

Supporting Information

Direct NF₂ Functionalization of Ketones: A Mild Strategy for Accessing High-Performance *gem*-Difluoroamino Compounds

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1. General Information

CAUTION: Gem-Bis(difluoramines) are potentially shock-sensitive and thermolabile. They should be handled with care!

Unless otherwise stated, NMR spectra were recorded in CDCl_3 or $\text{DMSO-}d_6$ at the following frequencies: 400 MHz for ^1H NMR, 283 MHz for ^{19}F NMR and 101 MHz (or 126 MHz) for ^{13}C NMR. Analytical thin layer chromatography (TLC) was carried out on 0.25 mm SiO_2 (silica gel 60 F254, Leyan), and the spots were visualized under ultraviolet light (254 and 365 nm). All chemical shifts are reported in ppm relative to TMS or CFCl_3 (positive values indicate downfield shifts) as external standards. The IR spectral data obtained by the liquid film method. Mass spectrometry experiments were conducted using an Agilent 6110A instrument for ESI-MS, an Agilent 5973N instrument for EI-MS, and a Waters Micromass GCT Premier instrument for LRMS.

2. Preparation procedure of $\text{Me}_4\text{NSO}_3\text{NF}_2$

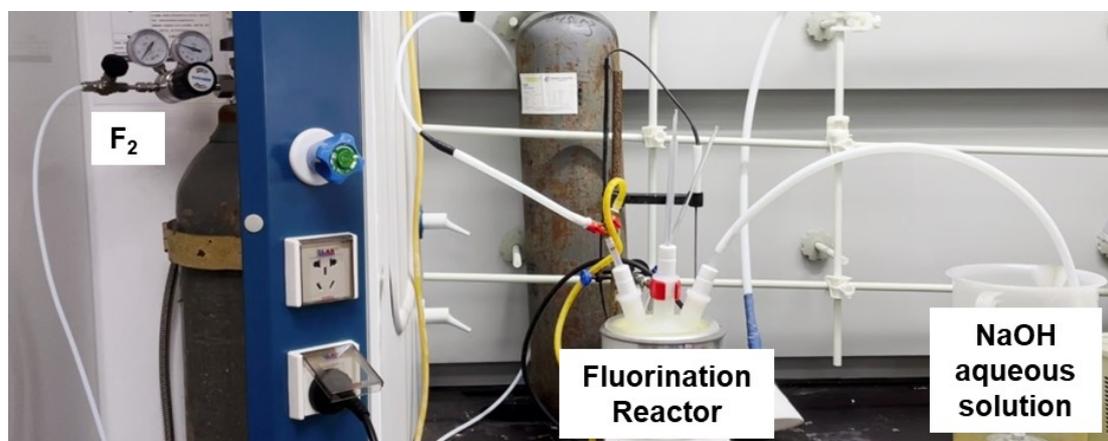


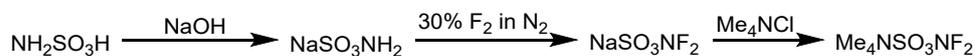
FIGURE 1 Fluorine gas fluorination reaction device

Fluorination Reactor: The fluorination reactor employed in this experiment consisted of a 1000 mL three-necked flask fabricated from polyfluoroalkoxy (PFA), with a thermometer positioned in the central neck. The inlet and outlet gas lines were also constructed from PFA to ensure chemical compatibility.

Disposal methods: Waste is quenched using a wet scrubber with 10% aqueous NaOH solution and collected separately in a clearly labeled and chemical resistant container.

Safety precautions: All experimental procedures must be performed in a properly

functioning chemical fume hood with adequate ventilation capacity. Furthermore, all gas delivery systems should employ nickel/Monel alloy components to ensure compatibility with the highly corrosive nature of elemental fluorine.

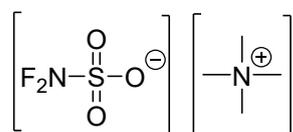


SCHEME 1 The synthesis method of Me₄NSO₃NF₂

Under a nitrogen atmosphere, aminosulfonic acid (77.7 g, 0.800 mol) and sodium hydroxide (38.4 g, 0.960 mol) were dissolved in water (250 mL) in a 1000 mL three-necked flask fabricated from polyfluoroalkoxy (PFA), which was cooled with an ice bath. Subsequently, 30% fluorine gas (F₂) in nitrogen (N₂) (1 mL/s) was introduced. The reaction was stirred at 0-5°C for 8 hours, with completion monitored by ¹⁹F NMR spectroscopy (30% F₂/N₂ gas flow was stopped, and the system was purged with nitrogen gas to remove any residual fluorine. After purging, aliquots were carefully withdrawn from the reaction mixture and analyzed by ¹⁹F NMR to monitor the progress of the reaction).

The ice bath was maintained, and a sodium hydroxide solution (68 g NaOH in 250 mL H₂O) was added dropwise to adjust the PH to neutral. The mixture was then filtered using a Buchner funnel, and the filtrate was transferred to a 1 L single-necked flask. A solution of tetramethylammonium chloride (87.7g Me₄NCl, 0.800 mol, in 100 mL H₂O) was added dropwise while stirring. After 20 minutes of dropwise addition, the mixture was stirred for an additional hour. The product was filtered through a Buchner funnel and then dried using a freeze dryer for 12 hours. The resulting Me₄NSO₃NF₂ was obtained as a white powder (141.0 g, 0.684 mol, 85.5 % yield) (**Scheme 1**). This reagent demonstrated long-term stability, with no detectable decomposition over a six-month period at room temperature, even in the absence of inert gas protection.

3. Characterization Data for Me₄NSO₃NF₂



Tetramethyl ammonium difluoroamine sulfonate. White solid. Yield: 85.5 %. $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 3.10 (s, 12H). $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 54.87 (t, $J=3.89$ Hz). $^{19}\text{F NMR}$ (283 MHz, $\text{DMSO-}d_6$) δ 34.88 ppm. **IR (KBr):** $\tilde{\nu}$ = 3433, 3044, 1491, 1420, 1282, 1067, 950, 851, 703, 614, 556, 527, 515. **Calcd for $\text{C}_4\text{H}_{12}\text{F}_2\text{N}_2\text{O}_3\text{S}$:** C 23.30, H 5.87, N 13.59, F 18.43, S 15.55; **Found** C 22.38, H 5.88, N 12.79, F 18.19, S 15.33.

4. Preparation procedure of *gem*-difluoroamination products

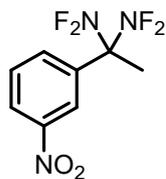
Aromatic ketones (4.0 mmol, 1.0 equiv.) and 2.474 g of $\text{Me}_4\text{NSO}_3\text{NF}_2$ (12.0 mmol, 3.0 equiv.) were dissolved in 12.0 mL of dichloromethane. The reaction flask was then transferred to an ice bath and cooled to 0-5 °C. Then, 1.6 mL of 20% fuming sulfuric acid was added dropwise, keeping the internal temperature below 10 °C. After addition, stirring was continued for 15 minutes, and then heated to 25 °C and stirred for 0.5 h. The reaction mixture was slowly poured into 30.0 mL of ice water, and the system was separated into layers. The organic phase was extracted three times with dichloromethane, and the organic phases were combined. Dry the organic phase with anhydrous sodium sulfate and concentrate to obtain crude product. The crude product is purified by column chromatography to obtain the pure product.

5. Product Characterization Data

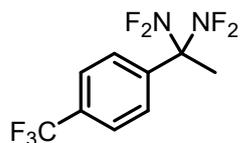


***N,N,N',N'*-tetrafluoro-1-(4-nitrophenyl)ethane-1,1-diamine (2a) Yellow liquid. Yield: 95.3 %.** $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.33 (d, $J = 8.98$ Hz, 2H), 7.85 (d, $J = 8.80$ Hz, 2H), 2.16 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 149.20, 136.12, 129.78, 123.57, 98.34 (t, $J = 9.40$ Hz), 10.52 (tt, $J = 8.26$, 6.32 Hz). $^{19}\text{F NMR}$ (283 MHz, CDCl_3) δ 29.49 (dd, $J = 622.6\text{Hz}$, 885.8 Hz). **IR (KBr):** $\tilde{\nu}$ = 3122, 3089, 2870, 1611, 1530, 1498, 1460, 1414, 1385, 1351, 1324, 1295, 1269, 1196, 1112, 978, 934,

895, 879, 851, 827, 748, 708, 696, 657, 619, 539, 475, 440 cm^{-1} . **HRMS(FI)** m/z : calculated for $[\text{M}+\text{H}]^+$ 254.0547. found 254.0554.



N,N,N',N'-tetrafluoro-1-(3-nitrophenyl)ethane-1,1-diamine (2b) Yellow liquid. Yield: 71.1 %. **^1H NMR (400 MHz, CDCl_3)**: δ 8.51 (q, $J = 1.65$ Hz, 1H), 8.39 (dd, $J = 8.27, 2.19$ Hz, 1H), 8.01 (d, $J = 7.95$ Hz, 1H), 7.72 (t, $J = 8.09$ Hz, 1H), 2.18 (s, 3H). **^{13}C NMR (101 MHz, CDCl_3)**: δ 148.29, 134.44, 131.72, 129.85, 125.68, 123.73, 98.33 (t, $J = 9.47$ Hz), δ 10.40 (tt, $J = 8.33, 6.49$ Hz). **^{19}F NMR (283 MHz, CDCl_3)** δ 29.26 (dd, $J = 619.8\text{Hz}, 863.2\text{Hz}$). **IR (KBr)**: $\tilde{\nu} = 3096, 2880, 1619, 1537, 1486, 1461, 1439, 1385, 1354, 1298, 1265, 1181, 1121, 1100, 1075, 979, 938, 899, 877, 838, 808, 759, 735, 709, 687, 642, 601, 545, 414$ cm^{-1} . **HRMS(FI)** m/z : calculated for $[\text{M}+\text{H}]^+$ 254.0547. found 254.0551.



N,N,N',N'-tetrafluoro-1-(4-(trifluoromethyl)phenyl)ethane-1,1-diamine (2c) Yellow liquid. Yield: 66.6 %. **^1H NMR (400 MHz, CDCl_3)**: δ 7.75 (q, $J = 8.61$ Hz, 4H), 2.12 (s, 3H). **^{13}C NMR (101 MHz, CDCl_3)**: δ 133.62, 132.87 (q, $J = 33.07$ Hz), 127.55, 125.54 (q, $J = 3.73$ Hz), 123.48 (q, $J = 272.43$ Hz), 98.55 (t, $J = 9.49$ Hz), 10.19 (tt, $J = 8.57, 6.37$ Hz). **^{19}F NMR (283 MHz, CDCl_3)** δ 29.09 (dd, $J = 619.6\text{Hz}, 871.5\text{Hz}$), -63.98 (d, $J = 7.13$ Hz). **IR (KBr)**: $\tilde{\nu} = 2968, 1623, 1450, 1417, 1385, 1328, 1271, 1175, 1136, 1068, 1021, 979, 934, 880, 856, 820, 743, 722, 689, 660, 621, 512, 422$ cm^{-1} . **HRMS(FI)** m/z : calculated for $[\text{M}]^+$ 276.0492. found 276.0488.

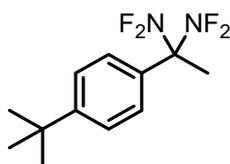


N,N,N',N'-tetrafluoro-1-(4-fluorophenyl)ethane-1,1-diamine (2d) Yellow liquid. Yield: 42.2 %. **^1H NMR (400 MHz, CDCl_3)**: δ 7.62 (dd, $J = 8.70, 5.14$ Hz, 2H), 7.16 (t, $J = 8.57$ Hz, 2H), 2.08 (s, 3H). **^{13}C NMR (101 MHz, CDCl_3)**: δ 164.00 (d, $J = 251.93$ Hz), 130.62 (d, $J = 8.71$ Hz), 125.81, 115.76 (d, $J = 21.91$ Hz), 98.68 (t, $J = 9.49$ Hz), 10.01 (p, $J = 7.60$ Hz). **^{19}F NMR (283 MHz, CDCl_3)**

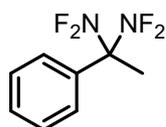
δ 29.06 (dd, $J = 611.3\text{Hz}$, 721.7Hz), -109.83 (dt, $J = 10.90$, 5.73 Hz). **IR (KBr):** $\tilde{\nu} = 2930$, 1608 , 1515 , 1460 , 1417 , 1383 , 1271 , 1245 , 1170 , 1102 , 997 , 977 , 932 , 877 , 859 , 821 , 734 , 659 , 583 , 569 , 546 , 511 , 482 cm^{-1} . **HRMS(FI)** m/z : calculated for $[\text{M}]^+$ 226.0524 . found 226.0525 .



1-(4-bromophenyl)-N,N,N',N'-tetrafluoroethane-1,1-diamine (2e) Yellow liquid. Yield: 91.4 %. **^1H NMR (400 MHz, CDCl_3):** δ 7.60 (d, $J = 8.74$ Hz, 2H), 7.49 (d, $J = 8.45$ Hz, 2H), 2.06 (s, 3H). **^{13}C NMR (101 MHz, CDCl_3):** δ 131.91, 130.01, 128.88, 125.61, 98.76 (t, $J = 9.54$ Hz), δ 9.98 (tt, $J = 8.69$, 6.67 Hz). **^{19}F NMR (283 MHz, CDCl_3)** δ 29.12(dd, $J = 616.9\text{Hz}$, 792.4Hz). **IR (KBr):** $\tilde{\nu} = 3023$, 2966 , 1913 , 1593 , 1496 , 1460 , 1404 , 1382 , 1194 , 1095 , 1074 , 1013 , 997 , 977 , 930 , 877 , 852 , 807 , 728 , 685 , 657 , 613 , 541 , 512 , 420 cm^{-1} . **HRMS(FI)** m/z : calculated for $[\text{M}]^+$ 285.9723 . found 285.9728 .



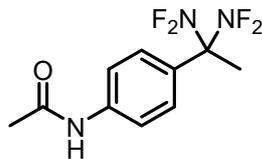
1-(4-(tert-butyl)phenyl)-N,N,N',N'-tetrafluoroethane-1,1-diamine (2f) Brown solid. Yield: 51.5 %. **^1H NMR (400 MHz, CDCl_3):** δ 7.54 (d, $J = 8.40$ Hz, 2H), 7.47 (d, $J = 8.71$ Hz, 2H), 2.07 (s, 3H), 1.33 (s, 9H). **^{13}C NMR (101 MHz, CDCl_3):** δ 154.00, 128.07, 126.95, 125.56, 99.08 (t, $J = 9.54$ Hz), 34.74, 31.08, 9.93 (tt, $J = 8.75$, 6.53 Hz).. **^{19}F NMR (283 MHz, CDCl_3)** δ 29.08 (dd, $J = 611.3\text{Hz}$, 781.1Hz). **IR (KBr):** $\tilde{\nu} = 3437$, 2967 , 2907 , 2871 , 1613 , 1514 , 1477 , 1462 , 1416 , 1382 , 1366 , 1272 , 1204 , 1165 , 1123 , 1085 , 975 , 929 , 875 , 815 , 696 , 659 , 571 cm^{-1} . **HRMS(FI)** m/z : calculated for $[\text{M}]^+$ 264.1244 . found 264.1239 .



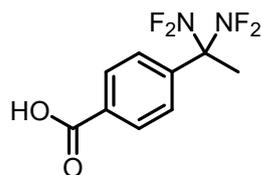
N,N,N',N'-tetrafluoro-1-phenylethane-1,1-diamine (2g) Yellow liquid. Yield: 51.4 %. **^1H NMR (400 MHz, CDCl_3):** δ 7.63 – 7.61 (m, 2H), 7.50 – 7.42 (m, 3H), 2.08 (p, $J = 2.22$ Hz, 3H). **^{13}C NMR (101 MHz, CDCl_3):** δ 130.75, 130.03, 128.61, 128.36, 99.14 (t, $J = 9.23$ Hz), 9.82 (tt, $J = 8.88$, 6.74 Hz). **^{19}F NMR (283 MHz, CDCl_3)** δ 29.13 (dd, $J = 611.3\text{Hz}$, 772.6Hz). **IR (KBr):** $\tilde{\nu} = 3068$, 1500 ,

1451, 1383, 1271, 1131, 1076, 976, 933, 878, 851, 753, 698, 657, 641, 594, 542, 497 cm^{-1} .

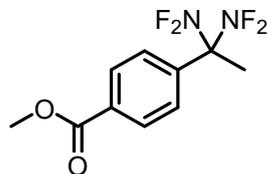
HRMS(FI) m/z : calculated for $[\text{M}]^+$ 208.0618. found 208.0620.



N-(4-(1,1-bis(difluoroamino)ethyl)phenyl)acetamide (2h) White solid. Yield: 94.5 %. ^1H NMR (400 MHz, CDCl_3): δ 7.70 (s, 1H), 7.62 (d, $J = 8.51$ Hz, 2H), 7.55 (d, $J = 8.50$ Hz, 2H), 2.18 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 168.77, 140.12, 129.30, 125.26, 119.40, 98.88 (t, $J = 8.76$ Hz), 24.54, 9.86 (t, $J = 7.22$ Hz). ^{19}F NMR (283 MHz, CDCl_3) δ 29.09 (dd, $J = 614.1\text{Hz}, 741.5\text{Hz}$). IR (KBr): $\tilde{\nu} = 3298, 3261, 3193, 3120, 3061, 2917, 1673, 1610, 1552, 1462, 1410, 1383, 1326, 1271, 1190, 1038, 997, 977, 931, 890, 871, 814, 740, 689, 550$ cm^{-1} . **HRMS(FI)** m/z : calculated for $[\text{M}]^+$ 265.0833. found 265.0837.

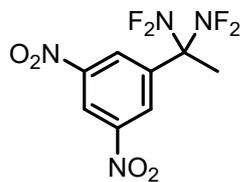


4-(1,1-bis(difluoroamino)ethyl)benzoic acid (2i) White solid. Yield: 80.9 %. ^1H NMR (400 MHz, CDCl_3): δ 11.58 (s, 1H), 8.21 (d, $J = 8.17$ Hz, 2H), 7.76 (d, $J = 8.18$ Hz, 2H), 2.14 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 171.35, 135.29, 131.40, 130.28, 128.68, δ 98.71 (t, $J = 9.30$ Hz), 10.25 (t, $J = 7.34$ Hz). ^{19}F NMR (283 MHz, CDCl_3) δ 29.34 (dd, $J = 619.8\text{Hz}, 860.3\text{Hz}$). IR (KBr): $\tilde{\nu} = 3020, 2673, 2549, 1698, 1615, 1578, 1422, 1384, 1324, 1286, 1198, 1131, 977, 931, 893, 871, 857, 831, 767, 713, 616, 542$ cm^{-1} . **HRMS(FI)** m/z : calculated for $[\text{M}+\text{H}]^+$ 253.0595. found 253.0598.

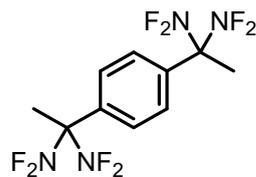


methyl 4-(1,1-bis(difluoroamino)ethyl)benzoate (2j) Yellow liquid. Yield: 76.0 %. ^1H NMR (400 MHz, CDCl_3): δ 8.12 (d, $J = 8.53$ Hz, 2H), 7.71 (d, $J = 8.37$ Hz, 2H), 3.94 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 165.99, 134.25, 132.33, 129.62, 128.48, 98.76 (t, $J = 9.46$ Hz), 52.32, 10.09 (tt, $J = 8.60, 6.43$ Hz). ^{19}F NMR (283 MHz, CDCl_3) δ 29.25 (dd, $J = 620.4\text{Hz}, 844.2\text{Hz}$). IR (KBr): $\tilde{\nu} = 3005, 2957, 2848, 1943, 1731, 1615, 1578, 1438, 1414, 1384, 1285, 1196, 1119, 1021,$

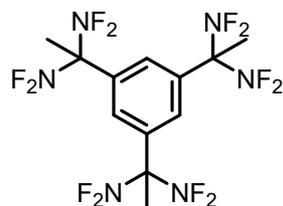
977, 932, 878, 857, 827, 765, 714, 658, 619, 544, 495, 424 cm^{-1} . **HRMS(FI)** m/z : calculated for $[\text{M}]^+$ 266.0673. found 266.0668.



1-(3,5-dinitrophenyl)-N,N,N',N'-tetrafluoroethane-1,1-diamine (2k) Yellow liquid. Yield: 37.6%. **^1H NMR (400 MHz, CDCl_3)**: δ 9.21 (t, $J = 2.12$ Hz, 1H), 8.83 (d, $J = 2.03$ Hz, 2H), 2.26 (t, $J = 2.26$ Hz, 3H). **^{13}C NMR (101 MHz, CDCl_3)**: δ 148.69, 133.65, 128.92, 121.06, 97.73 (t, $J = 9.25$ Hz), 10.97 (p, $J = 7.35, 6.85$ Hz). **^{19}F NMR (283 MHz, CDCl_3)** δ 29.79 (dd, $J = 630.2\text{Hz}, 934.0\text{Hz}$). **IR (KBr)**: $\tilde{\nu} = 3108, 2886, 1843, 1633, 1599, 1549, 1463, 1387, 1345, 1321, 1276, 1151, 1114, 1081, 981, 947, 921, 879, 837, 771, 731, 712, 673, 605, 434$ cm^{-1} . **HRMS(FI)** m/z : calculated for $[\text{M}+\text{H}]^+$ 299.0398. found 299.0393.

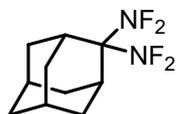


1,1'-(1,4-phenylene)bis(N,N,N',N'-tetrafluoroethane-1,1-diamine) (2l) White solid. Yield: 80.7%. *Except for 2l, the equivalent of other reagents is twice that of acetophenone.* **^1H NMR (400 MHz, CDCl_3)**: δ 7.73 (s, 4H), 2.11 (s, 6H). **^{13}C NMR (101 MHz, CDCl_3)**: δ 132.50, 128.66, 98.54 (t, $J = 9.62$ Hz), 10.48-10.19 (m). **^{19}F NMR (283 MHz, CDCl_3)** δ 29.26 (dd, $J = 620.9\text{Hz}, 916.3\text{Hz}$). **IR (KBr)**: $\tilde{\nu} = 3445, 3030, 2924, 1942, 1816, 1520, 1462, 1418, 1384, 1271, 1244, 1128, 1110, 975, 932, 893, 873, 849, 811, 707, 685, 659, 553, 540, 518, 482$ cm^{-1} . **HRMS(FI)** m/z : calculated for $[\text{M}]^+$ 338.0772. found 338.0776.

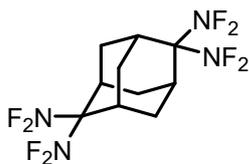


1,1',1''-(benzene-1,3,5-triyl)tris(N,N,N',N'-tetrafluoroethane-1,1-diamine) (2m) White solid. Yield: 22.5%. *Except for 2m, the equivalent of other reagents is three times that of acetophenone.* **^1H NMR (400 MHz, CDCl_3)**: δ 8.00 (s, 3H), 2.15 (s, 9H). **^{13}C NMR (101 MHz, CDCl_3)**: δ 131.32,

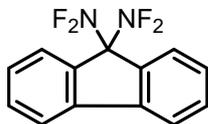
130.82, 98.28 (t, $J = 9.27$ Hz), 10.6-10.43 (m). ^{19}F NMR (283 MHz, CDCl_3) δ 28.90 (dd, $J = 624.1$ Hz, 970.6 Hz). IR (KBr): $\tilde{\nu} = 3110, 2921, 2850, 1611, 1465, 1386, 1249, 1130, 1081, 981, 952, 925, 899, 876, 827, 795, 720, 691, 662, 634, 606, 486$ cm^{-1} . HRMS(FI) m/z : calculated for $[\text{M}-\text{NF}_2]^+$ 416.0928. found 416.0933.



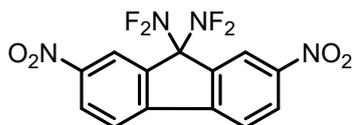
2,2-bis-difluoroaminoadamantane (2q) White solid. Yield: 98.2 %. ^1H NMR (400 MHz, CDCl_3): δ 2.49 (s, 2H), 2.23 (d, $J = 13.16$ Hz, 4H), 1.99 (t, $J = 3.39$ Hz, 2H), 1.77 (d, $J = 8.91$ Hz, 4H), 1.73 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ 94.79, 37.42, 32.64, 31.83 (p, $J = 3.45$ Hz), 26.40. ^{19}F NMR (283 MHz, CDCl_3) δ 12.95. IR (KBr): $\tilde{\nu} = 3448, 2950, 2928, 2871, 2679, 1456, 1361, 1344, 1283, 1252, 1105, 1067, 1018, 969, 913, 878, 834, 670, 512$ cm^{-1} . HRMS(FI) m/z : calculated for $[\text{M}-\text{H}]^-$ 237.1003. found 237.1009.



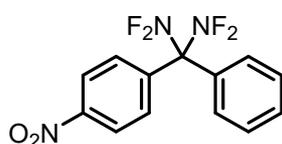
2,2,6,6-tetra-difluoroaminoadamantane (2r) White solid. Yield: 98.0 %. Except for Ir, the equivalent of other reagents is twice that of acetophenone. ^1H NMR (400 MHz, CDCl_3): δ 2.61 (s, 4H), 2.27 (s, 8H). ^{13}C NMR (101 MHz, CDCl_3): δ 92.53 (t, $J = 4.65$ Hz), 30.16 (p, $J = 3.58$ Hz), 27.32. ^{19}F NMR (283 MHz, CDCl_3) δ 13.09. IR (KBr): $\tilde{\nu} = 2973, 2882, 1460, 1350, 1322, 1293, 1057, 966, 917, 886, 836, 686, 666, 507, 467$ cm^{-1} . HRMS(FI) m/z : calculated for $[\text{M}]^+$ 340.0929. found 340.0925.



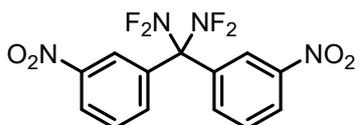
N,N,N',N'-tetrafluoro-9H-fluorene-9,9-diamine (2s) White solid. Yield: 34.3 %. ^1H NMR (400 MHz, CDCl_3): δ 7.78 (d, $J = 7.67$ Hz, 2H), 7.69 (d, $J = 7.62$ Hz, 2H), 7.55 (t, $J = 7.57$ Hz, 2H), 7.38 (td, $J = 7.56, 1.09$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ 142.55, 132.38, 128.58, 128.25, 128.23, 128.21, 120.67. ^{19}F NMR (283 MHz, CDCl_3) δ 35.07. IR (KBr): $\tilde{\nu} = 3448, 3068, 2926, 1607, 1489, 1477, 1454, 1405, 1304, 1205, 1186, 1159, 1081, 1032, 980, 961, 910, 893, 874, 856, 758, 732, 691, 671, 649, 621, 418$ cm^{-1} . HRMS(FI) m/z : calculated for $[\text{M}]^+$ 268.0618. found 268.0621.



N,N,N',N'-tetrafluoro-2,7-dinitro-9H-fluorene-9,9-diamine (2t) Yellow solid. Yield: 98.2 %. ¹H NMR (400 MHz, CDCl₃): δ 8.70 (d, *J* = 2.08 Hz, 2H), 8.60 (dd, *J* = 8.45, 2.10 Hz, 2H), 8.04 (d, *J* = 8.41 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 149.01, 145.63, 134.54, 128.79, 123.86, 122.69. ¹⁹F NMR (283 MHz, CDCl₃) δ 35.89. IR (KBr): $\tilde{\nu}$ = 3111, 2862, 1616, 1597, 1522, 1488, 1457, 1344, 1268, 1231, 1202, 1127, 1089, 971, 934, 896, 847, 738, 706, 672, 649, 424 cm⁻¹. HRMS(FI) *m/z*: calculated for [M]⁺ 358.0320. found 358.0323.



