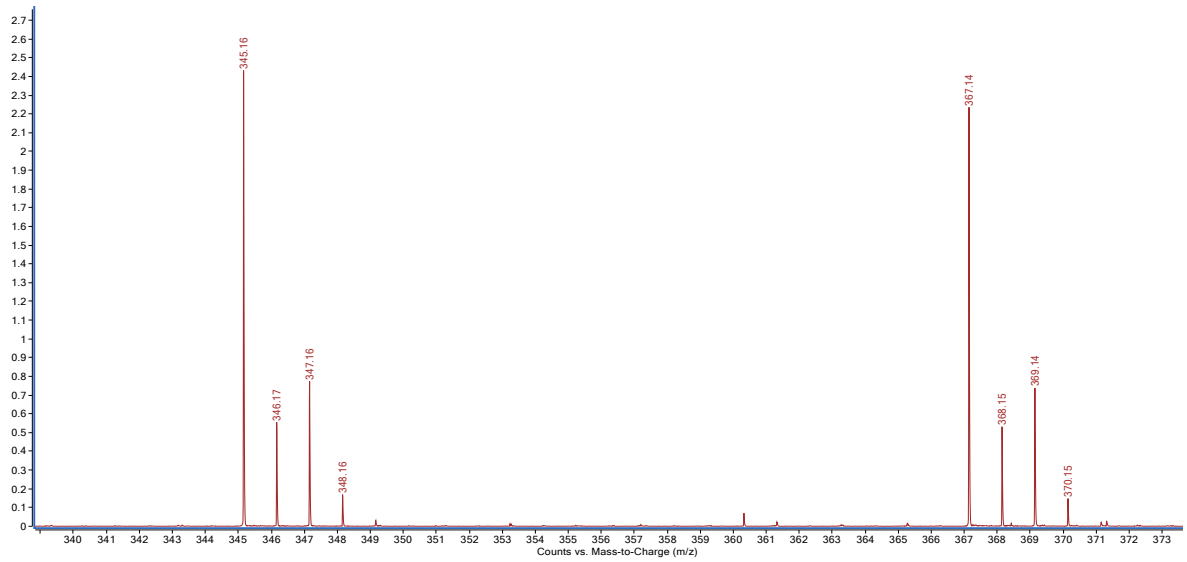
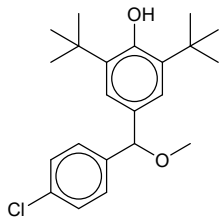


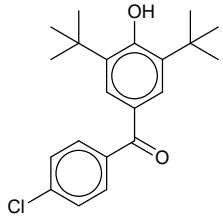
Figure S8: LC-MS spectra of compound **1a**

Spectroscopic data of the prepared compounds



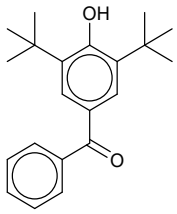
2,6-di-tert-butyl-4-((4-chlorophenyl)(methoxy)methyl)phenol (Compound 8a)

^{1}H NMR (600 MHz,) δ 7.40 – 7.33 (m, 1H), 7.25 (s, 5H), 7.03 (s, 2H), 5.10 (d, J = 14.9 Hz, 2H), 3.31 (s, 1H), 1.36 (s, 18H). **^{13}C NMR** (151 MHz,) δ 153.40, 141.16, 135.91, 132.13, 128.53, 128.31, 123.85, 85.40, 57.10, 34.43, 30.35.



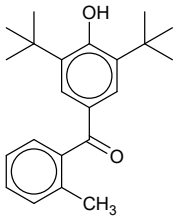
(4-chlorophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methanone (Compound 1a)

White solid (99%), MP: 162-163 °C, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, 2H), 7.69 (s, 2H), 7.45 (d, 2H), 5.76 (s, 1H), 1.45 (s, 18H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 195.14, 158.40, 137.00, 135.84, 131.28, 128.49, 128.15, 34.48, 30.23. **IR (Solid): υ_{max}** 3560, 2949, 1647, 1584, 1420, 1300, 1241, 1110, 891, 747 cm^{-1}. **LC-MS (EI) m/z** 345.16 (100%), 346.17, 347.16, 348.16, 367.14, 368.15, 369.14, 370.15.



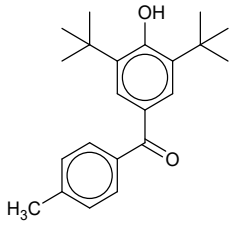
(3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methanone (compound 1b)

White solid (97%), MP:-124-126 °C, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.7 Hz, 2H), 7.73 (s, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 5.73 (s, 1H), 1.45 (s, 18H) ppm. **^{13}C NMR** (151 MHz) δ 196.41, 158.22, 138.68, 135.68, 131.76, 129.86, 128.93, 128.28, 128.15, 34.47, 30.25 ppm. **IR (Solid): υ_{max}** 3580, 2963, 1650, 1573, 1427, 1307, 1236, 1102, 864, 830, 627 cm^{-1}**. LC-MS (EI) m/z** 333.16, 349.21, 350.19 (100%), 351.6.



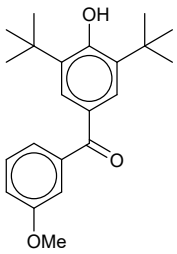
(3,5-di-tert-butyl-4-hydroxyphenyl)(o-tolyl) methanone (Compound 1c)

Off white solid (92%), MP: 132-142°C, **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.70 (s, 2H), 7.35 (td, *J* = 7.6, 1.4 Hz, 1H), 7.30 – 7.27 (m, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 5.77 (s, 1H), 2.33 (s, 3H), 1.42 (s, 18H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 128.30, 125.06, 34.42, 30.19, 20.03ppm. **IR (Solid): υ_{max}** 3583, 3501, 2953, 1630, 1589, 1414, 1265, 1228, 1137, 772 $cm^{-1.}$ **LC-MS (EI) m/z** 347.20 (100%), 348.34, 360.25, 363.17.



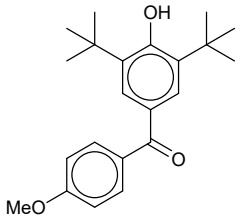
(3,5-di-tert-butyl-4-hydroxyphenyl)(p-tolyl) methanone (Compound 1d)

White solid (95%), **MP: 131-132°C ^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.77 – 7.64 (m, 4H), 7.31 – 7.22 (m, 2H), 5.71 (s, 1H), 2.44 (s, 3H), 1.46 (s, 18H) **^{13}C NMR (151 MHz, $CDCl_3$)** δ 196.19, 157.99, 142.41, 135.87, 135.58, 130.15, 129.25, 128.85, 128.14, 34.47, 30.27, 21.69 ppm. **IR (Solid): υ_{max}** 3518, 2957, 1636, 1546, 1424, 1241, 1105, 836, 752, 631 cm^{-1} . **LC-MS (EI) m/z** 347.20, 348.20, 349.20, 363.17, 364.17, 365.17.



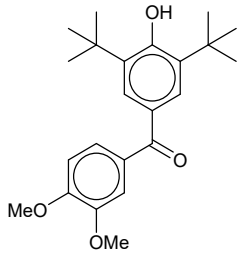
(3, 5-di-tert-butyl-4-hydroxyphenyl)(3-methoxyphenyl) methanone (Compound 1e)

White solid (90%), MP: 140-148°C ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (s, 2H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 6.8 Hz, 2H), 7.26 (s, 1H), 7.12 – 7.08 (m, 1H), 5.73 (s, 1H), 3.86 (s, 3H), 1.45 (s, 18H) ppm. **^{13}C NMR (151 MHz, $CDCl_3$)** δ 196.11, 159.53, 158.25, 139.99, 135.64, 129.05, 128.88, 128.30, 122.57, 118.36, 114.16, 55.52, 34.48, 30.26 ppm . **IR (Solid): υ_{max}** 3543, 2955, 1634, 1421, 1310, 1223, 1104, 1041, 759 cm^{-1} . **LC-MS (EI) m/z** 379.17 (100%), 380.17, 381.17.



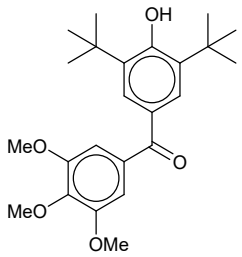
(3, 5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl) methanone (compound 1f)

White Solid (95%), MP: 143-144 °C .^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 – 7.80 (m, 2H), 7.68 (s, 2H), 6.97 – 6.95 (m, 2H), 5.69 (s, 1H), 3.89 (s, 3H), 1.46 (s, 18H) ppm. **^{13}C NMR (151 MHz, $CDCl_3$)** δ 195.38, 162.75, 157.78, 135.56, 132.34, 131.13, 129.51, 127.94, 113.43, 55.51, 34.47, 30.28 ppm. **IR (Solid): υ_{max}** 3521, 2956, 1633, 1568, 1414, 1308, 1239, 1107, 1035, 769, 610 cm^{-1}**.**



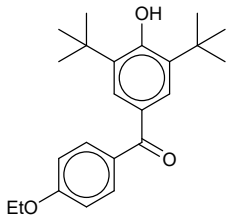
(3, 5-di-tert-butyl-4-hydroxyphenyl)(3, 4-dimethoxyphenyl) methanone (Compound 1g)

White Solid (96%), MP: 132-140 °C, ^{1}H NMR (600 MHz,$CDCl_3$) δ 7.70 (s, 2H), 7.44 (d, *J* = 1.8 Hz, 1H), 7.43 – 7.39 (m, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 5.71 (s, 1H), 3.97 (s, 3H), 3.94 (s, 3H), 1.46 (s, 18H) ppm. **^{13}C NMR (151 MHz, $CDCl_3$)** δ 195.33, 157.81, 152.46, 148.77, 135.56, 131.15, 129.43, 127.98, 124.82, 112.54, 109.84, 56.10, 56.08, 34.48, 30.29 ppm. **IR (Solid): υ_{max}** 3582.3, 3505.5, 2948.5, 1634.1, 1573.0, 1513.3, 1263.2, 1136.7, 1020.2, 771.60 cm^{-1}. **LC-MS (EI) m/z** 391.31, 393.29 (100%), 394.24, 395.29, 399.41, 407.30, 408.39, 409.26, 410.26, 411.26, 412.26, 413.35, 415.27, 416.38, 419.31.



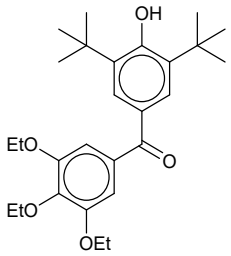
(3, 5-di-tert-butyl-4-hydroxyphenyl)(3, 4, 5-trimethoxyphenyl) methanone (Compound 1h)

White Solid (94%), MP: 128-135°C, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.06 (s, 1H), 6.99 (s, 2H), 5.66 (s, 1H), 3.87 (d, *J* = 3.1 Hz, 6H), 3.82 (s, 3H), 1.39 (s, 18H) ppm. **^{13}C NMR (151 MHz, $CDCl_3$)** δ 195.22, 158.12, 152.81, 141.43, 135.65, 133.59, 128.90, 128.20, 107.59, 61.05, 56.32, 34.51, 30.33 ppm. **IR (Solid): υ_{max}** 3521, 2947, 1636, 1573, 1414, 1222, 1127, 1002, 860, 769, 693, 614 cm^{-1}. **LC-MS (EI) m/z** 423.18, 425.25, 429.23(100%), 430.24, 432.15, 434.10, 441.44, 445.25, 446.37.



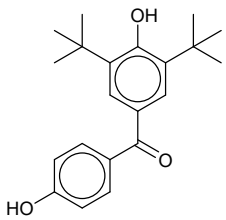
(3,5-di-tert-butyl-4-hydroxyphenyl)(4-ethoxyphenyl) methanone (compound 1i)

Off White (97%), MP: 132-136°C, ^{1}H NMR (600 MHz,$CDCl_3$) δ 7.96 – 7.78 (m, 2H), 7.72 (s, 2H), 7.07 – 6.94 (m, 2H), 5.73 (s, 1H), 4.17 (q, *J* = 7.0 Hz, 2H), 1.62 – 1.32 (m, 21H) ppm.**^{13}C NMR (151 MHz,)** δ 190.16, 161.38, 134.71, 131.57, 131.30, 128.74, 127.14, 114.00, 113.06, 62.96, 33.67, 29.47, 14.04 ppm. **IR (Solid) υ_{max}** 3543, 2955, 1739, 1604, 1423, 1119, 770, 622 cm^{-1}.



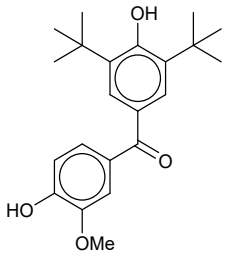
(3, 5-di-tert-butyl-4-hydroxyphenyl)(3,4,5-triethoxyphenyl)methanone (Compound 1j)

White solid (92%), MP: 127-135°C, ^{1}H NMR (600 MHz, ppm) δ 7.74 (s, 2H), 7.06 (s, 2H), 5.74 (s, 1H), 3.89 (s, 6H), 1.68 – 1.22 (m, 27H).. **^{13}C NMR (151 MHz, $CDCl_3$)** δ 81.58, 54.91, 51.77, 51.51, 48.94, 47.35, 34.20, 33.26 ppm. **IR (Solid): υ_{max}** 3527, 2956, 1636, 1570, 1412, 1329, 1222, 1127, 1002, 859, 769, 693, 613 cm^{-1}.



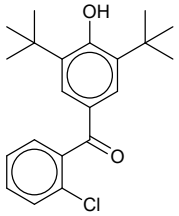
(3,5-di-tert-butyl-4-hydroxyphenyl)(4-hydroxyphenyl) methanone (compound 1k)

White Solid (93%), MP: 158-164°C, ^{1}H NMR (600 MHz,$CDCl_3$) δ 7.76 – 7.73 (m, 2H), 7.69 (s, 2H), 7.39 (s, 1H), 6.93 (t, *J* = 5.6 Hz, 2H), 5.71 (s, 1H), 1.44 (s, 18H) ppm.**^{13}C NMR (151 MHz, $CDCl_3$)** δ 196.53, 160.28, 158.09, 135.66, 132.82, 130.46, 129.26, 128.21, 115.26, 34.47, 30.24 ppm. **IR (Solid): υ_{max}** 359, 2950, 1592, 1437, 1318, 1232, 1103, 1032, 773, 611 cm^{-1} .



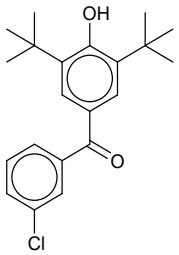
(3,5 -di-tert-butyl-4-hydroxyphenyl)(4-hydroxy-3-methoxyphenyl) methanone (Compound 1l)

White Solid (93%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.75 (s, 1H), 7.60 (s, 1H), 7.36 (ddd, *J* = 9.1, 4.4, 1.9 Hz, 3H), 7.27 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.87 (m, 1H), 5.62 (s, 1H), 3.89 (s, 3H), 1.38 (s, 18H) ppm. **^{13}C NMR (151 MHz, $CDCl_3$)** δ 157.78, 151.80, 149.57, 135.54, 127.97, 127.66, 125.65, 114.48, 108.84, 77.33, 77.11, 76.90, 56.19, 34.47, 30.28 ppm.



(2-chlorophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methanone (Compound 1m)

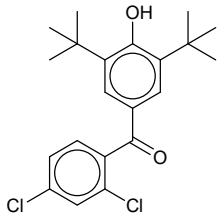
White Solid (96%), MP 158-164 °C, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (s, 2H), 7.50 – 7.18 (m, 4H), 5.82 (s, 1H), 1.42 (s, 18) ppm. **^{13}C NMR (151 MHz,)** δ 194.54, 159.26, 139.37, 135.99, 131.19, 130.66, 129.97, 129.00, 128.36, 126.54, 77.32, 77.11, 76.89, 34.41, 30.15 ppm. **IR (Solid): υ_{max}** 3578, 2950, 1936, 1652, 1576, 1422, 1307, 994, 626 cm^{-1} .



(3-chlorophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methanone (Compound 1n)

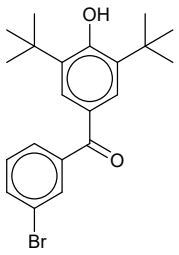
White Solid (99%), MP: 155-160 °C, **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.76 (t, *J* = 1.7 Hz, 1H), 7.71 (d, *J* = 4.2 Hz, 2H), 7.64 – 7.61 (m, 1H), 7.54 – 7.51 (m, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 5.78 (s, 1H), 1.45 (s, 18H) ppm. **^{13}C NMR (151 MHz, $CDCl_3$)** δ 194.83, 158.58, 140.36, 135.89, 134.45, 131.71, 129.84,

129.45, 128.33, 128.30, 127.86, 34.48, 30.22 ppm. **LC-MS (EI) m/z** 305, 319.29, 325.29, 345.24, 348.28, 357.28, 360.40, 367.22 (100%), 368.22, 369.22, 370.22, 377.29, 383.20, 384.20, 385.20.



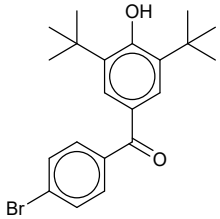
(3,5-di-tert-butyl-4-hydroxyphenyl)(2,4-dichlorophenyl)methanone (Compound 1o)

White Solid (94%), MP: 155-164 °C, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.45 (d, *J* = 2.1 Hz, 1H), 7.30 (t, *J* = 5.0 Hz, 1H), 7.27 (s, 1H), 7.23 (s, 1H), 5.81 (s, 1H), 1.39 (s, 18H) ppm. **^{13}C NMR (151 MHz, $CDCl_3$)** δ 193.47, 159.45, 137.78, 136.13, 136.04, 132.33, 130.05, 129.93, 128.30, 127.78, 126.98, 34.43, 30.15 ppm. **IR (Solid): υ_{max}** 3585, 3287, 3094, 2966, 1652, 1575, 1428, 1308, 1240, 1141, 830, 627 cm^{-1} **LC-MS (EI) m/z** 376.38, 377.29, 379.20, 391.31, 393.29, 394.29,401.18 (100%) 402.18,404.12, 405.19, 406.17.



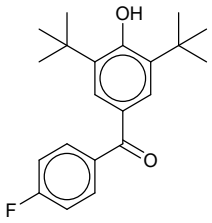
(3-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methanone (Compound 1p)

White Solid (94%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.72 – 7.66 (m, 4H), 7.35 (t, *J* = 7.8 Hz, 1H), 5.79 (s, 1H), 1.46 (s, 18H)ppm. **^{13}C NMR (151 MHz, $CDCl_3$)** δ 194.68, 158.59, 140.56, 135.90, 134.62, 132.79, 129.72, 128.32, 122.47, 34.49, 30.23ppm. **IR (Solid): υ_{max}** 3513, 2952, 1644, 1561, 1423, 1310, 1119, 744 cm^{-1}.



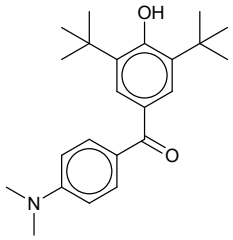
(4-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methanone (Compound 1q)

White Solid (96%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (t, *J* = 1.5 Hz, 1H), 7.70 (s, 2H), 7.70 – 7.66 (m, 2H), 7.35 (t, *J* = 7.8 Hz, 1H), 5.79 (s, 1H), 1.46 (s, 18H) ppm. **^{13}C NMR (151 MHz, $CDCl_3$)** δ 194.67, 158.59, 135.90, 134.62, 132.79, 128.31, 122.47, 34.49, 30.25, 30.21ppm. **IR (Solid): υ_{max}** 3584, 3505, 2952, 2347, 1635, 1596, 1514, 1415, 1226, 1138, 1017, 770 cm^{-1} . **LC-MS (EI) m/z** 411.18, 412.18, 413.18 (100%), 414.18, 415.18, 427.17, 428.17.



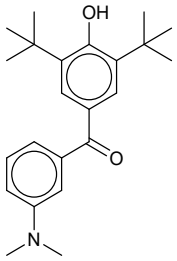
(3,5-di-tert-butyl-4-hydroxyphenyl)(4-fluorophenyl) methanone (Compound 1r)

White Solid (91%), MP: 163-170 °C, ^{1}H NMR (600 MHz,$CDCl_3$) δ 7.44 (dd, *J* = 8.3, 5.4 Hz, 3H), 7.17 – 7.13 (m, 3H), 7.00 (d, *J* = 2.0 Hz, 1H), 1.31 (s, 18H)ppm. **^{13}C NMR (151 MHz, $CDCl_3$)** δ 195.02, 158.26, 135.78, 134.85, 132.39, 132.33, 128.84, 128.11, 115.35, 115.20, 77.30, 77.09, 76.88, 34.47, 30.23 ppm. **LC-MS (EI) m/z** 351.17, 367.15 (100%), 369.15



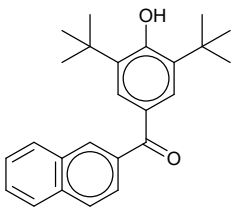
(3,5-di-tert-butyl-4-hydroxyphenyl)(4-(dimethylamino) phenyl) methanone (Compound 1s)

Off White (82%), MP: 125-139°C, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 – 7.72 (m, 2H), 7.62 (s, 2H), 6.77 – 6.56 (m, 2H), 5.56 (s, 1H), 2.14 (s, 6H), 1.43 (s, 18H).. **^{13}C NMR (151 MHz, $CDCl_3$)** δ 157.12, 153.00, 135.32, 132.62, 130.41, 127.59, 125.69, 110.59, 40.16, 34.47, 30.33 ppm.



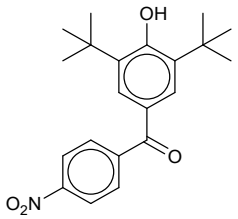
(3,5-di-tert-butyl-4-hydroxyphenyl)(3-(dimethylamino)phenyl)ethanone (compound 1t)

Off White (85%), MP: 129-135°C, **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.84 – 7.74 (m, 2H), 7.63 (s, 2H), 6.67 (d, J = 9.0 Hz, 2H), 5.58 (s, 1H), 3.05 (s, 6H), 1.44 (s, 18H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 157.12, 153.00, 135.32, 132.62, 130.41, 127.59, 125.69, 110.59, 40.16, 34.47, 30.33ppm. **LC-MS (EI) m/z** 354.24, 355.25, 356.25, 376.22, 377.23, 392.22, 393.20, 413.26, 434.27, 483.32 (100%), 441.34.



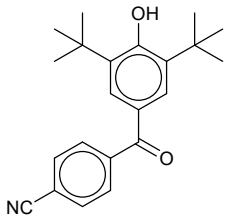
(3,5-di-tert-butyl-4-hydroxyphenyl)(naphthalen-2-yl) methanone (Compound 1u)

White Solid (93%), MP: 196-210 ^{1}H NMR (600 MHz,) δ 8.09 (d, J = 8.3 Hz, 1H), 7.98 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 7.8 Hz, 1H), 7.80 (s, 2H), 7.60 – 7.47 (m, 3H), 7.27 (s, 1H), 5.80 (s, 1H), 1.41 (s, 18H) ppm. **^{13}C NMR (151 MHz, CDCl3)** δ 197.39, 158.89, 137.25, 135.78, 133.81, 131.18, 130.66, 129.73, 128.63, 128.37, 127.07, 126.93, 126.35, 126.06, 124.35, 34.44, 30.19 ppm. **IR (Solid): υ_{max}** 3585, 2955, 1636, 1547, 1423, 1309, 1224, 1107, 1042, 758 cm^{-1}. **LC-MS (EI) m/z** 361.22 (100%), 362.22, 383.20, 384.20, 399.17.



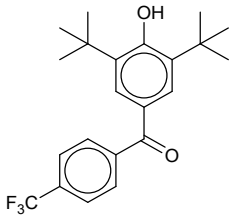
(3,5-di-tert-butyl-4-hydroxyphenyl)(4-nitrophenyl) methanone (Compound 1v)

White Solid (87%), MP: 121-130°C, **IR (Solid) ^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.36 (d, *J* = 8.6 Hz, 2H), 7.91 (d, *J* = 8.6 Hz, 2H), 7.72 (s, 2H), 5.88 (s, 1H), 1.47 (s, 18H)ppm .**^{13}C NMR (151 MHz, $CDCl_3$)** δ 194.33, 159.11, 149.50, 144.36, 136.19, 130.40, 128.36, 127.79, 123.46, 34.50, 30.18ppm. **υ_{max}** 3558, 2924, 2350, 1650, 1519, 1307, 1116, 842, 721 cm^{-1}. **LC-MS (EI) m/z** 360.40, 400.23, 413.36 (100%), 416.21, 441.39, 458.28.



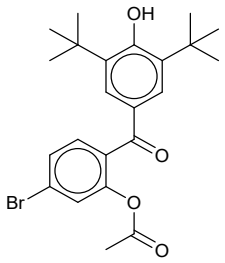
4-(3,5-di-tert-butyl-4-hydroxybenzoyl)benzonitrile (Compound 1w)

White Solid (80%), MP: 129-134°C, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 3H), 7.68 (d, *J* = 8.0 Hz, 3H), 7.41 (s, 1H), 7.15, 1.44 (s,18H) ppm. **^{13}C NMR (151 MHz, $CDCl_3$)** δ 186.50, 150.63, 149.04, 140.45, 138.88, 134.50, 134.10, 132.47, 130.63, 126.74, 118.51, 112.23, 35.64, 35.21, 29.57 ppm. **IR (Solid): υ_{max}** 3491, 2956, 2235, 1640, 1570, 1314, 1235, 1106, 767 cm^{-1} **LC-MS (EI) m/z** 358.18 (100%), 359.13, 360.32, 374.14.



