Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Water Facilitated Photolysis of Perfluoroalkyl Iodides via Halogen Bonding

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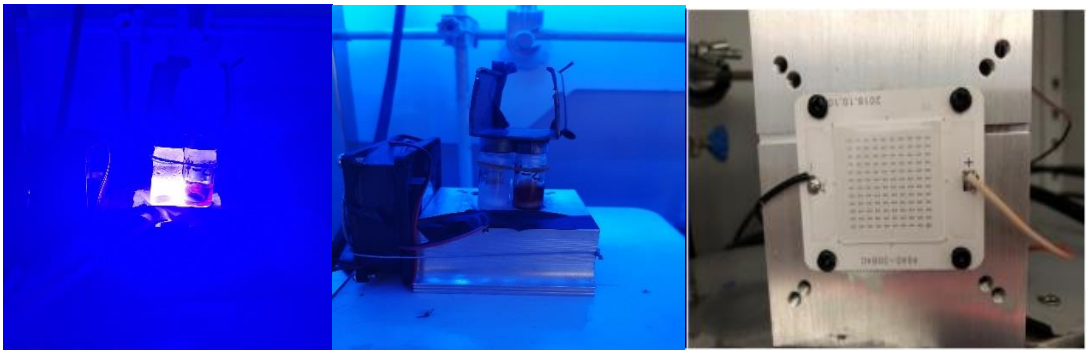
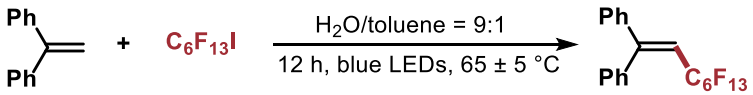
1.General Information

- Chemicals were purchased from Alfa Aesar, Heowns, Innochem and Bidepharm and used without further purification unless otherwise noted. Solvents were purified using a solvent-purification system (VSPS-8, Vigor) that contained activated alumina and molecular sieves.
- Flash column chromatography was performed using 200-300 mesh silica gel.
- IR spectra were taken on a Vertex 70 spectrophotometer and reported as wavenumbers (cm^{-1}).
- UV-vis absorption spectra were acquired on UV-1900 spectrophotometer (Shimadzu, Japan).
- The WRS-2 was used to measure the melting point of solids.
- ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Shimadzu Avance 400 and Shimadzu Avance 500 spectrometers at ambient temperature. Chemical shifts (δ) are reported in ppm downfield of tetramethylsilane (TMS) and the residual solvent peaks were used as an internal reference, for ^{1}H NMR: $CDCl_3$ = 7.26 ppm; for ^{13}C NMR: $CDCl_3$ = 77.16 ppm. The order of citation in parentheses is a) multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd= doublet of doublet, ddd= doublet of doublet of doublet, td = triplet of doublet, m = multiplet), b) coupling constants, c) number of protons. Coupling constants (J) are reported in Hertz (Hz). Photochemical experiments were performed magnetically stirred in 10 mL glass Sample bottle, sealed with a rubber septum. The tubes were irradiated with blue light (450 nm,) using a LED lamp with a power output of 50 W and directly contacted with the light source to keep the reaction temperature at 65 ± 5 °C (The purchase link of LED lamp is https://item.m.jd.com/product/47264027233.html).



2. Experimental Procedures

Scheme S1. Optimization of the Reaction Conditions[a]



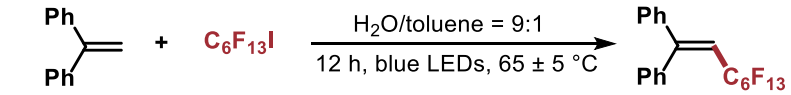
1 (1.0 equiv.) **2** (2.0 equiv.)

Entry	Variations from standard conditions	Yield (%)[b]
1	none	90
2	hexane	35
3	THF	60
4	DCM	33
5	H_2O	43
6	Toluene	50
7	acetonitrile	24
8	hexane: H_2O = 1:1	61
9	THF: H_2O = 1:1	58
10	DCM: H_2O = 1:1	62
11	toluene: H_2O = 1:1	83
12	acetone: H_2O = 1:1	65
13	xylene: H_2O = 1:1	67
14	PE: H_2O = 1:1	62
15	acetonitrile: H_2O = 1:1	80
16	acetonitrile: H_2O = 1:9	90
17	toluene: H_2O = 3:7	85
18	toluene: H_2O = 1:5	71
19	toluene: H_2O = 1:6	69
20	toluene: H_2O = 1:7	75
21	toluene: H_2O = 1:8	82
22	toluene: H_2O = 1:10	76
23	toluene: H_2O = 1:15	58
24	toluene: H_2O = 1:20	46
25	38 °C	33
26	50 °C	62
27	without irradiation (65 °C)	trace

[a] **1** (0.2 mmol), **2** (0.4 mmol), solvent (0.5 mL), irradiation with 50 W blue LEDs. [b] Yield is based on ^{1}H NMR analysis of crude reaction mixture.

3.General Procedures

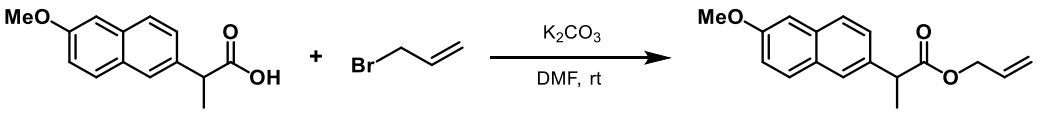
General procedure A



1 (1.0 equiv.) **2** (2.0 equiv.)

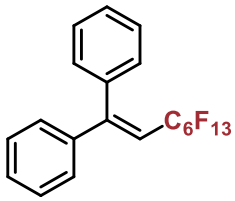
To a dry sample flask equipped with a stirring bar, the olefin (0.2 mmol, 1.0 equiv.), perfluoroalkyl iodide (0.4 mmol, 2.0 equiv.) were added. The tube was evacuated and filled with nitrogen (three times). After the addition of toluene (0.05 mL) and H_2O (0.45 mL) to the mixture via gas-tight syringe, the mixture was stirred overnight at about 65 °C via a 50W blue LED (450 nm) lamp. Then the reaction mixture was subjected to silica gel chromatography to afford the desired product (PE:EA = 200:1 – 5:1).

General procedure B

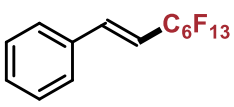


According to a literature procedure[1]: A round-bottom flask was charged with 2-(6-methoxynaphthalen-2-yl)propanoic acid (2 mmol, 1.0 equiv.) and allyl bromide (3 mmol, 1.5 equiv.) in the presence of K_2CO_3 (3 mmol, 1.5 equiv.) in DMF. The reaction was stirred for 4 hours at room temperature, then the organic phase was washed with water and extracted with Et_2O, dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel to afford the product.

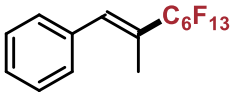
4. Compound Characterization Data



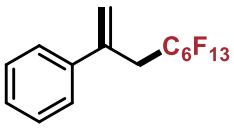
(3-n-perfluorohexyl-1-ene-1,1-diyl)dibenzene (3): Following the general procedure A, the title product was obtained after purification by column chromatography (PE) as a white solid (89.4 mg, 0.180 mmol, 90 % yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.39 - 7.31 (m, 6H), 7.25 - 7.22 (m, 4H), 6.1 (t, *J* = 14.7 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 154.5, 140.8, 137.6, 129.7, 129.1 (t, *J* = 3.0 Hz), 128.7, 128.5, 128.1, 128.0, 112.9 (t, *J* = 21.1 Hz). **^{19}F NMR** (471 MHz, Chloroform-d) δ -80.7 (t, *J* = 10.1 Hz, 3F), -103.5 (q, *J* = 14.1, 13.4 Hz, 2F), -121.4 – -121.5 (m, 2F), -122.7 – -122.8 (m, 2F), -122.85 – -122.93 (m, 2F), -126.0 – -126.1 (m, 2F). These data are in agreement with those reported previously in the literature.[2]



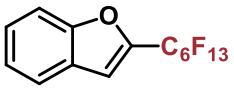
(E)-(3-n-perfluorohexyl-1-octen-1-yl)benzene (4): Following the general procedure A, the title product was obtained after purification by column chromatography (PE) as a transparent oil liquid (50.7 mg, 0.120 mmol, 60 % yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.51 – 7.38 (m, 4H), 7.18 (dt, *J* = 16.2, 2.5 Hz, 1H), 6.21 (dt, *J* = 16.2, 12.2 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 140.1 – 139.7 (t, *J* = 8.8 Hz), 133.7, 130.4, 129.1, 127.8, 114.4 (t, *J* = 23.0 Hz). **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -80.66 (t, *J* = 10.7 Hz, 3F), -111.0– -111.1 (m, 2F), -121.4– -121.6 (m, 2F), -122.7– -122.8 (m, 2F), -123.1– -123.2 (m, 2F), -126.0– -126.1 (m, 2F). These data are in agreement with those reported previously in the literature.[3]



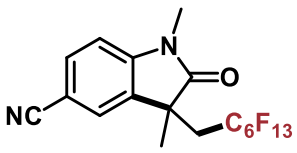
(E)-(3-n-perfluorohexyl-2-methyloct-1-en-1-yl)benzene (5): Following the general procedure A, the title product was obtained after purification by column chromatography (PE) as a transparent oil liquid (28.0 mg, 0.064 mmol, 32 % yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.43 – 7.38 (m, 2H), 7.36 – 7.32 (m, 3H), 7.03 (s, 1H), 2.04 – 2.03 (m, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 135.0 (t, J = 8.8 Hz), 134.9, 129.4, 128.6, 128.5, 126.1 (t, J = 20.7 Hz), 13.3. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -80.6 (t, J = 10.0 Hz,3F), -112.7 (t, J = 14.6 Hz, 2F), -121.5 – -121.6 (m, 2F), -121.7 – -121.8 (m, 2F), -122.6 – -122.8 (m, 2F), -126.0 – -126.1 (m, 2F). These data are in agreement with those reported previously in the literature.[4]



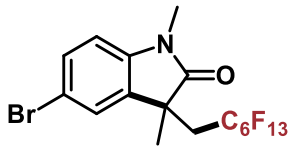
(4-n-perfluorohexyl-1-en-2-yl)benzene (6): Following the general procedure A, the title product was obtained after purification by column chromatography (PE) as a transparent oil liquid (56.5 mg, 0.13 mmol, 65% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.42 – 7.29 (m, 5H), 5.65 (s, 1H), 5.38 (s, 1H), 3.29 (t, J = 18.6 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 140.4, 137.1, 128.6, 128.1, 126.2, 120.8, 36.3 (t, J = 22.0 Hz). **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -80.7 (t, *J* = 10.0 Hz, 2F), -112.3 (p, *J* = 17.9, 17.4 Hz, 2F), -121.7 – -121.8 (m, 2F), --122.7 – -122.8 (m, 2F), -122.9 – -123.0 (m, 2F), -126.0 – -126.1 (m,2F). These data are in agreement with those reported previously in the literature.[5]



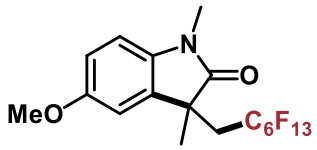
2-(n-perfluorohexyl)benzofuran (7): Following the general procedure A, the title product was obtained after purification by column chromatography (PE) as a transparent oil liquid (46.5 mg, 0.107 mmol, 53 % yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.69 - 7,66 (m, 1H), 7.59 - 7.57 (m, 1H), 7.47 - 7.45 (m, 1H), 7.35 -7.32 (m, 1H), 7.255 - 7.248 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 155.9, 127.2,126.3, 124.2, 122.6, 112.3, 110.7. **^{19}F NMR** (376 MHz, Chloroform-d) δ -80.7 (s, 3F), -111.8 (s, 2F), -121.9 (s,2F), -122.4 (s,2F), -122.7 (s,2F), -126.1 (s,2F). These data are in agreement with those reported previously in the literature.[6]



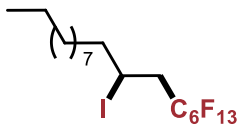
1,3-dimethyl-2-oxo-3-(2-n-perfluorohexyl)indoline-5-carbonitrile (8): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as a white solid (89 mg, 0.170 mmol, 85% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.66 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.542 – 7.535 (m, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 3.29 (s, 3H), 3.03 - 2.85 (m, 1H), 2.70 - 2.56 (m, 1H), 1.46 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 178.3, 146.8, 134.0, 132.4, 127.2, 119.1, 109.2, 106.1, 44.1, 37.2 (t, *J* = 20.5 Hz), 26.9, 25.9. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.8 (s, 3F), -106.0 – -115.0 (m, 2F), -121.7 (s, 2F), -122.8 (s, 2F), -123.8 (s, 2F), -126.1 (s, 2F). **IR** (neat): 3058, 2920, 2849, 2218, 1722, 1615, 1499, 1368, 1346, 1228, 1122, 822, 470 cm^{-1}. **HRMS** (ESI): m/z [M+Na]$^{+}$ calcd for $C_{18}H_{11}ON_2F_{13}Na^{+}$: 541.0556; found 541.0556. **Melting Point** (Experimental): 140 °C – 142 °C.



5-bromo-1,3-dimethyl-3-(2-n-perfluorohexyl)indolin-2-one (9): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as a white solid (71 mg, 0.124 mmol, 62% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.45 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.40 (d, *J* = 2.1 Hz, 1H), 6.78 (d, *J* = 8.3 Hz, 1H), 3.23 (s, 3H), 3.00 - 2.79 (m, 1H), 2.65 - 2.51 (m, 1H), 1.43 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 178.1, 142.0, 133.4, 131.6, 127.0, 115.4, 110.1, 44.5, 37.2 (t, *J* = 20.5 Hz), 26.7, 26.0. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.7 (s, 3F), -107.8 – -114.7 (m, 2F), -121.6 (s, 2F), -122.8 (s, 2F), -123.5 (s, 2F), -126.1 (s, 2F). **IR** (neat): 2986, 1710, 1609, 1493, 1362, 1185, 1143, 804, 696, 653, 563, 538, 466 cm^{-1}. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{17}H_{11}ONBrF_{13}Na^+$: 593.9709; found 593.9695. **Melting Point** (Experimental): 101 °C – 103 °C.

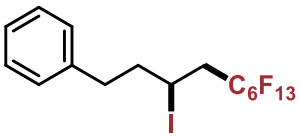


5-methoxy-1,3-dimethyl-3-(2-n-perfluorohexyl)indolin-2-one (10): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as a white solid (49 mg, 0.093 mmol, 47% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.90 (d, *J* = 2.5 Hz, 1H), 6.84 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 3.81 (s, 3H), 3.23 (s, 3H), 2.97 - 2.79 (m, 1H), 2.65 - 2.51 (m, 1H), 1.43 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 178.4, 156.2, 136.5, 132.8, 112.7, 111.5, 108.9, 56.0, 44.8, 37.1 (t, *J* = 20.5 Hz), 26.7, 26.1. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.7 (s, 3F), -107.6 – -115.4 (m, 2F), -121.7 (s, 2F), -122.8 (s, 2F), -123.6 (s, 2F), -126.1 (s, 2F). **IR** (neat): 2919, 2849, 1705, 1602, 1496, 1361, 1288, 1232, 1182, 1141, 1121, 797, 696, 564, 536, 466cm^{-1}. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{18}H_{14}O_2F_{13}Na^+$: 546.0709; found 546.0696. **Melting Point** (Experimental): 106 °C – 108 ˚C.

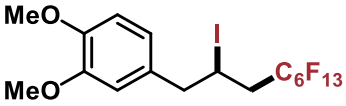


2-(n-perfluorohexyl)benzofuran (11): Following the general procedure A, the title product was obtained after purification by column chromatography (PE) as a transparent oil liquid (115.7 mg, 0.188 mmol, 94 % yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.37 - 4.30 (m, 1H), 3.02 - 2.68 (m, 2H), 1.88 - 1.72 (m, 2H), 1.58 - 1.51 (m, 1H), 1.46 - 1.34 (m, 2H), 1.32 - 1.26 (m, 13H), 0.90 - 0.86 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 41.8 (t, *J* = 21.0 Hz), 40.5, 32.1, 29.9, 29.72, 29.69, 29.53, 29.48, 28.7,

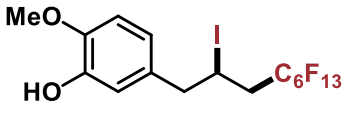
22.8, 21.1, 14.2. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.9 (s, 3F), -111.4 – -115.0 (m. 2F), -121.8 (s, 2F), -122.9 (s, 2F), -123.7 (s, 2F), -126.2 (s, 2F). **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{18}H_{24}F_{13}INa^+$: 637.0607; found 637.0596.



(5-n-perfluorohexyl-3-iododecyl)benzene (12): Following the general procedure A, the title product was obtained after purification by column chromatography (PE) as a transparent oil liquid (92 mg, 0.160 mmol, 80 % yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.33 - 7.28 (m, 2H), 7.24 - 7.20 (m, 3H), 4.30 - 4.22 (m, 1H), 3.05 - 2.66 (m, 4H), 2.21 - 2.02 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 140.0, 128.8, 128.6, 126.5, 41.8 (t, *J* = 20.8 Hz), 41.6, 35.8, 20.3. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.7 (s, 3F), -110.9 – 114.9 (m,2F), -121.7 (s, 2F), -122.8 (s, 2F), -123.5 (s, 2F), -126.1 (s, 2F). **IR** (neat): 2926, 1233, 1188, 1142, 1121, 733, 697, 656 cm^{-1}. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{15}H_{10}F_{13}INa^+$: 602.94610; found 602.9456.

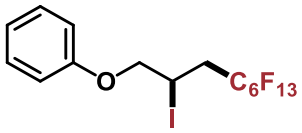


1,2-dimethoxy-4-(n-perfluorohexyl-2-iodononyl)benzene (13): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as a pale yellow solid (101.9 mg, 0.164 mmol, 82% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.83 (d, *J* = 8.2 Hz, 1H), 6.75 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.71 (d, *J* = 2.1 Hz, 1H), 4.45 (dq, *J* = 8.3, 6.4 Hz, 1H), 3.894 (s, 3H), 3.885 (s, 3H), 3.27 – 3.13 (m, 2H), 2.98 – 2.77 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 149.0, 148.4, 131.1, 121.4, 112.1, 111.2, 55.99, 55.95, 46.8, 40.6 (t, *J* = 20.8 Hz), 19.9. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.7 (s, 3F), -111.1 – -114.9 (m, 2F), -121.7 (s, 2F), -122.8 (s, 2F) , -123.5 (s, 2F) , -126.1 (s, 2F). **IR** (neat): 2958, 2839, 1518, 1233, 1188, 1140, 1073, 1022, 698, 653 $cm^{-1.}$ **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{17}H_{14}O_2F_{13}INa^+$: 646.9723; found 646.9718. **Melting Point** (Experimental): 60 °C – 62 °C.

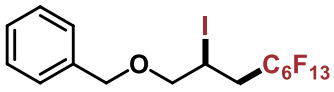


2-methoxy-5-(3-n-perfluorohexane-2-iodononyl)phenol (14): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA =

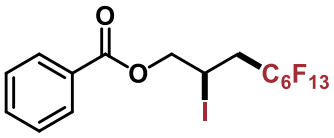
5:1) as a white solid (85 mg, 0.140 mmol, 70% yield). **^{1}H NMR** (500 MHz, Chloroform-d) δ 6.89 - 6.84 (m, 1H), 6.68 (d, *J* = 7.4 Hz, 2H), 5.56 (s, 1H), 4.44 - 4.39 (m, 1H), 3.89 (s, 3H), 3.11 - 3.21(m, 2H), 2.92 - 2.75 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 146.6, 145.0, 130.5, 122.1, 114.6, 111.5, 56.1, 46.9, 40.6 (t, *J* = 20.8 Hz), 20.1. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.6 (s, 3F), -111.0 – -114.6 (m,2F), -121.7 (s, 2F), -122.8 (s, 2F), -123.5 (s, 2F), -126.0 (s, 2F). **IR** (neat): 2969, 1693, 1515, 1188, 1143, 698, 653 cm$^{-1.}$ **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{16}H_{12}O_2F_{13}INa^+$: 632.9567; found 632.9548. **Melting Point** (Experimental): 58 °C – 59 °C.



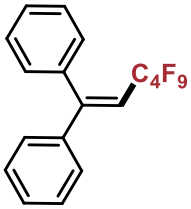
(4-n-perfluorohexyl-2-iodobutoxy)benzene (15): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 20:1) as a transparent oil liquid (103.2 mg, 0.178 mmol, 89% yield). **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.37 - 7.28 (m, 2H), 7.01 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.94 - 6.88 (m, 2H), 4.56 - 4.48 (m, 1H), 4.30 (dd, J = 10.4, 4.9 Hz, 1H), 4.18 (dd, J = 10.4, 6.7 Hz, 1H), 3.13 - 3.25 (m, 1H), 2.90 - 2.71 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.8, 129.8, 122.0, 115.0, 72.8, 37.8 (t, *J* = 20.8 Hz), 12.9. **^{19}F NMR** (471 MHz, Chloroform-d) δ -80.8 (t, *J* = 9.9 Hz,3F), -111.9 – -114.2 (m, 2F), -121.6 – -121.8 (m, 2F), -122.8 – -122.9 (m, 2F), -123.1 – -123.9 (m, 2F), -126.1 – -126.2 (m, 2F). **IR** (neat): 2988, 1599, 1496, 1232, 1190, 1142, 752, 691 cm^{-1}. **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{16}H_{13}F_{13}I^+$: 578.9849; found 578.9859.



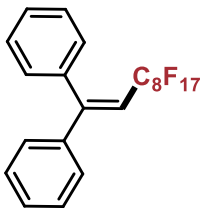
(((4-n-perfluorohexyl-2-iodononyl)oxy)methyl)benzene (16): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 20:1) as a pale yellow oil liquid (102 mg, 0.170 mmol, 86% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 151.5 Hz, 5H), 4.59 (d, *J* = 1.5 Hz, 2H), 4.40 - 4.33 (m, 1H), 3.78 - 3.63 (m, 2H), 3.17 - 3.01 (m, 1H), 2.77 - 2.60 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 140.0, 128.8, 128.6, 126.5, 41.9, 41.8 (t, *J* = 20.8 Hz), 35.8, 20.3. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.7 (s, 3F), -110.3 – -115.1 (m, 2F), -121.7 (s, 2F), -122.8 (s, 2F), -123.5 (s, 2F), -126.0 (s, 2F). **IR** (neat): 2865, 1233, 1190, 1142, 1073, 734, 697, 656 cm$^{-1.}$ **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{16}H_{12}OF_{13}INa$: 616.9617$^+$; found 616.9606.



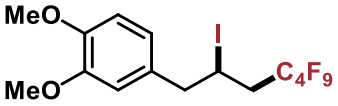
4-n-perfluorohexyl-2-iodononyl benzoate (17): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 20:1) as a white solid (110 mg, 0.180 mmol, 90% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.11 - 8.04 (m, 2H), 7.66 - 7.57 (m, 1H), 7.53 - 7.44 (m, 2H), 4.66 - 4.50 (m, 3H), 3.13 - 2.81 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 165.7, 133.7, 129.9, 129.4, 128.7, 68.9, 38.6 (t, *J* = 20.8 Hz), 12.2. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.7 (s, 3F), -111.6 – -114.7 (m, 2F), -121.7 (s, 2F), -122.8 (s, 2F), -123.4 (s, 2F), -126.0 (d, *J* = 11.9 Hz, 2F). **IR** (neat): 2973, 2902, 1727, 1265, 1231, 1140, 1115, 1025, 698, 653, 567, 530, 405 cm^{-1}. **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{16}H_{10}O_2F_{13}INa^+$: 630.9410; found 630.9410. **Melting Point** (Experimental): 40 °C – 42 °C.



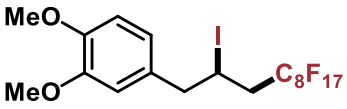
(3,3,4,4,5,5,6,6,6-Nonafluorohex-1-ene-1,1-diyl)dibenzene (18): Following the general procedure A, the title product was obtained after purification by column chromatography (PE) as a transparent oil liquid (55 mg, 0.138 mmol, 69% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.5 - 7.3 (m, 7H), 7.3 - 7.2 (m, 3H), 6.1 (t, *J* = 14.9 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 154.4, 140.8, 137.6, 129.7, 129.1, 128.6, 128.5, 128.1, 128.0, 112.7 (t, *J* = 20.7 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.9 (s 3F), -103.7 (s,2F), -123.8 (s,2F), -125.6 (s,2F). **IR** (neat): 3061, 2987, 2901, 1353, 1229, 1129, 1027, 878, 773, 695, 590 cm^{-1}. These data are in agreement with those reported previously in the literature.[7]



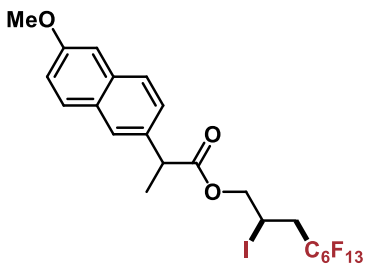
(3-n-perfluorooctane -1-ene-1,1-diyl)dibenzene (19): Following the general procedure A, the title product was obtained after purification by column chromatography (PE) as a white solid (77 mg, 0.129 mmol, 65% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.41 - 7.30 (m, 7H), 7.25 - 7.21 (m, 3H), 6.09 (t, *J* = 14.7 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 154.5, 140.9, 137.6, 129.7, 129.2, 128.7, 128.5, 128.1, 128.0, 112.9 (t, *J* = 21.2 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.8 (s, 3F), -103.5 (s, 2F), -121.3 (s, 2F), -121.9 (s, 4F), -122.7 (s, 2F), -122.9 (s, 2F), -126.1 (s, 2F). **IR** (neat): 2969, 1195, 1143, 1099, 977, 695, 652, 558 cm^{-1}. **HRMS** (ESI): m/z [M+H]$^+$ calcd for $C_{22}H_{12}F_{17}^+$: 599.0662; found 599.0649.



1,2-dimethoxy-4-(n-perfluorobutane-2-iodononyl)benzene (20): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as a transparent oil liquid (81 mg, 0.155 mmol, 77% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.84 (d, *J* = 8.2 Hz, 1H), 6.75 (dd, *J* = 8.1, 2.2 Hz, 1H), 6.71 (d, *J* = 2.2 Hz, 1H), 4.48 – 4.41 (m, 1H), 3.89 (s, 3H), 3.89 (s, 3H), 3.25 - 3.13 (m, 2H), 2.96 - 2.78 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.0, 148.4, 131.1, 121.4, 112.1, 111.2, 56.0, 56.0, 46.8, 40.5 (t, *J* = 20.7 Hz), 19.8. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.9 (s, 3F), -111.6 – -114.7 (m,2F), -124.5 (s, 2F), -125.8 (s, 2F). **IR** (neat): 2959, 2838, 1517, 1349, 1215, 1130, 1027, 879, 804, 720, 533, 465 cm^{-1}. **HRMS** (ESI): m/z [M+Na]$^{+}$ calcd for $C_{15}H_{14}F_9INa^{+}$: 546.9787; found 546.9774.

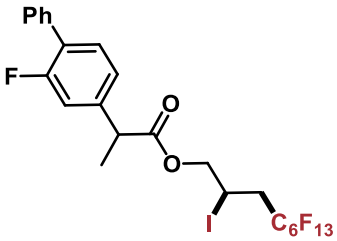


1,2-dimethoxy-4-(n-perfluorooctane-2-iodononyl)benzene (21): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as a white solid (88 mg, 0.122 mmol, 61% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.84 (d, *J* = 8.2 Hz, 1H), 6.75 (dd, *J* = 8.1, 2.1 Hz, 1H), 6.71 (d, *J* = 2.1 Hz, 1H), 4.52 - 4.39 (m, 1H), 3.90 (s, 3H), 3.89 (s, 3H), 3.25 - 3.13 (m, 2H), 2.94 - 2.79 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.0, 148.3, 131.1, 121.3, 112.1, 111.1, 55.9, 55.9, 46.7, 40.6 (t, *J* = 21.0 Hz), 19.8. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.7 (s, 3F), -111.5 – -114.5 (m, 2F), -121.5 (s, 2F), -121.8 (s, 4F), -122.6 (s, 2F), -123.5 (s, 2F), -126.0 (s, 2F). **IR** (neat): 2958, 2921, 2851, 1519, 1238, 1198, 1143, 1116, 1022, 657, 560, 530, 505 cm^{-1} **HRMS** (ESI): m/z [M+Na]$^{+}$ calcd for $C_{19}H_{14}O_2F_{17}INa$: 746.9659^{+}; found 746.9651. **Melting Point** (Experimental): 91 °C – 93 °C.

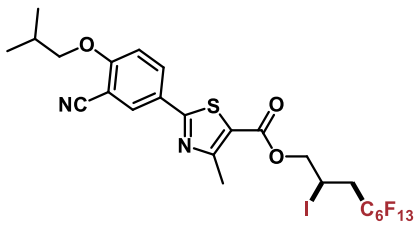


4-n-perfluorohexyl-2-iodononyl 2-(6-methoxynaphthalen-2-yl)propanoate (22): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as a white solid (123 mg, 0.171 mmol, 86% yield, dr = 1:1). **^{1}H NMR** (400 MHz, Chloroform-d) δ

7.81 - 7.59 (m, 3H), 7.41 - 7.37 (m, 1H), 7.15 - 7.09 (m, 2H), 4.47 - 4.17 (m, 3H), 3.95 - 3.87 (m, 4H), 2.85 - 2.44 (m, 2H), 1.64 - 1.61(dd, J = 7.2, 2.7 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 173.8, 173.7, 157.9, 135.0, 134.96, 134.0, 129.4, 129.3, 129.1, 127.5, 127.4, 126.3, 126.2, 126.15, 119.3, 105.7, 105.7, 68.6, 55.4, 55.3, 45.5, 45.47, 37.9 (t, *J* = 21.0 Hz), 37.8 (t, *J* = 20.9 Hz), 18.2, 18.16, 11.8, 11.7.**^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.7 (s, 3F), -105.1 – -120.2 (m,2F), -121.8 (s, 2F), -122.8 (s, 2F), -123.6 (s, 2F), -126.1 (s, 2F). **IR** (neat): 2971, 1633, 1606, 1228, 1139, 1034, 815, 790, 696, 652, 529, 475 cm^{-1} **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{17}H_{14}F_{13}INa^+$: 738.9985; found 738.9984. **Melting Point** (Experimental): 95 °C – 97 °C.

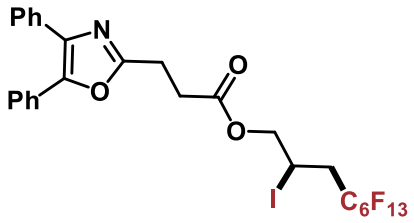


4-n-perfluorohexyl-2-iodononyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (23): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 10:1) as a pale yellow solid (121 mg, 0.166 mmol, 83% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.53 - 7.49 (m, 2H), 7.46 - 7.31 (m, 4H), 7.19 - 7.09 (m, 2H), 4.47 - 4.23 (m, 3H), 3.84 - 3.78 (m, 1H), 2.88 - 2.57 (m, 2H), 1.59 - 1.56 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 173.1, 161.1, 158.6, 141.2 (d, *J* = 4.4 Hz), 141.1 (d, *J* = 4.4 Hz), 135.5, 131.0, 129.0, 128.58, 128.56, 127.9, 123.8 (d, *J* = 3.4 Hz), 123.7 (d, *J* = 3.4 Hz) 115.6 (d, *J* = 5.8 Hz), 115.4 (d, *J* = 5.8 Hz), 68.8, 45.1, 38.1 (t, *J* = 20.8 Hz), 38.0 (t, *J* = 20.8 Hz), 18.1, 11.7, 11.6. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.7 (s, 3F), -112.1 – -115.6 (m, 2F), -117.4 (s, 1F), -121.7 (s, 2F), -122.8 (s, 2F), -123.5 (s, 2F), -126.1 (s, 2F). **IR** (neat): 2977, 1734, 1483, 1420, 1232, 1141, 765, 695, 657, 516 cm^{-1}. **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{24}H_{17}F_{13}INa^+$: 752.9942; found 752.9930. **Melting Point** (Experimental): 56 °C – 58 °C.

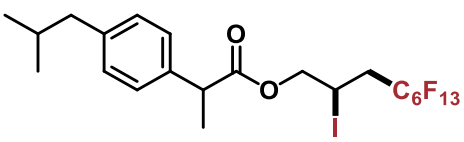


4-n-perfluorohexyl-2-iodononyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (24): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as a white solid (143 mg, 0.179 mmol, 89% yield, dr = 1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 2.3 Hz, 1H), 8.11 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.02 (d, *J* = 8.9 Hz,

1H), 4.59 - 4.51 (m, 3H), 3.91 (d, *J* = 6.5 Hz, 2H), 3.10 - 2.81 (m, 2H), 2.79 (s, 3H), 2.32 - 2.13 (m, 1H), 1.10 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 168.2, 162.8, 162.5, 161.1, 132.8, 132.4, 125.9, 120.7, 115.5, 112.8, 103.2, 75.9, 69.1, 38.6 (t, *J* = 20.7 Hz), 28.3, 19.2, 17.8, 11.8. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.7 (s, 3F), -111.1 – -115.2 (m, 2F), -121.6 (s, 2F), -122.7 (s, 2F), -123.3 (s, 2F), -126.0 (s, 2F). **IR** (neat): 1694, 1606, 1339, 1228, 1187, 1111, 829, 698, 653 cm^{-1}. **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{17}H_{14}F_{13}INa^+$: 824.9924; found 824.9905. **Melting Point** (Experimental): 113 °C - 115 °C.