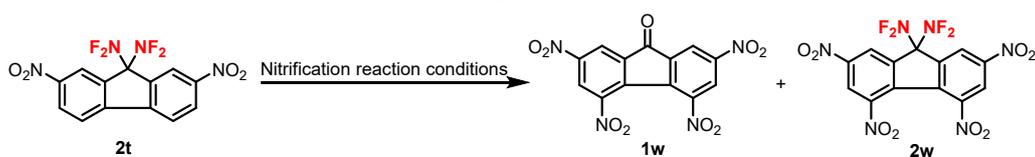
N,N,N',N'-tetrafluoro-1-(4-nitrophenyl)-1-phenylmethanediamine (2u) Yellow solid. Yield: 16.0 %. ¹H NMR (400 MHz, CDCl₃): δ 8.33 – 8.31 (m, 2H), 7.78 (d, *J* = 8.63 Hz, 2H), 7.57 (h, *J* = 4.13 Hz, 1H), 7.50 (d, *J* = 4.44 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃): δ 149.06, 135.25, 132.49, 131.12, 131.00, 128.14, 127.53, 122.71, 101.37, 101.27, 101.18. ¹⁹F NMR (283 MHz, CDCl₃) δ 28.71. IR (KBr): $\tilde{\nu}$ = 3449, 3099, 1617, 1583, 1529, 1483, 1444, 1350, 1305, 1295, 1253, 1109, 1013, 934, 920, 876, 860, 813, 748, 727, 700, 681, 629, 594 cm⁻¹. HRMS(FI) *m/z*: calculated for [M]⁺ 315.0625. found 315.0622.



N,N,N',N'-tetrafluoro-1,1-bis(3-nitrophenyl)methanediamine (2v) Yellow solid. Yield: 55.7 %. ¹H NMR (400 MHz, CDCl₃): δ 8.50 – 8.47 (m, 2H), 8.42 (d, *J* = 2.20 Hz, 2H), 7.89 (d, *J* = 7.96 Hz, 2H), 7.77 (t, *J* = 8.07 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 148.03, 136.61, 132.28, 129.56, 129.40, 126.19, 126.02, 123.22, 100.41. ¹⁹F NMR (283 MHz, CDCl₃) δ 29.16. IR (KBr): $\tilde{\nu}$ = 3449, 3099, 1617, 1583, 1529, 1483, 1444, 1350, 1305, 1295, 1253, 1109, 1013, 934, 920, 876, 860, 813, 748, 727, 700, 681, 629, 594 cm⁻¹. HRMS(FI) *m/z*: calculated for [M+H]⁺ 361.0554. found 361.0556.

6. Optimization of Nitrification Conditions for 2w

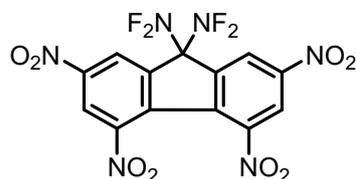
TABLE 1 Screening of reaction conditions^a



Entry	Reaction conditions	1r	2r
1	Fe(NO ₃) ₃ ·9H ₂ O, HFIP, 25°C, 12h	trace	trace
2	Fe(NO ₃) ₃ ·9H ₂ O, HFIP, T _f OH, 60°C, 12h	trace	trace
3	V(65% HNO ₃ /96% H ₂ SO ₄)=1/2, 110°C, 12h	50.2%	trace
4	V(90% HNO ₃ /96% H ₂ SO ₄)=1/2, 110°C, 12h	75.2%	15.0%
5	V(90% HNO₃/96% H₂SO₄)=1/2, 110°C, 8h	45.3%	42.2%
6	V(90% HNO ₃ /96% H ₂ SO ₄)=1/2, 110°C, 4h	50.5%	26.3%
7	V(90% HNO ₃ /96% H ₂ SO ₄)=1/2, 110°C, 2h	56.4%	10.6%
8	V(90% HNO ₃ /96% H ₂ SO ₄)=1/3, 110°C, 8h	46.9%	40.8%
9	V(90% HNO ₃ /96% H ₂ SO ₄)=1/1, 110°C, 8h	48.8%	41.6%

a. Reaction conditions: **2o** (1.0 eq, 7.0 mmol), Isolated yield.

By screening the nitration reaction conditions of **2t** (Table 1), entry 5 was ultimately determined as the optimal reaction condition. **2w** was synthesized by using the methods described by Newman et al^[1], with slight modifications. Add concentrated sulfuric acid 90mL and **2t** (2.507g 7.0 mmol) to the reaction flask, and then transfer the reaction flask to an ice bath. Under ice bath conditions, add fuming nitric acid 45mL dropwise to the bottle. After the mixed acid releases heat, remove the ice bath and heat it up to 110 °C for 8 hours of reaction. The reaction mixture was slowly poured into 600 mL of ice water, and the system was separated into layers. The organic phase was extracted three times with dichloromethane, and the organic phases were combined. Dry the organic phase with anhydrous sodium sulfate and concentrate to obtain crude product. The crude product is purified by column chromatography to obtain **2w** (42.2%, 2.954 mmol, 1.324g).



N,N,N',N'-tetrafluoro-2,4,5,7-tetranitro-9H-fluorene-9,9-diamine (2w) Yellow solid. Yield: 42.2 %. ¹H NMR (400 MHz, CDCl₃) δ 9.11 (d, *J* = 2.06 Hz, 2H), 8.97 (d, *J* = 2.04 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 149.28, 147.09, 137.27, 135.74, 126.32, 124.65. ¹⁹F NMR (283 MHz, CDCl₃) δ 35.78. IR (KBr): $\tilde{\nu}$ = 3446, 3100, 2960, 1734, 1618, 1603, 1557, 1538, 1446, 1345, 1308, 1220,

1190, 1100, 983, 945, 929, 904, 886, 792, 772, 732, 721, 706, 658, 423 cm^{-1} . **HRMS(FI)** m/z :
calculated for $[\text{M}]^+$ 448.0021. found 448.0026.

7. Crystal structure of **2m** and **2r**

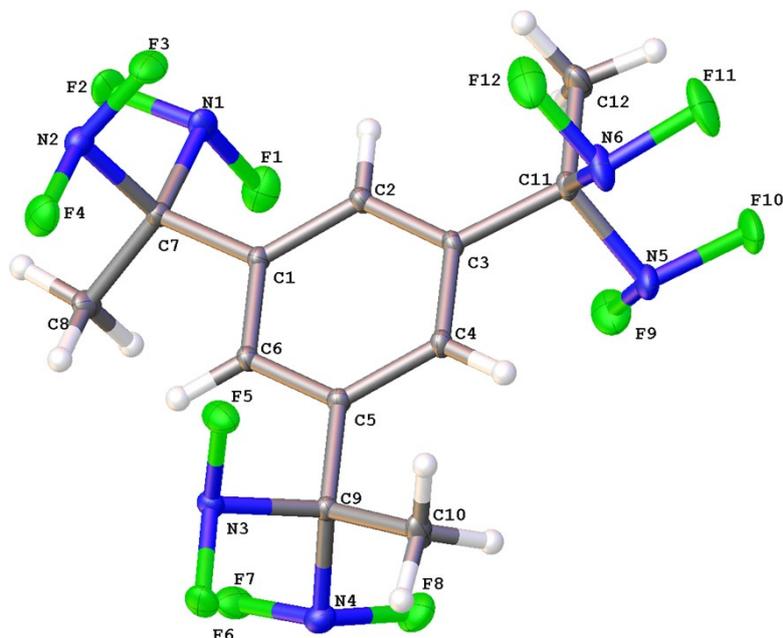


FIGURE 2 Molecular structure of **2m**

Figure 2 shows the molecular structure of compounds **2m**. The crystal of compound **2m** was obtained by volatilizing from a mixed solvent of petroleum ether and ethyl acetate. Specific crystal data are shown in **Table 2**. Crystal analysis results show that **2m** crystal belongs to monoclinic, P 1 21/n 1 space group with $a=9.60800(10)$ Å, $b=9.00020(10)$ Å, $c=20.4814(3)$ Å, $\alpha=\gamma=90^\circ$, $\beta=95.0680(10)^\circ$ unit cell parameters, The unit cell volume is $1764.18(4)$ Å³, each unit cell contains 4 molecules ($Z=4$), and the crystal density is 1.763 $\text{g}\cdot\text{cm}^{-3}$ (170.00 K).

TABLE 2 Crystal structure data of **2m**

Compound	2m
CCDC	2515239
Empirical formula	$\text{C}_{12}\text{H}_{12}\text{F}_{12}\text{N}_6$
Formula weight	468.28
Temperature	170.00 K
Crystal system	Monoclinic
Space group	P 1 21/n 1

a	9.60800(10) Å
b	9.00020(10) Å
c	20.4814(3) Å
α	90°
β	95.0680(10)°
γ	90°
Volume	1764.18(4) Å ³
Z	4
Density (calculated)	1.763 Mg/m ³
Absorption coefficient	1.204 mm ⁻¹
F(000)	936
Crystal size	0.18 x 0.17 x 0.05 mm ³
Theta range for data collection	3.770 to 63.449°
Index ranges	-12<=h<=12, -12<=k<=9, -26<=l<=27
Reflections collected	14636
Independent reflections	4341 [R(int) = 0.0386]
Data / restraints / parameters	4341 / 0 / 274
Goodness-of-fit on F ²	1.052
Final R indices [I>2 σ (I)]	R1 = 0.0401, wR2 = 0.1128
R indices (all data)	R1 = 0.0460, wR2 = 0.1165
Largest diff. peak and hole	0.804 and -0.288 e.Å ⁻³

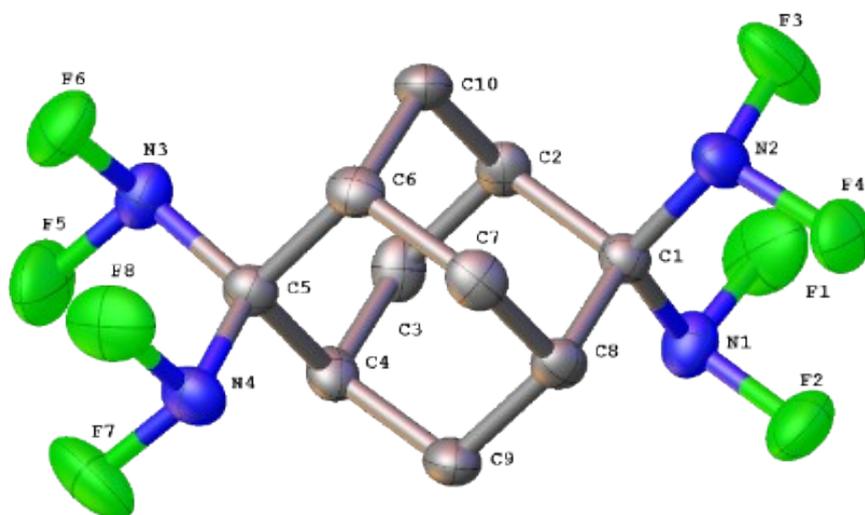


FIGURE 3 Molecular structure of **2r**

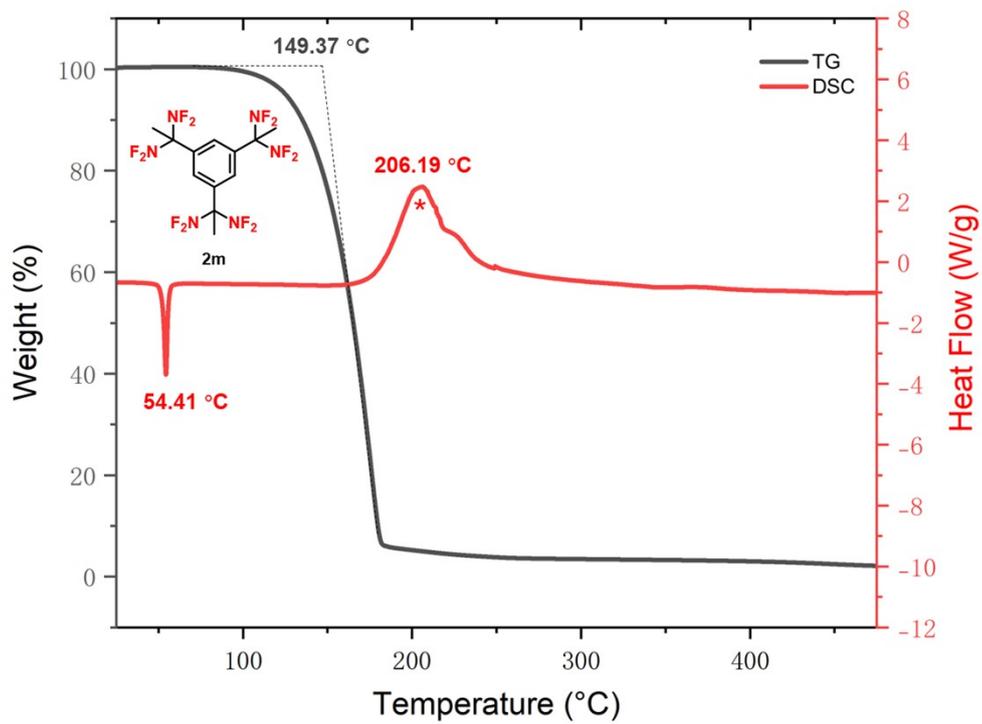
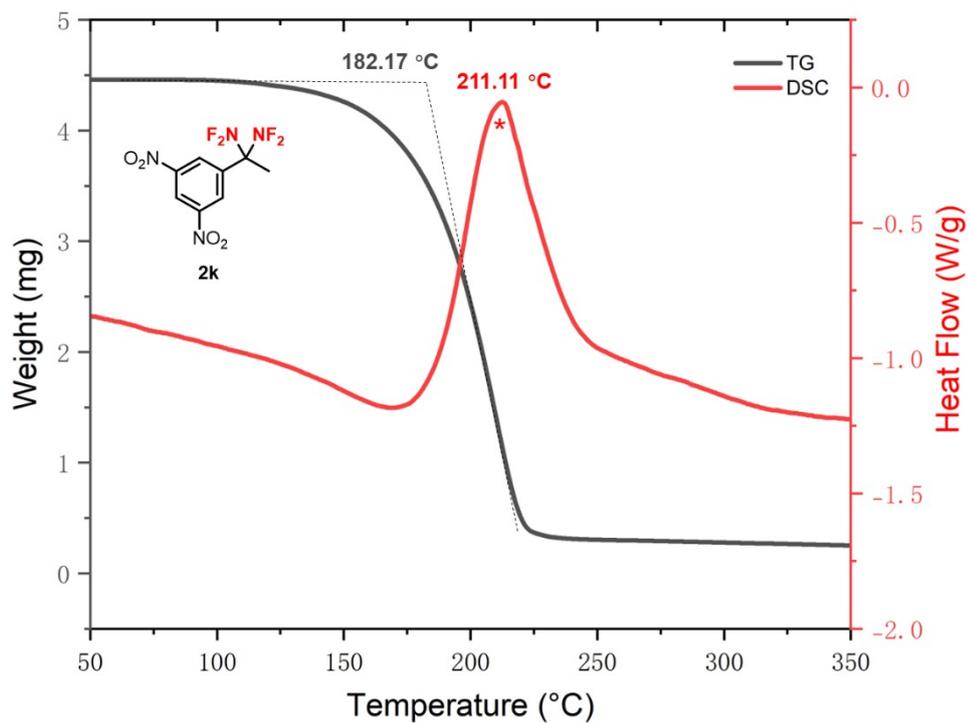
Figure 3 shows the molecular structure of compounds **2r**. The crystal of compound **2r** was obtained by volatilizing from a mixed solvent of petroleum ether and ethyl acetate. Specific crystal

data are shown in **Table 3**. Crystal analysis results show that **2r** crystal belongs to orthorhombic, $P2_12_12_1$ space group with $a=7.4094(4)$ Å, $b=7.8335(4)$ Å, $c=21.8556(11)$ Å, $\alpha=\beta=\gamma=90^\circ$ unit cell parameters, The unit cell volume is $1268.53(11)$ Å³, each unit cell contains 4 molecules ($Z=4$), and the crystal density is 1.782 g·cm⁻³(296.00 K).

TABLE 3 Crystal structure data of **2r**

Compound	2r
CCDC	2518732
Empirical formula	C ₁₀ H ₁₂ F ₈ N ₄
Formula weight	340.24
Temperature	296.00 K
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a	7.4094(4) Å
b	7.8335(4) Å
c	21.8556(11) Å
a	90°.
b	90°.
g	90°.
Volume	1268.53(11) Å ³
Z	4
Density (calculated)	1.782 Mg/m ³
Absorption coefficient	0.193 mm ⁻¹
F(000)	688
Crystal size	0.18 x 0.17 x 0.05 mm ³
Theta range for data collection	1.864 to 32.917°.
Index ranges	-10<=h<=10, -11<=k<=11, -32<=l<=32
Reflections collected	18161
Independent reflections	3928 [R(int) = 0.0605]
Data / restraints / parameters	3928 / 0 / 199
Goodness-of-fit on F ²	1.025
Final R indices [I>2σ(I)]	R1 = 0.0466, wR2 = 0.1179
R indices (all data)	R1 = 0.0725, wR2 = 0.1344
Largest diff. peak and hole	0.191 and -0.152 e.Å ⁻³

8. TG-DSC of 2k and 2m and 2r and 2w



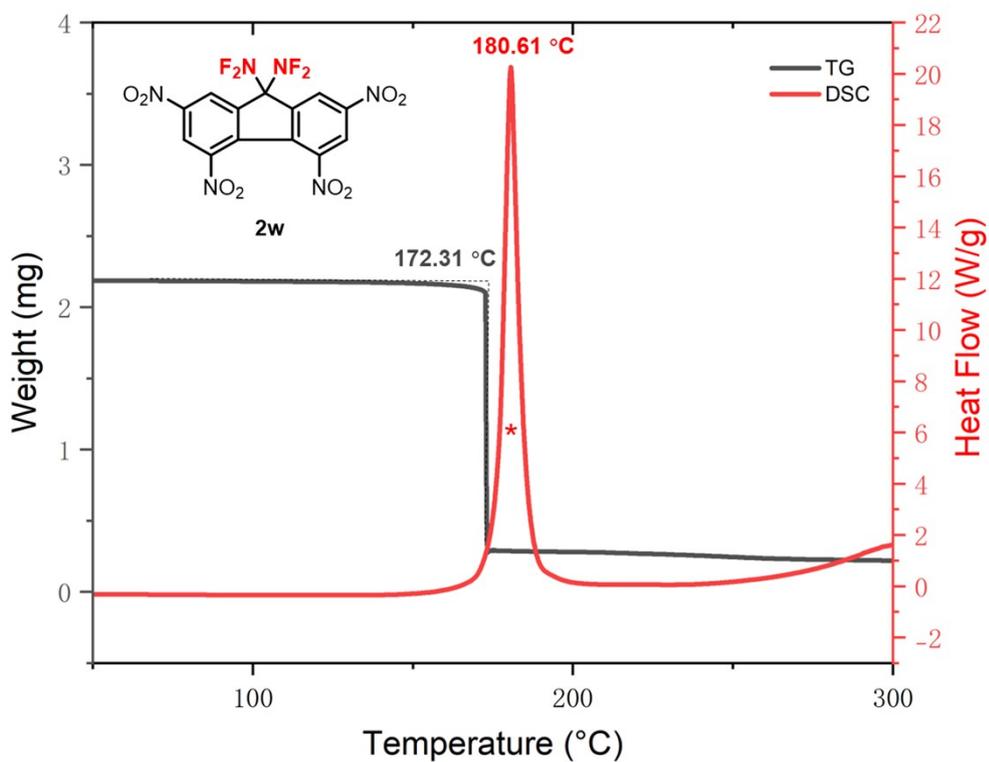
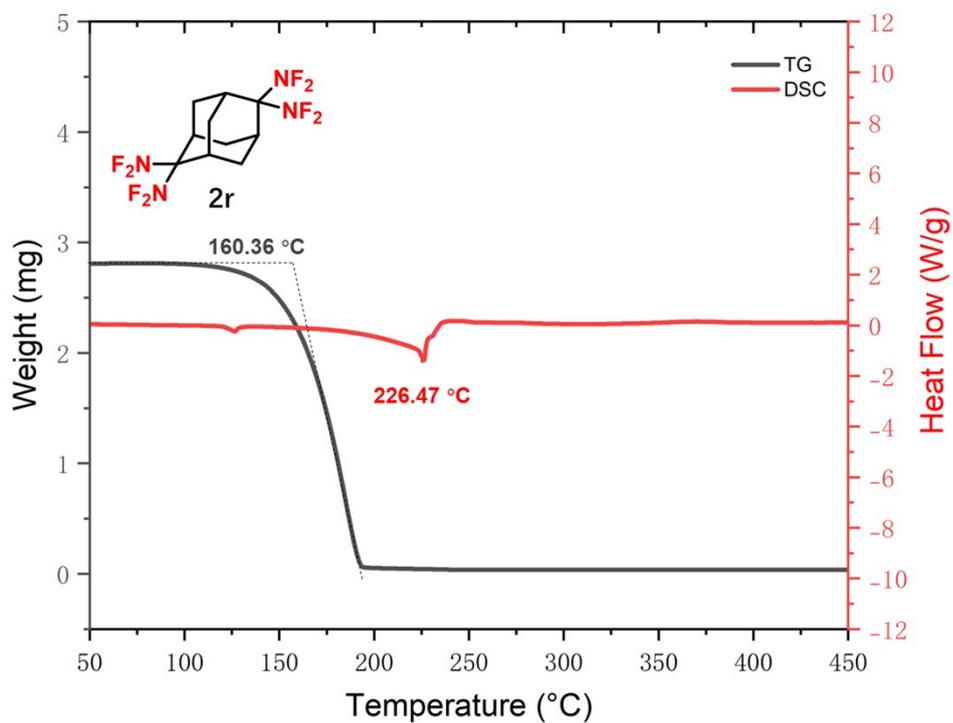
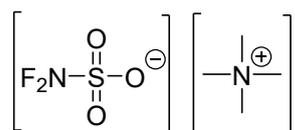


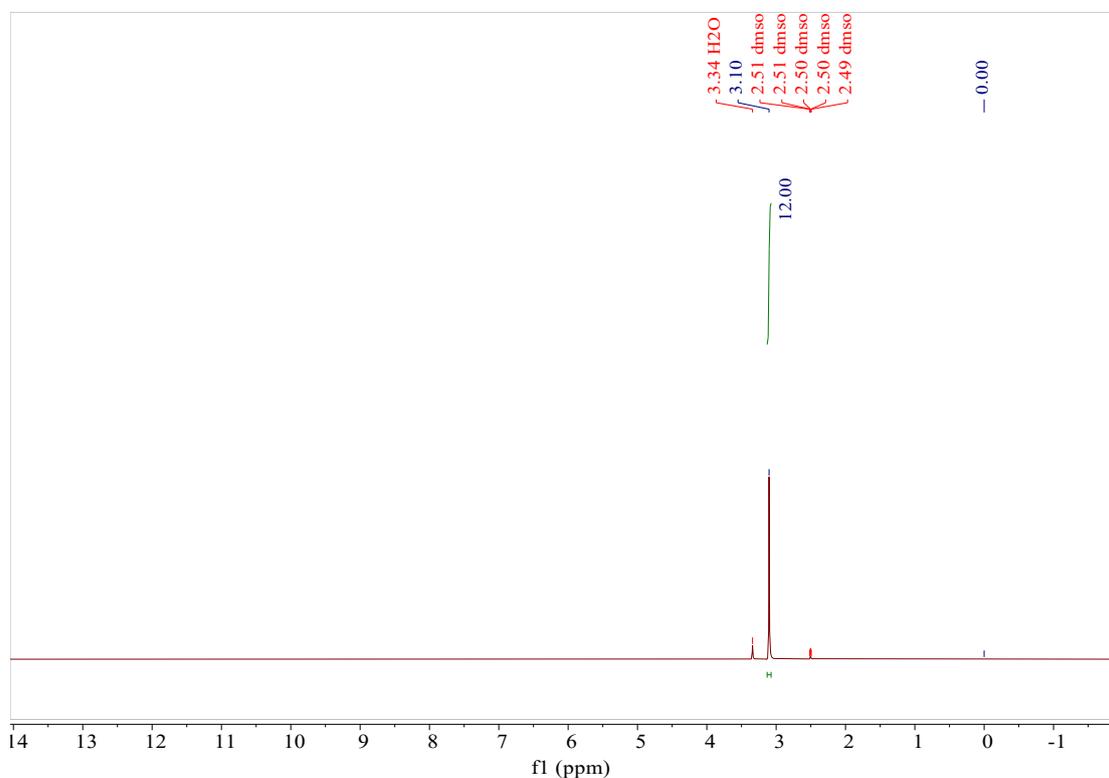
FIGURE 4 The thermal decomposition performance of compound **2k**, **2m**, **2r** and **2w**

The thermal decomposition performance of compound **2k**, **2m**, **2r** and **2w** were measured using TG-DSC synchronous thermal analyzer (**Figure 4**). It can be seen from the TG curve that compound **2k** begins to decompose at 182.17 °C. There is a clear exothermic peak at 211.11 °C in the DSC curve. It also can be observed from the TG curve that compound **2m** begins to decompose at 149.37 °C. There is a clear endothermic peak at 54.41 °C in the DSC curve, which is the melting point of **2m**. There is an exothermic peak in the DSC curve, and the peak temperature is 206.19 °C. It also can be observed from the TG curve that compound **2r** begins to decompose at 160.36 °C. There is a clear endothermic peak at 226.47 °C in the DSC curve, which is the melting point of **2r**. However, no obvious exothermic peak was observed in the DSC curve. Compound **2w** begins to decompose at 172.31 °C. The decomposition peak is sharp in the DSC curve, which shows that compound **2w** decomposes rapidly near this temperature and releases a large amount of heat.