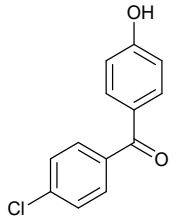
(3,5-di-tert-butyl-4-hydroxyphenyl)(4-(trifluoromethyl)phenyl)methanone (Compound 1x)

Yellow liquid, MP: 96.4-97.2 °C, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (1 H, s), 7.92 (1 H, d, *J* = 7.7), 7.77 (1 H, d, *J* = 7.8), 7.67 (2 H, s), 7.57 (1 H, t, *J* = 7.8), 5.78 (1 H, s), 1.40 (18 H, s). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 194.64, 158.73, 139.30, 136.04, 128.36, 126.81, 126.79, 34.49, 30.18.



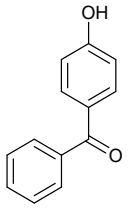
5-bromo-2-(3,5-di-tert-butyl-4-hydroxybenzoyl)phenyl acetate (Compound 1y)

Yellow liquid, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (2 H, s), 7.38 (1 H, dd, *J* = 8.3, 1.6), 7.31 (2 H, dd, *J* = 15.7, 4.9), 5.73 (1 H, s), 1.83 (3 H, s), 1.34 (18 H, s). **δ C (151 MHz, $CDCl_3$)** 193.39, 168.59, 158.80, 149.09, 135.98, 131.42, 131.33, 128.94, 128.90, 127.73, 126.74, 125.00, 34.43, 30.13, 20.44.



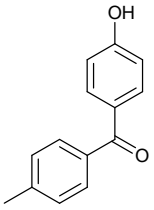
(4-chlorophenyl)(4-hydroxyphenyl) methanone (Compound 9a)

Brown solid (80%), MP: 178-180 °C, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 – 7.63 (m, 4H), 7.48 – 7.39 (m, 2H), 7.22 (s, 1H), 6.94 – 6.73 (m, 2H) ppm. **^{13}C NMR (151 MHz, $CDCl_3$)** δ 195.30, 160.69, 160.53, 138.69, 136.41, 133.03, 131.32, 128.70, 115.51.



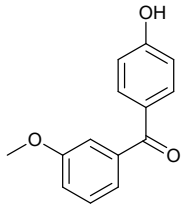
(4-hydroxyphenyl)(phenyl)methanone compound 9b)

Brown solid (80%), MP: 132-135 °C, ^{1}H NMR (600 MHz, DMSO) δ 9.15 (s, 1H), 6.42 – 6.31 (m, 5H), 6.24 (t, J = 7.6 Hz, 2H), 5.62 (d, J = 8.6 Hz, 2H). **^{13}C NMR (151 MHz)** δ 194.83, 162.52, 138.64, 133.03, 129.64, 128.88, 115.78**..**



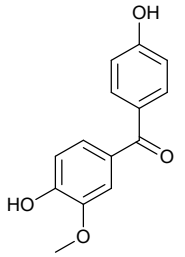
(4-hydroxyphenyl)(p-tolyl)methanone (Compound 9d)

Brown Solid (75%) MP: 173-175 °C, ^{1}H NMR (600 MHz, DMSO) δ 7.97 (s, 2H), 5.19 – 5.01 (m, 5H), 4.40 (d, *J* = 8.6 Hz, 2H), 0.90 (s, 3H) ppm. **^{13}C NMR (151 MHz, DMSO)** δ 194.85, 162.51, 138.60, 133.05, 132.34, 129.66, 128.90, 128.40, 115.78 ppm.



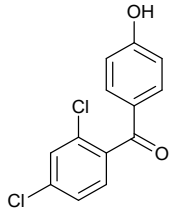
(4-hydroxyphenyl)(3-methoxyphenyl) methanone (Compound 9f)

Brown solid (73%), MP: 138-140 °C, ^{1}H NMR (600 MHz, $CDCl_3$) , ^{1}H NMR (600 MHz,$CDCl_3$) δ 7.74 – 7.64 (m, 2H), 7.41 – 7.35 (m, 1H), 7.21 (s, H), 6.86 (d, J = 8.6 Hz, 1H), 2.12 (s, 1H), 1.50 – 1.41 (m, 4H) ppm. **^{13}C NMR (151 MHz, $CDCl_3$)** δ 132.83, 131.22, 128.62, 115.32 ppm.



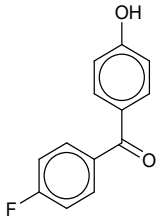
(4-hydroxy-3-methoxyphenyl)(4-hydroxyphenyl)methanone (Compound 9l)

Brown solid (71%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 – 7.61 (m, 1H), 7.31 – 6.86 (m, 5H), 2.33 (s, 2H), 1.59 – 1.24 (m, 3H) ppm. **^{13}C NMR (151 MHz, $CDCl_3$)** δ 160.31, 138.56, 136.48, 132.92, 131.27, 128.66, 115.42 ppm.



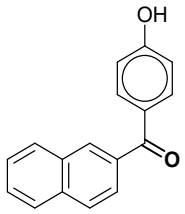
(2,4-dichlorophenyl)(4-hydroxyphenyl)methanone (Compound 9o)

Brown solid (78%), MP: 138-140 °C, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 27.5, 8.6 Hz, 3H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.26 (s, 1H), 6.93 (d, *J* = 8.7 Hz, 2H) ppm. **^{13}C NMR (151 MHz, $CDCl_3$)** δ 195.30, 160.69, 160.53, 138.69, 136.41, 133.03, 131.32, 128.70, 115.51 ppm.



(4-fluorophenyl)(4-hydroxyphenyl)methanone (Compound 9r)

White Solid (82%), MP: 168-171 °C, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 – 7.66 (m, 4H), 7.43 – 7.40 (m, 2H), 6.90 (dd, J = 9.0, 2 Hz, 2H), 6.80 (s, 1H).. **^{13}C NMR (151 MHz, $CDCl_3$)** δ 193.49, 165.52, 164.73, 163.86, 162.54, 132.99, 132.55, 132.49, 128.33, 116.01, 115.87, 115.80 ppm.



(3,5-di-tert-butyl-4-hydroxyphenyl)(naphthalen-2-yl)methanone (Compound 9u)

White solid (79%), MP: 140 °C, ^{1}H NMR (600 MHz, DMSO-D$_6$) δ 9.33 (s, 1H), 6.89 – 6.77 (m, 2 H), 6.61 (dd, J = 40.6, 8.5 Hz, 1H), 6.46 – 6.26 (m, 6H), 5.65 (d, J = 8.2 Hz, 2H). **^{13}C NMR (151 MHz,**) δ 196.04, 163.23, 137.43, 133.70, 133.11, 130.68, 130.60, 129.41, 128.98, 127.53, 126.93, 126.62, 125.59, 125.35, 116.00.