4-n-perfluorohexyl-2-iodononyl 3-(4,5-diphenyloxazol-2-yl)propanoate (25): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 5:1) as a pale yellow solid (141 mg, 0.181 mmol, 90% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.66 - 7.60 (m, 2H), 7.59 - 7.54 (m, 2H), 7.40 - 7.28 (m, 6H), 4.48 - 4.32 (m, 3H), 3.22 (t, *J* = 7.6 Hz, 2H), 3.01 (t, *J* = 7.6 Hz, 2H), 2.97 - 2.69 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 171.2, 161.5, 145.7, 135.3, 132.5, 129.1, 128.8, 128.70, 128.65, 128.2, 128.0, 126.6, 68.8, 38.3 (t, *J* = 21.2 Hz), 31.0, 23.5, 12.0. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -80.7 (t, *J* = 9.9 Hz, 3F), -109.2 – -116.4 (m,2F), -121.5 – -121.8 (m.2F), -122.7 (q, *J* = 12.4 Hz, 2F), -123.2 – -123.6 (m, 2F), -126.0 (dd, *J* = 15.4, 9.9 Hz, 2F). **IR** (neat): 2988, 2902, 1738, 1607, 1594, 1360, 1326, 1238, 1175, 1142, 694, 600, 504 cm^{-1}. **HRMS** (ESI): m/z [M+K]$^+$ calcd for $C_{27}H_{19}O_3NF_{13}IK^+$: 817.9834; found 817.9825. **Melting Point** (Experimental): 72 °C – 73 °C.

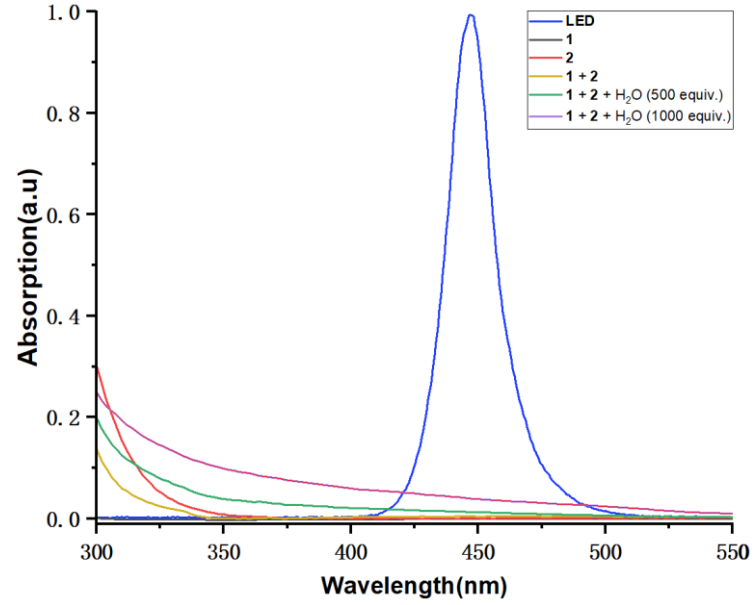


4-n-perfluorohexyl-2-iodononyl 2-(4-isobutylphenyl)propanoate (26): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 10:1) as a white solid (120 mg, 0.173 mmol, 87% yield, dr = 1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.23 - 7.18 (m, 2H), 7.10 - 7.08 (m, 2H), 4.47 - 4.15 (m, 3H), 3.78 - 3.71 (m, 1H), 2.91 - 2.50 (m, 2H), 2.45 - 2.42 (m, 2H), 1.88 - 1.78 (m, 1H), 1.54 - 1.52 (m, 3H), 0.89 - 0.88 (m, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 173.9, 173.8, 141.0,

137.13, 137.07, 129.6, 127.4, 127.3, 68.5, 45.2, 45.13, 45.11, 45.09, 37.9 (t, *J* = 21.5 Hz), 37.7 (t, *J* = 21.8 Hz), 30.3, 30.28, 22.4, 18.2, 11.8, 11.7. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.67 (s, 3F), -111.4 – -115.8 (m, 2F), -121.7 (s, 2F), -122.8 (s, 2F), -123.5 (s, 2F), -126.0 (s, 2F). **IR** (neat): 2966, 2932, 2873, 1732, 1232, 1140, 1071, 695, 652, 567, 547, 530, 505 cm^{-1}. **HRMS** (ESI): m/z $[M+K]^+$ calcd for $C_{22}H_{22}O_2F_{13}IK^+$: 731.0089; found 731.0083. **Melting Point** (Experimental): 45 °C – 46 °C.

5. Mechanism Studies

5.1 UV/Vis absorption spectrometry



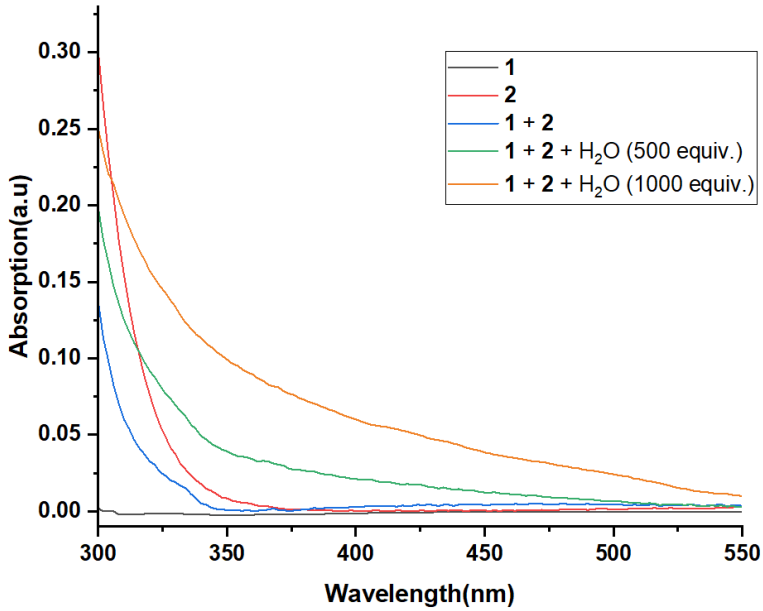


Figure S1: UV/vis spectrum of blue LED, **1**, **2**, **1**+**2**+H_2O (500 equiv.) and **1**+**2**+H_2O (1000 equiv.), [**1**] = 10^{-4} M, [**2**] = $2*10^{-4}$ M, [water] = 0.05 M (500 equiv.);0.1 M (1000 equiv.) in toluene.

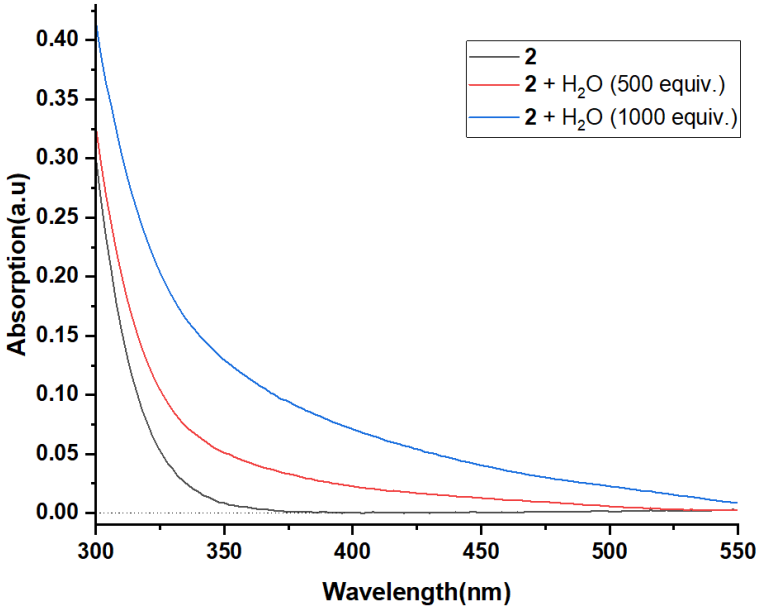


Figure S2: UV/vis spectrum of **2**, **2**+H_2O (500 equiv.) and **2**+H_2O (1000 equiv.), [**2**] = $1*10^{-4}$ M, [water] = 0.05 M (500 equiv.);0.1 M (1000 equiv.) in toluene.

5.2 Determination of binding stoichiometry of halogen bond complex

The binding stoichiometry between $C_6F_{13}I$ and halogen bond acceptors (XB acceptor: H_2O) were evaluated using Job's plot analysis[8]: ^{19}F NMR spectra of ten samples of mixtures of $C_6F_{13}I$ and XB acceptor in CD_3CN were recorded at 298 K. Trifluoroluorobenzene (δ F-Ph = -63.7200) was used as internal standard. The total volume of the mixture was 0.6 mL, and the total amount of $C_6F_{13}I$ and halogen bond acceptor was kept constant at 0.3 mmol (0.5 M), while the amount of $C_6F_{13}I$ was varied from 0 to 0.3 mmol (0-0.5 M). The molar ratios of $C_6F_{13}I/(C_6F_{13}I + H_2O)$ were 0.0, 0.07, 0.24, 0.35, 0.44, 0.56, 0.63, 0.81, 0.91, 1.0. ^{19}F NMR for each sample was recorded and the chemical shifts differences (Δδ) for $-CF_2I$ were used to draw the plot. The stoichiometry was determined by plotting ratios of $[C_6F_{13}I] \times \Delta\delta$ against ratios of $[C_6F_{13}I] / [C_6F_{13}I + H_2O]$ to afford a maximum at ratio $[C_6F_{13}I] / [C_6F_{13}I + H_2O] = 0.5$, which meant a 1:1 complex ratio between $C_6F_{13}I$ and H_2O (Figure

S3).

	[$C_6F_{13}I$] (M)	Δδ (ppm)	[$C_6F_{13}I$]/[$C_6F_{13}I$+H_2O]	[$C_6F_{13}I$]×Δδ (M.ppm)
1	0.50	0	1.00	0
2	0.45	0.032	0.91	0.0147
3	0.41	0.060	0.81	0.0244
4	0.31	0.122	0.63	0.0385
5	0.28	0.149	0.56	0.0414
6	0.22	0.187	0.44	0.0416
7	0.18	0.202	0.35	0.0356
8	0.12	0.237	0.24	0.0285
9	0.04	0.273	0.07	0.0101
10	0	0	0	0

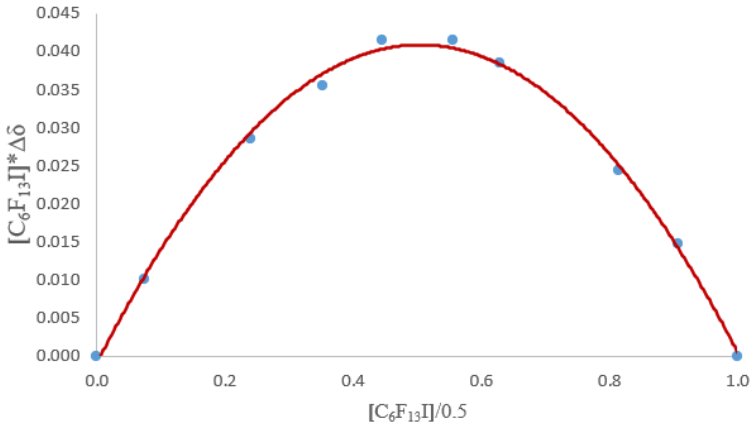


Figure S3

$y = -0.1645x^2 + 0.1659x - 0.0009$, $x_{max} = 0.1659/(-2\times(-0.1645)) = 0.50$

5.3 Determination of the association constant (K_{EDA})

The association constant (K_{EDA}) was calculated using Hanna and Ashbaugh's[9-12]. ^{19}F NMR spectra of eight samples of mixtures of $C_6F_{13}I$ and H_2O in CD_3CN were recorded at 298 K (trifluoroluorobenzene (δ F-Ph = -63.7200) was used as internal standard). The total volume of the mixture was 0.6 mL, the amount of $C_6F_{13}I$ was kept constant at 0.03 mmol (13.37 mg), while that

of H_2O was varied from 0.03 to 1.2 mmol. ^{19}F NMR for each sample was recorded and the chemical shifts differences (Δδ) for -CF_2I were used to draw the plot.

	H_2O (mol/L)	1/[H_2O] (L/mol)	Δδ (ppm)	1/Δδ (1/ppm)
1	0.06	15.43	0.012	83.3333
2	0.10	9.82	0.020	50.0000
3	0.20	4.91	0.035	28.8184
4	0.25	4.00	0.038	26.1097
5	0.32	3.09	0.054	18.6220
6	0.54	1.86	0.089	11.2108
7	0.98	1.02	0.142	7.0175
8	1.98	0.50	0.271	3.6846

According to equation 1, the equilibrium constant K_{EDA} (K_{EDA} = (1/Δ_0) / (1/kΔ_0) = 2.2204/5.1944 = 0.43) was readily obtained from the plot (Figure S4).

$$\frac{1}{\Delta} = \frac{1}{K\Delta_0}\frac{1}{[LB]} + \frac{1}{\Delta_0}$$ Equation 1

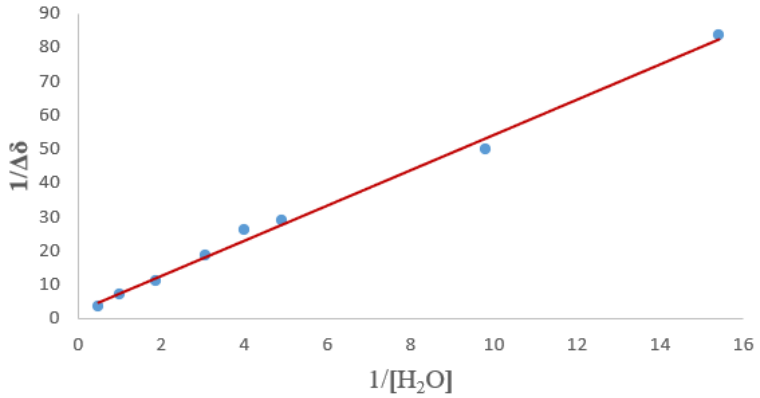
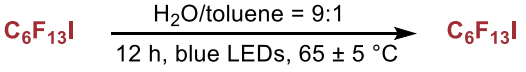


Figure S4

5.4 Photolysis reaction

procedure A

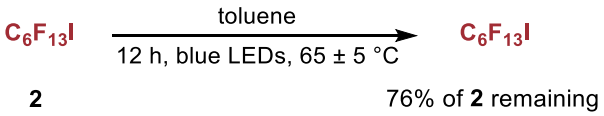


2 58% of **2** remaining

To a dry sample flask equipped with a stirring bar, the perfluoroalkyl iodide (0.4 mmol) was added. The tube was evacuated and filled with nitrogen (three times). After the addition of toluene (0.05 mL) and H_2O (0.45 mL) to the mixture via gas-tight syringe, the mixture was stirred overnight at

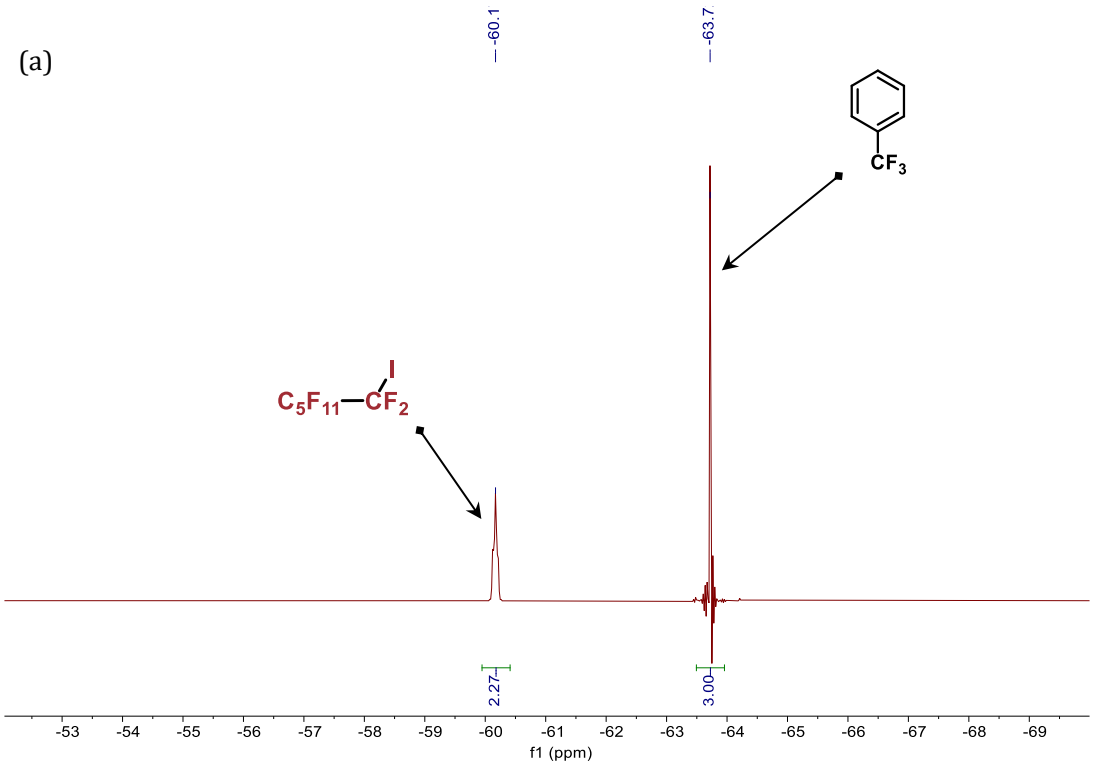
about 65 °C via a 50W blue LED (450 nm) lamp. (Trifluoromethyl)benzene (24 μL, 0.2 mmol) was added and the mixture was analyzed by **^{19}F NMR** spectroscopy. There is 58% of perfluoro iodine remaining. (Figure S5a).

procedure B



To a dry sample flask equipped with a stirring bar, the perfluoroalkyl iodide (0.4 mmol) was added. The tube was evacuated and filled with nitrogen (three times). After the addition of toluene (0.5 mL) to the mixture via gastight syringe, the mixture was stirred overnight at about 65 °C via a 50W blue LED (450 nm) lamp. (Trifluoromethyl)benzene (24 μL, 0.2 mmol) was added and the mixture was analyzed by **^{19}F NMR** spectroscopy. There is 76% of perfluoro iodine remaining (Figure S5b).

(a)



(b)

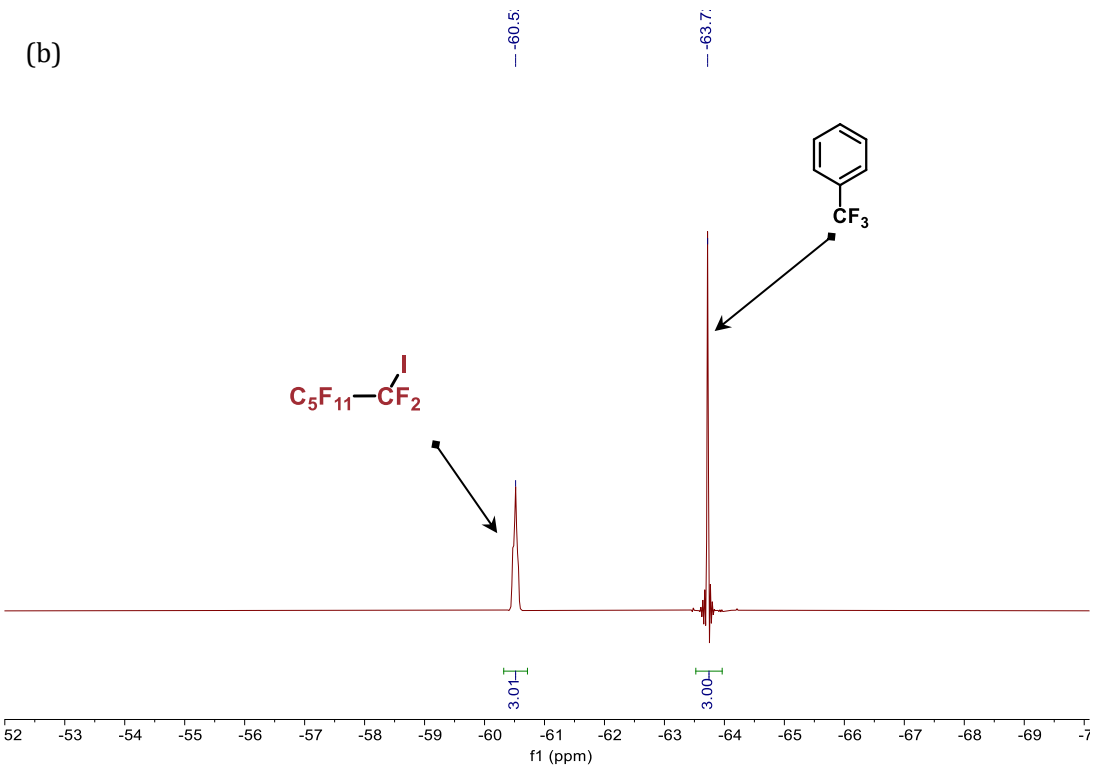
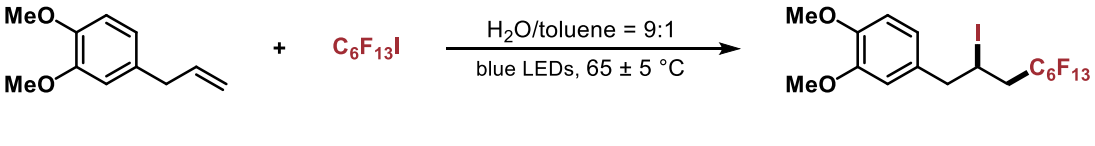

-60.5
-63.7
CF3
C5F11—CF2
I
3.01
3.00
52 -53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -7
f1 (ppm)

Figure S5.

5.5 Light On-Off Experiments



0.2 mmol 0.4 mmol

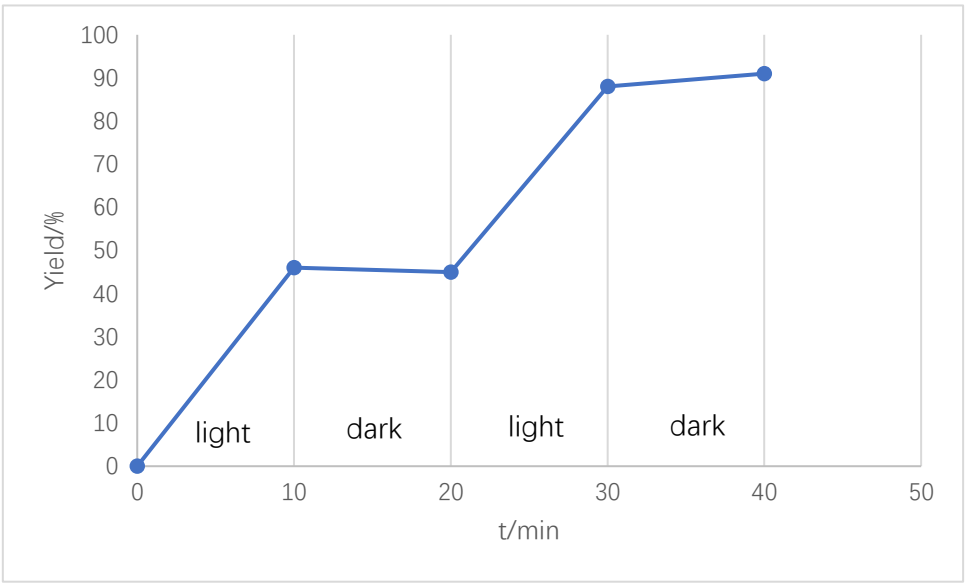
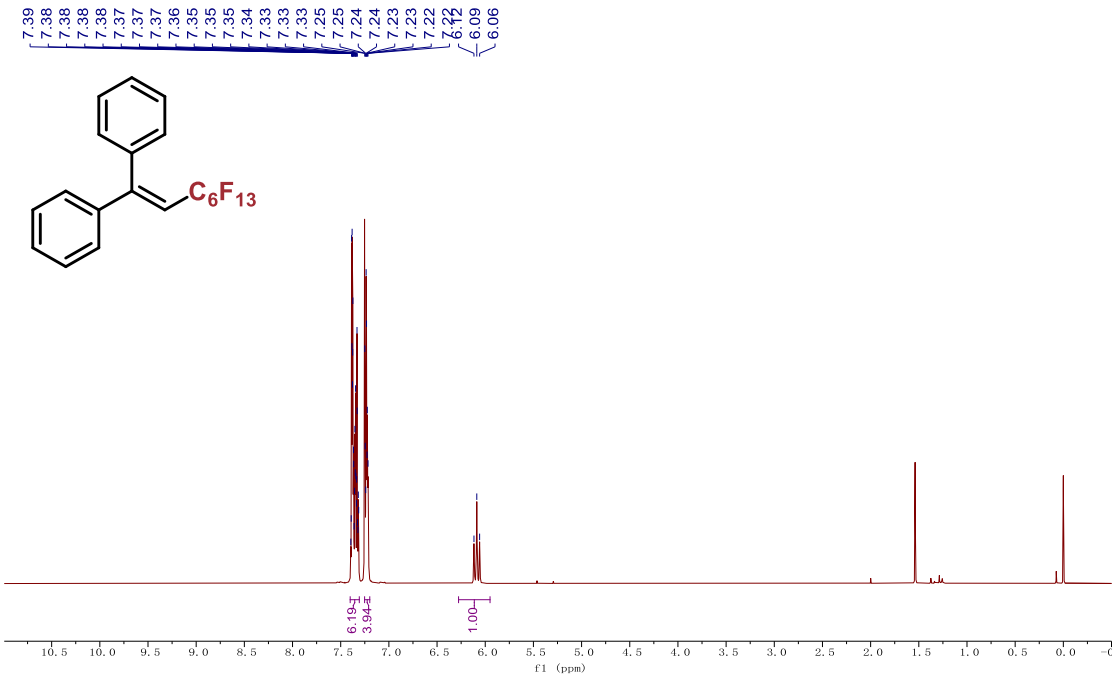


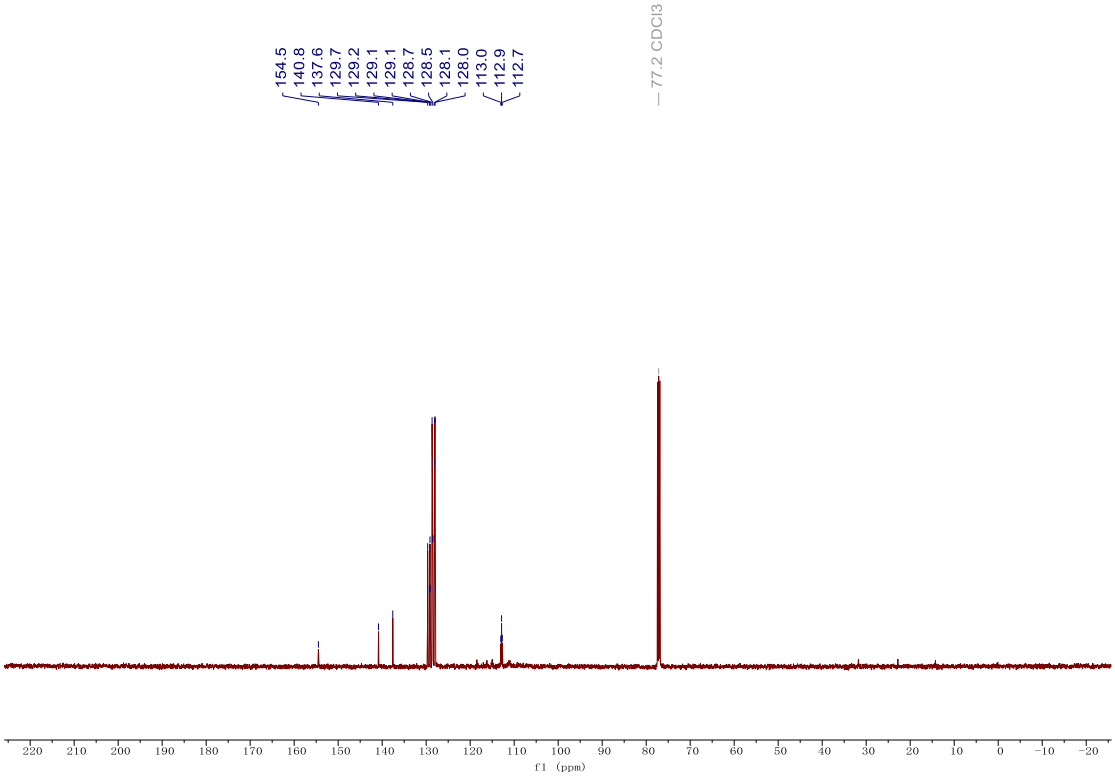
Figure S6. The yield was determined by 1H NMR using 1,1,2,2-Tetrachloroethane as an external standard.

6. NMR Spectra

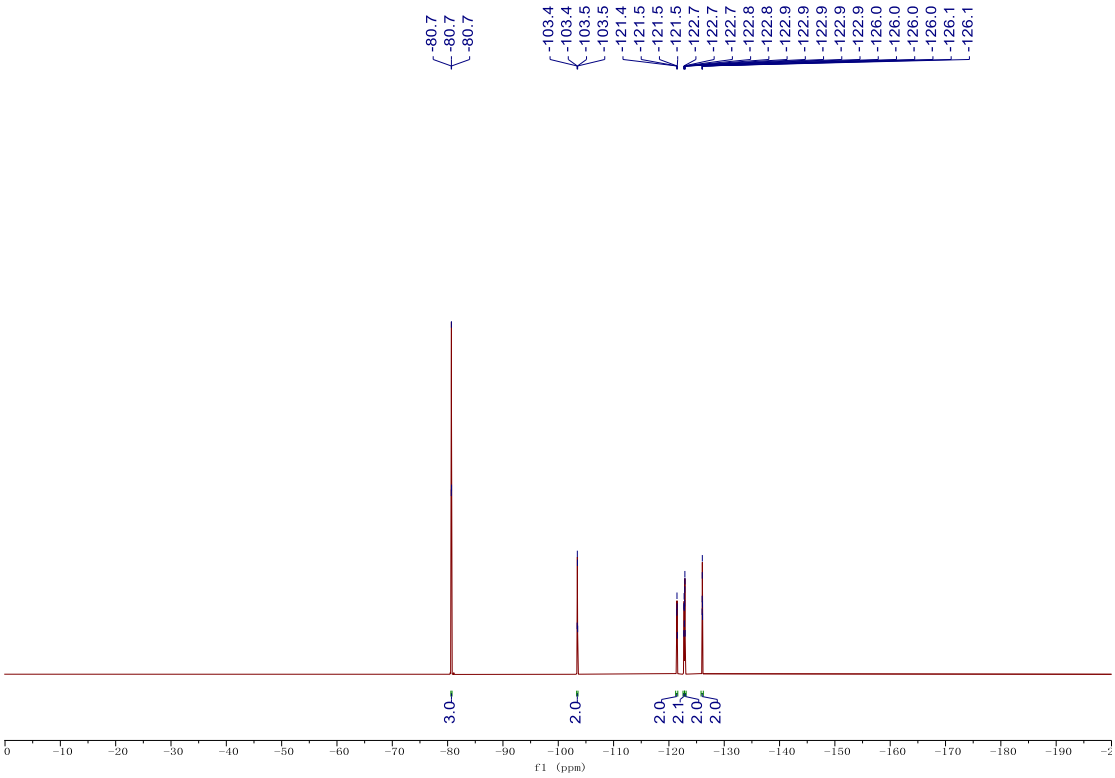
^{1}H NMR of compound **3** (500 MHz in $CDCl_3$)



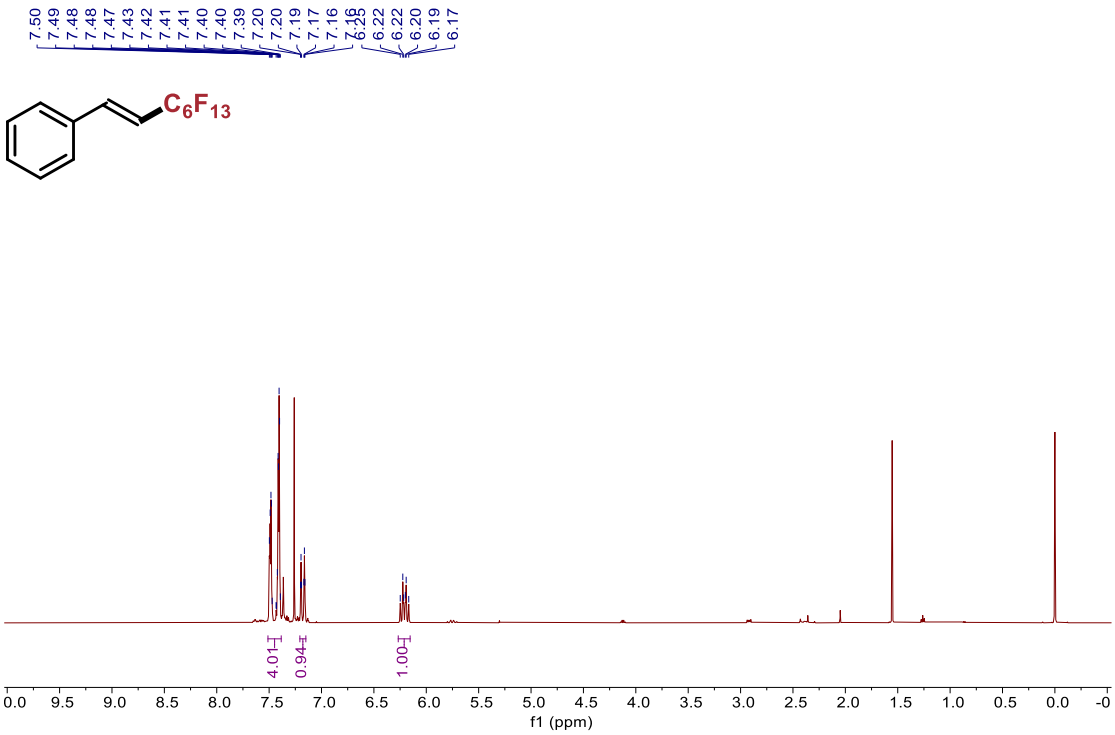
^{13}C NMR of compound **3** (126 MHz in $CDCl_3$)