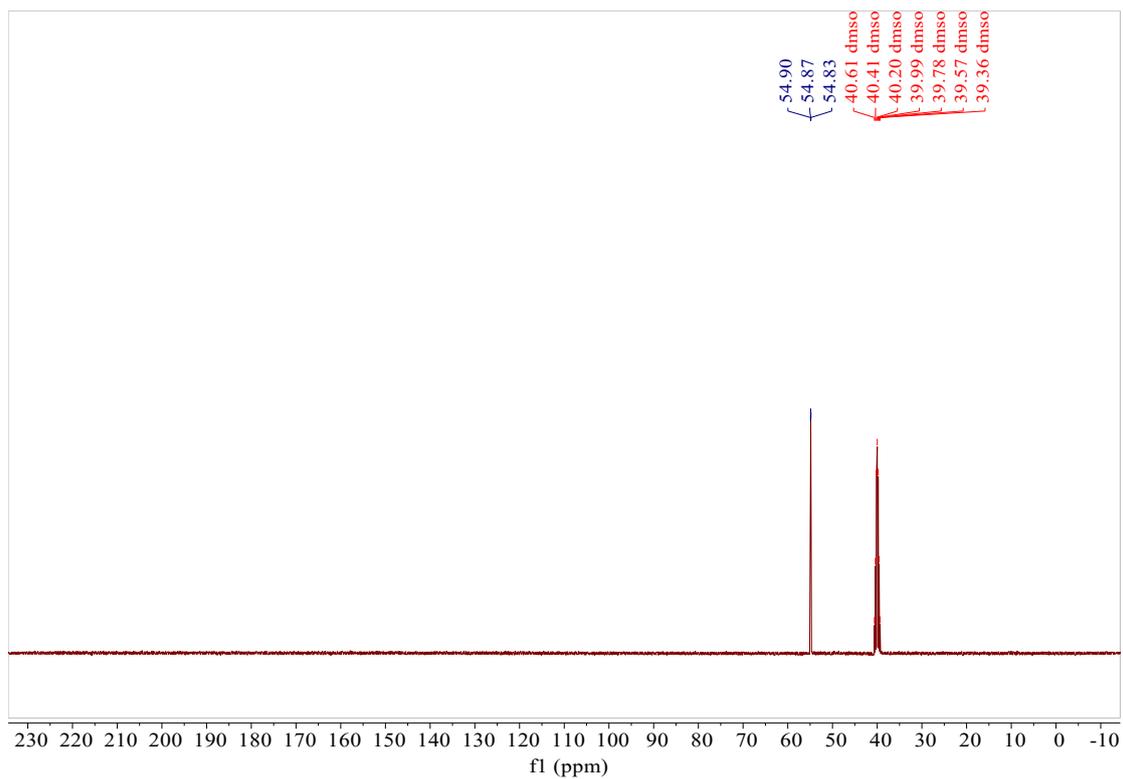
9. ¹H, ¹³C and ¹⁹F NMR Spectra



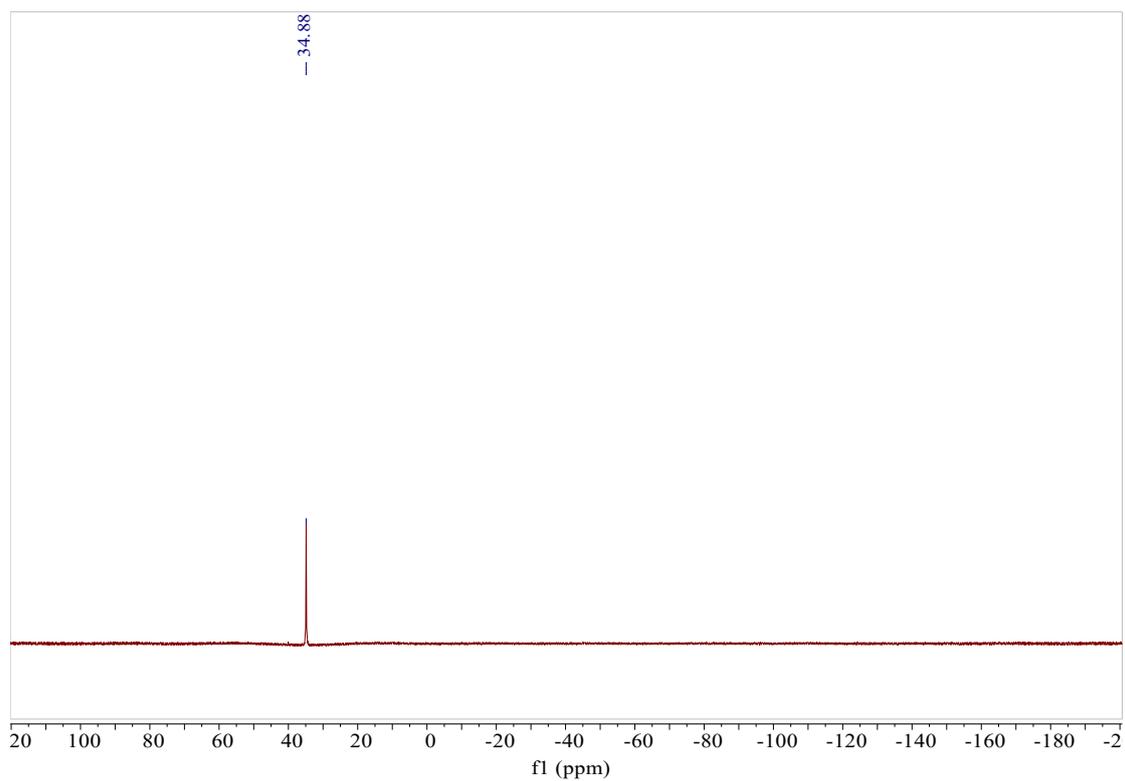
¹H NMR (400 MHz, DMSO-*d*₆)



¹³C NMR (101 MHz, DMSO-*d*₆)



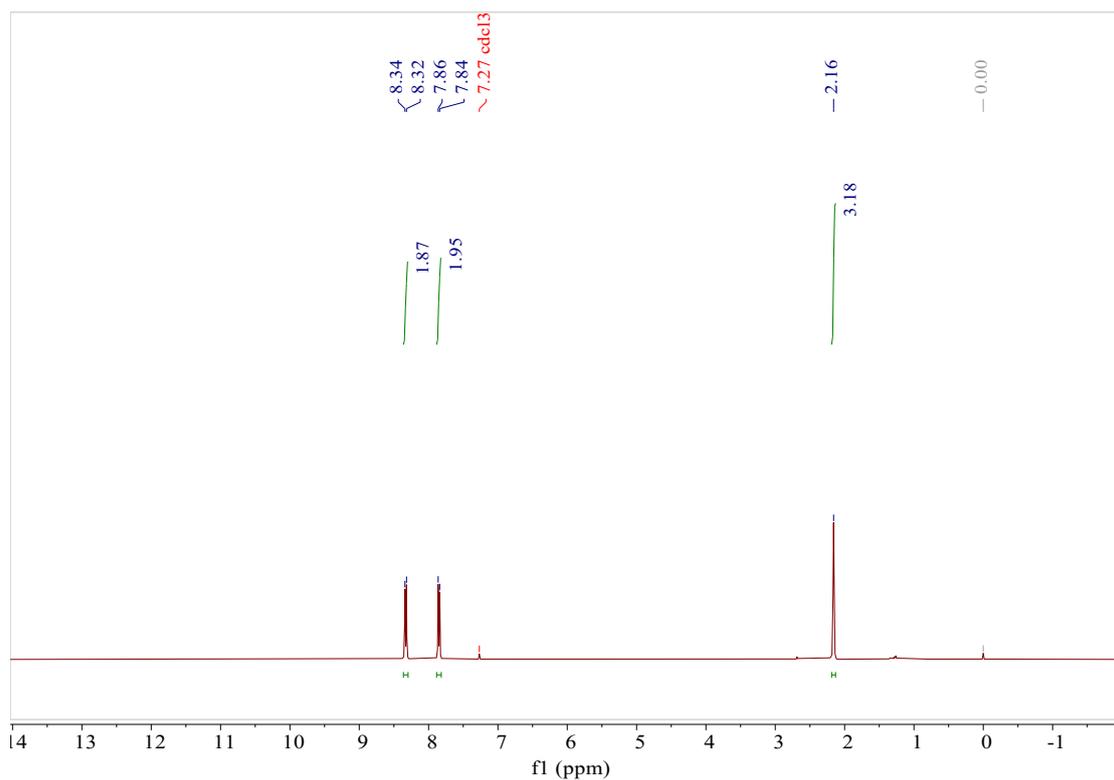
¹⁹F NMR (283 MHz, DMSO-*d*₆)



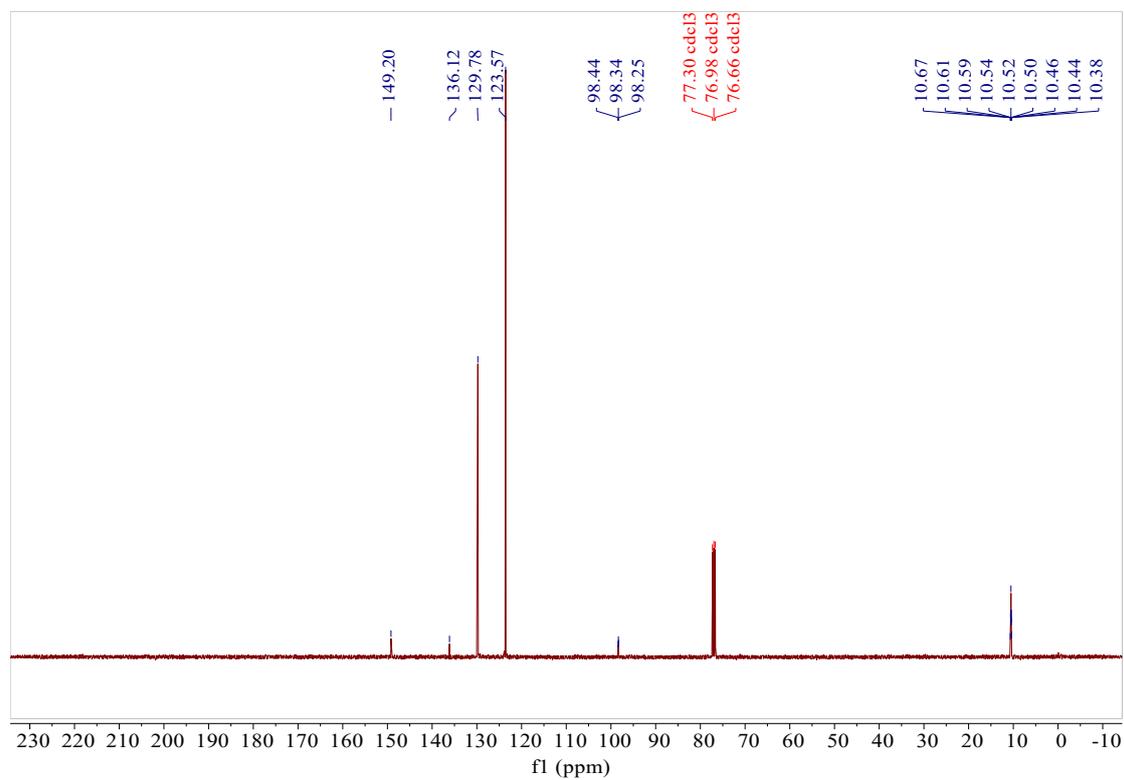
2a



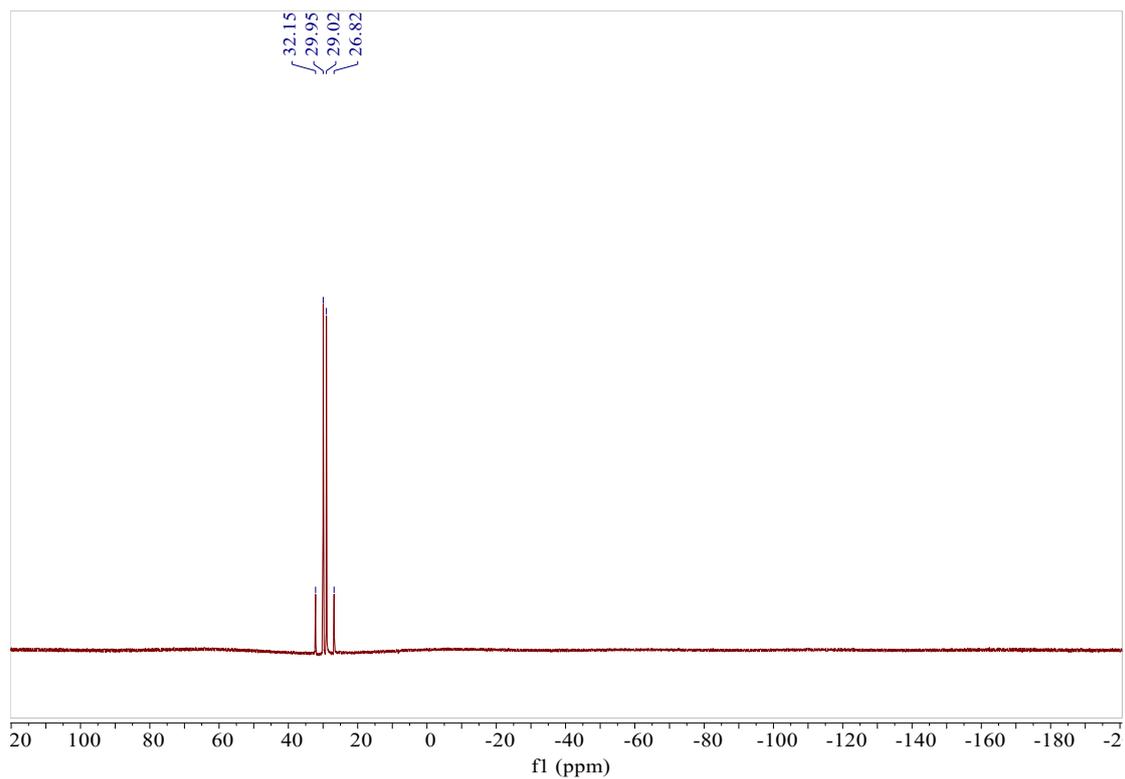
¹H NMR (400 MHz, CDCl₃)



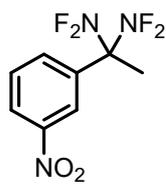
¹³C NMR (101 MHz, CDCl₃)



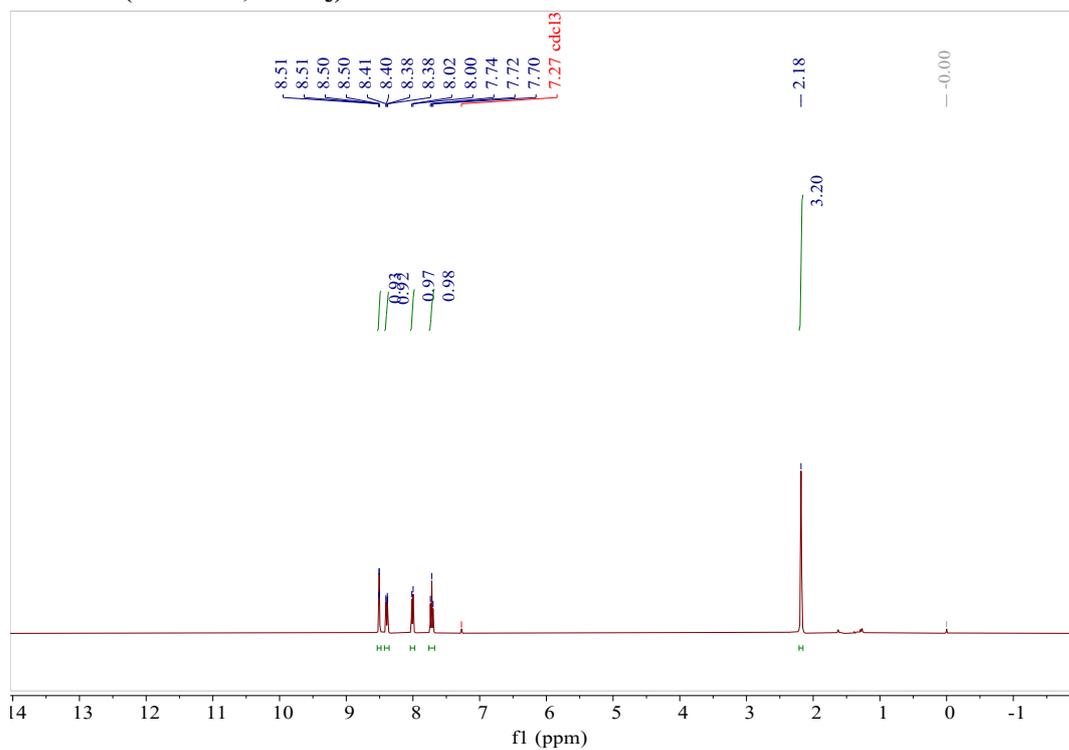
¹⁹F NMR (283 MHz, CDCl₃)



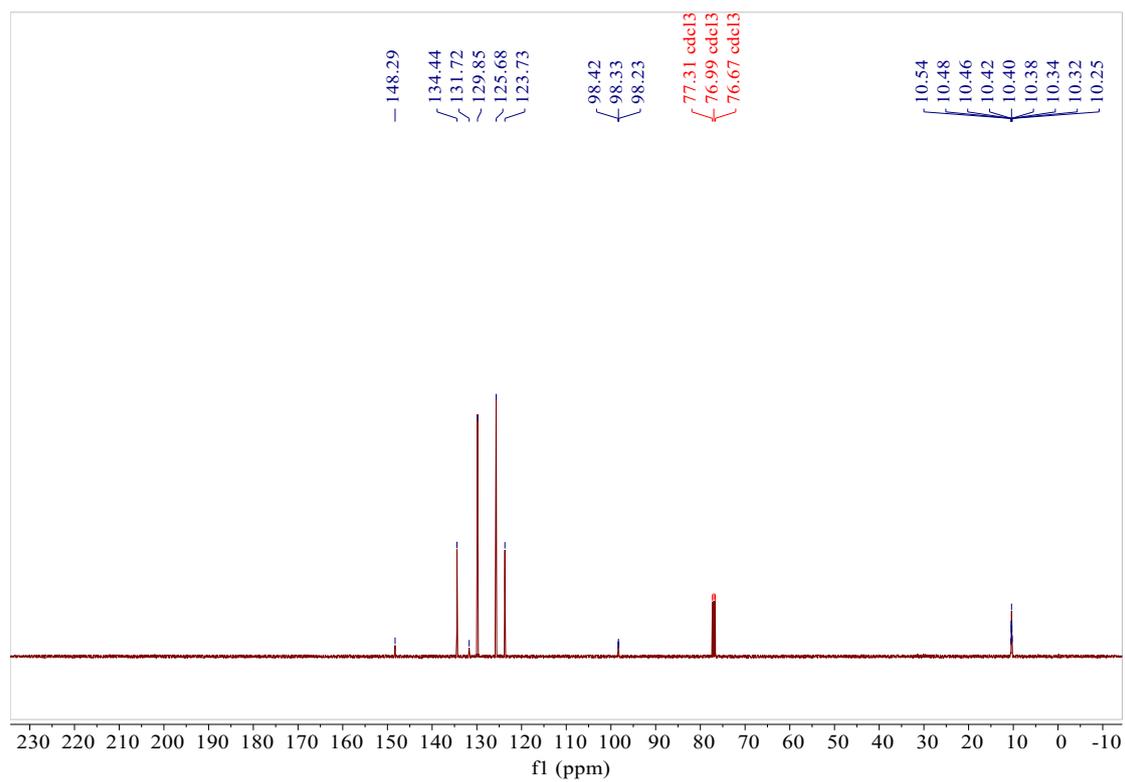
2b



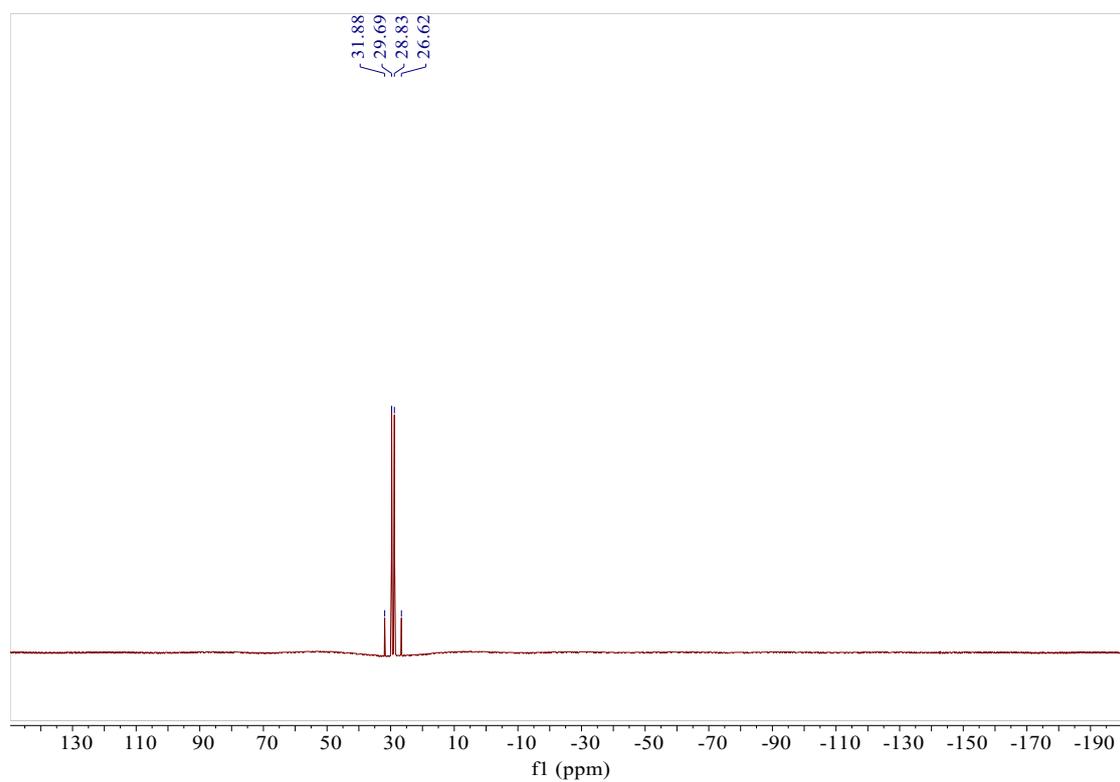
¹H NMR (400 MHz, CDCl₃)



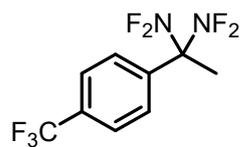
¹³C NMR (101 MHz, CDCl₃)



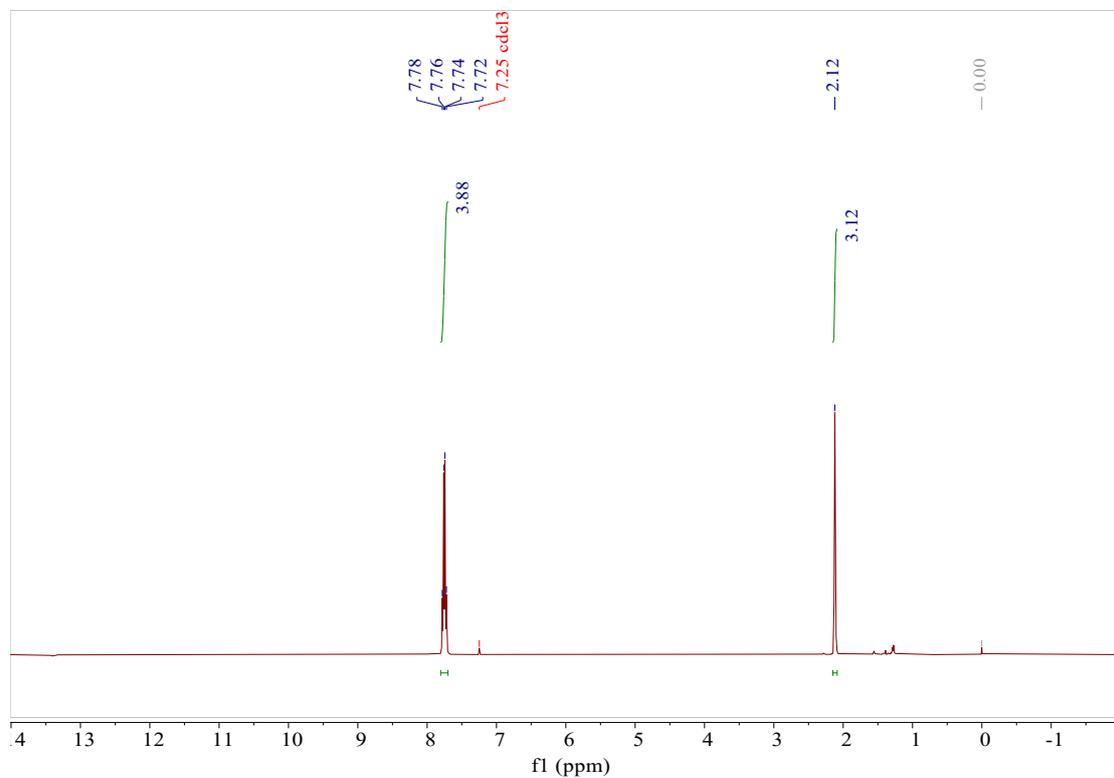
¹⁹F NMR (283 MHz, CDCl₃)



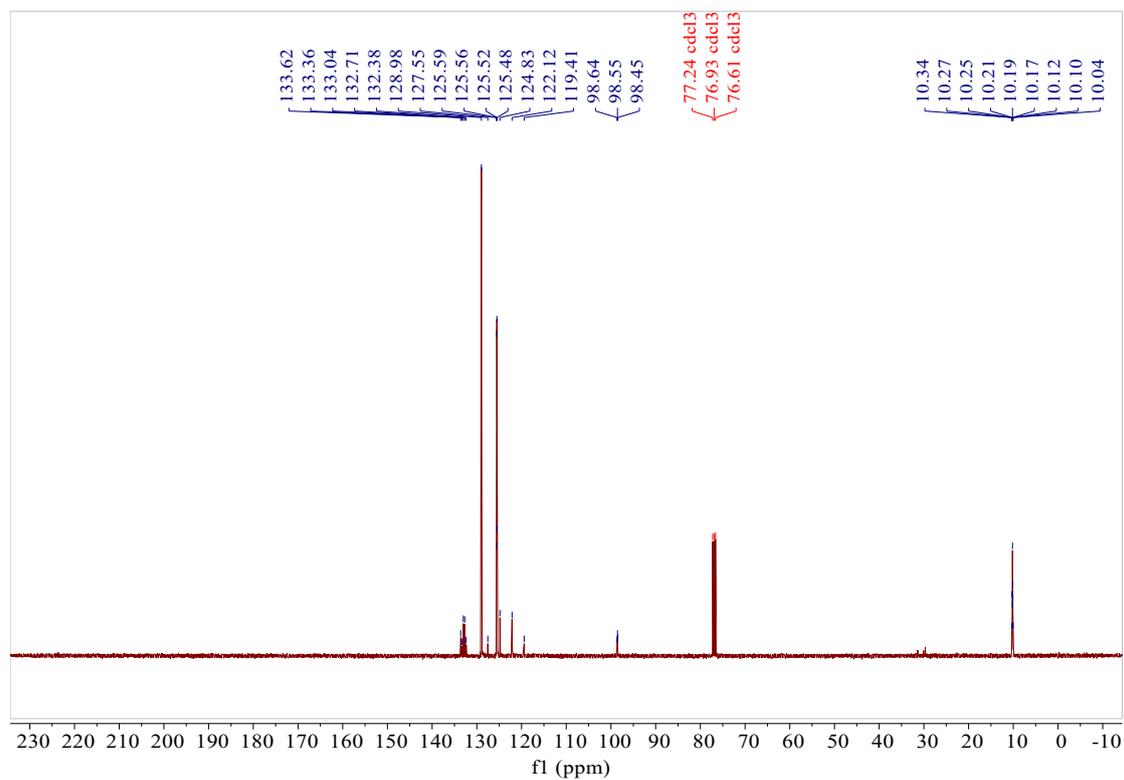
2c



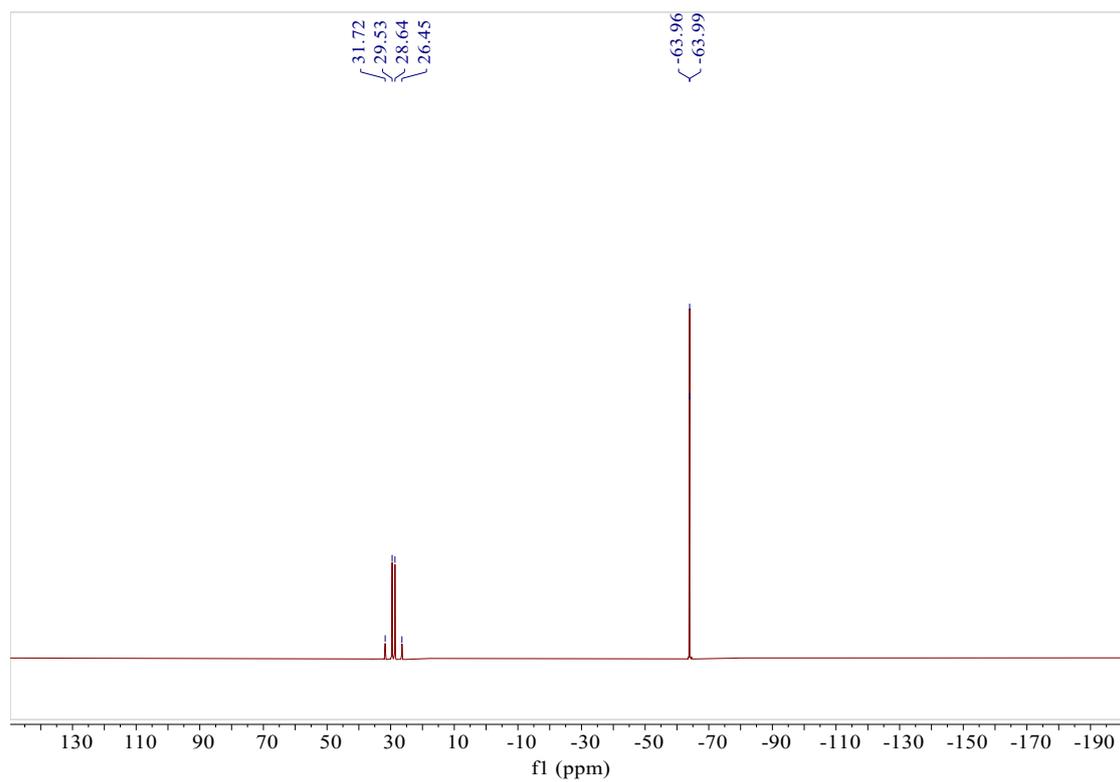
¹H NMR (400 MHz, CDCl₃)