^{1}H and ^{13}C NMR spectra of all the synthesized compounds

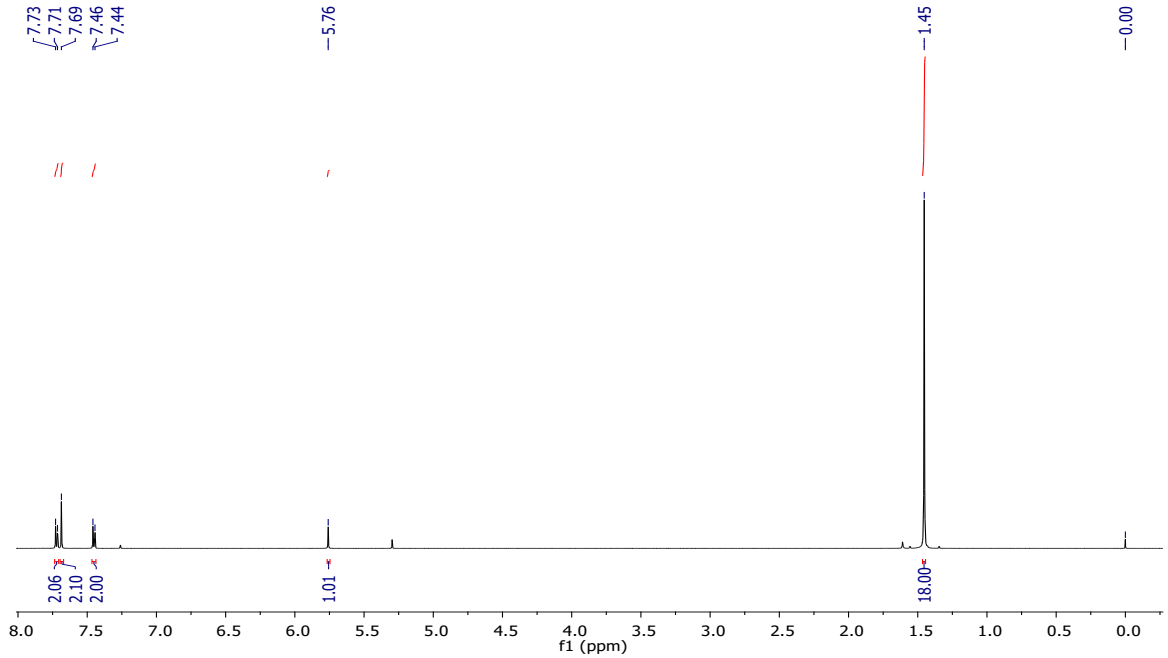


Figure S9. ^{1}H-NMR spectra of compound **1a**

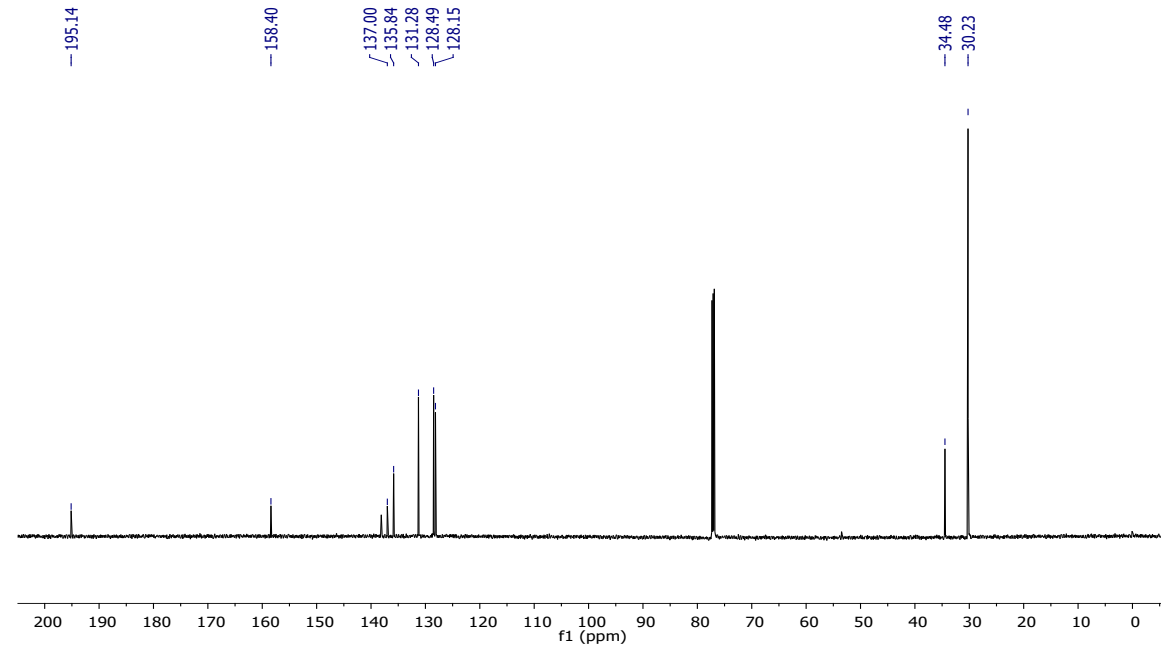


Figure S10. ^{13}C-NMR spectra of compound **1a**

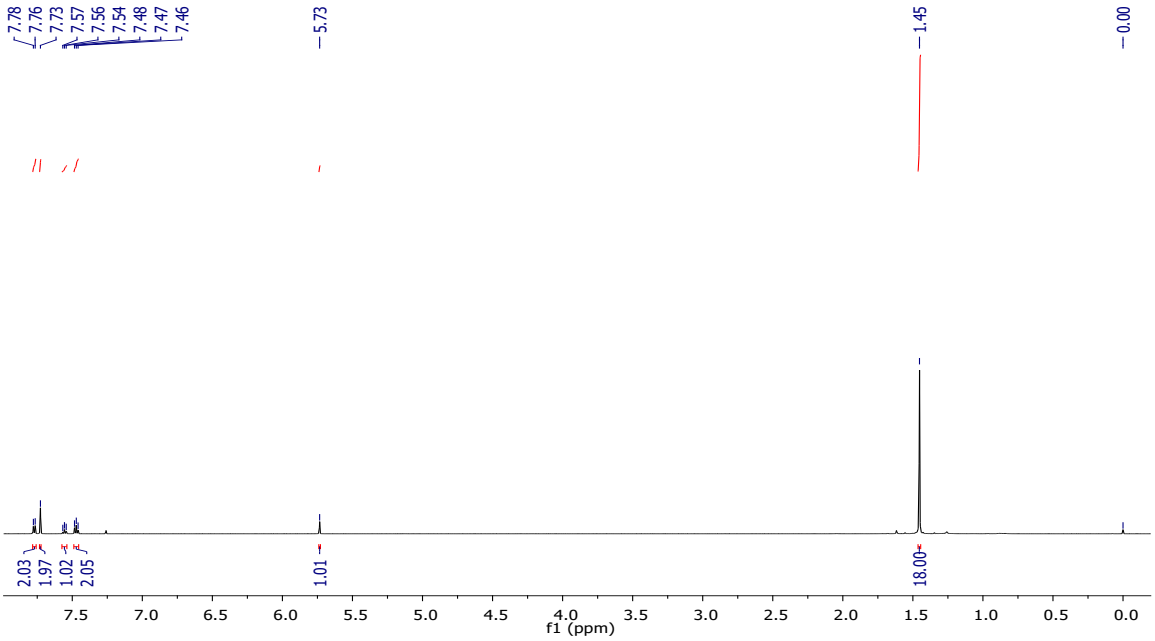


Figure S11. ^{1}H-NMR spectra of compound **1b**

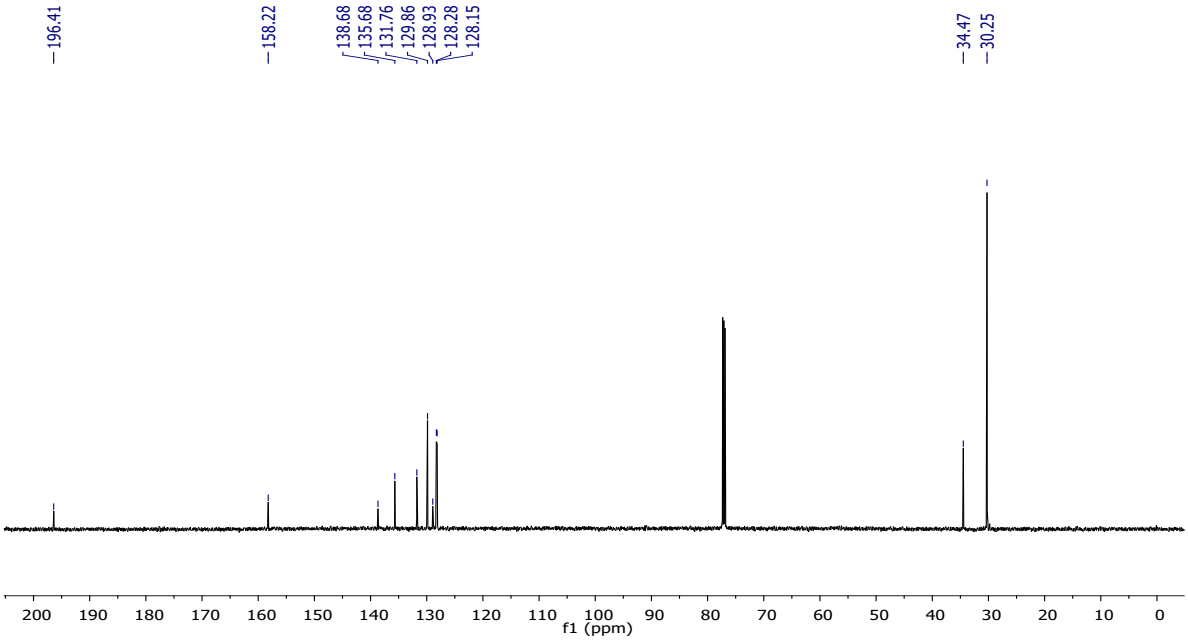


Figure S12. ^{13}C-NMR spectra of compound **1b**

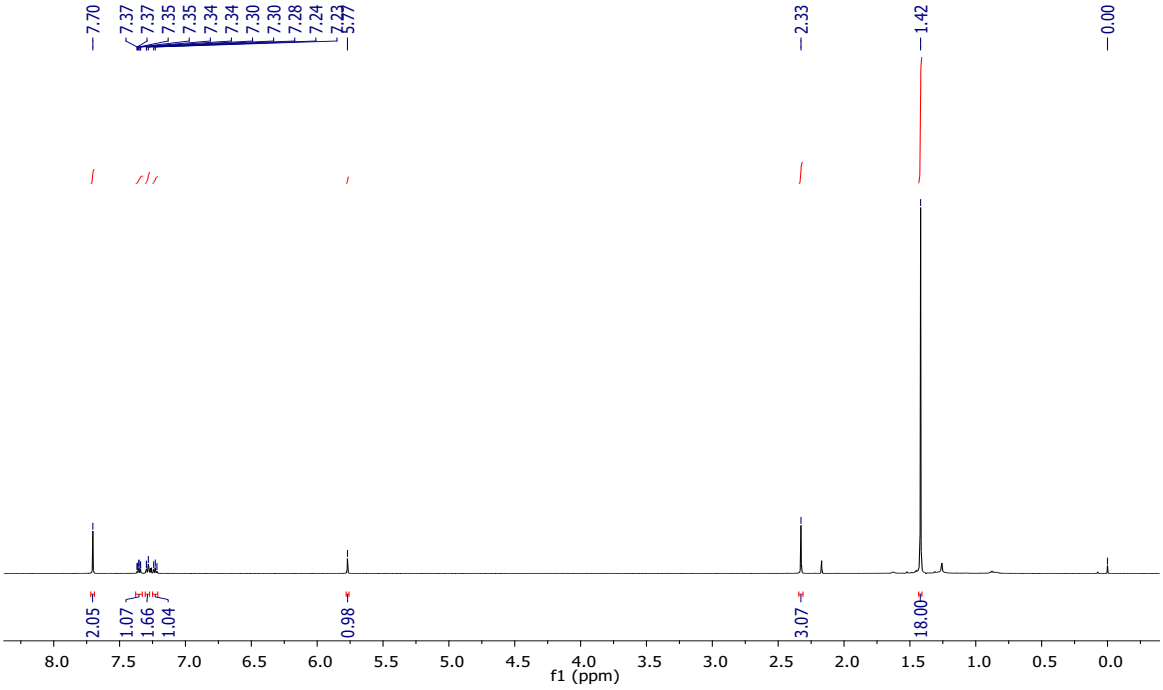


Figure S13. ^{1}H-NMR spectra of compound **1c**

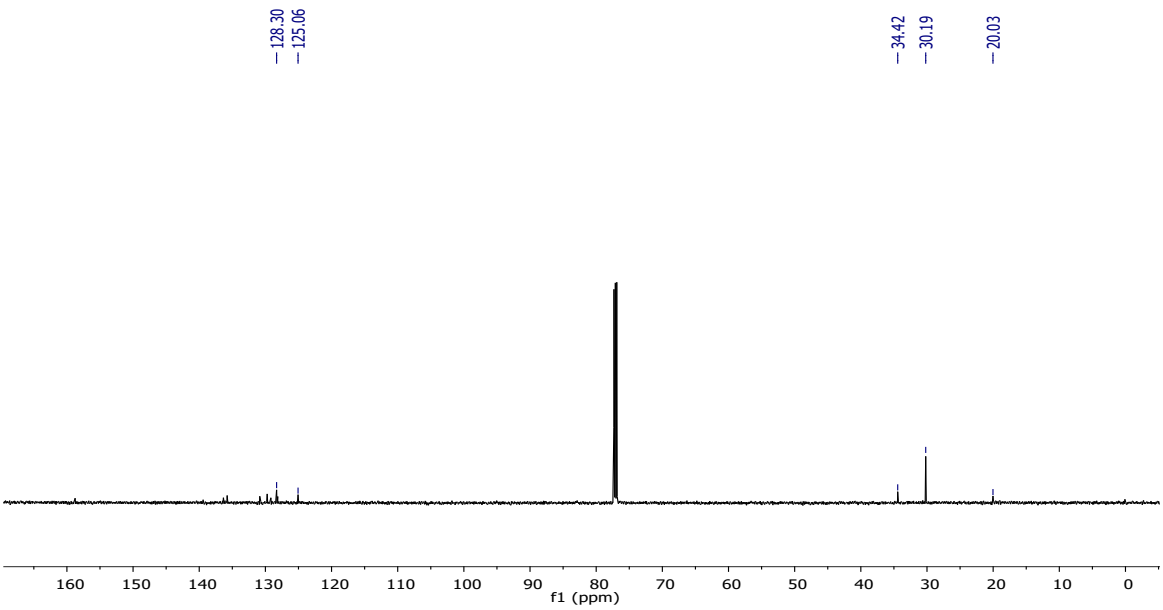


Figure S14. ^{13}C-NMR spectra of compound **1c**

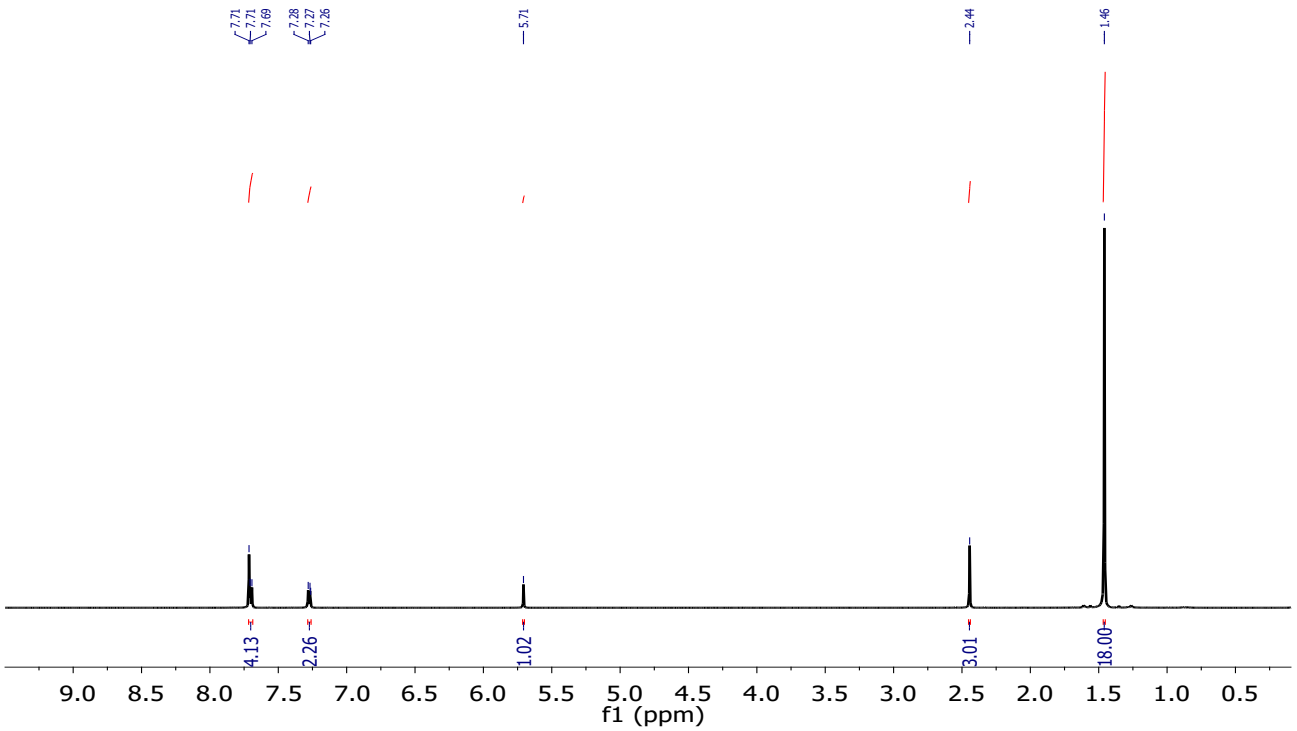


Figure S15. [1]H-NMR spectra of compound **1d**

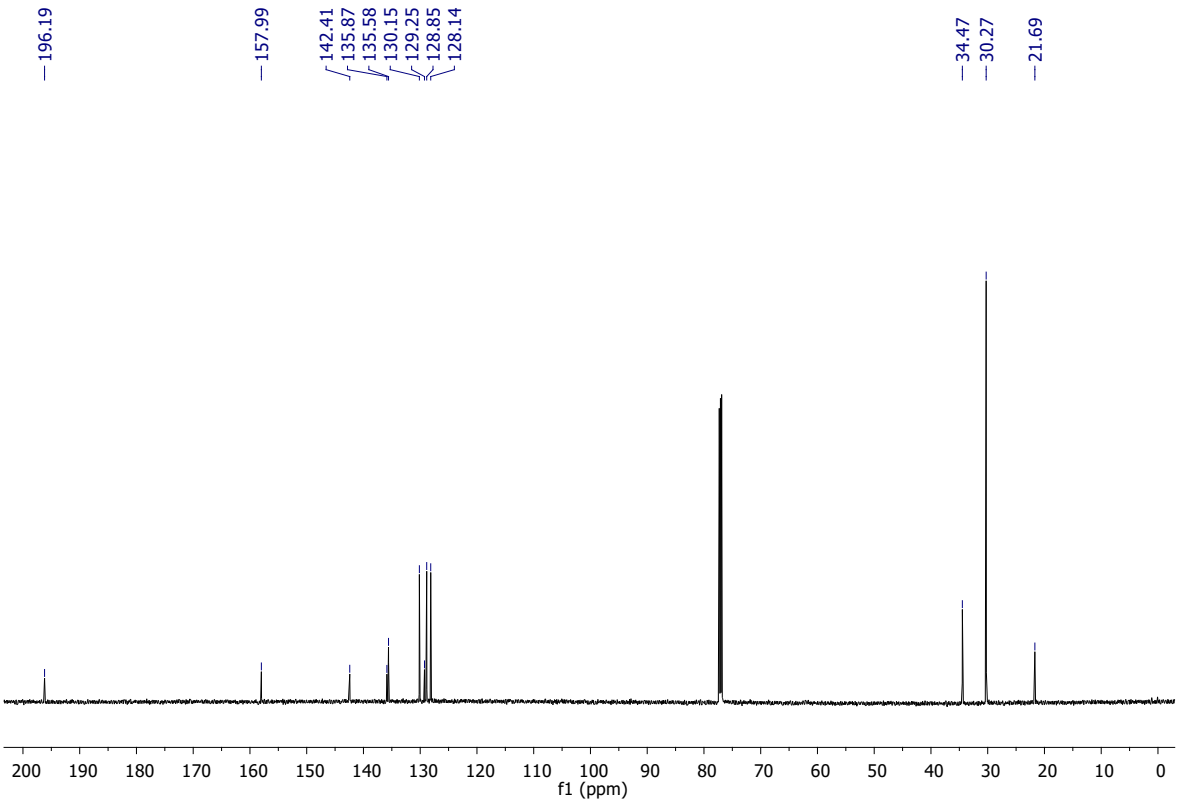


Figure S16. [13]C-NMR spectra of compound **1d**

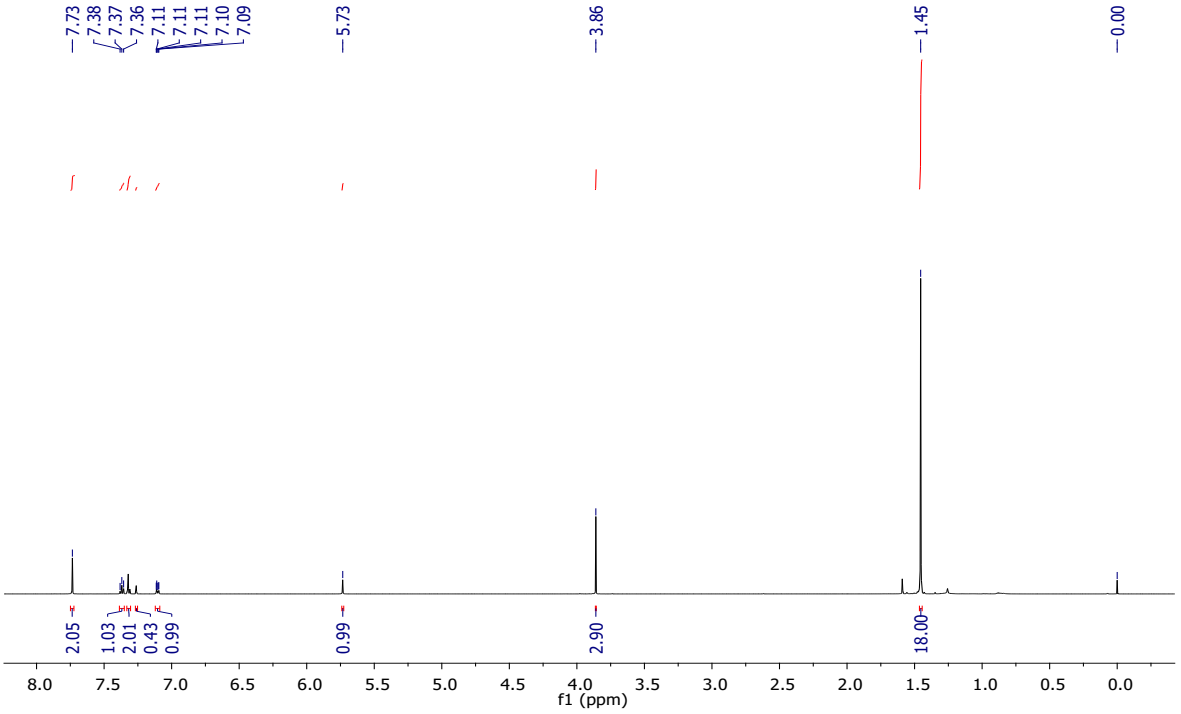


Figure S17. [1]H-NMR spectra of compound **1e**

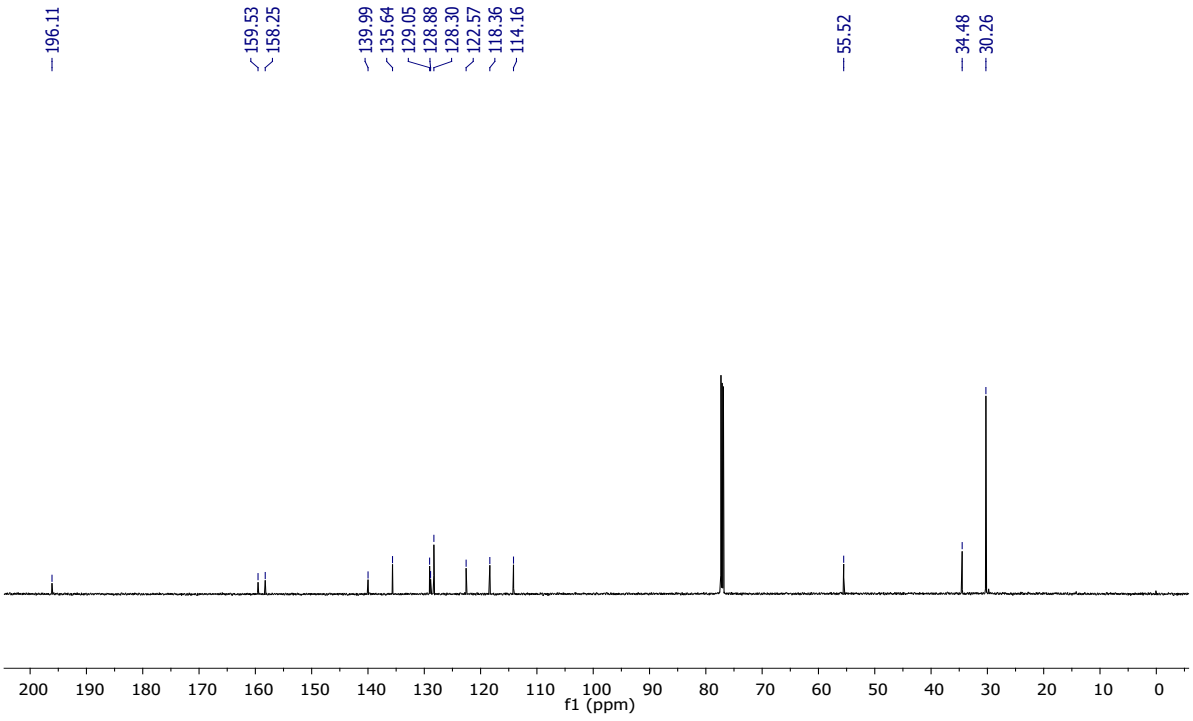


Figure S18. [13]C-NMR spectra of compound **1e**

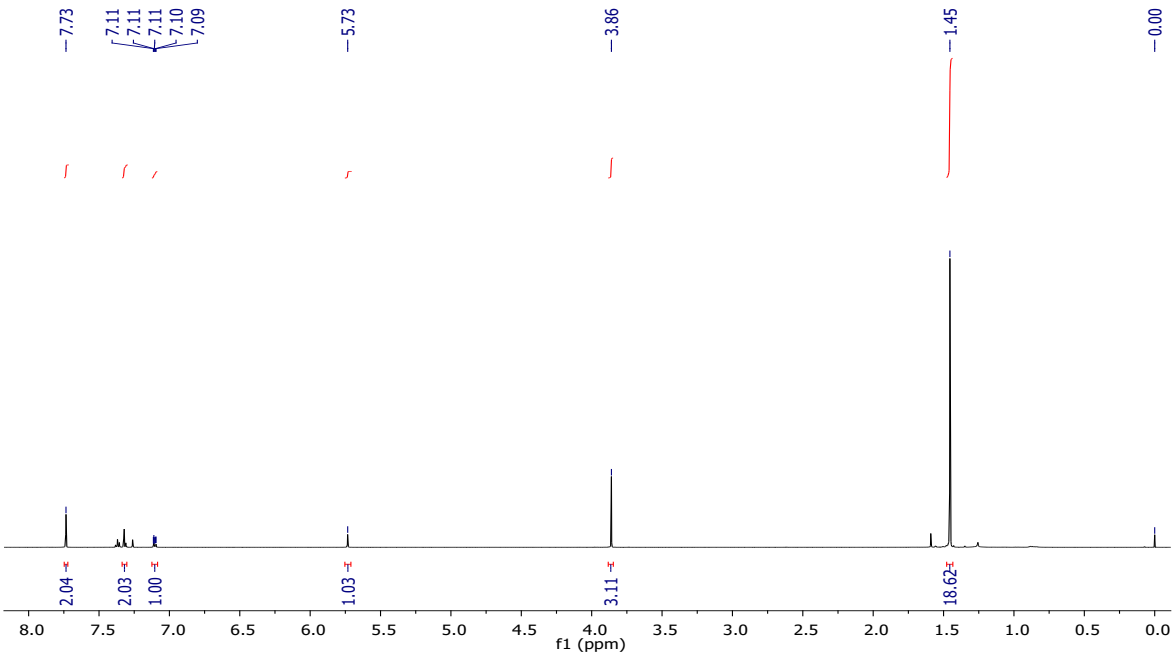


Figure S19. [1]H-NMR spectra of compound **1f**

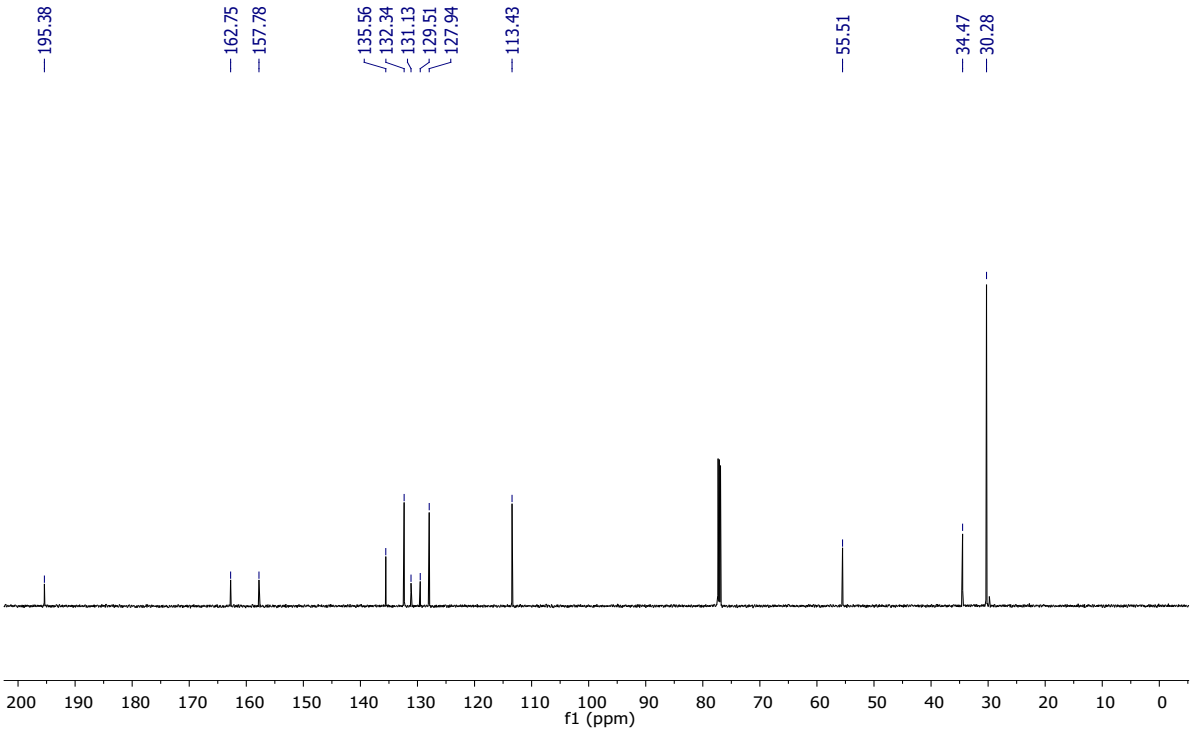


Figure S20. [13]C-NMR spectra of compound **1f**