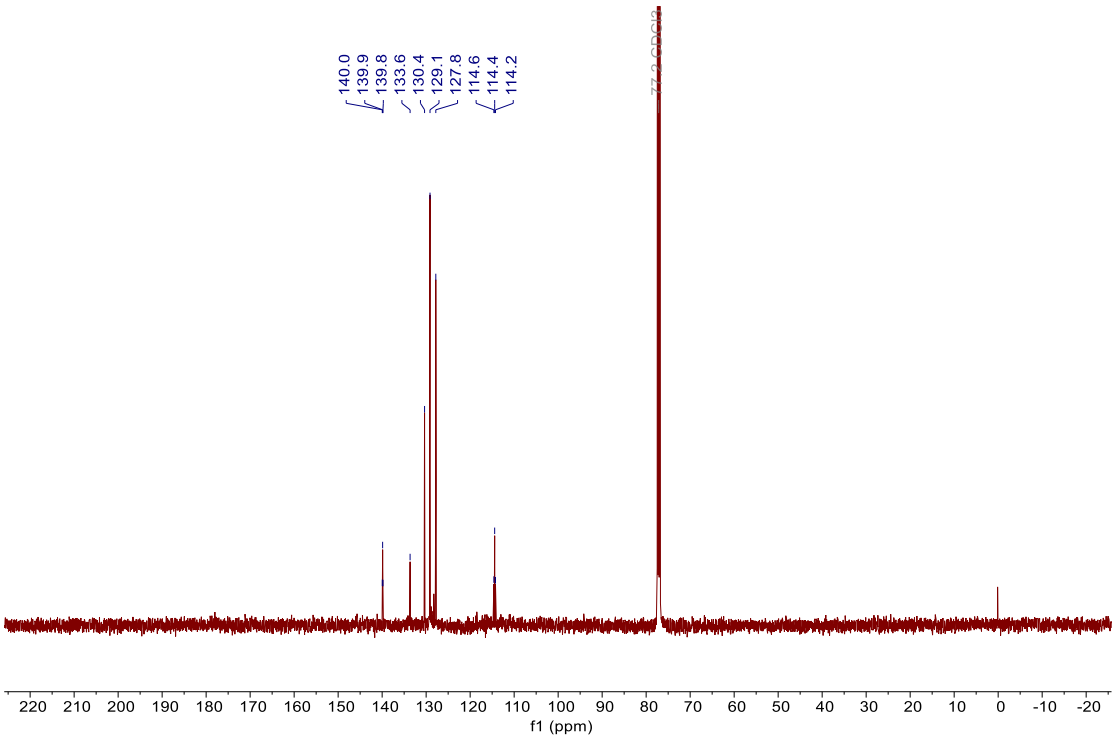
^{19}F NMR of compound **3** (376 MHz in $CDCl_3$)



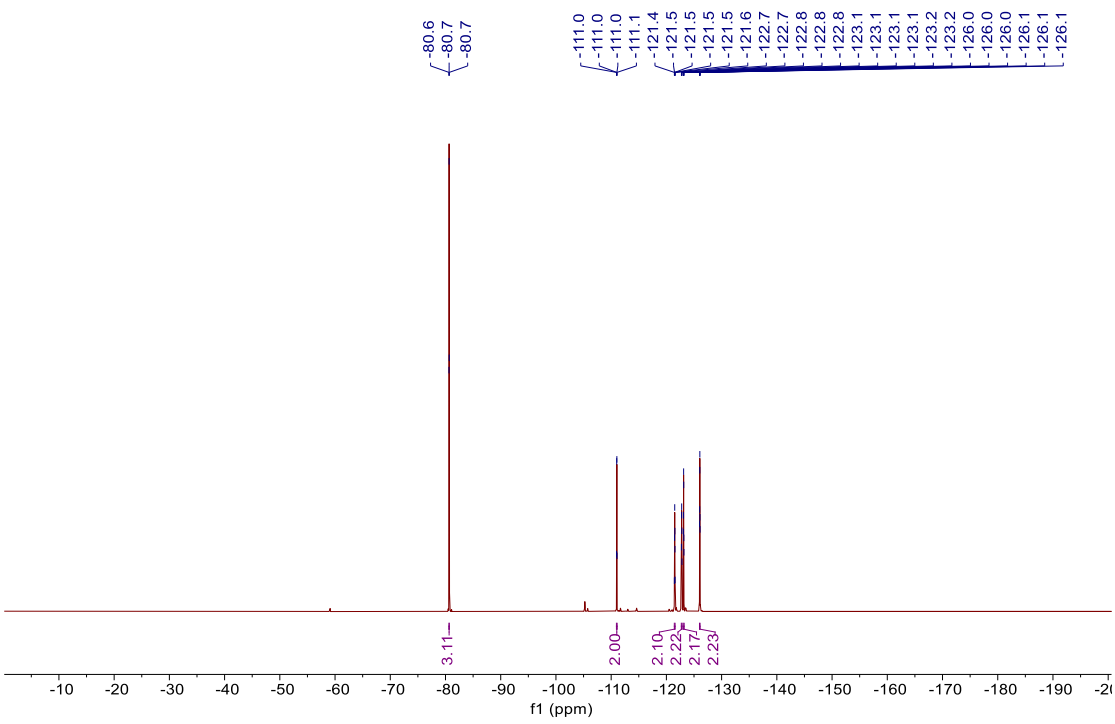
^{1}H NMR of compound **4** (500 MHz in $CDCl_3$)



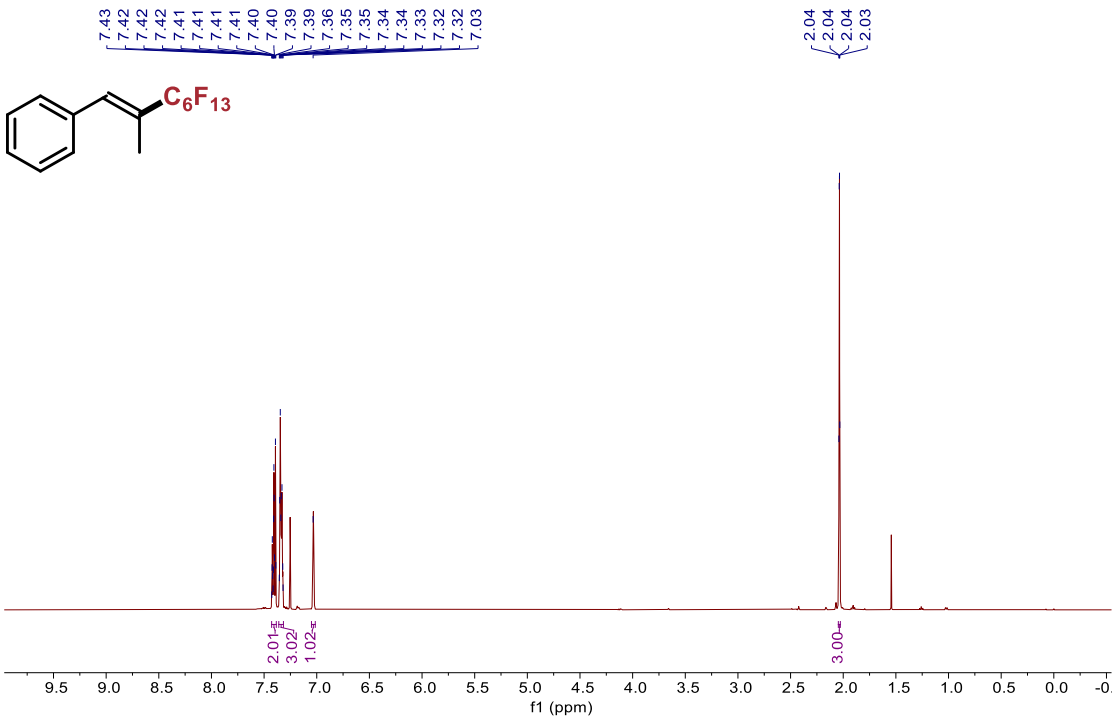
^{13}C NMR of compound **4** (126 MHz in $CDCl_3$)



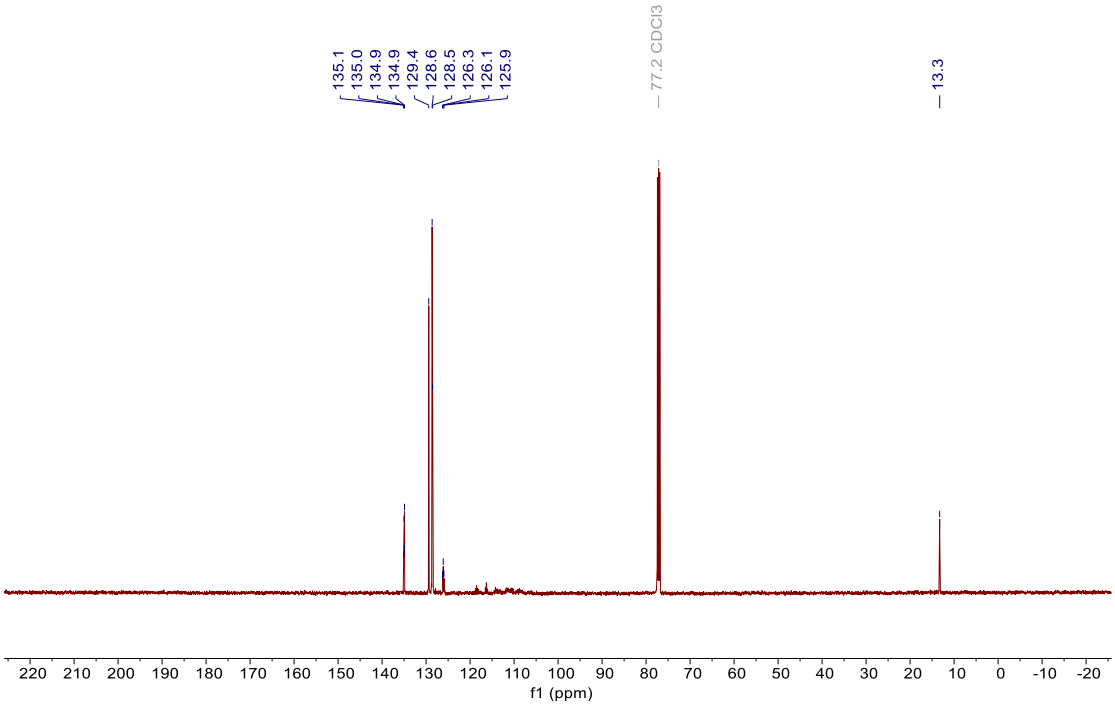
^{13}F NMR of compound **4** (376 MHz in $CDCl_3$)



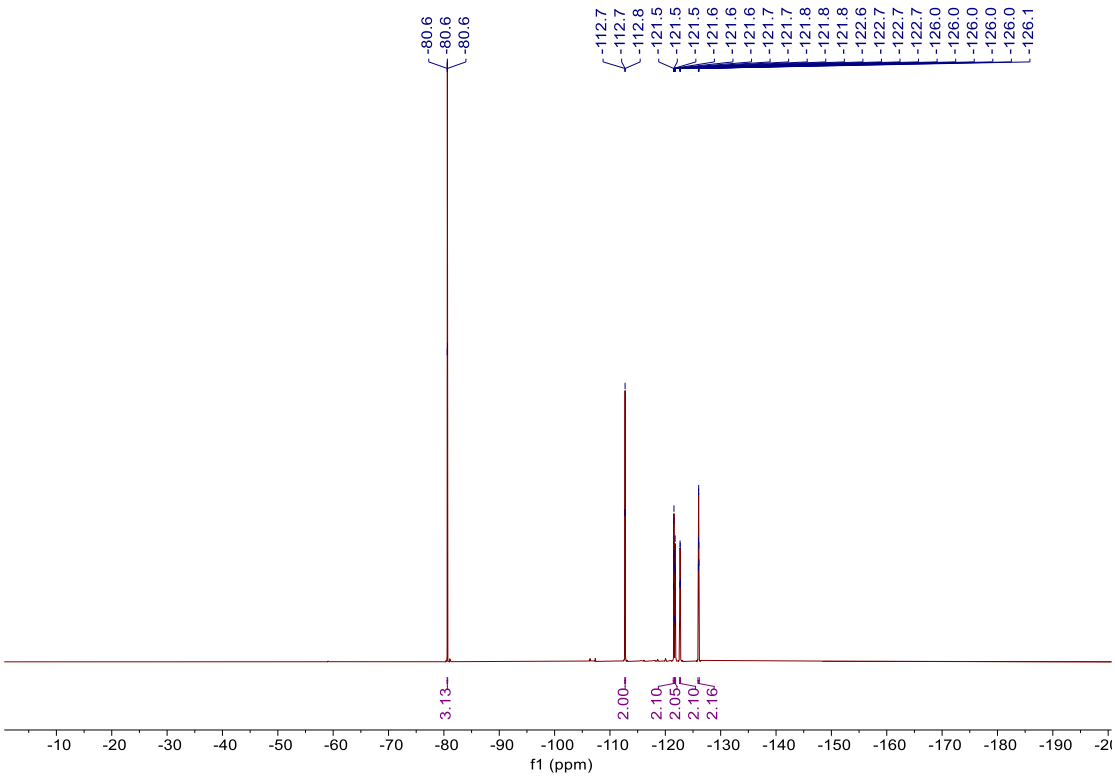
^{1}H NMR of compound **5** (500 MHz in $CDCl_3$)



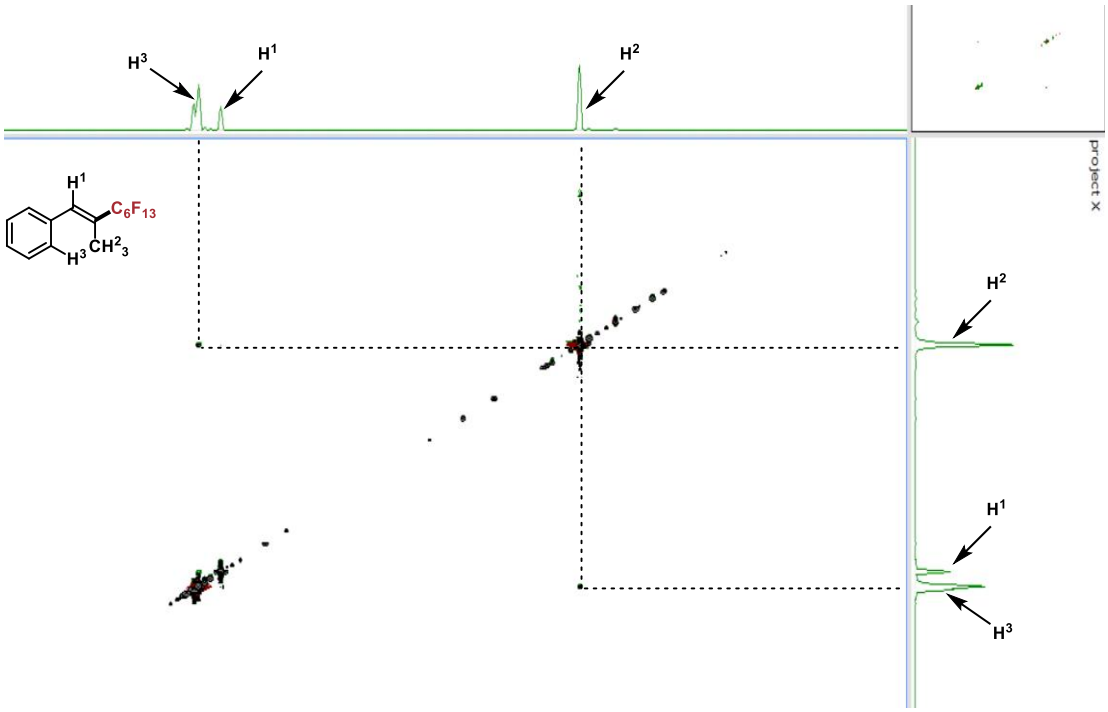
^{13}C NMR of compound **5** (126 MHz in $CDCl_3$)



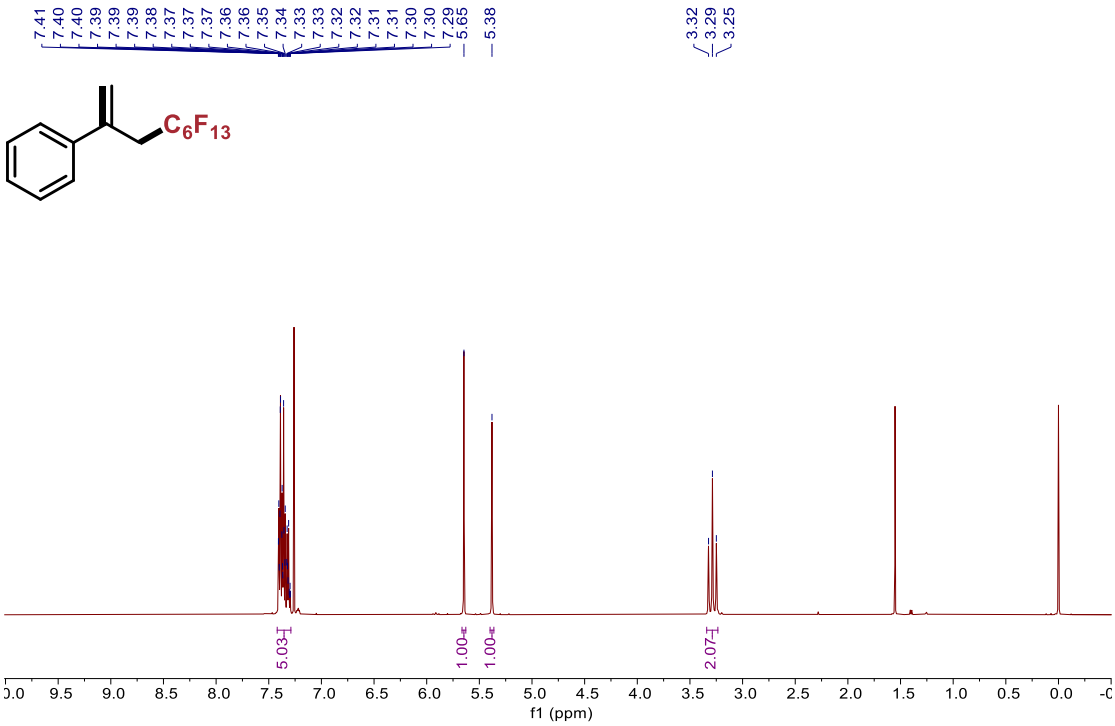
^{13}F NMR of compound **5** (376 MHz in $CDCl_3$)



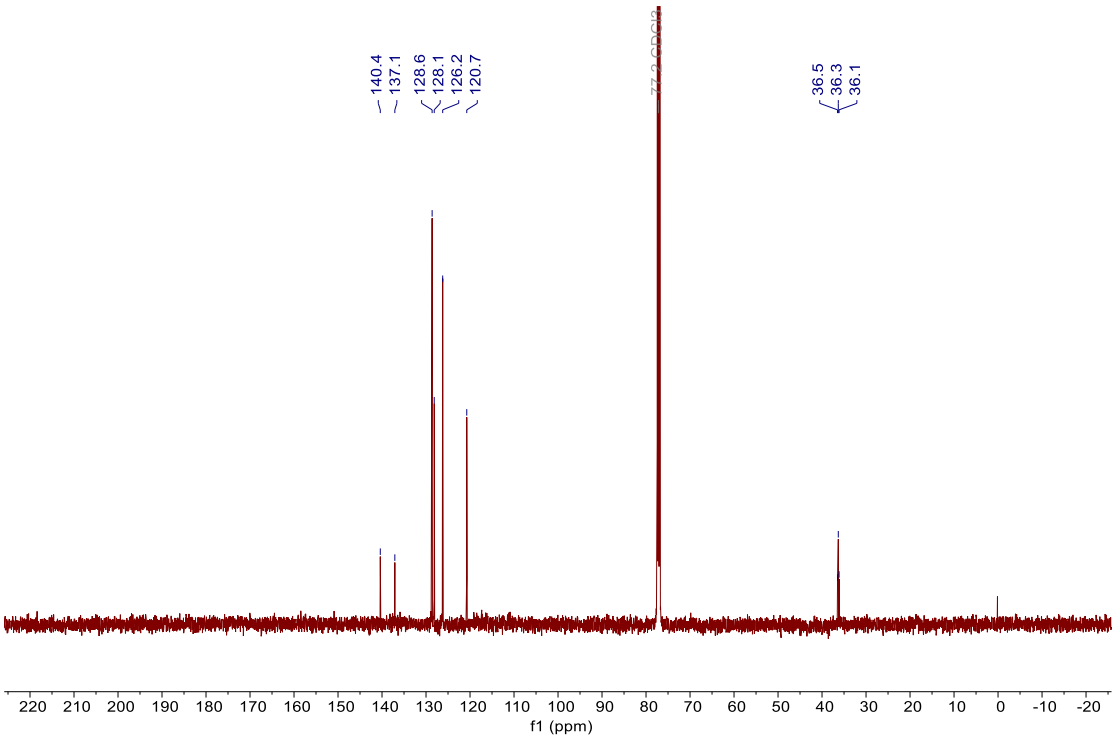
NOESY of compound **5** (500 MHz in $CDCl_3$)



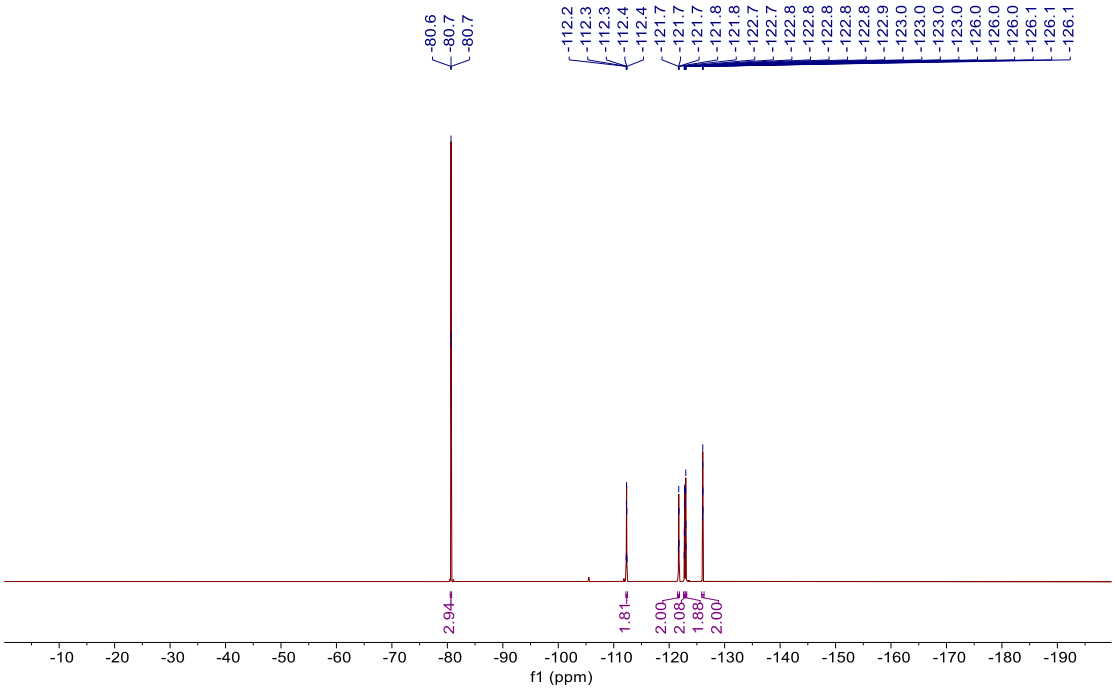
^{1}H NMR of compound **6** (500 MHz in $CDCl_3$)



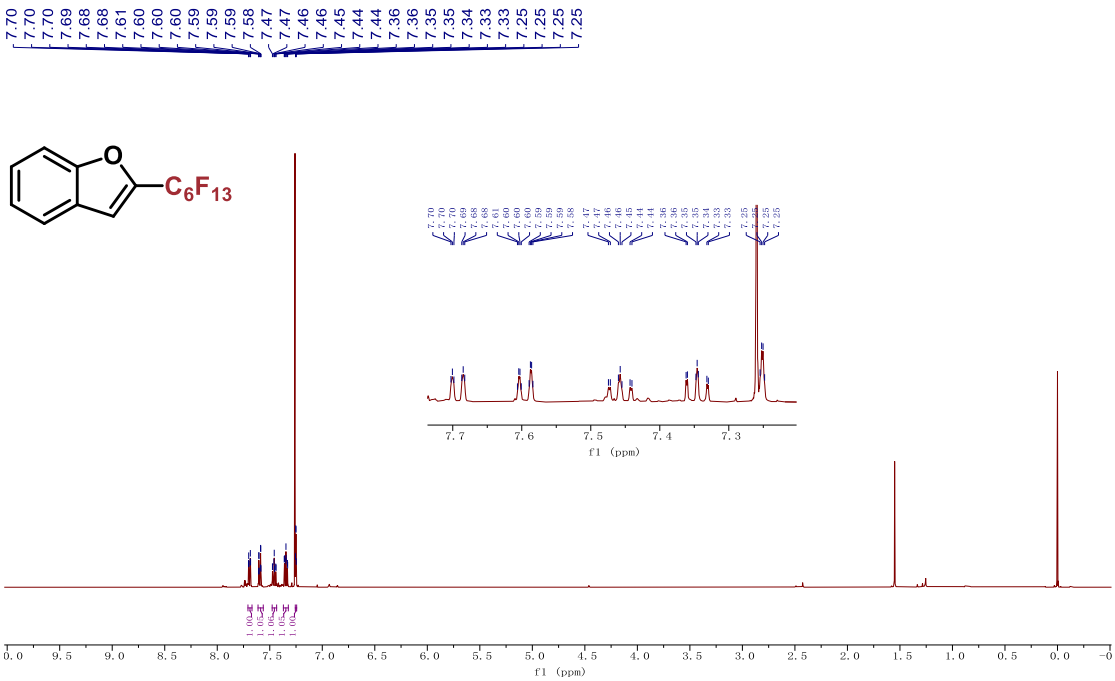
^{13}C NMR of compound **6** (126 MHz in $CDCl_3$)



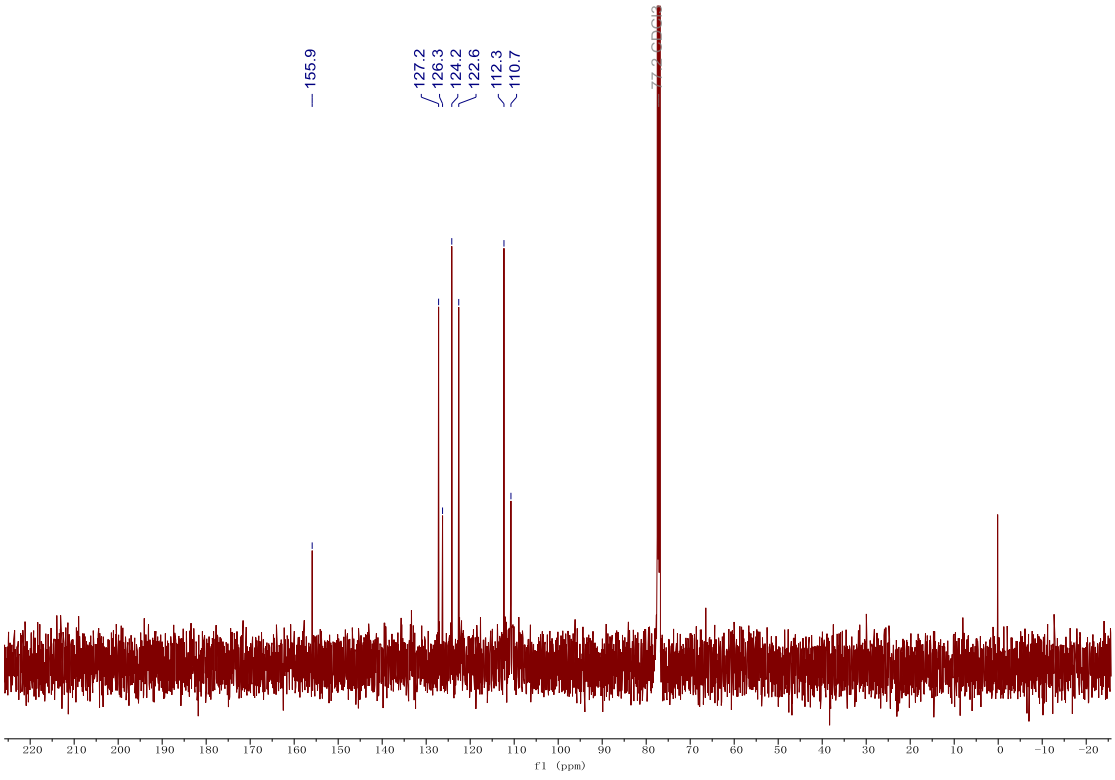
^{13}F NMR of compound **6** (376 MHz in $CDCl_3$)



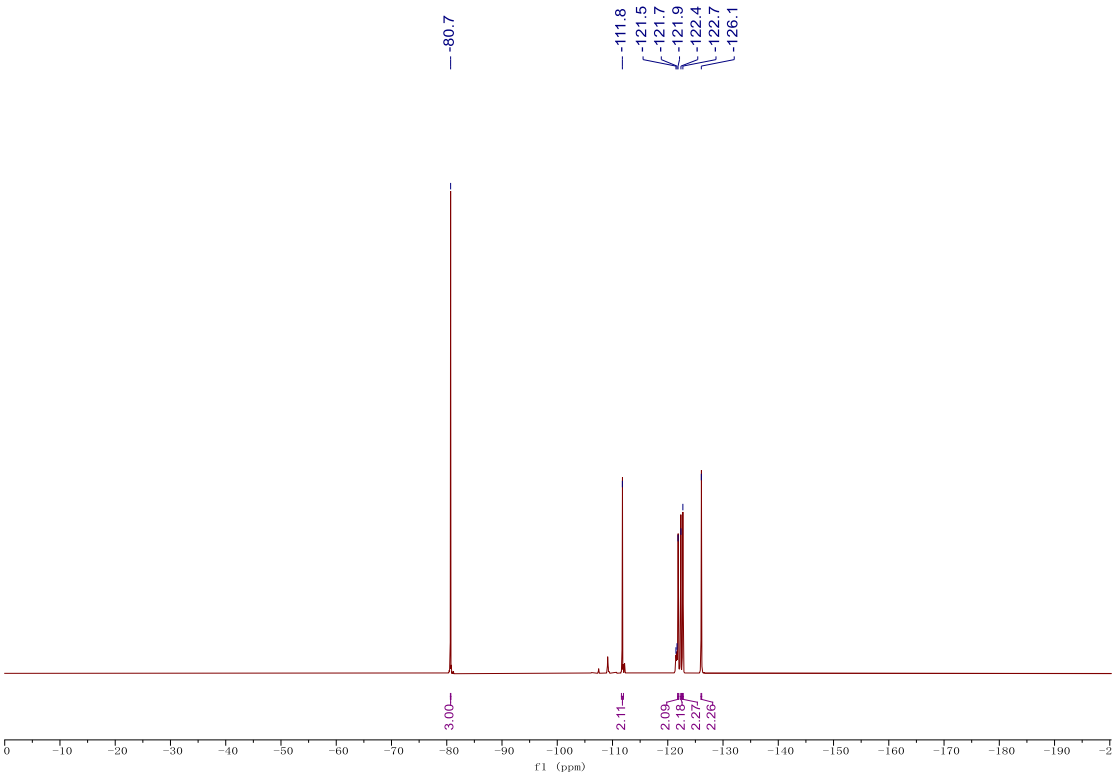
^{1}H NMR of compound **7** (500 MHz in $CDCl_3$)



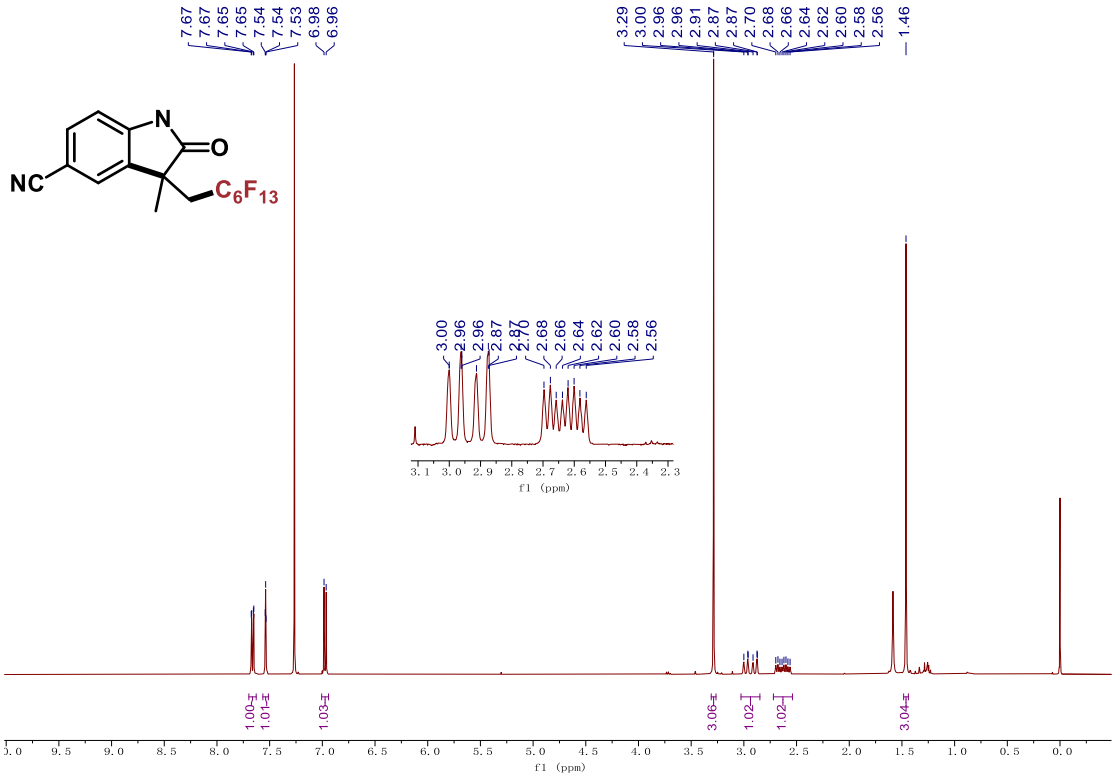
^{13}C NMR of compound **7** (126 MHz in $CDCl_3$)



