

Supporting Information

Direct Heptafluoroisopropylation of Arylboronic Acids *via* Hexafluoropropene (HFP)

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General Information

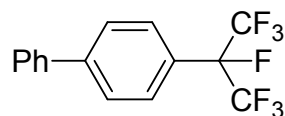
Melting points were measured on a Melt-Temp apparatus and were uncorrected. ^1H NMR spectra were recorded in CDCl_3 on a Bruker AM-300 spectrometer (300 MHz) with TMS as internal standard. ^{19}F NMR spectra were taken on a Bruker AM-300(282 MHz) spectrometer using PhCF_3 as external standard. ^{13}C NMR spectra were taken a Bruker AM-400(100 MHz) spectrometer. ^1H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet, dd = doublet of doublet, m = multiplet, etc.), integration, and coupling constants (Hz). ^{13}C NMR data are reported in parts per million (ppm) on the δ scale. IR spectra were obtained with a Nicolet AV-360 spectrophotometer. Mass spectra and elemental analyses were recorded in this institute. Solvents were purchased from commercial sources and purified before used by standard procedures. Unless otherwise specified, all reactions were carried out under a nitrogen atmosphere in a flame-dried Schlenk tube and magnetic stirring. TLC analysis was performed on silica gel plates, column chromatography over silica gel (mesh 300-400) and petroleum ethyl acetate combination was used as the eluent.

General procedure for heptafluoroisopropylation of various arylboronic acid derivatives

Preparation of heptafluoroisopropyl silver reagent:¹ to 0.2 mmol of silver fluoride in CH_3CN was added 0.2 mmol of HFP as a gas in 0.5h at rt. When all the solid disappeared, a clean solution was obtained, which was used in the next step directly.

General procedures for preparation of heptafluoroisopropylated arenes: after removing solvent of the above solution by evaporation, 2 ml of DMF was added. 5 mins later, 0.2 mmol of CuOAc was added, and 0.1 mmol of arylboronic acid and 50 mg of 4Å MS was added successively. Then the mixture was stirred at rt until the reaction was over. Excess amount of ethyl acetate was added to dilute the solution. Filtered, washed with water, dried, and then concentrated to get the crude product. The crude residue was purified by flash column chromatography (combined solvent ethyl acetate and petrol ether as eluent) to afford the pure product.

2b, 4-(perfluoropropan-2-yl)-1,1'-biphenyl

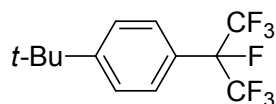


White solid, mp: 89-91 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.69 (q, $J = 8.7$ Hz, 4H), 7.64 – 7.56 (m, 2H), 7.47 (m, 2H), 7.41 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.02, 139.64, 129.01, 128.21, 127.55 (d, $J = 2.0$ Hz), 127.25, 126.18 (d, $J = 10.4$ Hz), 125.60 (d, $J = 20.6$ Hz), 120.75 (qd, $J = 285.3, 26.4$ Hz), 91.65 (dq, $J = 201.8, 31.1$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -75.66 (d, $J = 7.4$ Hz), -182.49 (hept, $J = 7.2$ Hz); IR (KBr, cm^{-1}): ν 3078, 1446, 1280, 1218, 1101, 981, 835, 736, 697; MS (EI) m/z (relative intensity) 322 [M^+], 253 (100); HRMS (EI) calcd. For $\text{C}_{15}\text{H}_9\text{F}_7$: 322.0592, Found: 322.0590.

2c, 1-(tert-butyl)-4-(perfluoropropan-2-yl)benzene²

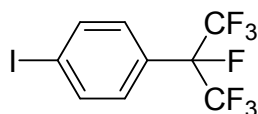
¹ W. T. Miller, R. J. Burnard, *J. Am. Chem. Soc.* **1968**, *90*, 7367.

² E. E. Gilbert, *J. Org. Chem.*, **1970**, *35*, 850.



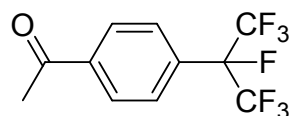
Colourless liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.59 – 7.46 (m, 4H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.26, 125.80, 125.39 (d, J = 10.2 Hz), 123.75 (d, J = 20.7 Hz), 120.71 (qd, J = 286.8, 28.5 Hz), 92.90-89.92 (m), 34.76, 31.05; ^{19}F NMR (376 MHz, CDCl_3) δ -75.85 (d, J = 7.3 Hz), -182.59 – -182.76 (m); IR (film, cm^{-1}): ν 2968, 1611, 1308, 1218, 1100, 982, 832, 711; MS (EI) m/z (relative intensity) 302 [M^+], 287 (100); HRMS (EI) calcd. For $\text{C}_{13}\text{H}_{13}\text{F}_7$: 302.0905, Found: 302.0906.

2d, 1-iodo-4-(perfluoropropan-2-yl)benzene³



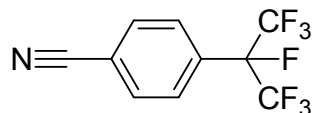
Colourless liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.20, 127.31 (d, J = 10.5 Hz), 126.47 (d, J = 20.8 Hz), 120.33 (qd, J = 287.8, 27.5 Hz), 97.91, 93.72 – 88.83 (m); ^{19}F NMR (376 MHz, CDCl_3) δ -75.74 (d, J = 7.3 Hz), -182.91 (hept, J = 7.2 Hz); IR (film, cm^{-1}): ν 2926, 1591, 1491, 1301, 1213, 984, 950, 816, 748; MS (EI) m/z (relative intensity) 372 (100) [M^+]; HRMS (EI) calcd. For $\text{C}_9\text{H}_4\text{F}_7\text{I}$: 371.9246, Found: 371.9250.

2e, 1-(4-(perfluoropropan-2-yl)phenyl)ethanone



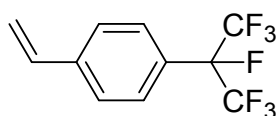
Colourless liquid; ^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, J = 8.3 Hz, 2H), 7.74 (d, J = 8.4 Hz, 2H), 2.65 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.87, 139.09, 131.07 (d, J = 20.5 Hz), 128.61 (d, J = 2.1 Hz), 126.13 (d, J = 10.6 Hz), 120.36 (qd, J = 285.8, 28.3 Hz), 93.04-89.70 (m), 26.63; ^{19}F NMR (376 MHz, CDCl_3) δ -75.58 (d, J = 7.3 Hz), -182.66 (hept, J = 7.1 Hz); IR (film, cm^{-1}): ν 3372, 3008, 1696, 1613, 1414, 1362, 1273, 1214, 1103, 985, 830, 708; MS (EI) m/z (relative intensity) 288 [M^+], 273 (100); HRMS (EI) calcd. For $\text{C}_{11}\text{H}_7\text{OF}_7$: 288.0385, Found: 288.0388.

2f, 4-(perfluoropropan-2-yl)benzonitrile

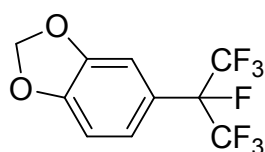


Colourless liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 132.82 (d, J = 2.1 Hz), 131.53 (d, J = 20.8 Hz), 126.86 (d, J = 10.8 Hz), 120.35 (qd, J = 285.1, 27.6 Hz), 117.51, 115.76, 92.93 – 89.45 (m); ^{19}F NMR (376 MHz, CDCl_3) δ -75.38 (d, J = 7.3 Hz), -182.69 (hept, J = 7.2 Hz); IR (film, cm^{-1}): ν 2911, 1611, 1510, 1497, 1453, 1307, 1277, 1095, 1044, 979, 755; MS (EI) m/z (relative intensity) 271 (7) [M^+], 221 (100); HRMS (EI) calcd. For $\text{C}_{10}\text{H}_4\text{NF}_7$: 271.0232, Found: 271.0230.

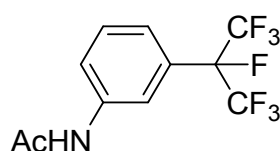
³ K. Kuroda, N. Ishikawa, *Nippon Kagaku Kaishi* **1972**, 10, 1876.

2g, 1-(perfluoropropan-2-yl)-4-vinylbenzene⁴

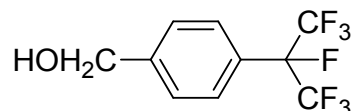
Colourless liquid; ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.7 Hz, 2H), 6.75 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.85 (dd, *J* = 17.6, 0.5 Hz, 1H), 5.39 (dd, *J* = 10.9, 0.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 140.25, 135.50, 126.55 (d, *J* = 2.1 Hz), 125.92 (d, *J* = 10.5 Hz), 125.70, 120.59 (qd, *J* = 287.2, 27.8 Hz), 116.44, 93.97 – 89.07 (m); ¹⁹F NMR (376 MHz, CDCl₃) δ -75.74 (d, *J* = 7.3 Hz), -182.54 (hept, *J* = 7.2 Hz); IR (film, cm⁻¹): ν 2922, 1513, 1277, 1212, 1103, 983, 750; MS (EI) *m/z* (relative intensity) 272 (45) [M⁺], 203 (100); HRMS (EI) calcd. For C₁₁H₇F₇: 272.0436, Found: 272.0439.

2h, 5-(perfluoropropan-2-yl)benzo[d][1,3]dioxole

Colourless liquid; ¹H NMR (400 MHz, CDCl₃) δ 7.11 (d, *J* = 8.3 Hz, 1H), 7.04 (s, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 6.05 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 149.99, 148.48 (d, *J* = 2.8 Hz), 120.74 (qd, *J* = 284.9, 27.5 Hz), 120.29 (d, *J* = 11.6 Hz), 120.07 (d, *J* = 20.8 Hz), 108.70 (d, *J* = 2.0 Hz), 106.41 (d, *J* = 11.6 Hz), 102.06, 93.20 – 89.88 (m); ¹⁹F NMR (376 MHz, CDCl₃) δ -75.90 (d, *J* = 7.2 Hz), -180.50 (hept, *J* = 7.1 Hz); IR (film, cm⁻¹): ν 2934, 2237, 1508, 1310, 1277, 1212, 986, 836, 749, 705; MS (EI) *m/z* (relative intensity) 290 (13) [M⁺], 193 (100); HRMS (EI) calcd. For C₁₀H₅O₂F₇: 290.0178, Found: 290.0176.

2i, N-(3-(perfluoropropan-2-yl)phenyl)acetamide

White solid; mp: 78-81 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 8.4 Hz, 1H), 7.70 (s, 1H), 7.61 (s, 1H), 7.45 (t, *J* = 8.1 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 2.20 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 169.36, 138.76, 129.58, 127.46 (d, *J* = 20.5 Hz), 122.50, 121.24 (d, *J* = 9.9 Hz), 120.50 (qd, *J* = 286.3, 28.2 Hz), 117.07 (d, *J* = 11.7 Hz), 93.83 – 87.74 (m), 24.27; ¹⁹F NMR (376 MHz, CDCl₃) δ -75.66 (d, *J* = 7.2 Hz), -182.42 (hept, *J* = 7.1 Hz); IR (KBr, cm⁻¹): ν 3274, 1673, 1558, 1281, 1224, 982, 750, 727; MS (EI) *m/z* (relative intensity) 303 (21) [M⁺], 261 (100); HRMS (EI) calcd. For C₁₁H₈NOF₇: 303.0494, Found: 303.0495.

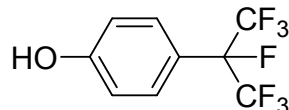
2j, (4-(perfluoropropan-2-yl)phenyl)methanol

Colourless liquid; ¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H),

⁴ B. Boemer, H. Hagemann, *Angewandte Makromolekulare Chemie* **1982**, 109/110, 285.

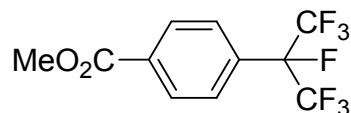
4.77 (s, 2H), 1.91 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.97, 128.81, 127.06 (d, $J = 2.1$ Hz), 125.90 (d, $J = 10.8$ Hz), 120.59 (qd, $J = 286.4, 28.1$ Hz), 93.54 – 89.23 (m), 64.40; ^{19}F NMR (376 MHz, CDCl_3) δ -75.77 (d, $J = 7.3$ Hz), -182.57 (hept, $J = 7.1$ Hz); IR (film, cm^{-1}): ν 3314, 1276, 1261, 1213, 984, 751; MS (EI) m/z (relative intensity) 276 (44) [M^+], 107 (100); HRMS (EI) calcd. For $\text{C}_{10}\text{H}_7\text{OF}_7$: 276.0385, Found: 276.0388.

2k, 4-(perfluoropropan-2-yl)phenol⁵



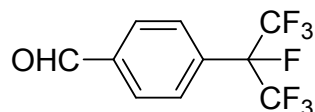
Colourless liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, $J = 8.8$ Hz, 2H), 6.94 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.68, 127.51 (d, $J = 10.6$ Hz), 120.66 (qd, $J = 287.2, 28.3$ Hz), 118.83 (d, $J = 20.8$ Hz), 115.79 (d, $J = 1.9$ Hz), 93.30 – 89.70 (m); ^{19}F NMR (376 MHz, CDCl_3) δ -76.00 (d, $J = 7.4$ Hz), -181.75 (hept, $J = 7.2$ Hz); IR (film, cm^{-1}): ν 3251, 1519, 1450, 1276, 981, 764, 750; MS (EI) m/z (relative intensity) 262 (43) [M^+], 193 (100); HRMS (EI) calcd. For $\text{C}_9\text{H}_5\text{OF}_7$: 262.0229, Found: 262.0232.

2l, methyl 4-(perfluoropropan-2-yl)benzoate⁶



Colourless liquid; ^1H NMR (400 MHz, CDCl_3) δ 8.17 (d, $J = 8.3$ Hz, 2H), 7.71 (d, $J = 8.4$ Hz, 2H), 3.96 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.81, 132.75, 131.02 (d, $J = 20.5$ Hz), 129.94 (d, $J = 2.3$ Hz), 125.83 (d, $J = 10.7$ Hz), 120.33 (qd, $J = 287.8, 28.3$ Hz), 93.02 – 89.41 (m), 52.45; ^{19}F NMR (376 MHz, CDCl_3) δ -75.55 (d, $J = 7.0$ Hz), -182.59 (hept, $J = 7.1$ Hz); IR (film, cm^{-1}): ν 2958, 1736, 1439, 1279, 1212, 1105, 985, 956, 723; MS (EI) m/z (relative intensity) 304 (24) [M^+], 273 (100); HRMS (EI) calcd. For $\text{C}_{11}\text{H}_7\text{O}_2\text{F}_7$: 304.0334, Found: 304.0333.

2m, 4-(perfluoropropan-2-yl)benzaldehyde⁷



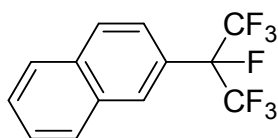
Colourless liquid; ^1H NMR (400 MHz, CDCl_3) δ 10.10 (s, 1H), 8.02 (d, $J = 8.2$ Hz, 2H), 7.81 (d, $J = 8.2$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 190.93, 138.13, 132.41 (d, $J = 20.5$ Hz), 129.83, 126.59 (d, $J = 10.5$ Hz), 120.33 (qd, $J = 287.6, 27.9$ Hz), 93.34 – 88.47 (m); ^{19}F NMR (376 MHz, CDCl_3) δ -75.40 (d, $J = 7.2$ Hz), -182.33 (hept, $J = 7.1$ Hz); IR (film, cm^{-1}): ν 2853, 1709, 1276, 1261, 984, 750; MS (EI) m/z (relative intensity) 274 [M^+], 273 (100); HRMS (EI) calcd. For $\text{C}_{10}\text{H}_5\text{OF}_7$: 274.0229, Found: 274.0228.

2n, 2-(perfluoropropan-2-yl)naphthalene⁶

⁵ T. Umemoto, S. Furukawa, O. Miyano, S. Nakayama, *Nippon Kagaku Kaishi* **1985**, 2146.

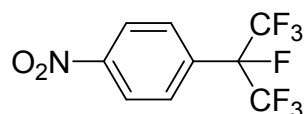
⁶ N. Ishikawa, M. Ochiai, *Nippon Kagaku Kaishi* **1973**, 2351.

⁷ A. Conte, H. Kuehne, T. Luebbbers, P. Mattei, C. Maugeais, W. Mueller, P. Pflieger, PCT Int. Appl. WO 2007090752 A1, 2007.



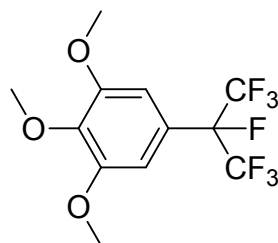
White solid, mp: 65-66 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.14 (s, 1H), 8.07 – 7.82 (m, 3H), 7.74 – 7.51 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 133.99, 132.44 (d, $J = 2.1$ Hz), 128.85 (d, $J = 2.3$ Hz), 128.71, 127.96, 127.67, 127.13, 126.44 (d, $J = 11.9$ Hz), 123.96 (d, $J = 20.3$ Hz), 121.56 (d, $J = 9.4$ Hz), 120.70 (qd, $J = 287.4, 27.8$ Hz), 94.09 – 88.83 (m); ^{19}F NMR (376 MHz, CDCl_3) δ -75.43 (d, $J = 7.3$ Hz), -181.92 (hept, $J = 7.2$ Hz); IR (KBr, cm^{-1}): ν 3060, 1276, 1220, 981, 907, 751; MS (EI) m/z (relative intensity) 296 (71) [M^+], 177 (100); HRMS (EI) calcd. For $\text{C}_{13}\text{H}_7\text{F}_7$: 296.0436, Found: 296.0431.

2p, 1-nitro-4-(perfluoropropan-2-yl)benzene⁸



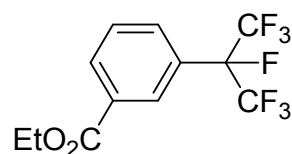
Colourless liquid; ^1H NMR (400 MHz, CDCl_3) δ 8.38 (d, $J = 8.7$ Hz, 2H), 7.85 (d, $J = 8.8$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.61, 132.91 (d, $J = 20.7$ Hz), 127.22 (d, $J = 10.8$ Hz), 124.01 (d, $J = 2.2$ Hz), 120.12 (qd, $J = 286.9, 27.2$ Hz), 93.28 – 89.60 (m); ^{19}F NMR (376 MHz, CDCl_3) δ -75.36 (d, $J = 7.3$ Hz), -181.96 (hept, $J = 7.2$ Hz); IR (film, cm^{-1}): ν 3118, 1611, 1536, 1276, 1217, 1106, 986, 854, 760; MS (EI) m/z (relative intensity) 291 [M^+], 145 (100); HRMS (EI) calcd. For $\text{C}_9\text{H}_4\text{NO}_2\text{F}_7$: 291.0130, Found: 291.0133.

2q, 1,2,3-trimethoxy-5-(perfluoropropan-2-yl)benzene



Colourless liquid; ^1H NMR (400 MHz, CDCl_3) δ 6.79 (s, 2H), 3.90 (s, 3H), 3.89 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.45 (d, $J = 2.1$ Hz), 140.12, 121.57 (d, $J = 20.7$ Hz), 120.52 (qd, $J = 286.9, 27.9$ Hz), 103.09 (d, $J = 11.4$ Hz), 93.77 – 89.17 (m), 60.78, 56.20; ^{19}F NMR (376 MHz, CDCl_3) δ -75.68 (d, $J = 7.2$ Hz), -181.23 (hept, $J = 7.1$ Hz); IR (film, cm^{-1}): ν 2945, 1595, 1514, 1465, 1422, 1290, 1168, 980, 835, 727; MS (EI) m/z (relative intensity) 336 (100) [M^+]; HRMS (EI) calcd. For $\text{C}_{12}\text{H}_{11}\text{O}_3\text{F}_7$: 336.0596, Found: 336.0593.

2r, ethyl 3-(perfluoropropan-2-yl)benzoate

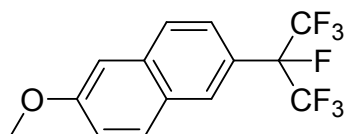


Colourless liquid; ^1H NMR (400 MHz, CDCl_3) δ 8.31 (s, 1H), 8.23 (d, $J = 7.9$ Hz, 1H), 7.80 (d, J

⁸ W. A. Sheppard, *J. Am. Chem. Soc.* **1965**, 87, 2410.

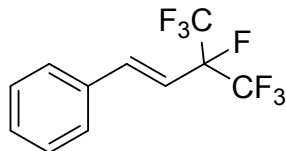
= 7.9 Hz, 1H), 7.60 (t, $J = 7.9$ Hz, 1H), 4.43 (q, $J = 7.1$ Hz, 2H), 1.42 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.26, 132.05, 131.52 (d, $J = 2.2$ Hz), 129.67 (d, $J = 10.1$ Hz), 129.06 (d, $J = 2.2$ Hz), 127.25 (d, $J = 20.8$ Hz), 126.87 (d, $J = 11.5$ Hz), 120.40 (qd, $J = 286.4$, 28.0 Hz), 93.04 – 89.25 (m), 61.53, 14.19; ^{19}F NMR (376 MHz, CDCl_3) δ -75.67 (d, $J = 7.3$ Hz), -182.48 (hept, $J = 7.2$ Hz); IR (film, cm^{-1}): ν 2986, 1728, 1281, 1206, 984, 723; MS (EI) m/z (relative intensity) 318 (15) [M^+], 273 (100); HRMS (EI) calcd. For $\text{C}_{12}\text{H}_9\text{O}_2\text{F}_7$: 318.0491, Found: 318.0494.

2s, 2-methoxy-6-(perfluoropropan-2-yl)naphthalene



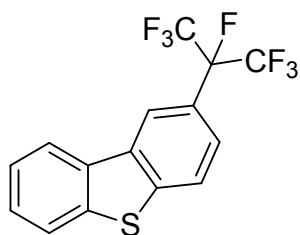
White solid, mp: 53-55 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.04 (s, 1H), 7.84 (d, $J = 8.3$ Hz, 1H), 7.81 (d, $J = 8.7$ Hz, 1H), 7.59 (d, $J = 8.8$ Hz, 1H), 7.32 – 7.20 (m, 1H), 7.17 (d, $J = 2.3$ Hz, 1H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.22, 135.51, 130.19, 127.95 (d, $J = 2.2$ Hz), 127.55 (d, $J = 2.3$ Hz), 126.09 (d, $J = 11.8$ Hz), 122.16 (d, $J = 9.4$ Hz), 121.53 (d, $J = 20.5$ Hz), 120.40 (qd, $J = 285.4$, 28.0 Hz), 120.15, 105.39, 93.64 – 89.22 (m), 55.33; ^{19}F NMR (376 MHz, CDCl_3) δ -75.74 (d, $J = 7.2$ Hz), -182.51 (hept, $J = 7.2$ Hz); IR (KBr, cm^{-1}): ν 2962, 1637, 1610, 1488, 1277, 1220, 1102, 981, 900, 854, 724; MS (EI) m/z (relative intensity) 326 (53) [M^+], 257 (100); HRMS (EI) calcd. For $\text{C}_{14}\text{H}_9\text{OF}_7$: 326.0542, Found: 326.0541.

2u, (E)-(3,4,4,4-tetrafluoro-3-(trifluoromethyl)but-1-en-1-yl)benzene⁹



Colourless liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.48-7.46 (m, 2H), 7.44 – 7.35 (m, 3H), 7.14 (d, $J = 16.1$ Hz, 1H), 6.14 (dd, $J = 20.1$, 16.1 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.53 (d, $J = 10.8$ Hz), 133.87, 129.85, 128.94, 127.37, 125.43 – 115.31 (m), 120.39 (qd, $J = 287.0$, 27.5 Hz), 92.78 – 88.83 (m); ^{19}F NMR (376 MHz, CDCl_3) δ -77.10 (d, $J = 7.7$ Hz), -186.02 – -186.28 (m); IR (film, cm^{-1}): ν 3003, 1275, 1261, 764, 750; MS (EI) m/z (relative intensity) 272 (73) [M^+], 203 (100); HRMS (EI) calcd. For $\text{C}_{11}\text{H}_7\text{F}_7$: 272.0436, Found: 272.0434.