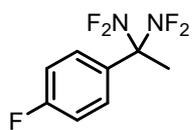
¹³C NMR (101 MHz, CDCl₃)



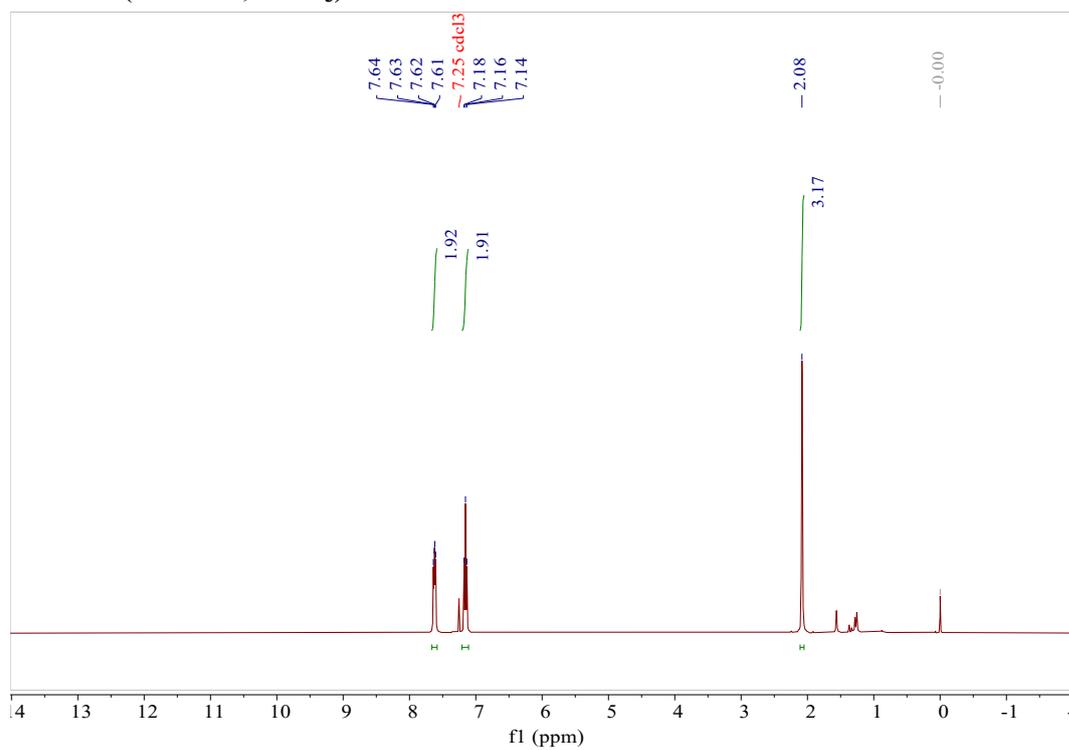
^{19}F NMR (283 MHz, CDCl_3)



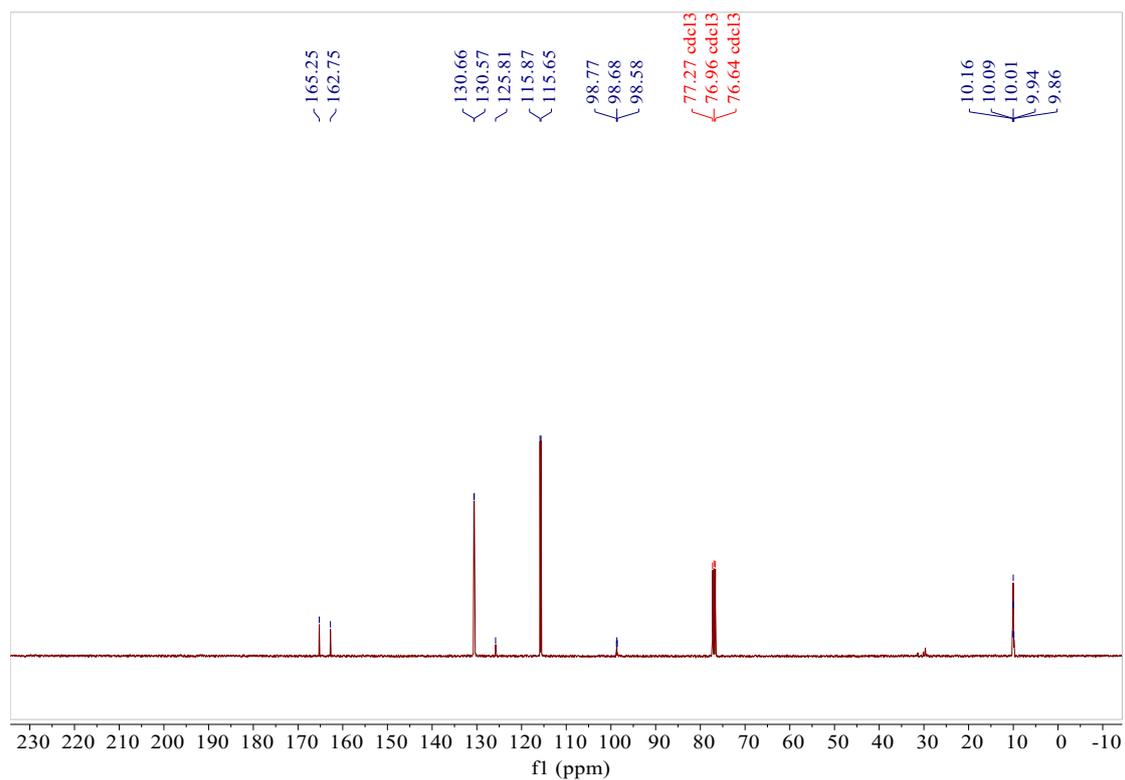
2d



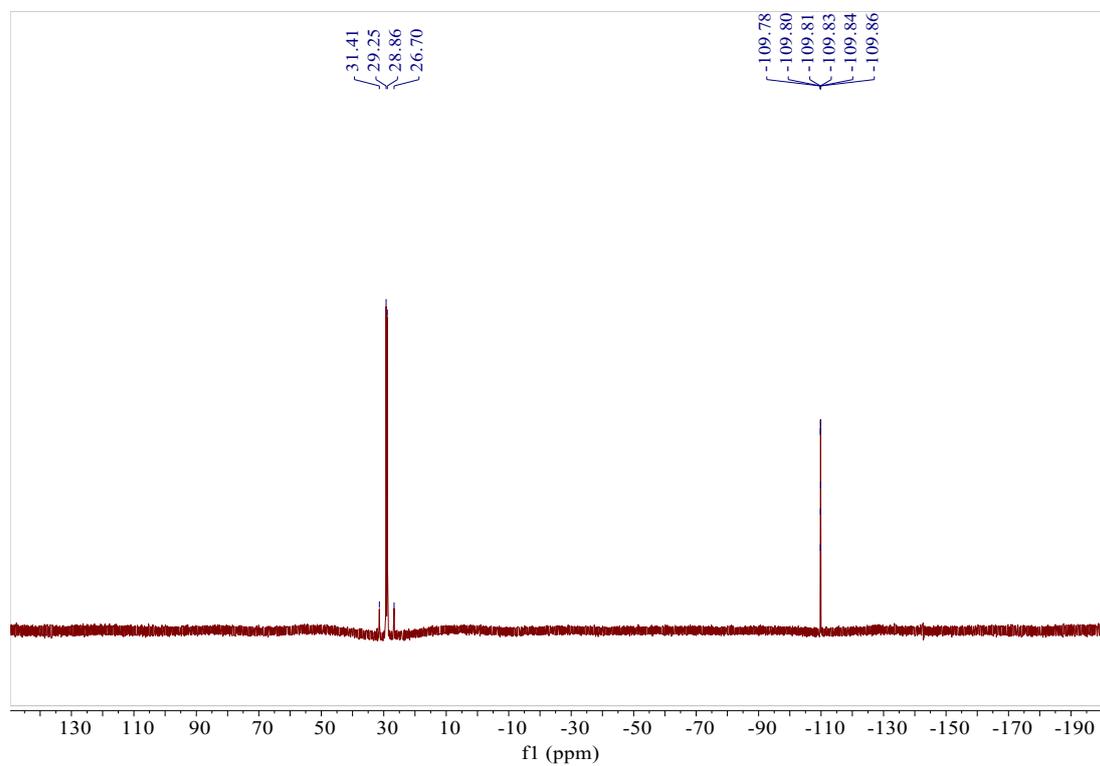
^1H NMR (400 MHz, CDCl_3)



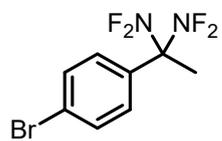
¹³C NMR (101 MHz, CDCl₃)



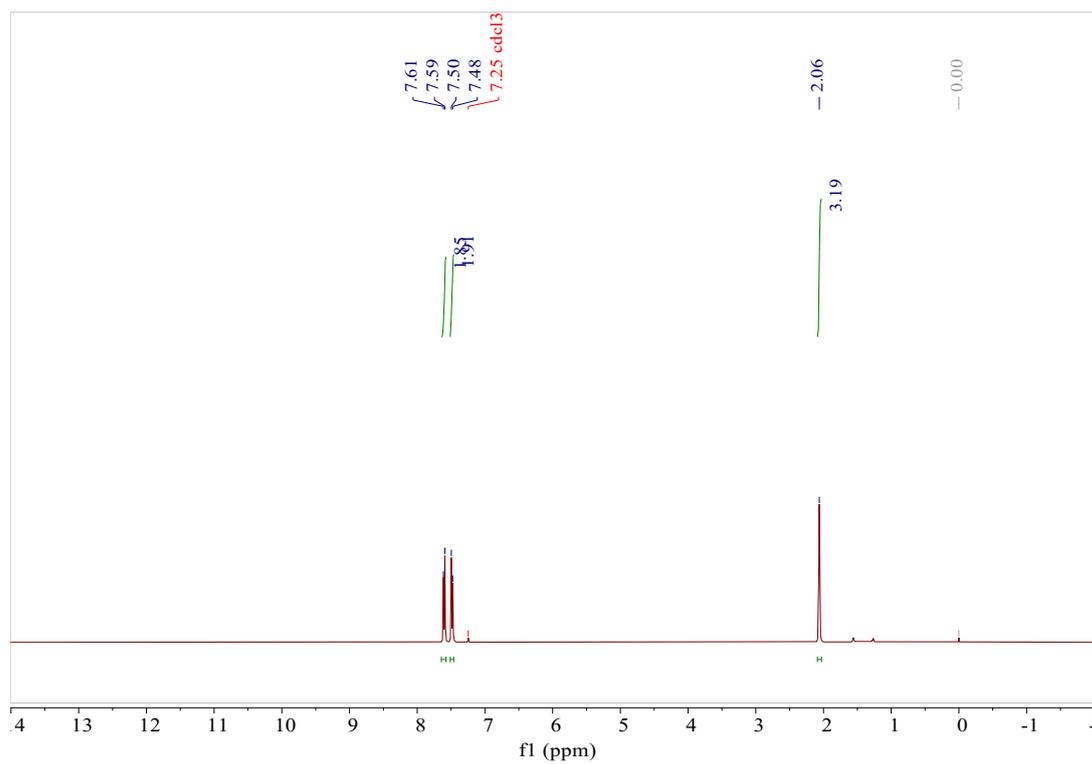
¹⁹F NMR (283 MHz, CDCl₃)



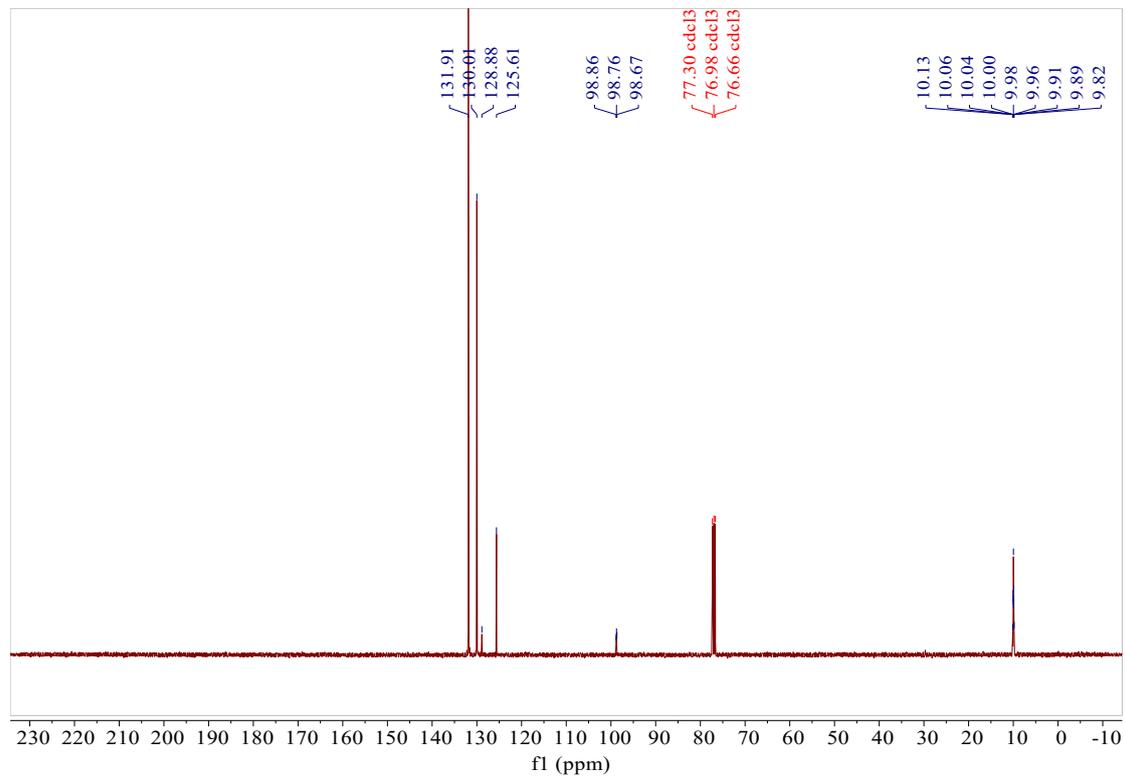
2e



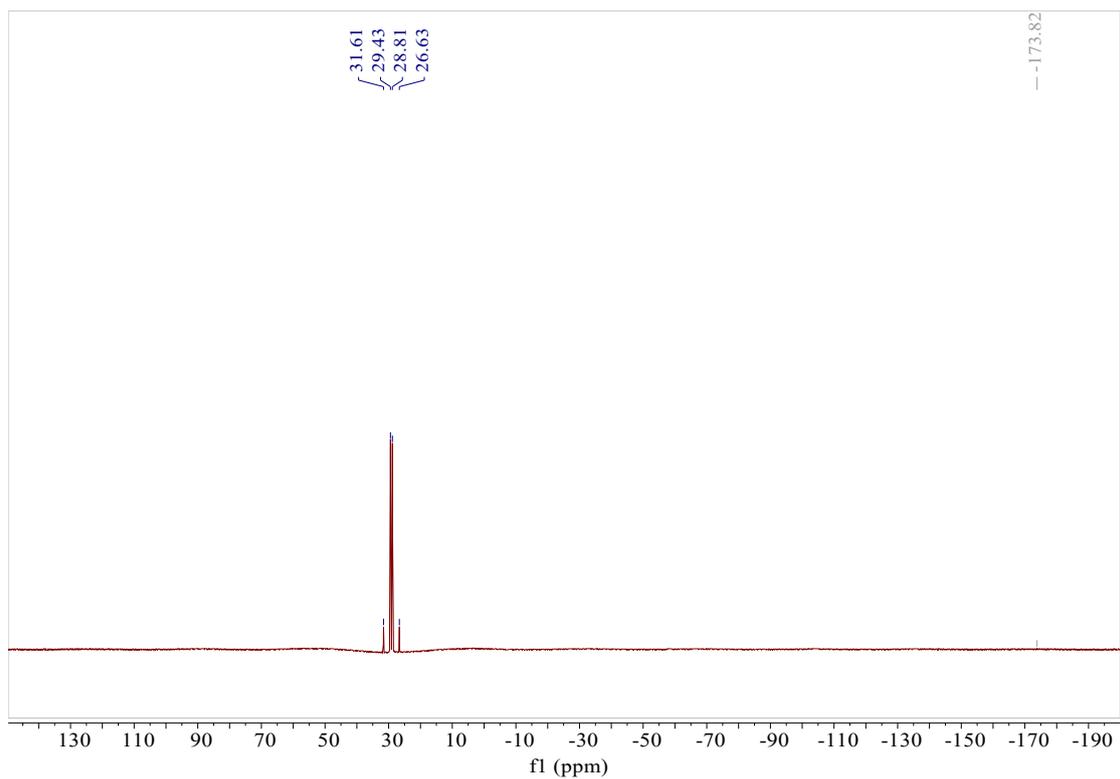
¹H NMR (400 MHz, CDCl₃)



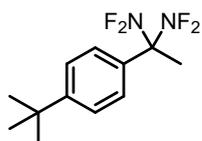
¹³C NMR (101 MHz, CDCl₃)



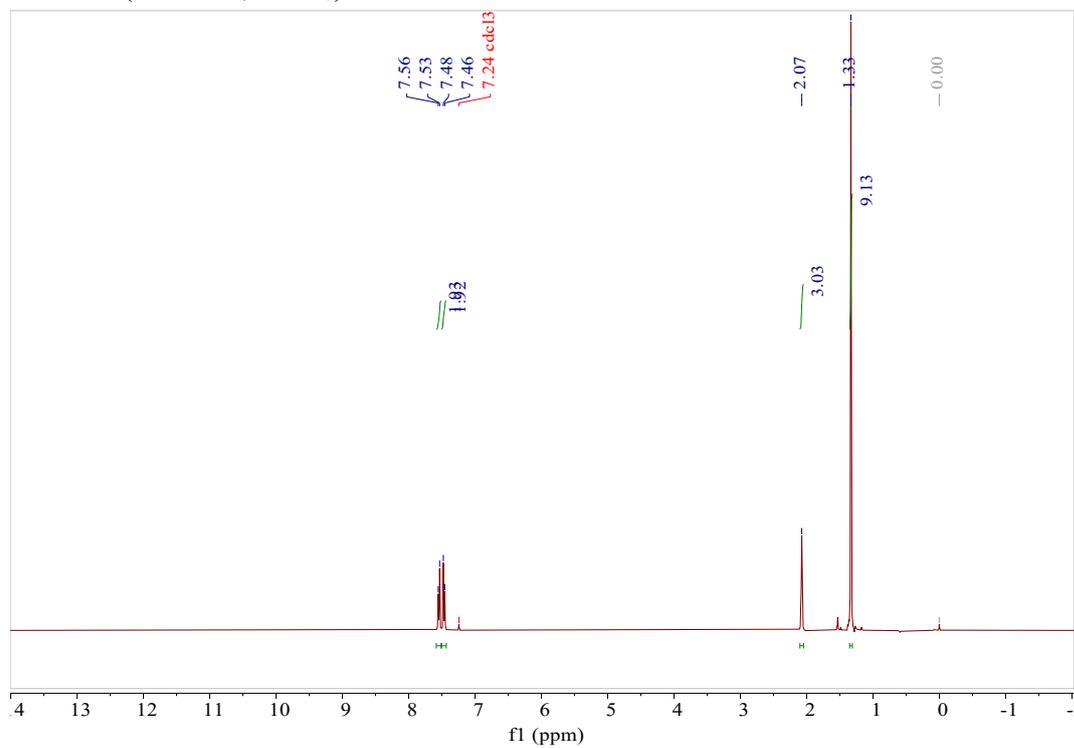
¹⁹F NMR (283 MHz, CDCl₃)



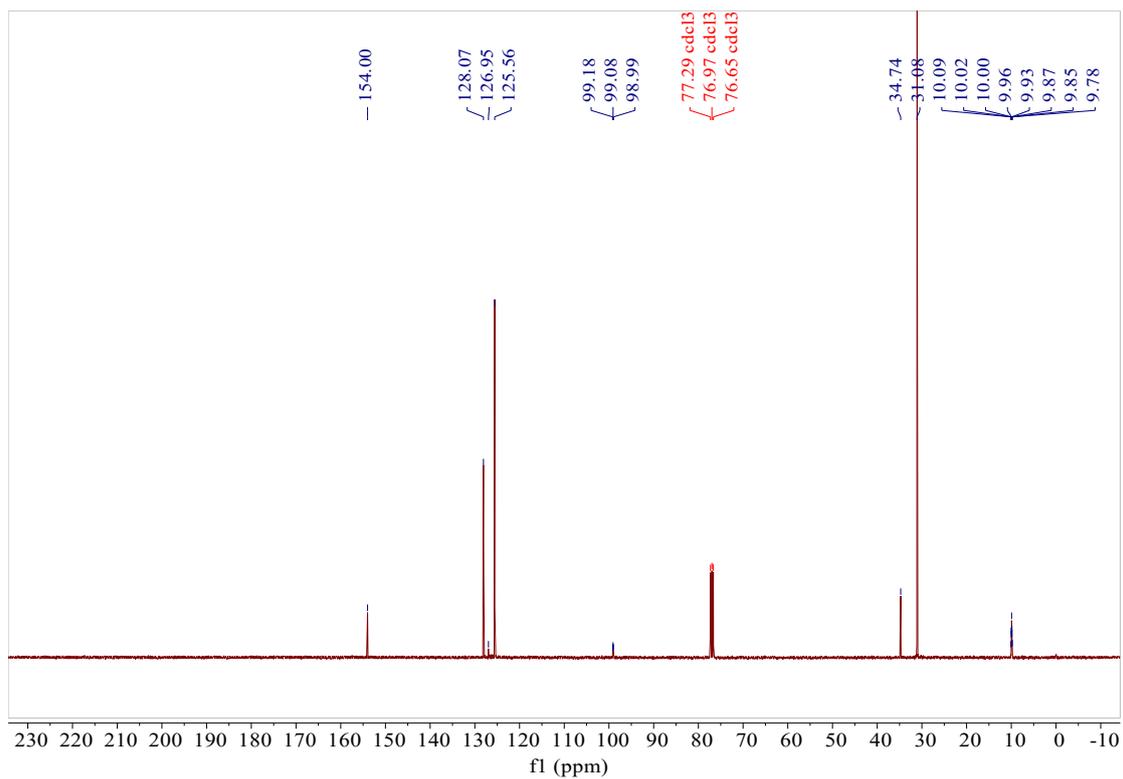
2f



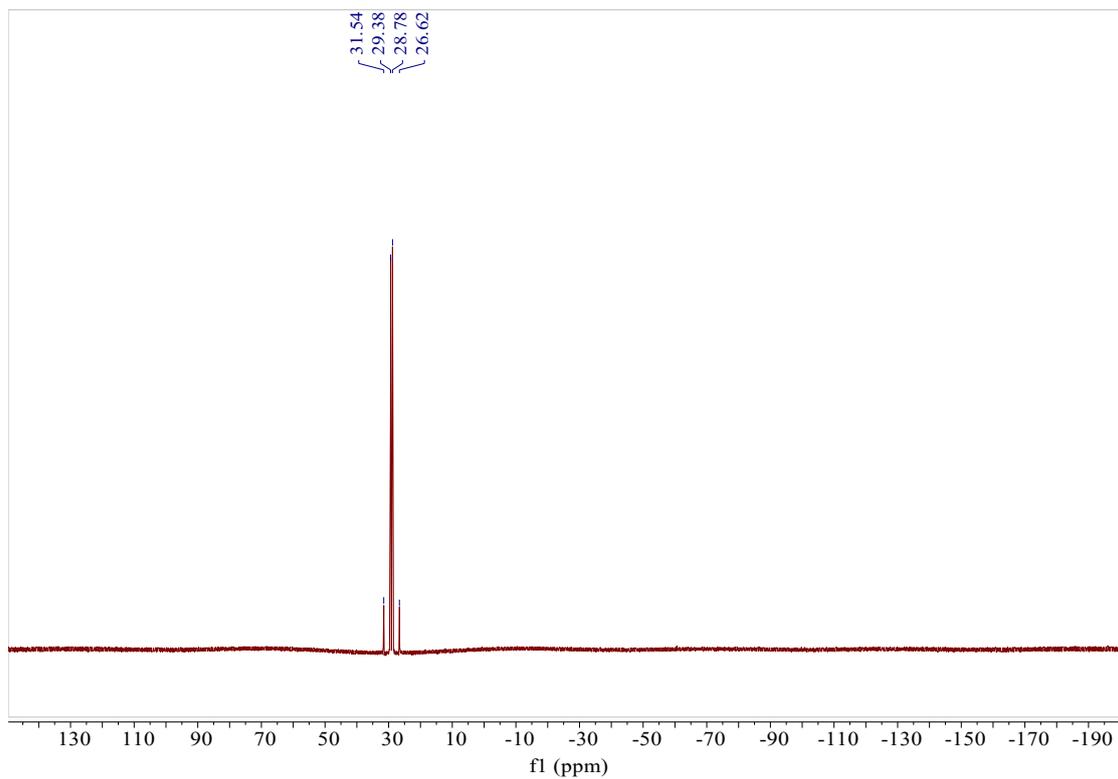
¹H NMR (400 MHz, CDCl₃)



¹³C NMR (101 MHz, CDCl₃)