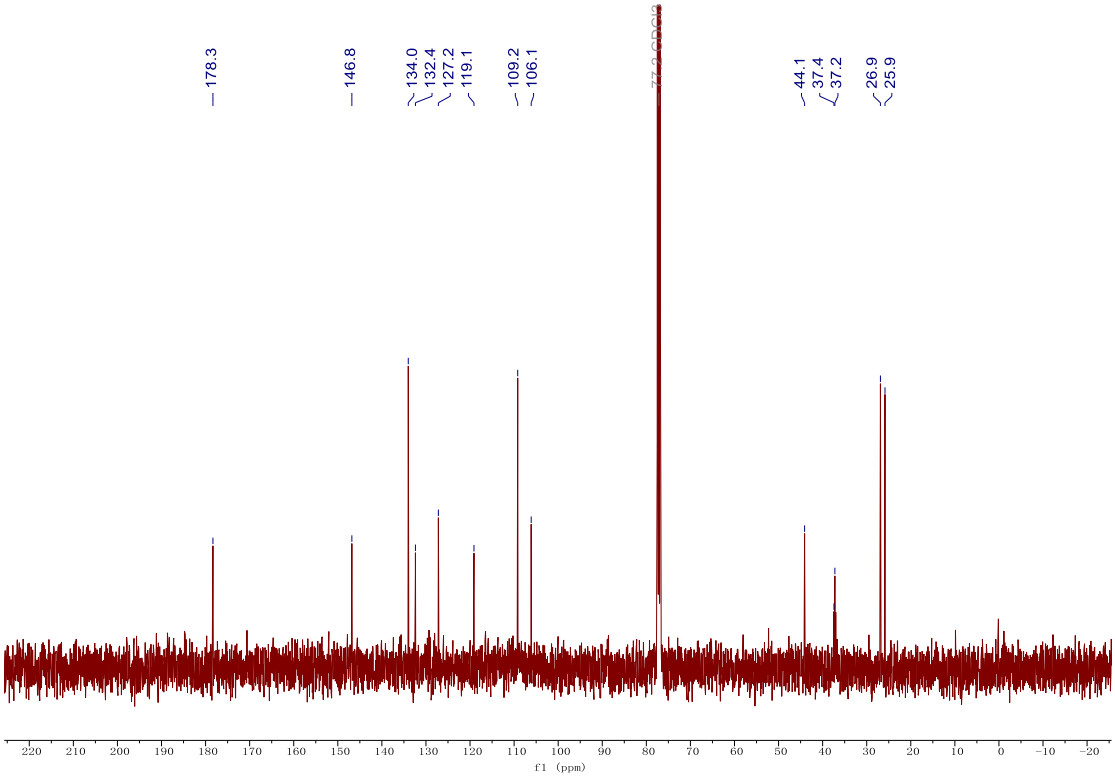
^{19}F NMR of compound **7** (376 MHz in $CDCl_3$)



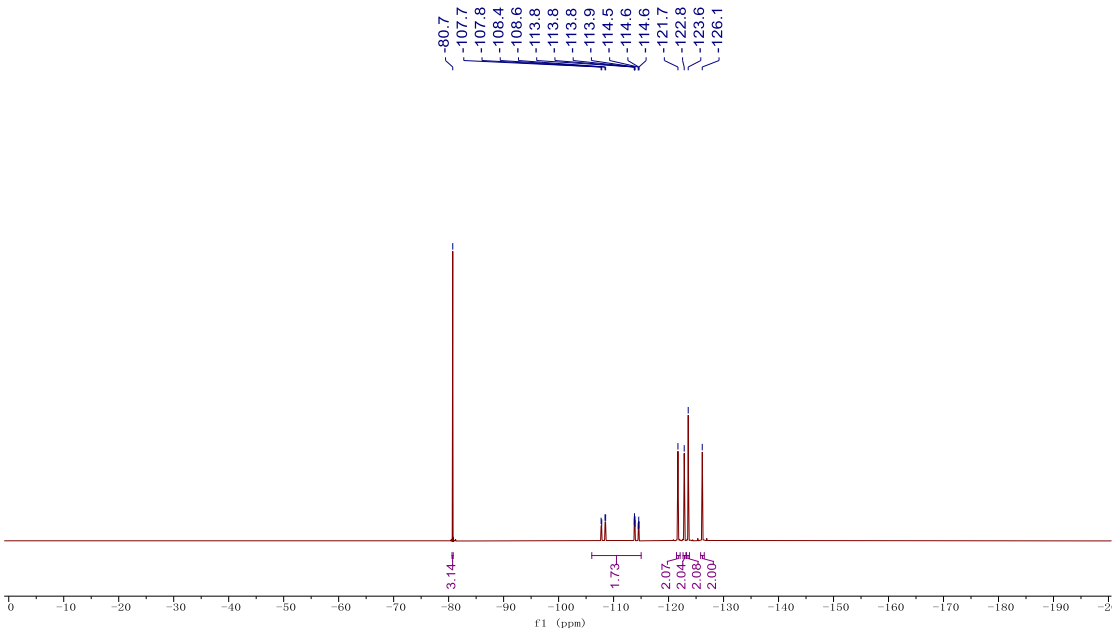
^{1}H NMR of compound **8** (400 MHz in $CDCl_3$)



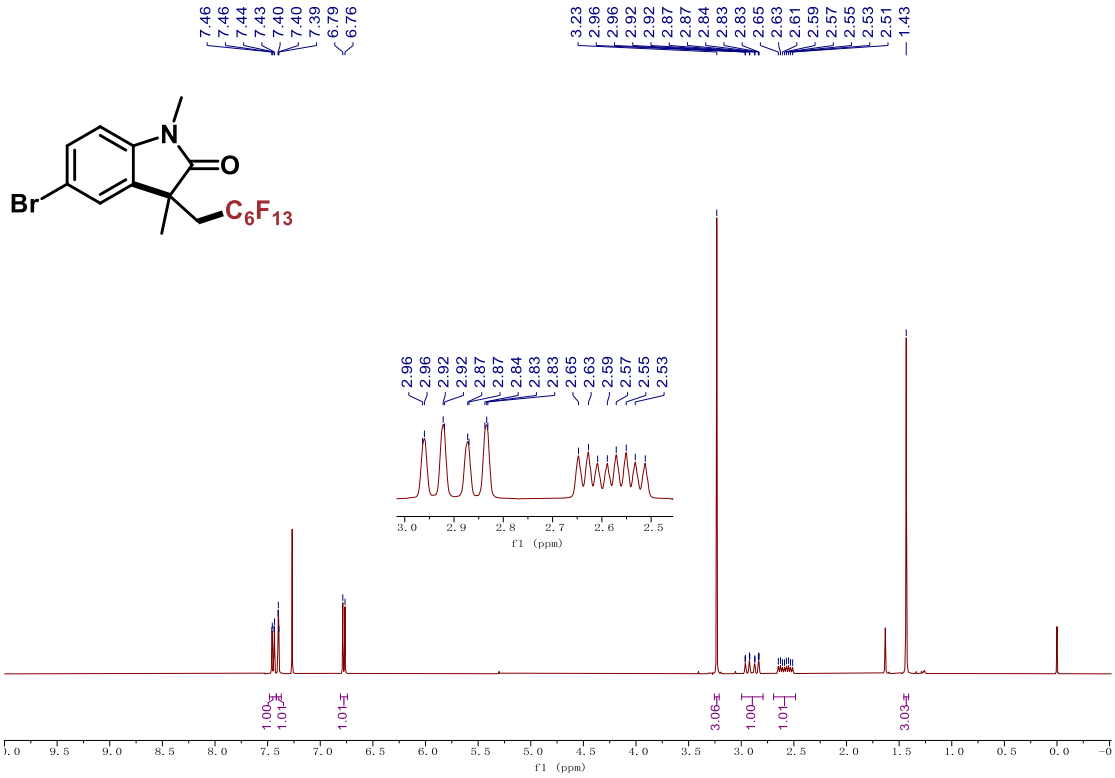
^{13}C NMR of compound **8** (101 MHz in $CDCl_3$)



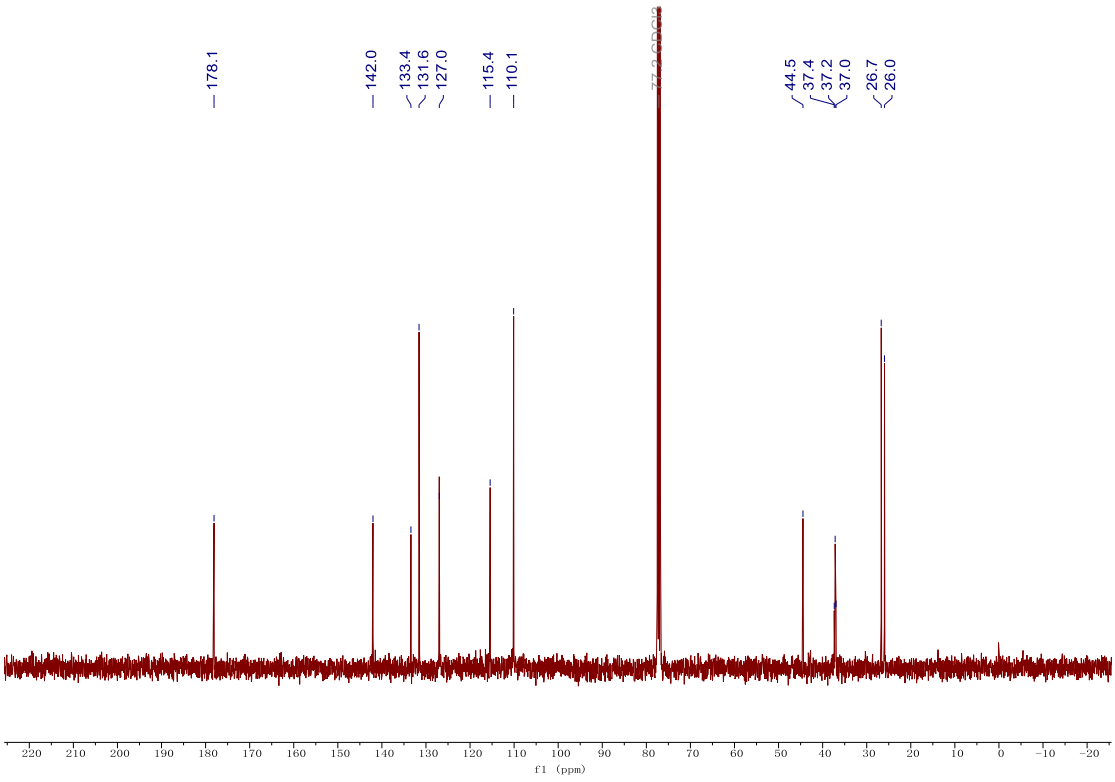
^{19}F NMR of compound **8** (376 MHz in $CDCl_3$)



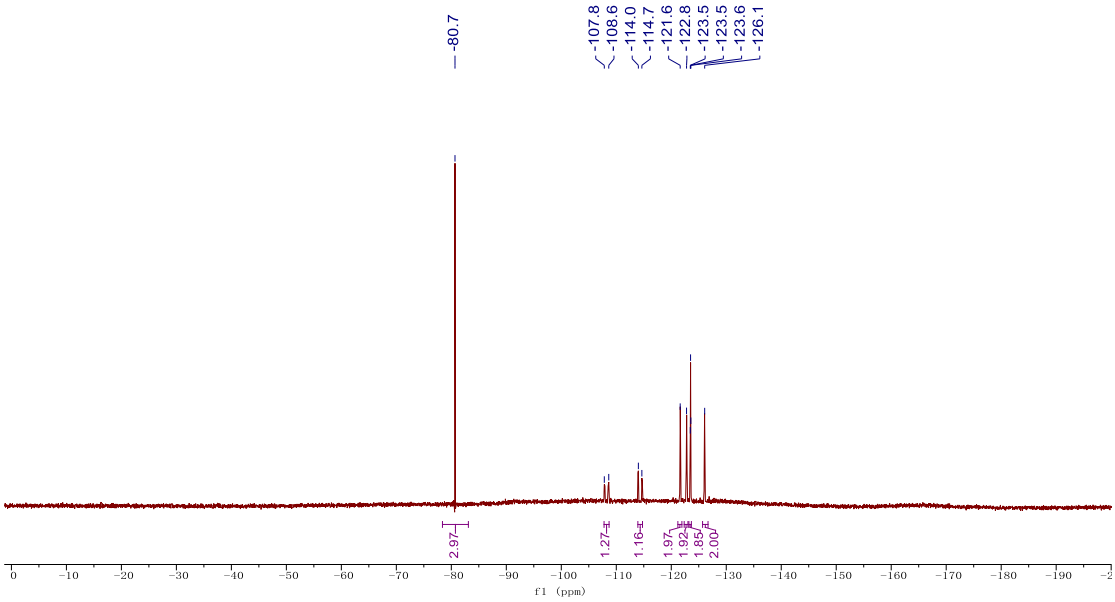
^{1}H NMR of compound **9** (400 MHz in $CDCl_3$)



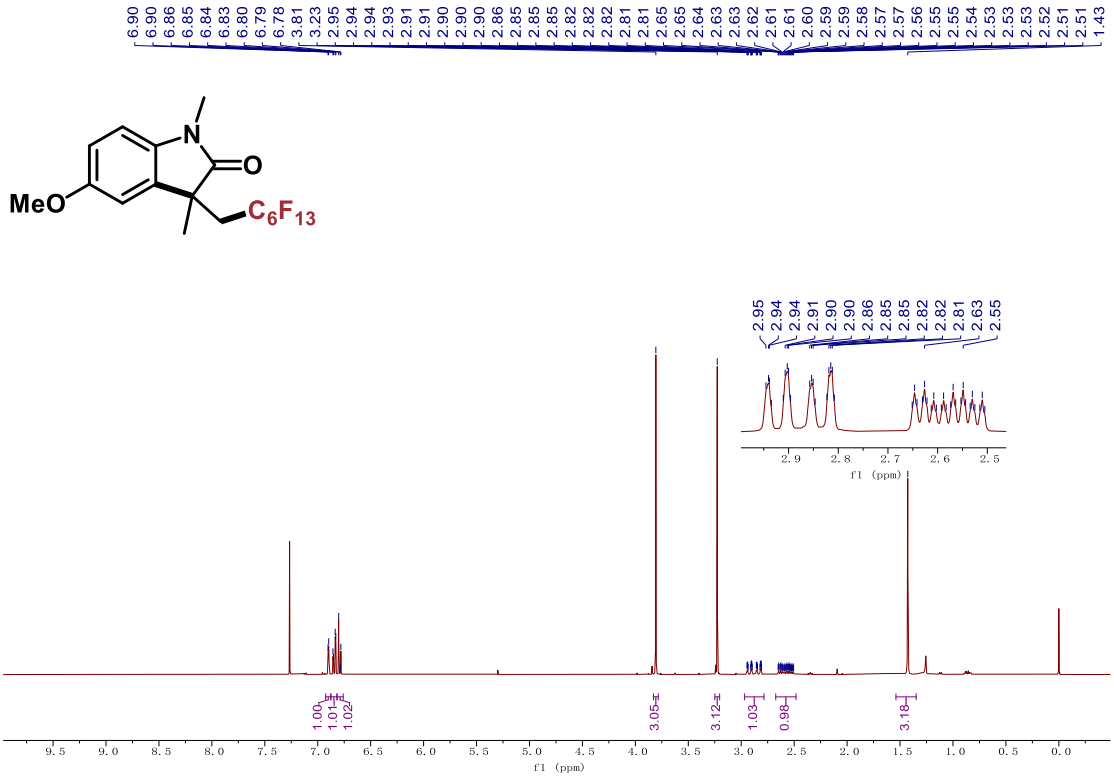
^{13}C NMR of compound **9** (101 MHz in $CDCl_3$)



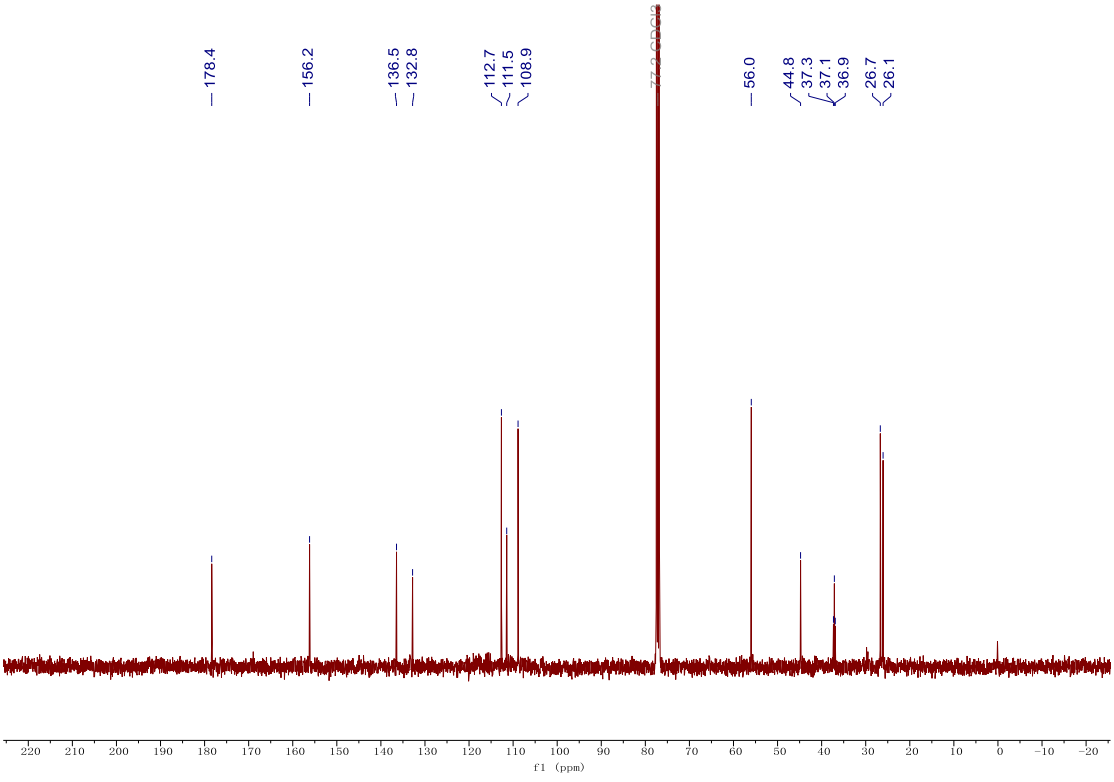
^{19}F NMR of compound **9** (376 MHz in $CDCl_3$)



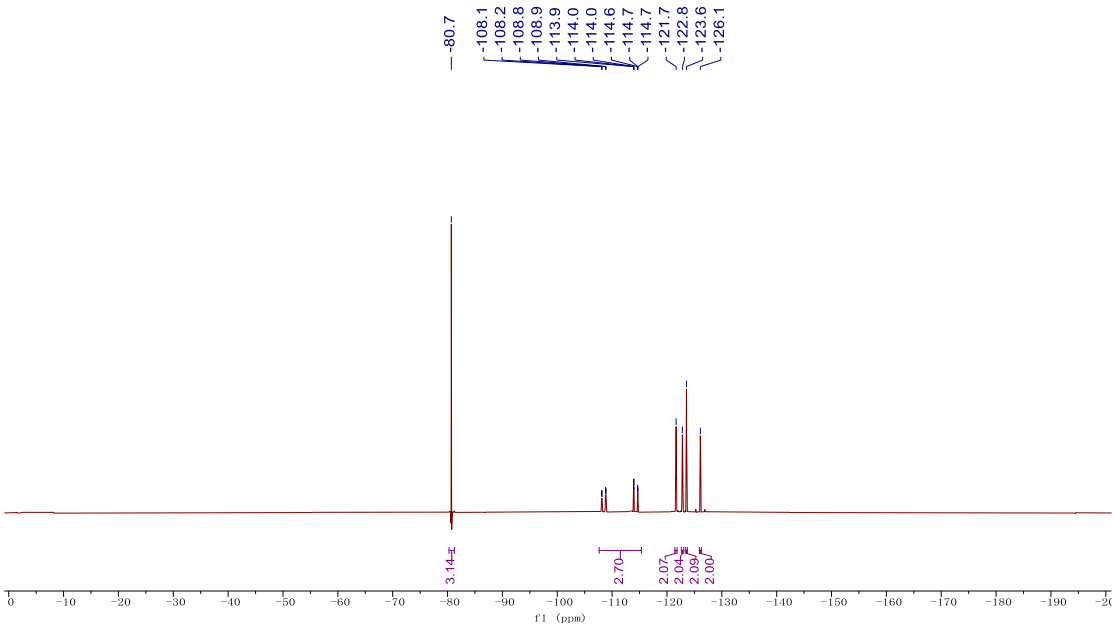
^{1}H NMR of compound **10** (400 MHz in $CDCl_3$)



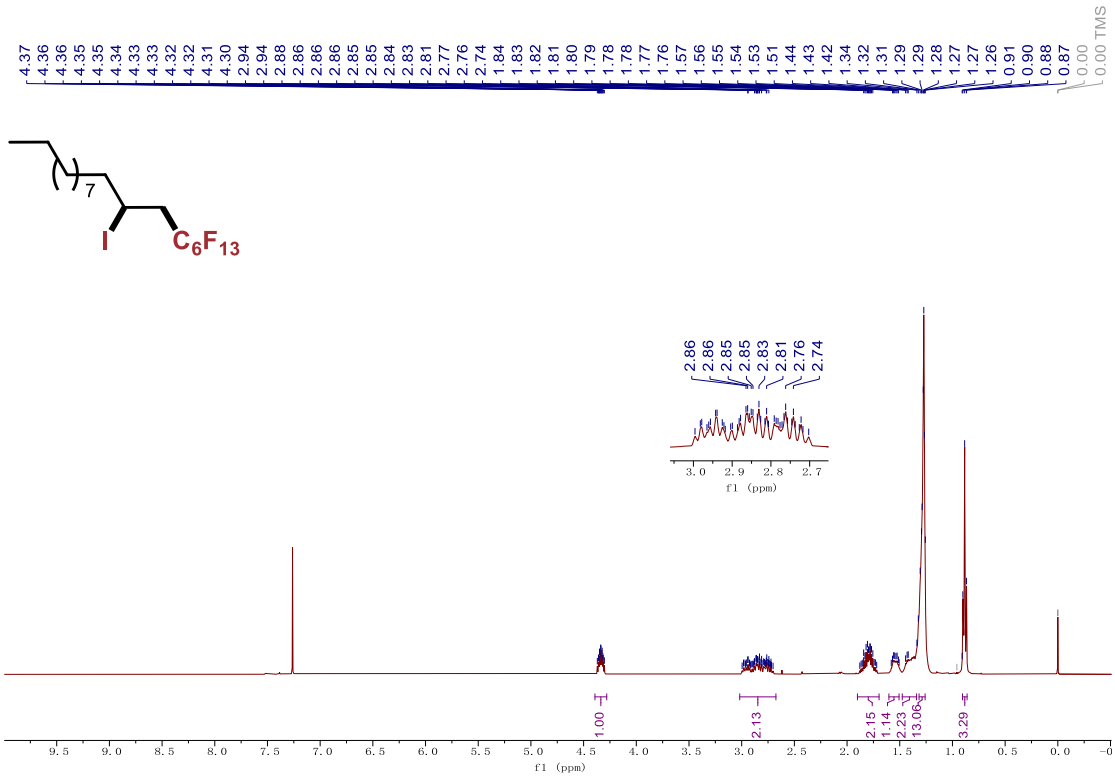
^{13}C NMR of compound **10** (101 MHz in $CDCl_3$)



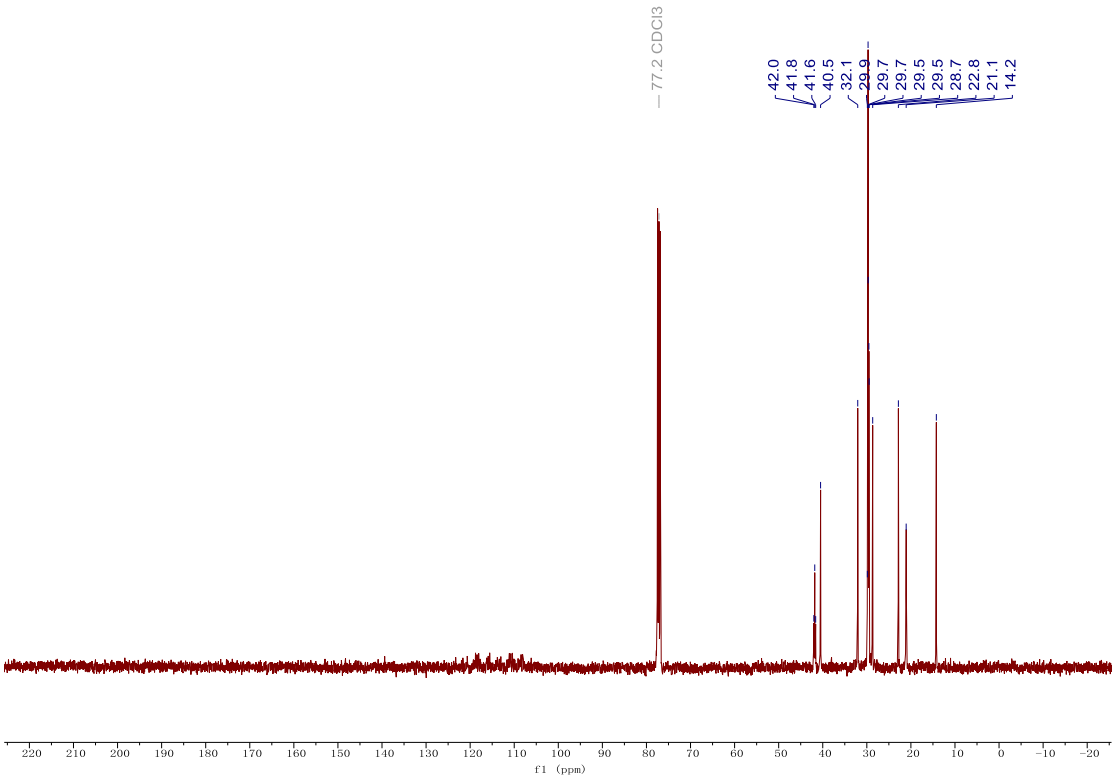
^{19}F NMR of compound **10** (376 MHz in $CDCl_3$)



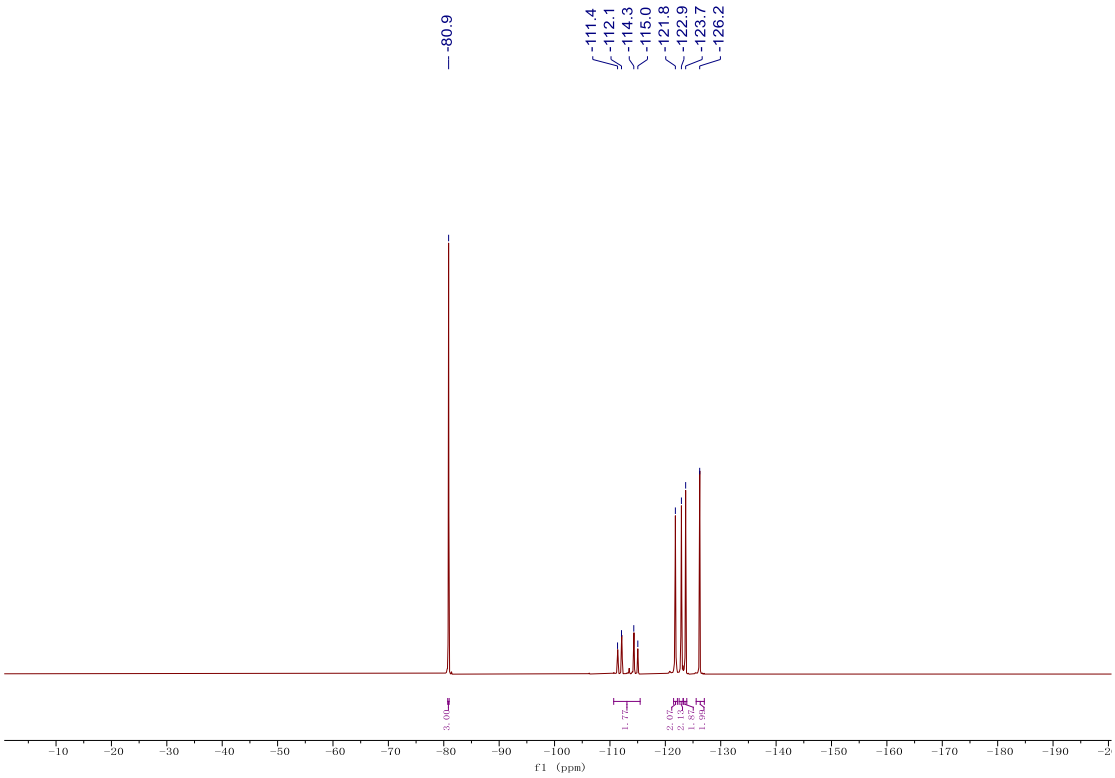
^{1}H NMR of compound **11** (400 MHz in $CDCl_3$)



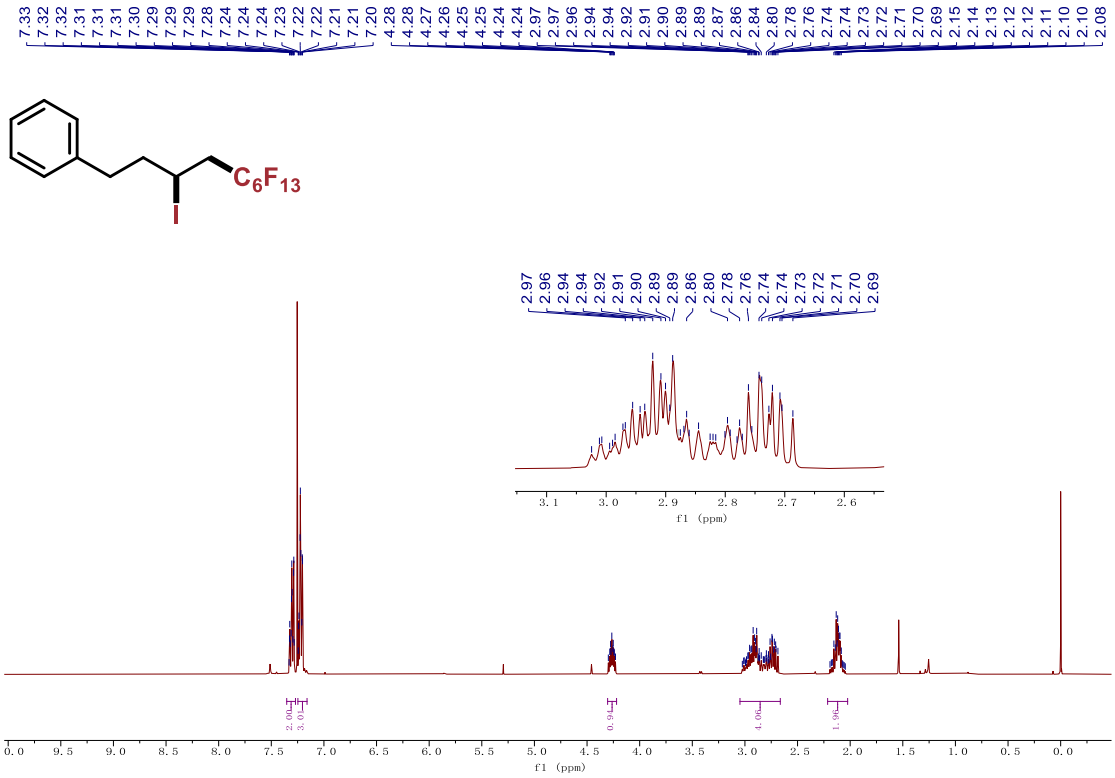
^{13}C NMR of compound **11** (101 MHz in $CDCl_3$)



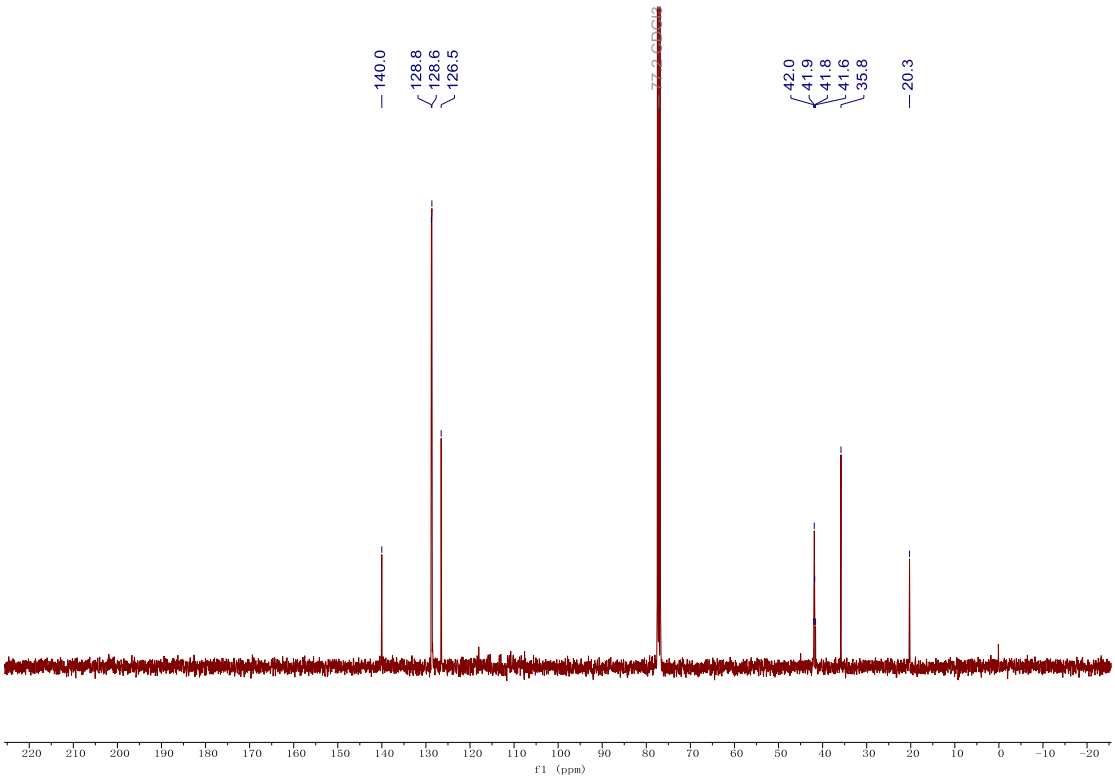
^{19}F NMR of compound **11** (376 MHz in $CDCl_3$)