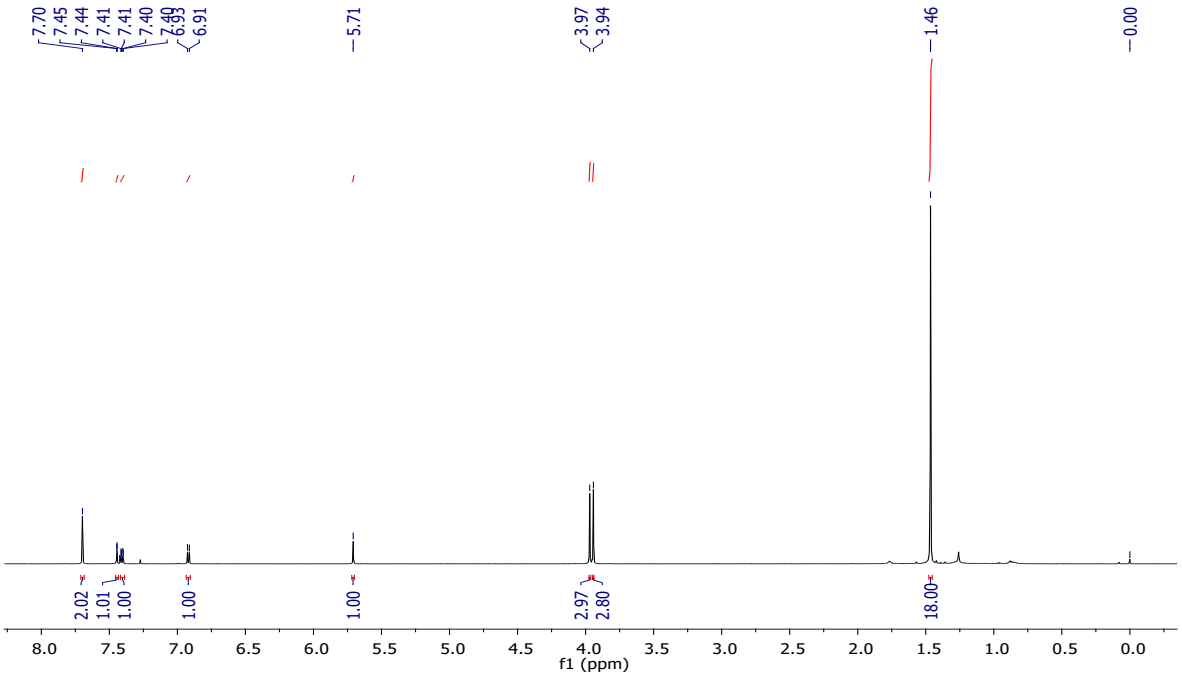


Figure S21. ^{1}H-NMR spectra of compound **1g**

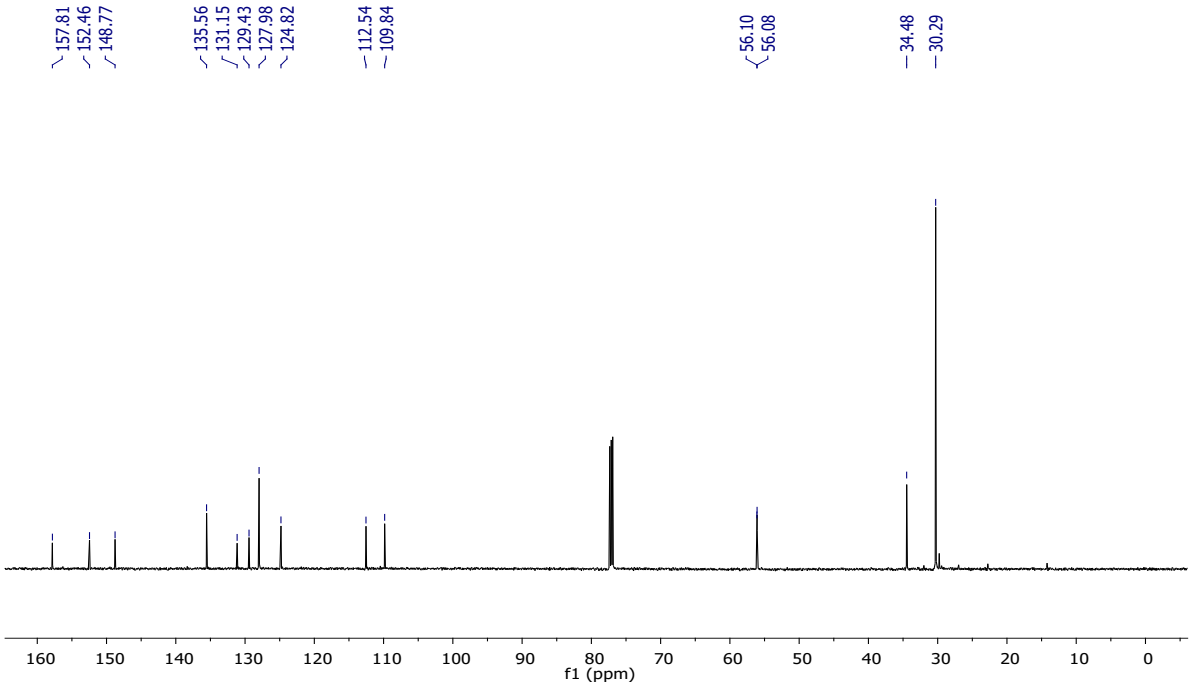


Figure S22. ^{13}C-NMR spectra of compound **1g**

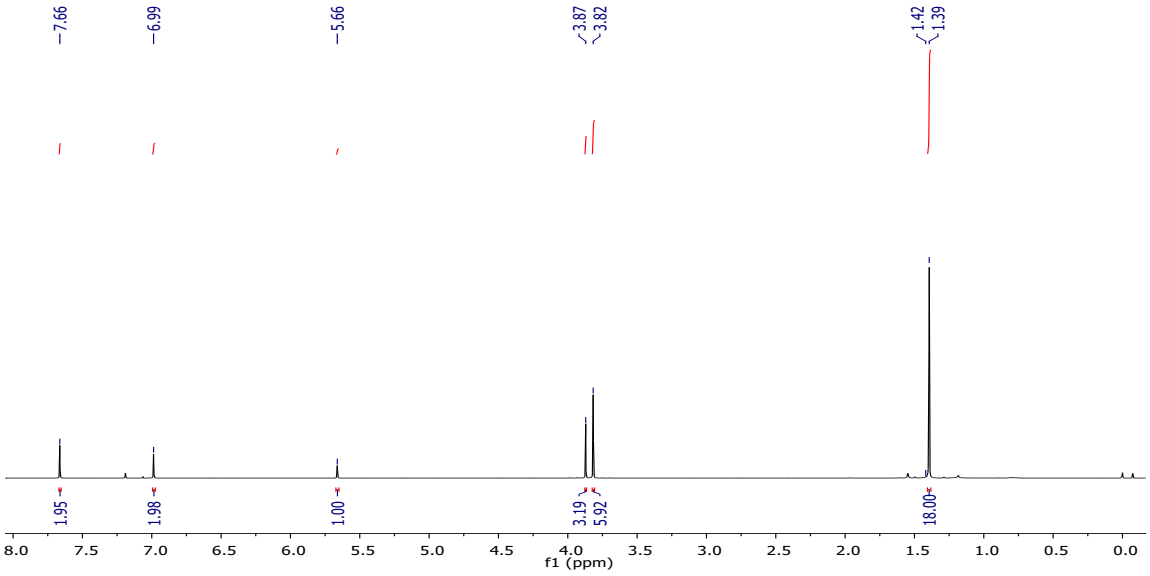


Figure S23. ^{1}H-NMR spectra of compound **1h**

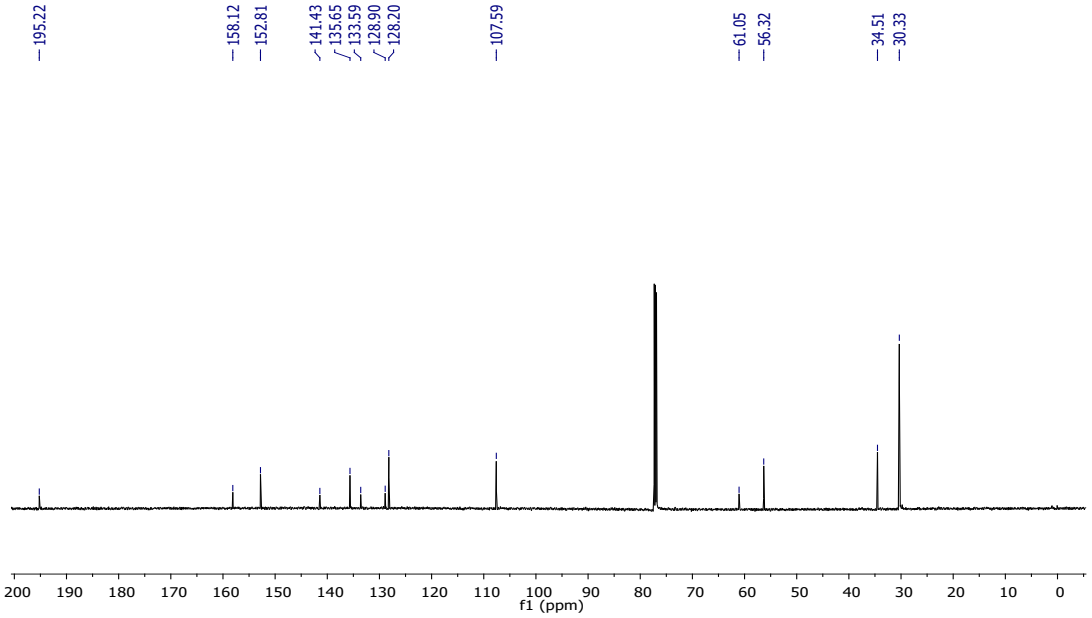


Figure S24. ^{13}C-NMR spectra of compound **1h**

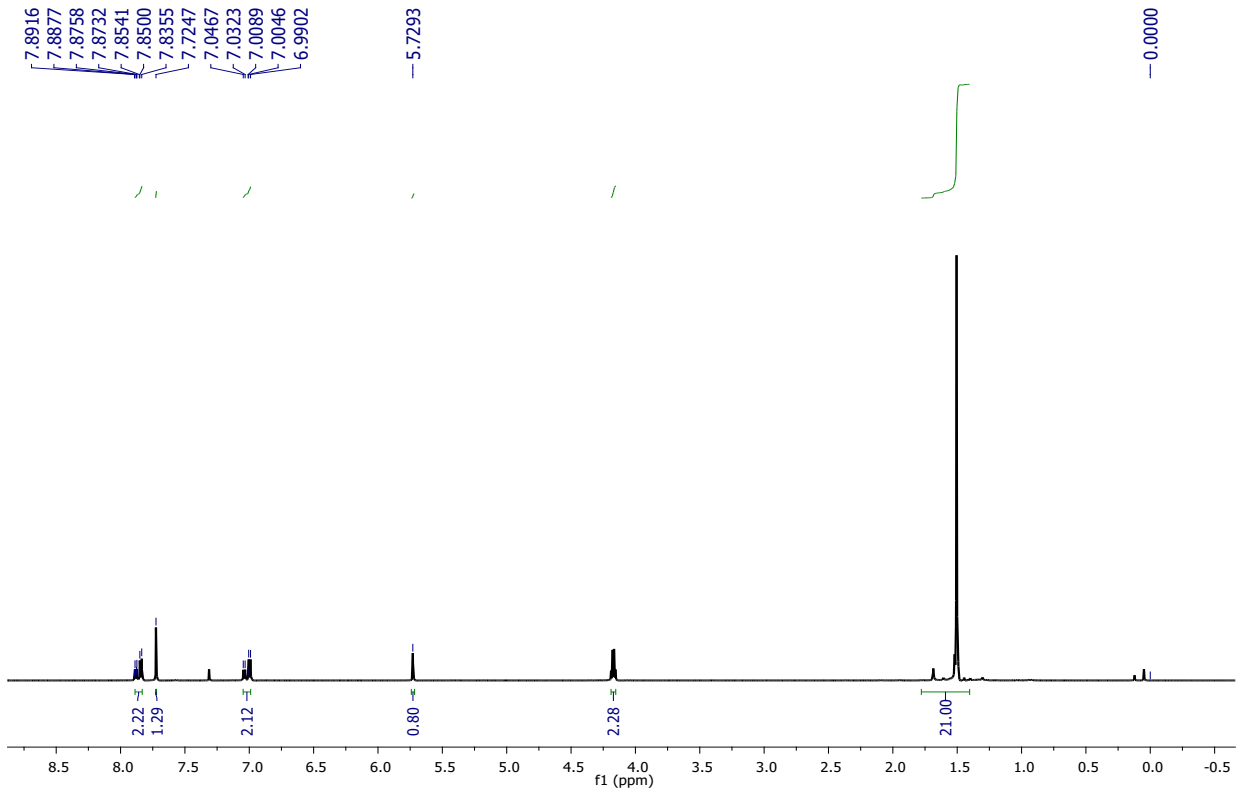


Figure S25. [1]H-NMR spectra of compound **1i**

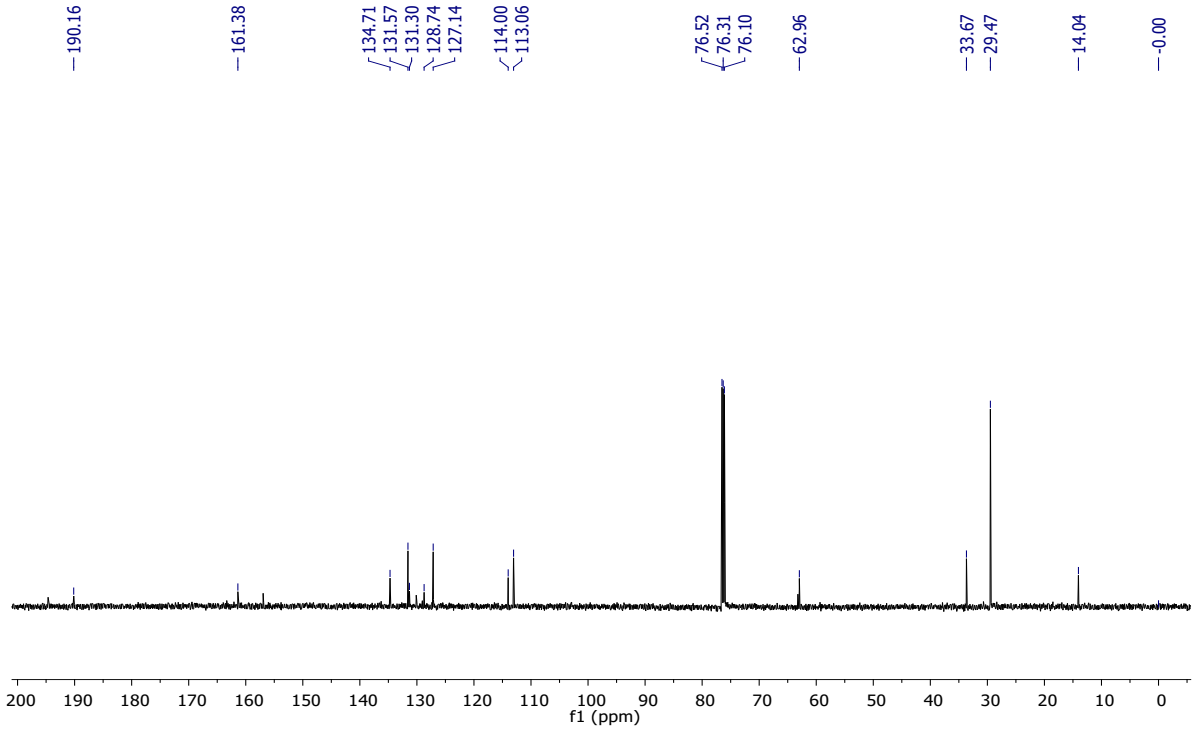


Figure S26. [13]C-NMR spectra of compound **1i**

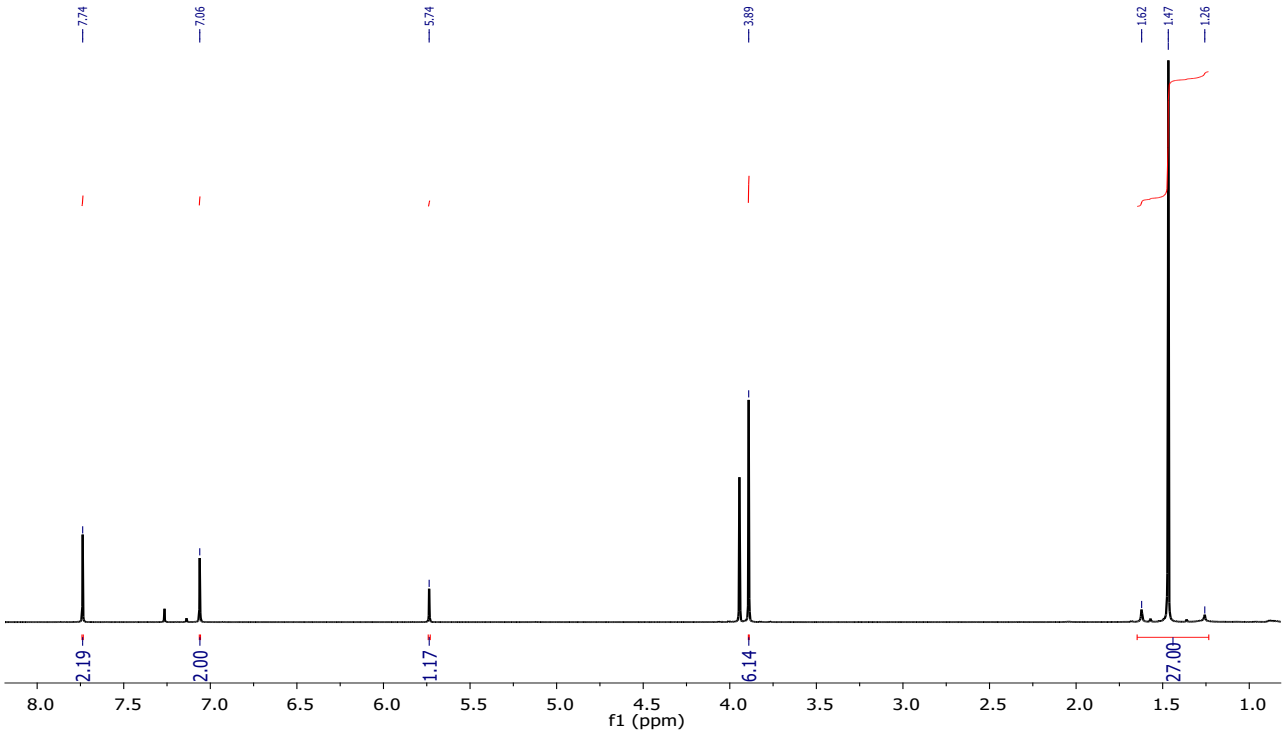


Figure S27. ^{1}H-NMR spectra of compound **1j**

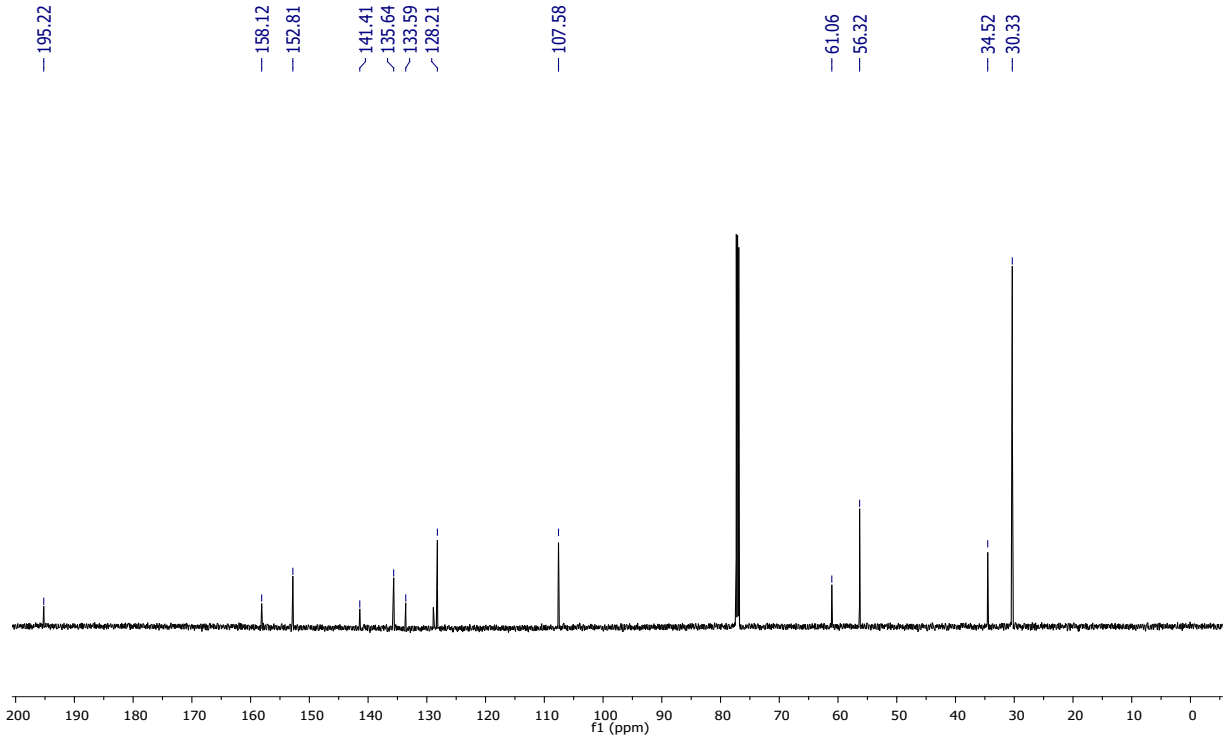


Figure S28. ^{13}C-NMR spectra of compound **1j**

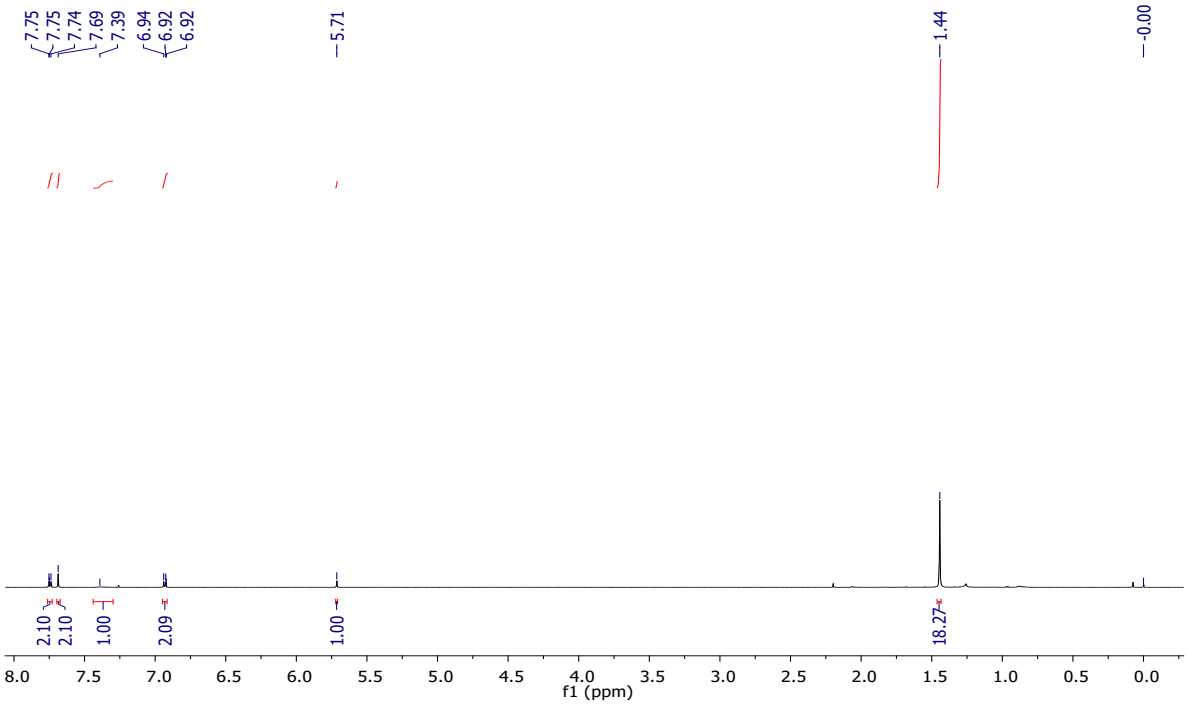


Figure S29. [1]H-NMR spectra of compound **1k**

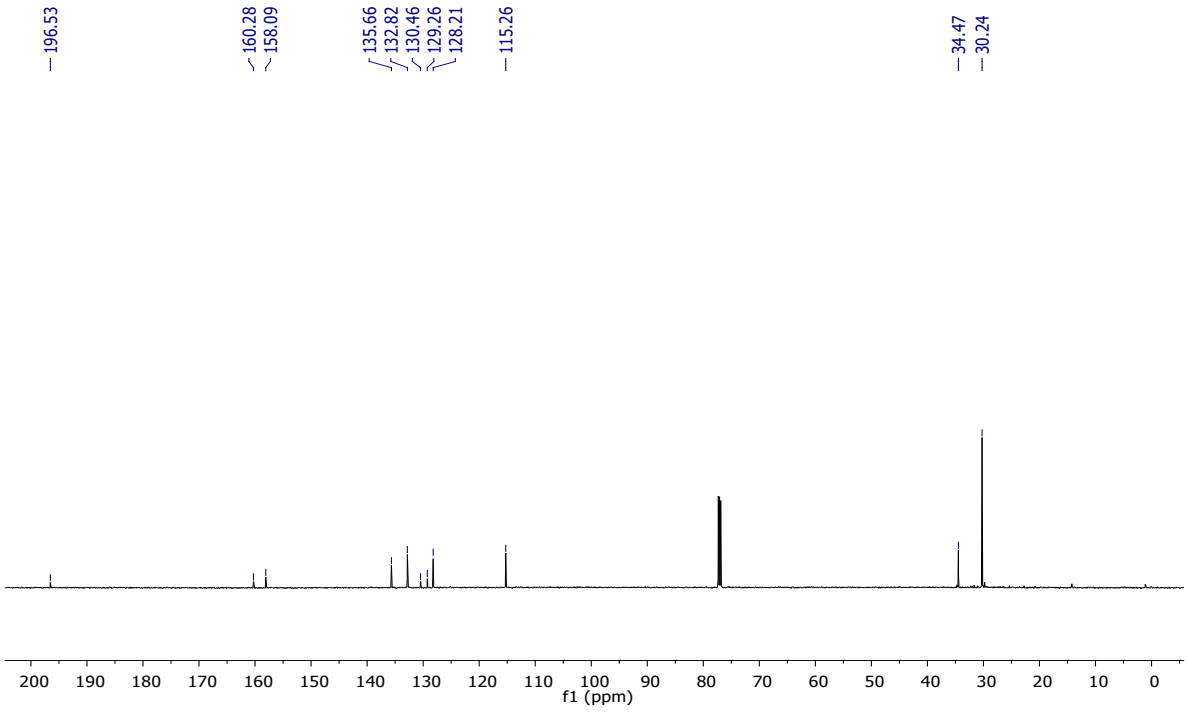


Figure S30. [13]C-NMR spectra of compound **1k**

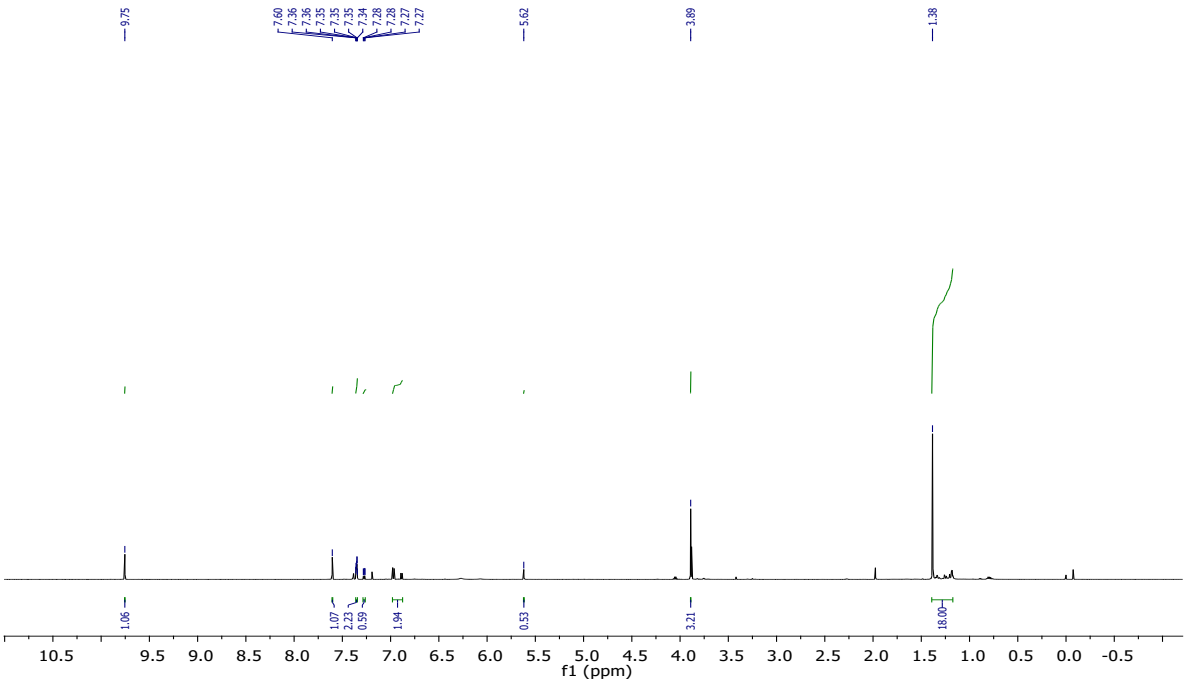


Figure S31. ^{1}H-NMR spectra of compound **1l**

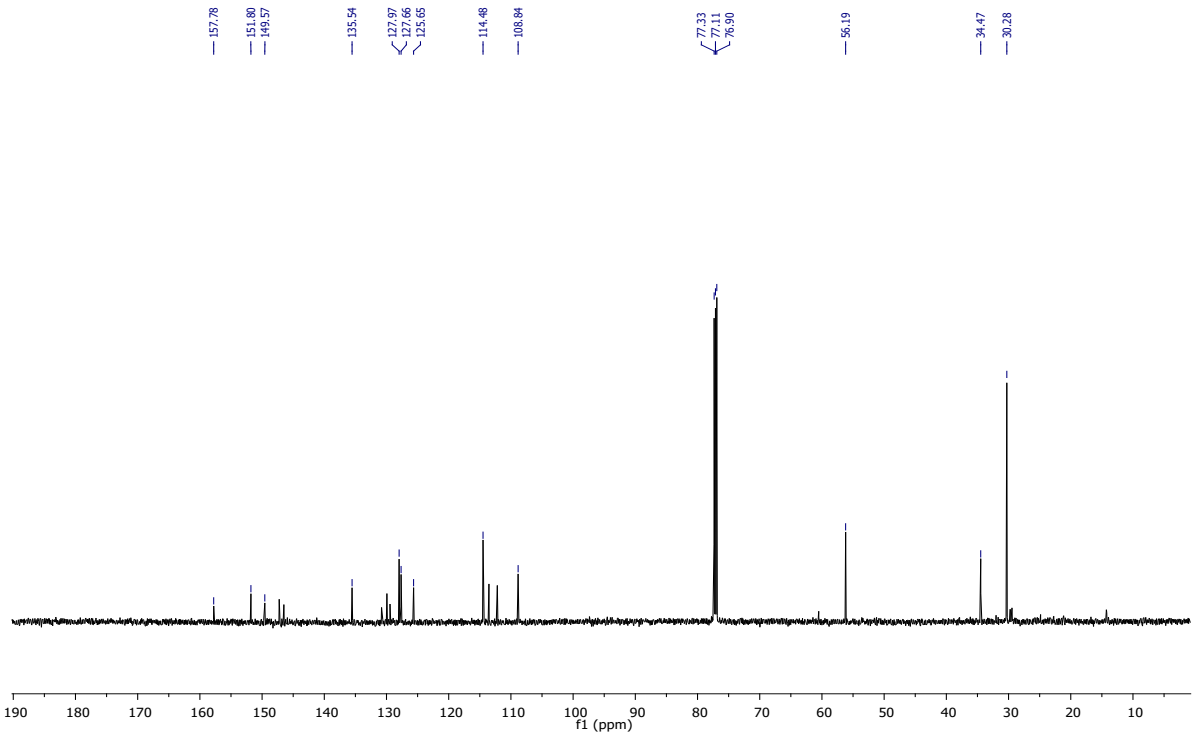


Figure S32. ^{13}C-NMR spectra of compound **1l**

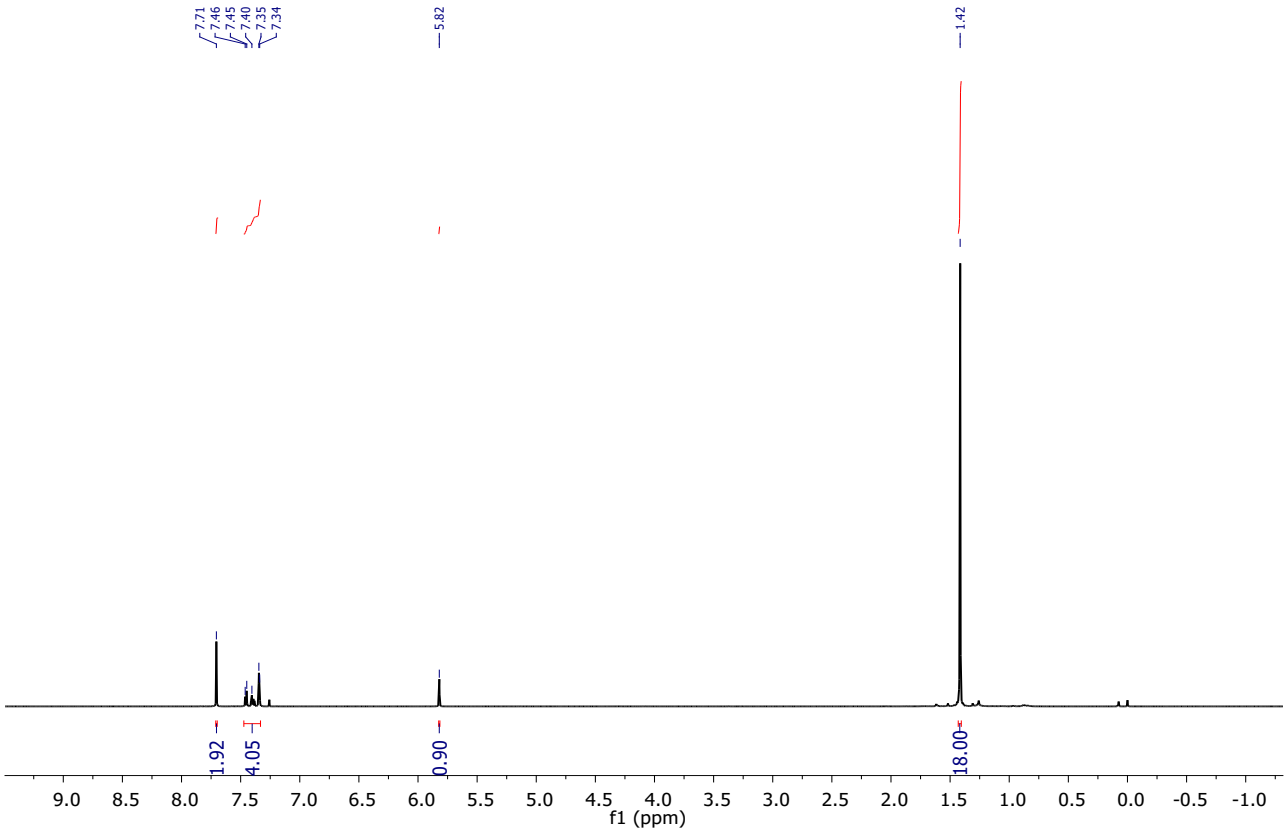


Figure S33. [1]H-NMR spectra of compound **1m**