2v, 2-(perfluoropropan-2-yl)dibenzo[b,d]thiophene

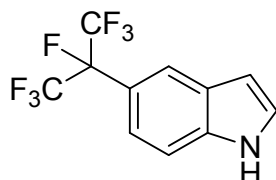


White solid, mp: 102-103 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.39 (s, 1H), 8.29 – 8.17 (m, 1H), 7.98 (d, $J = 8.6$ Hz, 1H), 7.93 – 7.83 (m, 1H), 7.67 (d, $J = 8.5$ Hz, 1H), 7.62 – 7.47 (m, 2H); ^{13}C

⁹ T. Kitazume, N. Ishikawa, *J. Am. Chem. Soc.* **1985**, *107*, 5186.

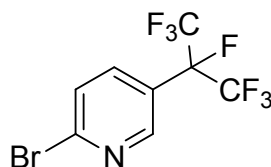
NMR (100 MHz, CDCl₃) δ 142.30, 139.84, 135.85 (d, J = 2.3 Hz), 134.66, 127.61, 124.84, 123.34 (d, J = 2.2 Hz), 123.19 (d, J = 9.9 Hz), 122.96 (d, J = 20.5 Hz), 122.90, 120.70 (qd, J = 288.7, 27.8 Hz); 121.84, 119.03 (d, J = 12.1 Hz), 93.63 – 89.89 (m); ¹⁹F NMR (376 MHz, CDCl₃) δ -75.54 (d, J = 7.3 Hz), -181.49 (hept, J = 7.2 Hz); IR (KBr, cm⁻¹): ν 3066, 1945, 1899, 1470, 1280, 1221, 1104, 980, 765, 729; MS (EI) m/z (relative intensity) 352 (77) [M⁺], 233 (100); HRMS (EI) calcd. For C₁₅H₇SF₇: 352.0157, Found: 352.0161.

2w, 5-(perfluoropropan-2-yl)-1H-indole



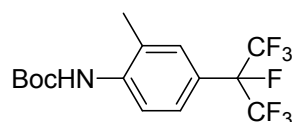
White solid, mp: 100-101 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.31 (b, 1H), 7.93 (s, 1H), 7.48 (d, J = 8.8 Hz, 1H), 7.41 (d, J = 8.7 Hz, 1H), 7.36 – 7.28 (m, 1H), 6.64 (d, J = 2.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 136.63, 127.67 (d, J = 2.3 Hz), 125.74, 120.98 (qd, J = 286.9, 27.9 Hz), 118.96 (d, J = 8.1 Hz), 118.85 (d, J = 6.7 Hz), 117.96 (d, J = 20.2 Hz), 111.39 (d, J = 2.3 Hz), 103.46, 93.98 – 89.99 (m); ¹⁹F NMR (376 MHz, CDCl₃) δ -75.70 (d, J = 7.2 Hz), -180.53 (hept, J = 7.1 Hz); IR (KBr, cm⁻¹): ν 3476, 3388, 2248, 1476, 1280, 1216, 1097, 978, 909, 733; MS (EI) m/z (relative intensity) 285 (48) [M⁺], 216 (100); HRMS (EI) calcd. For C₁₁H₆NF₇: 285.0388, Found: 285.0392.

2x, 2-bromo-5-(perfluoropropan-2-yl)pyridine



Colourless liquid; ¹H NMR (400 MHz, CDCl₃) δ 8.63 (d, J = 2.2 Hz, 1H), 7.78 (dd, J = 8.5, 2.4 Hz, 1H), 7.68 (d, J = 8.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 148.43 – 146.59 (m), 145.61 (d, J = 1.1 Hz), 135.69 (d, J = 9.9 Hz), 128.34 (d, J = 2.3 Hz), 122.53 (d, J = 20.9 Hz), 120.02 (qd, J = 287.3, 27.5 Hz), 93.15 – 87.51 (m); ¹⁹F NMR (376 MHz, CDCl₃) δ -75.91 (d, J = 7.7 Hz), -184.73 (hept, J = 7.6 Hz); IR (KBr, cm⁻¹): ν 3072, 2922, 1584, 1466, 1381, 1306, 1278, 1220, 1093, 988, 950, 831, 743, 715; MS (EI) m/z (relative intensity) 325 (100, ⁷⁹Br) [M⁺], 327 (97, ⁸¹Br) [M⁺]; HRMS (EI) calcd. For C₈H₃F₇NBr: 324.9337, Found: 324.9341.

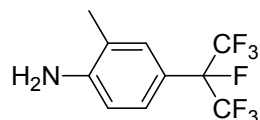
2y, tert-butyl (2-methyl-4-(perfluoropropan-2-yl)phenyl)carbamate



¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, J = 8.7 Hz, 1H), 7.34 (d, J = 8.9 Hz, 1H), 7.28 (s, 1H), 6.35 (s, 1H), 2.22 (s, 3H), 1.46 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 152.47, 139.07, 127.38 (d, J = 10.8 Hz), 126.33 (d, J = 1.8 Hz), 126.90 – 114.82 (m), 124.44 (d, J = 10.3 Hz), 120.67 (d, J =

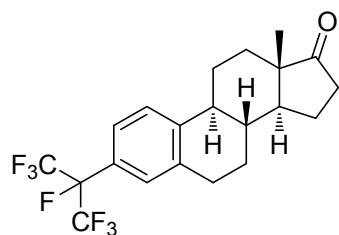
20.7 Hz), 120.60 (qd, $J = 287.9, 27.3$ Hz), 119.57, 93.54 – 88.21 (m), 81.19, 28.21, 17.82; ^{19}F NMR (376 MHz, CDCl_3) δ -75.86 (d, $J = 7.4$ Hz), -182.36 (hept, $J = 7.3$ Hz); IR (KBr, cm^{-1}): ν 3275, 2976, 1719, 1694, 1593, 1538, 1455, 1370, 1278, 1233, 1167, 981, 736; MS (EI) m/z (relative intensity) 375 (3) [M^+], 57 (100); HRMS (EI) calcd. For $\text{C}_{15}\text{H}_{16}\text{NO}_2\text{F}_7$: 375.1069, Found: 375.1071.

2y', 2-methyl-4-(perfluoropropan-2-yl)aniline¹⁰



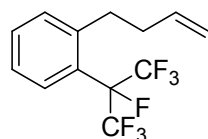
^1H NMR (400 MHz, CDCl_3) δ 7.23 (m, 2H), 6.70 (d, $J = 9.0$ Hz, 1H), 3.82 (br, 2H), 2.18 (s, 3H); ^{19}F NMR (376 MHz, CDCl_3) δ -75.84 (d, $J = 7.4$ Hz), -182.37 (hept, $J = 7.3$ Hz); the pure product was spectrally identical to material previously synthesized.

2z, 13-methyl-3-(perfluoropropan-2-yl)-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one



^1H NMR (400 MHz, CDCl_3) δ 7.44-7.37 (m, 2H), 7.33 (s, 1H), 3.09 – 2.90 (m, 2H), 2.55 (dd, $J = 18.8, 8.7$ Hz, 1H), 2.49-2.44 (m, 1H), 2.39-2.33 (m, 1H), 2.33 – 2.00 (m, 4H), 1.70 – 1.49 (m, 6H), 0.95 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.94, 137.37 (d, $J = 1.9$ Hz), 128.23, 126.10 (d, $J = 10.5$ Hz), 124.14 (d, $J = 20.5$ Hz), 122.89 (d, $J = 10.1$ Hz), 120.67 (qd, $J = 288.3, 27.3$ Hz), 95.78 – 88.03 (m), 50.51, 47.90, 44.33, 37.77, 35.81, 31.54, 29.70, 26.25, 25.49, 21.57, 13.81; ^{19}F NMR (376 MHz, CDCl_3) δ -75.74 (d, $J = 6.6$ Hz), -182.56 – -182.78 (m); IR (KBr, cm^{-1}): ν 2929, 2856, 1743, 1558, 1541, 1507, 1457, 1277, 1219, 981, 764, 750; MS (EI) m/z (relative intensity) 422 [M^+], 378 (100); HRMS (EI) calcd. For $\text{C}_{21}\text{H}_{21}\text{OF}_7$: 422.1481, Found: 422.1484.

4, 1-(but-3-en-1-yl)-2-(perfluoropropan-2-yl)benzene

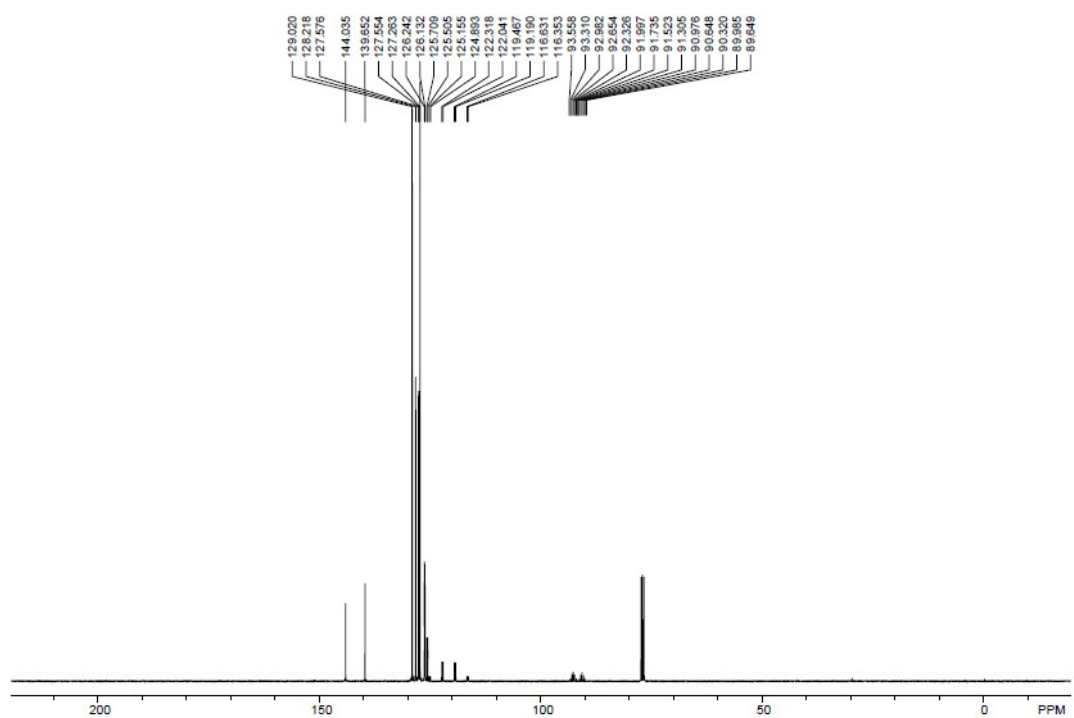
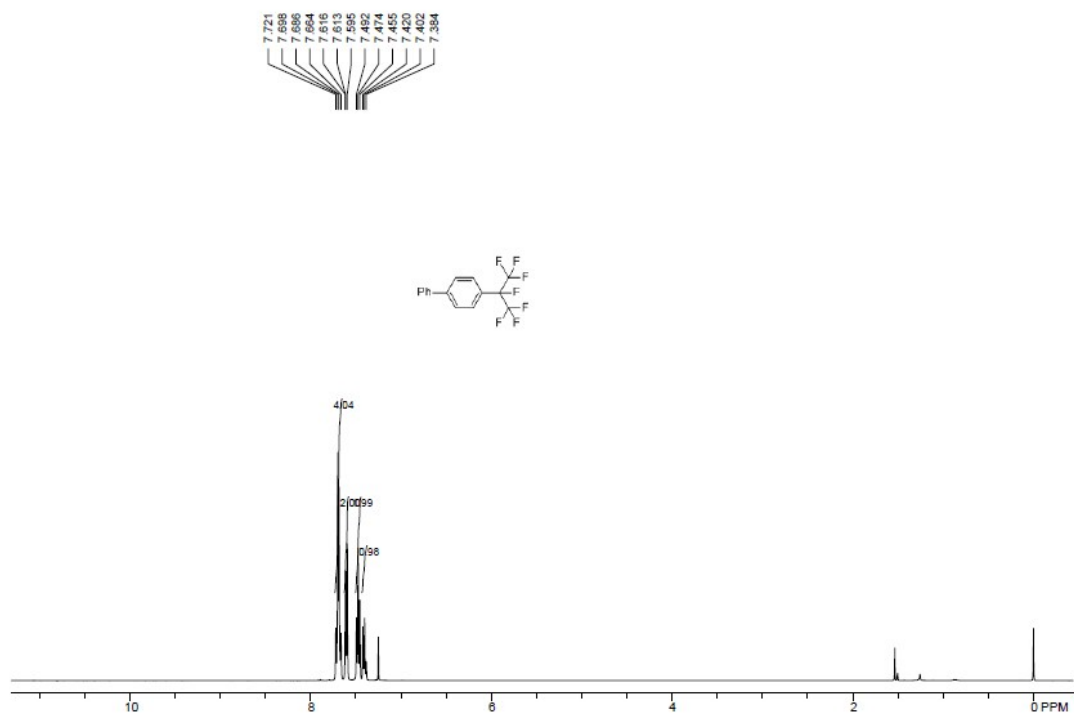


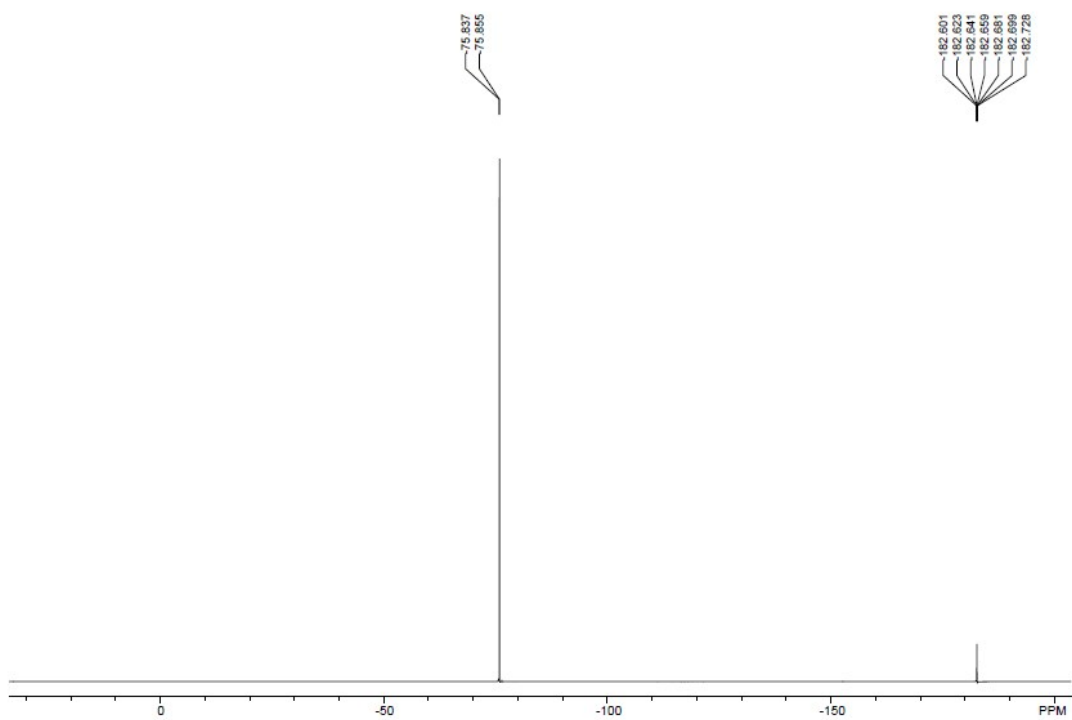
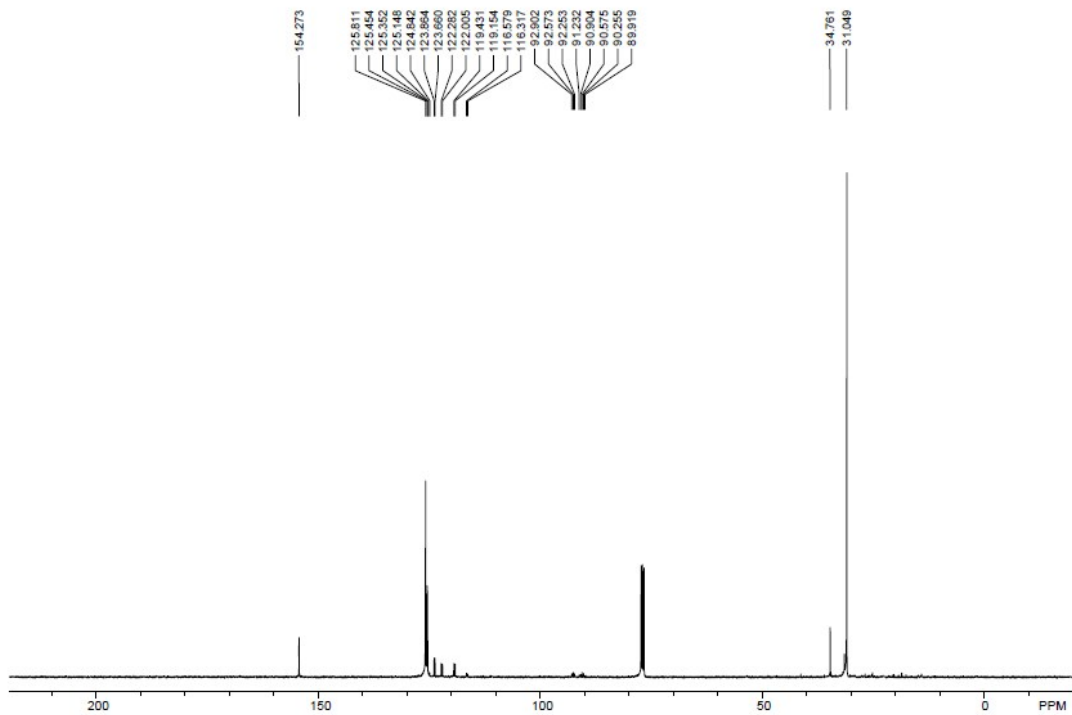
^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, $J = 8.1$ Hz, 1H), 7.41 (t, $J = 7.5$ Hz, 1H), 7.33 – 7.27 (m, 2H), 5.91-5.81 (m, 1H), 5.11 – 4.92 (m, 2H), 2.97 – 2.82 (m, 2H), 3.00 – 2.80 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.60, 137.68, 133.39, 130.60, 126.81 – 126.38 (m), 126.11 (d, $J = 1.5$ Hz), 123.85 (d, $J = 19.2$ Hz), 122.99 (qd, $J = 289.8, 28.3$ Hz), 115.06, 96.59 – 92.25 (m), 36.69, 34.76; ^{19}F NMR (376 MHz, CDCl_3) δ -74.67 (d, $J = 6.5$ Hz), -179.11 – -179.25 (m); IR (KBr, cm^{-1}): ν

¹⁰ S. Zhou, T. Yan, Y. Li, Z. Jia, B. Wang, Y. Zhao, Y. Qiao, L. Xiong, Y. Li, Z. Li, *Org. Biomol. Chem.* **2014**, *12*, 6643.

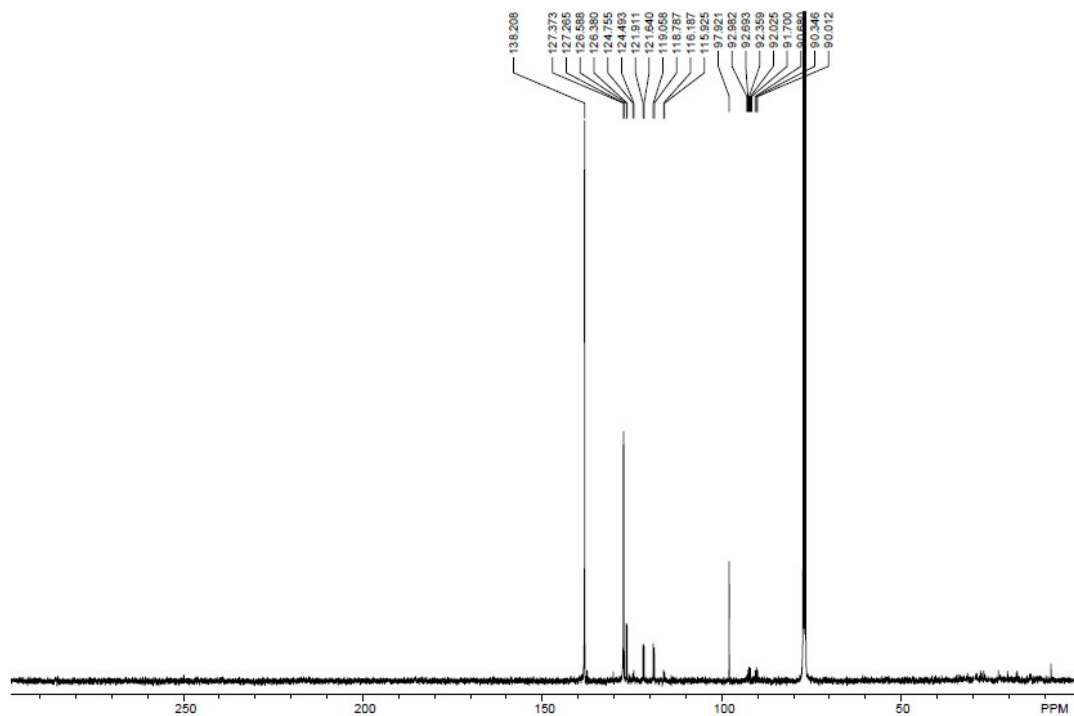
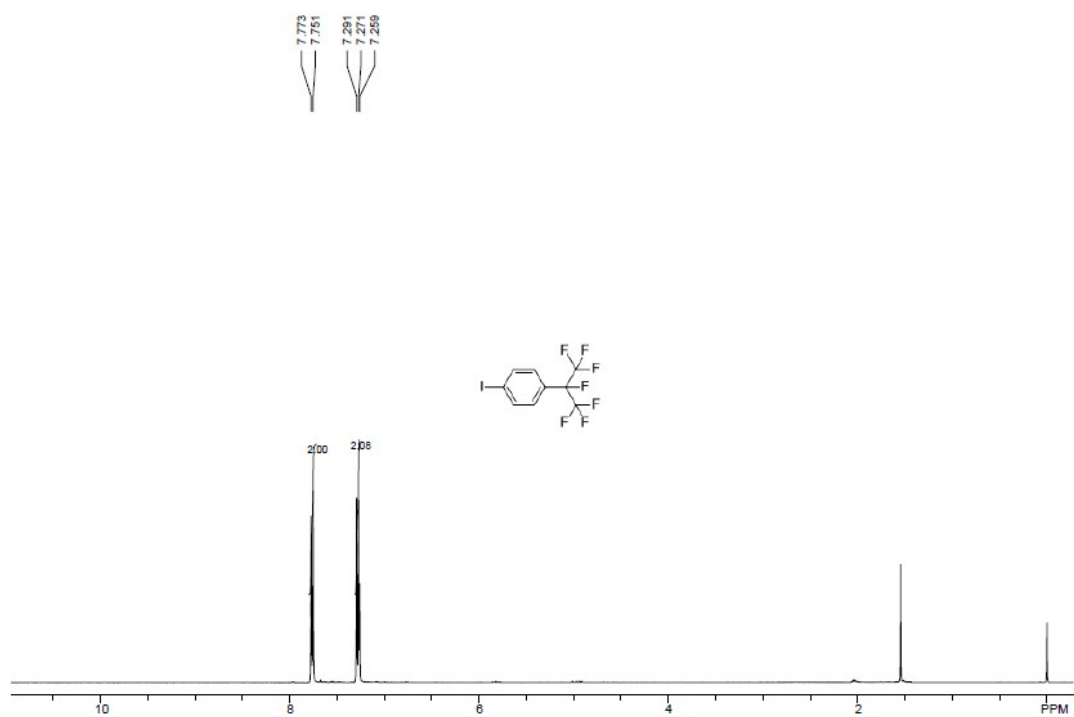
2926, 1558, 1541, 1507, 1278, 1206, 976, 749; MS (EI) m/z (relative intensity) 300 [M⁺], 259 (100); HRMS (EI) calcd. For C₁₃H₁₁F₇: 300.0749, Found: 300.0750.