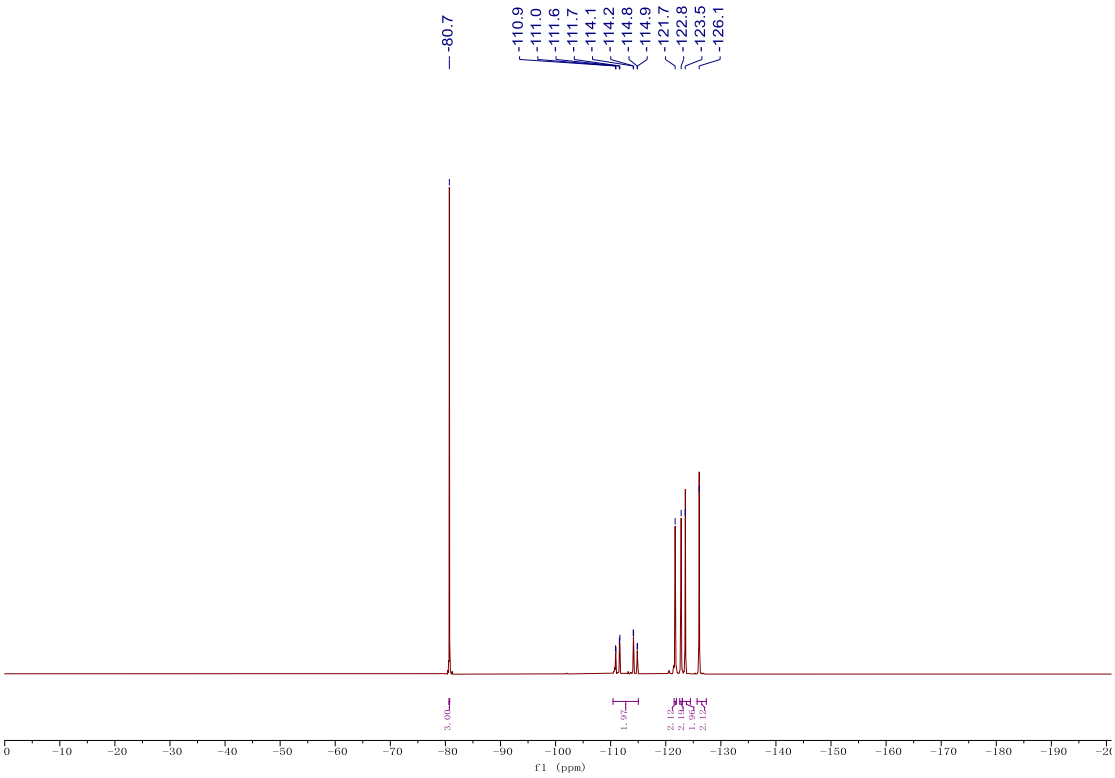
^{1}H NMR of compound **12** (400 MHz in $CDCl_3$)



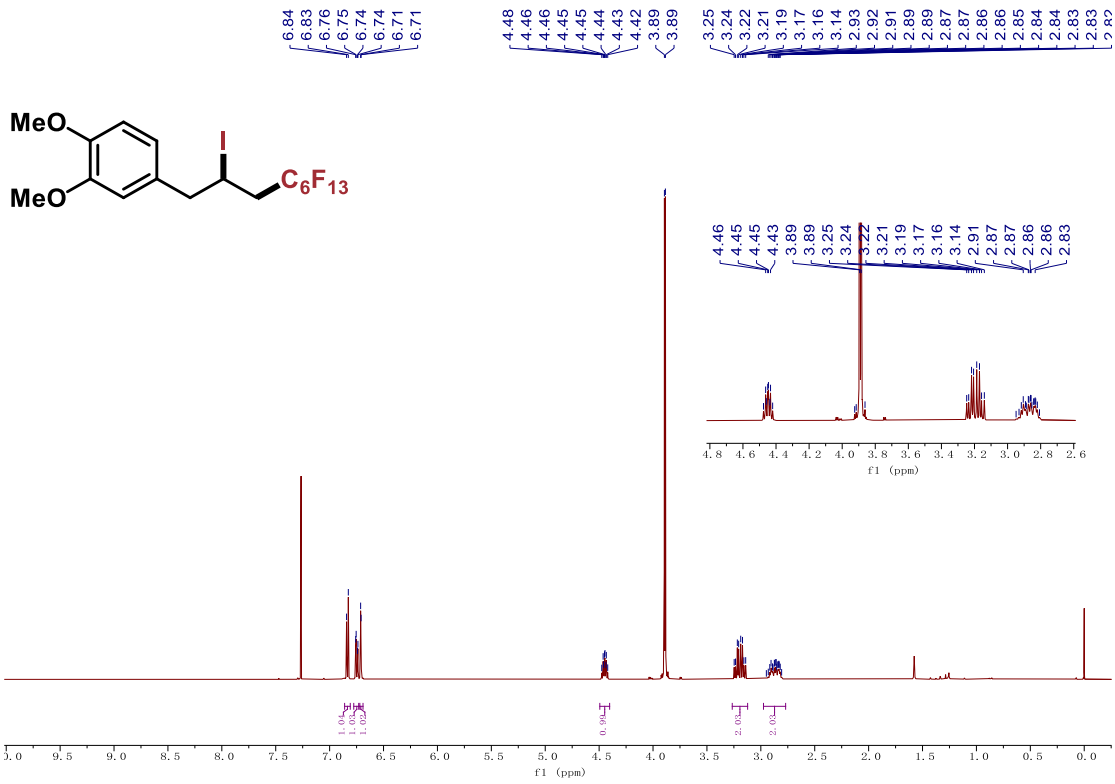
^{13}C NMR of compound **12** (101 MHz in $CDCl_3$)



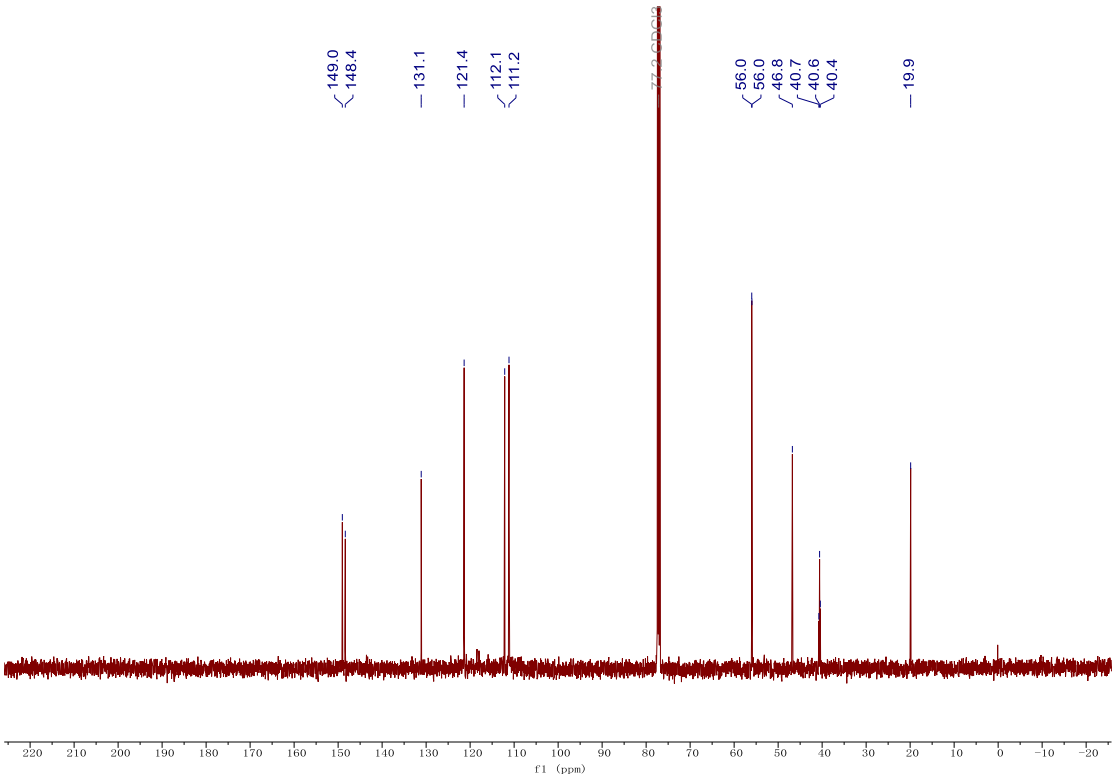
^{19}F NMR of compound **12** (376 MHz in $CDCl_3$)



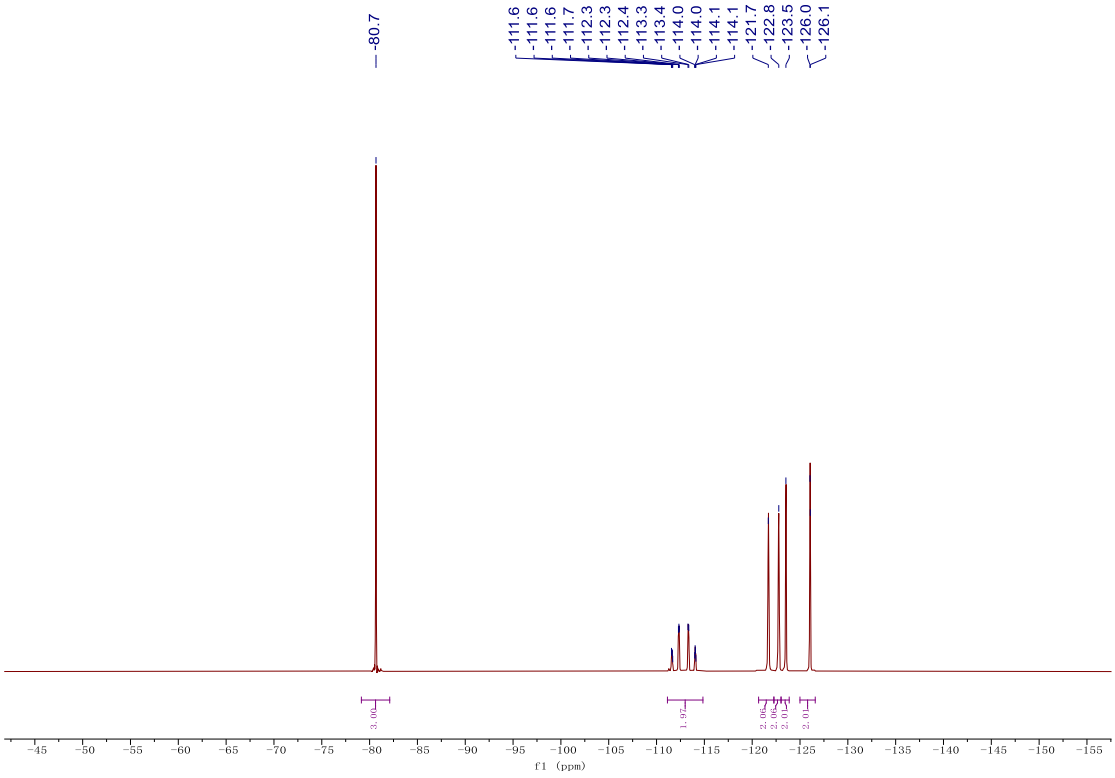
^{1}H NMR of compound **13** (500 MHz in $CDCl_3$)



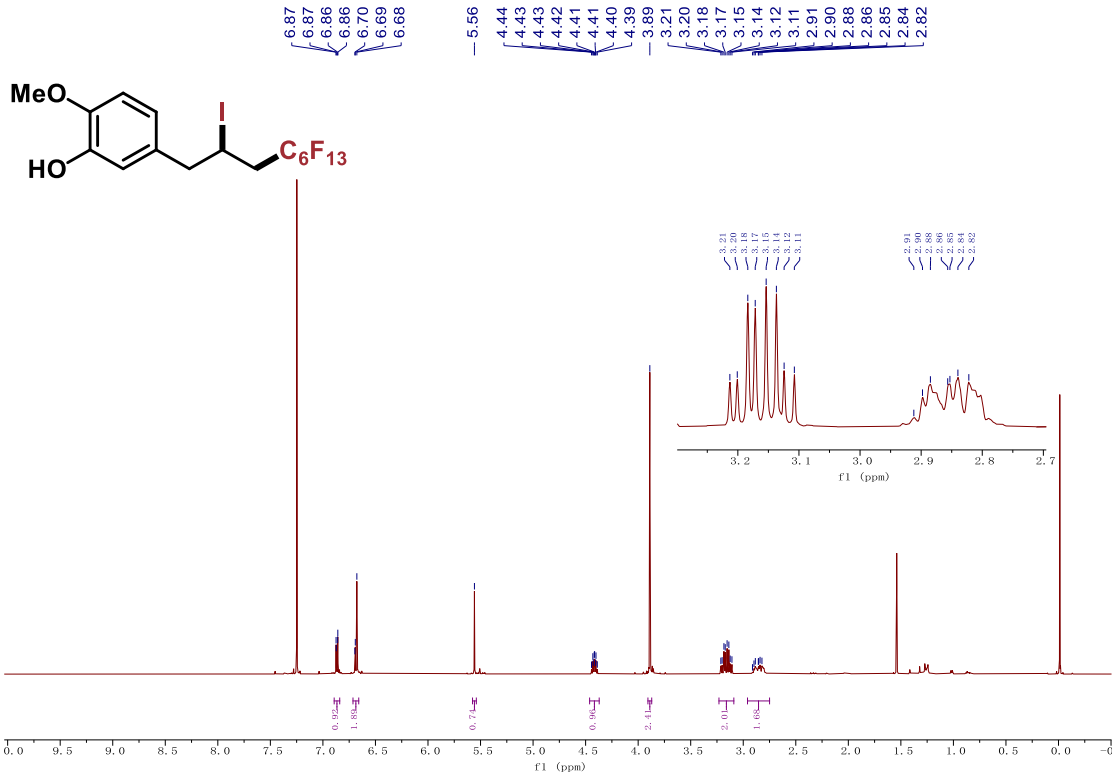
^{13}C NMR of compound **13** (126 MHz in $CDCl_3$)



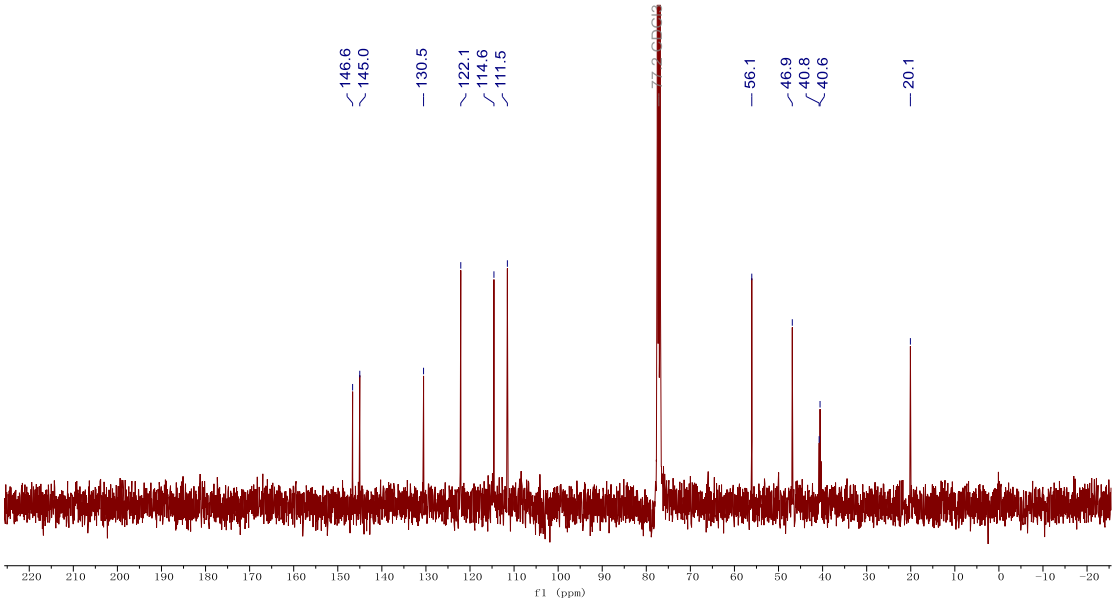
^{19}F NMR of compound **13** (376 MHz in $CDCl_3$)



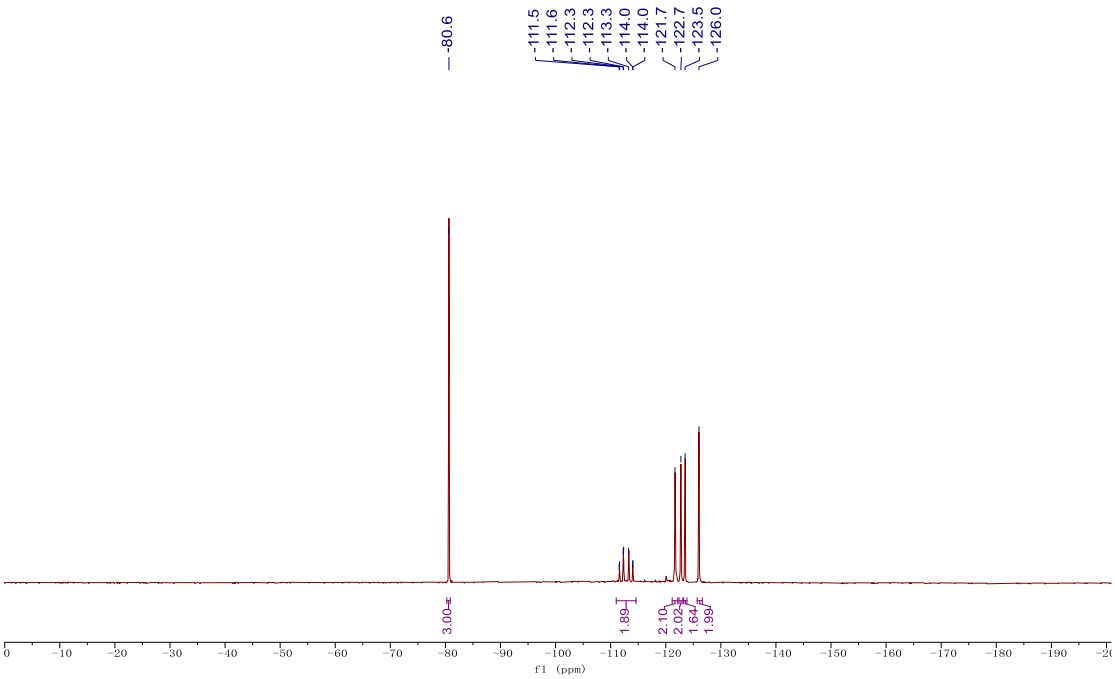
^{1}H NMR of compound **14** (500 MHz in $CDCl_3$)



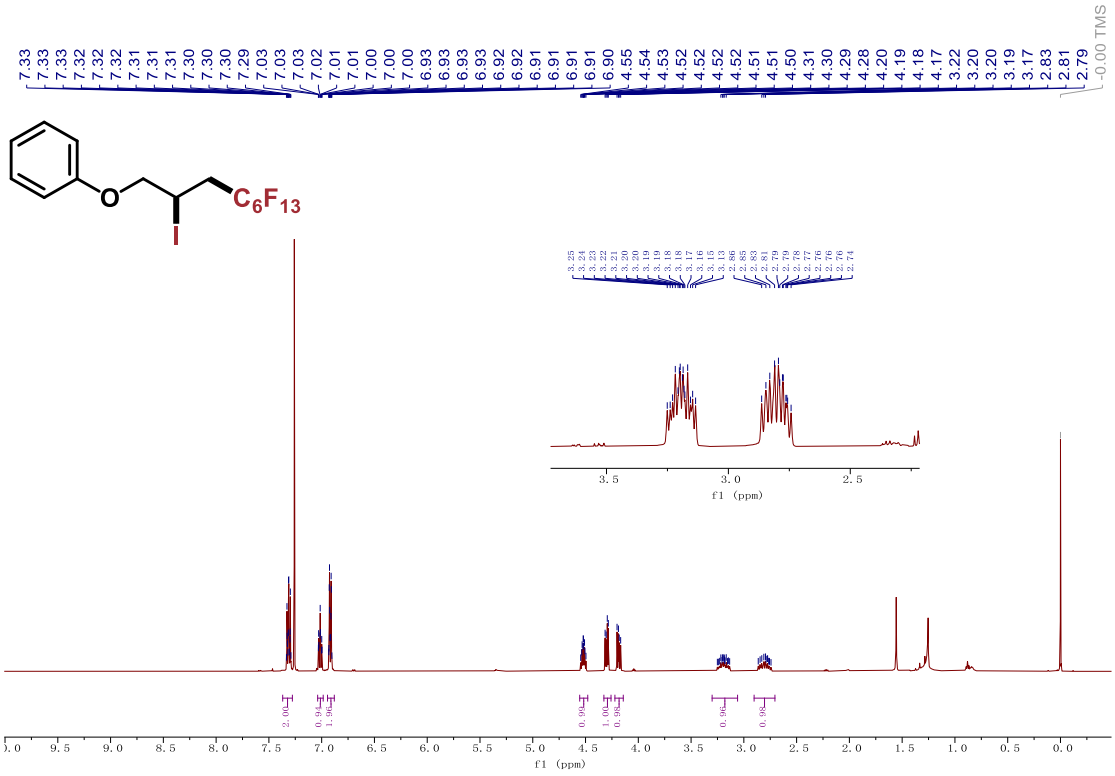
^{13}C NMR of compound **14** (101 MHz in $CDCl_3$)



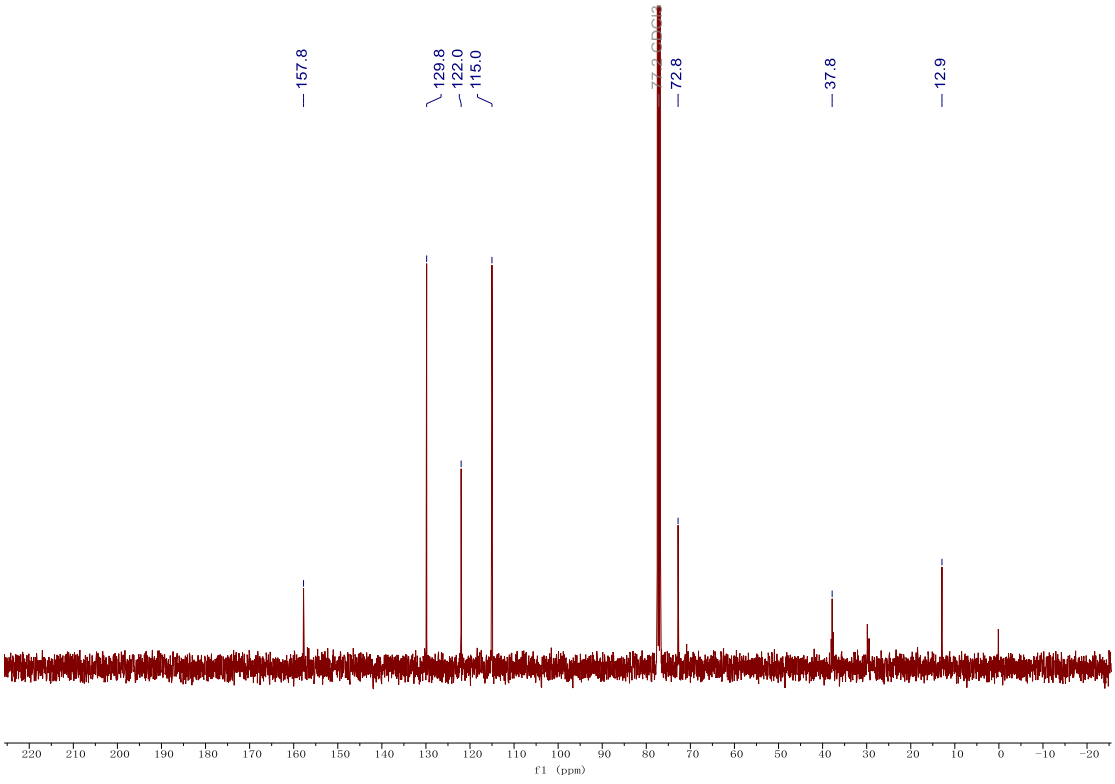
^{19}F NMR of compound **14** (376 MHz in $CDCl_3$)



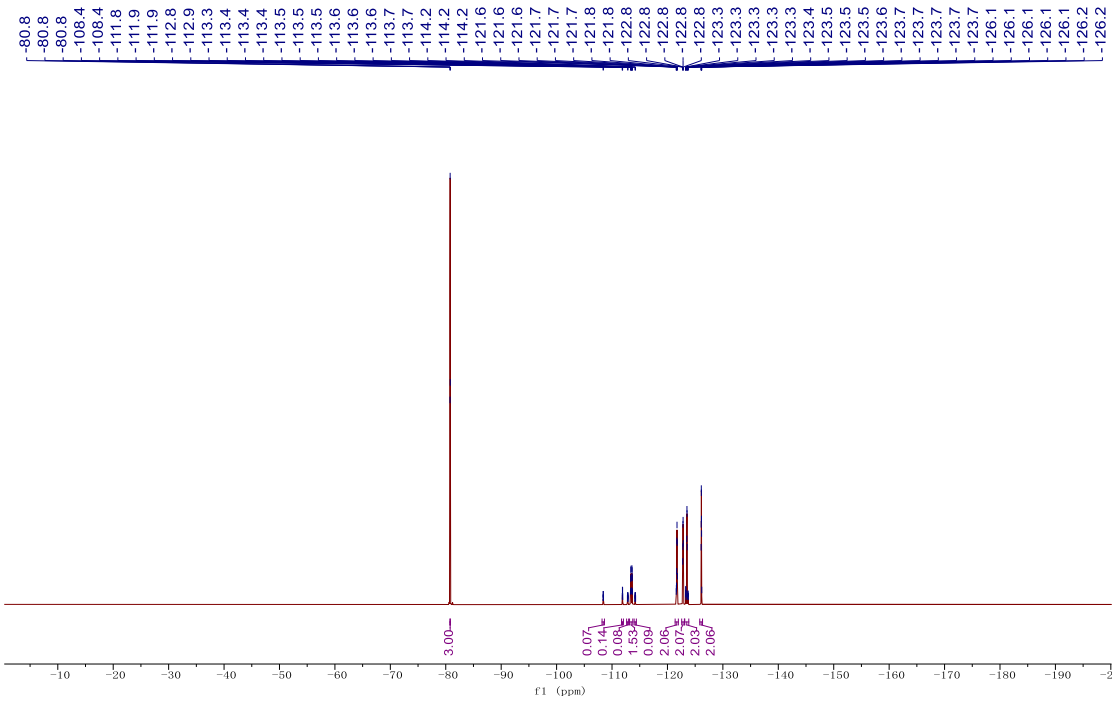
^{1}H NMR of compound **15**(500 MHz in $CDCl_3$)



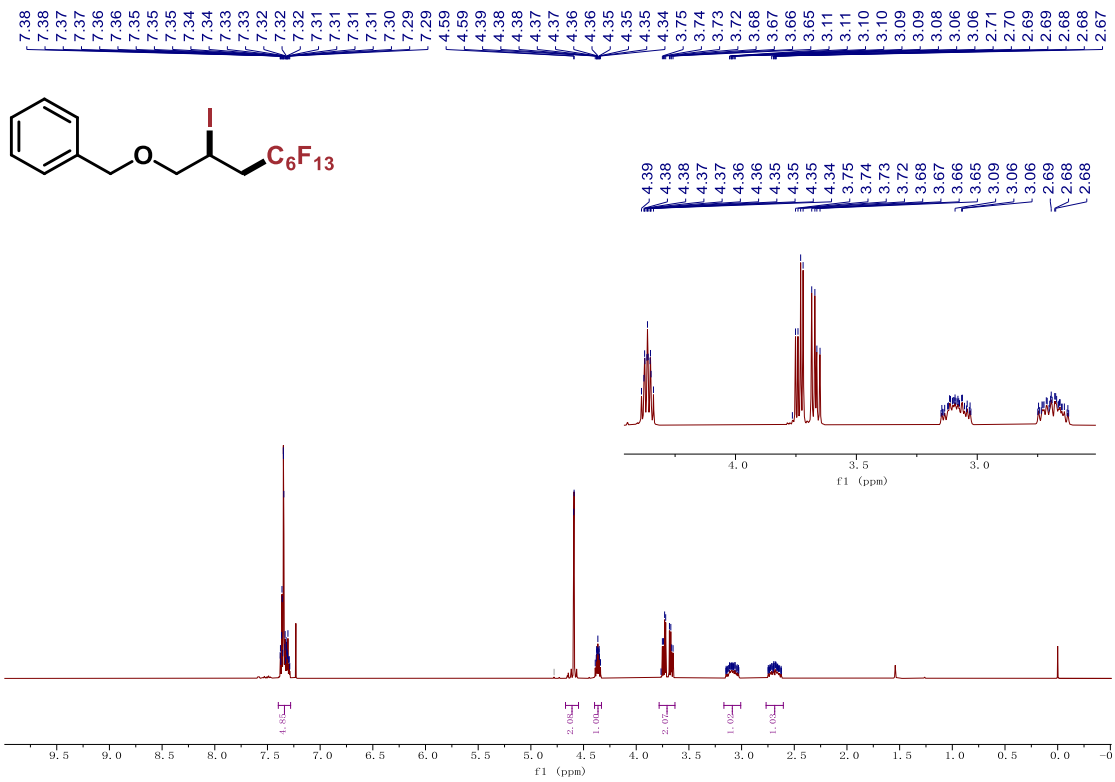
^{13}C NMR of compound **15** (101 MHz in $CDCl_3$)



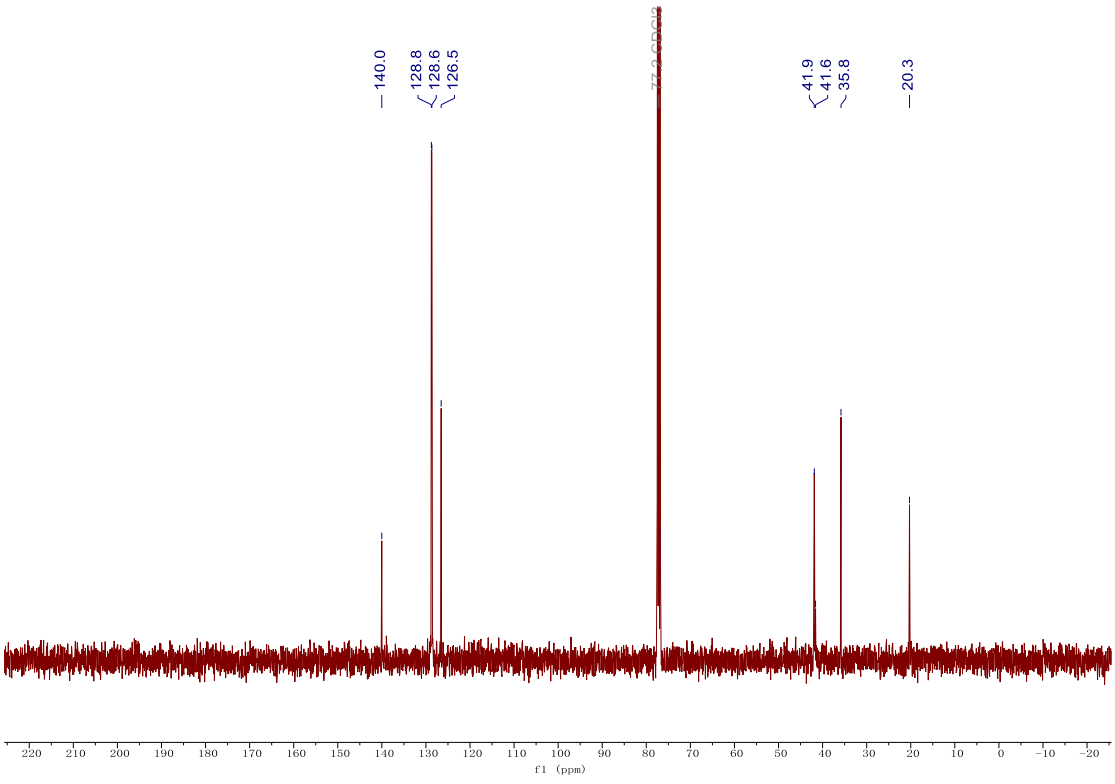
^{19}F NMR of compound **15** (471 MHz in $CDCl_3$)