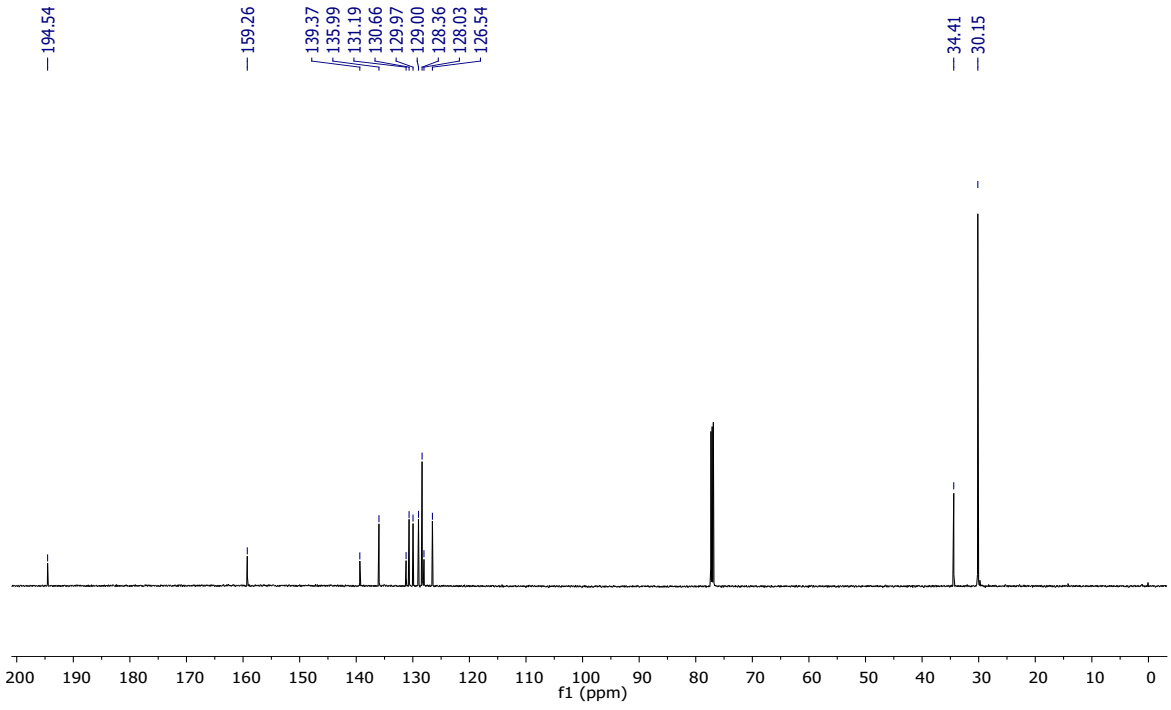


Figure S34. [13]C-NMR spectra of compound **1m**

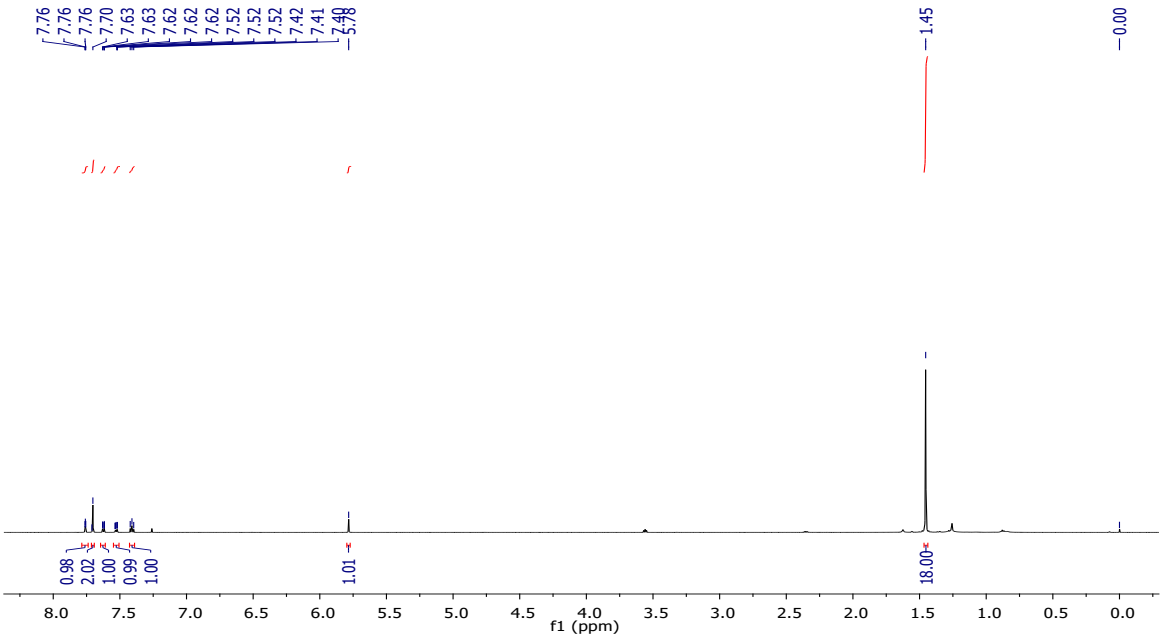


Figure S35. [1]H-NMR spectra of compound **1n**

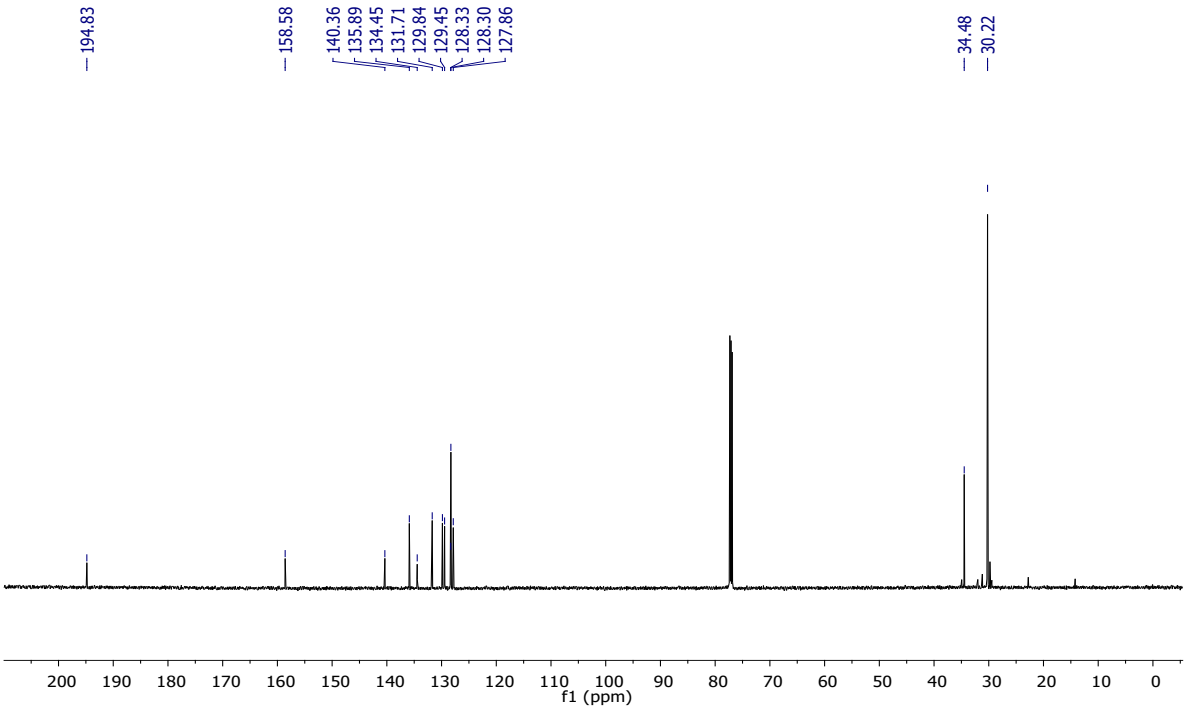


Figure S36. [13]C-NMR spectra of compound **1n**

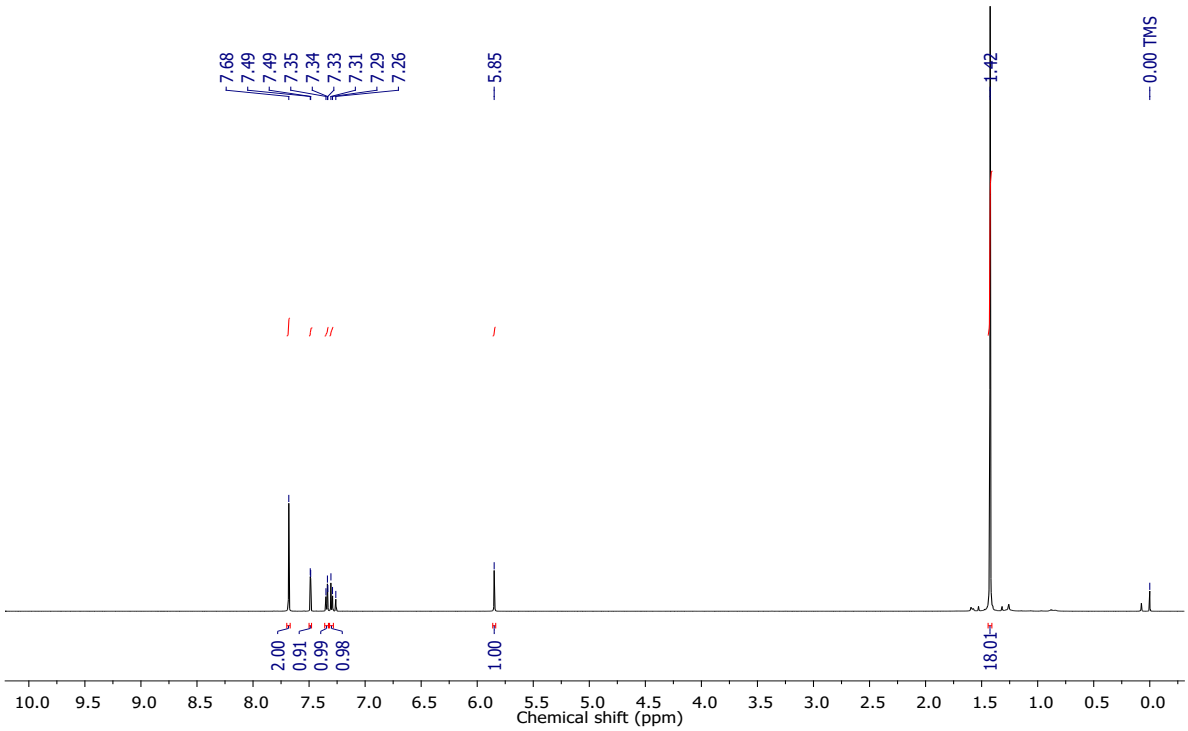


Figure S37. ^{1}H-NMR spectra of compound **1o**

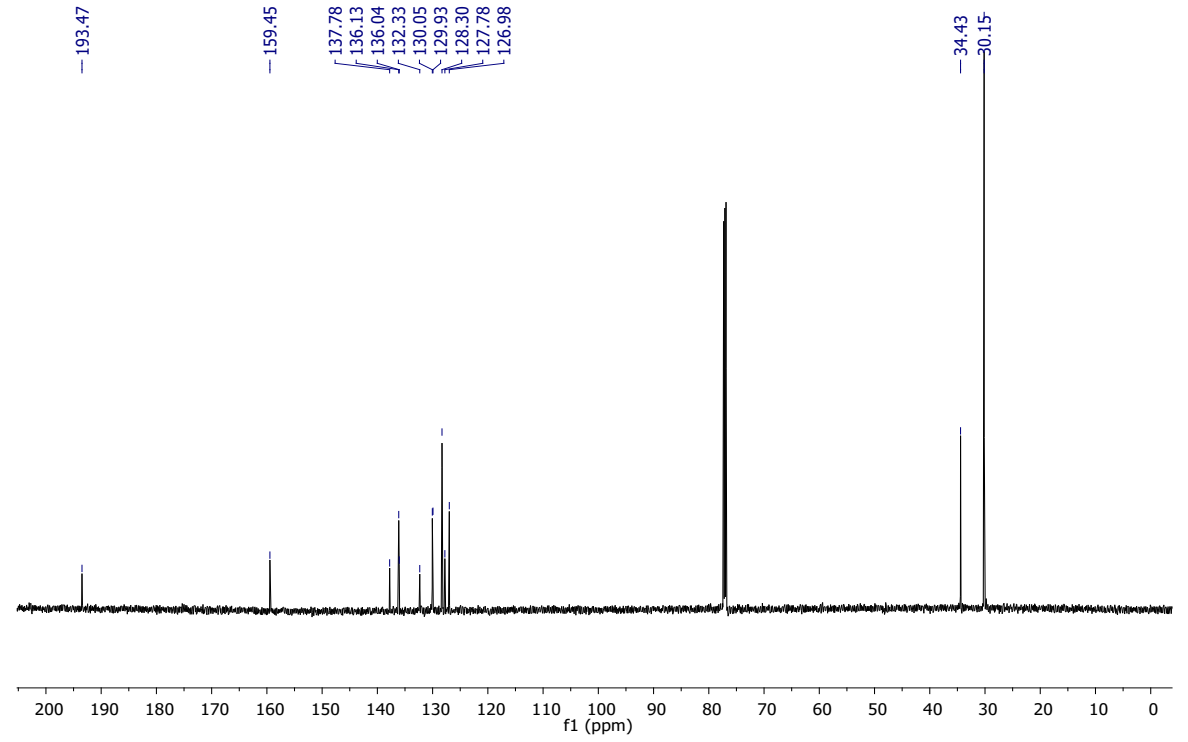


Figure S38. ^{13}C-NMR spectra of compound **1o**

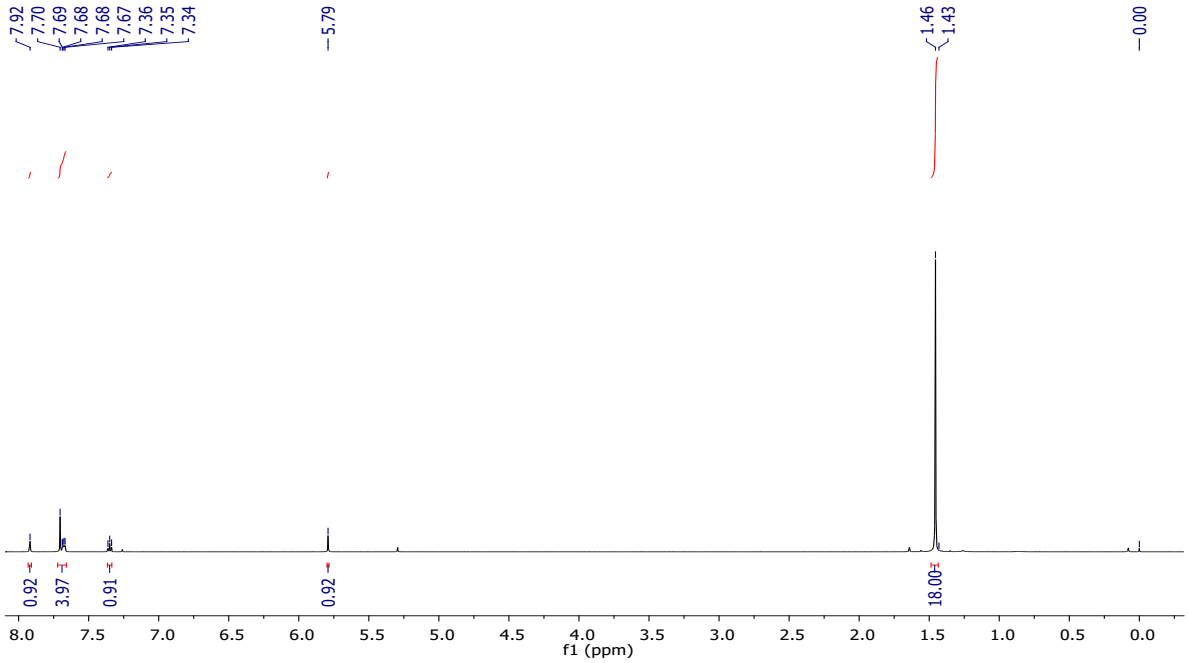


Figure S39. ^{1}H-NMR spectra of compound **1p**

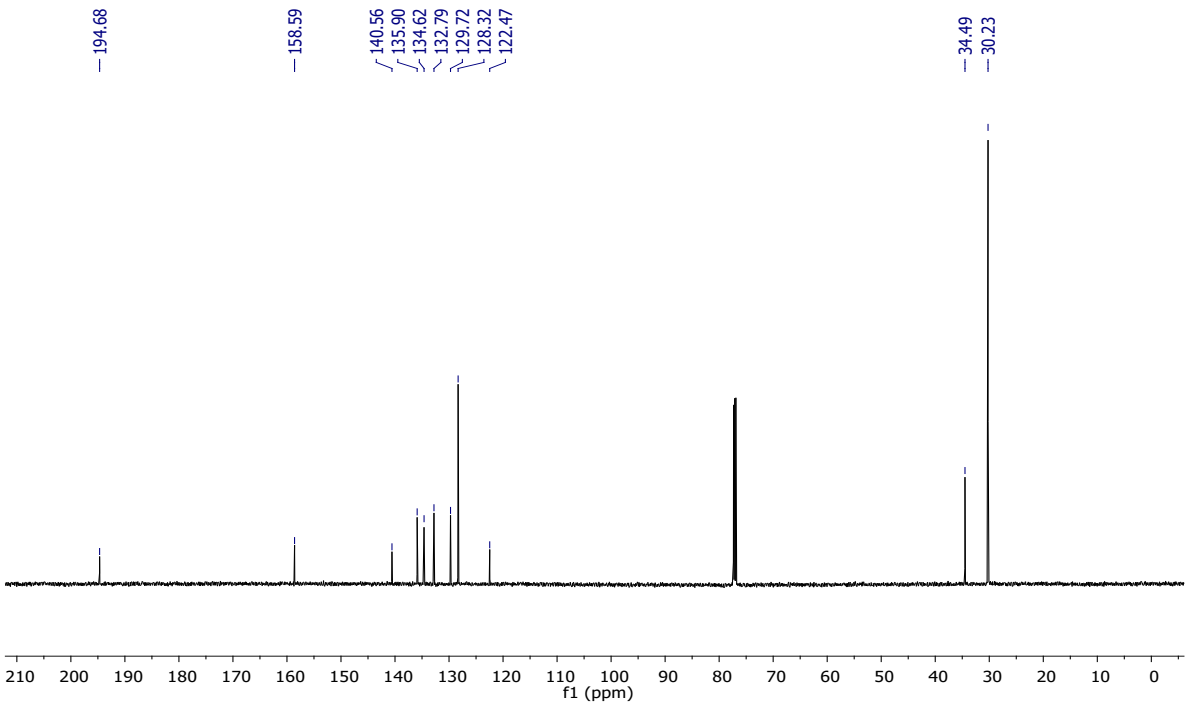


Figure S40. ^{13}C-NMR spectra of compound **1p**

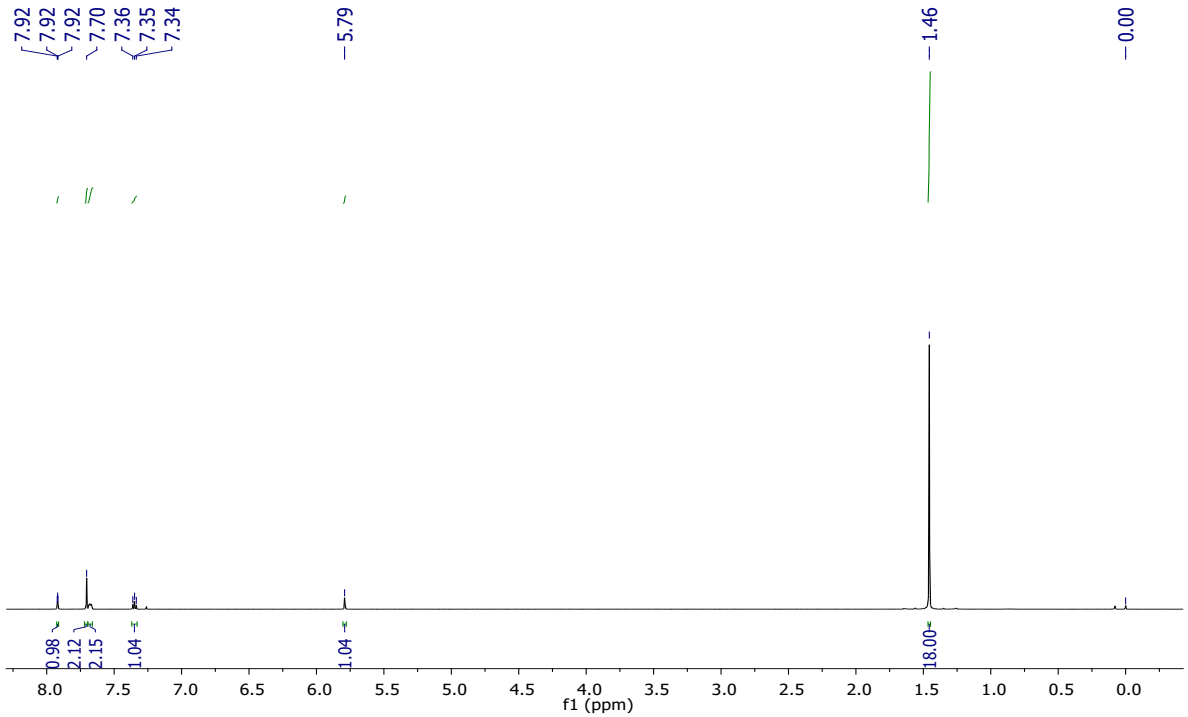


Figure S41. ^{1}H-NMR spectra of compound **1q**

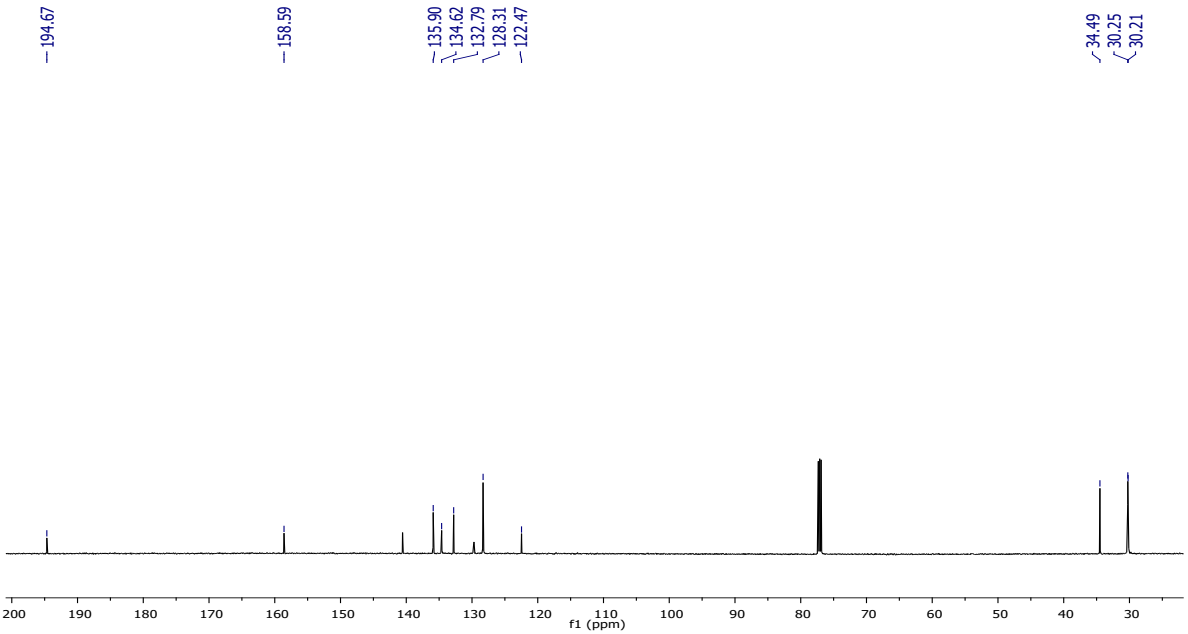


Figure S42. ^{13}C-NMR spectra of compound **1q**

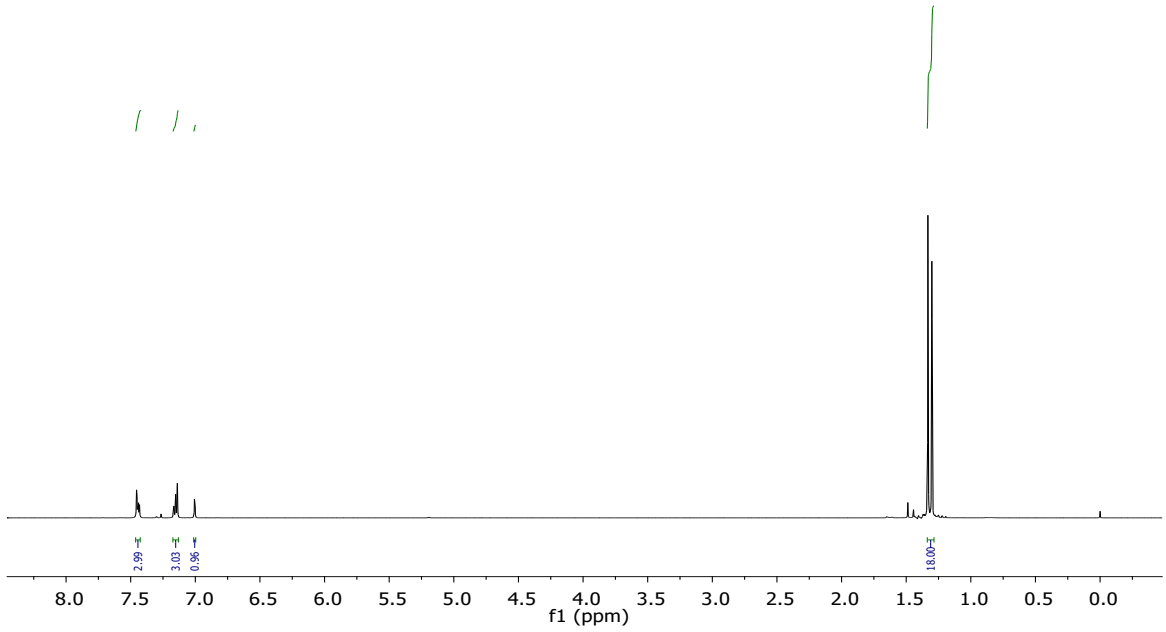


Figure S43. [1]H-NMR spectra of compound **1r**

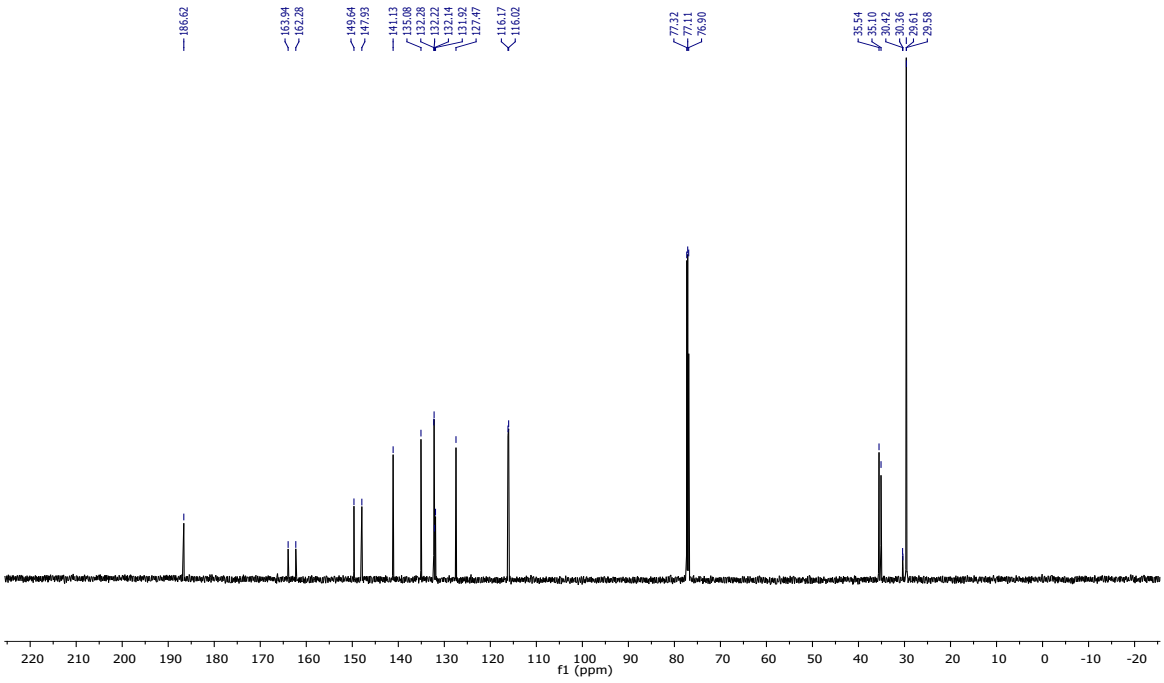


Figure S44. [13]C-NMR spectra of compound **1r**

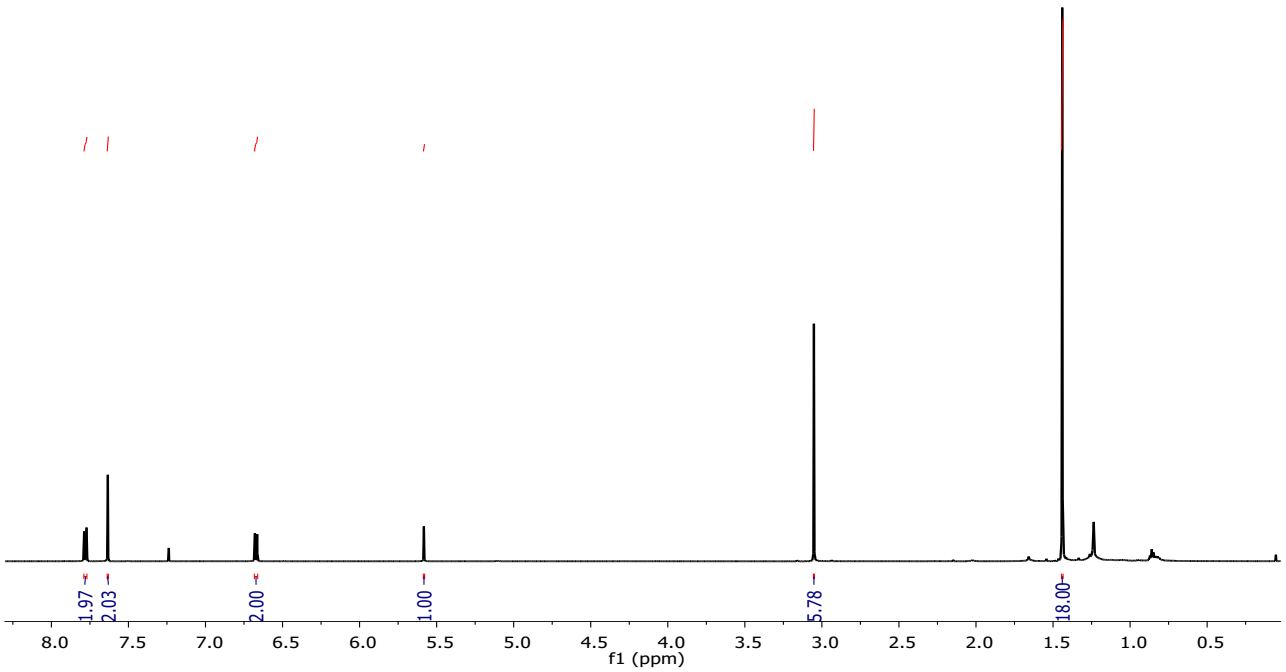


Figure S45. ^{1}H-NMR spectra of compound **1s**

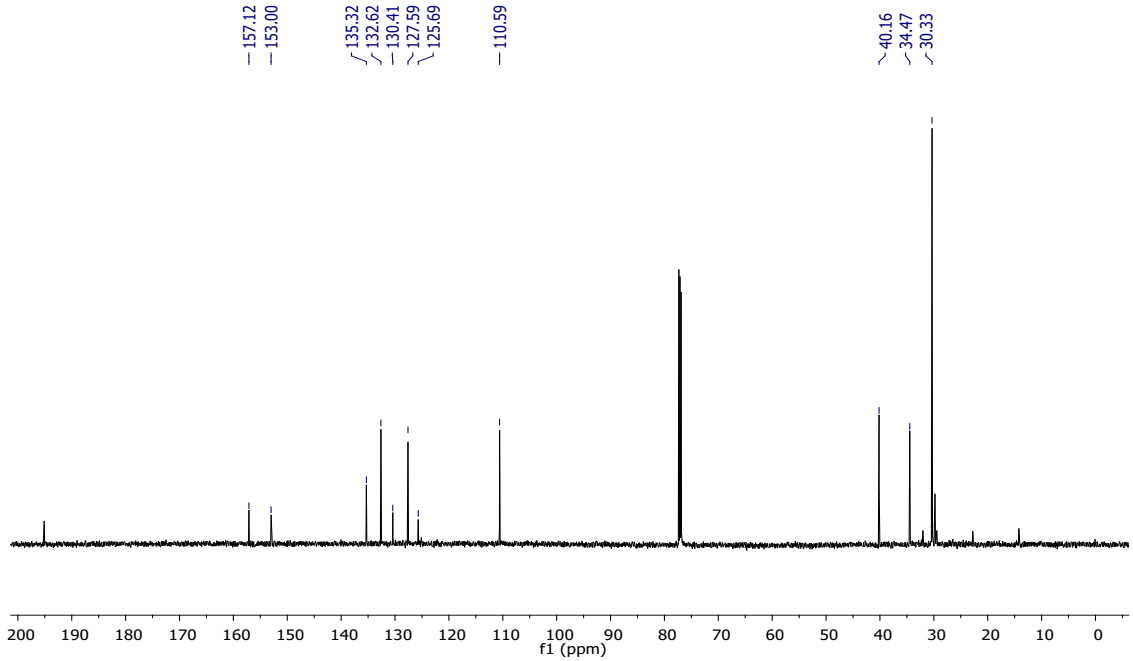