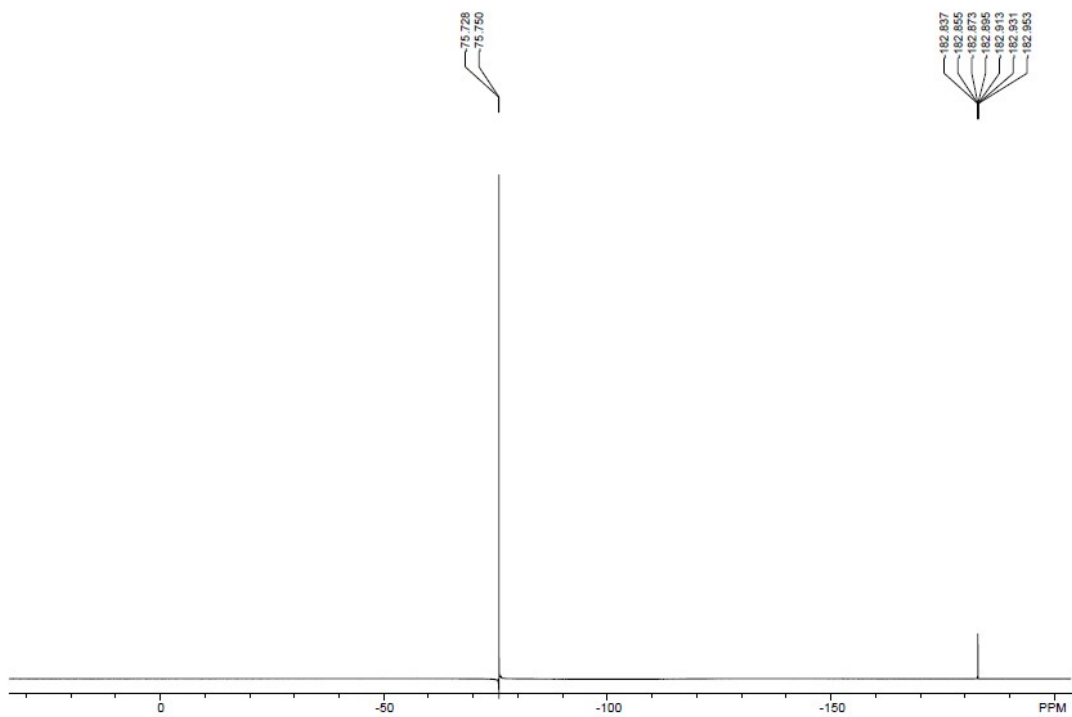
2b



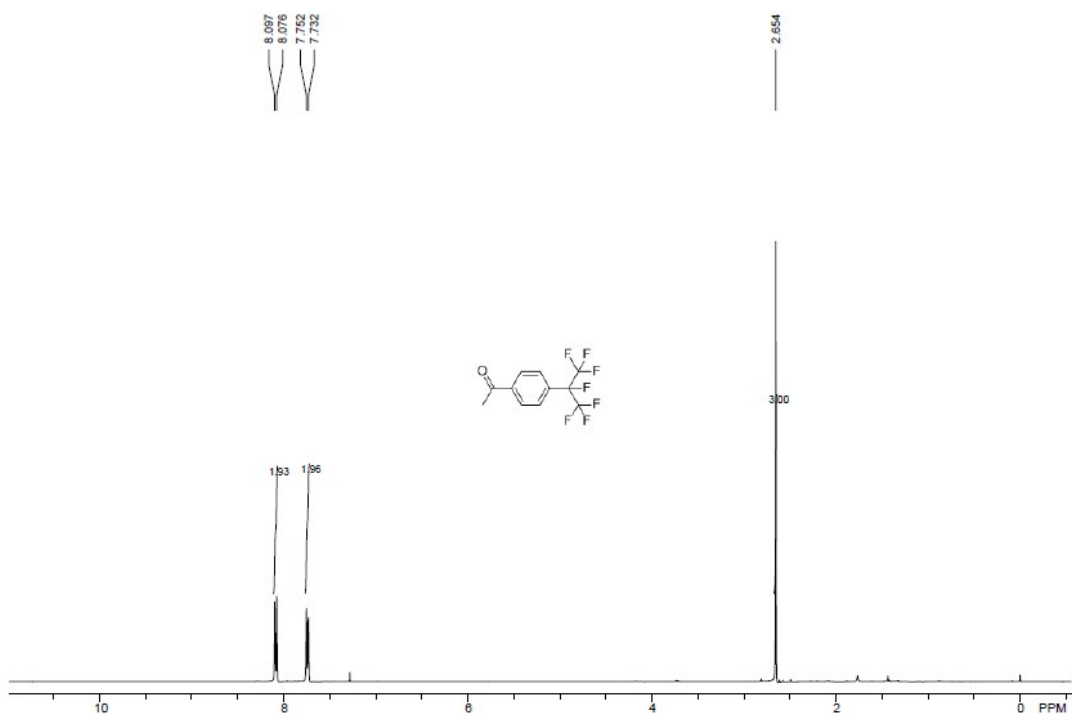


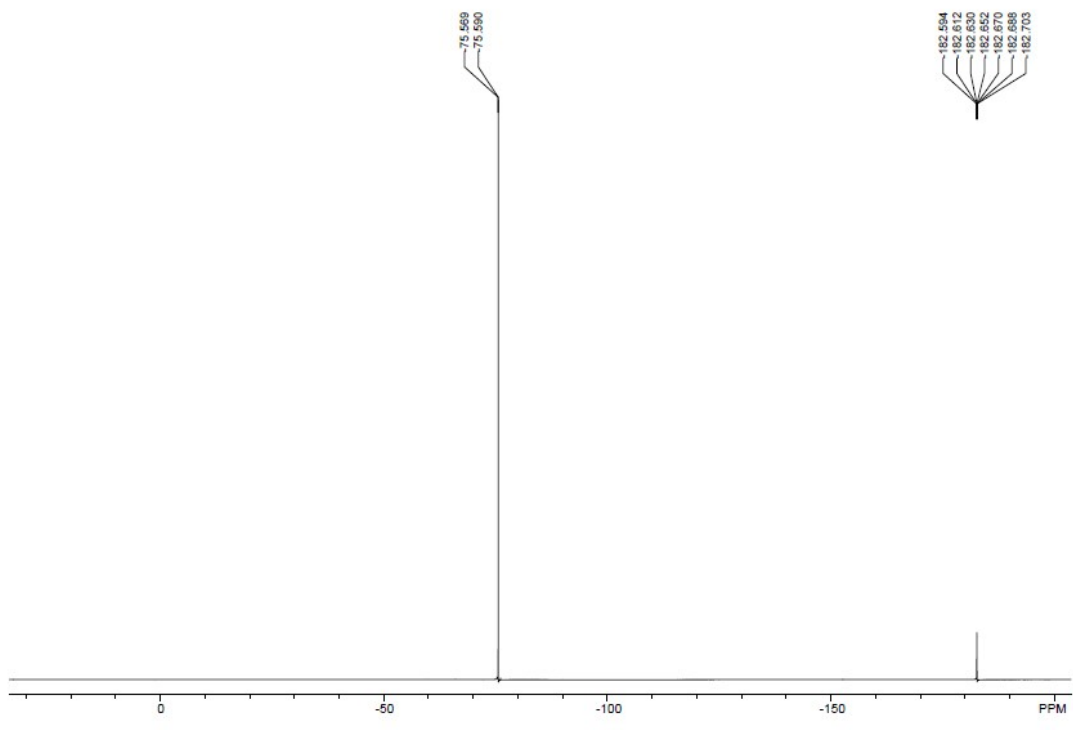
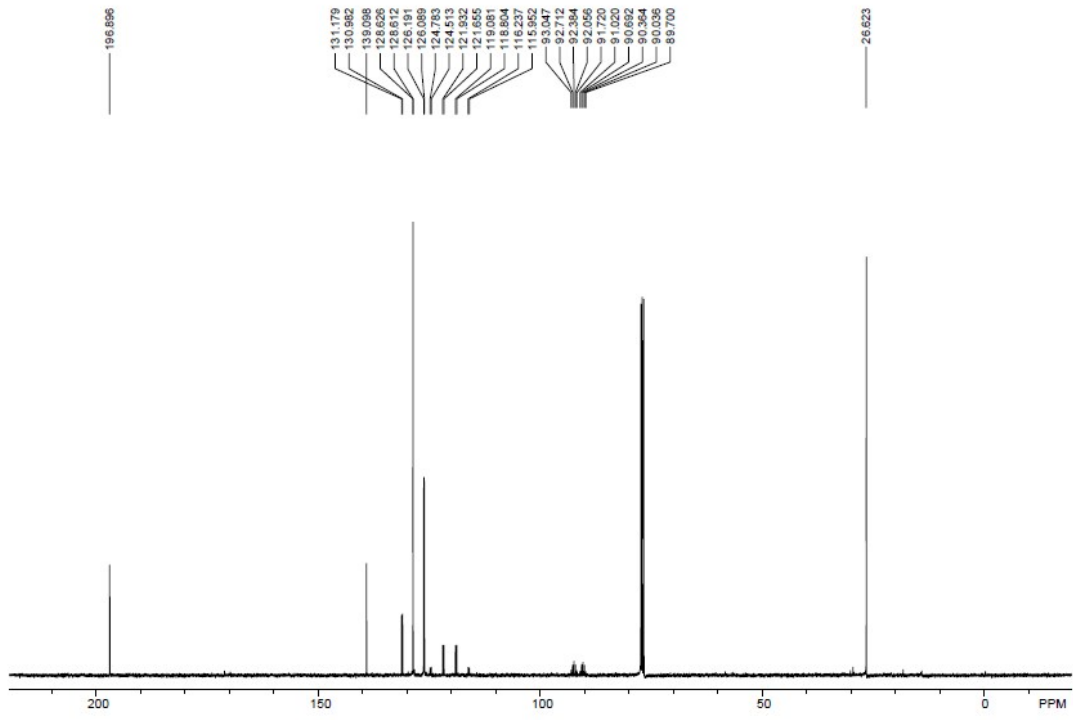
2d



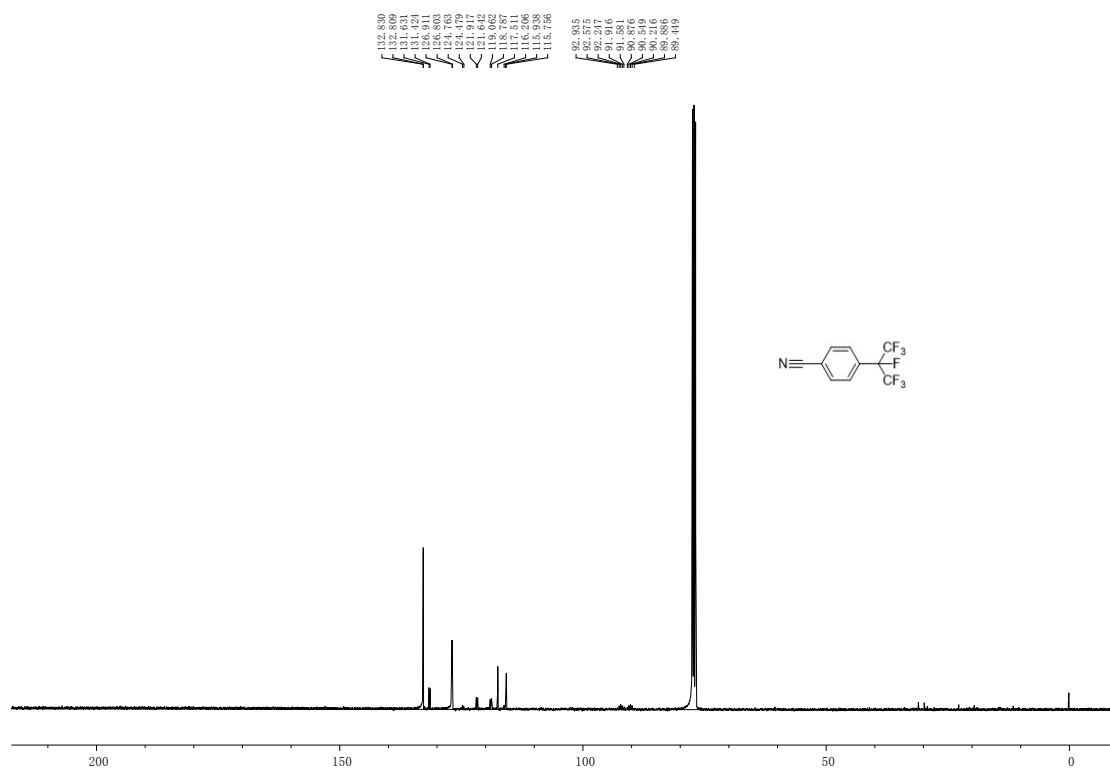
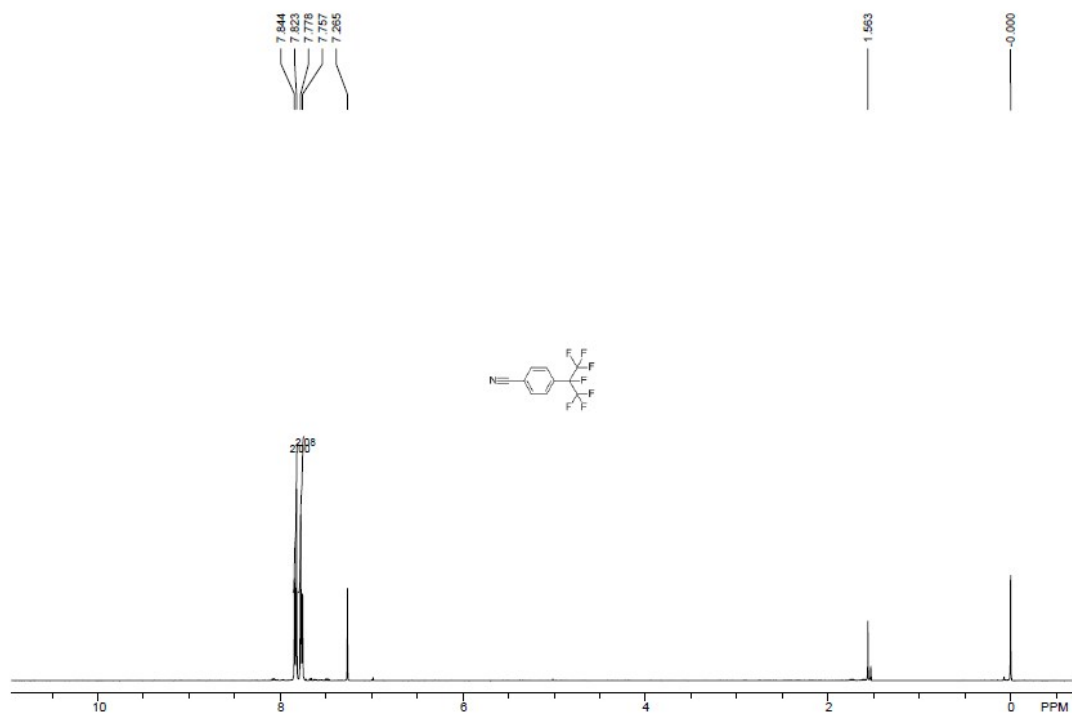


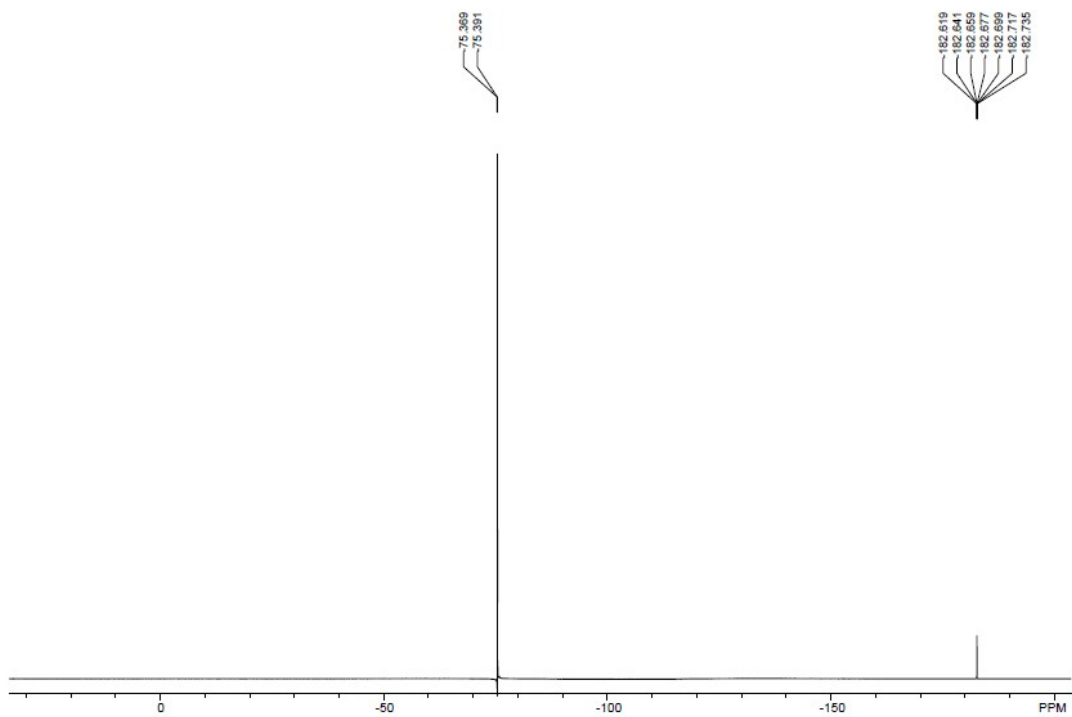
2e



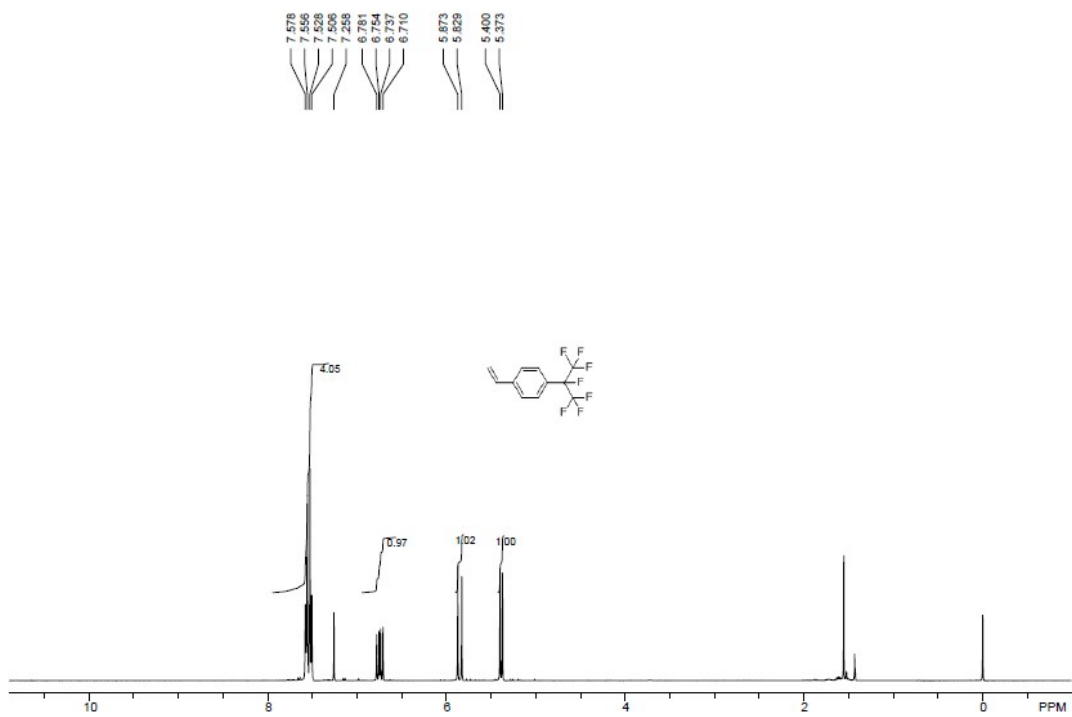


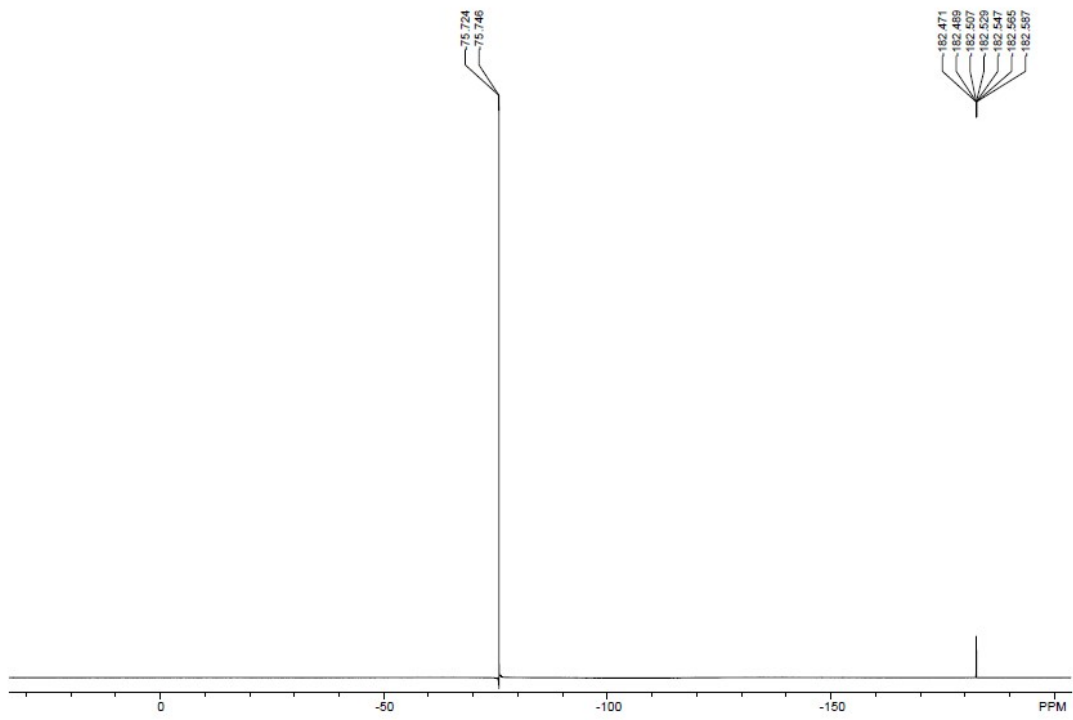
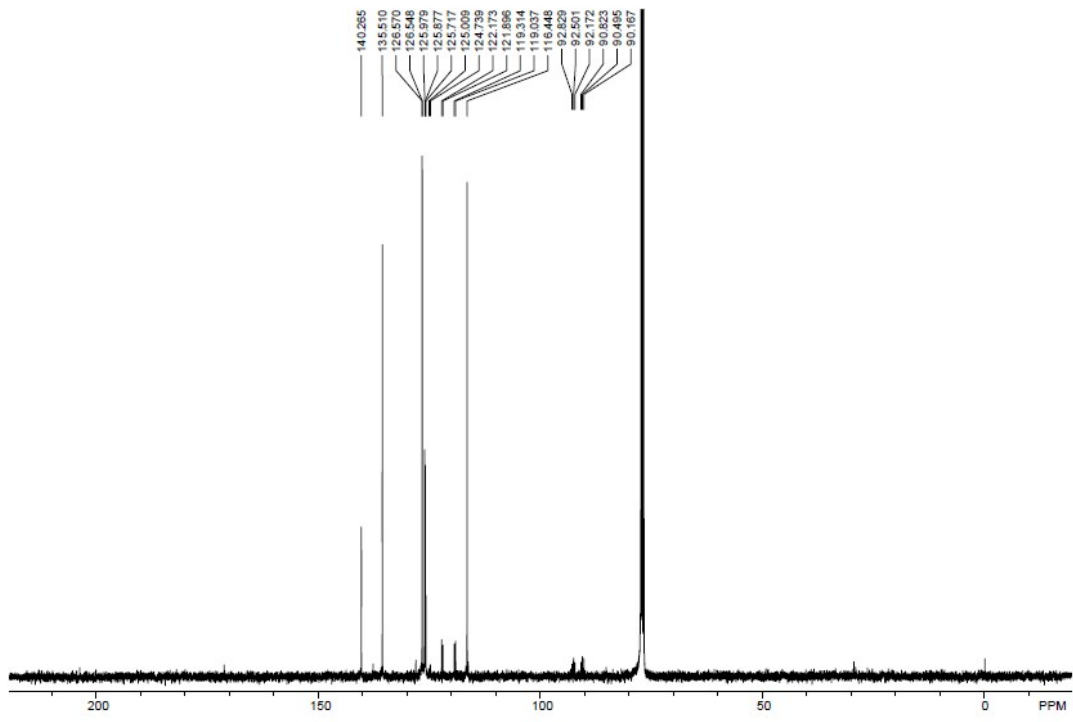
2f