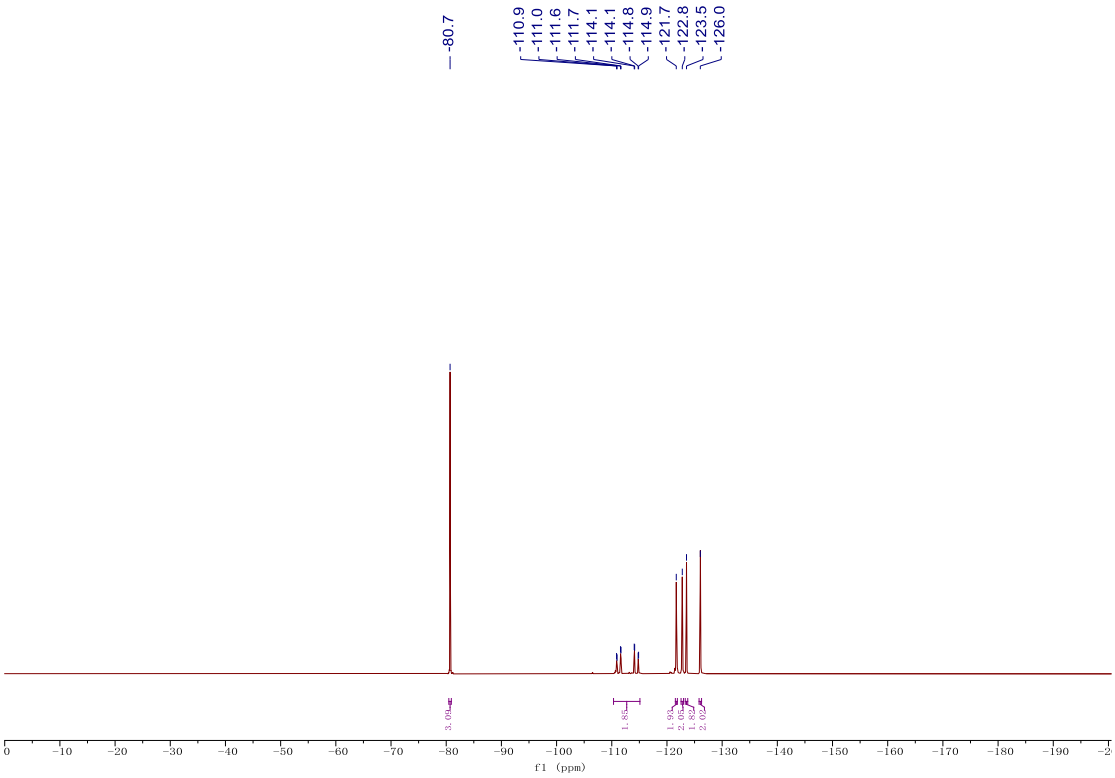
^{1}H NMR of compound **16** (500 MHz in $CDCl_3$)



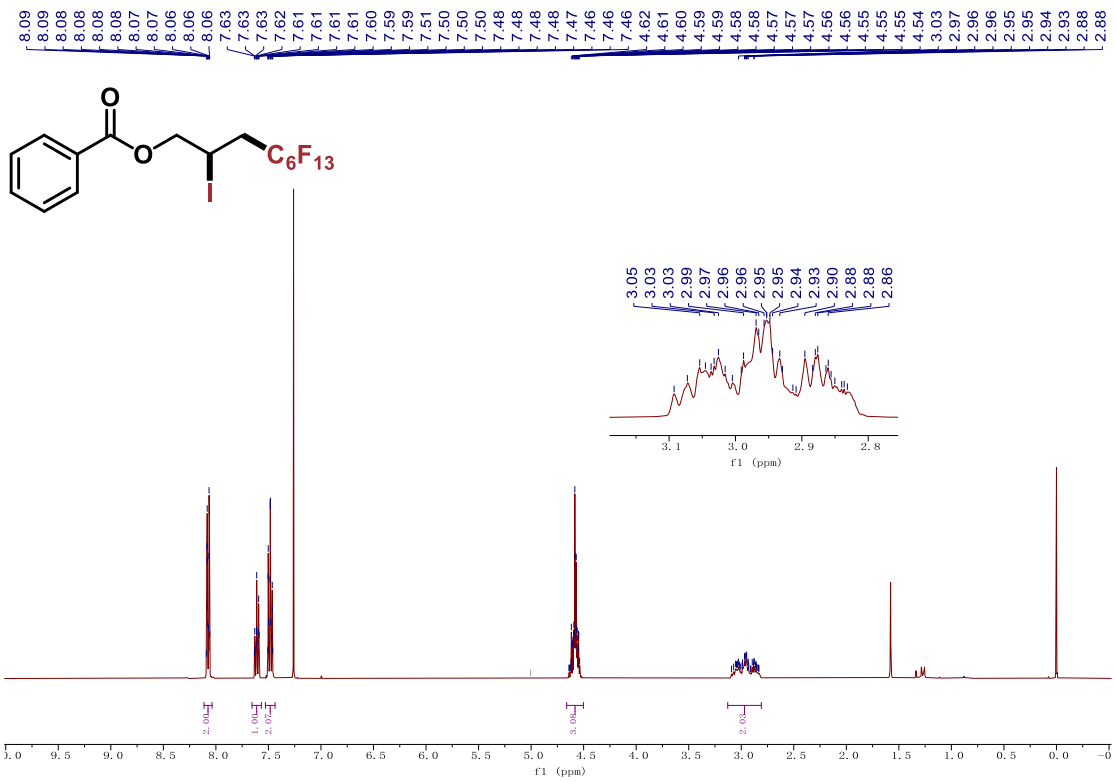
^{13}C NMR of compound **16** (101 MHz in $CDCl_3$)



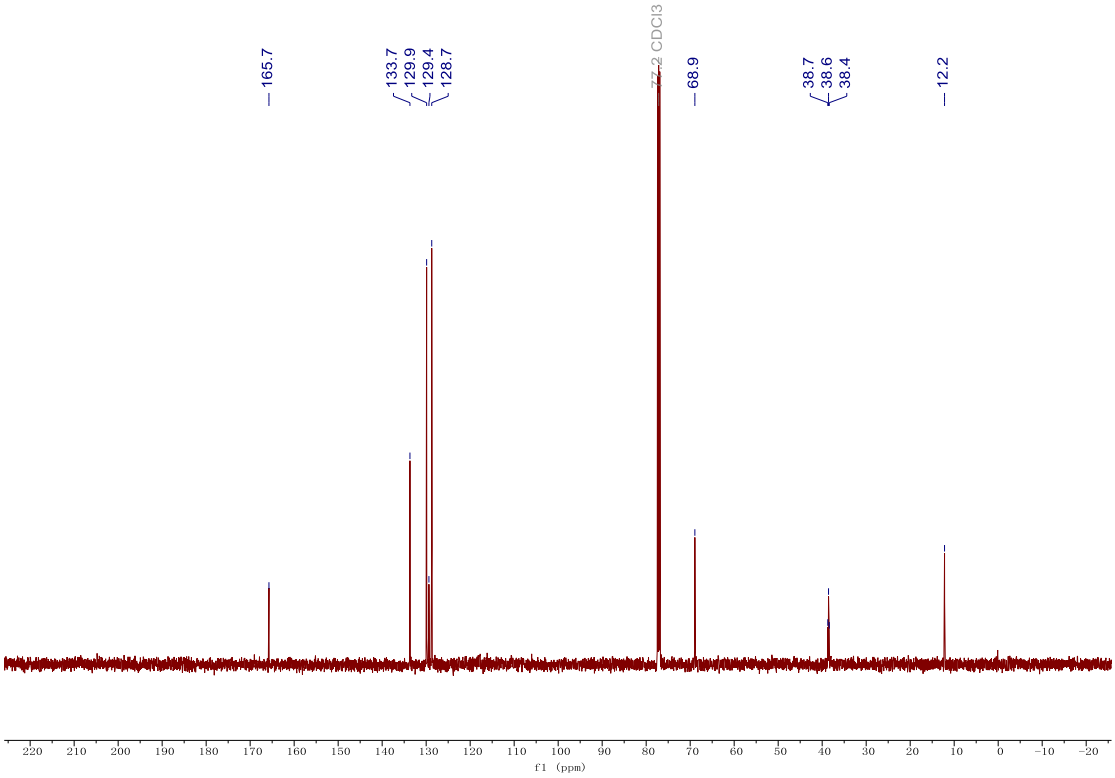
^{19}F NMR of compound **16** (376 MHz in $CDCl_3$)



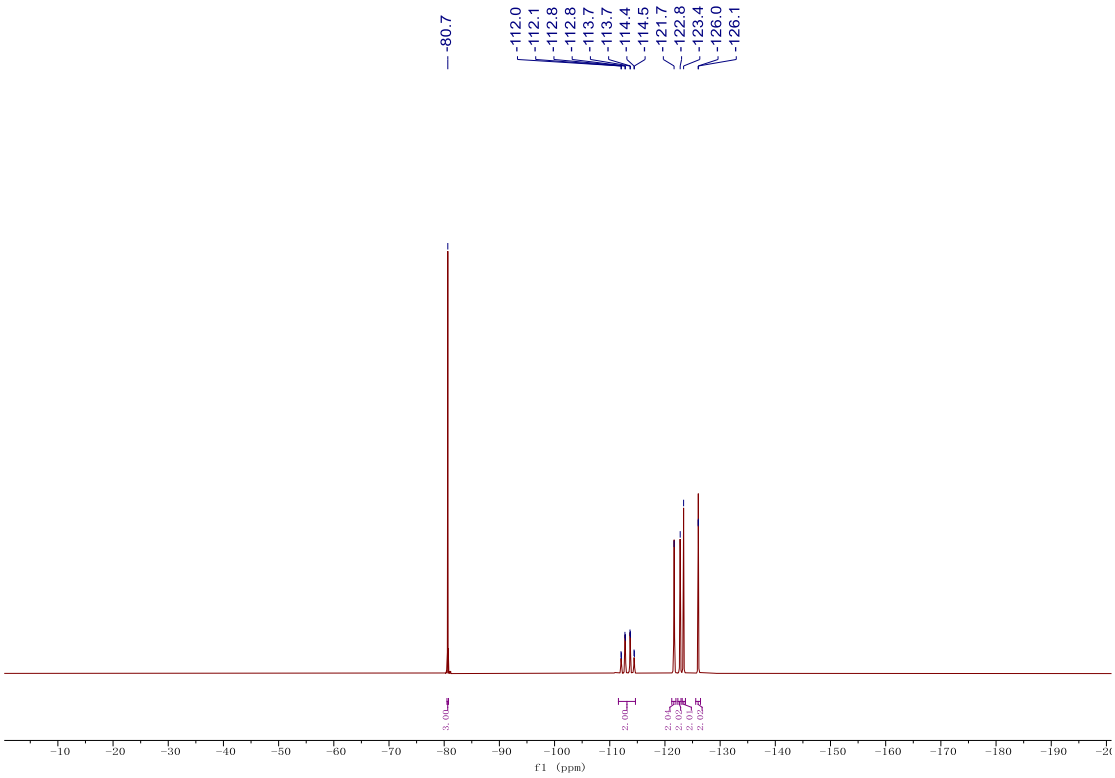
^{1}H NMR of compound **17** (400 MHz in $CDCl_3$)



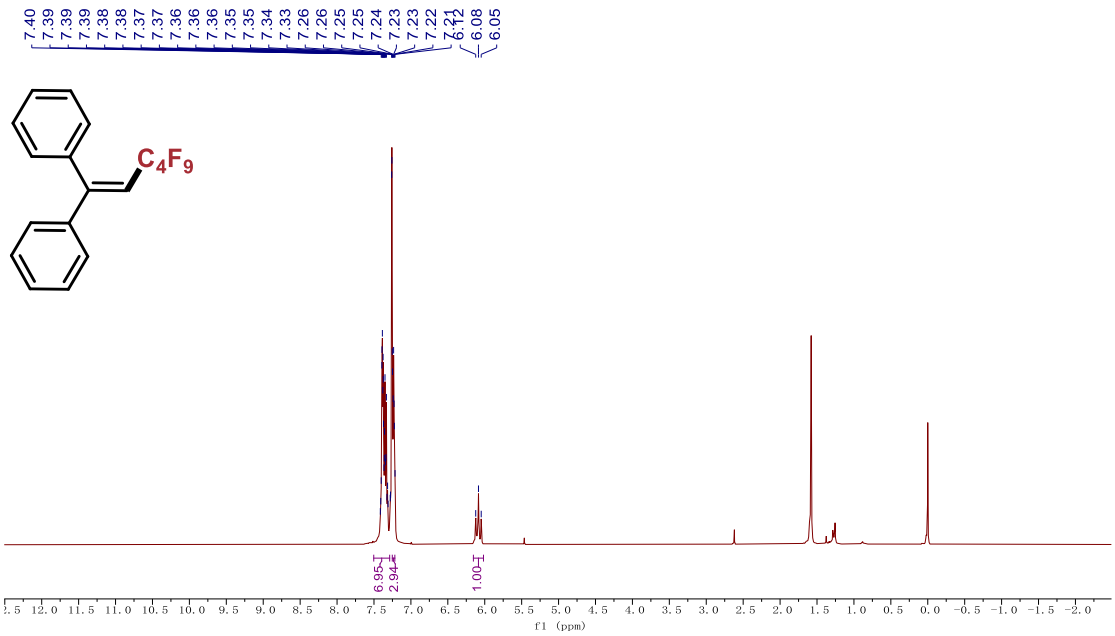
^{13}C NMR of compound **17** (126 MHz in $CDCl_3$)



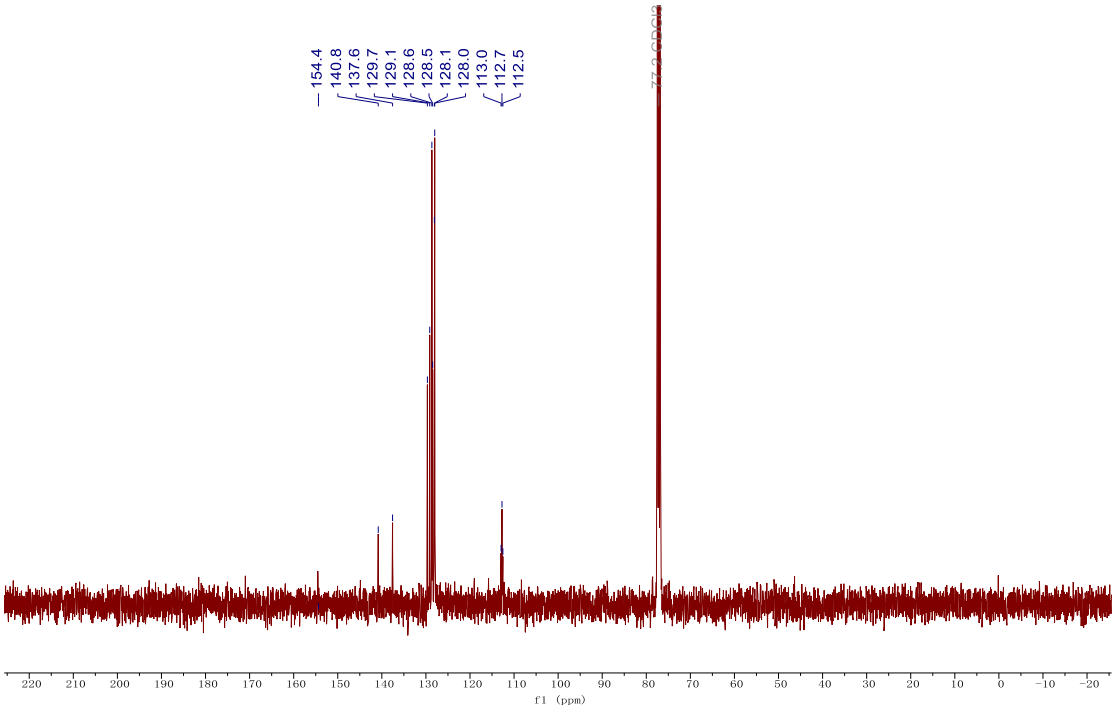
^{19}F NMR of compound **17** (376 MHz in $CDCl_3$)



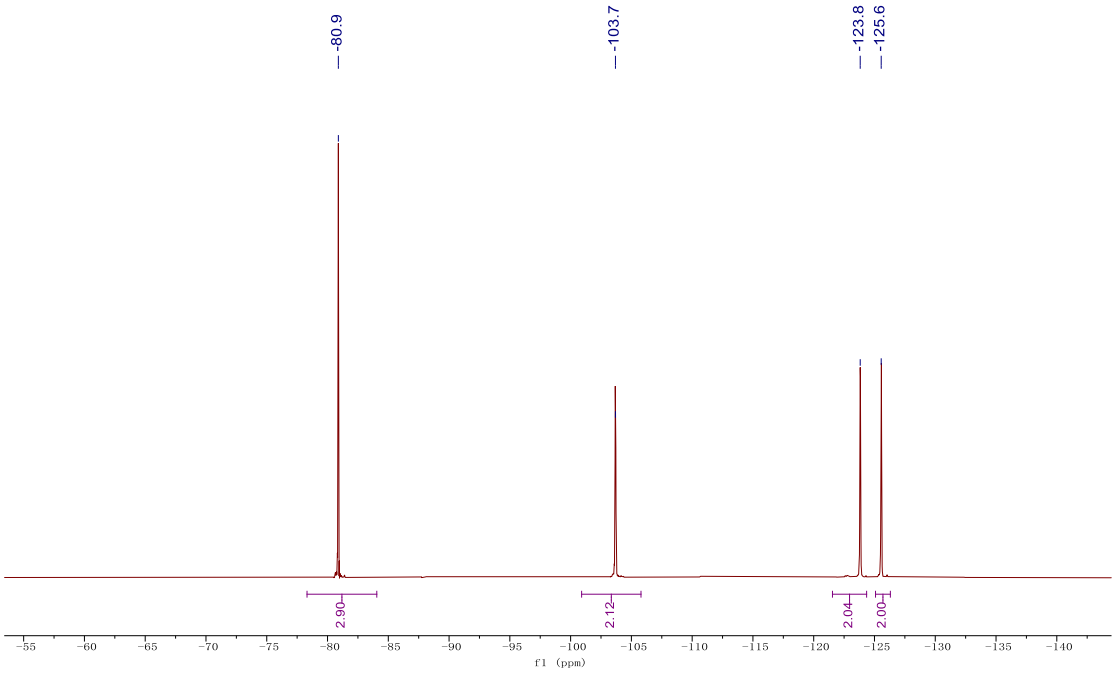
^{1}H NMR of compound **18** (400 MHz in $CDCl_3$)



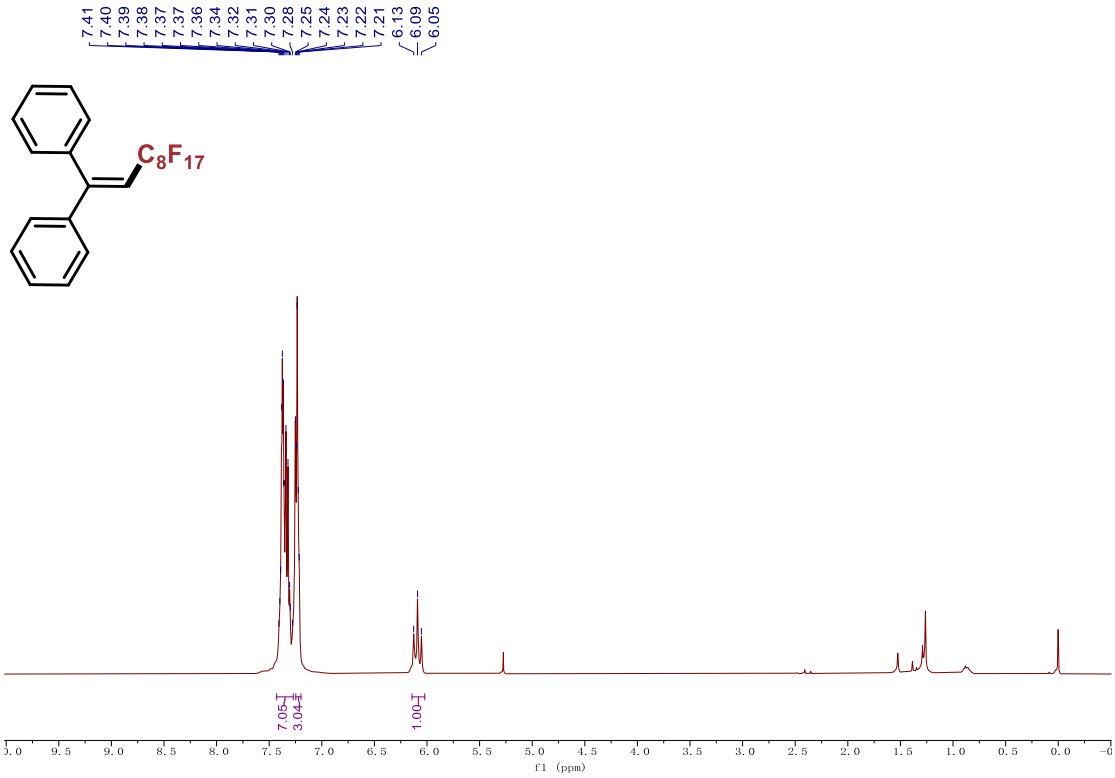
^{13}C NMR of compound **18** (101 MHz in $CDCl_3$)



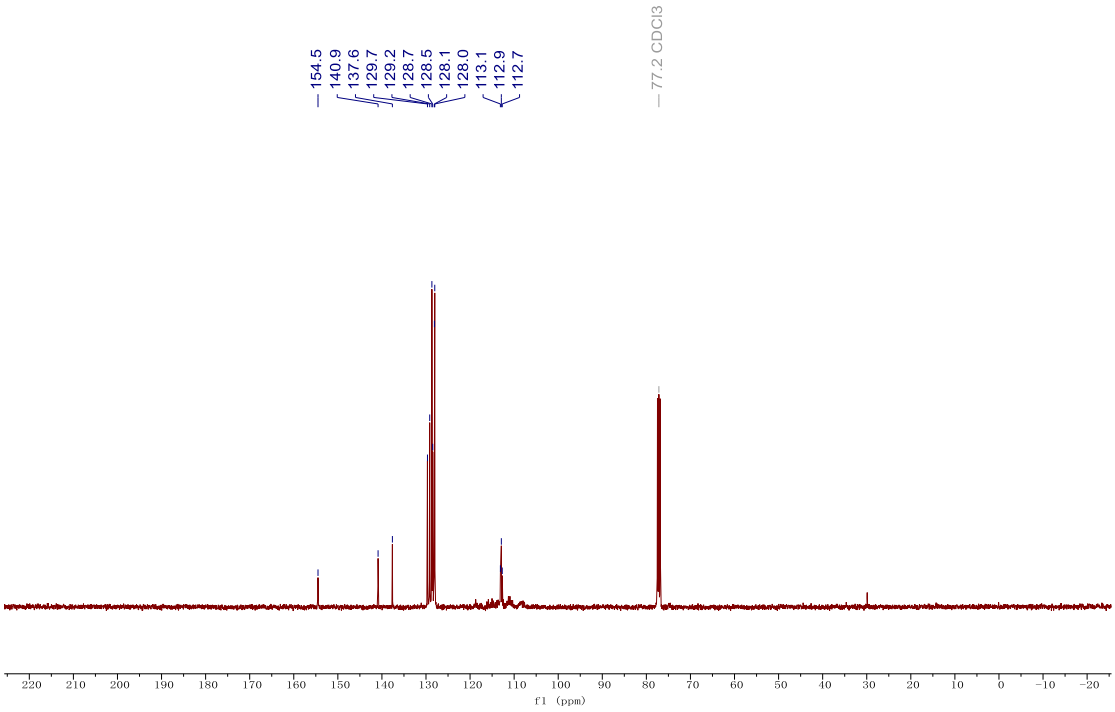
^{19}F NMR of compound **18** (376 MHz in $CDCl_3$)



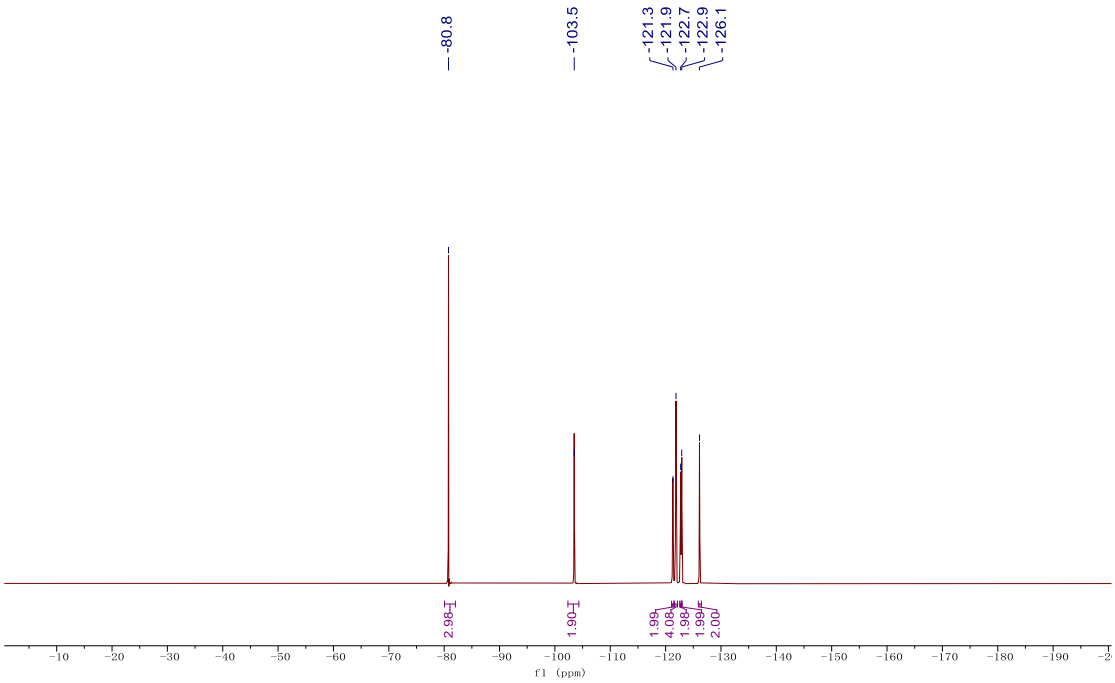
^{1}H NMR of compound **19** (400 MHz in $CDCl_3$)



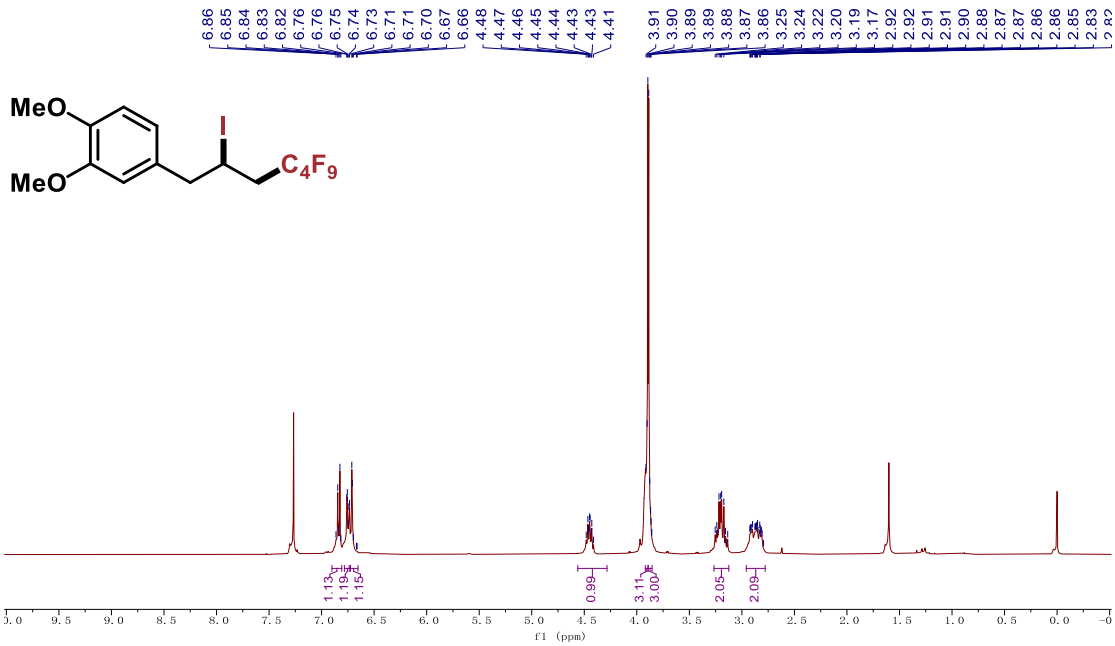
^{13}C NMR of compound **16** (101 MHz in $CDCl_3$)



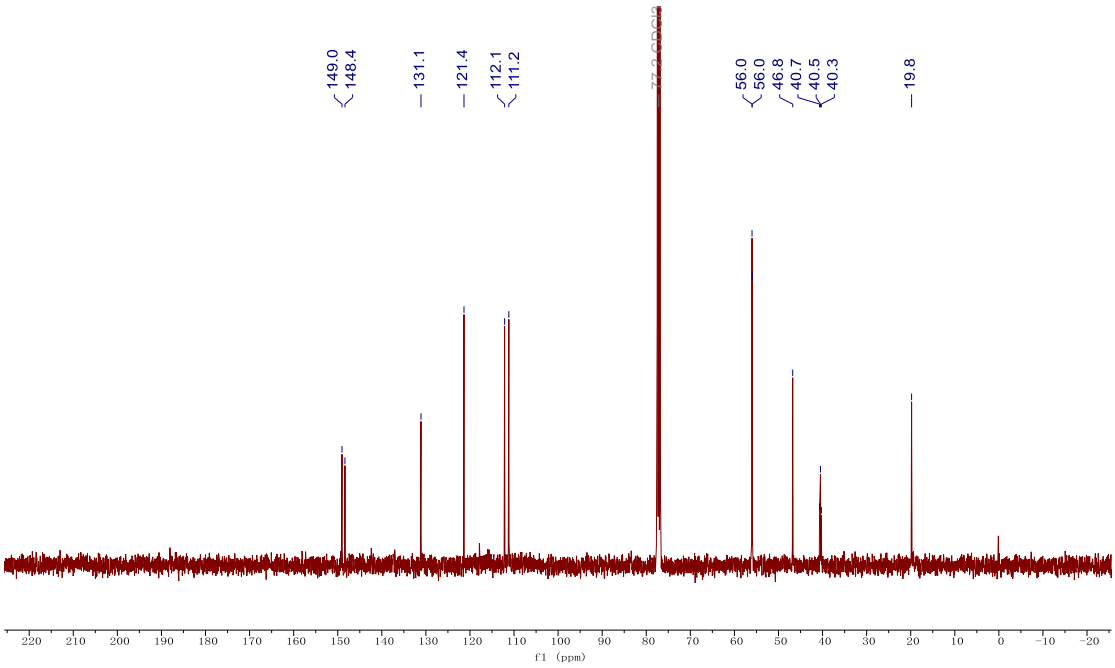
^{19}F NMR of compound **19** (376 MHz in $CDCl_3$)



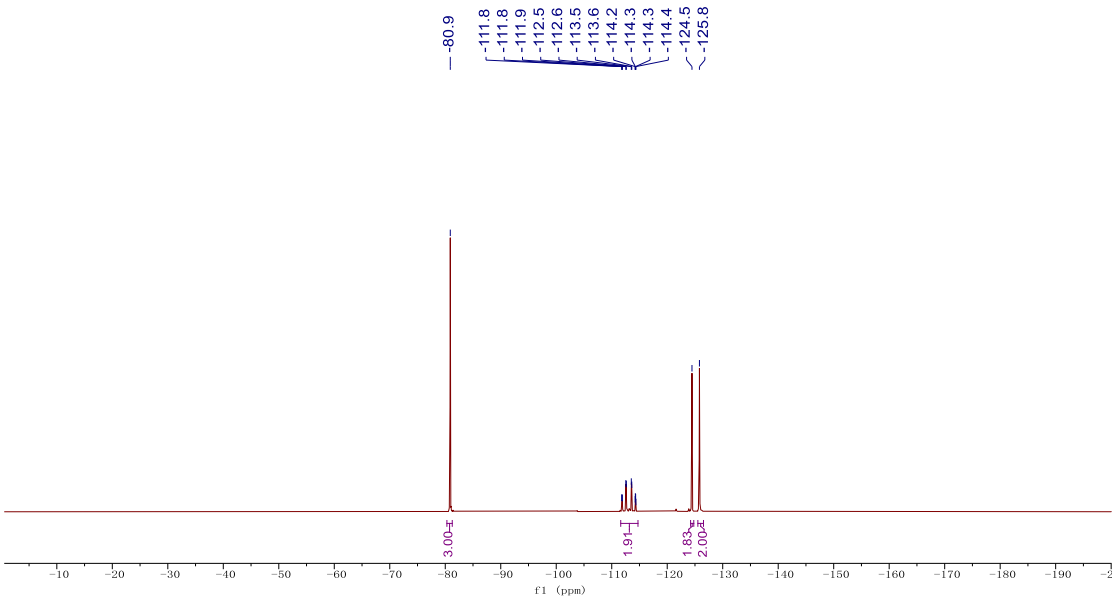
^{1}H NMR of compound **20** (400 MHz in $CDCl_3$)



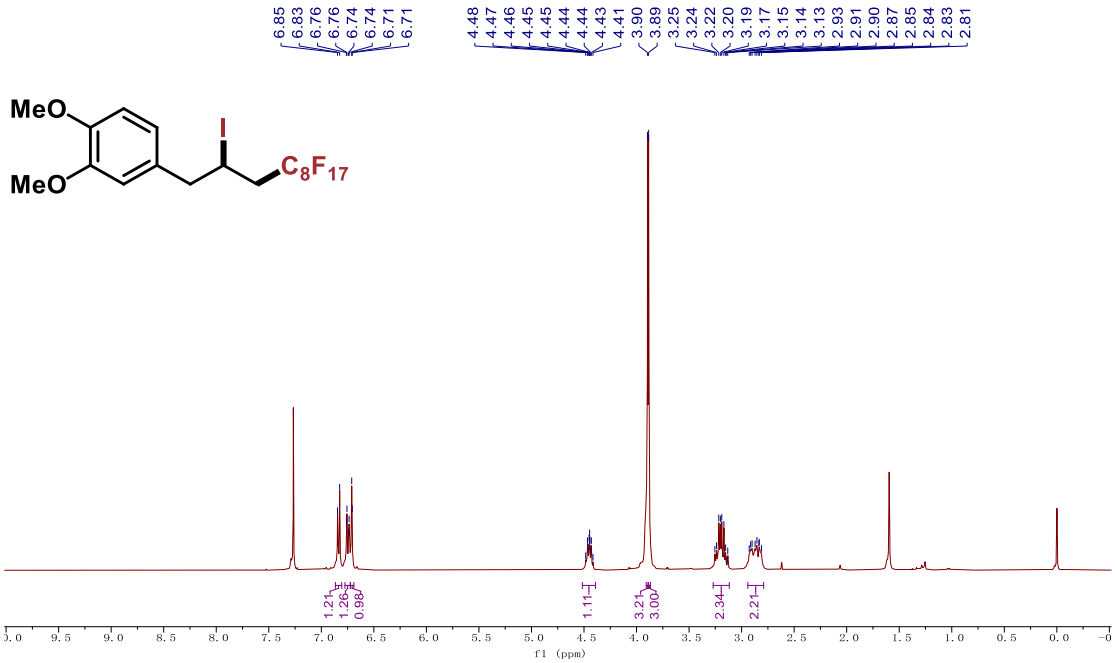
^{13}C NMR of compound **20** (101 MHz in $CDCl_3$)