Figure S46. ^{13}C-NMR spectra of compound **1s**

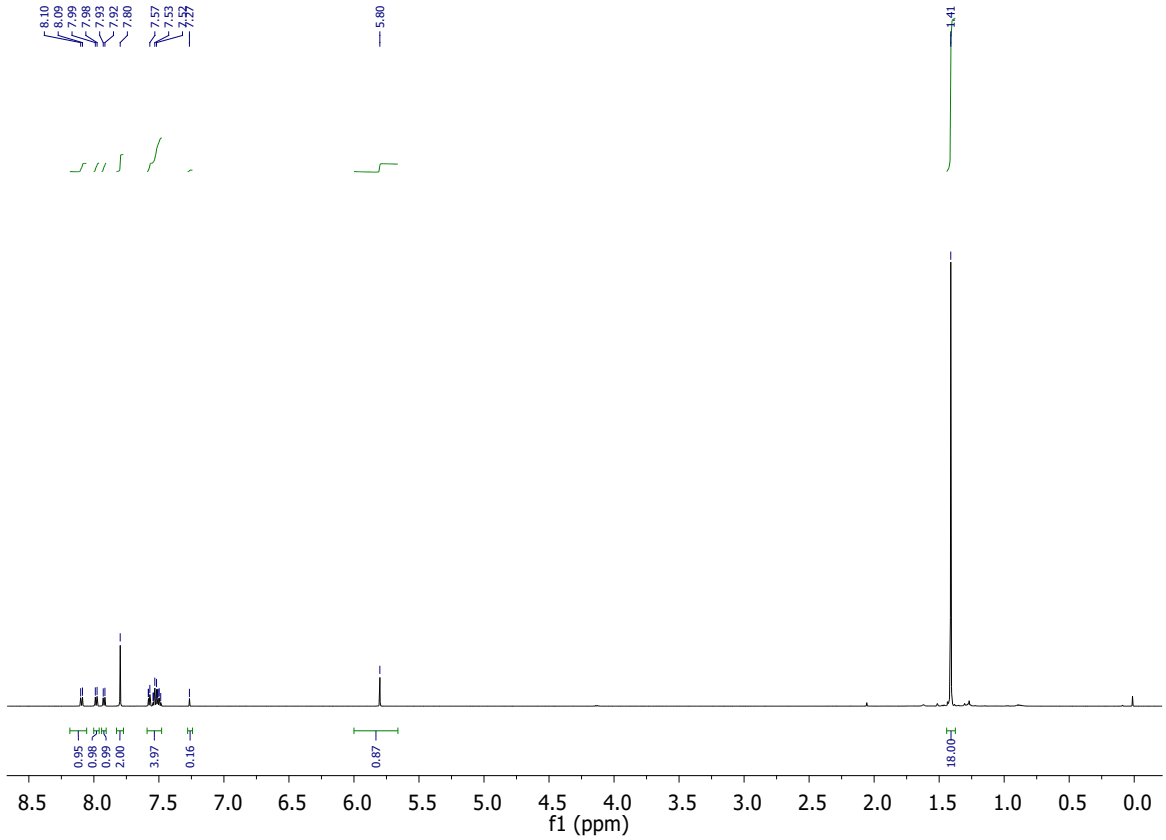


Figure S47. [1]H-NMR spectra of compound **1u**

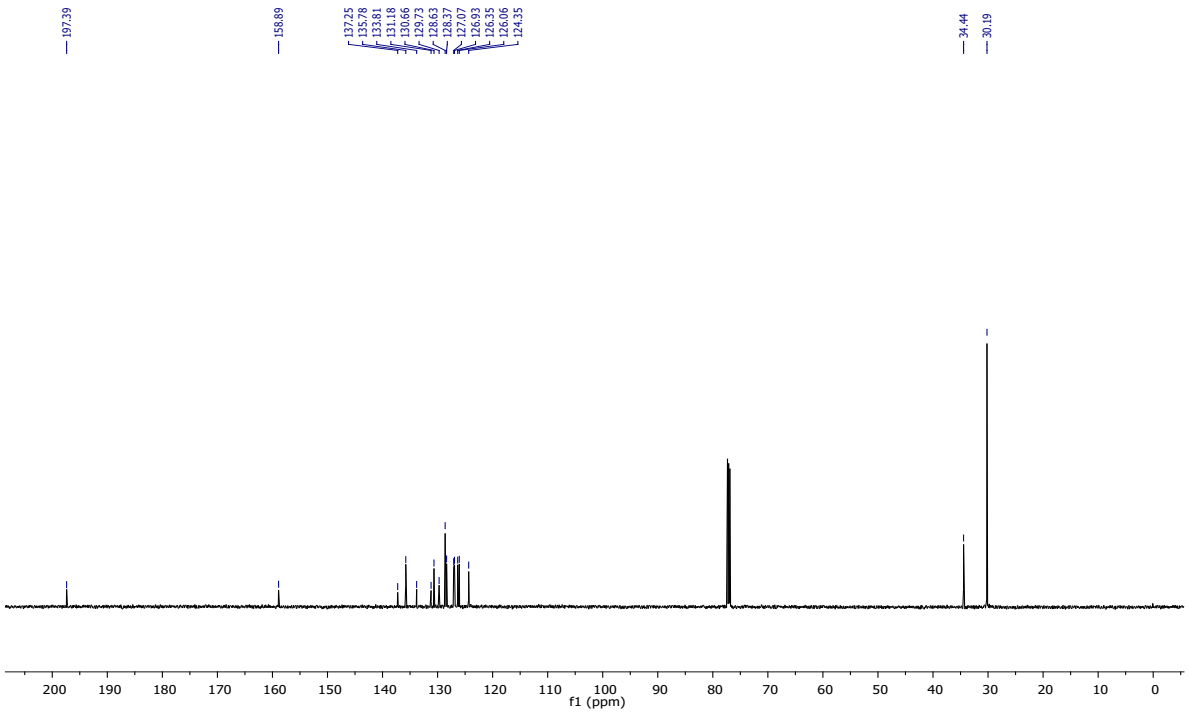


Figure S48. [13]C-NMR spectra of compound **1u**

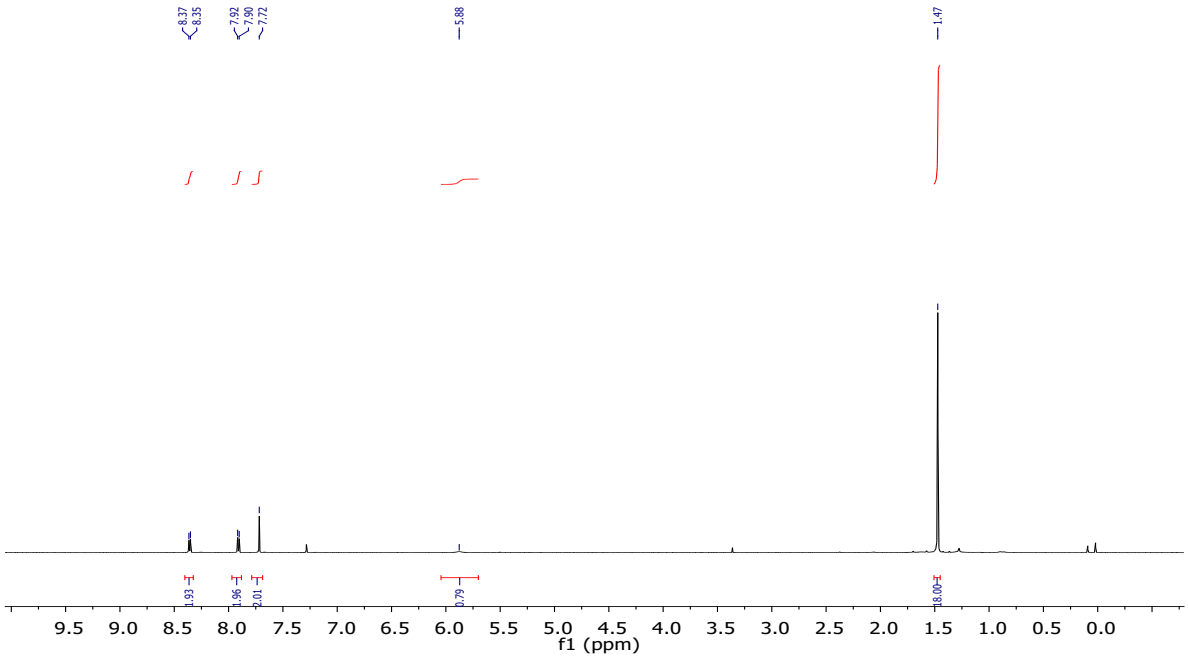


Figure S49. [1]H-NMR spectra of compound **1v**

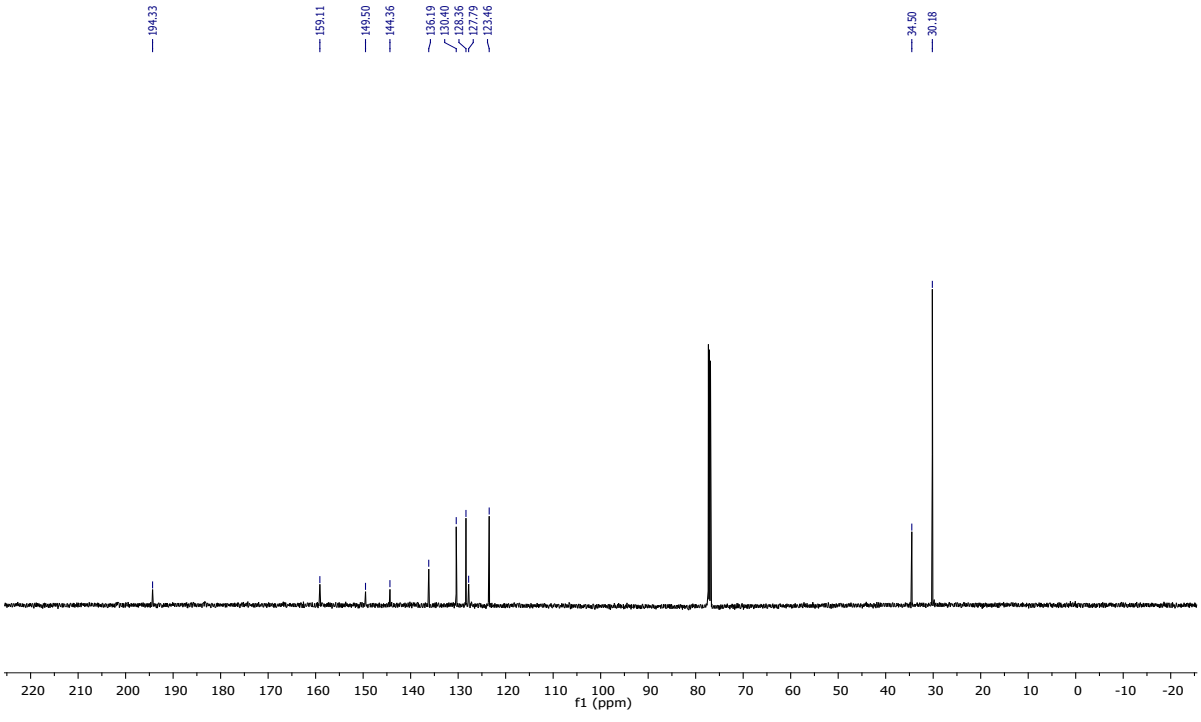


Figure S50. [13]C-NMR spectra of compound **1v**

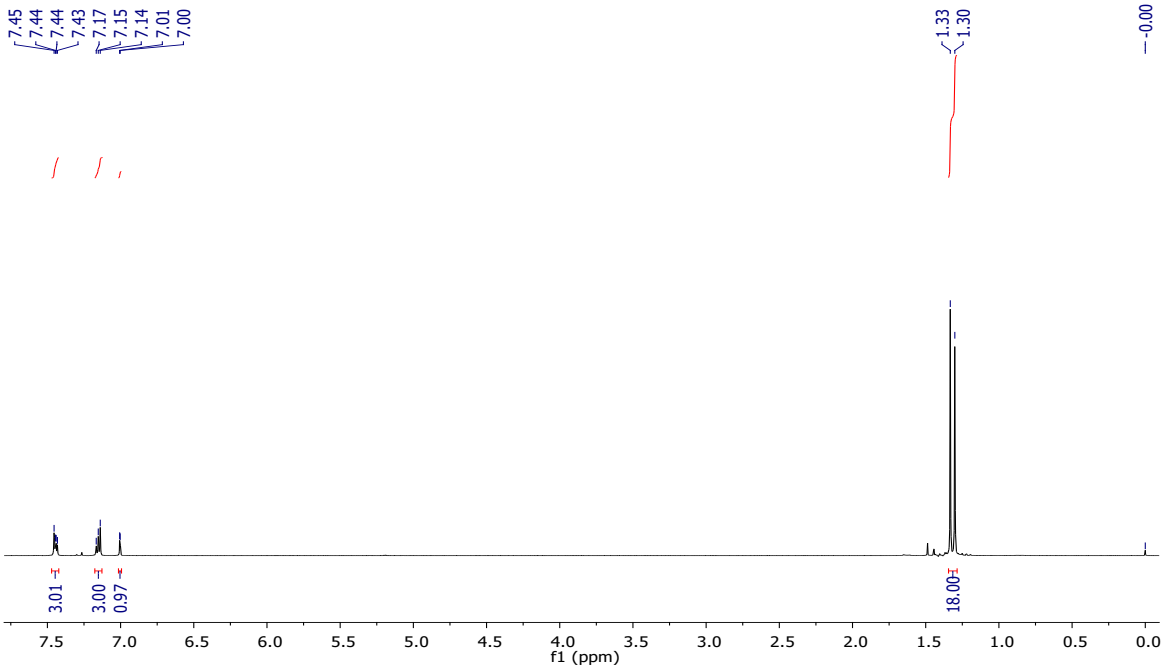


Figure S51. [1]H-NMR spectra of compound **1w**

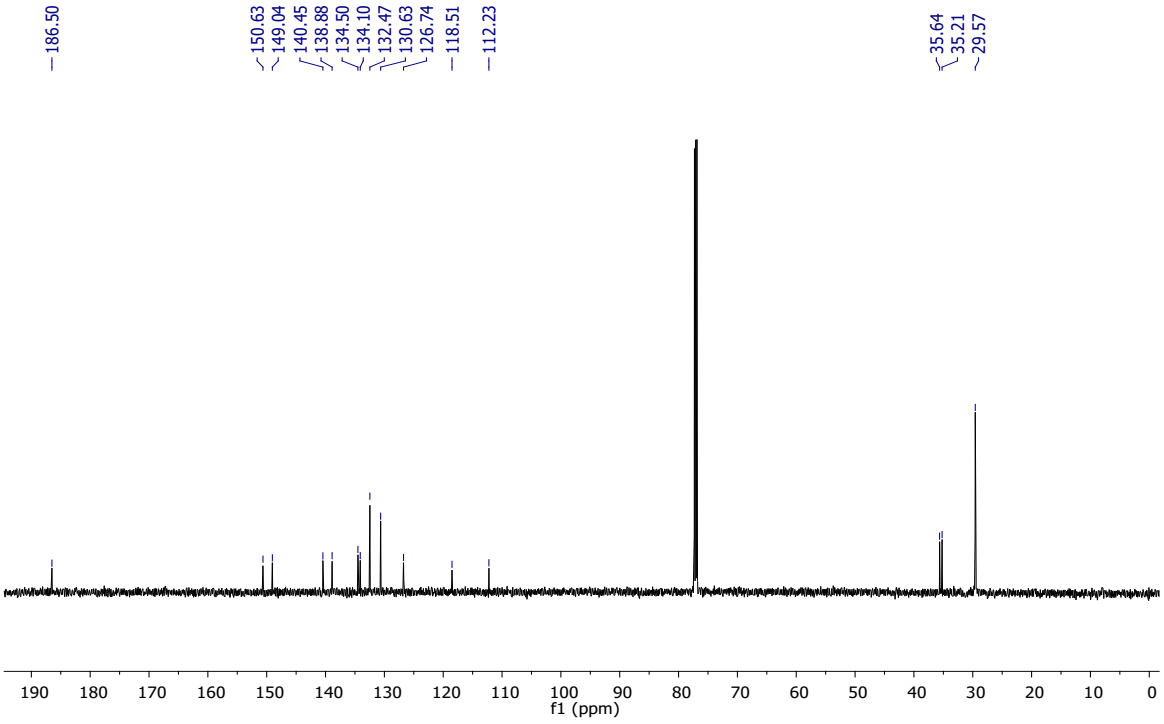


Figure S52. [13]C-NMR spectra of compound **1w**

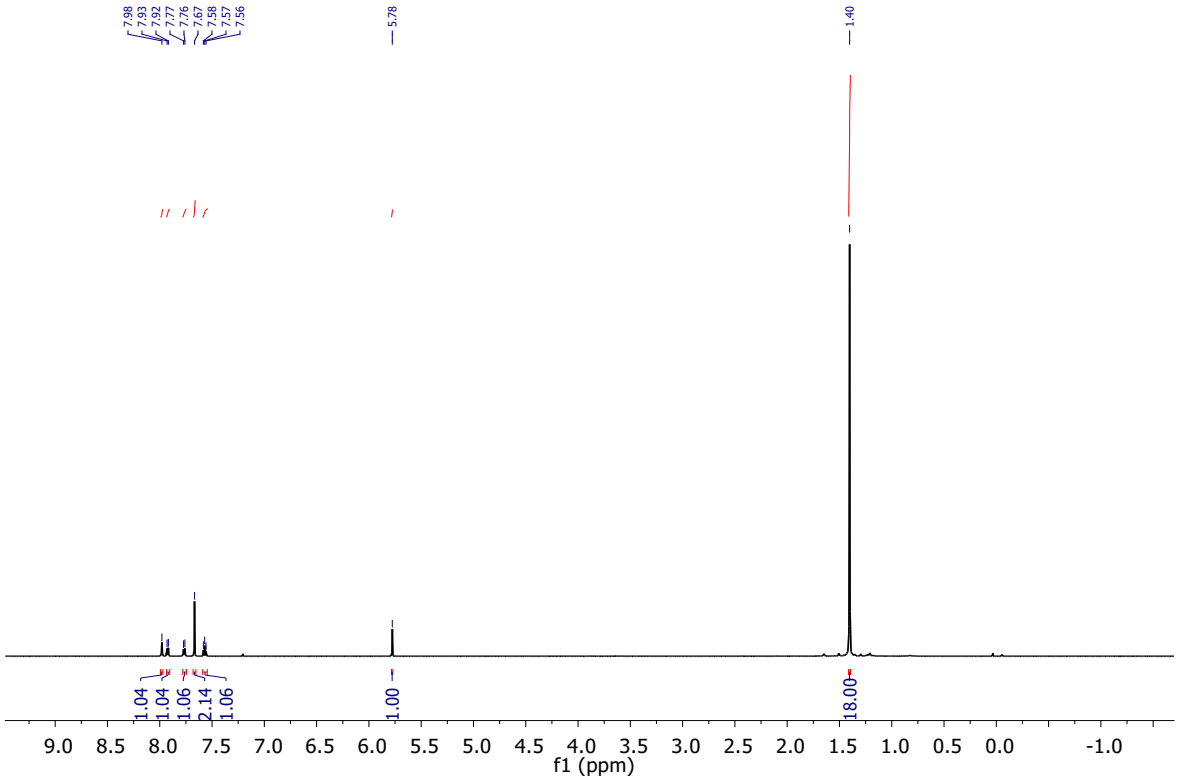


Figure S53. [1]H-NMR spectra of compound **1x**

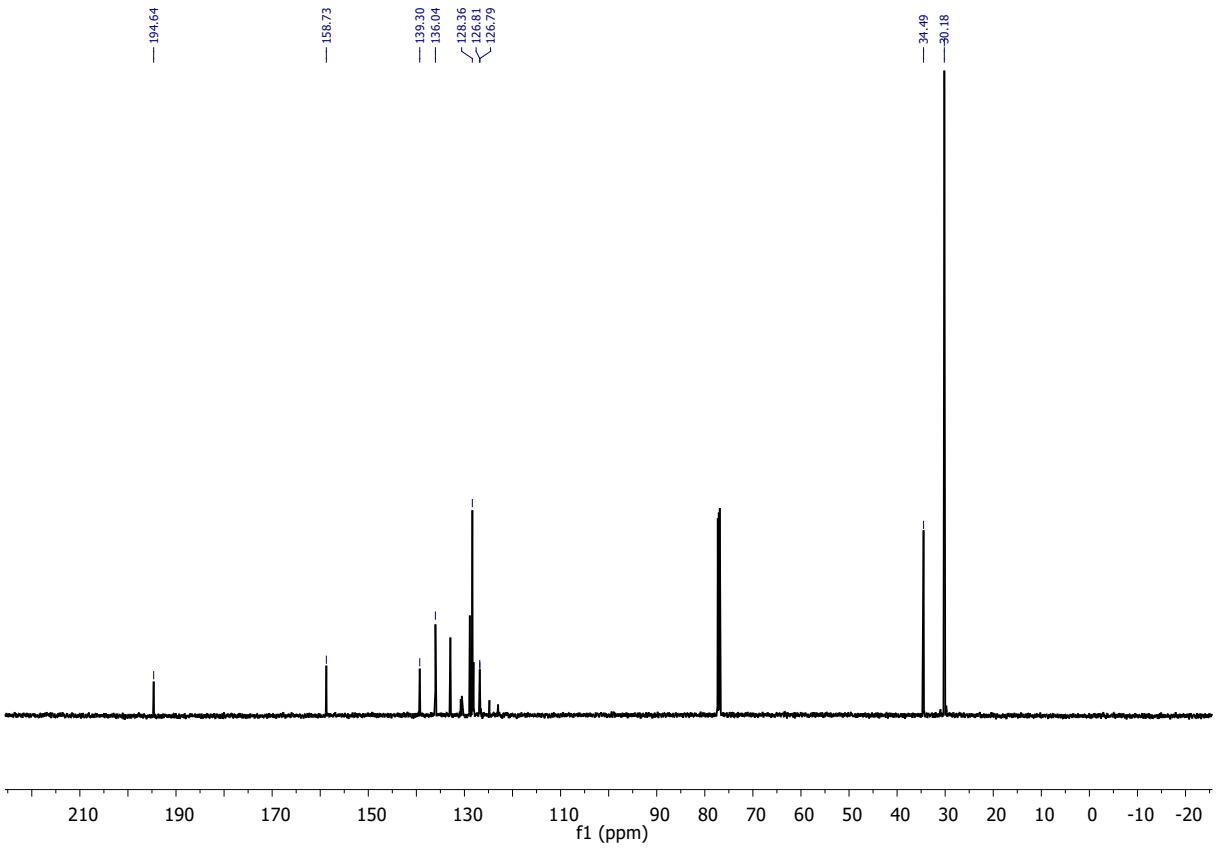


Figure S54. ^{13}C-NMR spectra of compound **1x**

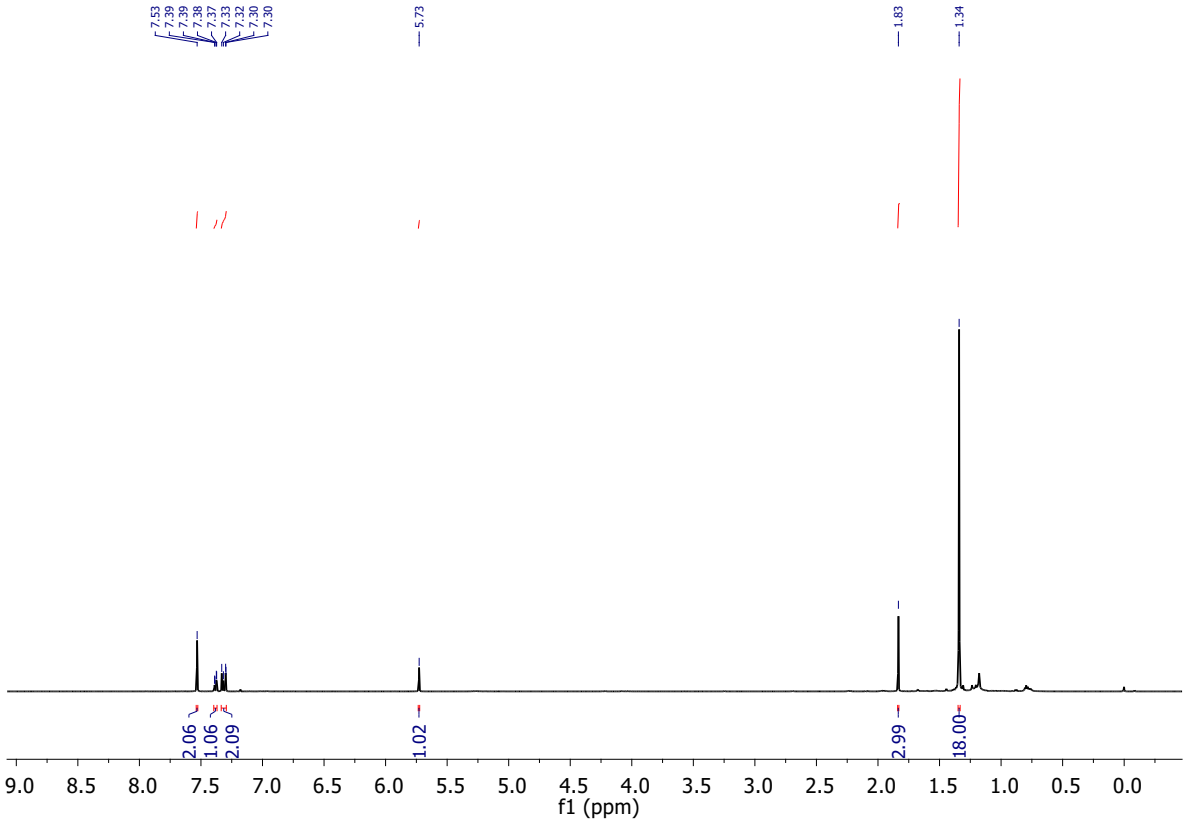


Figure S55. ^{1}H-NMR spectra of compound **1y**

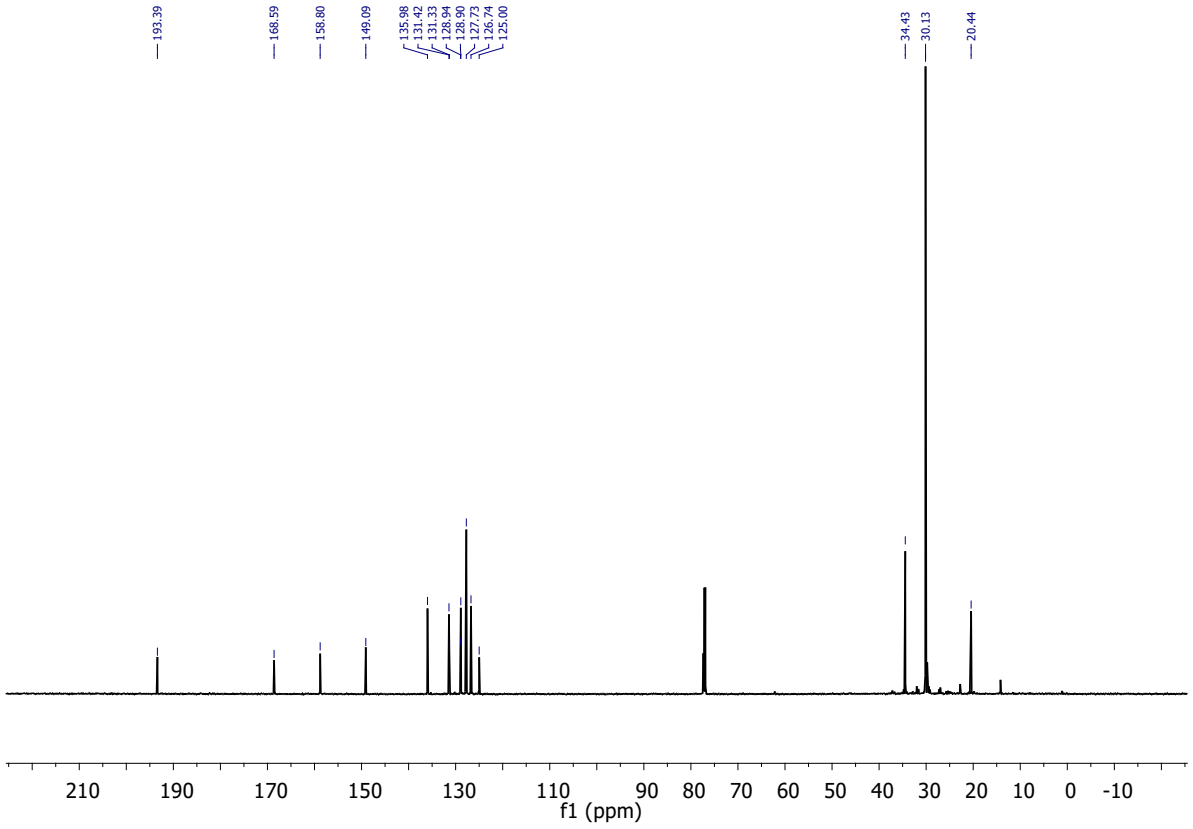


Figure S56. ^{13}C-NMR spectra of compound **1y**

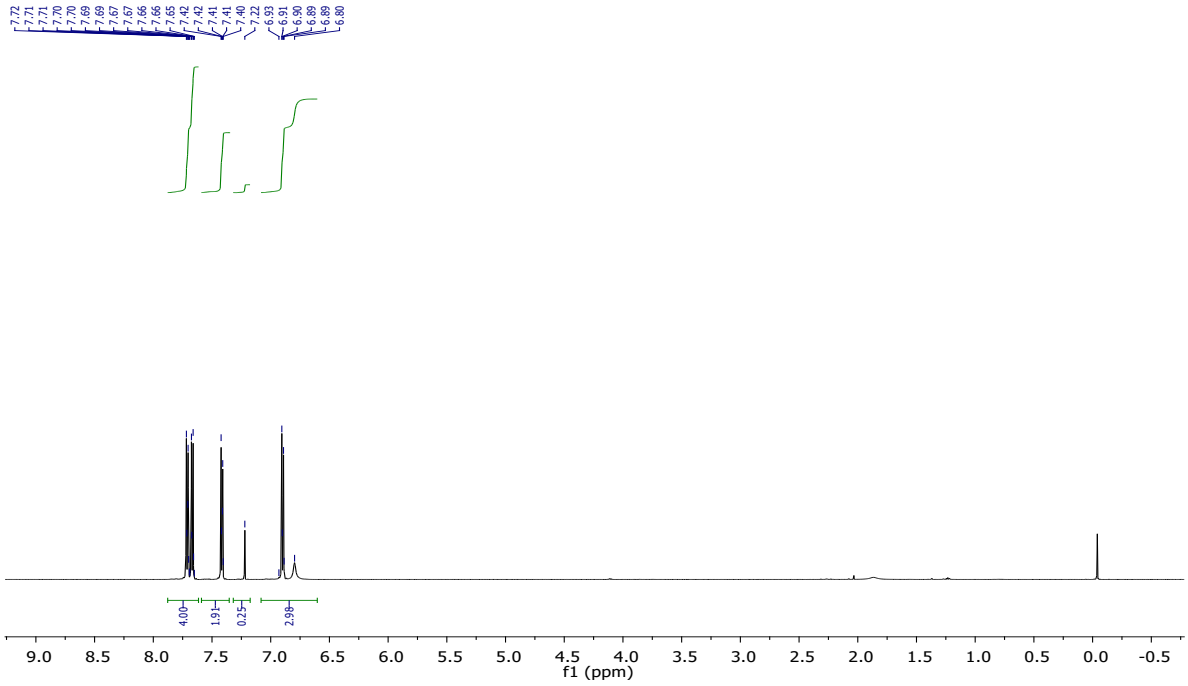


Figure S57. ^{1}H-NMR spectra of compound **9a**

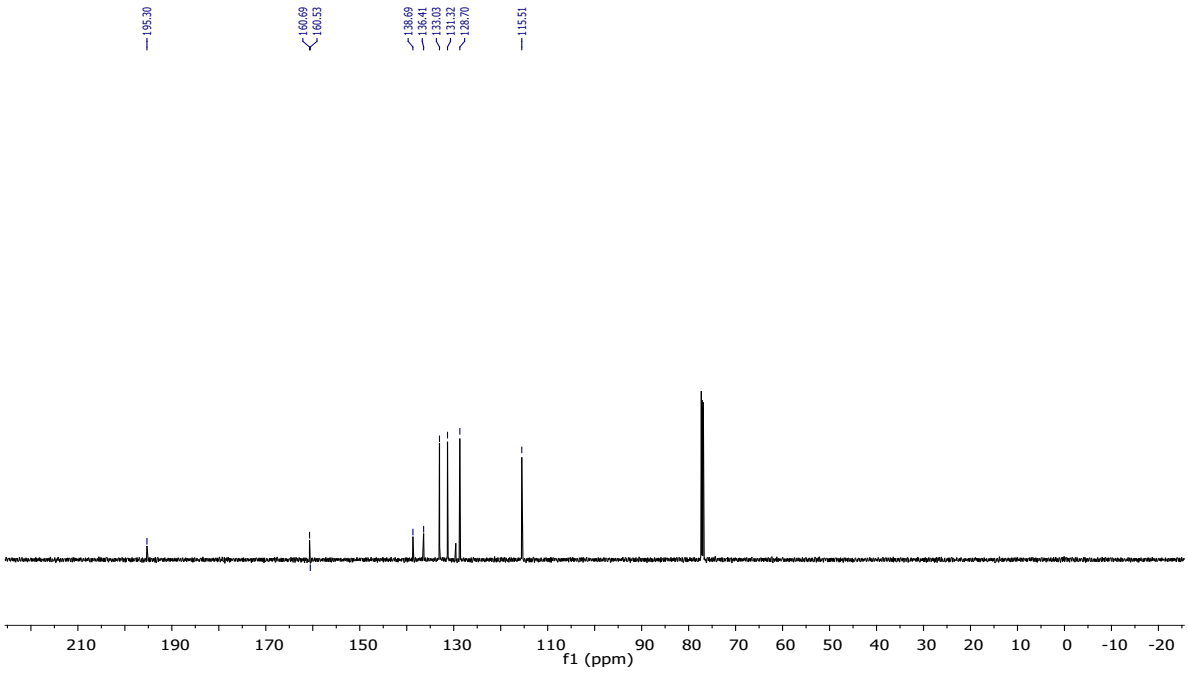


Figure S58. ^{13}C-NMR spectra of compound **9a**

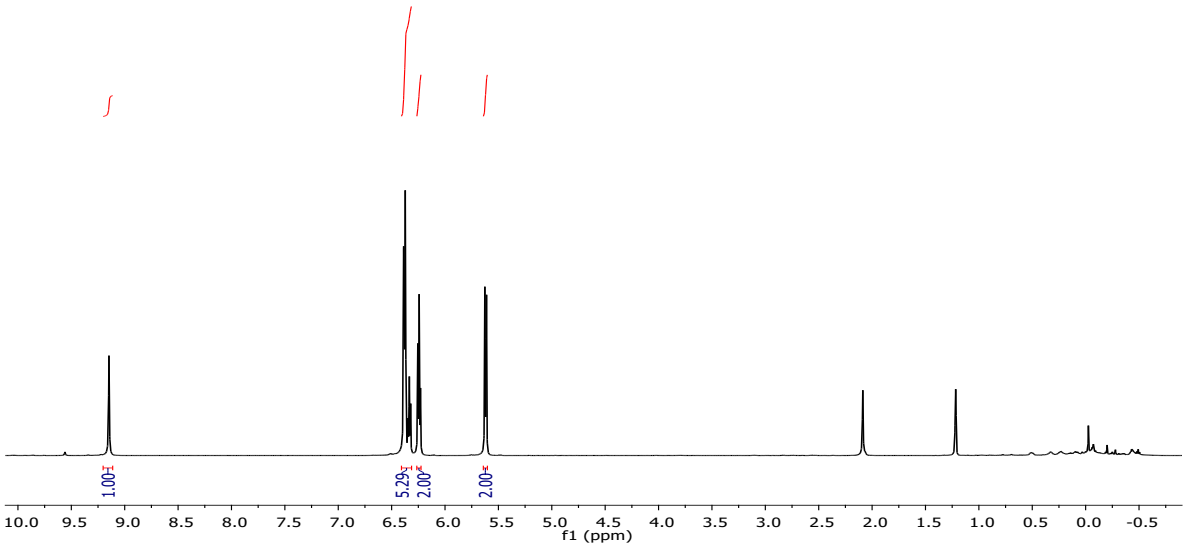