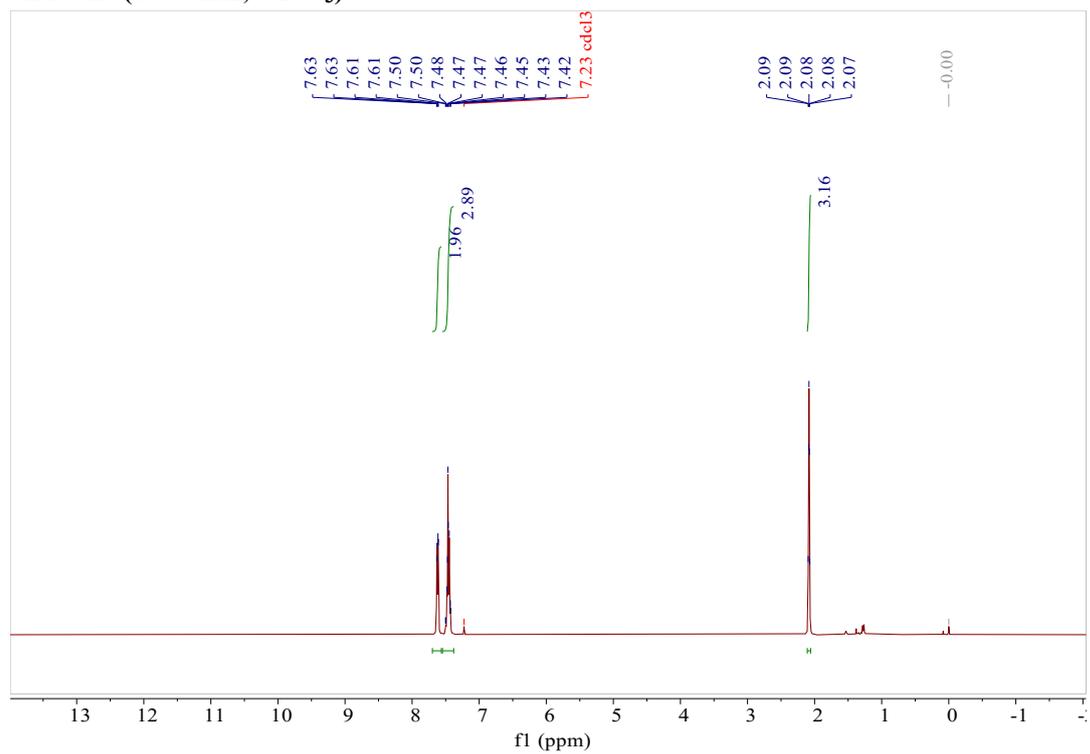
¹⁹F NMR (283 MHz, CDCl₃)



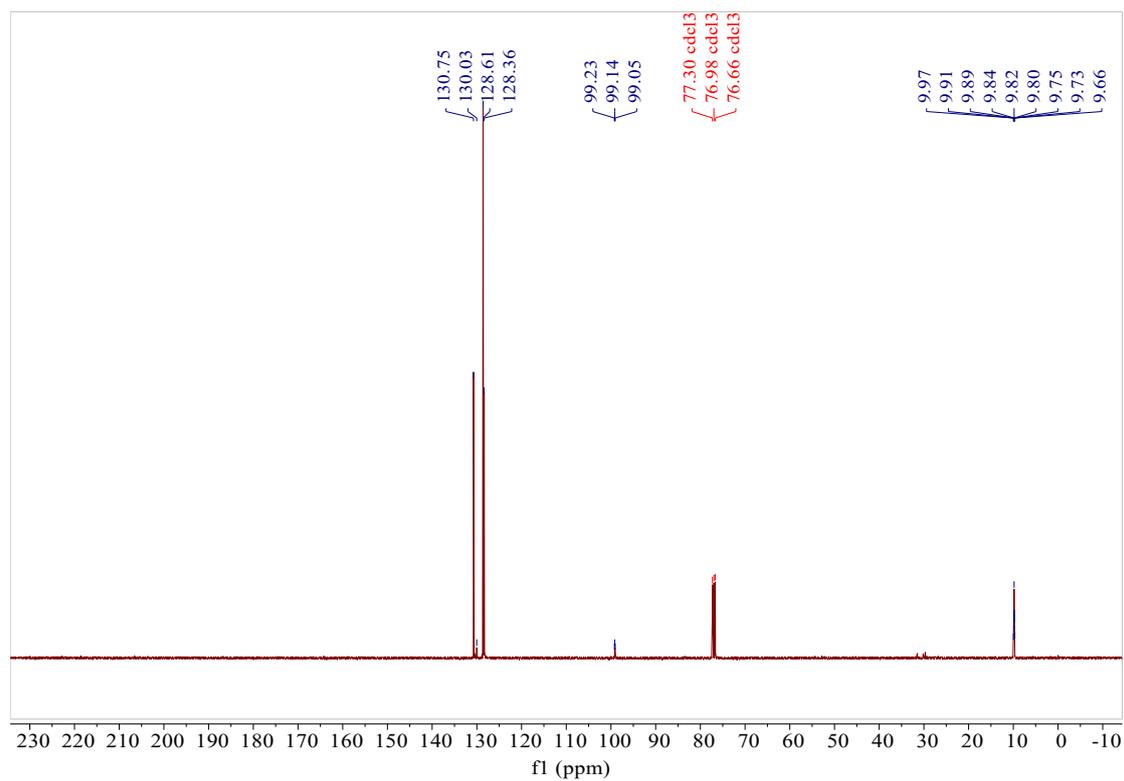
2g



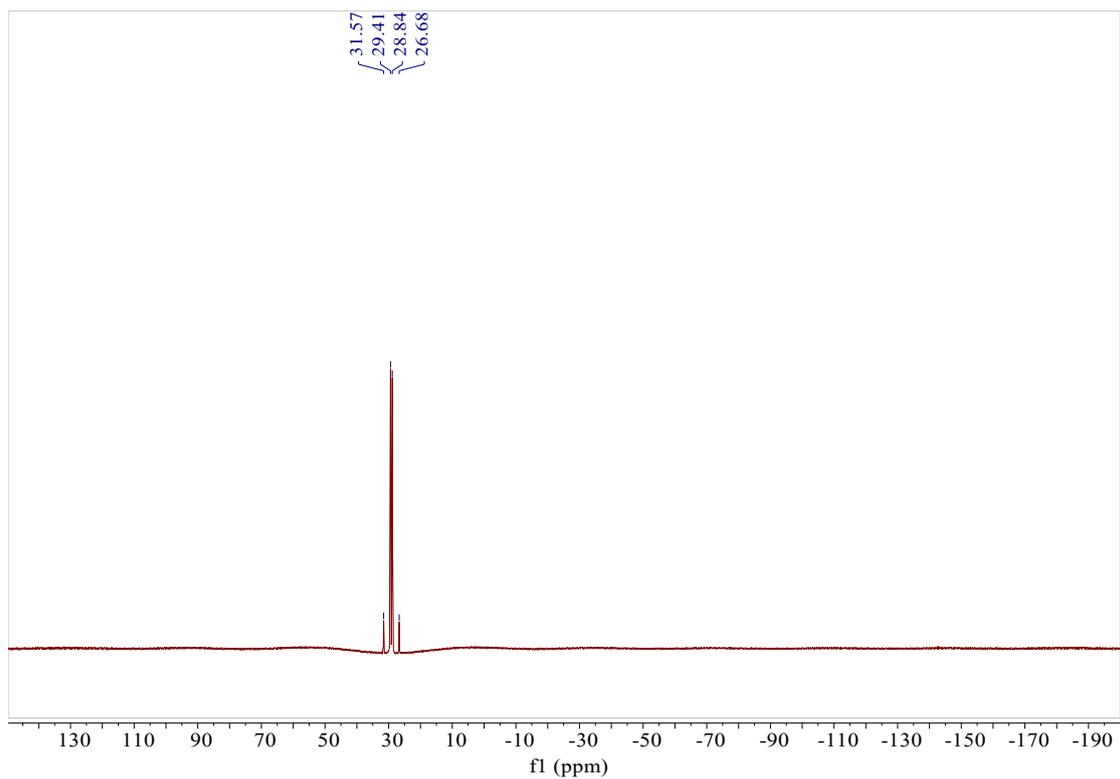
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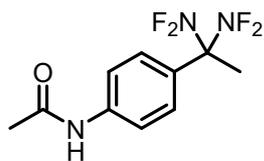
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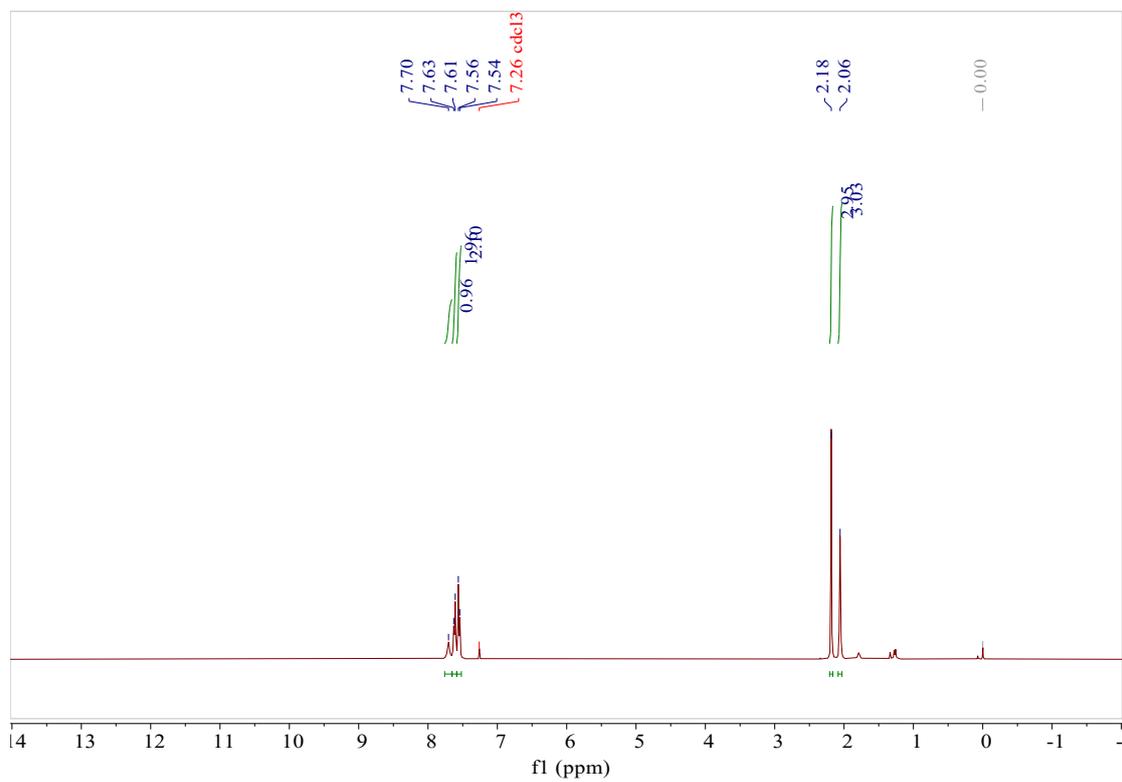
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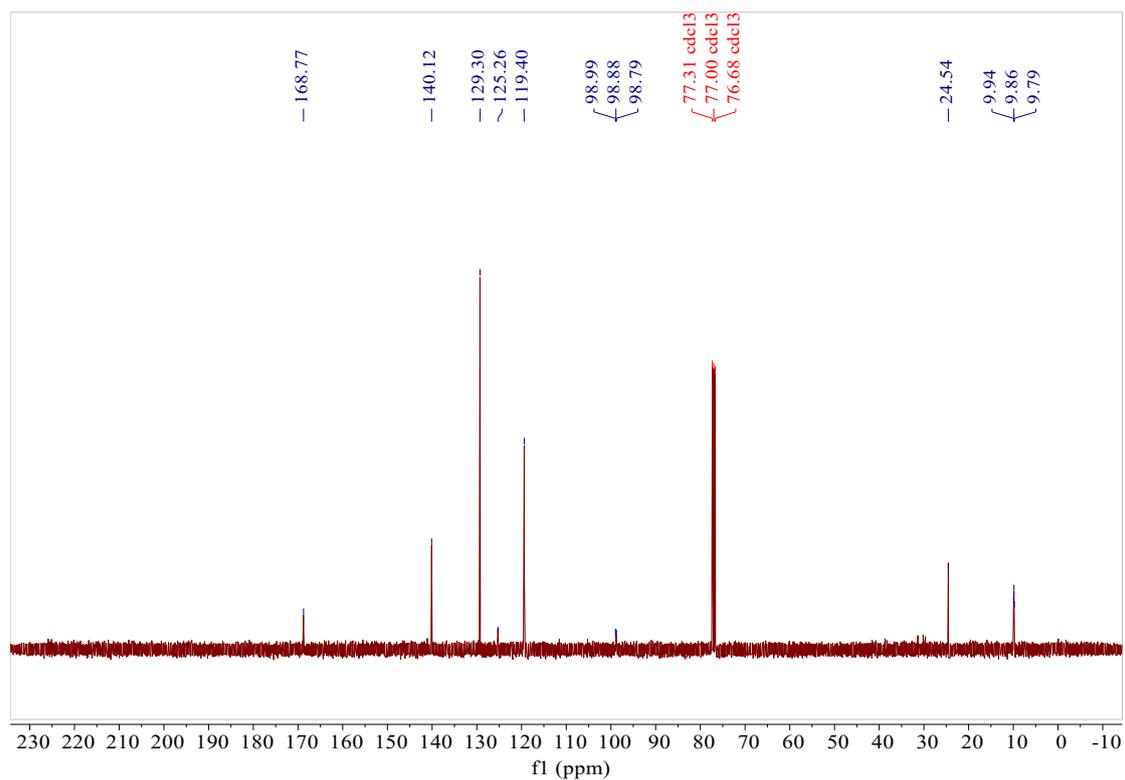
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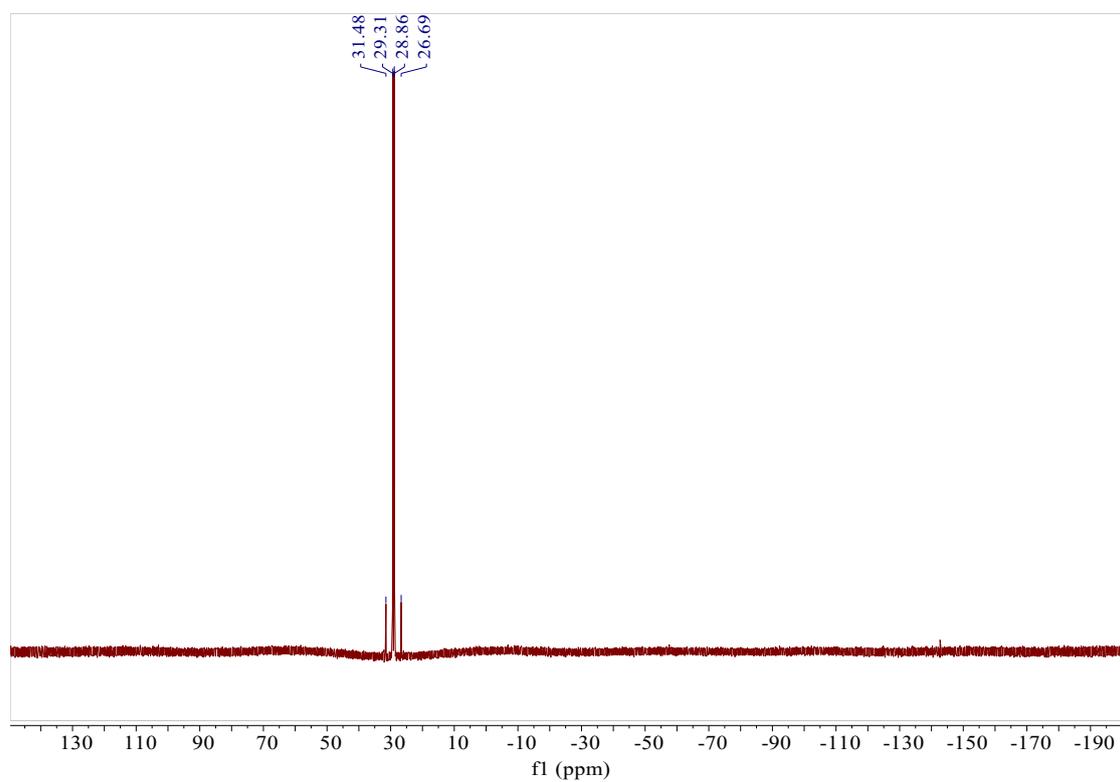
¹H NMR (400 MHz, CDCl₃)



¹³C NMR (101 MHz, CDCl₃)