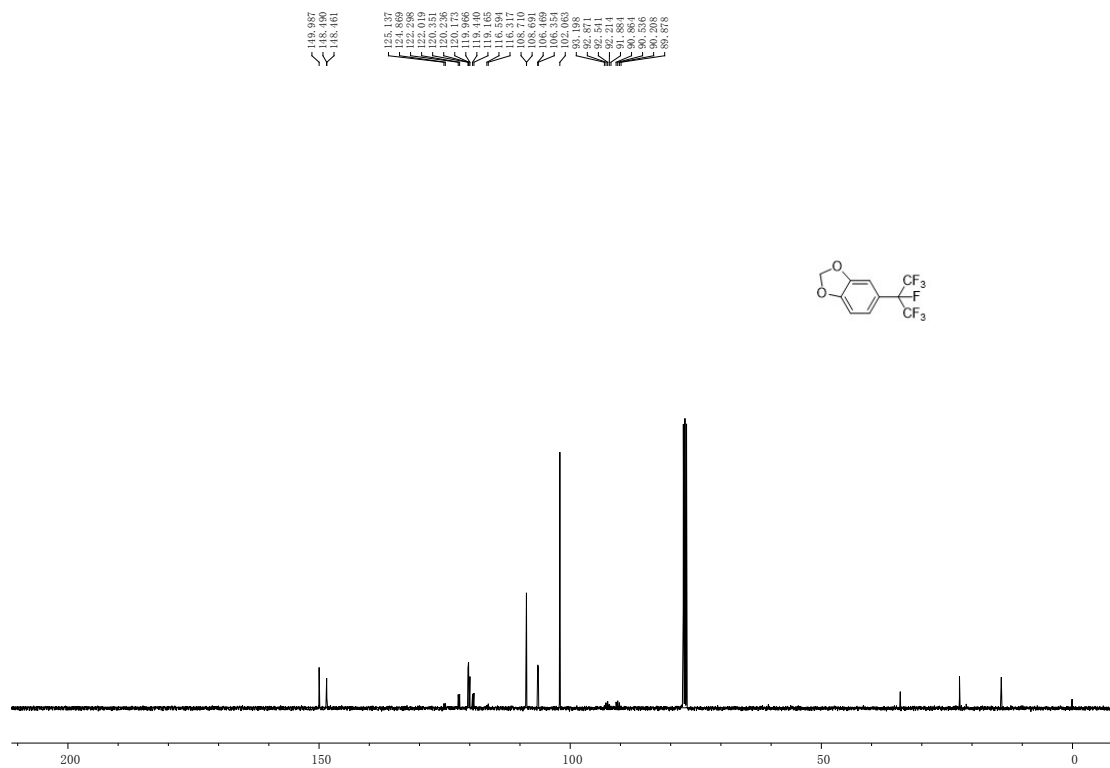
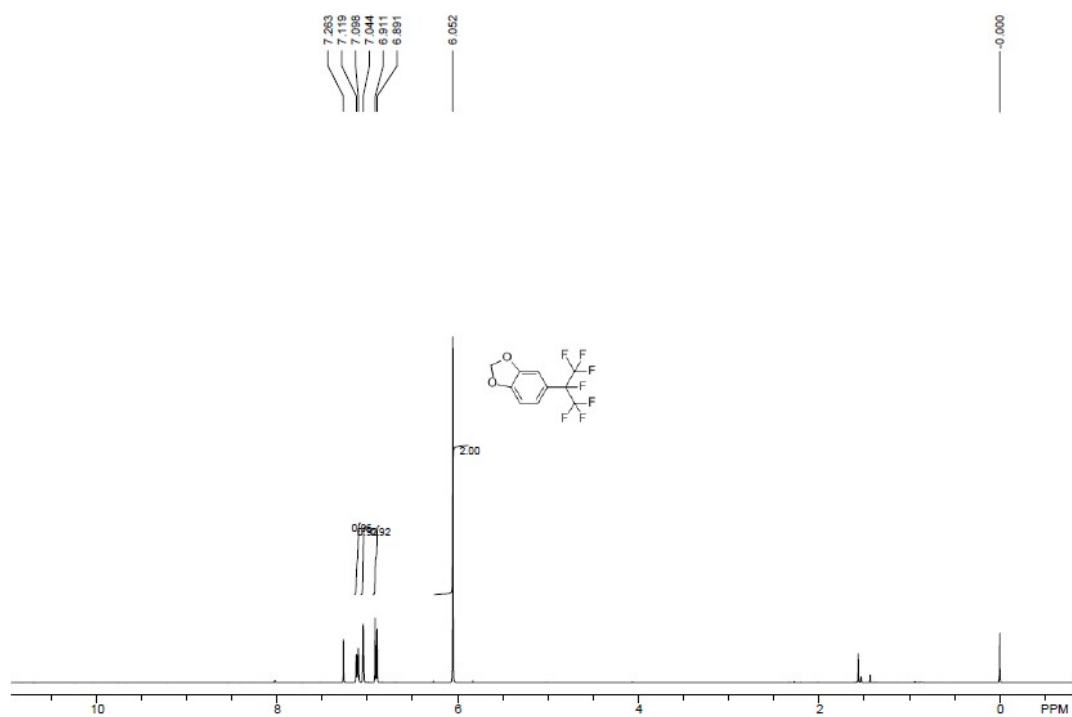


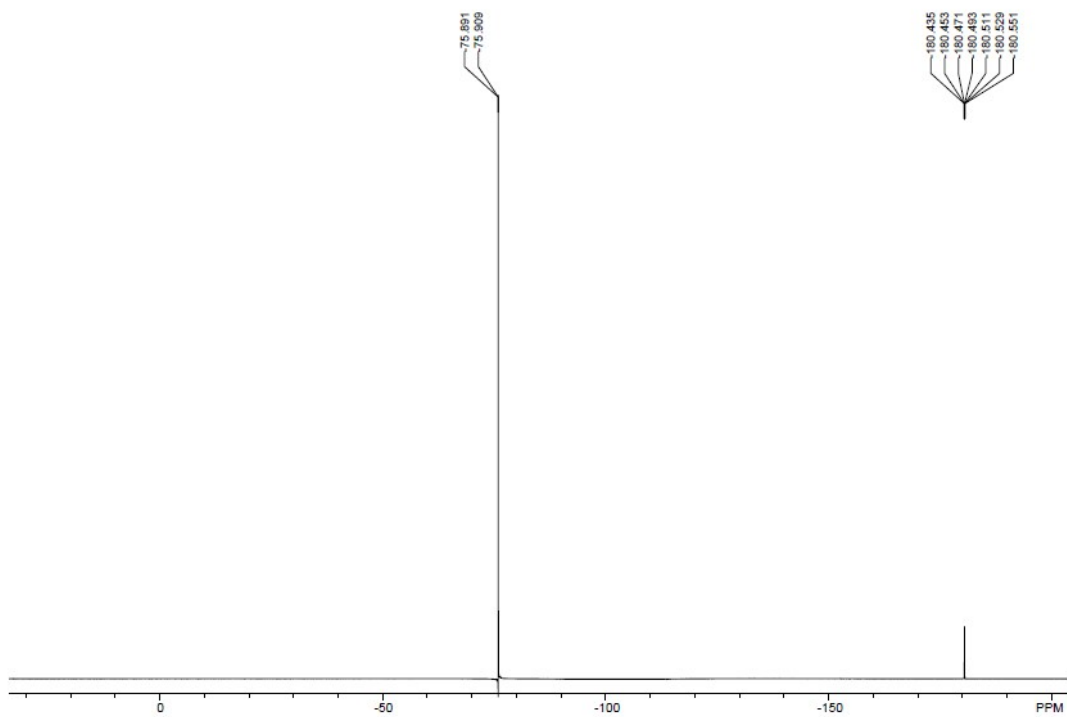
2g



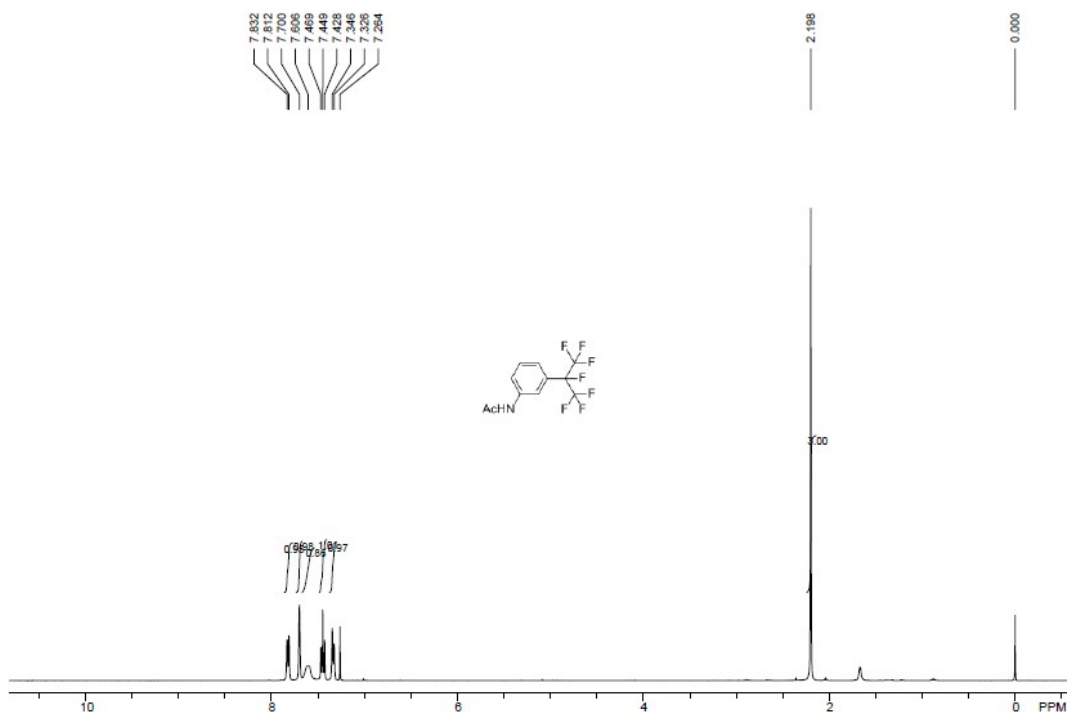


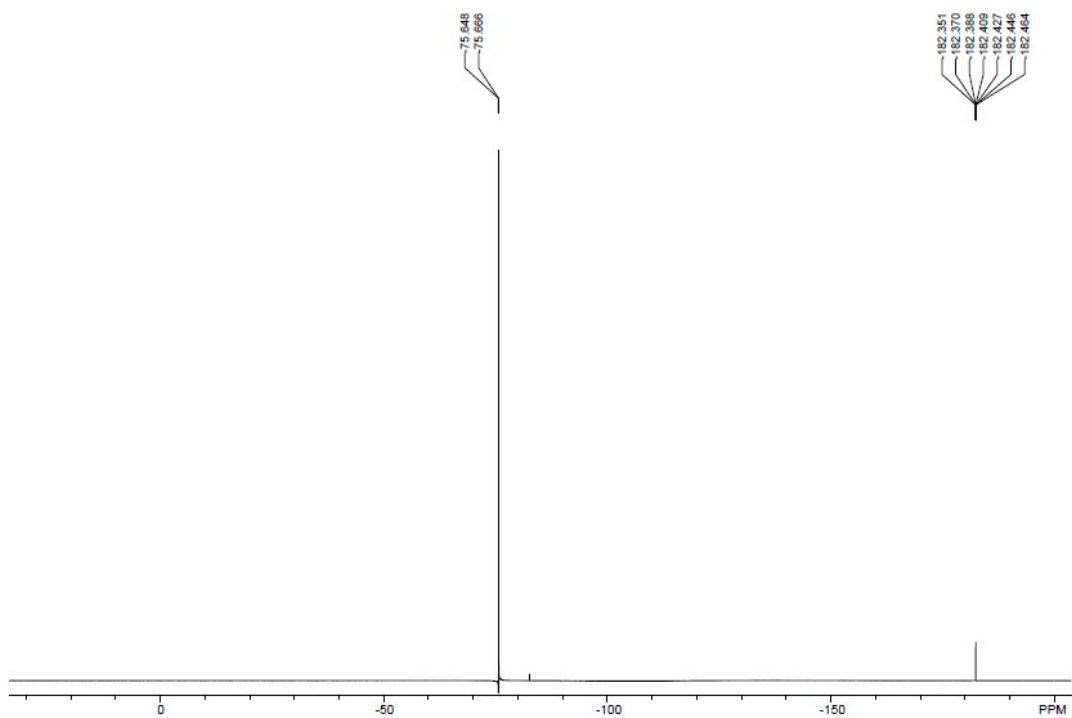
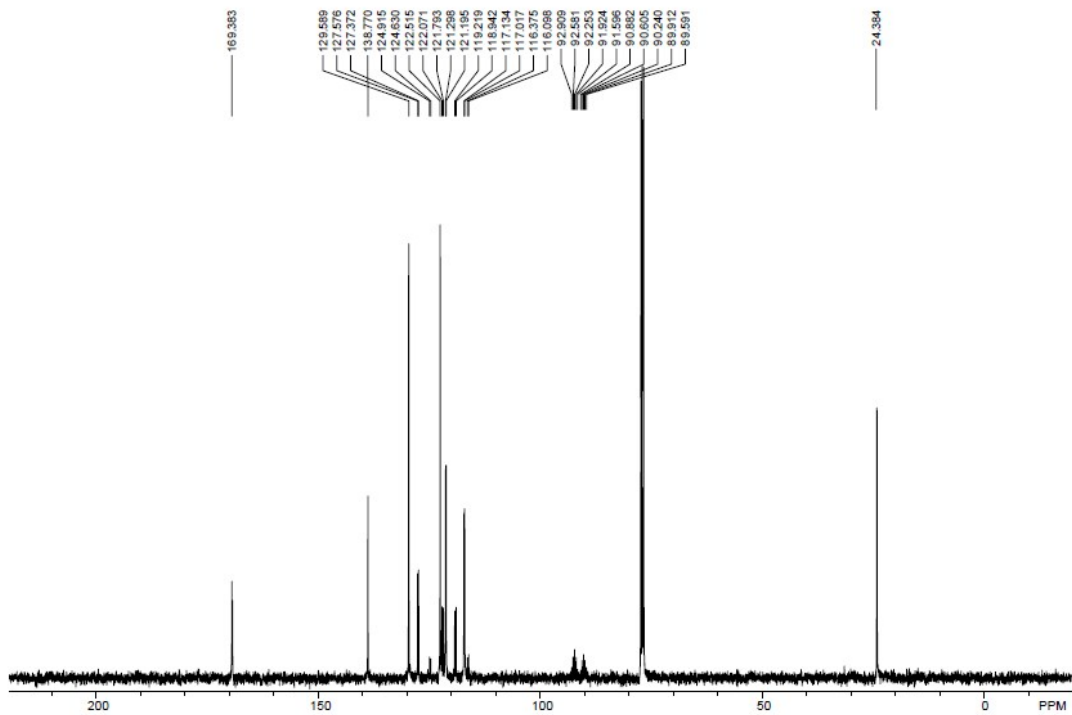
2h



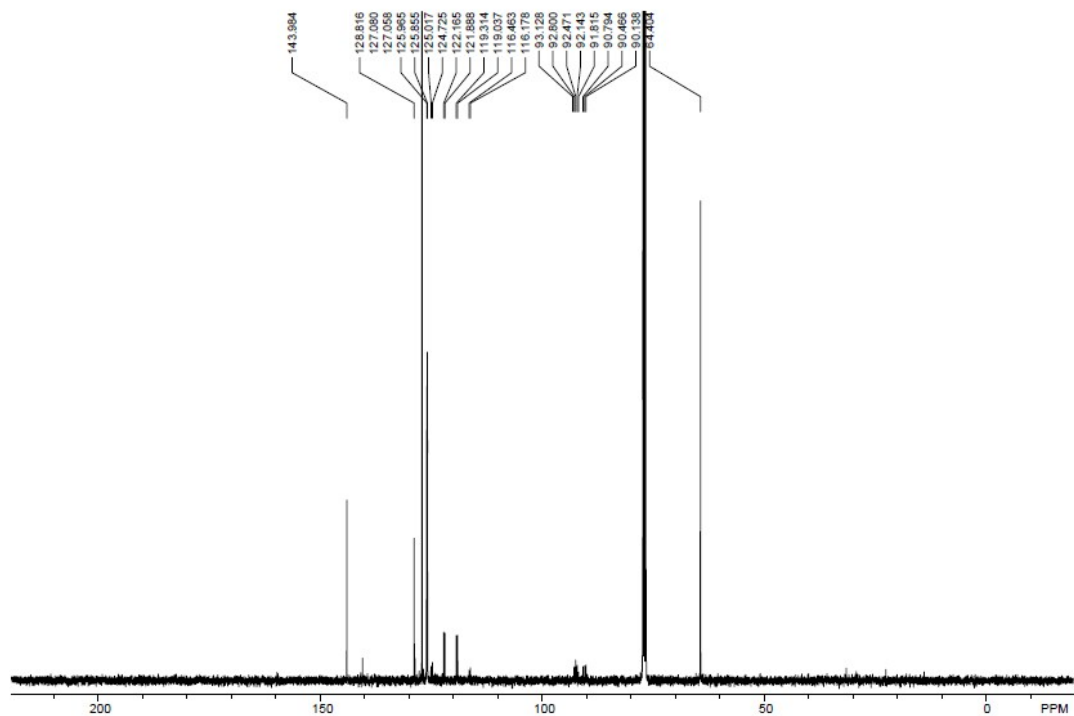
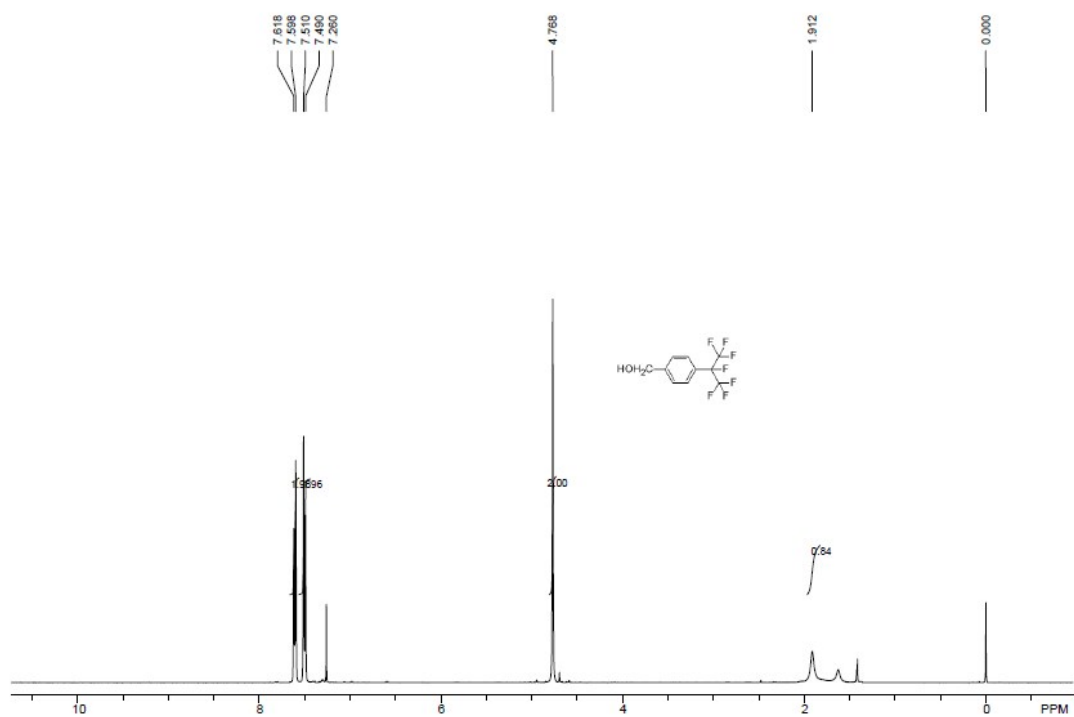