Figure S59. [1]H-NMR spectra of compound **9b**

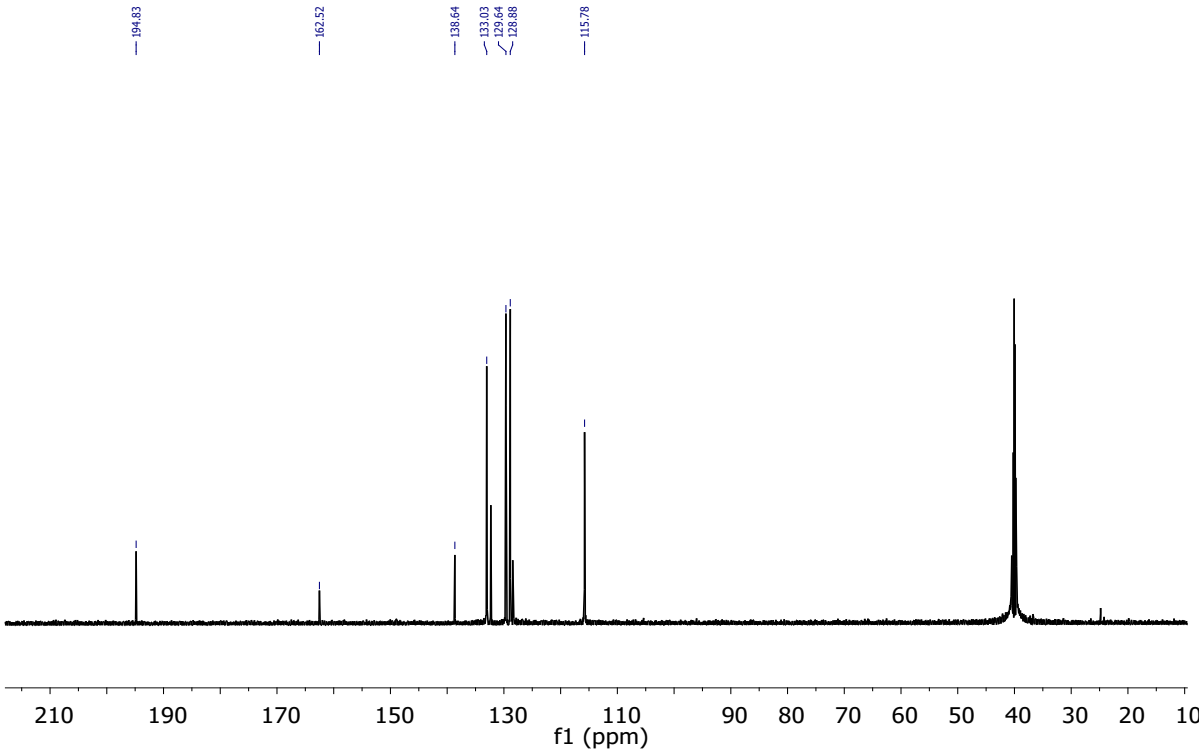


Figure S60. [13]C-NMR spectra of compound **9b**

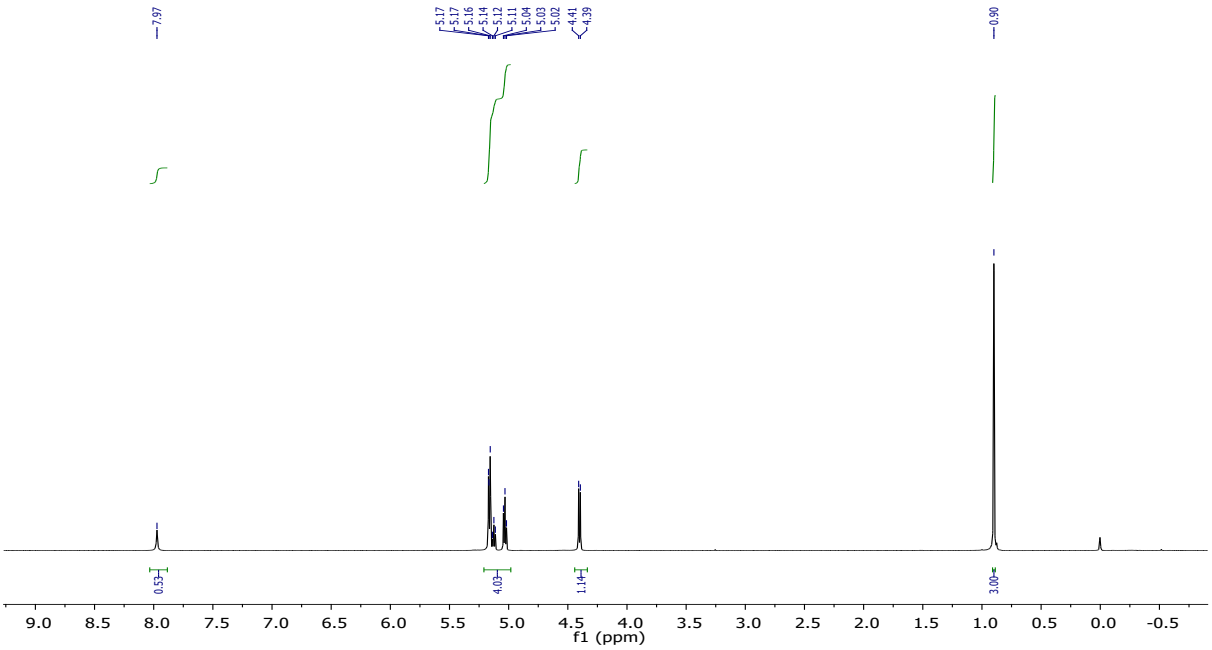


Figure S61. ^{1}H-NMR spectra of compound **9d**

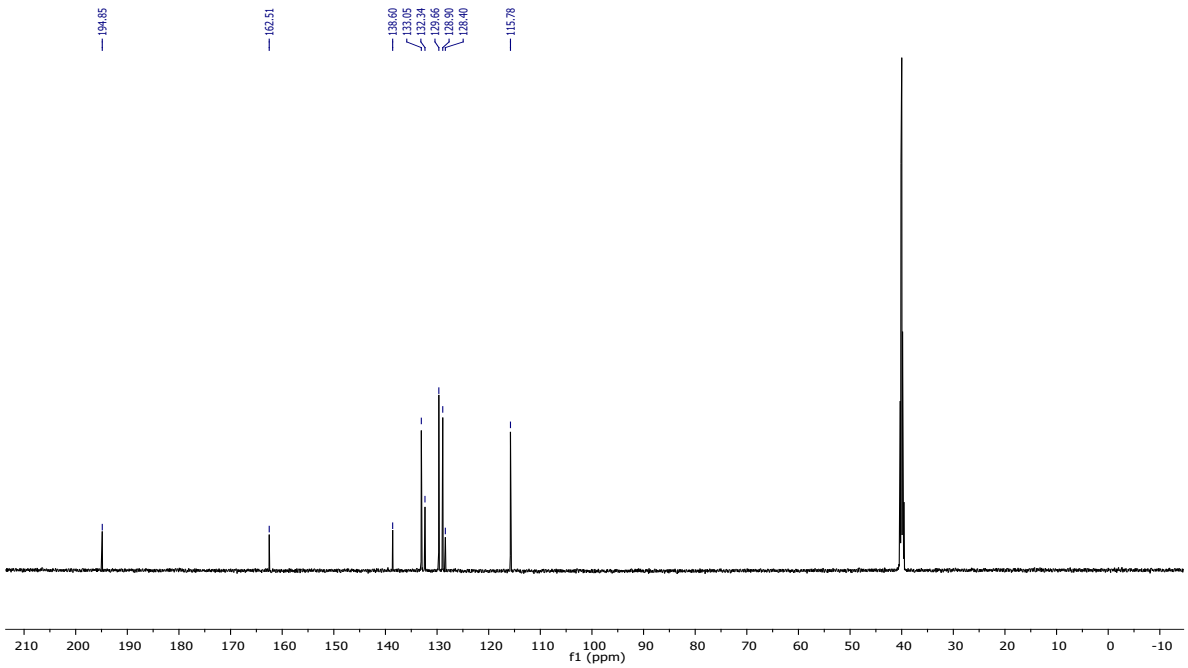


Figure S62. ^{13}C-NMR spectra of compound **9d**

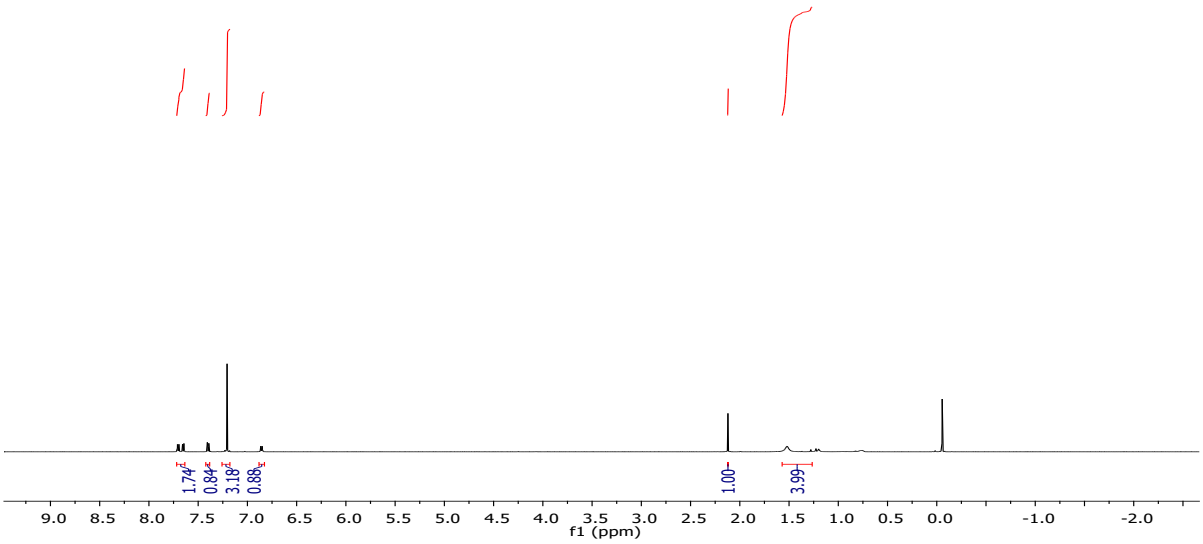


Figure S63. [1]H-NMR spectra of compound **9f**

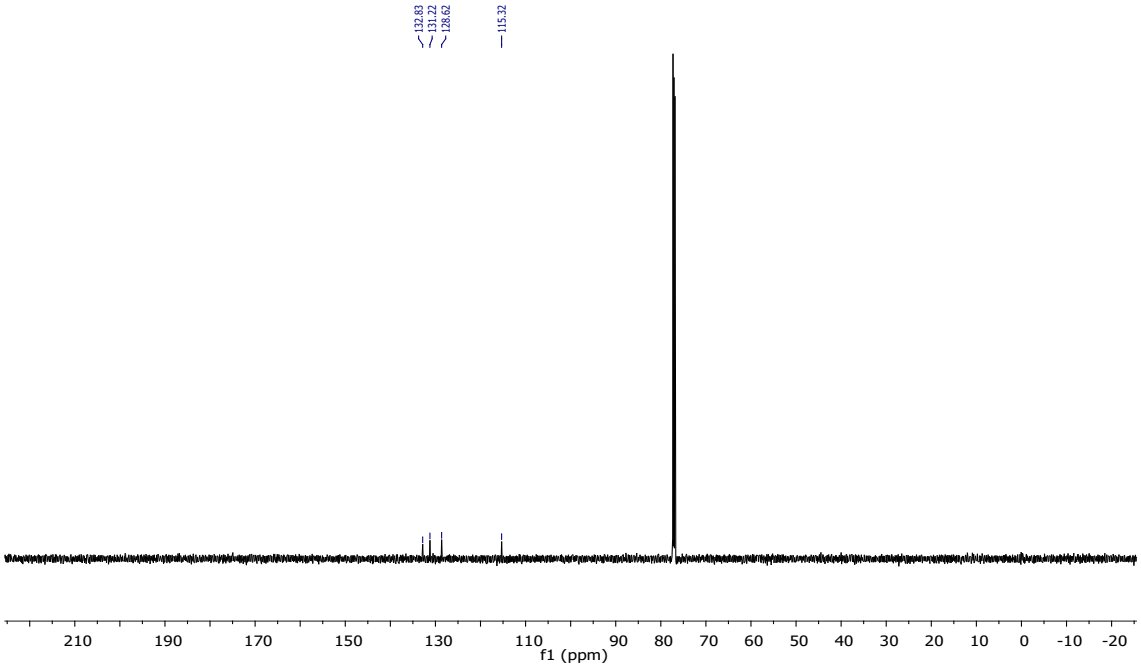


Figure S64. [13]C-NMR spectra of compound **9f**

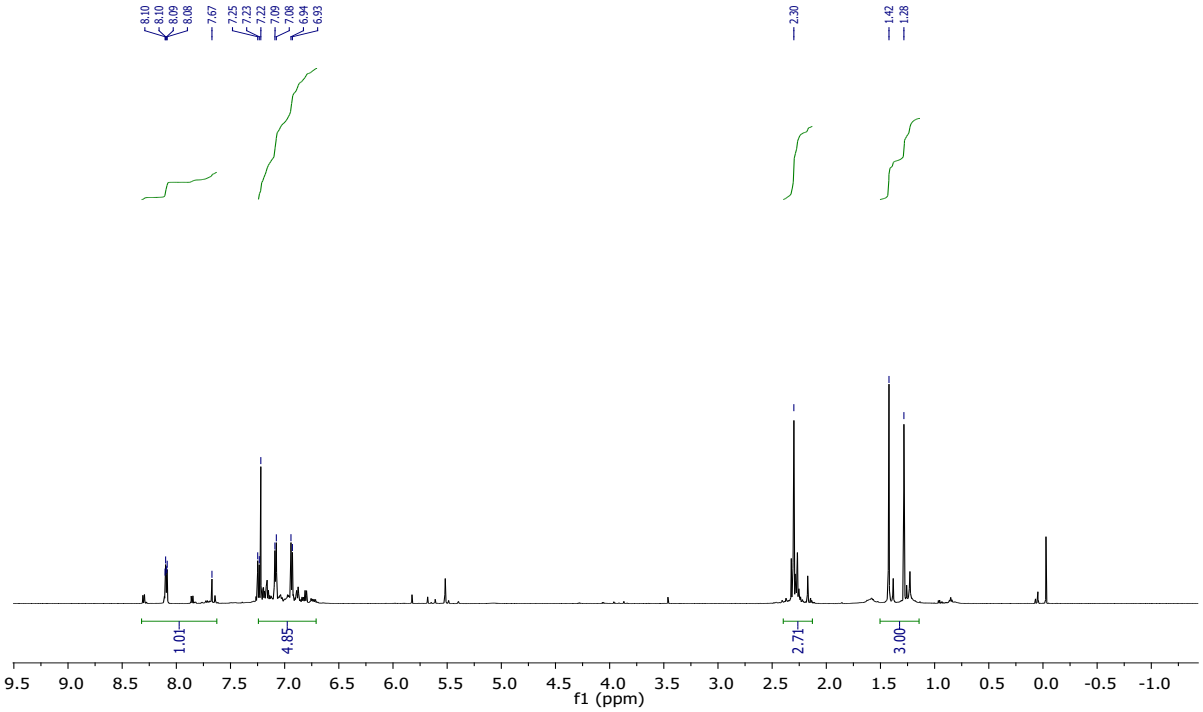


Figure S65. ^{1}H-NMR spectra of compound **9l**

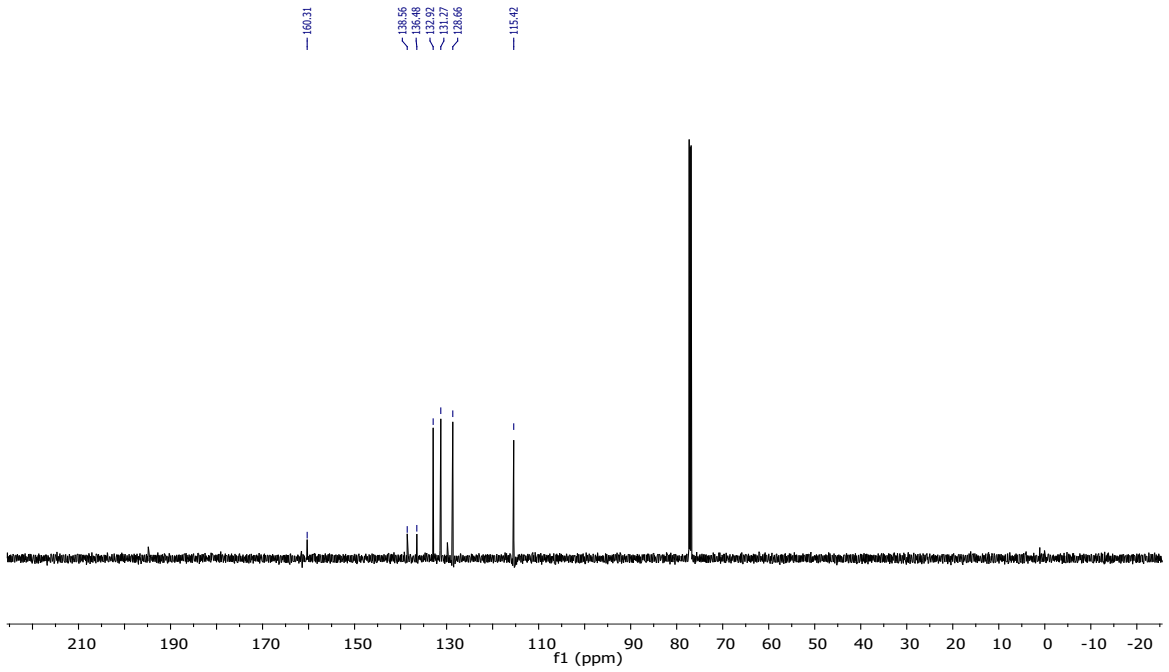


Figure S66. ^{13}C-NMR spectra of compound **9l**

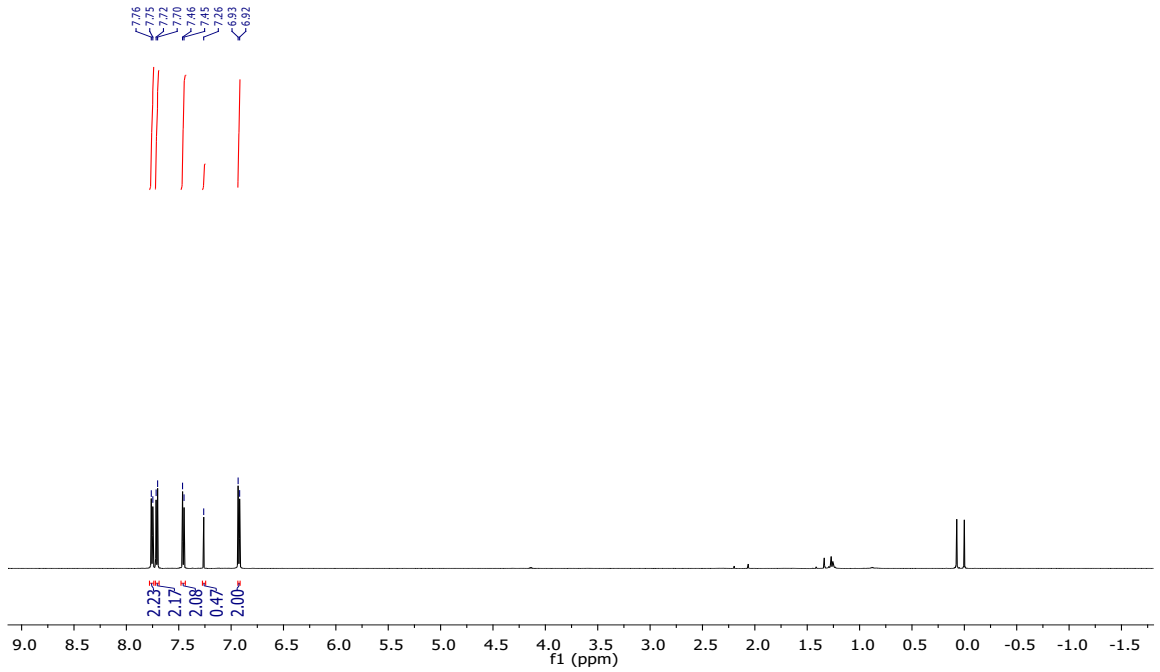


Figure S67. ^{1}H-NMR spectra of compound **9o**

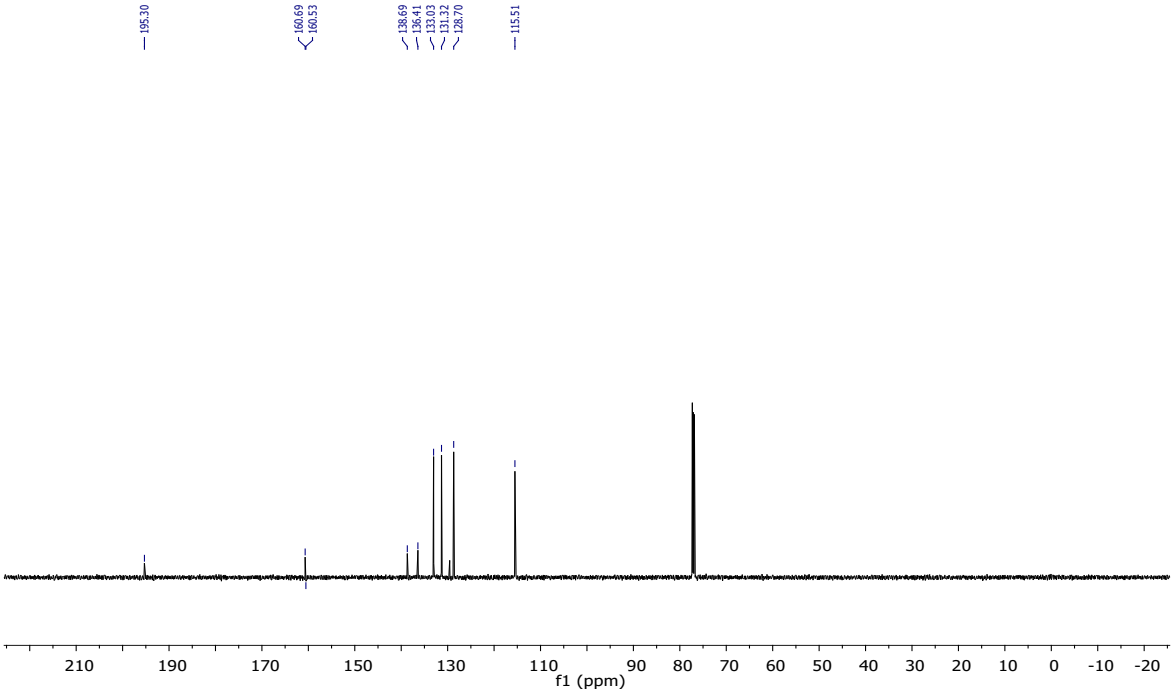


Figure S68. ^{13}C-NMR spectra of compound **9o**

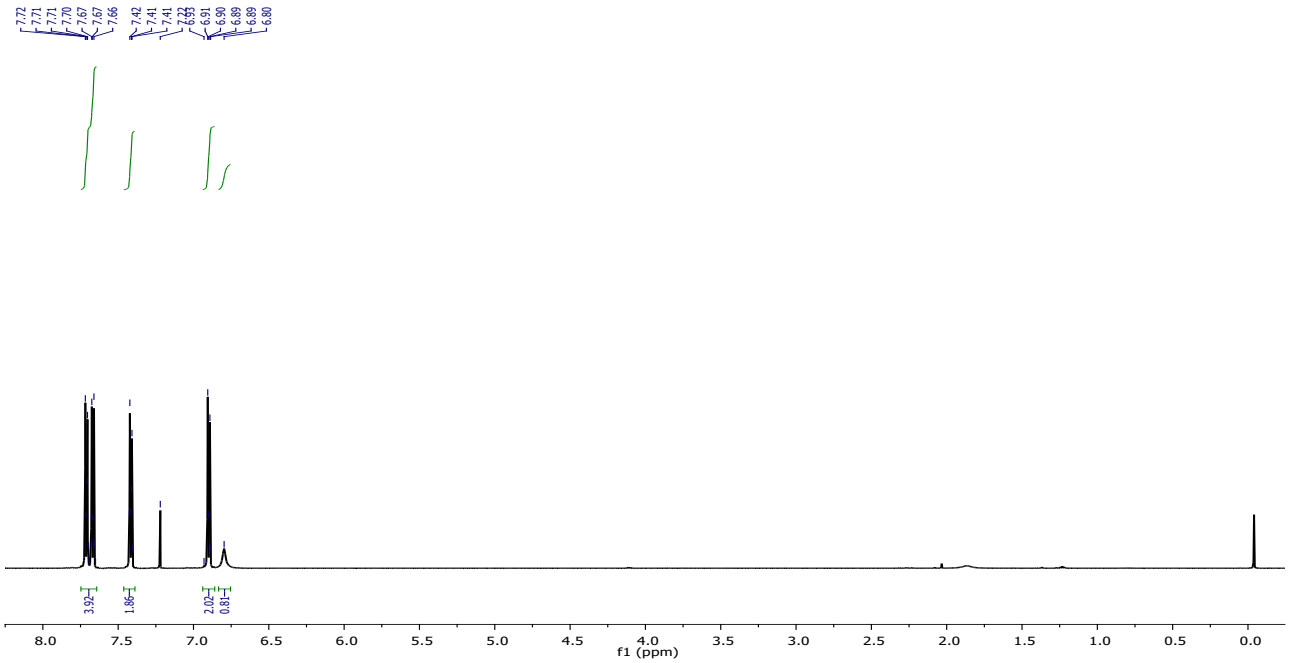


Figure S69. ^{1}H-NMR spectra of compound **9r**

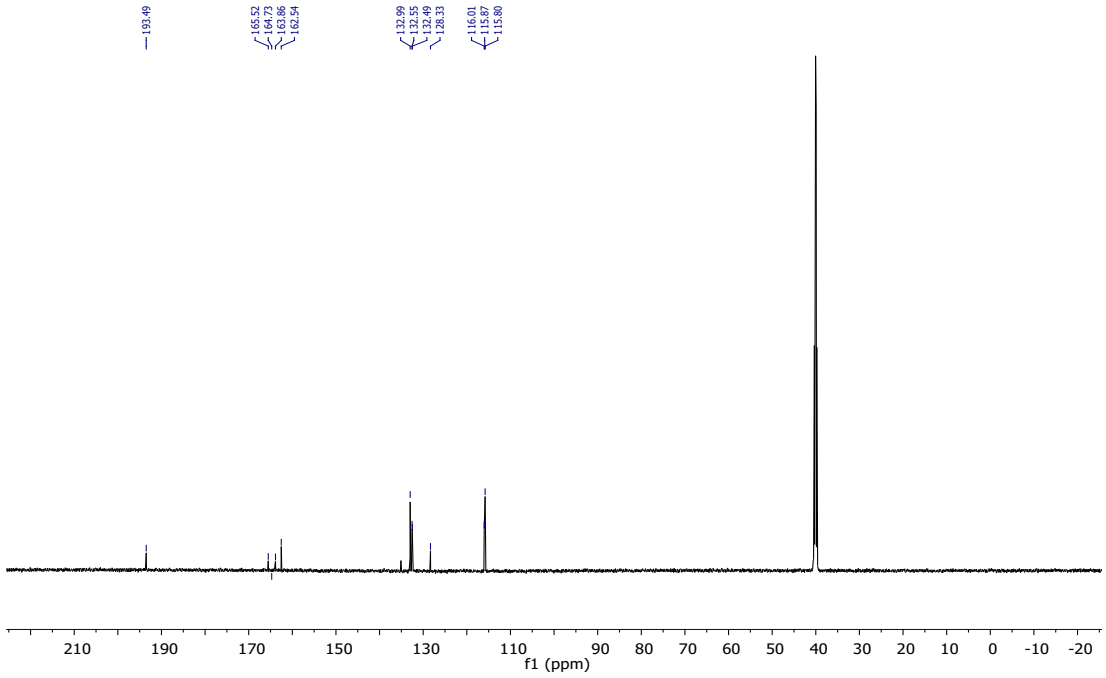


Figure S70. ^{13}C-NMR spectra of compound **9r**

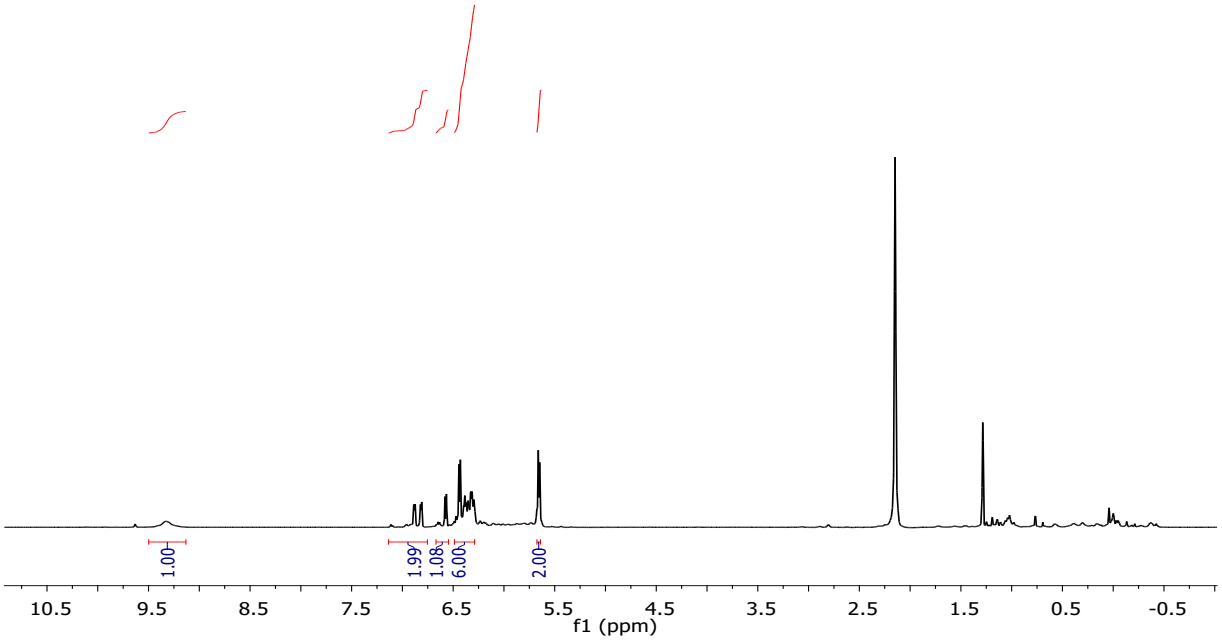


Figure S71. [1]H-NMR spectra of compound **9u**