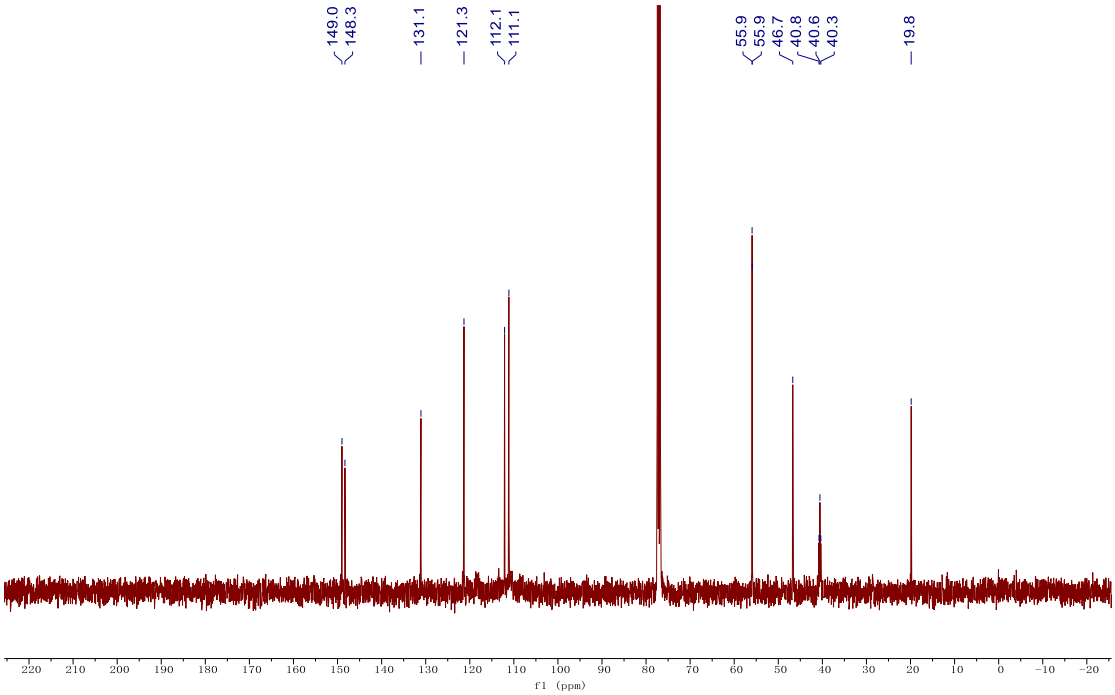
^{19}F NMR of compound **20** (376 MHz in $CDCl_3$)



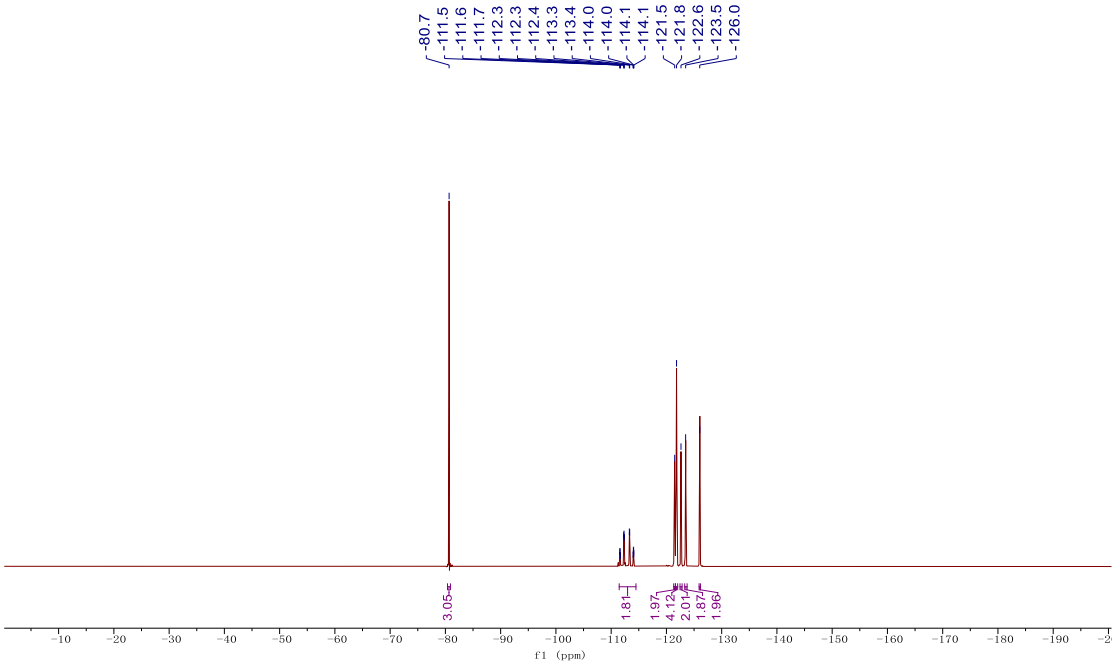
^{1}H NMR of compound **21** (400 MHz in $CDCl_3$)



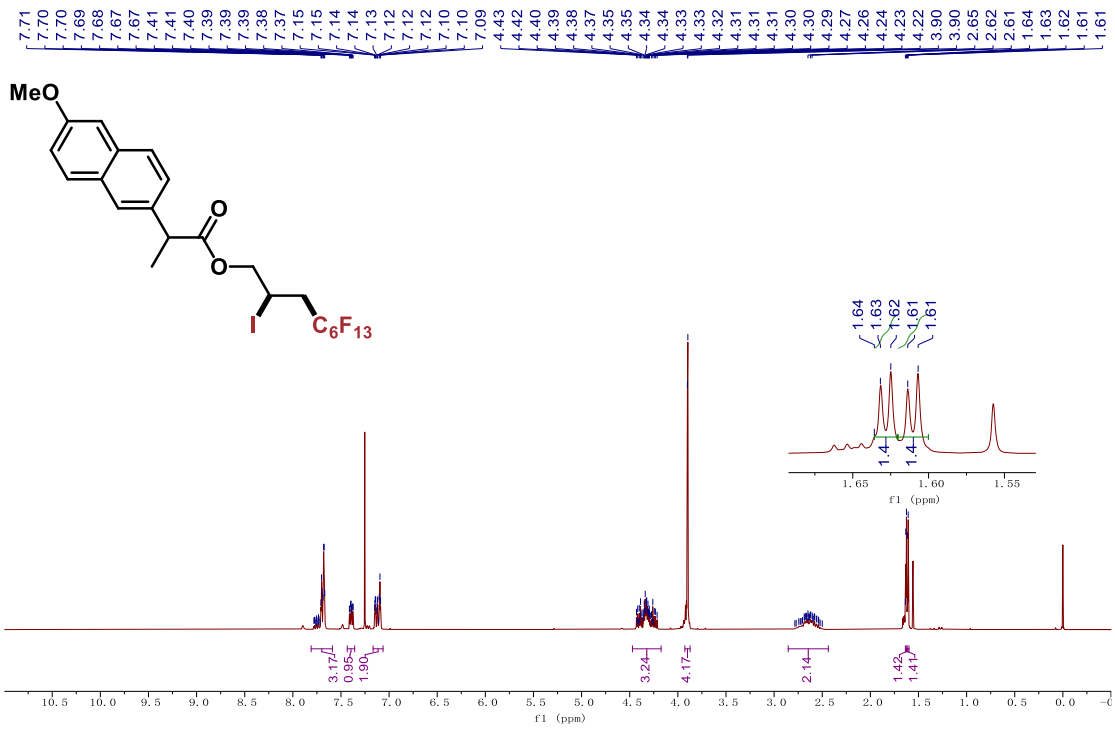
^{13}C NMR of compound **21** (101 MHz in $CDCl_3$)



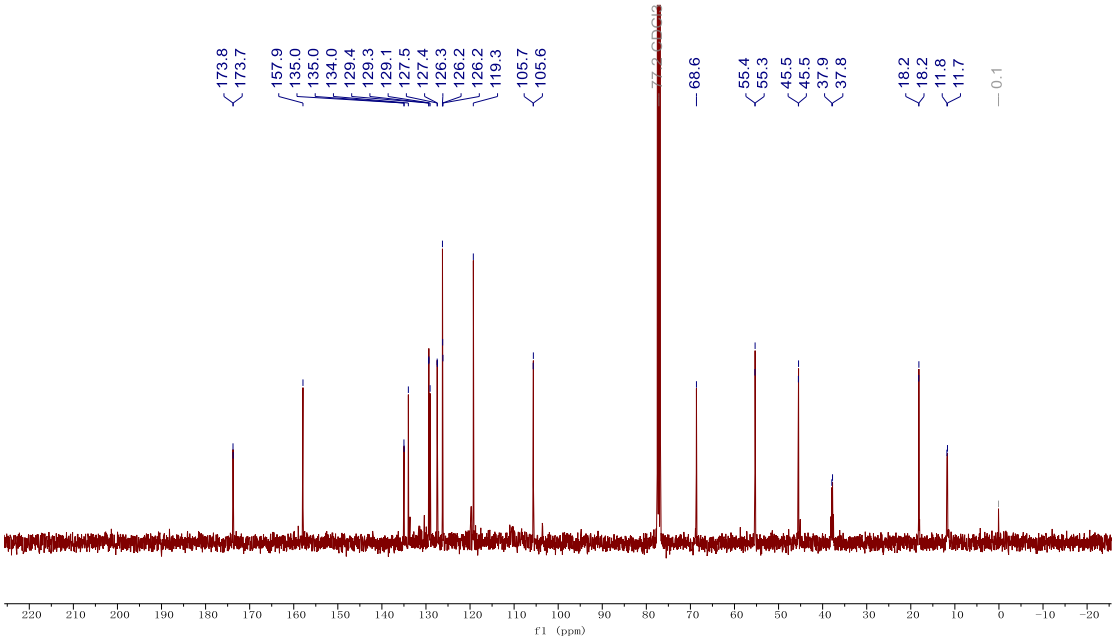
^{19}F NMR of compound **21** (376 MHz in $CDCl_3$)



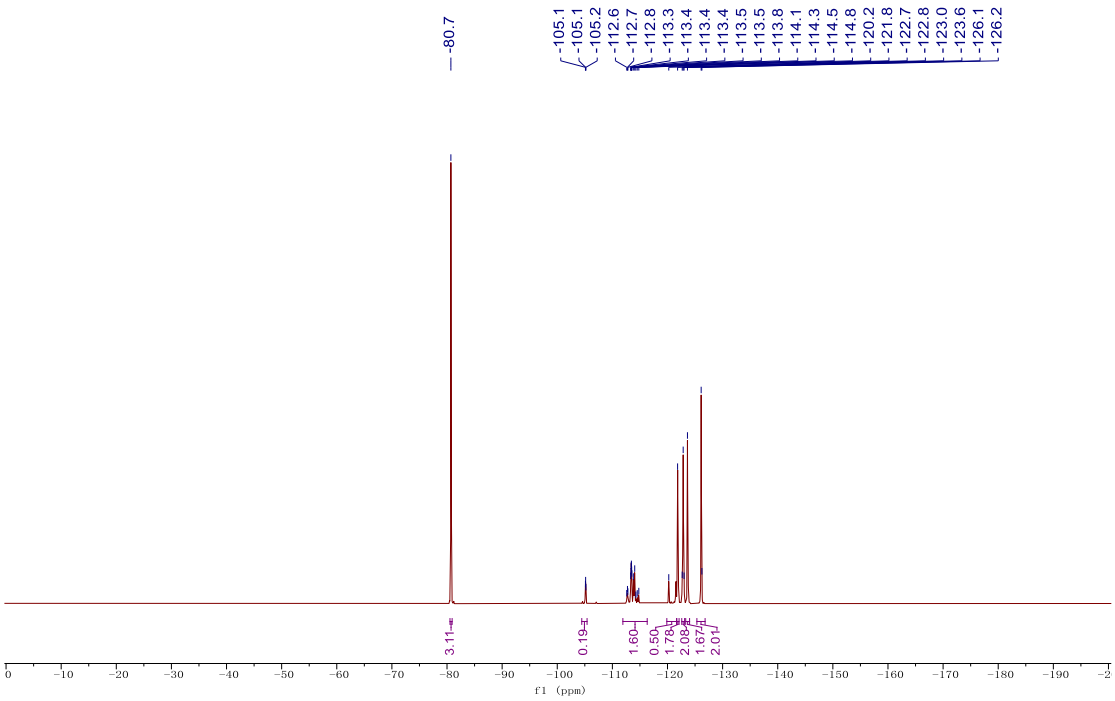
^{1}H NMR of compound **22** (400 MHz in $CDCl_3$)



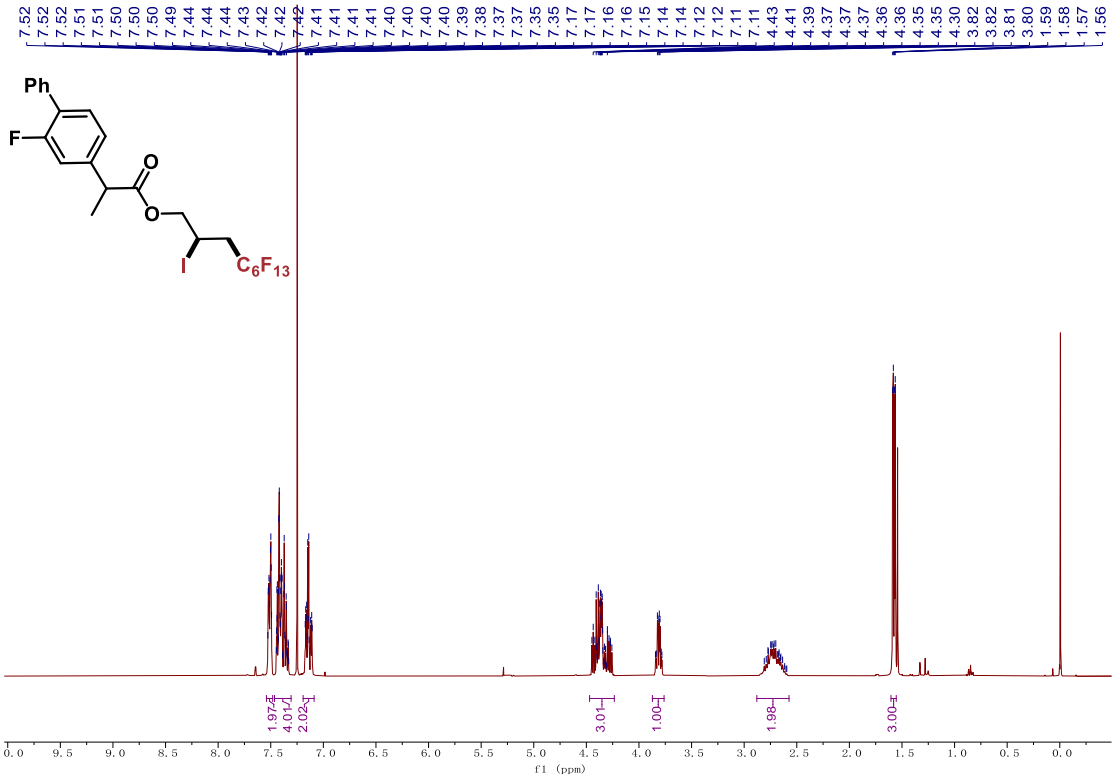
^{13}C NMR of compound **22** (101 MHz in $CDCl_3$)



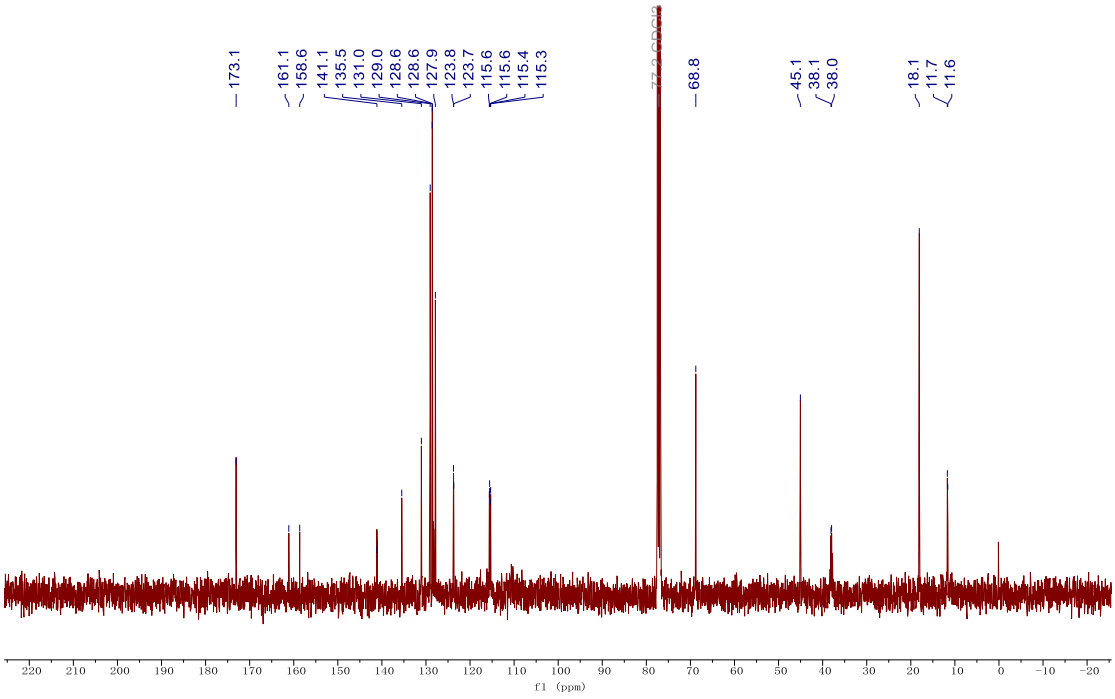
^{19}F NMR of compound **22** (376 MHz in $CDCl_3$)



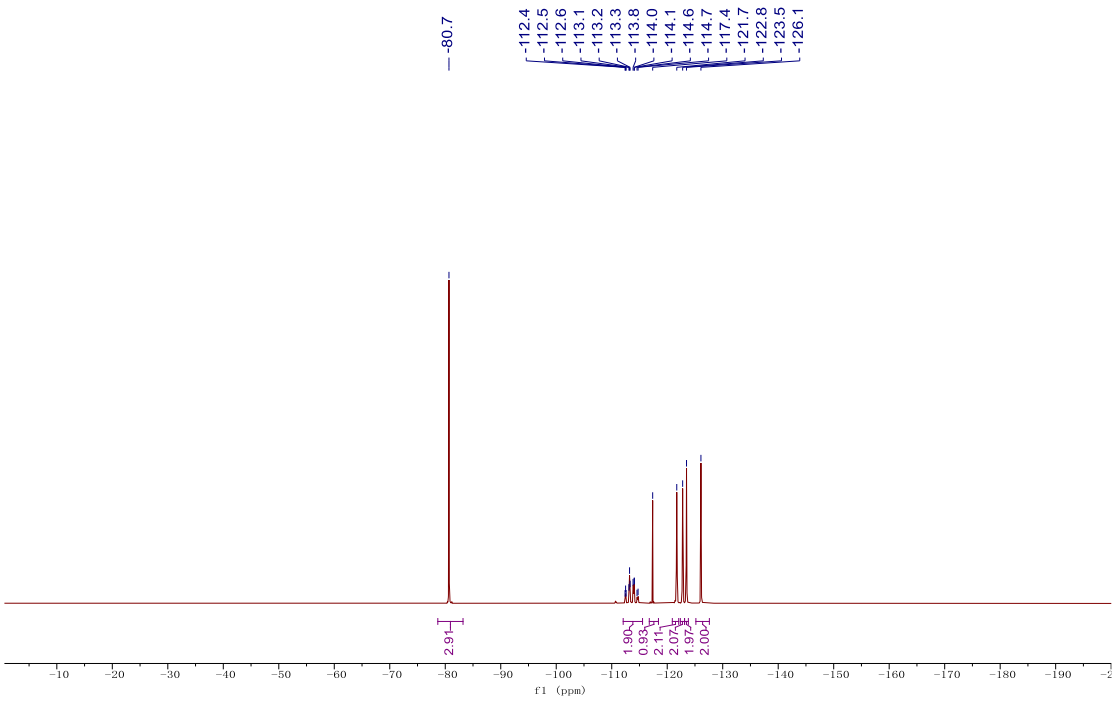
^{1}H NMR of compound **23** (400 MHz in $CDCl_3$)



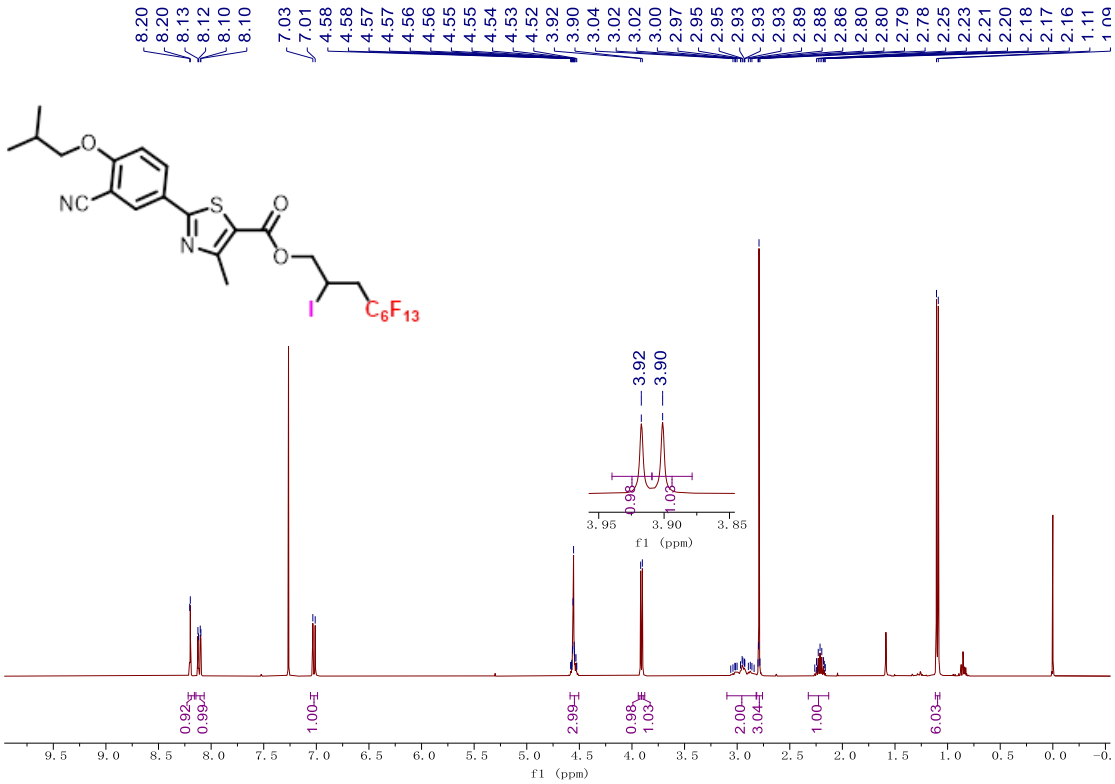
^{13}C NMR of compound **23** (101 MHz in $CDCl_3$)



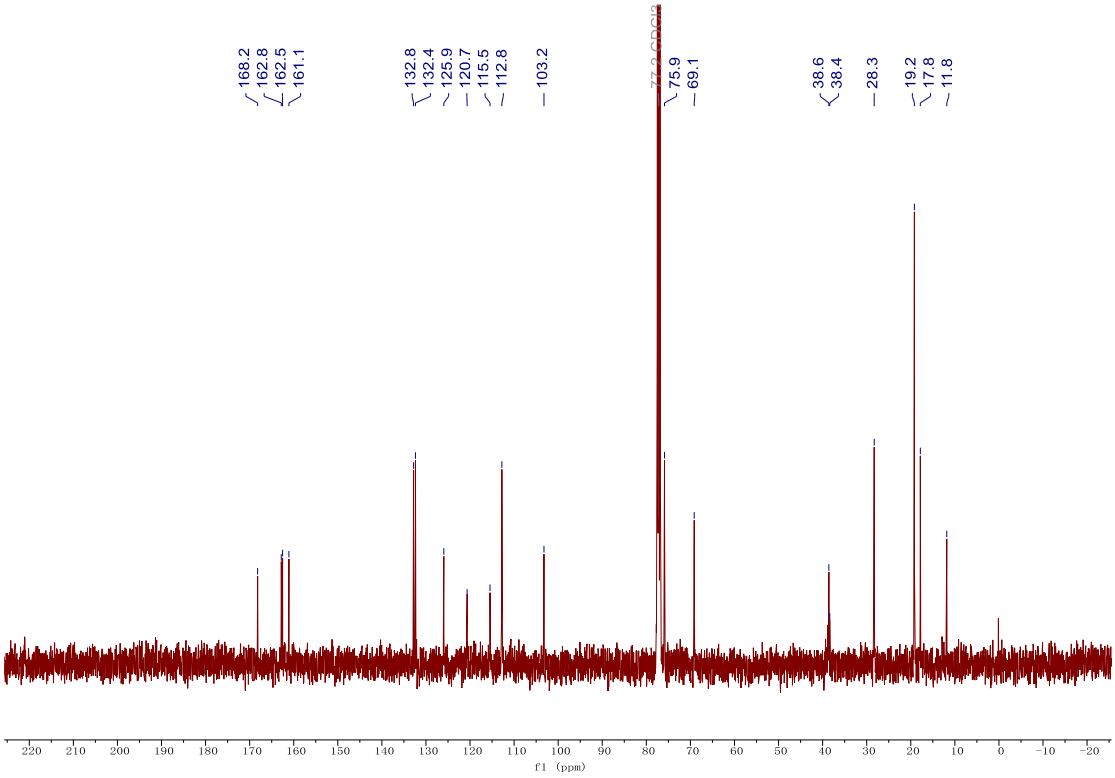
^{19}F NMR of compound **23** (376 MHz in $CDCl_3$)



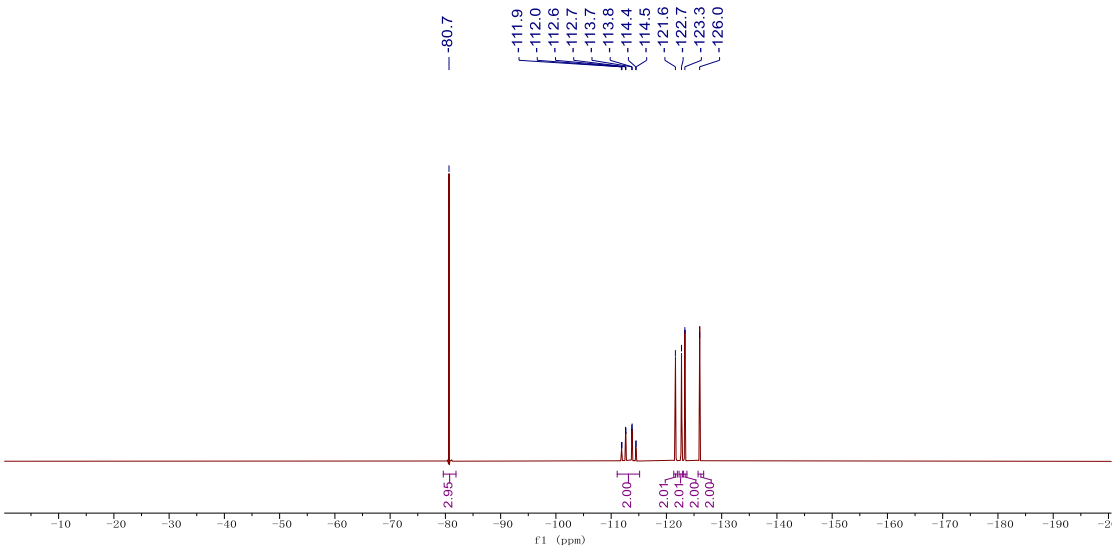
^{1}H NMR of compound **24** (400 MHz in $CDCl_3$)



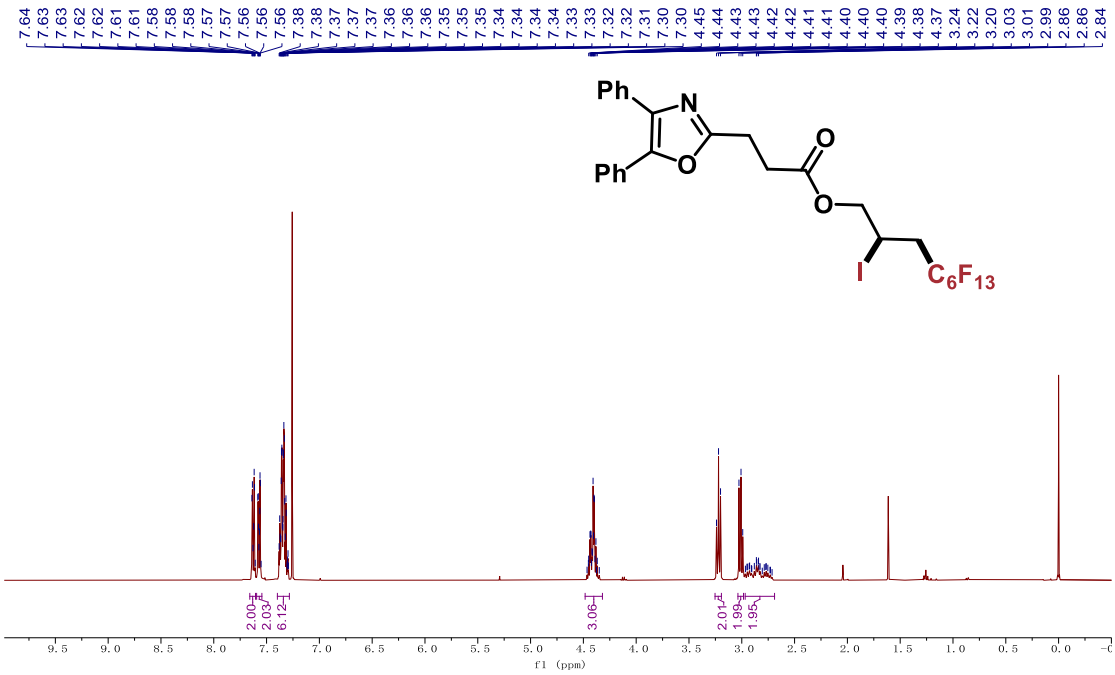
^{13}C NMR of compound **24** (101 MHz in $CDCl_3$)



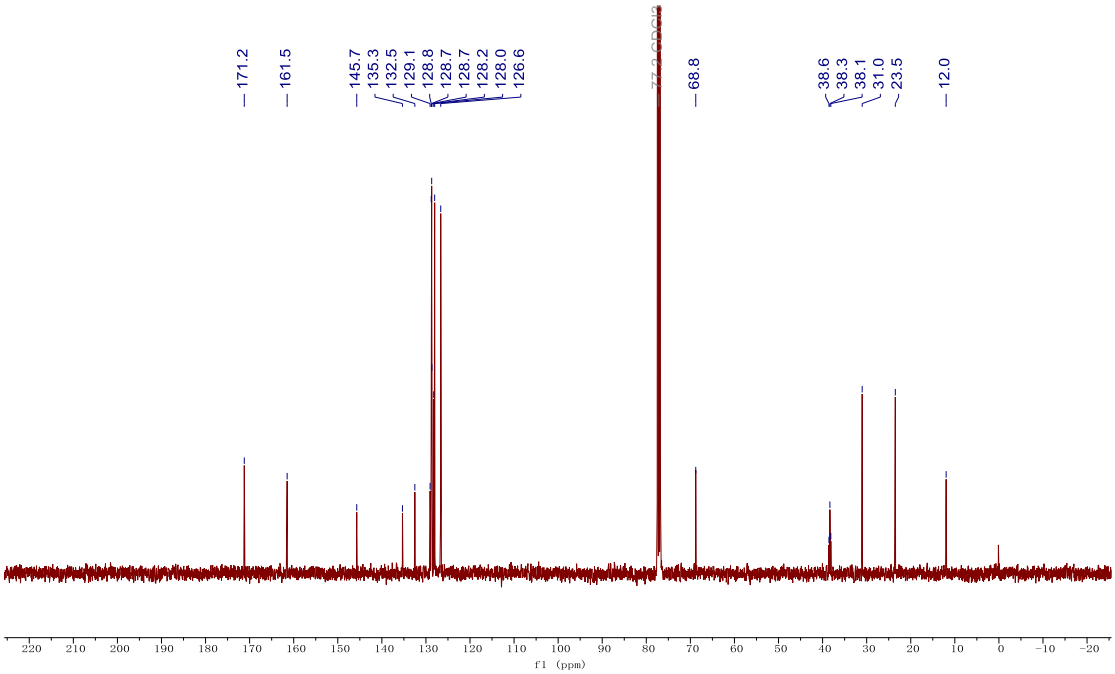
^{19}F NMR of compound **24** (376 MHz in $CDCl_3$)