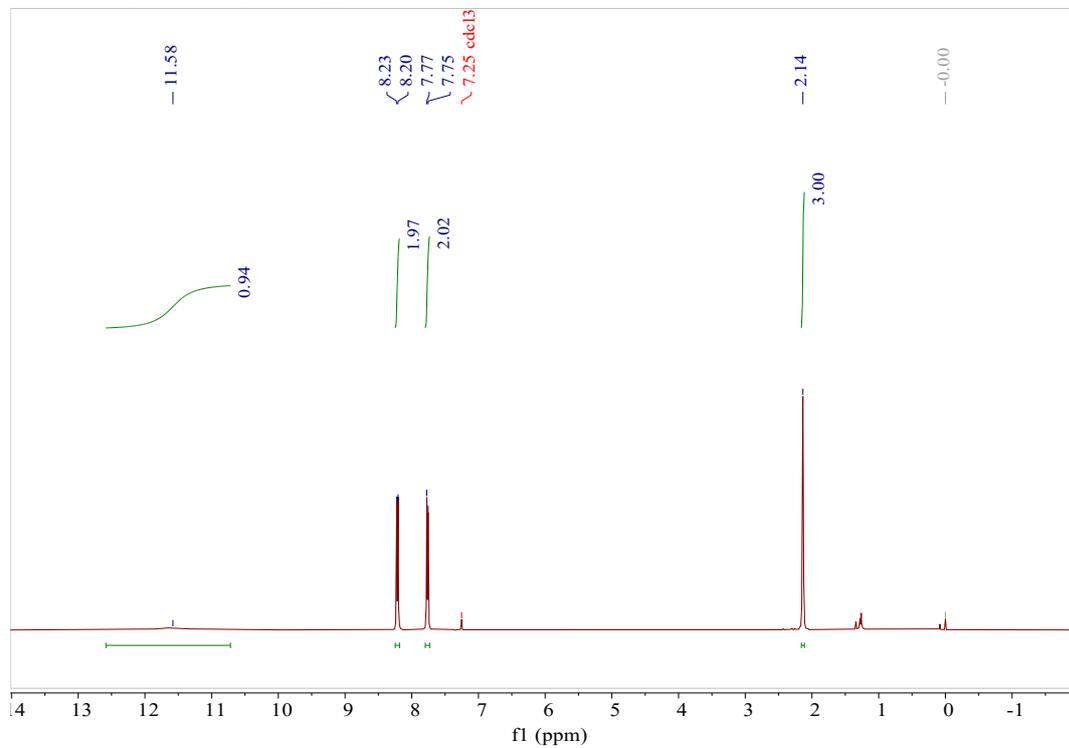
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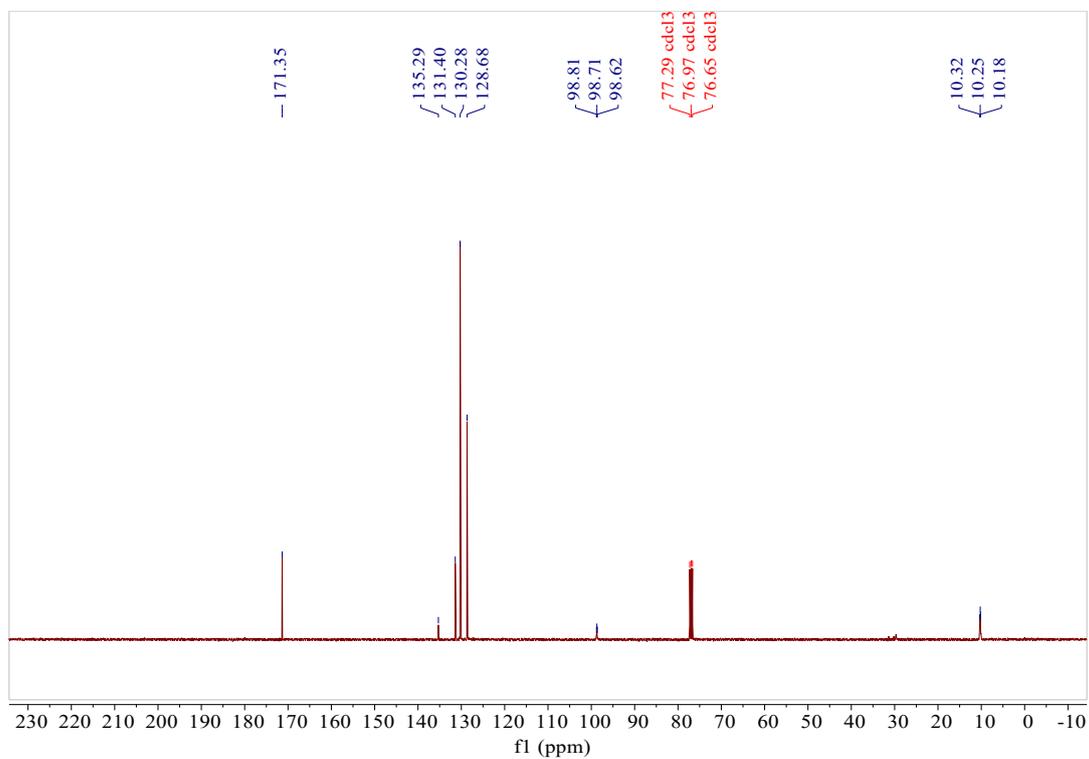
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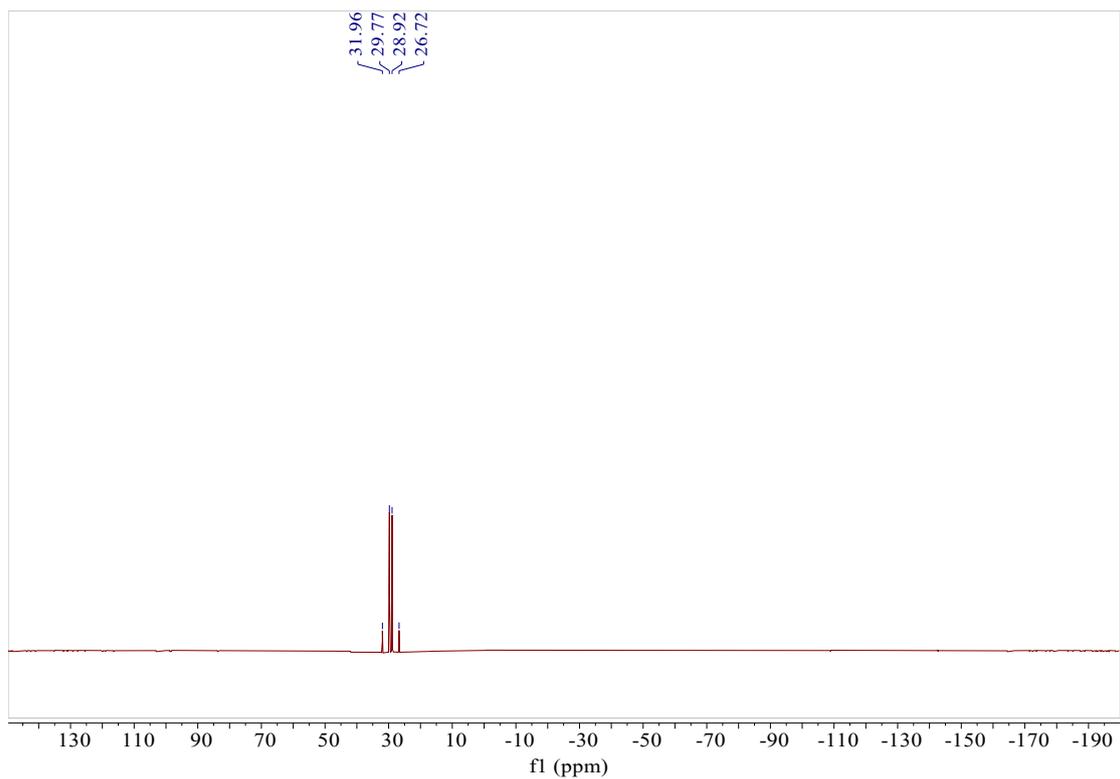
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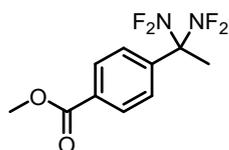
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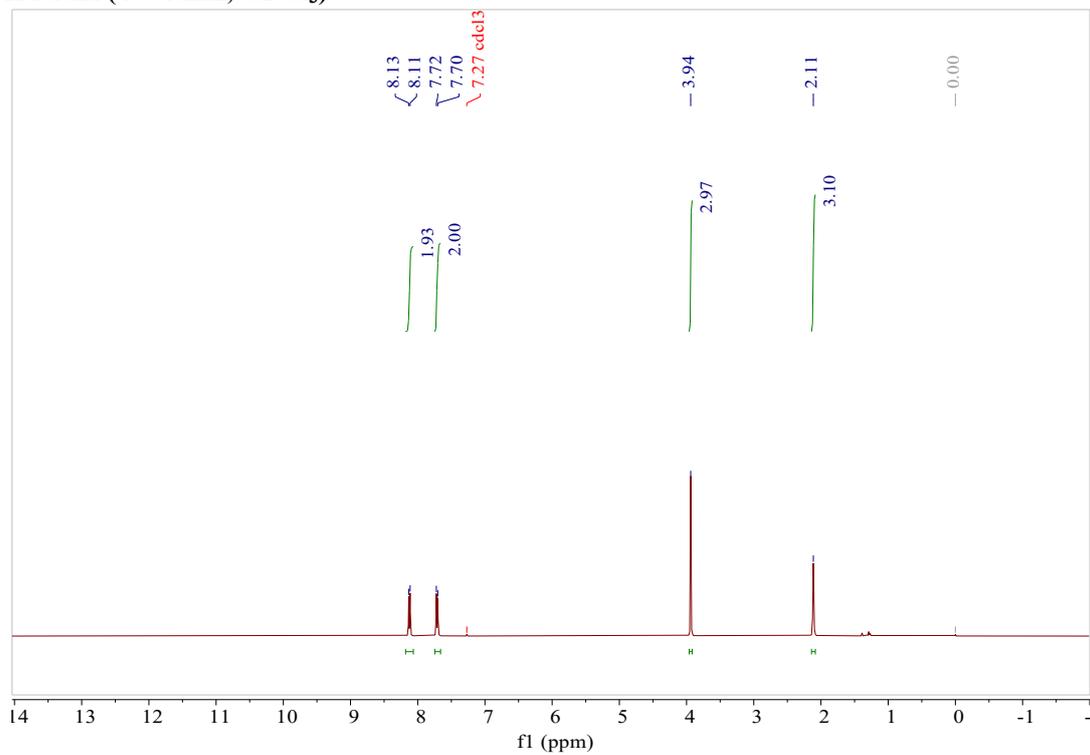
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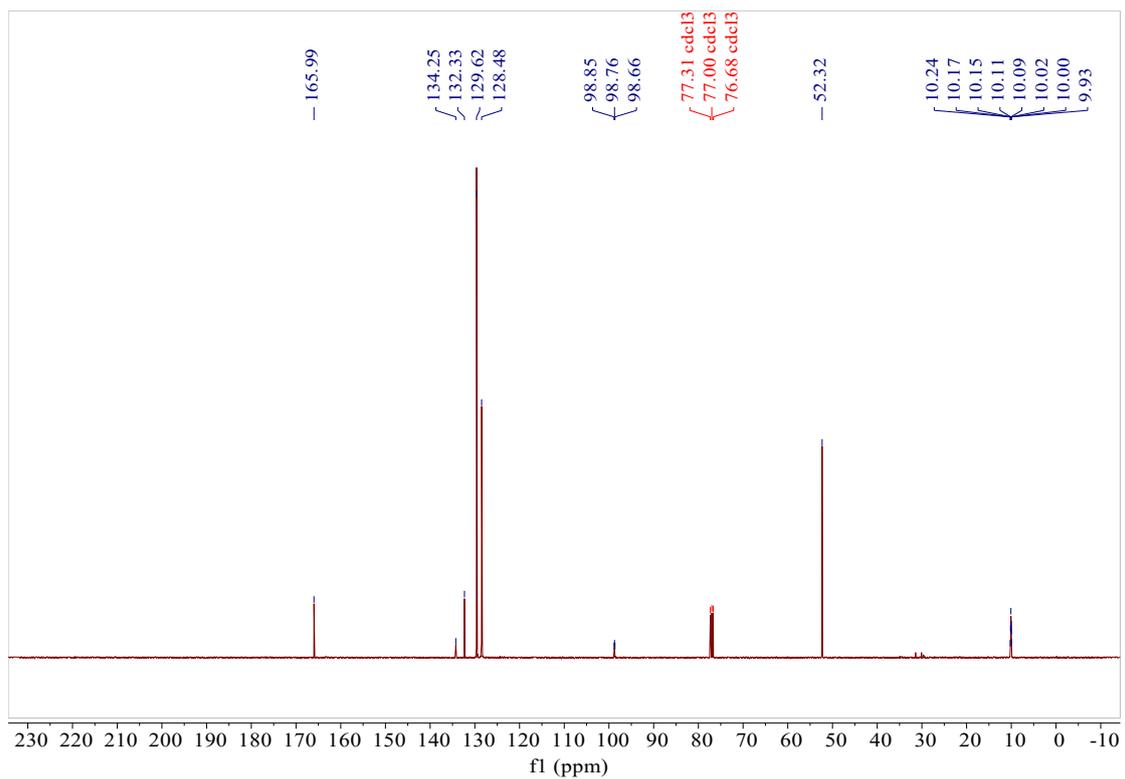
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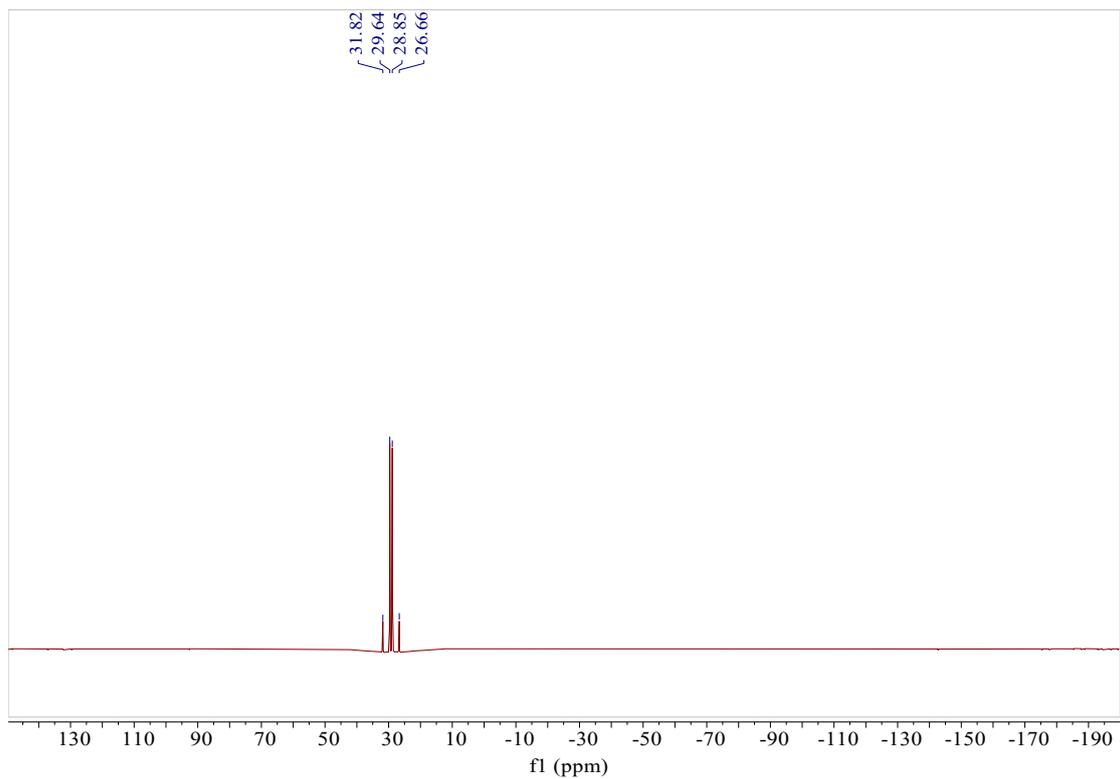
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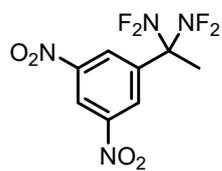
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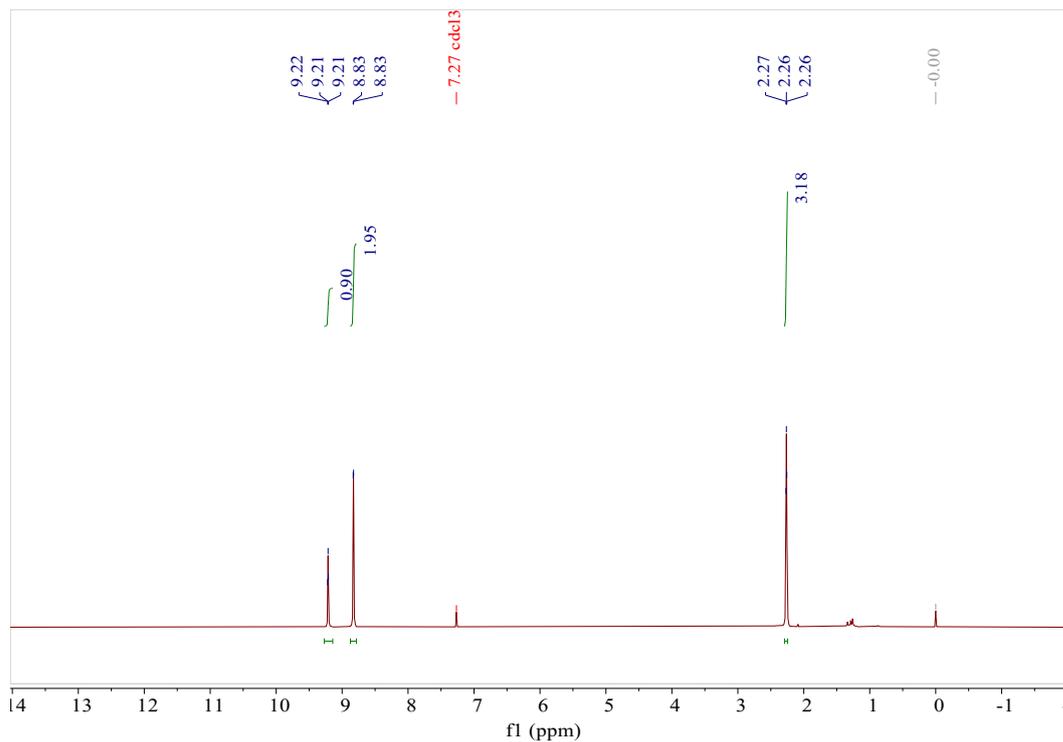
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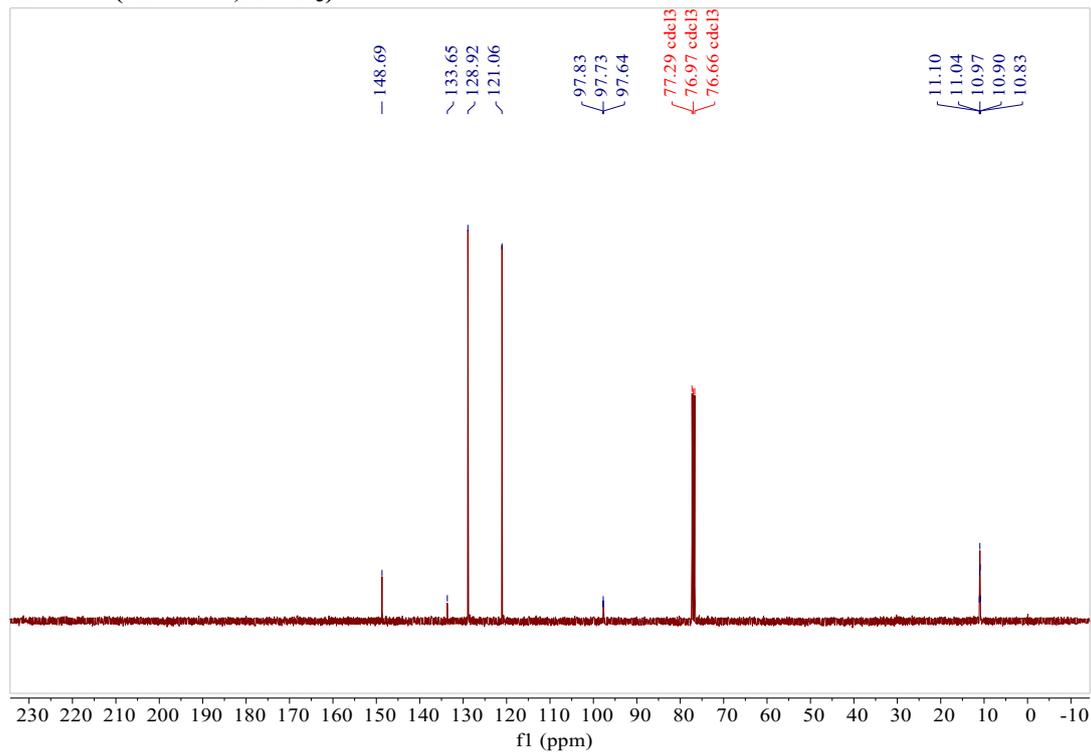
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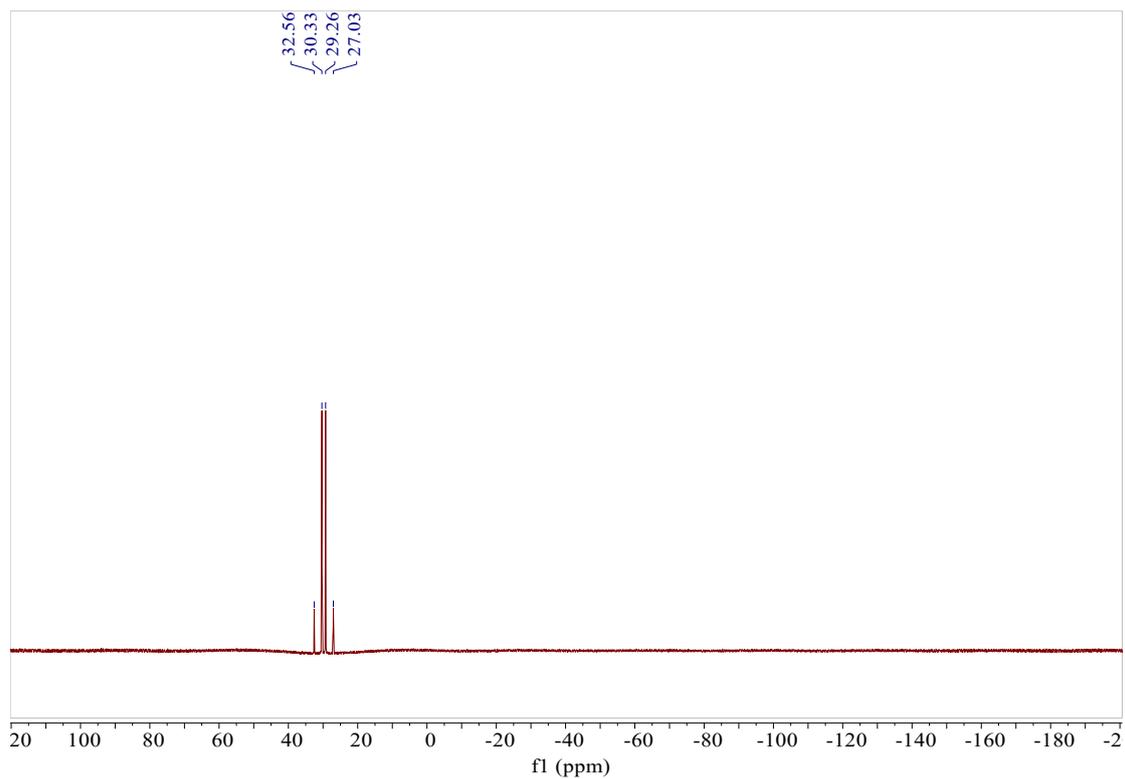
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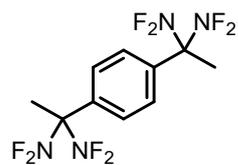
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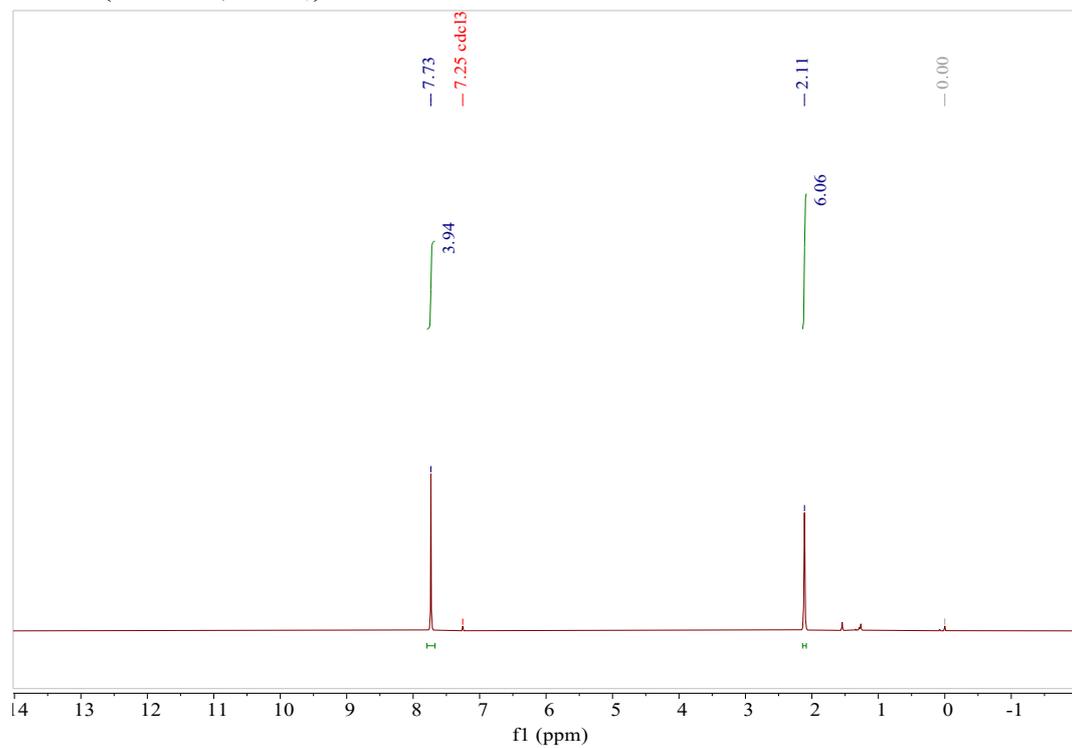
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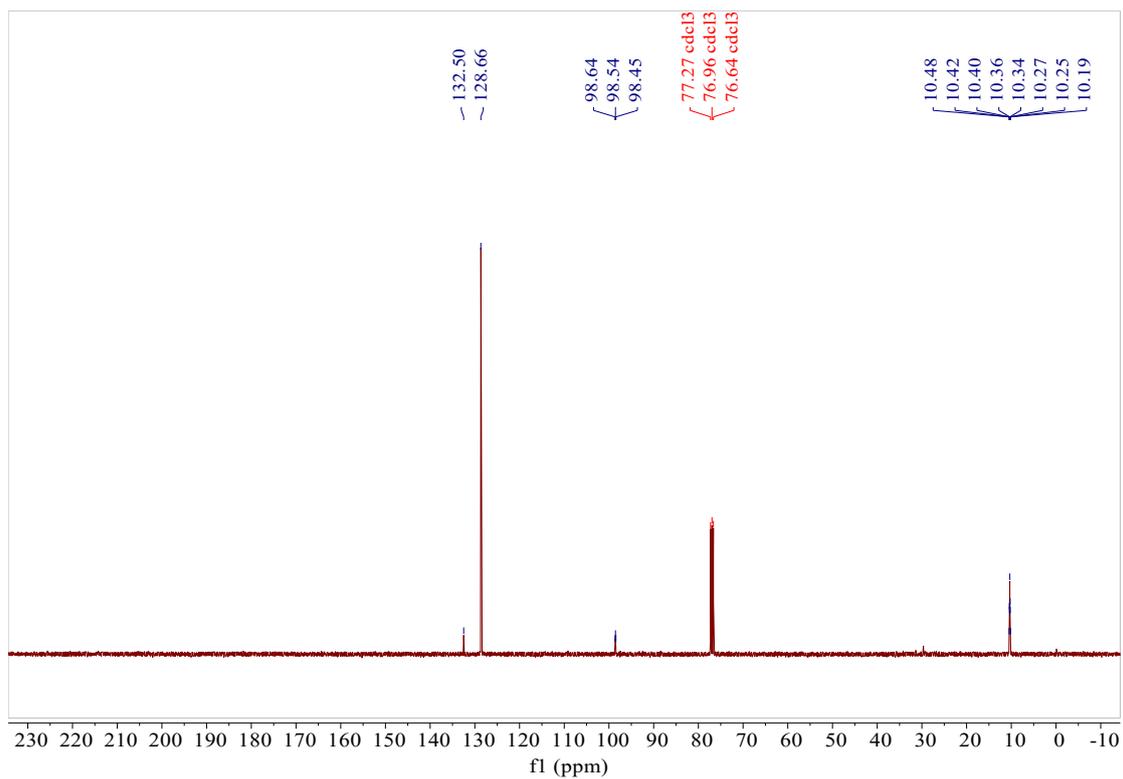
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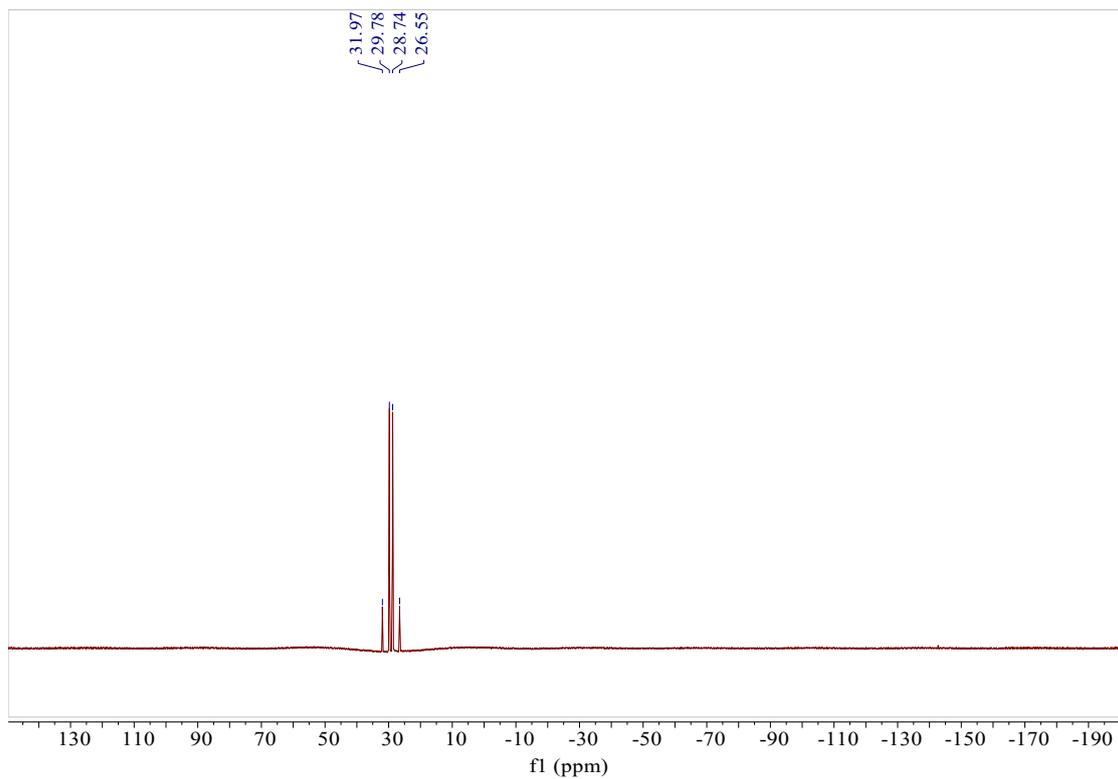
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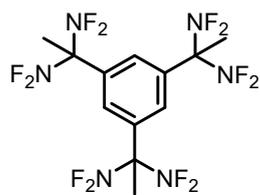
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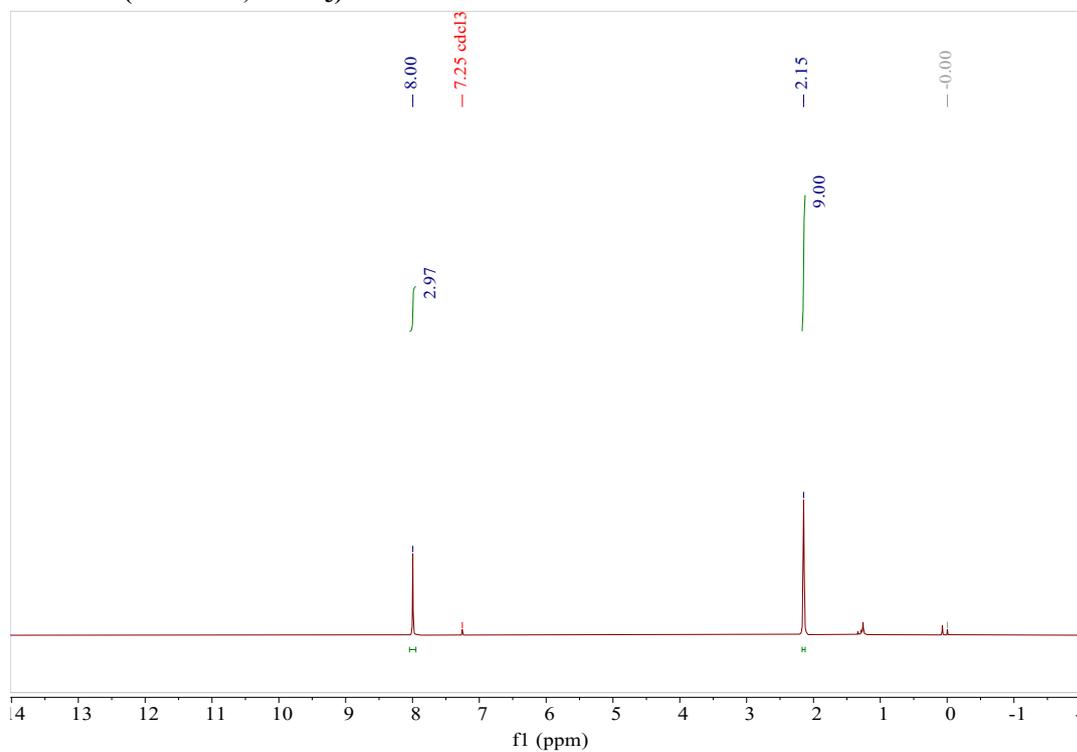
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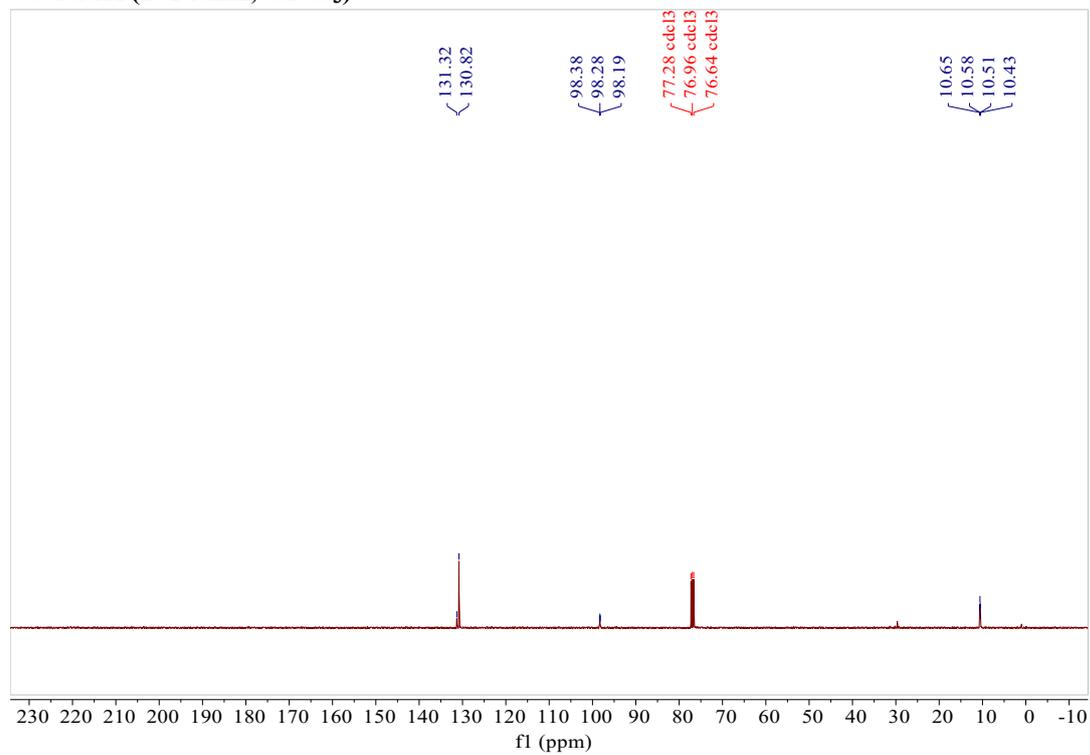
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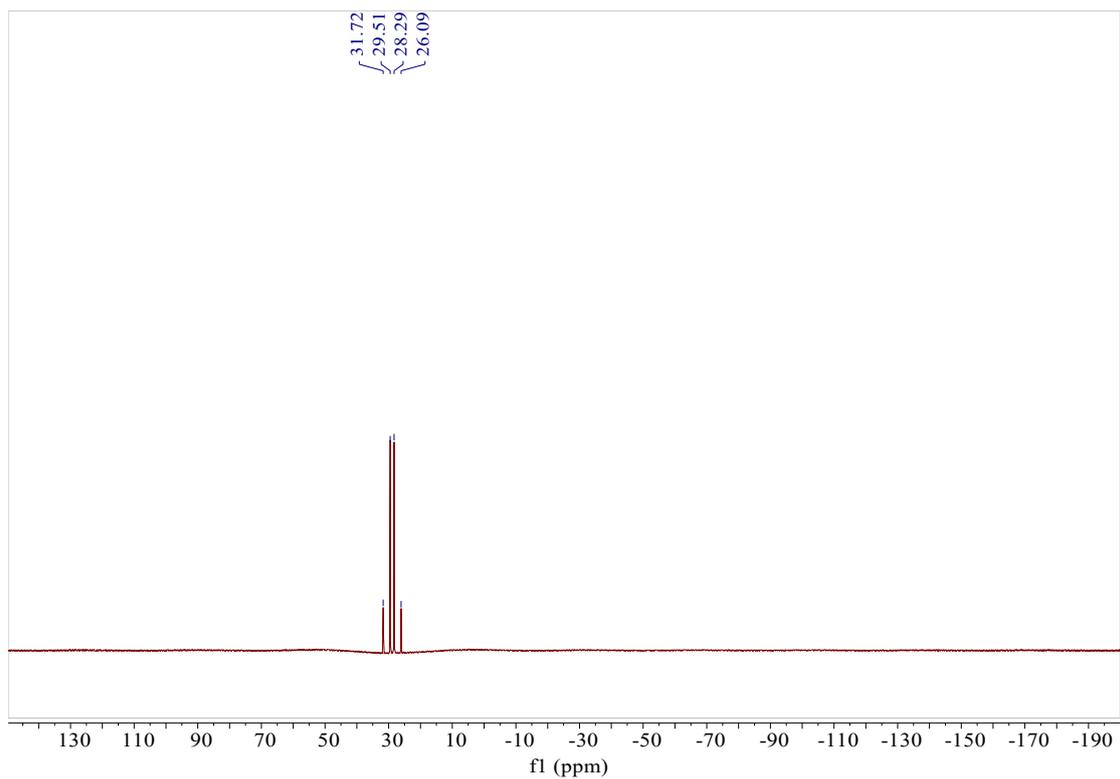
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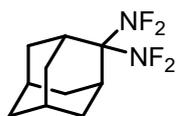
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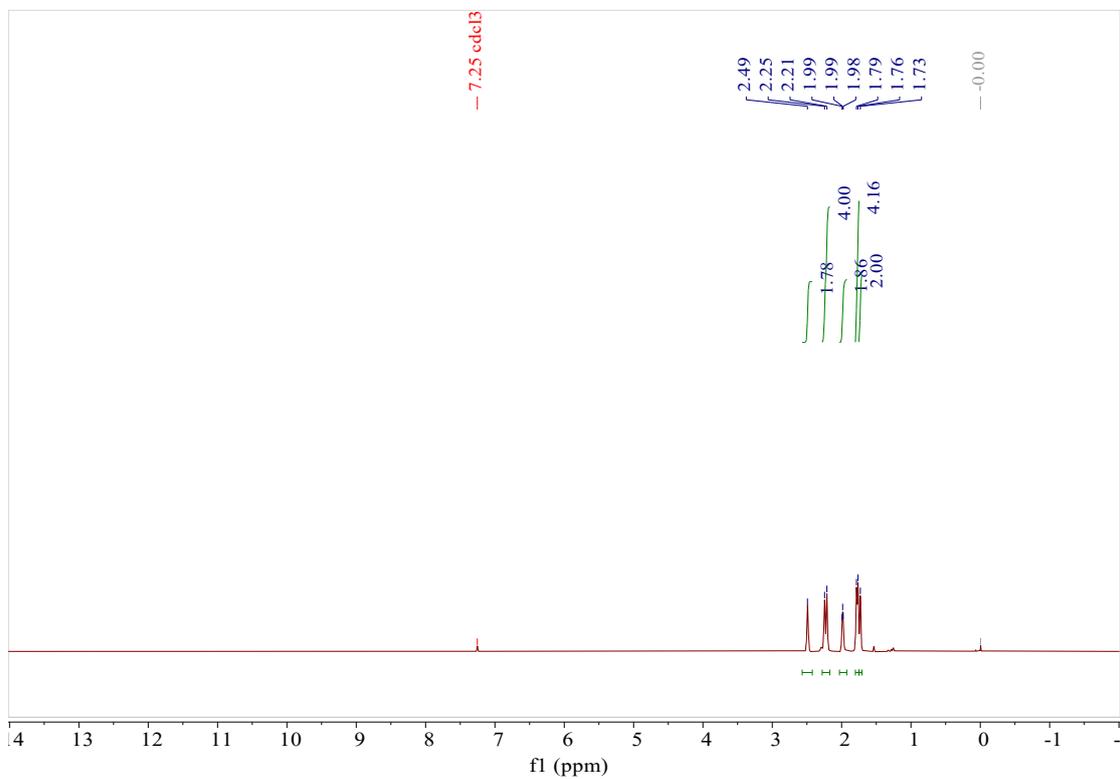
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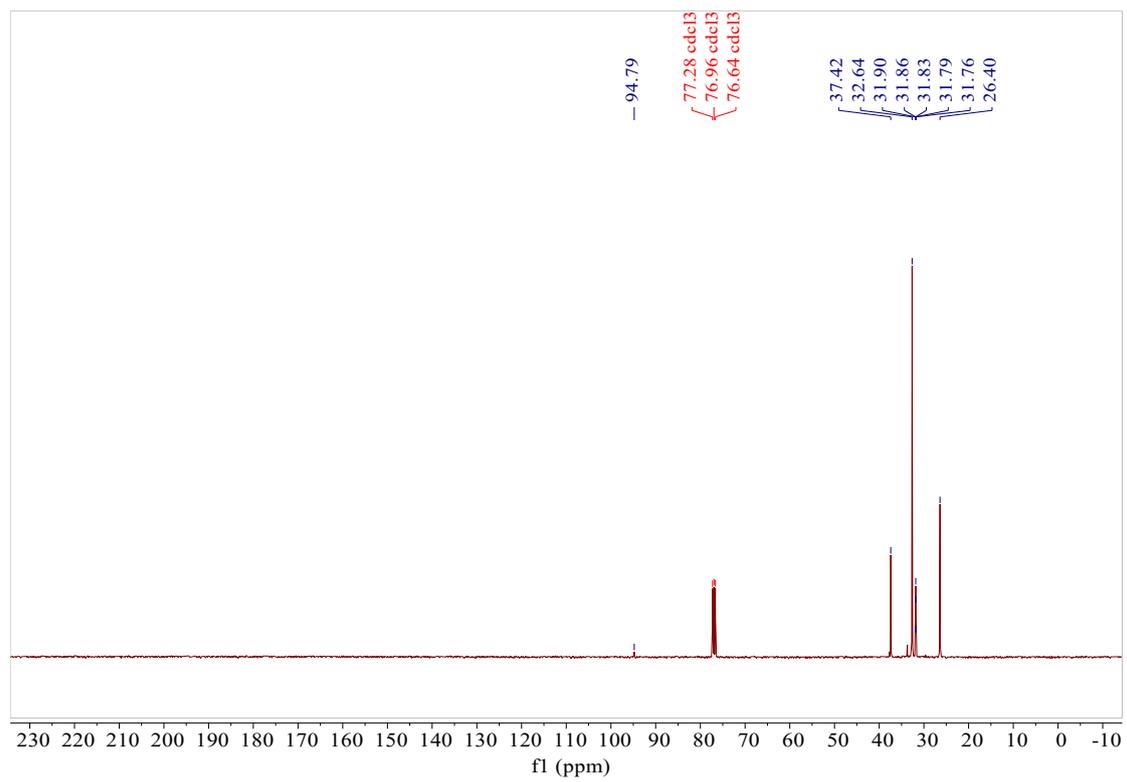
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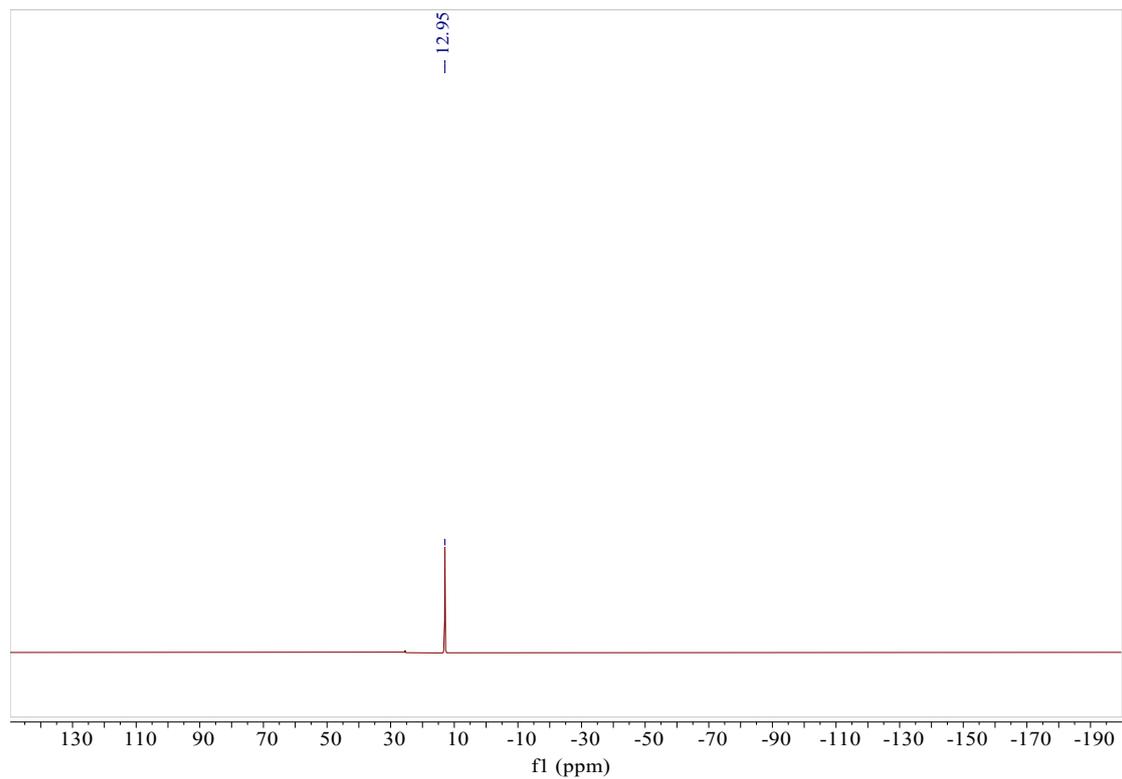
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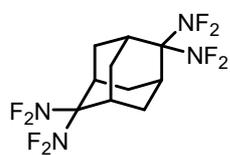
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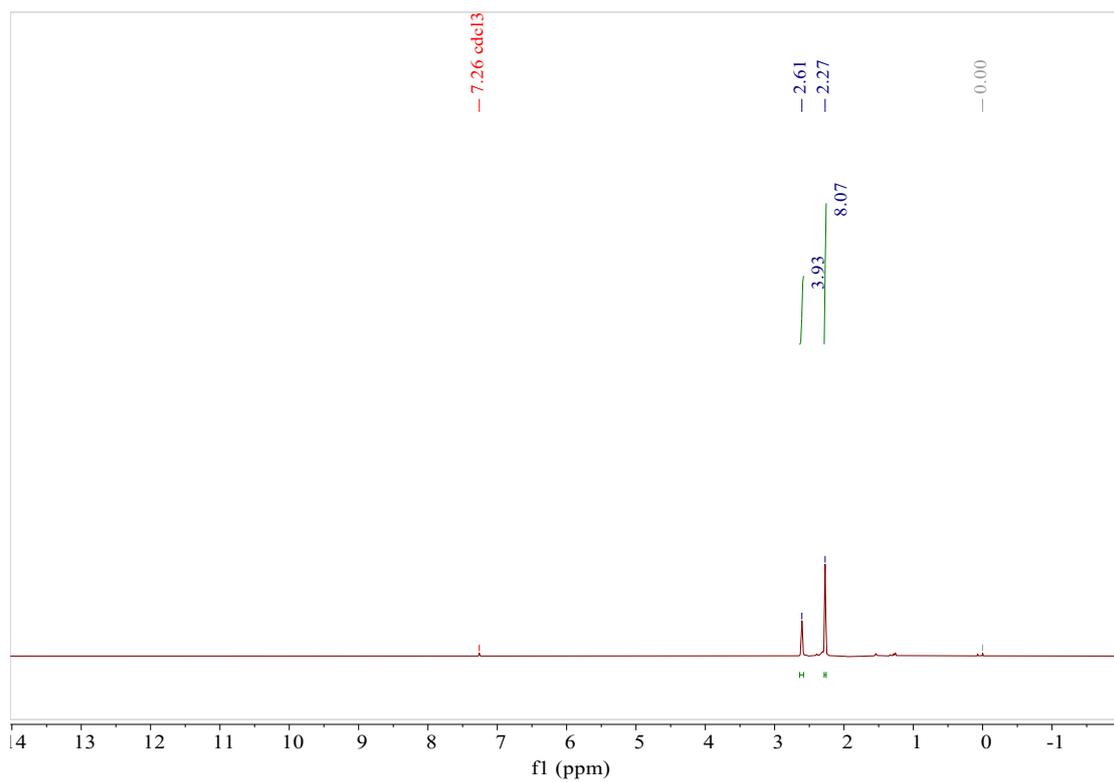
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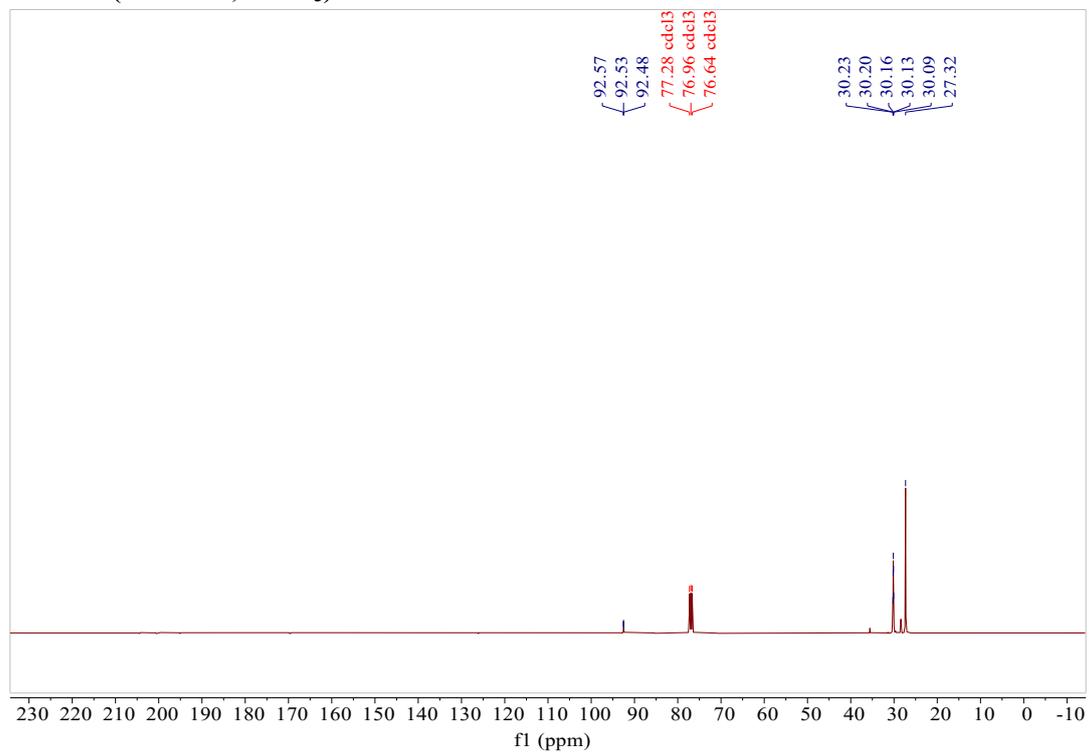
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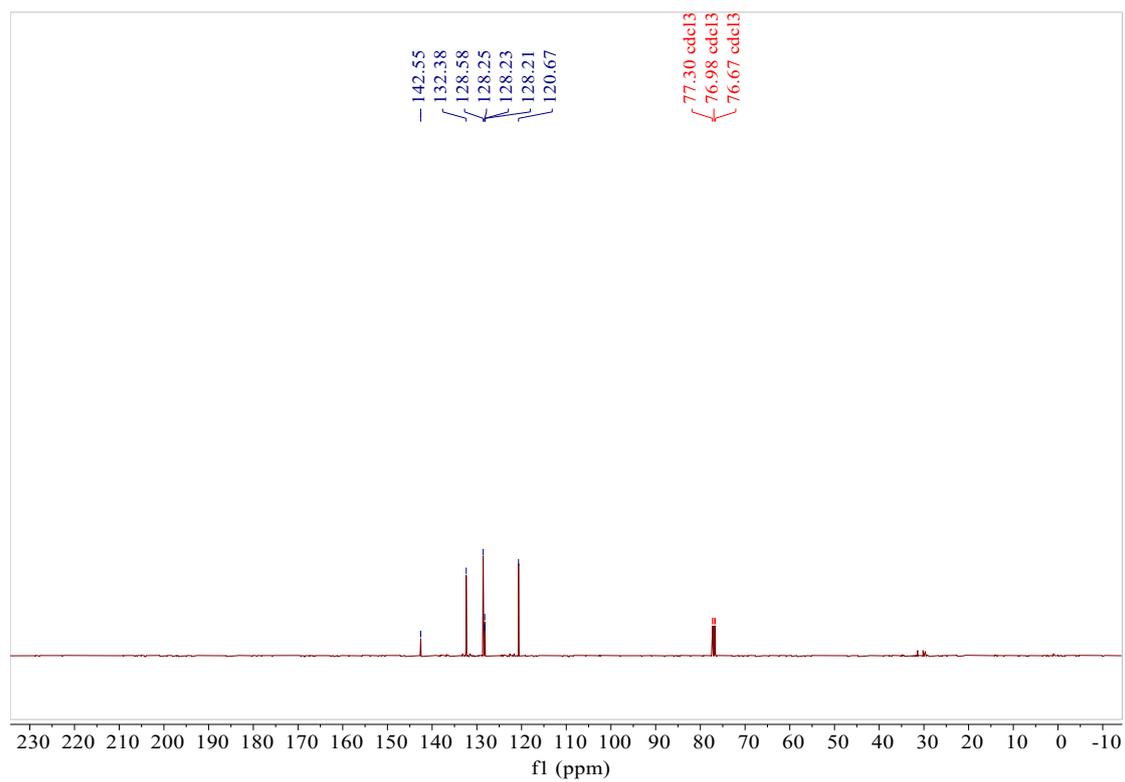