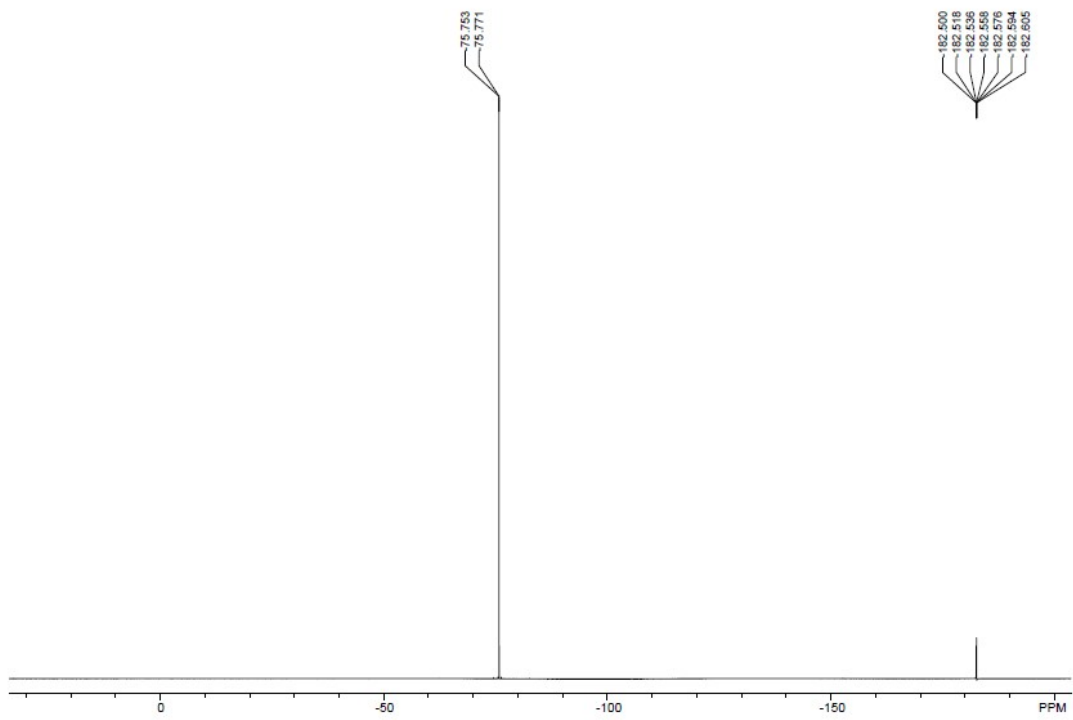
2i



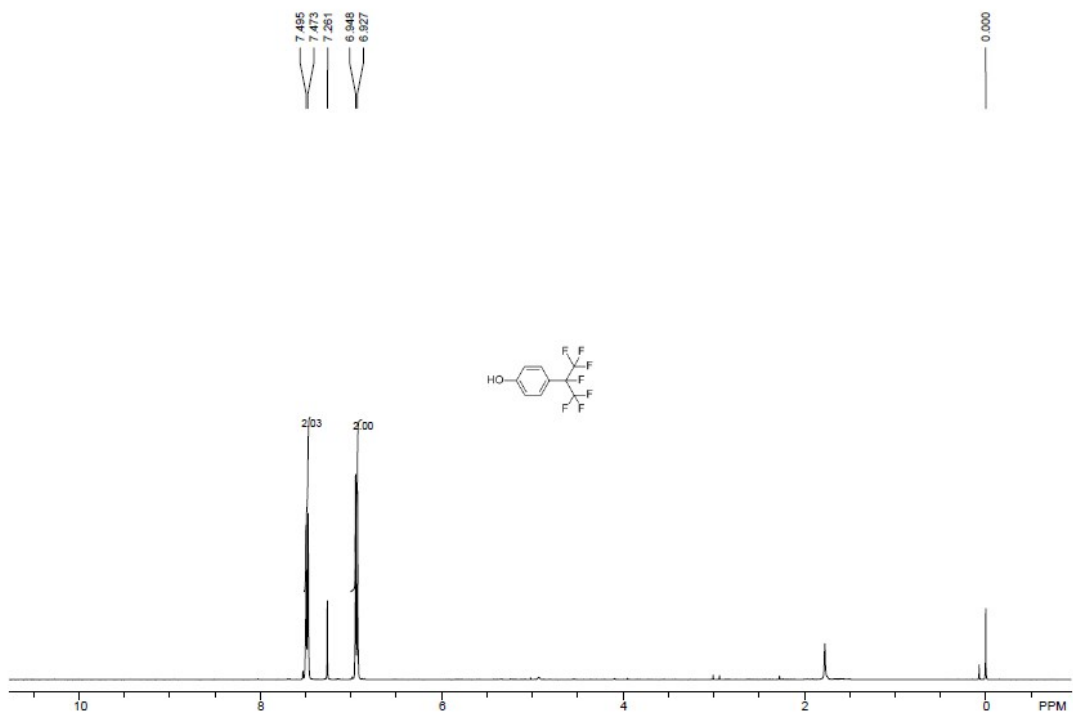


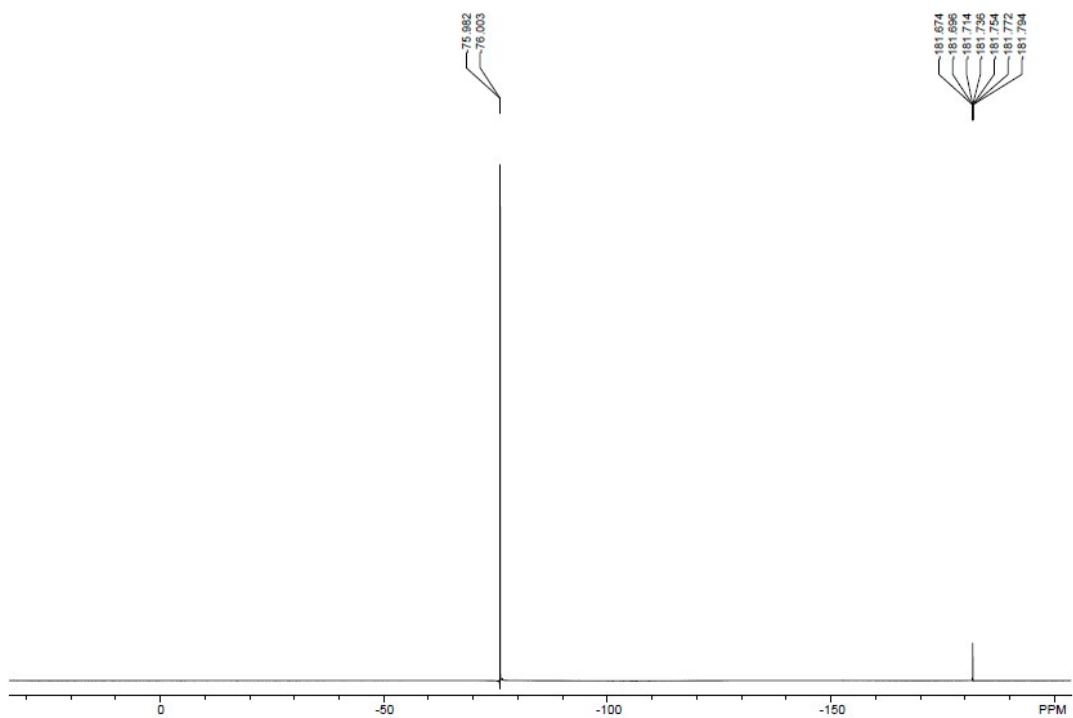
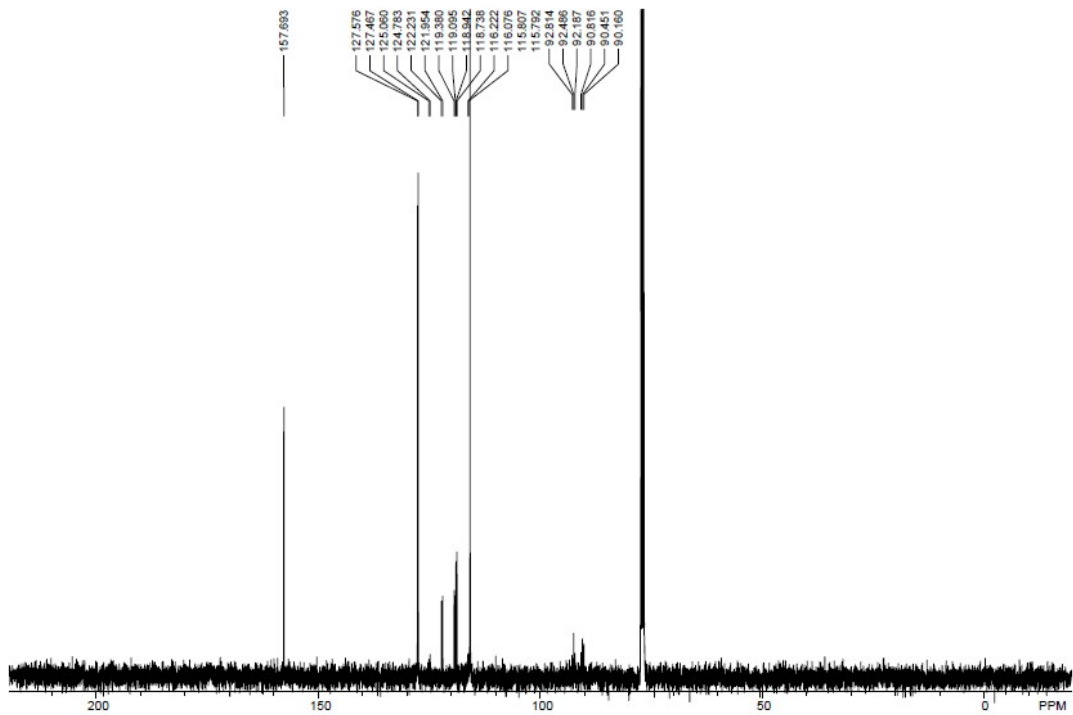
2j



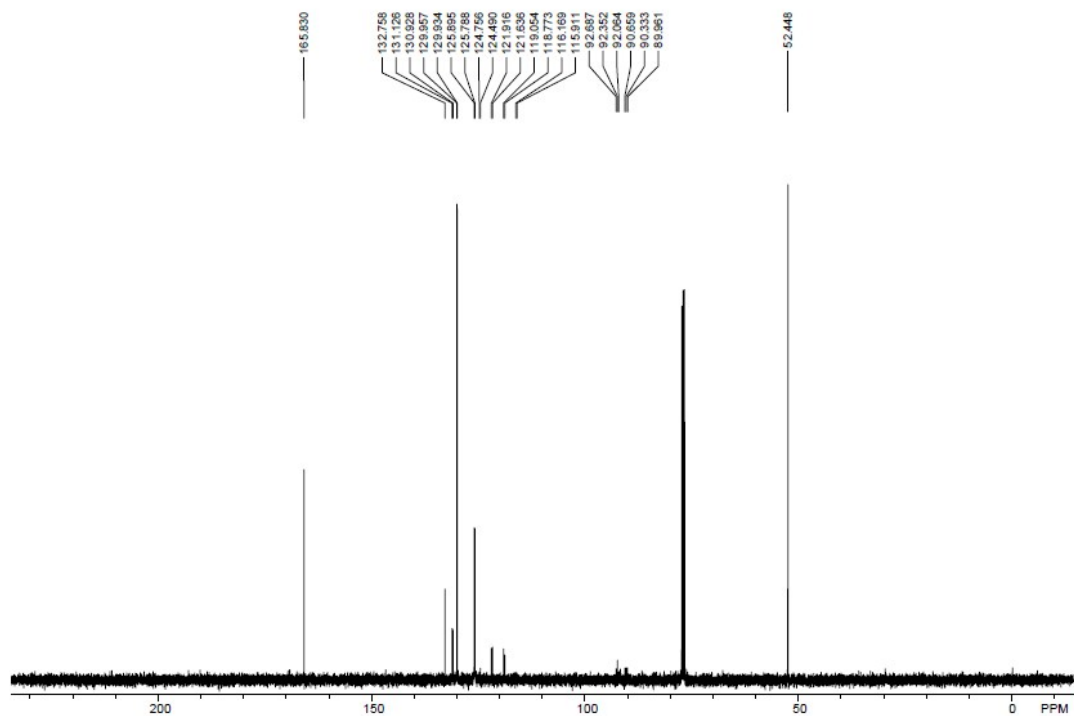
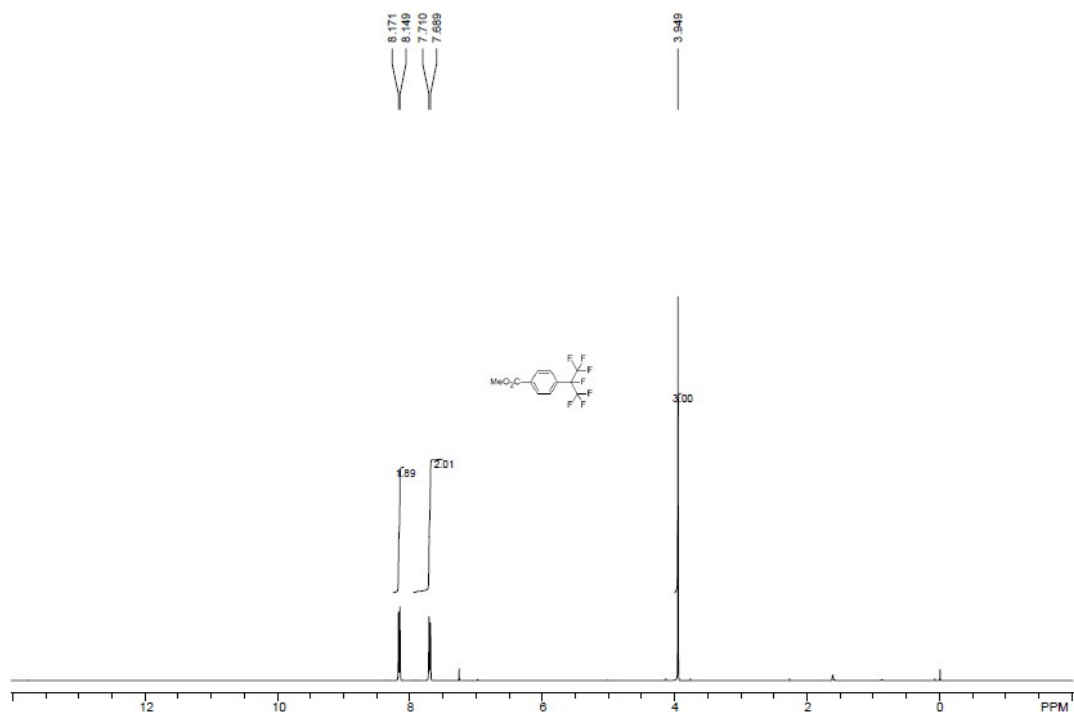


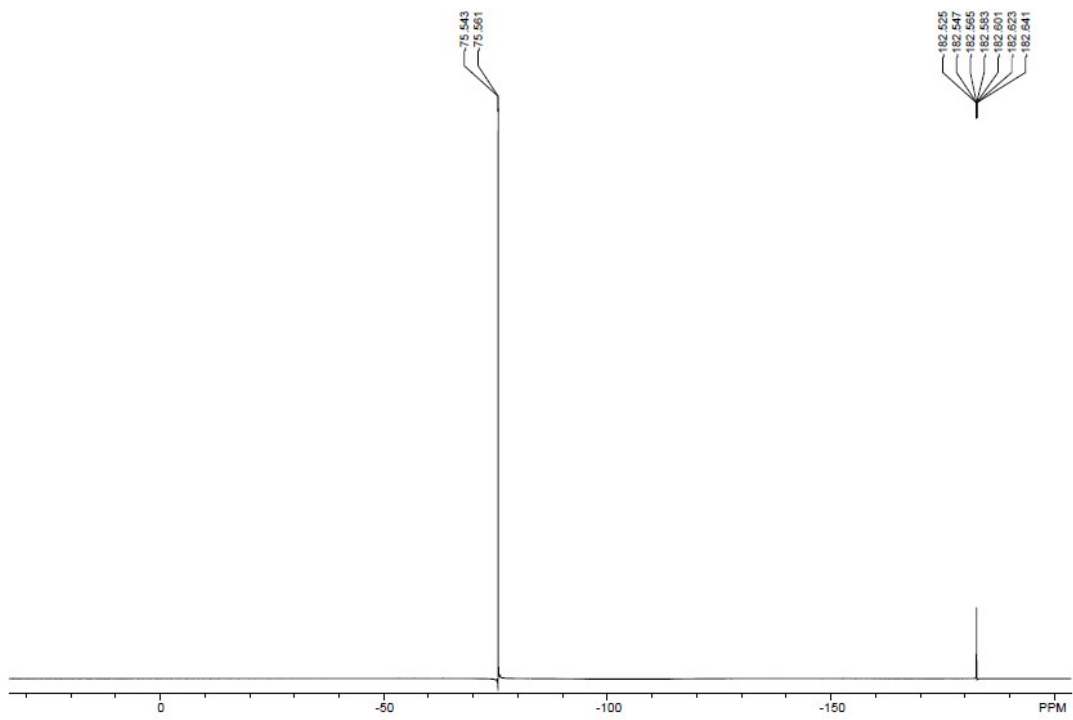
2k



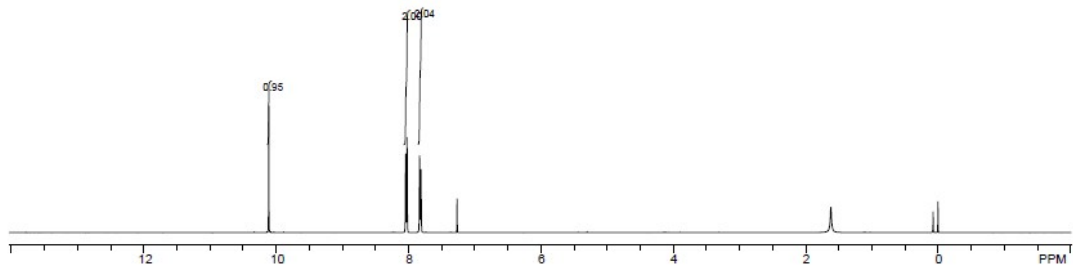
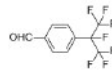


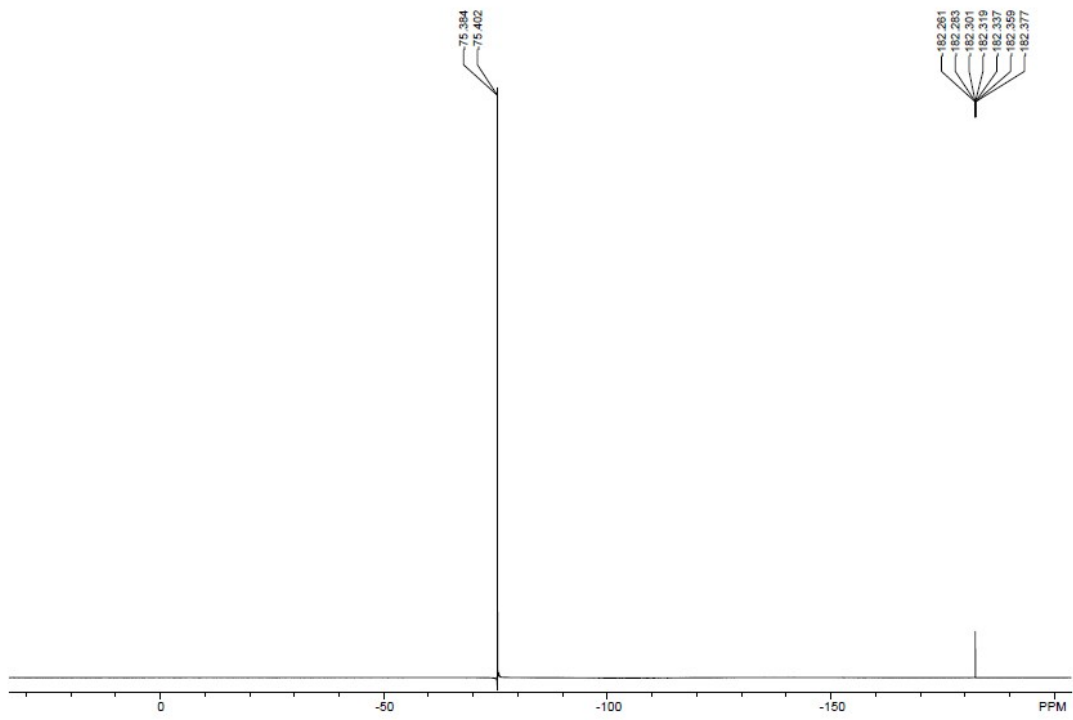
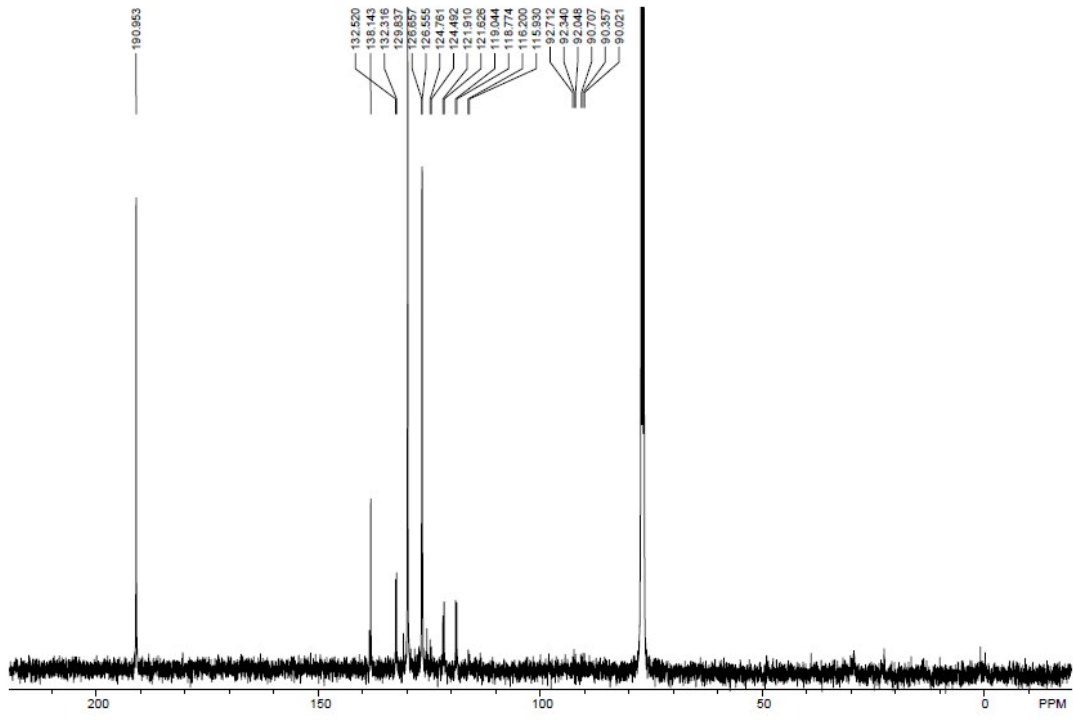
21



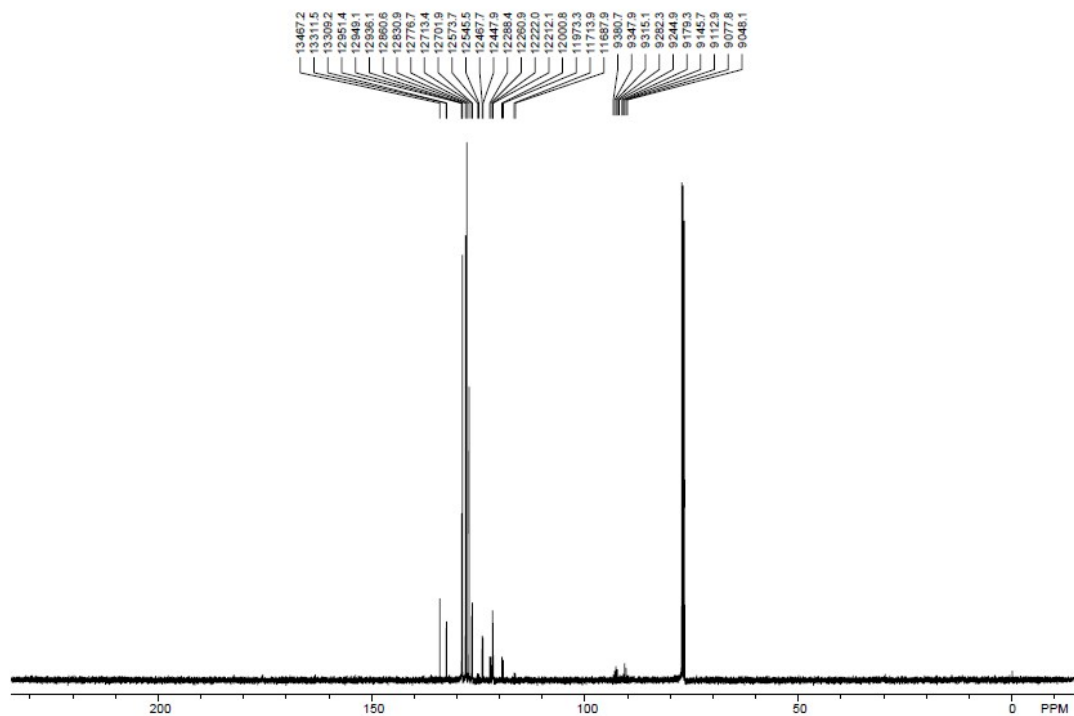
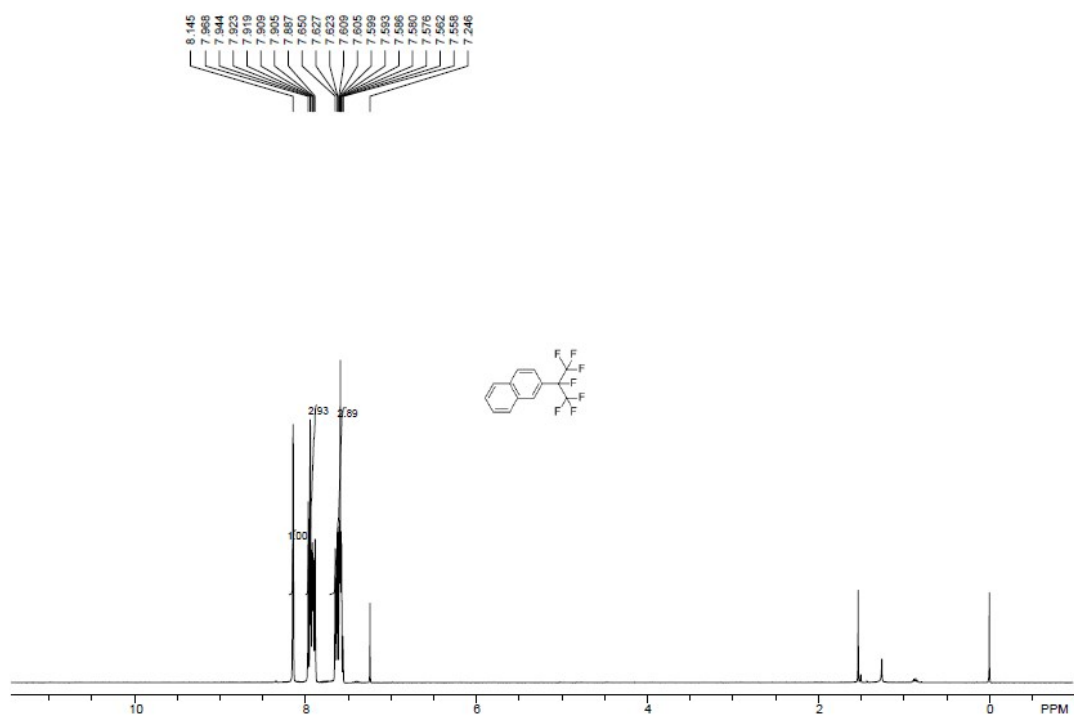