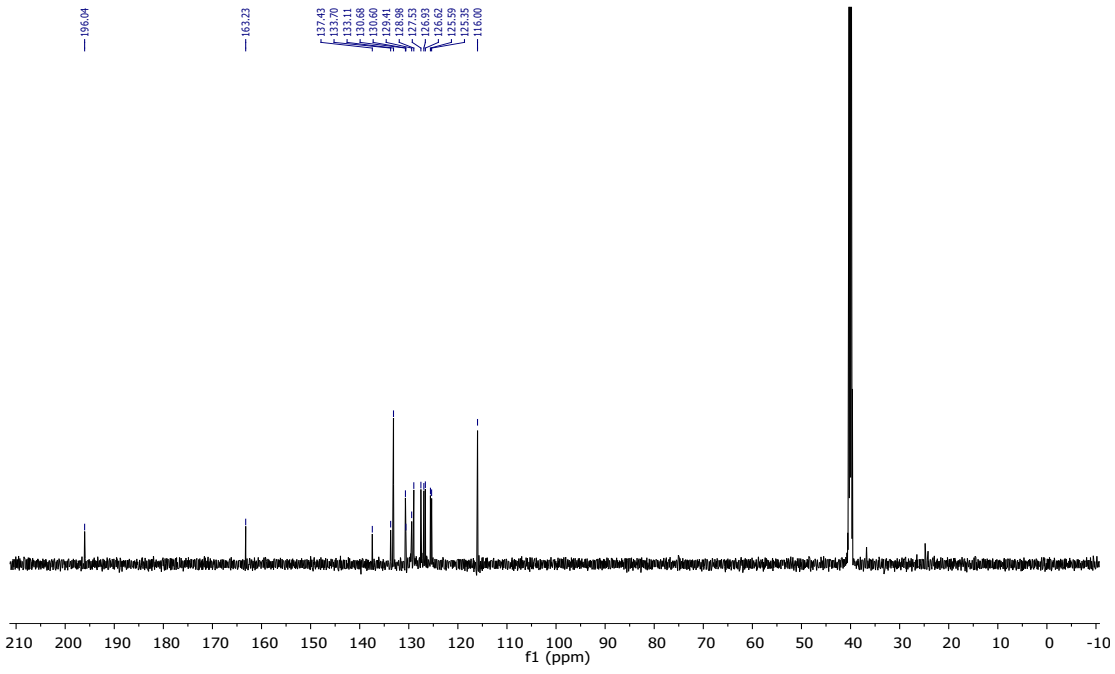


Figure S72. [13]C-NMR spectra of compound **9u**

Single crystal XRD data of the 1a

Crystals of compound **1a** was grown in ethyl acetate at room temperature and analyzed by applying the parameters depicted below. The CCDC number is 2256862, and also CIF file is attached separately.

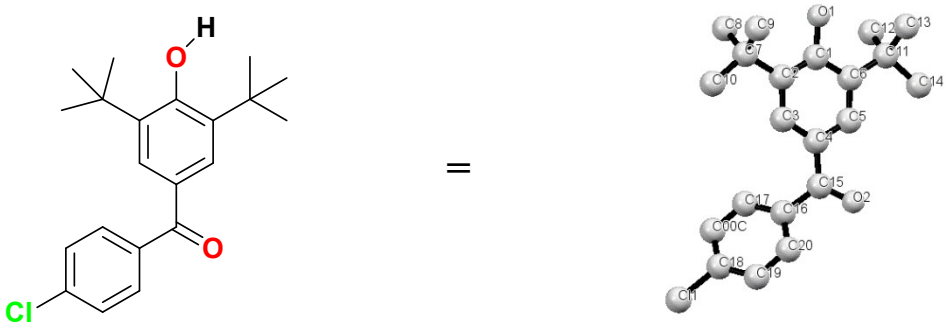


Figure SI. ORETP diagram of the compound **1a** with atom numbering (45% probability factor for the thermal ellipsoids)

Datablock of Compound 1a by single crystal study

Bond precision C-C = 0.0100 A
Wavelength = 0.71073
Cell a=6.0699(12) b=16.684(3) c=9.459(2) alpha=90 beta=101.436(6) gamma=90
Temperature = 100 K

Data	Calculated	Reported
Volume	938.9(3)	938.9(3)
Space group	P 21	P 21
Hall group	P 2yb	P 2yb
Moiety formula	C21 H25 Cl O2	-
Sum formula	C21 H25 Cl O2	C21 H25 Cl O2
Mr	344.86	344.86
Dx,g cm-3	1.220	1.220
Z	2	2
Mu (mm-1)	0.213	0.213
F000	368.0	368.0
F000’	368.44	-
h,k,lmax	7,20,11	7,20,11
Nref	3557(1844)	3542
Tmin,Tmax	0.970, 0.996	-
Tmin’	0.938	-

Correction method = Not given
Data completeness = 1.92/1.00
Theta(max) = 25.625
R(reflections) = 0.0625(2230)
wR2(reflections) = 0.1867(3542)
S = 0.938
Npar = 227