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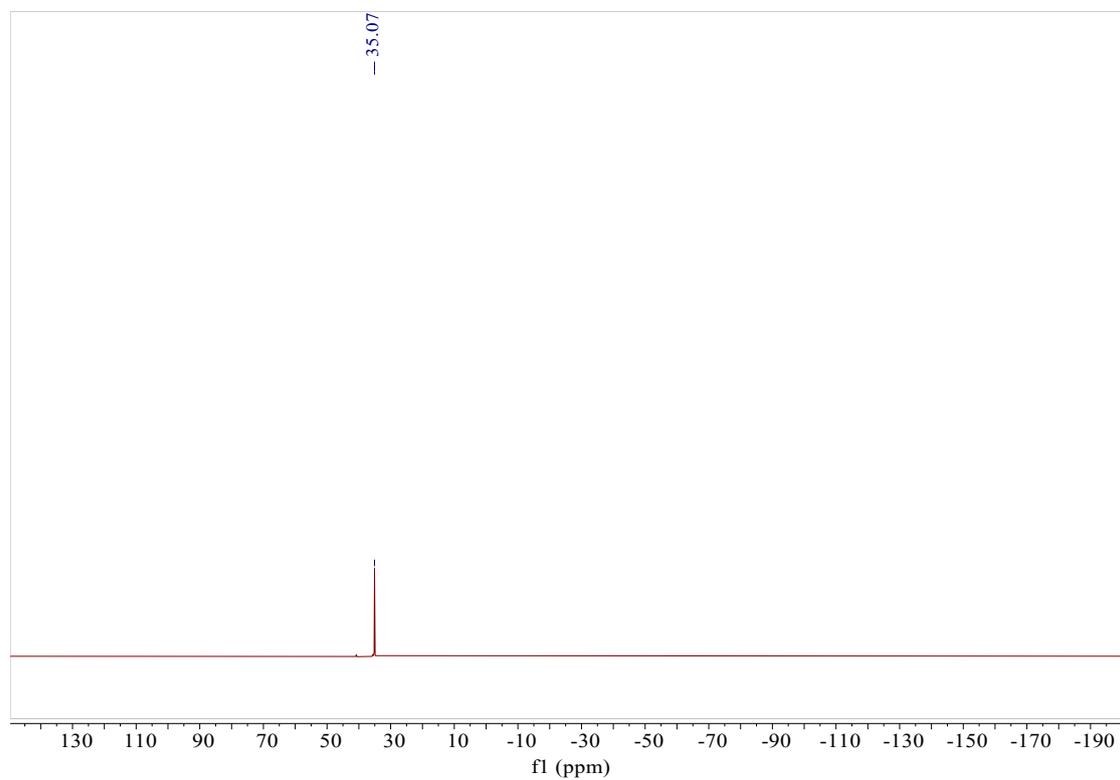