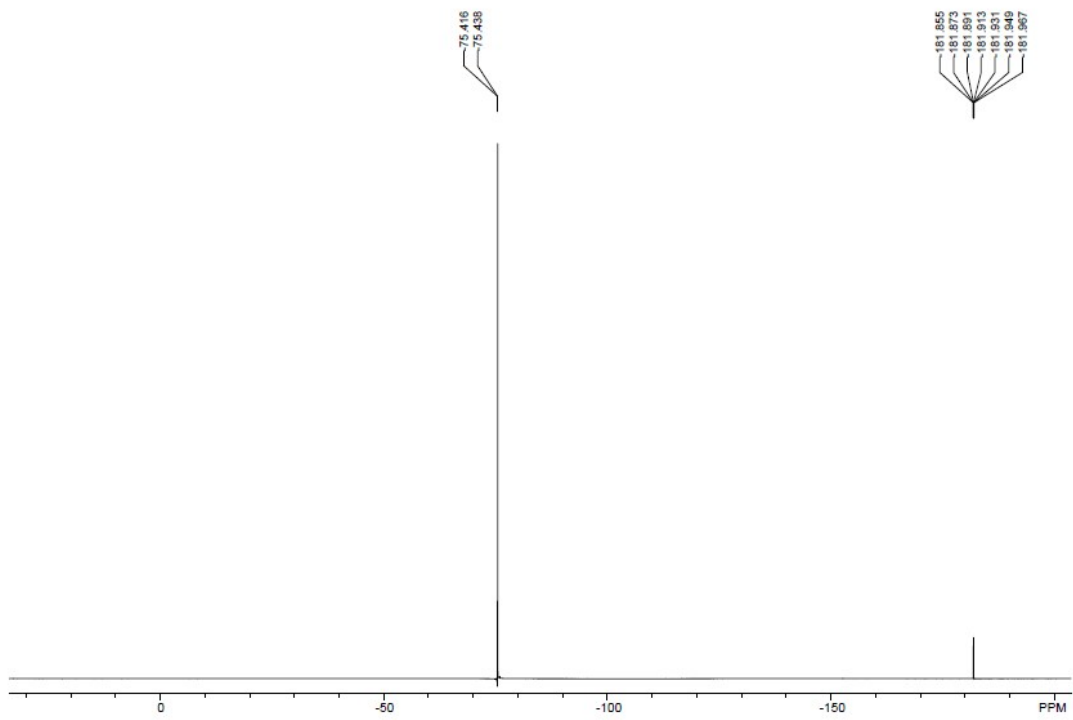
2m



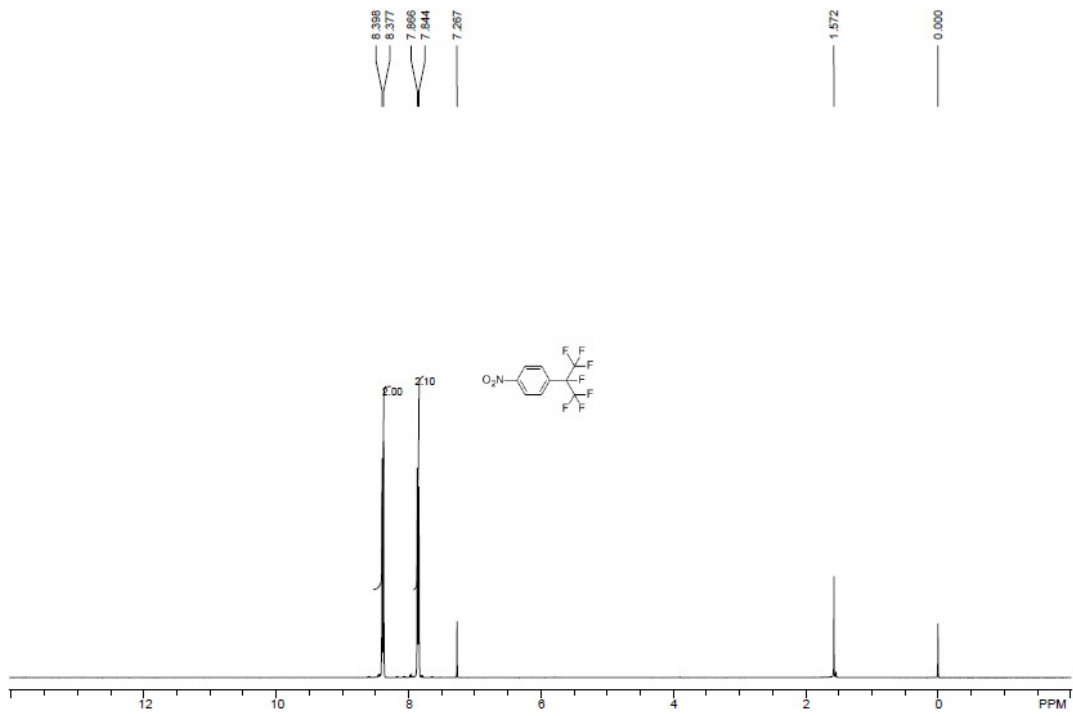


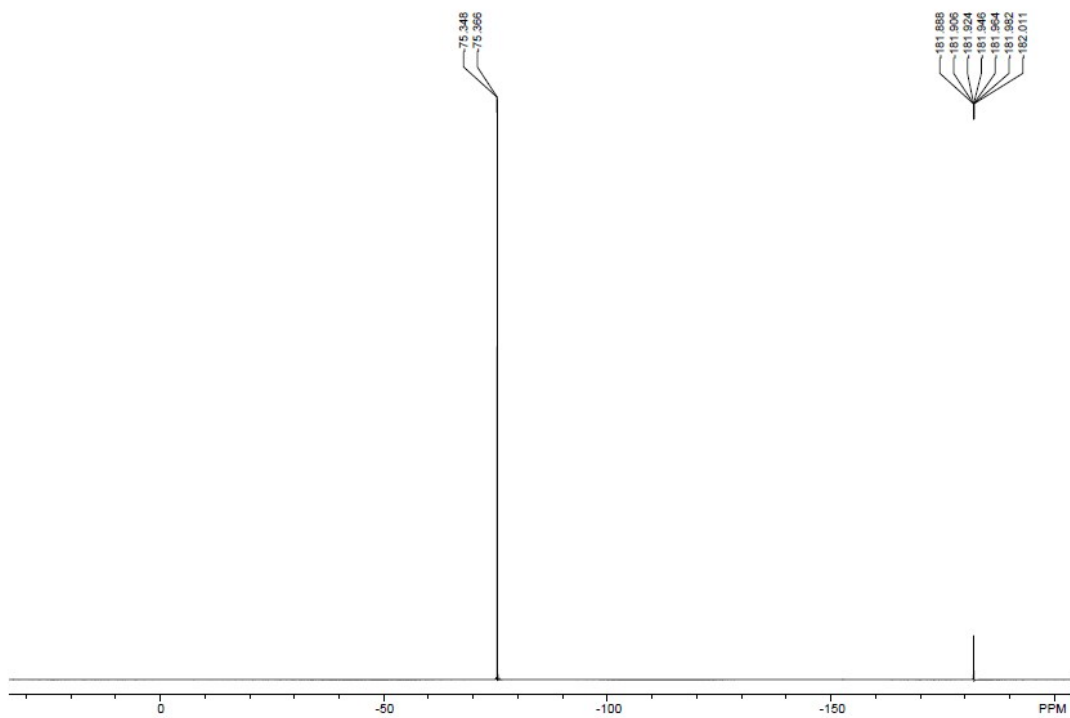
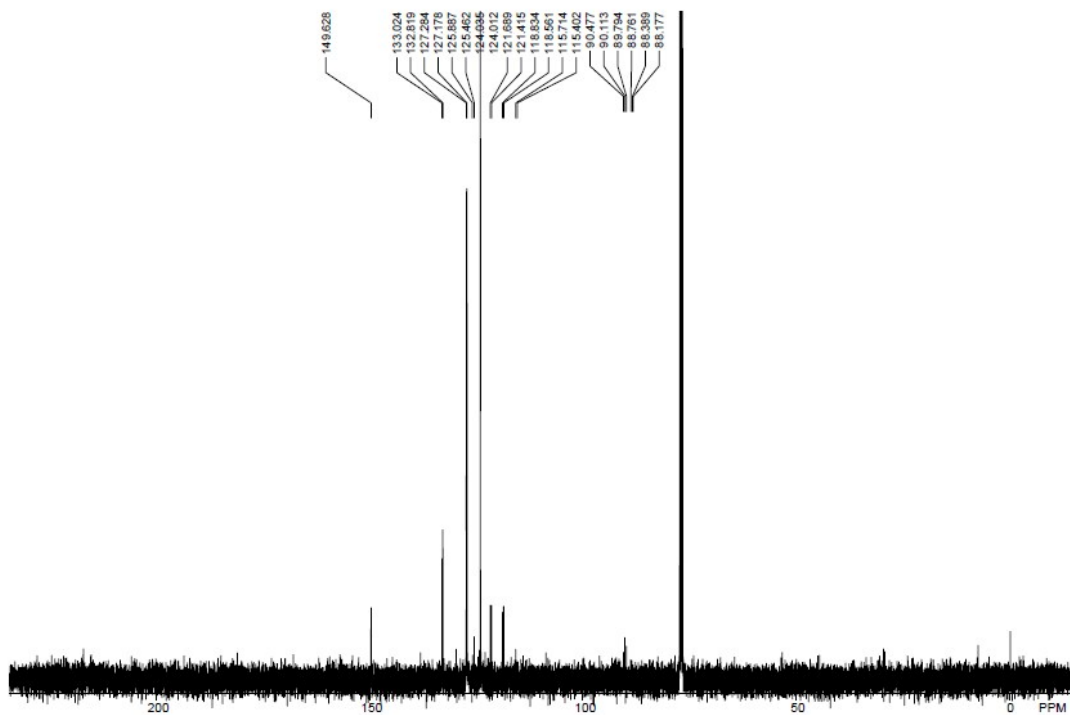
2n



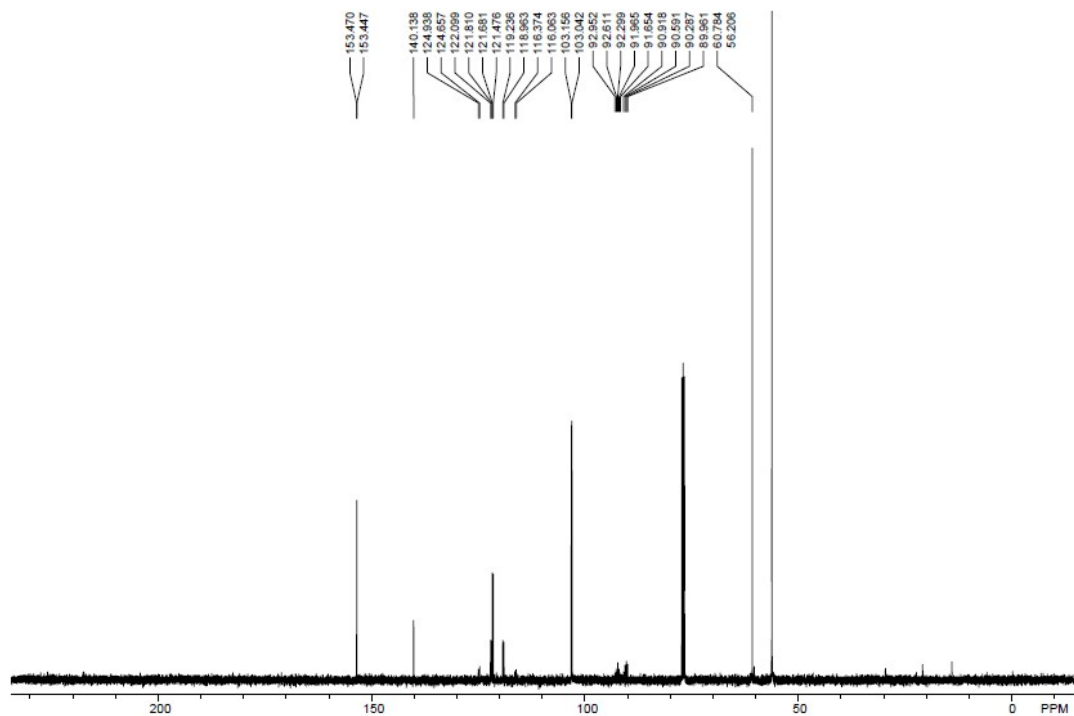
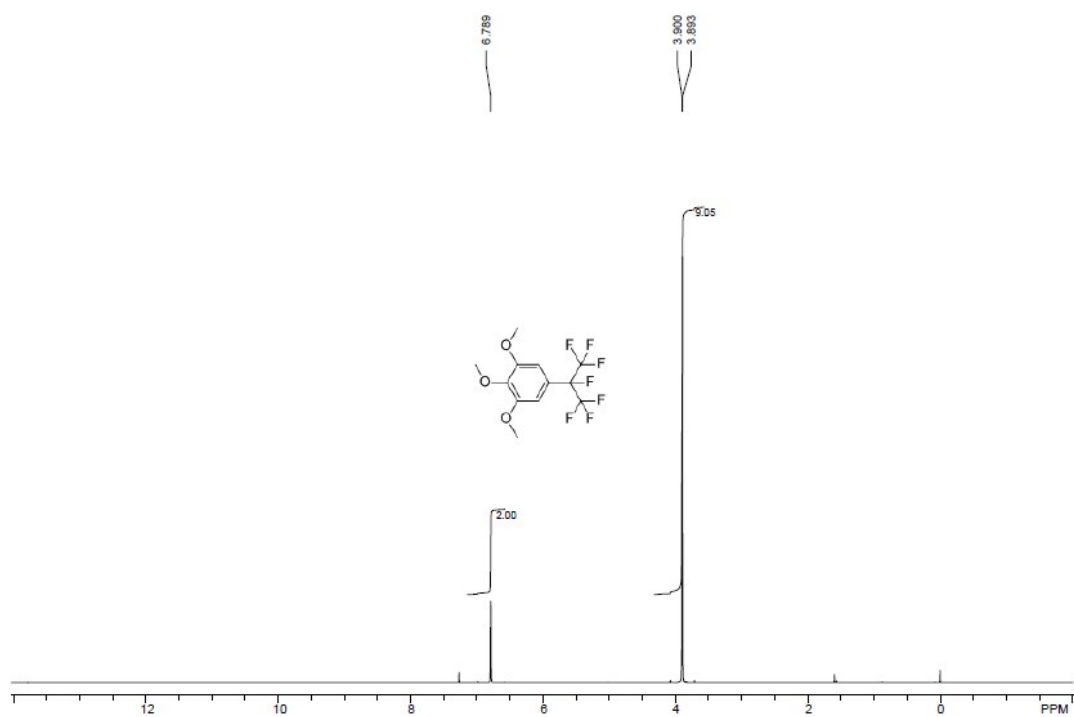


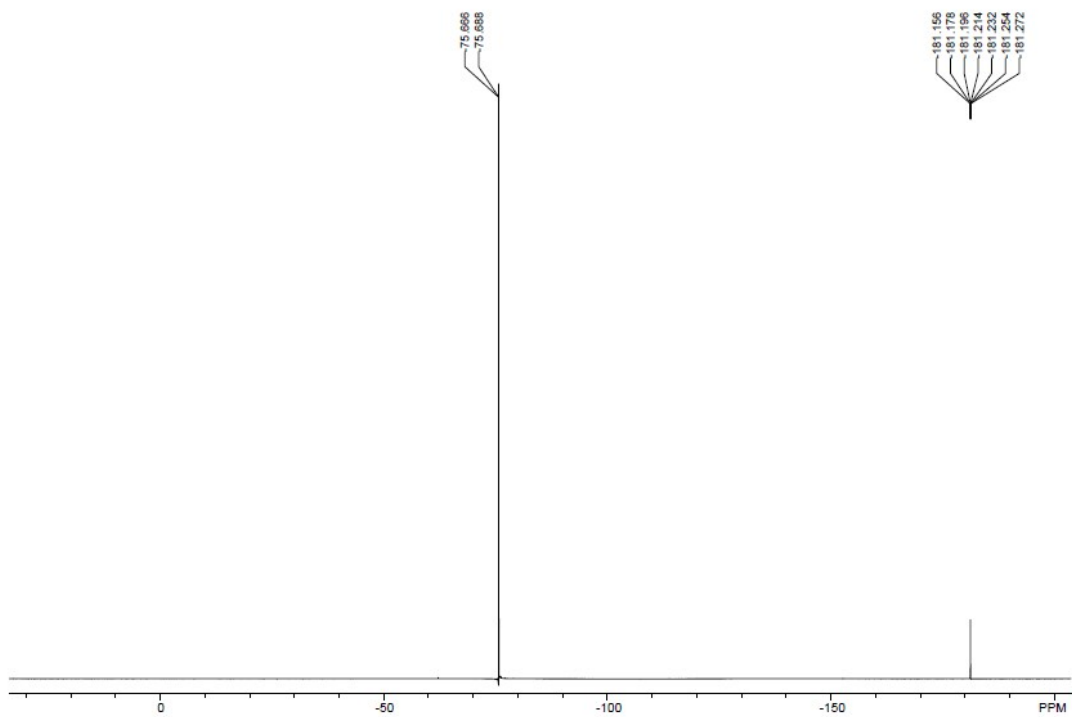
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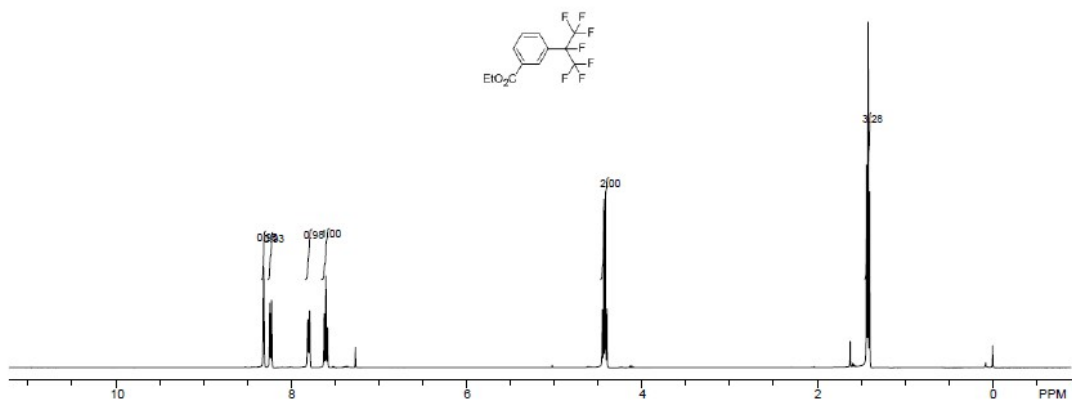
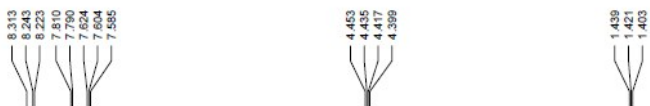