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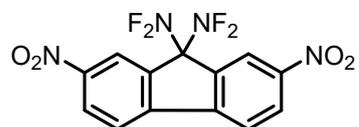
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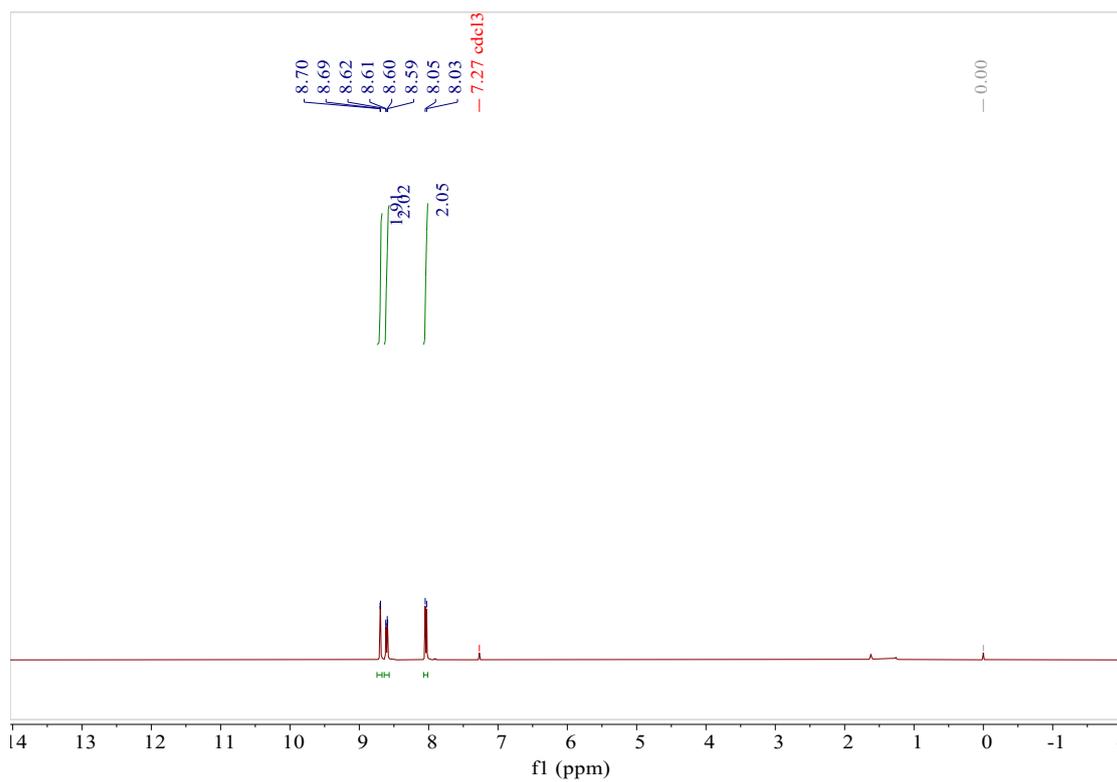
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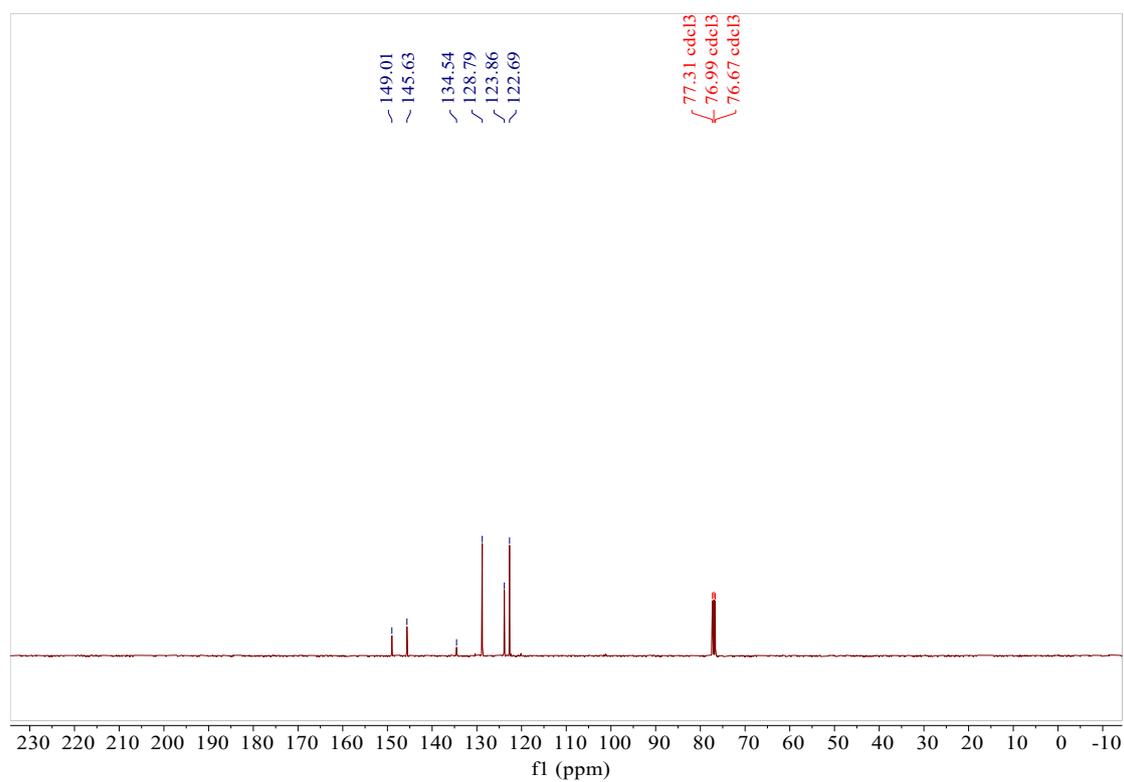
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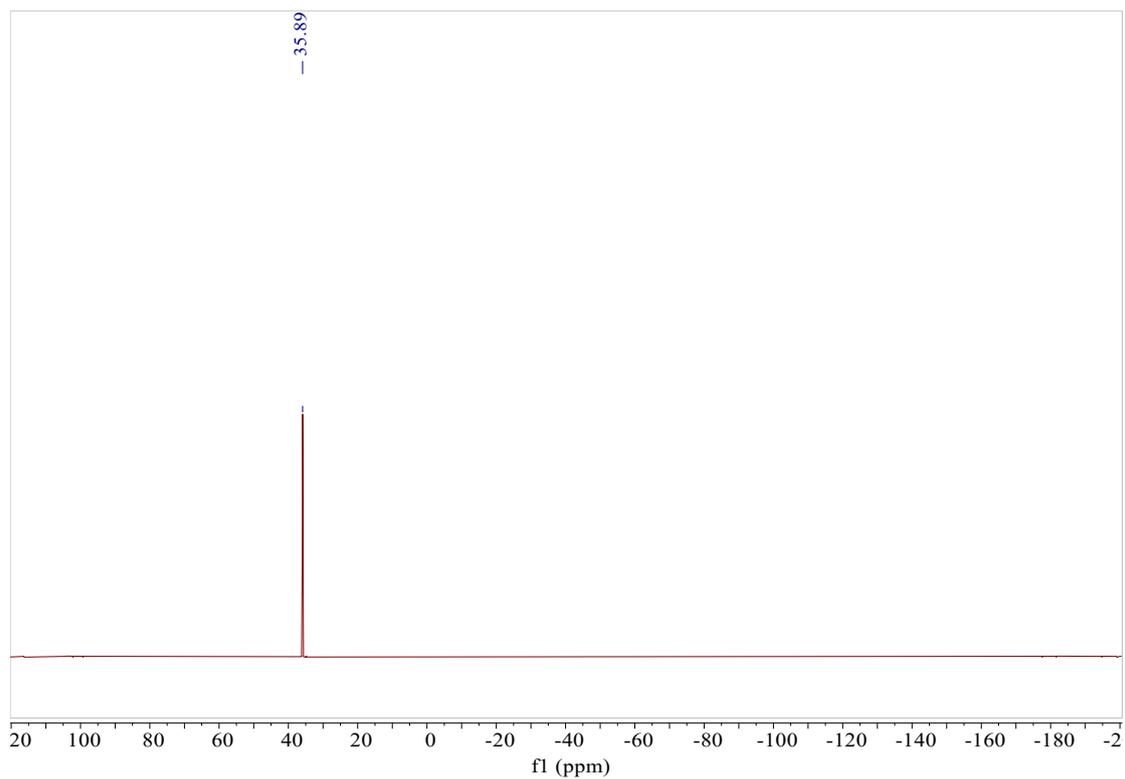
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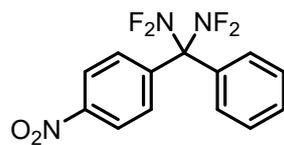
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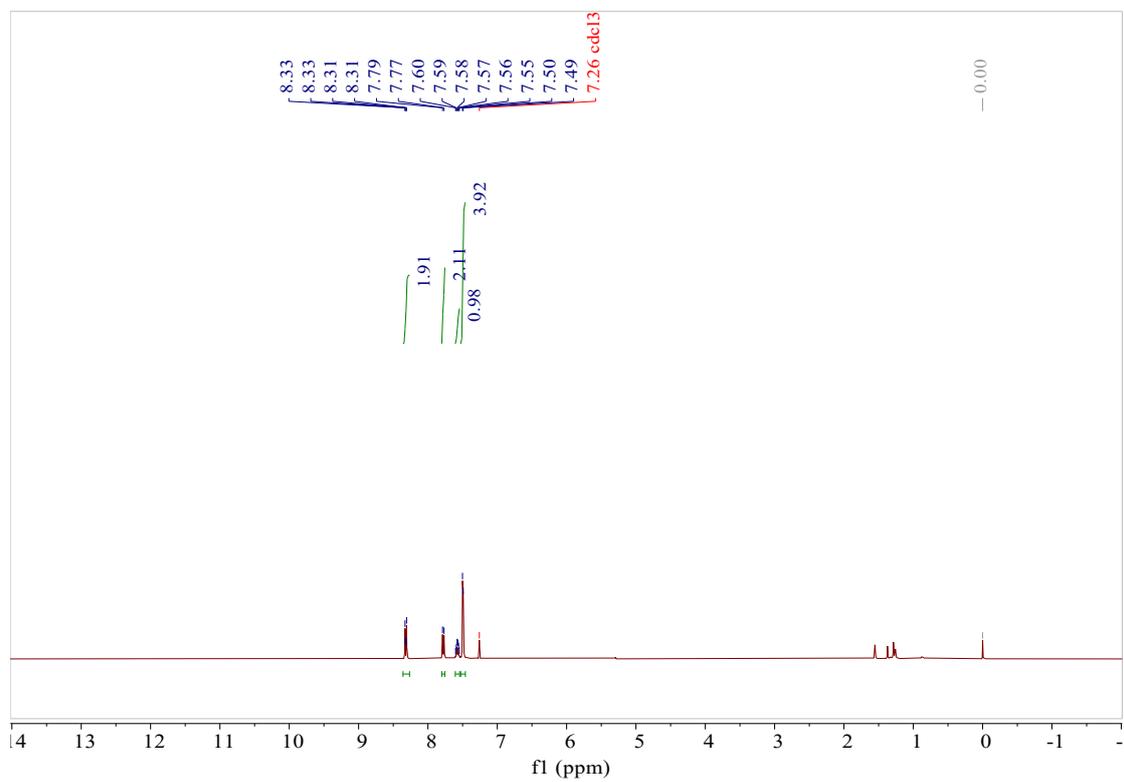
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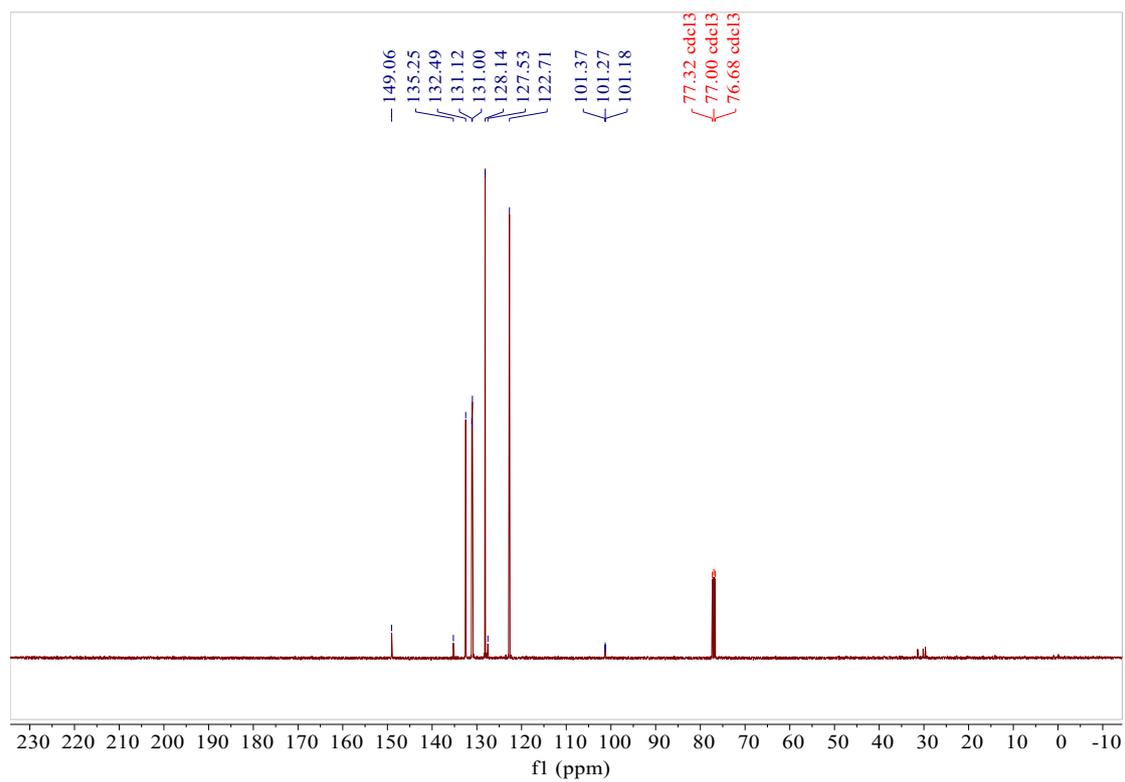
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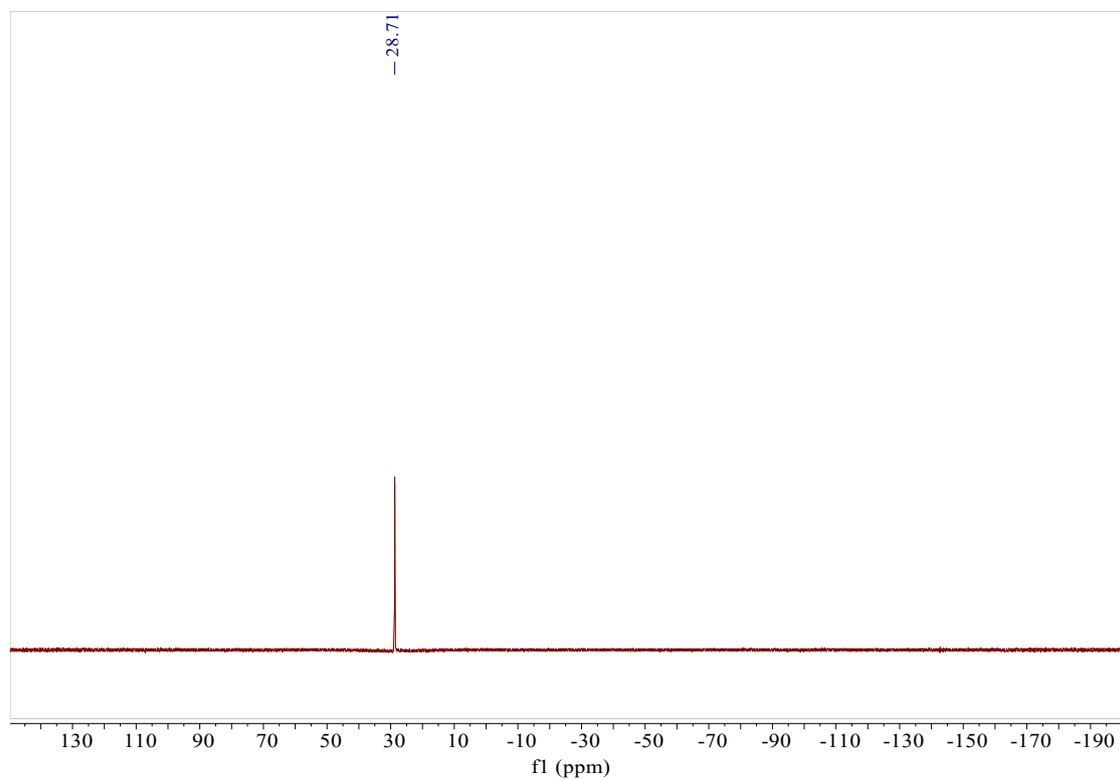
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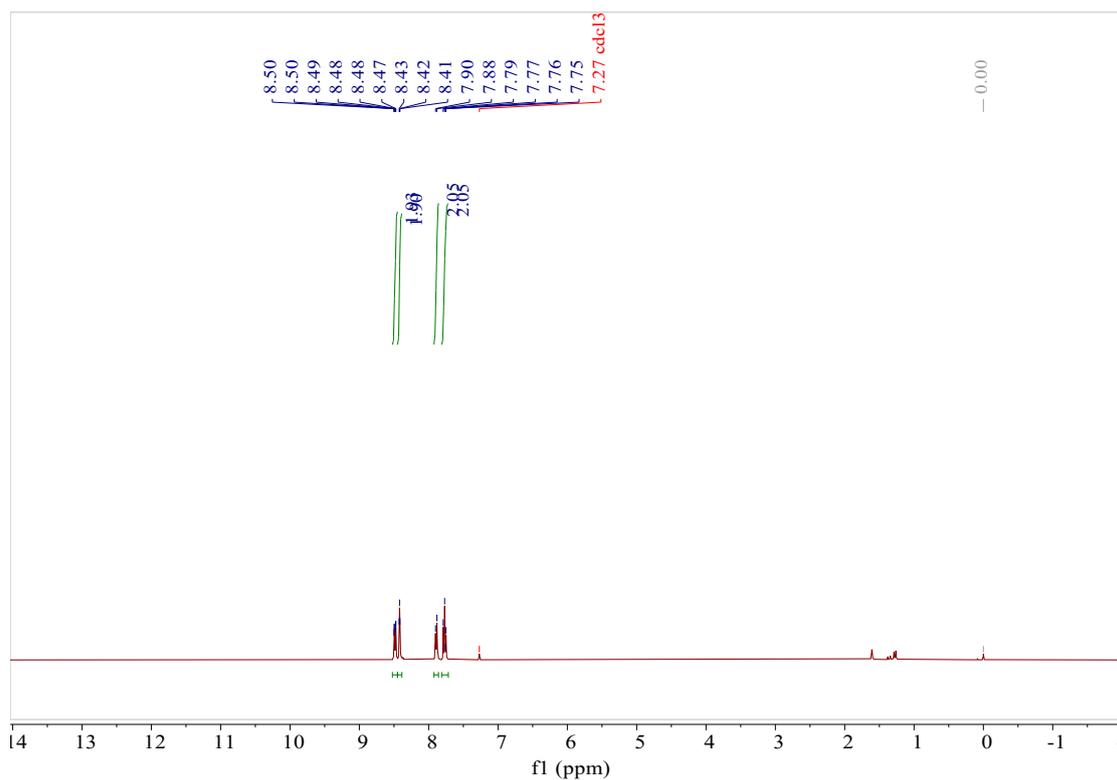
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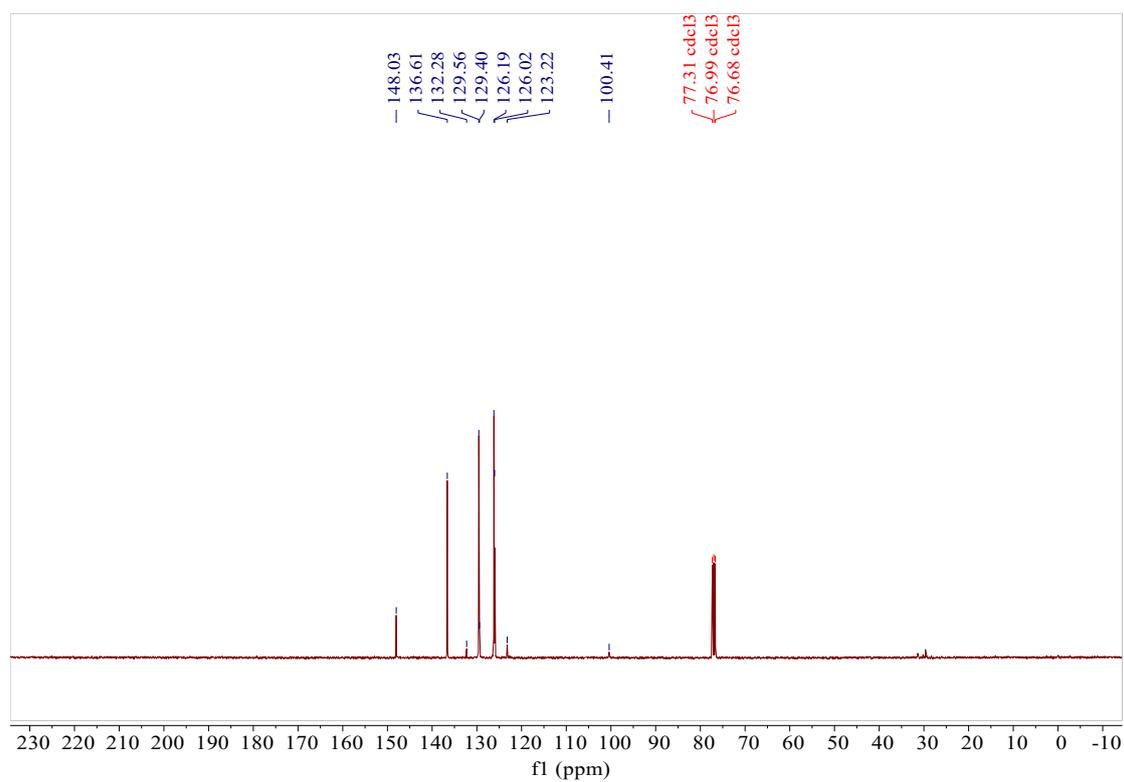
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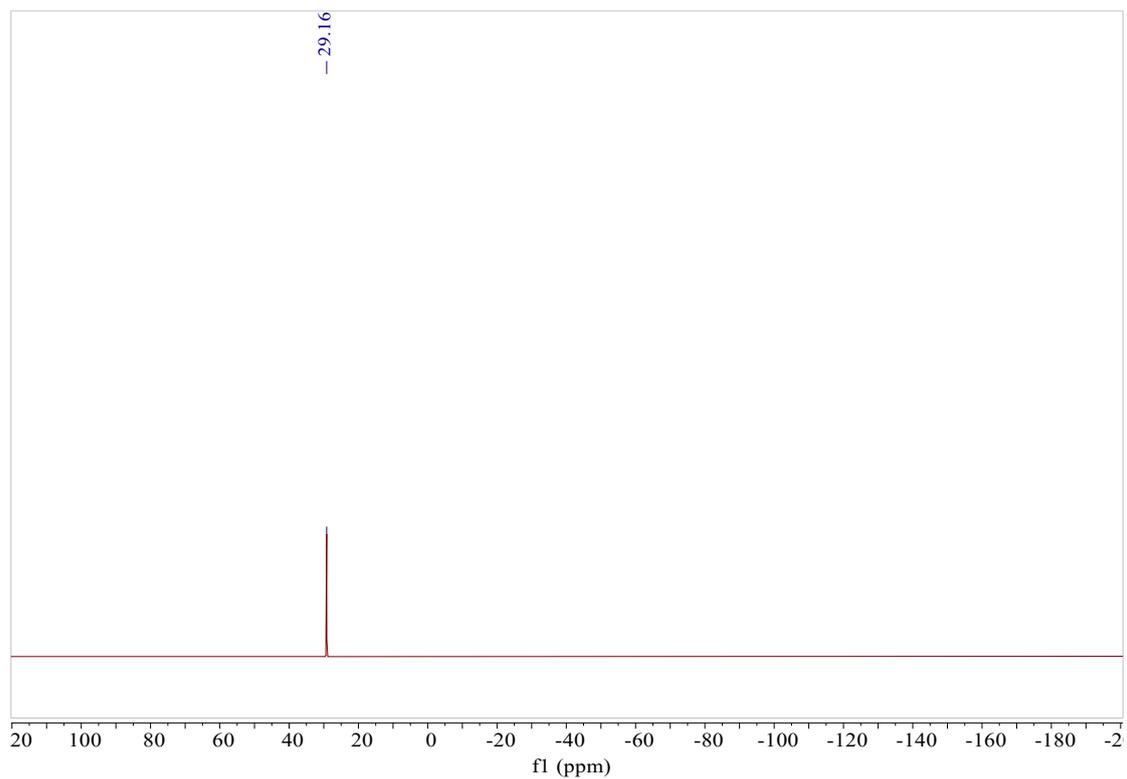
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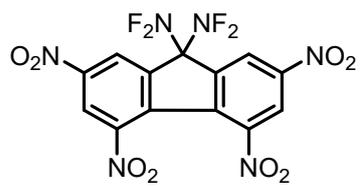
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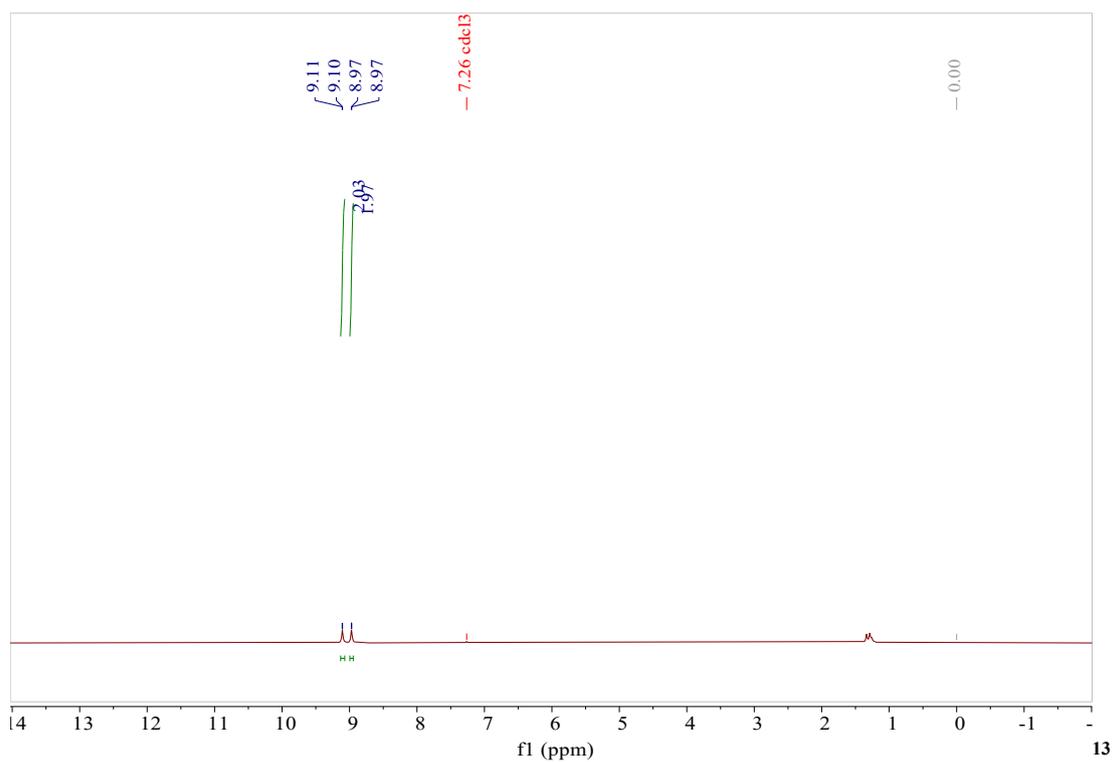
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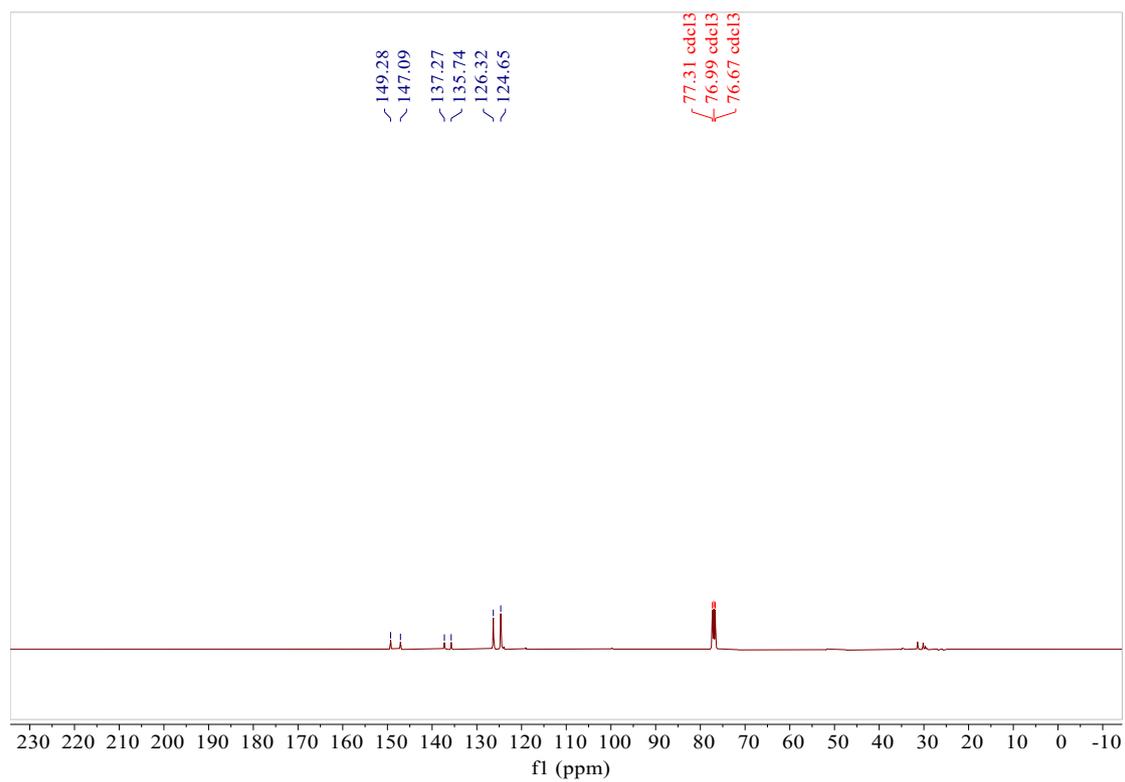
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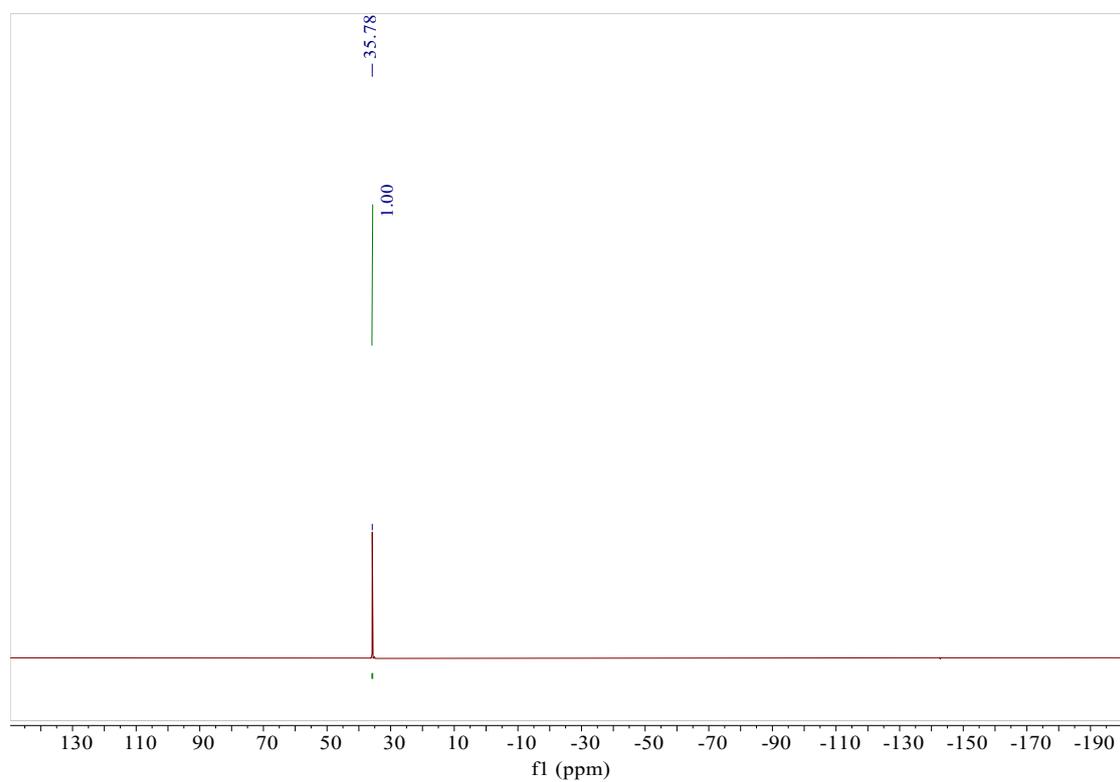
¹H NMR (400 MHz, CDCl₃)



C NMR (101 MHz, CDCl₃)



19F NMR (283 MHz, CDCl₃)



10. References

- [1] N M.S. Newman, W.B. Lutz, *J. Am. Chem. Soc.* **1956**, 78, 2469–2473.