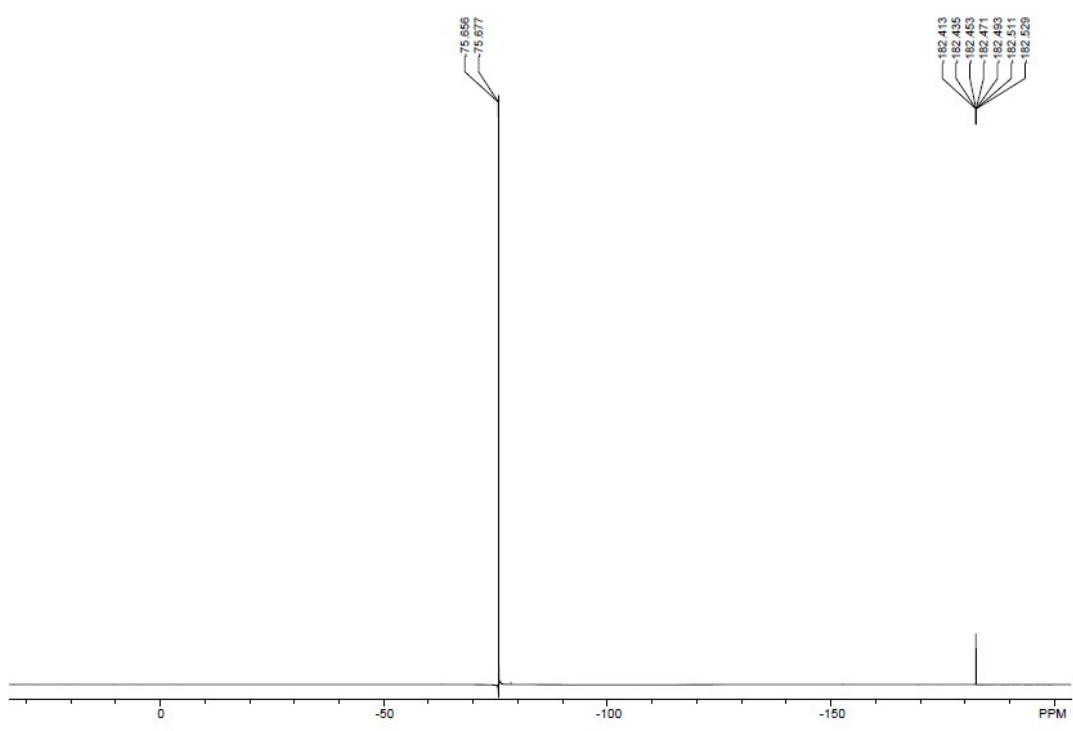
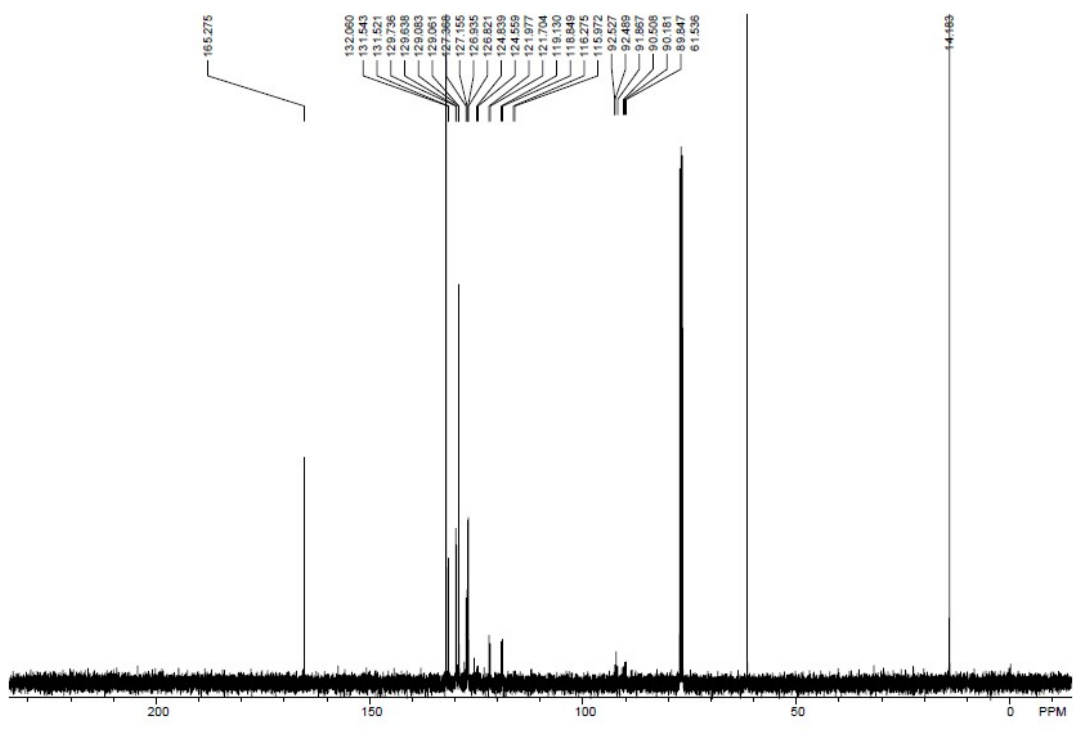
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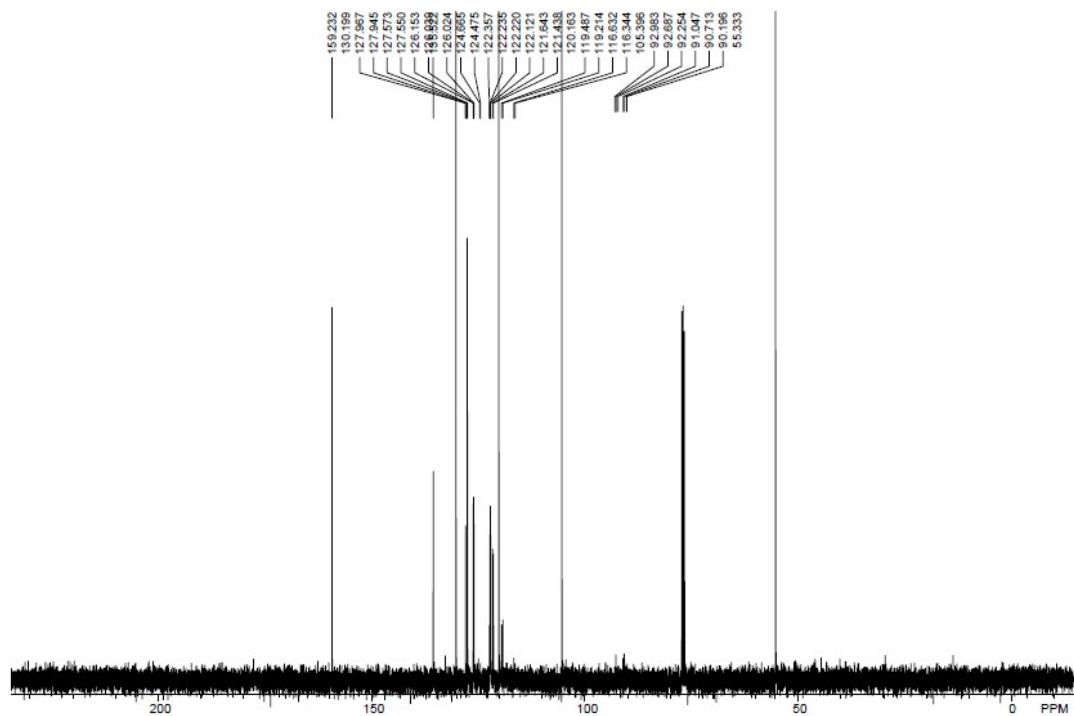
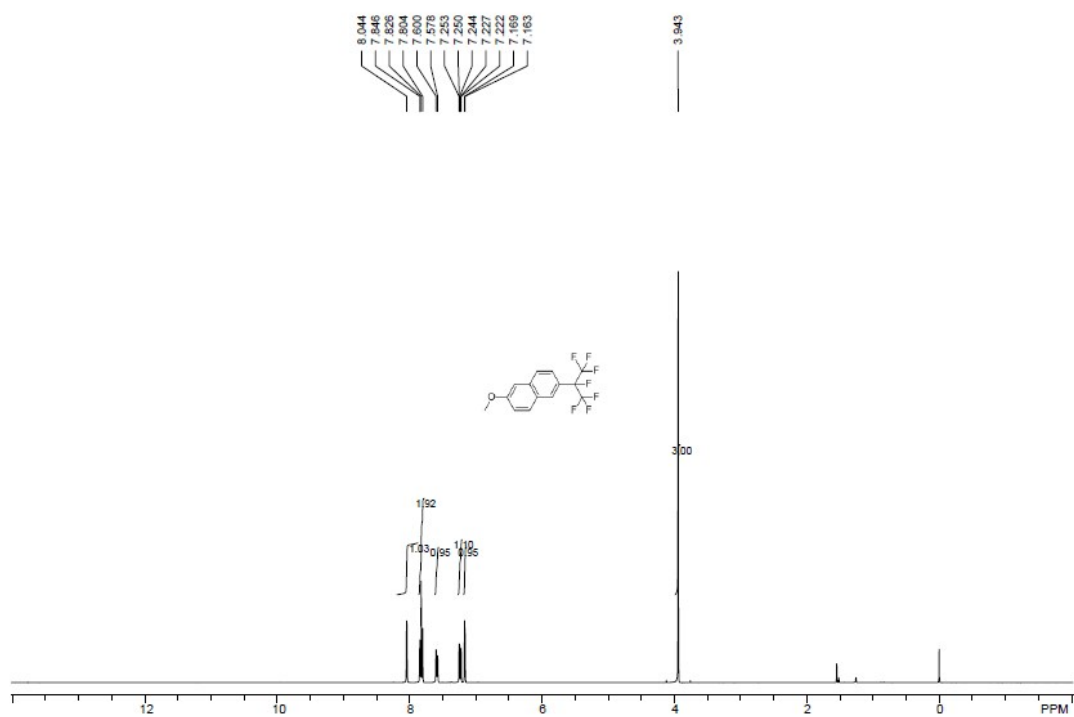


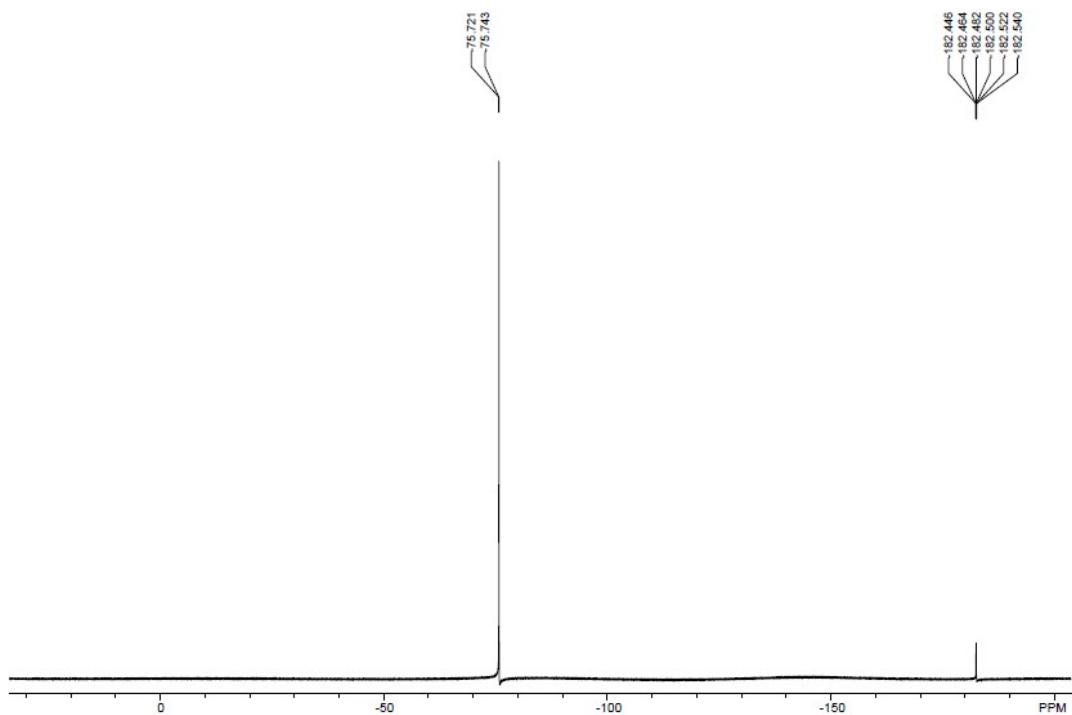
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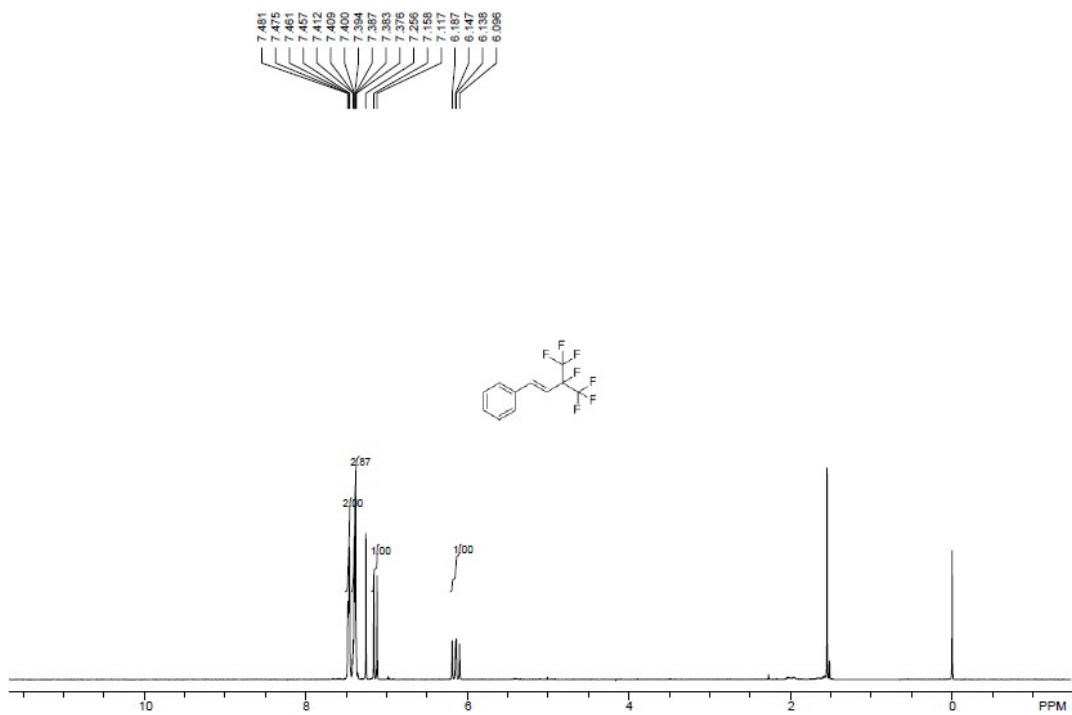


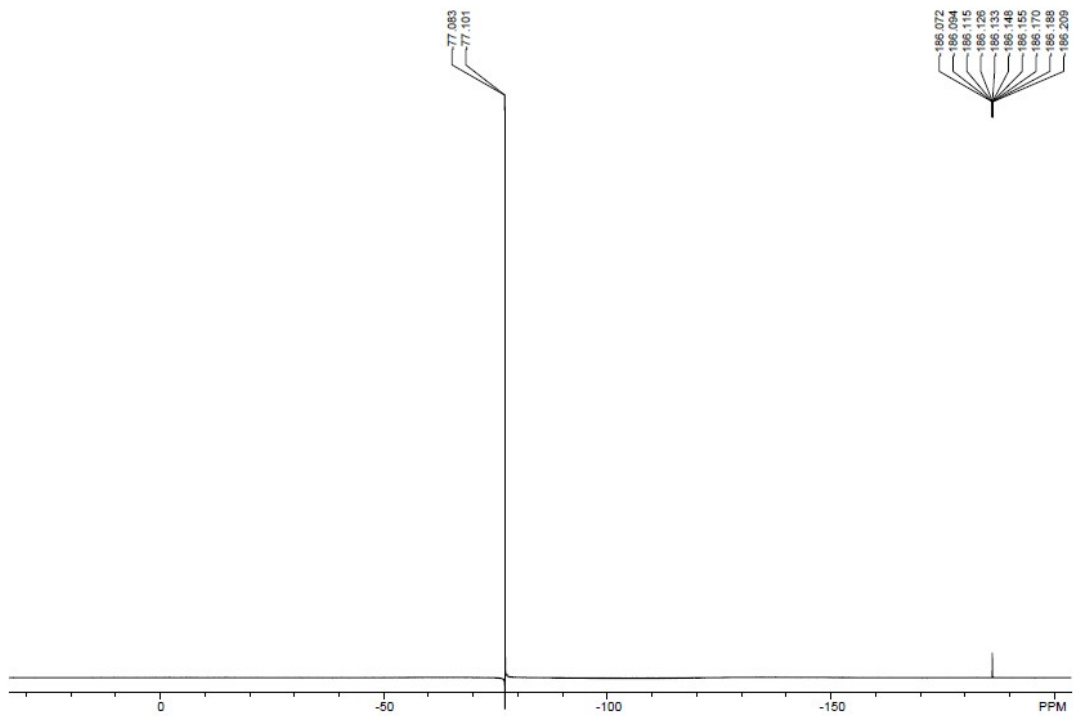
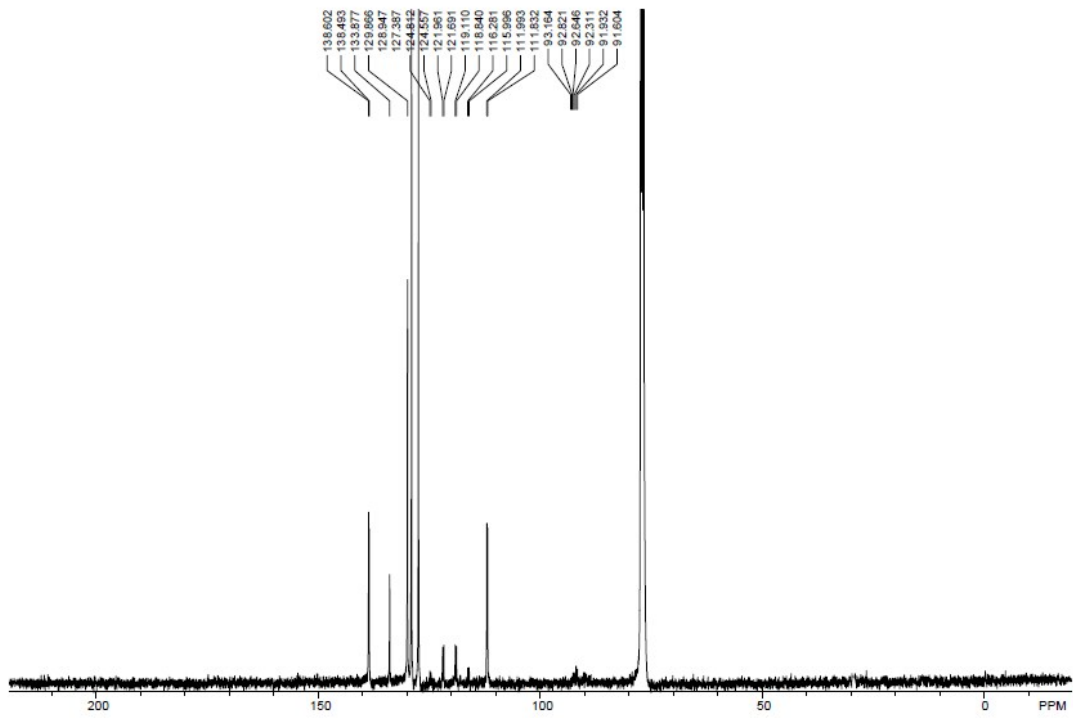
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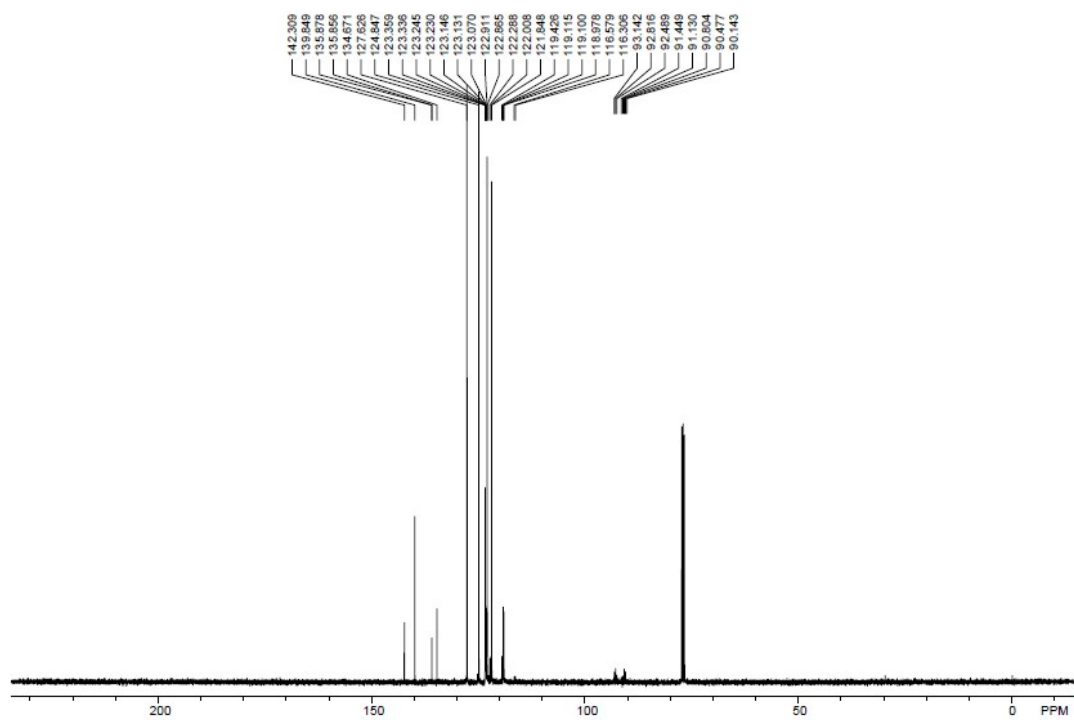
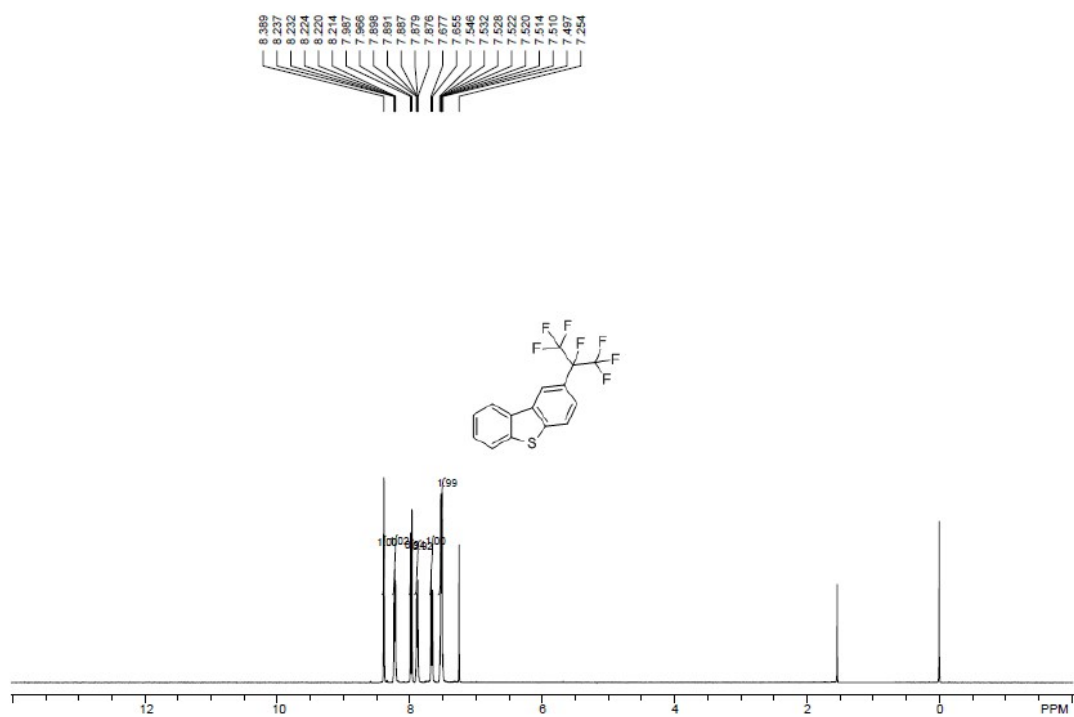


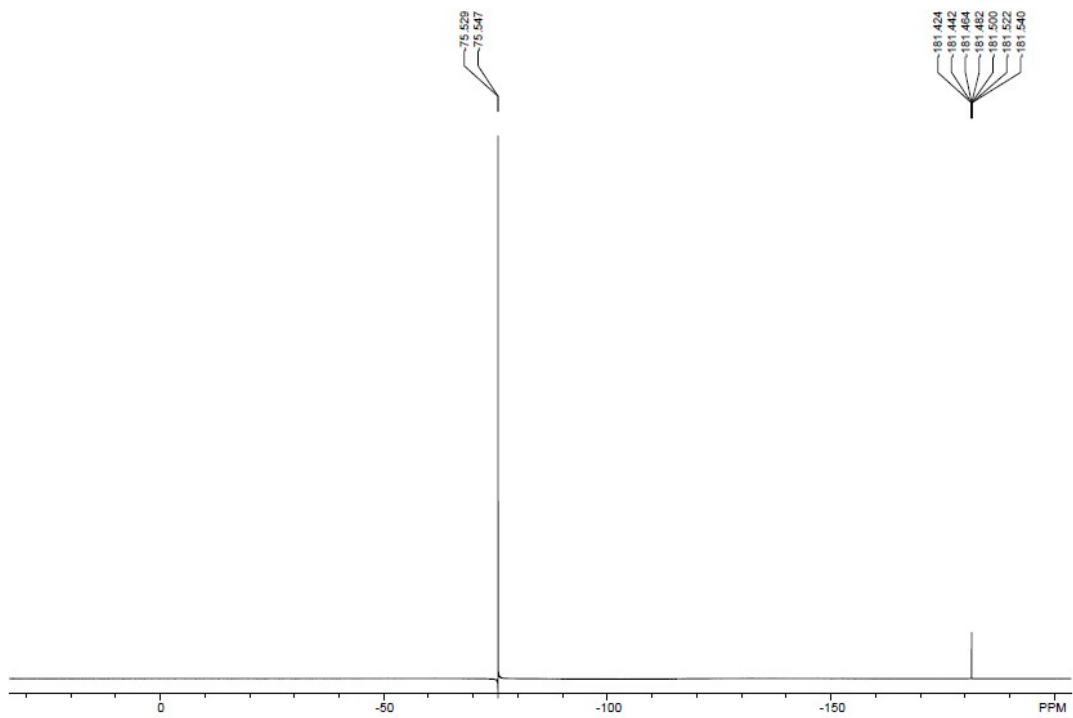
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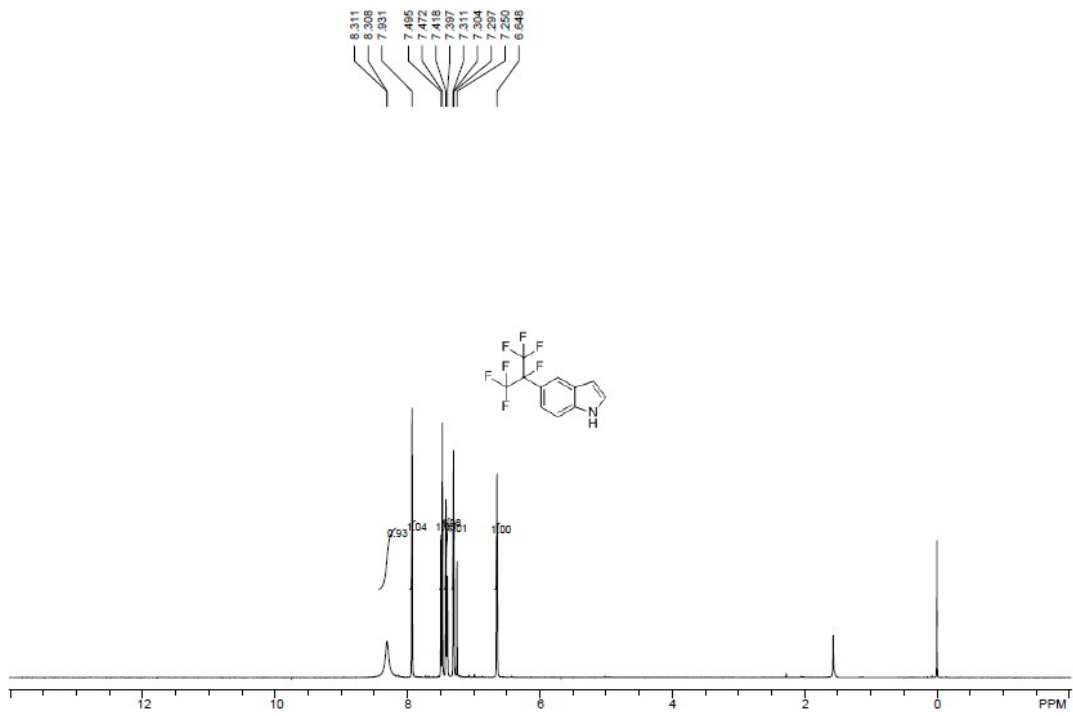


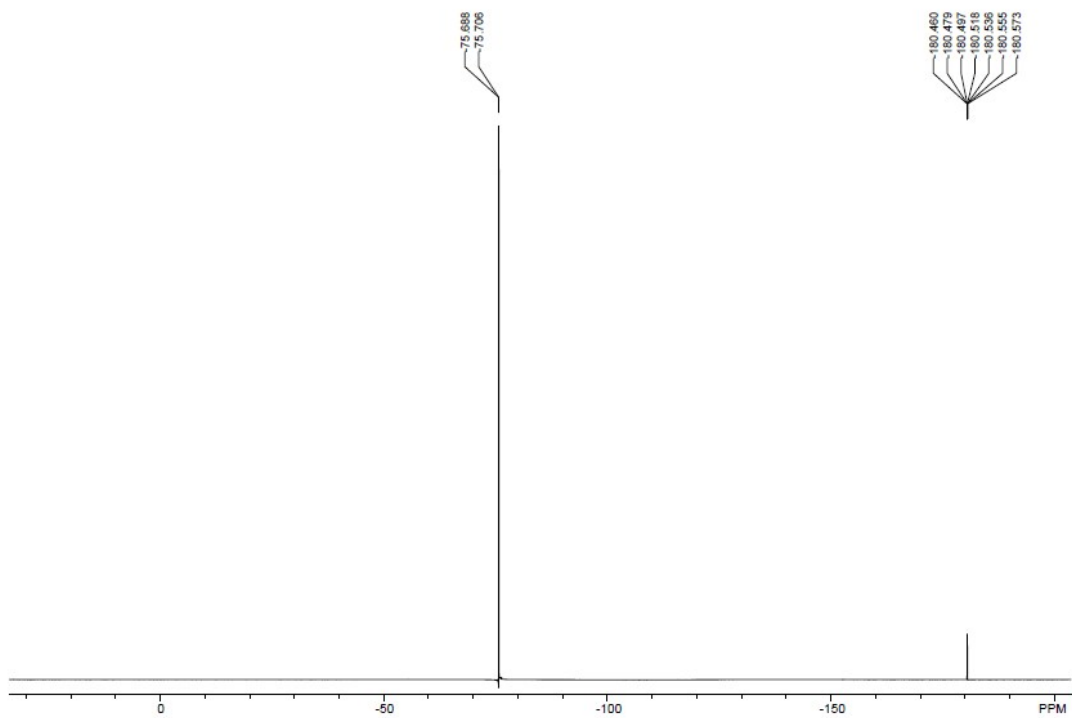
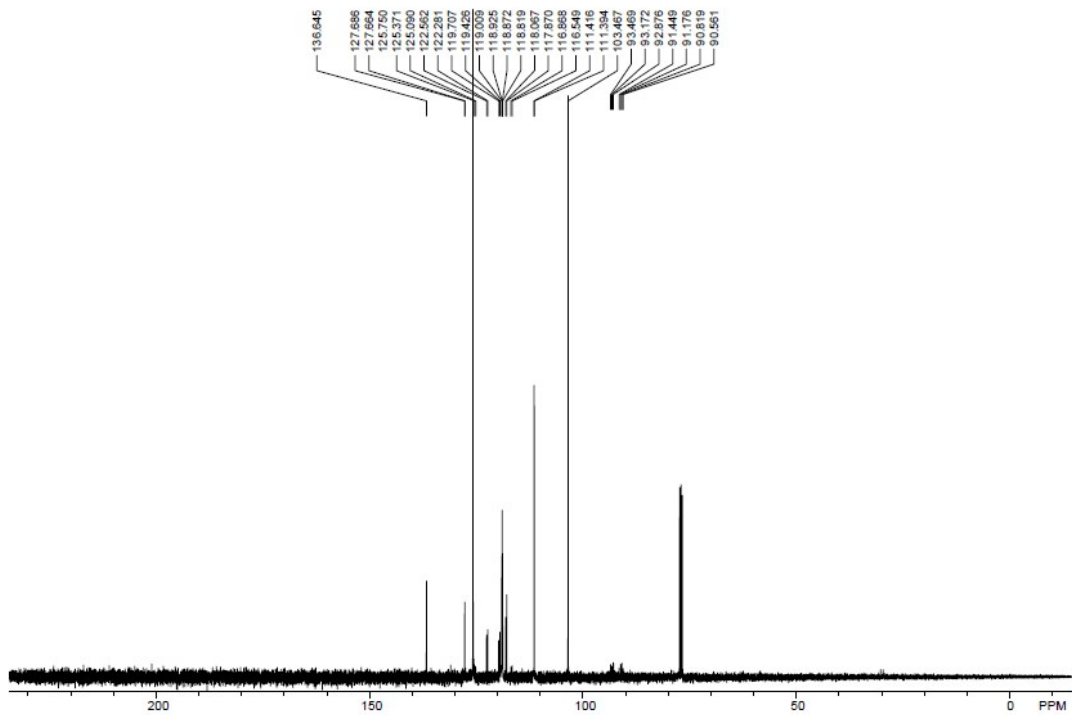
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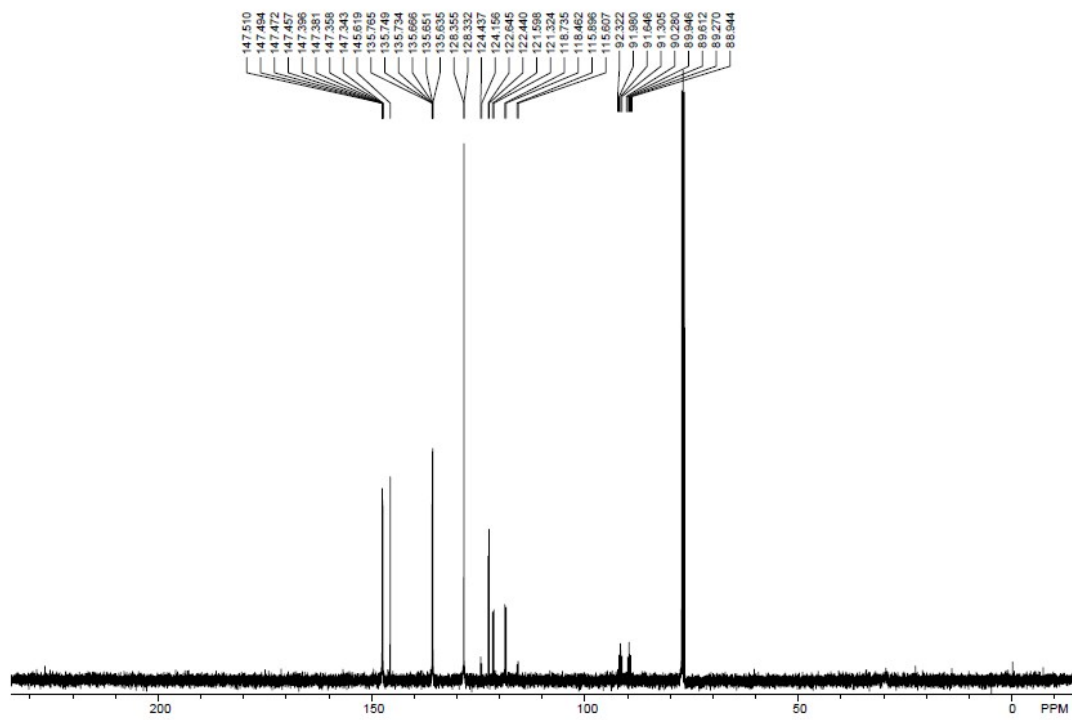
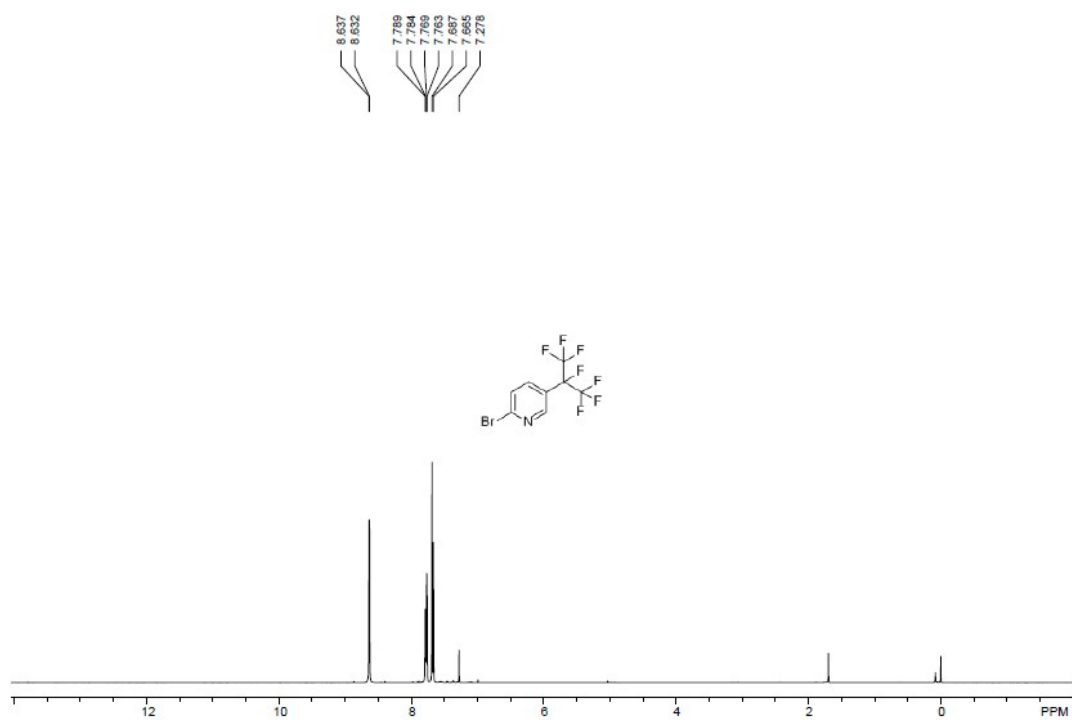


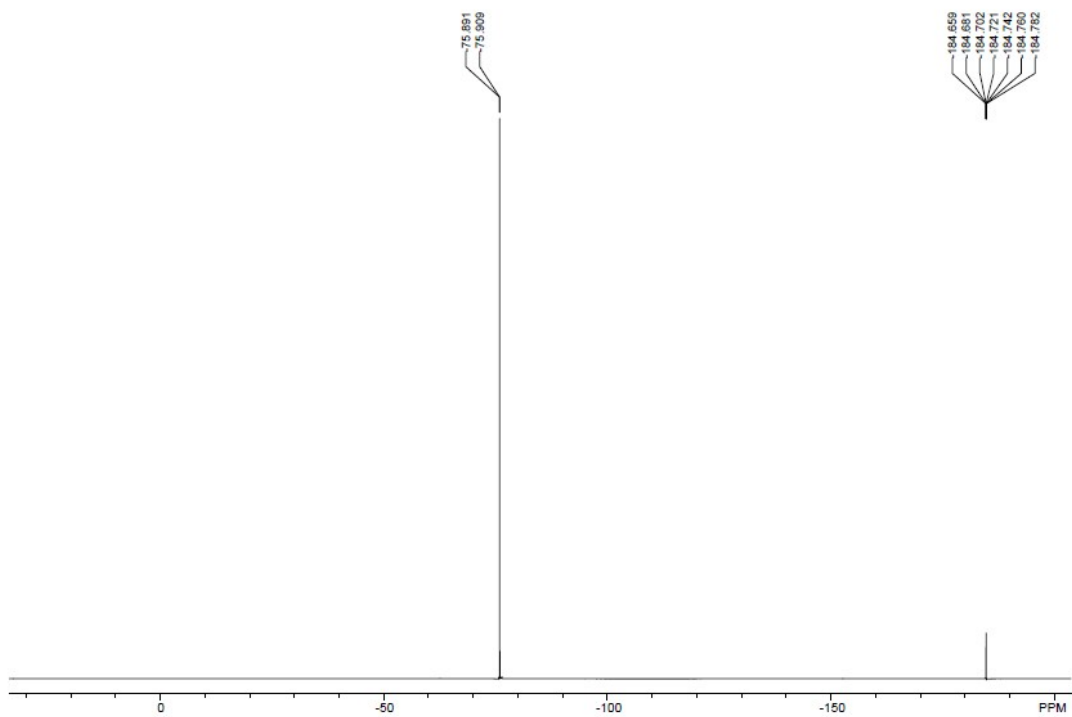
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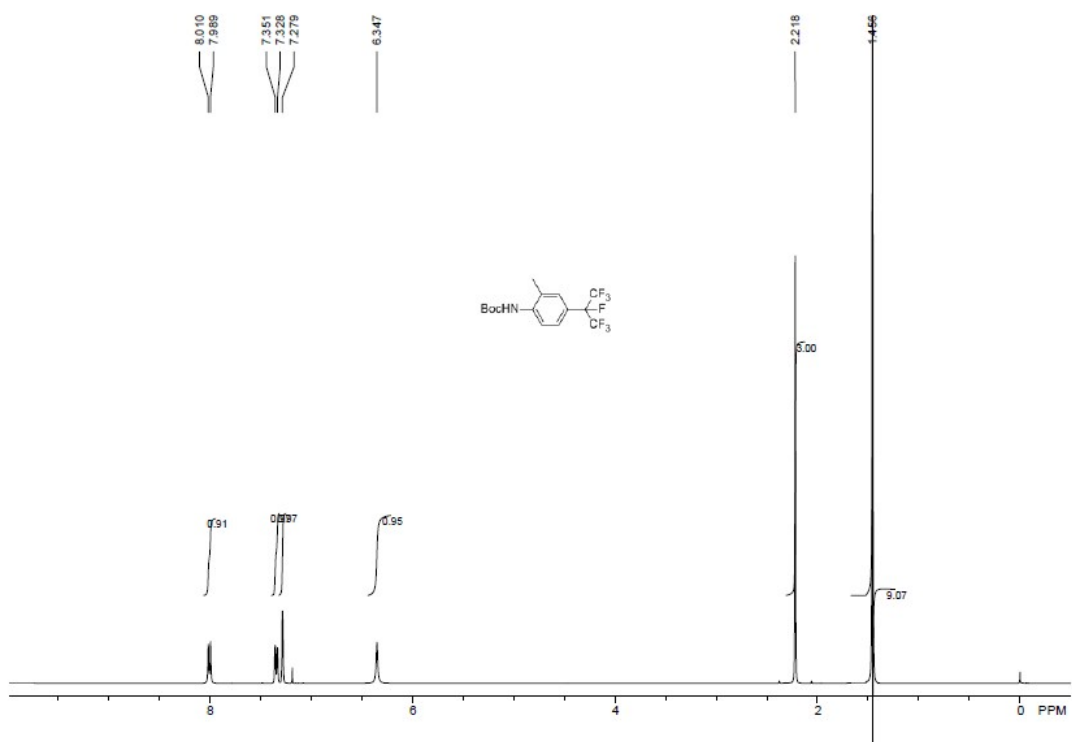


2x

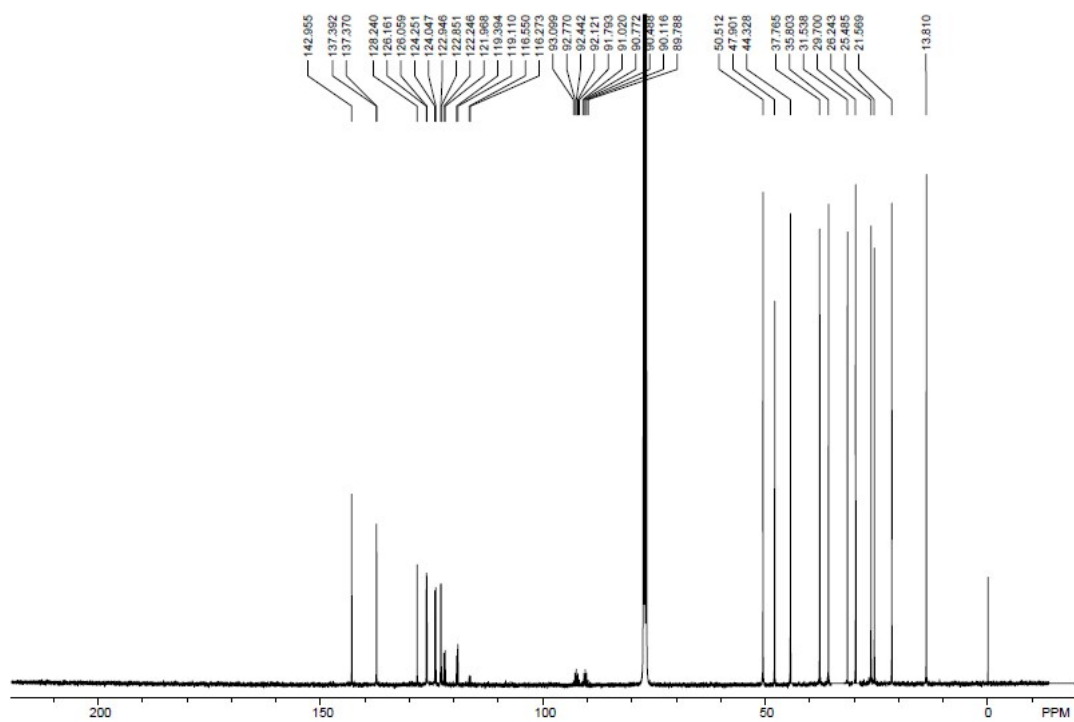
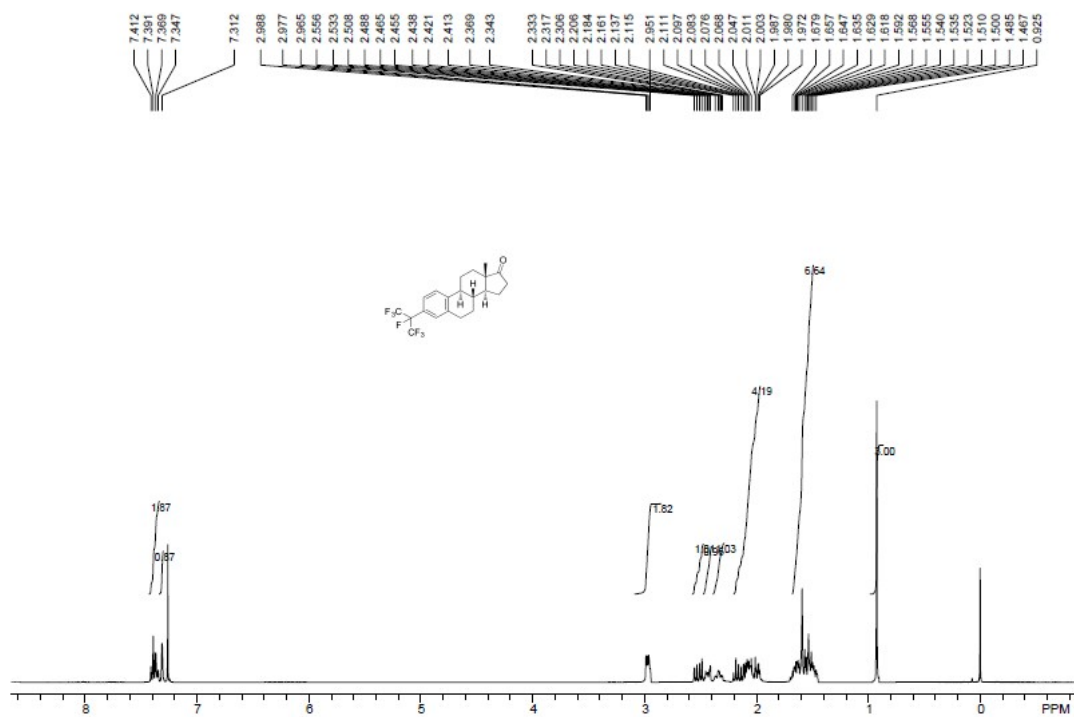


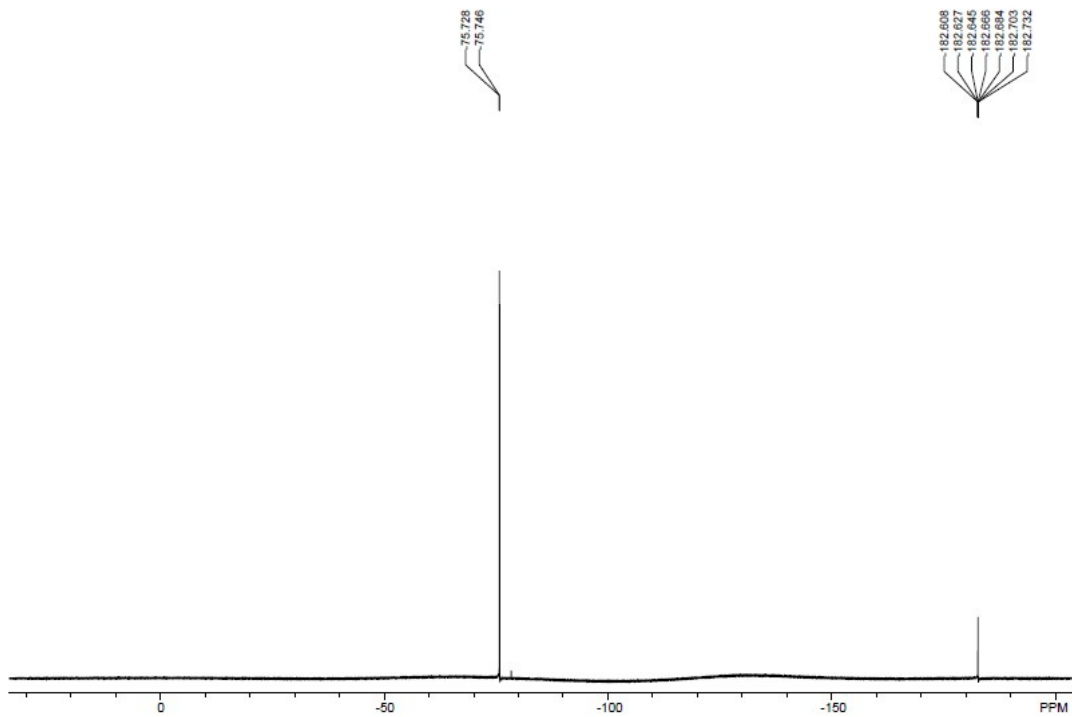


2y



2z





4