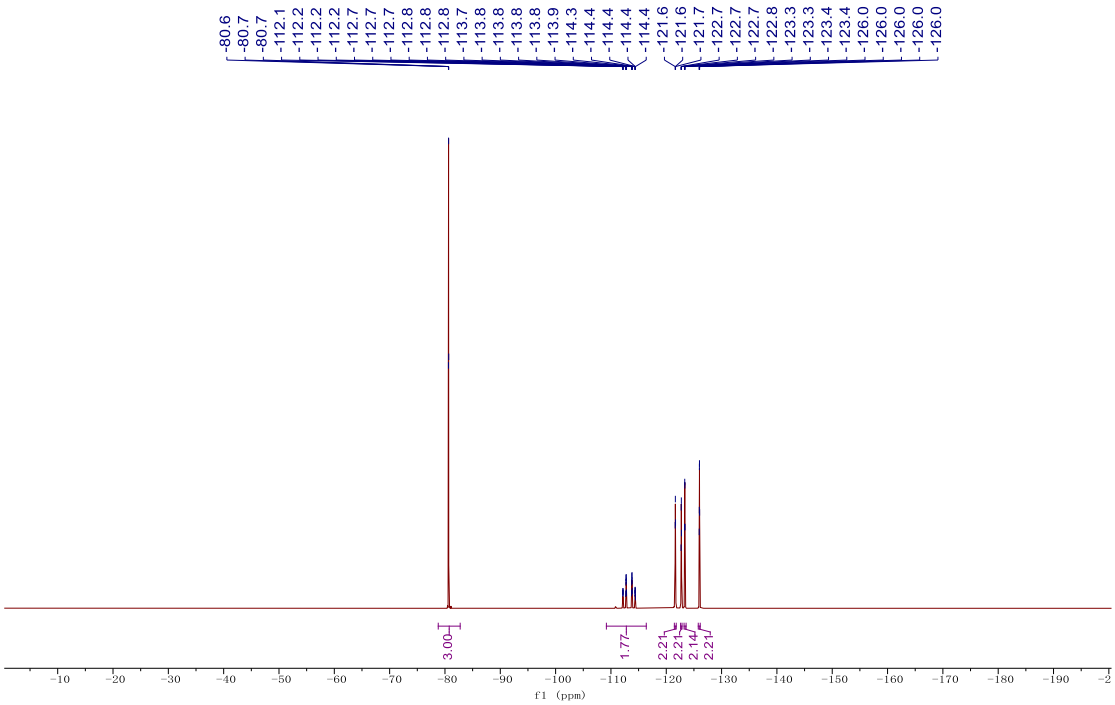
^{1}H NMR of compound **25** (400 MHz in $CDCl_3$)



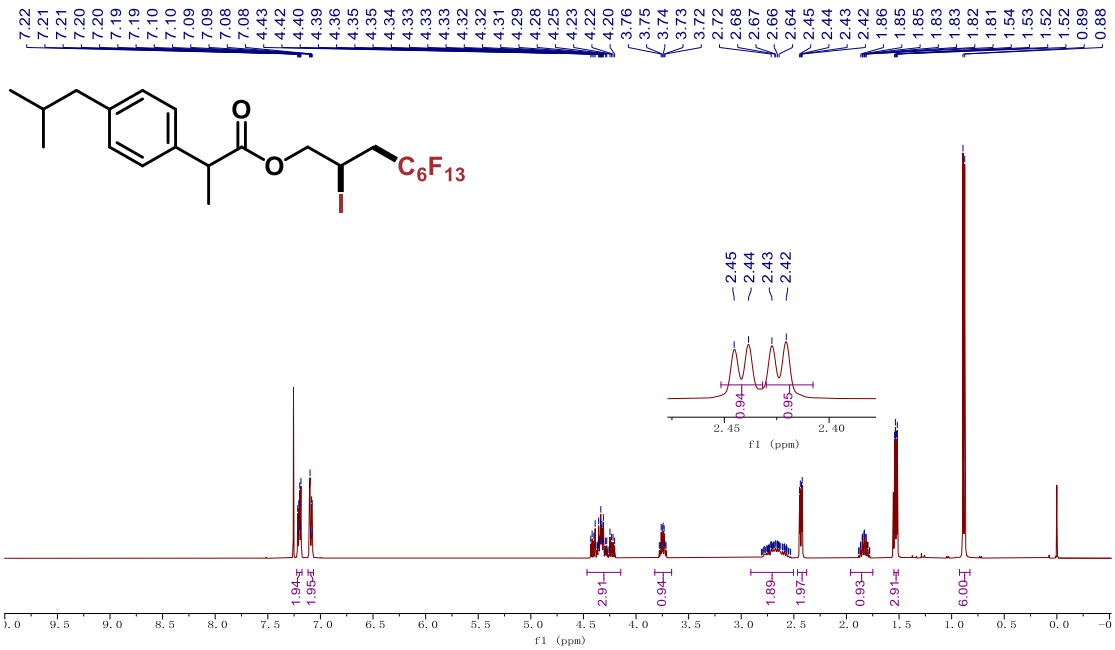
^{13}C NMR of compound **25** (101 MHz in $CDCl_3$)



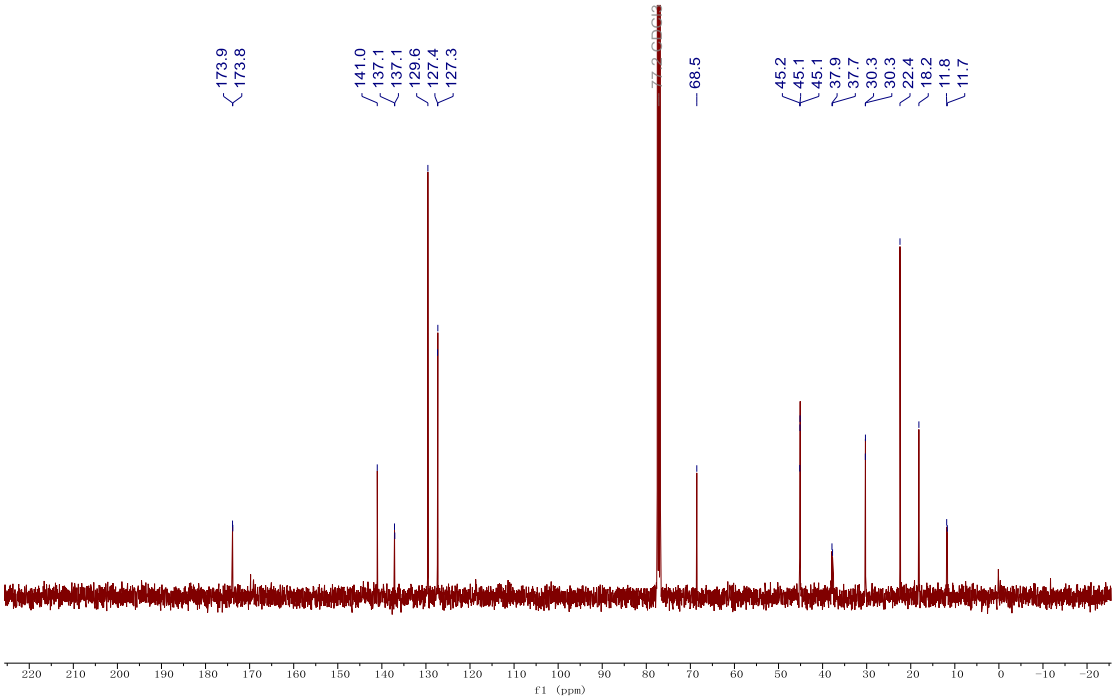
^{19}F NMR of compound **25** (471 MHz in $CDCl_3$)



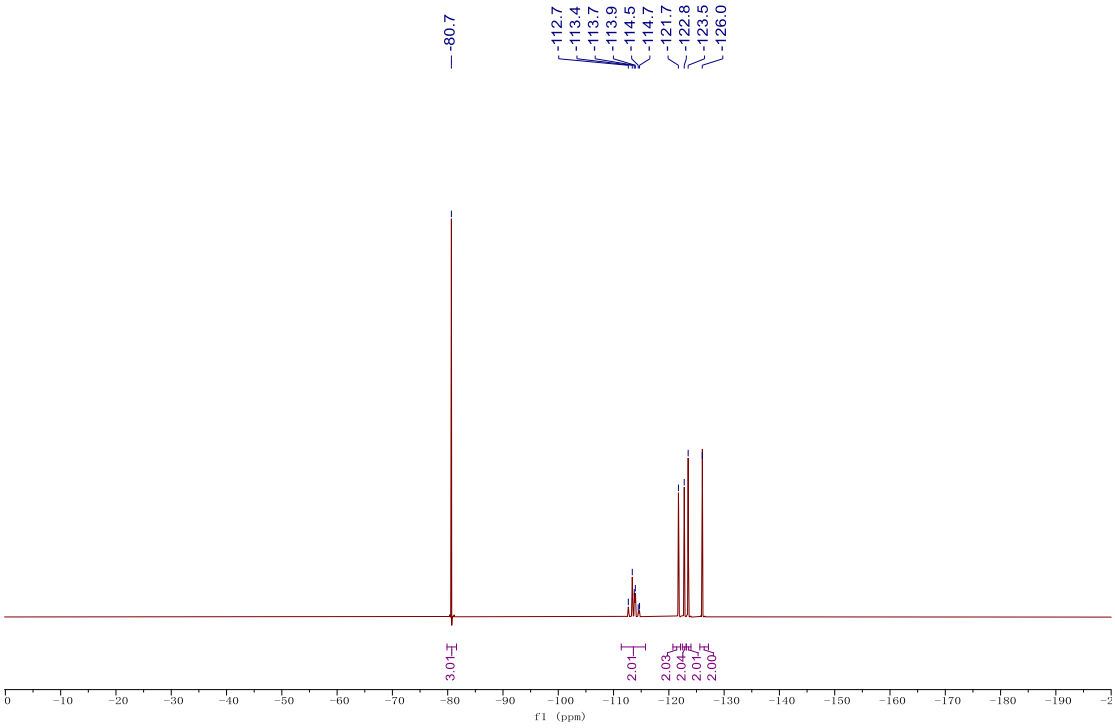
^{1}H NMR of compound **26** (400 MHz in $CDCl_3$)



^{13}C NMR of compound **26** (101 MHz in $CDCl_3$)



^{19}F NMR of compound **26** (376 MHz in $CDCl_3$)



7. Computational Details

All the calculations were carried out by using Gaussian16 program.[13] The structures were optimized at B3LYP[14]-D3BJ[15]/BSI level with the implicit solvation model SMD[16] in toluene solvent, BSI denoting a basis set with SDD[17] for I atom and 6-31G(d,p) for other atoms. The Coulomb radius for iodine in the SMD model was modified with 2.74 Å.[18] Harmonic vibrational frequencies were calculated at the same level to confirm that the minima have no imaginary frequency and transition states have unique one imaginary frequency, and obtain the thermal corrections simultaneously. The energies were further refined by the single-point-energy calculations at the B3LYP-D3BJ/BSII level with the same solvation model as the geometry optimizations, BSII representing a basis set with SDD for I atom and 6-311++G(d,p) for other atoms.

Cartesian Coordinates and Energetic Results of Optimized Structures

Coordinates are in Å, SCF energies and Gibbs free energy corrections (G_{corr} at 298.15 K) are in a.u. in toluene solvent.

$C_6F_{13}I$

B3LYP-D3BJ/BSI SCF energy:

-1537.946257

G_{corr} at B3LYP-D3BJ/BSI level:

0.024938

B3LYP-D3BJ/BSII SCF energy:

-1538.459413

C	-4.333552	-0.391563	0.149190
C	-3.061721	0.350031	-0.334350
C	-1.736306	-0.335416	0.093026
C	-0.496451	0.595599	-0.039457
C	0.851775	-0.187447	-0.039084
C	2.077569	0.723616	0.224782
I	3.976436	-0.395780	-0.072032
F	-5.400779	0.130266	-0.464915
F	-4.252535	-1.694761	-0.150480
F	-4.482474	-0.252017	1.469777
F	-3.100100	0.407891	-1.682022
F	-3.098226	1.604868	0.170473
F	-1.839016	-0.719505	1.385565
F	-1.558991	-1.428603	-0.682045
F	-0.582412	1.283902	-1.199580
F	-0.512814	1.465437	0.993725
F	0.809354	-1.132228	0.925606
F	0.985085	-0.775654	-1.244097
F	2.039223	1.172660	1.482954
F	2.042685	1.765232	-0.616845

H_2O

B3LYP-D3BJ/BSI SCF energy:

-76.422754

G_{corr} at B3LYP-D3BJ/BSI level:

0.003622

B3LYP-D3BJ/BSII SCF energy:

-76.463532

O	0.000000	0.000000	0.119432
H	0.000000	0.759178	-0.477728
H	0.000000	-0.759178	-0.477728

$C_6F_{13}I\_H_2O\_complex$

B3LYP-D3BJ/BSI SCF energy:

-1614.380303

G_{corr} at B3LYP-D3BJ/BSI level:

0.041471

B3LYP-D3BJ/BSII SCF energy:

-1614.929950

C	4.610265	-0.534453	0.166688
C	3.370050	0.203568	-0.398065
C	2.019027	-0.339384	0.139427
C	0.828155	0.632197	-0.103709
C	-0.559302	-0.067280	0.007459
C	-1.736793	0.921637	0.177232
I	-3.695478	-0.093852	0.021465
F	5.690179	-0.169809	-0.533262
F	4.800094	-0.217360	1.450862
F	4.450333	-1.860495	0.058910
F	3.486291	1.512620	-0.076330
F	3.383728	0.069925	-1.741163
F	1.768428	-1.518508	-0.473702
F	2.131202	-0.547902	1.471216
F	0.911350	1.628393	0.804588
F	0.937756	1.156441	-1.345885
F	-0.739386	-0.789354	-1.119523
F	-0.543842	-0.899069	1.075034
F	-1.637377	1.871873	-0.774109
F	-1.637701	1.508738	1.382885
O	-6.234895	-1.455929	-0.218365
H	-6.121747	-2.313292	0.215097
H	-6.336670	-1.672291	-1.155693

$C_6F_{13}I^{\bullet\cdot}$

B3LYP-D3BJ/BSI SCF energy:

-1538.050956

G_{corr} at B3LYP-D3BJ/BSI level:

0.020398

B3LYP-D3BJ/BSII SCF energy:

-1538.572529

C	-4.475534	-0.586992	0.143609
C	-3.268976	0.270646	-0.311643
C	-1.888788	-0.327452	0.072139
C	-0.722322	0.694396	-0.014723
C	0.700113	0.063494	-0.038900
C	1.843917	1.030932	0.168618
I	4.515008	-0.526495	-0.044308

F -5.589763 -0.114661 -0.433154

F -4.310407 -1.864725 -0.223699

F -4.625408 -0.528027 1.471043

F -3.335730 0.387294 -1.656116

F -3.410831 1.495101 0.249302

F -1.965645 -0.788126 1.344320

F -1.652138 -1.368854 -0.757847

F -0.884766 1.433980 -1.141476

F -0.826067 1.513777 1.060871

F 0.732652 -0.879224 0.940308

F 0.839872 -0.531998 -1.250207

F 1.827740 1.569661 1.401754

F 1.819836 2.012925 -0.756911

$H_2O^{\bullet+}$

B3LYP-D3BJ/BSI SCF energy:

-76.041605

G_{corr} at B3LYP-D3BJ/BSI level:

-0.000001

B3LYP-D3BJ/BSII SCF energy:

-76.066228

O 0.000000 0.000000 0.117500

H 0.000000 0.825367 -0.469999

H 0.000000 -0.825367 -0.469999

$(H_2O)_4$

B3LYP-D3BJ/BSI SCF energy:

-305.756723

G_{corr} at B3LYP-D3BJ/BSI level:

0.067794

B3LYP-D3BJ/BSII SCF energy:

-305.896834

O -0.817480 1.710056 0.020308

H 0.150542 1.482839 0.028053

H -0.960010 2.146187 -0.830016

O -1.710064 -0.817464 -0.020299

H -2.146232 -0.959864 0.830037

H -1.482948 0.150595 -0.028149

O 0.817464 -1.710009 0.020296

H -0.150625 -1.483048 0.028168

H 0.959855 -2.146270 -0.829996

O 1.710115 0.817459 -0.020304

H 1.482922 -0.150588 -0.028184

H 2.146213 0.959807 0.830080

$(H_2O)_4^{\bullet+}$

B3LYP-D3BJ/BSI SCF energy:

-305.461374

G_{corr} at B3LYP-D3BJ/BSI level:

0.063322

B3LYP-D3BJ/BSII SCF energy:

-305.581067

O 1.683334 0.828809 -0.063030

H 0.214774 1.307937 0.030202

H 2.060537 0.704477 0.834001

O	0.906562	-1.384188	-0.019908
H	1.401283	-1.956465	0.589272
H	1.328937	-1.499420	-0.886554
O	-1.719332	-0.763335	-0.066947
H	-0.896390	-1.301163	-0.018614
H	-2.324680	-1.060386	0.630171
O	-0.796533	1.474432	0.079684
H	-1.305467	0.489066	0.021282
H	-1.071241	2.070216	-0.638163

I•

B3LYP-D3BJ/SDD SCF energy:

-11.393961

G_{corr} at B3LYP-D3BJ/SDD level:

-0.017503

I	0.000000	0.000000	0.000000

1_Alk•

B3LYP-D3BJ/BSI SCF energy:

-2067.325472

G_{corr} at B3LYP-D3BJ/BSI level:

0.229359

B3LYP-D3BJ/BSII SCF energy:

-2067.961839

C	5.117075	-0.436024	-0.719241
C	3.814275	0.400450	-0.656816
C	2.645776	-0.311615	0.076204
C	1.502986	0.657905	0.495039
C	0.165812	-0.073923	0.807828
C	-0.864730	0.757831	1.607755
F	5.968359	0.146154	-1.571612
F	5.690861	-0.501453	0.486129
F	4.853166	-1.677306	-1.149509
F	4.102095	1.561233	-0.023629
F	3.431129	0.665053	-1.923849
F	2.153146	-1.262108	-0.750378
F	3.129996	-0.905342	1.192236
F	1.922004	1.342399	1.581494
F	1.280525	1.527542	-0.517762
F	-0.375339	-0.439730	-0.378047
F	0.445729	-1.199175	1.524284
F	-0.952982	1.973799	0.995495
F	-0.329851	0.962403	2.850311
C	-4.312132	3.372876	-0.257539
C	-3.851166	2.274113	0.457648
C	-3.559125	1.047998	-0.186081
C	-3.727200	0.999994	-1.591912
C	-4.179064	2.104544	-2.304067
C	-4.481343	3.298029	-1.642734
H	-4.542154	4.294517	0.269122
H	-3.737005	2.362413	1.532050
H	-3.465830	0.091433	-2.122340
H	-4.283965	2.038427	-3.383111
H	-4.835400	4.160264	-2.199387
C	-3.065233	-0.110112	0.545124
C	-2.238316	0.111890	1.785917

H	-2.083308	-0.819057	2.332718
H	-2.752821	0.785915	2.481575
C	-3.387898	-1.464614	0.140494
C	-4.583823	-1.747558	-0.570578
C	-2.562557	-2.569858	0.472011
C	-4.920721	-3.044307	-0.935856
H	-5.263510	-0.936343	-0.803258
C	-2.903898	-3.864227	0.098387
H	-1.624983	-2.413772	0.990626
C	-4.082740	-4.114847	-0.609041
H	-5.850554	-3.224084	-1.467834
H	-2.239342	-4.684268	0.354636
H	-4.346510	-5.127921	-0.896501

^{os}IM1

B3LYP-D3BJ/BSI SCF energy:

-2078.758894

G_{corr} at B3LYP-D3BJ/BSI level:

0.225347

B3LYP-D3BJ/BSII SCF energy:

-2079.388930

spin contaminant:

before annihilation 0.0747, after 0.0004

C	-6.183809	-0.758791	0.545912
C	-4.986243	0.213723	0.397584
C	-3.669700	-0.478710	-0.045959
C	-2.603954	0.518261	-0.586046
C	-1.167616	-0.076129	-0.599919
C	-0.144558	0.693872	-1.469501
F	-7.183099	-0.128206	1.171975
F	-6.609981	-1.160865	-0.654949
F	-5.825122	-1.829129	1.268098
F	-5.327399	1.153727	-0.513570
F	-4.777915	0.804498	1.593324
F	-3.163686	-1.138896	1.021265
F	-3.950194	-1.369727	-1.024154
F	-2.960234	0.873332	-1.838647
F	-2.593816	1.617527	0.202760
F	-0.718275	-0.088882	0.681061
F	-1.223104	-1.356353	-1.053608
F	-0.243358	2.011643	-1.141678
F	-0.522570	0.555628	-2.769632
C	2.771352	4.026440	0.096129
C	2.541104	2.749804	-0.395585
C	2.184128	1.698977	0.481070
C	2.027548	1.990280	1.858012
C	2.232156	3.277198	2.336432
C	2.613664	4.295894	1.459421
H	3.078828	4.815380	-0.582104
H	2.694830	2.552485	-1.449829
H	1.691462	1.207438	2.528153
H	2.086347	3.489847	3.390435
H	2.781748	5.300201	1.835443
C	1.948298	0.352062	0.000588
C	1.290088	0.180353	-1.339186
H	1.303492	-0.855589	-1.672865
H	1.860397	0.747800	-2.083017

C	2.389317	-0.773649	0.728024
C	3.464782	-0.644388	1.668180
C	1.839606	-2.079172	0.519773
C	3.868301	-1.736263	2.437677
H	3.940670	0.314182	1.805146
C	2.260264	-3.144079	1.280747
H	1.028544	-2.220871	-0.182706
C	3.268560	-2.972922	2.254583
H	4.676014	-1.615077	3.150784
H	1.805811	-4.119411	1.142670
H	3.587133	-3.823411	2.849148
I	5.841371	-0.595449	-0.528094

^{os}TS1

B3LYP-D3BJ/BSI SCF energy:

-2078.758644

G_{corr} at B3LYP-D3BJ/BSI level:

0.227636

B3LYP-D3BJ/BSII SCF energy:

-2079.388026

spin contaminant:

before annihilation 0.0515, after 0.0001

C	-6.195854	-0.691536	0.494544
C	-4.985483	0.264820	0.343663
C	-3.670451	-0.450956	-0.065492
C	-2.585867	0.522534	-0.610118
C	-1.156400	-0.088865	-0.590771
C	-0.116247	0.644750	-1.471275
F	-7.196716	-0.037669	1.093539
F	-6.609416	-1.113502	-0.703805
F	-5.858921	-1.750732	1.243291
F	-5.301978	1.188538	-0.592568
F	-4.788198	0.878967	1.529459
F	-3.186448	-1.093435	1.022733
F	-3.946354	-1.359072	-1.028986
F	-2.918909	0.855781	-1.874828
F	-2.574027	1.637449	0.156284
F	-0.719171	-0.067153	0.694954
F	-1.220938	-1.381658	-1.004551
F	-0.213991	1.973209	-1.187763
F	-0.474912	0.465390	-2.770606
C	2.675125	4.016219	0.129774
C	2.467687	2.737621	-0.361978
C	2.166653	1.671305	0.520012
C	2.046336	1.950509	1.905084
C	2.227883	3.239950	2.383980
C	2.551364	4.272898	1.500096
H	2.941725	4.817025	-0.551519
H	2.603853	2.547032	-1.419202
H	1.753191	1.155432	2.580469
H	2.109555	3.444052	3.442952
H	2.702891	5.279687	1.876608
C	1.950999	0.326613	0.042884
C	1.313542	0.127638	-1.302886
H	1.329397	-0.917503	-1.607003
H	1.906004	0.667694	-2.049210
C	2.389900	-0.795030	0.792098

C	3.506221	-0.657295	1.674115
C	1.814307	-2.090627	0.631744
C	3.966419	-1.746521	2.406132
H	4.012265	0.293556	1.747516
C	2.277747	-3.156769	1.372049
H	0.963521	-2.234123	-0.021641
C	3.353522	-2.987210	2.264569
H	4.822851	-1.628200	3.060621
H	1.809191	-4.129679	1.269587
H	3.716431	-3.838007	2.832877
I	5.562880	-0.288545	-1.024088

1HI

B3LYP-D3BJ/BSI SCF energy:

-2078.773621

G_{corr} at B3LYP-D3BJ/BSI level:

0.230415

B3LYP-D3BJ/BSII SCF energy:

-2079.407724

C	5.929079	0.499030	0.165763
C	4.647393	-0.363242	0.288311
C	3.376506	0.319835	-0.284564
C	2.204574	-0.674109	-0.533494
C	0.825694	0.039053	-0.663557
C	-0.288851	-0.817839	-1.306113
F	6.899602	-0.056043	0.900220
F	6.332256	0.561399	-1.106796
F	5.699403	1.739899	0.616616
F	4.868966	-1.525466	-0.368066
F	4.444820	-0.620726	1.598001
F	2.983777	1.271648	0.592789
F	3.691441	0.908258	-1.461906
F	2.481936	-1.365305	-1.659267
F	2.136857	-1.533933	0.509348
F	0.455236	0.401717	0.587727
F	0.986701	1.158884	-1.418143
F	-0.255640	-2.031416	-0.687194
F	0.084156	-1.013670	-2.608333
C	-2.900606	-3.506877	1.302944
C	-3.043477	-2.383157	0.498119
C	-2.476555	-1.152190	0.866578
C	-1.743191	-1.090692	2.062874
C	-1.595648	-2.221235	2.867135
C	-2.175304	-3.431391	2.495143
H	-3.360532	-4.442818	1.001261
H	-3.622280	-2.453317	-0.415998
H	-1.263563	-0.167064	2.357035
H	-1.021492	-2.148343	3.785684
H	-2.065811	-4.308741	3.125192
C	-2.488765	0.032801	-0.067773
C	-1.719289	-0.258952	-1.368846
H	-1.704409	0.610527	-2.025180
H	-2.238751	-1.049442	-1.912336
C	-2.329832	1.385428	0.558313
C	-2.980416	1.662523	1.775843
C	-1.600567	2.416918	-0.050335
C	-2.878285	2.911659	2.374910

H	-3.589699	0.895500	2.240123
C	-1.496122	3.670147	0.551724
H	-1.090331	2.257173	-0.990089
C	-2.130641	3.923874	1.766155
H	-3.391849	3.099941	3.312628
H	-0.915749	4.447671	0.064908
H	-2.051456	4.901439	2.231658
I	-4.750639	0.217561	-0.981597

TS2

B3LYP-D3BJ/BSI SCF energy:

-2078.761646

G_{corr} at B3LYP-D3BJ/BSI level:

0.228324

B3LYP-D3BJ/BSII SCF energy:

-2079.390104

C	6.199503	0.303771	-0.067133
C	4.881202	-0.414321	0.316392
C	3.620395	0.180436	-0.365654
C	2.384317	-0.762916	-0.297735
C	1.041139	-0.025967	-0.560285
C	-0.161184	-0.946867	-0.889070
F	7.176769	-0.119605	0.741659
F	6.532952	0.027949	-1.331014
F	6.061694	1.629475	0.073945
F	5.002988	-1.716214	-0.029326
F	4.730921	-0.317748	1.654610
F	3.323756	1.349901	0.248179
F	3.898135	0.422808	-1.666643
F	2.550101	-1.738156	-1.215539
F	2.324935	-1.315527	0.935943
F	0.740728	0.687768	0.556841
F	1.207404	0.840727	-1.594032
F	-0.155107	-1.948813	0.033634
F	0.067173	-1.500244	-2.108865
C	-2.781739	-2.405410	2.583610
C	-2.554798	-1.693049	1.418193
C	-2.222198	-0.312995	1.477344
C	-2.086699	0.301866	2.752838
C	-2.286594	-0.430198	3.911083
C	-2.646188	-1.780525	3.828339
H	-3.074055	-3.448172	2.526161
H	-2.707499	-2.171988	0.461504
H	-1.763543	1.333864	2.812223
H	-2.154390	0.041036	4.879125
H	-2.814168	-2.349530	4.737605
C	-1.999860	0.453796	0.287196
C	-1.502528	-0.216778	-0.954140
H	-1.456833	0.481488	-1.788776
H	-2.265475	-0.961098	-1.244947
C	-2.271860	1.868230	0.263504
C	-3.341243	2.391690	1.036866
C	-1.521288	2.758345	-0.546480
C	-3.635289	3.746034	1.006986
H	-3.978554	1.709899	1.586207
C	-1.805567	4.114378	-0.544716
H	-0.683072	2.397428	-1.128468

C	-2.864796	4.610946	0.224281
H	-4.477592	4.126889	1.574315
H	-1.206378	4.789775	-1.145930
H	-3.096973	5.671133	0.201305
I	-5.059469	-0.920461	-1.310441

IM2

B3LYP-D3BJ/BSI SCF energy:

-2078.765178

G_{corr} at B3LYP-D3BJ/BSI level:

0.225184

B3LYP-D3BJ/BSII SCF energy:

-2079.393515

C	6.045718	-0.073316	-0.175851
C	4.694210	-0.374965	0.519138
C	3.453234	-0.050973	-0.354607
C	2.143340	-0.705933	0.171066
C	0.860210	-0.048595	-0.410607
C	-0.435819	-0.889762	-0.261229
F	7.027546	-0.155096	0.728676
F	6.279727	-0.956375	-1.150502
F	6.034183	1.162920	-0.693941
F	4.681237	-1.687125	0.846033
F	4.632622	0.368270	1.644700
F	3.299598	1.293972	-0.381897
F	3.674880	-0.495450	-1.612408
F	2.170849	-2.014504	-0.154643
F	2.103339	-0.581518	1.518019
F	0.681487	1.136558	0.229230
F	1.051814	0.203873	-1.732793
F	-0.488522	-1.302828	1.033989
F	-0.305298	-1.983906	-1.051265
C	-3.102701	-0.199736	3.415100
C	-2.809186	-0.175307	2.059376
C	-2.344479	1.020035	1.453490
C	-2.147800	2.168469	2.266977
C	-2.406544	2.117442	3.626464
C	-2.894585	0.936991	4.201242
H	-3.490785	-1.109307	3.860832
H	-3.000424	-1.054958	1.457256
H	-1.741306	3.070262	1.824783
H	-2.223733	2.989839	4.245011
H	-3.105209	0.903324	5.265816
C	-2.074264	1.079158	0.041774
C	-1.682445	-0.126616	-0.702467
H	-1.576617	0.072379	-1.768199
H	-2.537180	-0.879522	-0.644710
C	-2.296321	2.303034	-0.695466
C	-3.329782	3.193577	-0.310320
C	-1.513490	2.622550	-1.832857
C	-3.564639	4.354841	-1.033587
H	-3.974928	2.931877	0.519363
C	-1.738716	3.798728	-2.531072
H	-0.695183	1.977034	-2.127031
C	-2.766660	4.663775	-2.138361
H	-4.376964	5.013904	-0.746162
H	-1.114812	4.046901	-3.383185

H -2.949427 5.574969 -2.699406

I -4.327175 -2.492759 -0.804951

TS3

B3LYP-D3BJ/BSI SCF energy:

-2078.753880

G_{corr} at B3LYP-D3BJ/BSI level:

0.218243

B3LYP-D3BJ/BSII SCF energy:

-2079.390383

C 6.086653 0.209723 -0.391964

C 4.775355 -0.110468 0.368673

C 3.491332 0.109296 -0.474871

C 2.232907 -0.576903 0.131177

C 0.899616 -0.011051 -0.431390

C -0.356382 -0.895778 -0.176338

F 7.102296 0.226867 0.478717

F 6.329520 -0.719533 -1.320892

F 6.000396 1.410257 -0.981428

F 4.835597 -1.401886 0.767211

F 4.720568 0.691169 1.453581

F 3.277262 1.442036 -0.569156

F 3.693870 -0.393178 -1.714887

F 2.317244 -1.898937 -0.130087

F 2.238636 -0.387925 1.471568

F 0.702640 1.202345 0.138919

F 1.023061 0.156937 -1.774583

F -0.342097 -1.232348 1.142967

F -0.190408 -2.040651 -0.899240

C -2.344287 0.541088 3.700945

C -2.359720 0.212508 2.347867

C -2.152318 1.206790 1.376228

C -1.936685 2.535269 1.791629

C -1.892996 2.850985 3.145013

C -2.101542 1.855112 4.103177

H -2.522667 -0.232904 4.440594

H -2.562368 -0.806010 2.043999

H -1.779253 3.307541 1.046600

H -1.702208 3.874081 3.453509

H -2.080350 2.104806 5.159614

C -2.199222 0.903183 -0.063856

C -1.612469 -0.210394 -0.644143

H -1.705927 -0.300257 -1.723293

H -2.713539 -1.314210 -0.377053

C -3.003455 1.787333 -0.920196

C -4.192851 2.363208 -0.432515

C -2.602899 2.066321 -2.241800

C -4.971326 3.171340 -1.254713

H -4.511983 2.149190 0.581045

C -3.375360 2.890365 -3.052937

H -1.661369 1.672400 -2.609933

C -4.564512 3.437781 -2.564250

H -5.896764 3.592648 -0.875259

H -3.047520 3.112949 -4.063363

H -5.169448 4.075999 -3.201021

I -3.904583 -2.655601 -0.232718

3

B3LYP-D3BJ/BSI SCF energy:

-2066.732735

G_{corr} at B3LYP-D3BJ/BSI level:

0.218849

B3LYP-D3BJ/BSII SCF energy:

-2067.370944

C	5.543240	-0.250189	-0.506277
C	4.193242	0.429309	-0.165191
C	2.978416	-0.536206	-0.199904
C	1.722107	0.030217	0.520649
C	0.407816	-0.696904	0.129170
C	-0.783192	-0.465855	1.105281
F	6.472107	0.694760	-0.692694
F	5.933237	-1.047342	0.492923
F	5.429263	-0.973470	-1.628574
F	4.305179	0.969059	1.070526
F	3.986883	1.413963	-1.065929
F	2.680404	-0.782293	-1.496483
F	3.327966	-1.697296	0.401074
F	1.923773	-0.080787	1.852157
F	1.593308	1.339514	0.197419
F	0.063625	-0.268780	-1.113318
F	0.642557	-2.032517	0.065685
F	-0.774573	0.846926	1.465644
F	-0.487337	-1.195029	2.231269
C	-4.349011	3.342823	0.597960
C	-4.260801	1.955796	0.692768
C	-3.210576	1.262898	0.070203
C	-2.271651	1.986326	-0.678574
C	-2.370405	3.372382	-0.785085
C	-3.404737	4.055466	-0.143729
H	-5.158335	3.866215	1.098158
H	-5.003032	1.401894	1.258612
H	-1.466763	1.461264	-1.177552
H	-1.637645	3.918379	-1.371730
H	-3.478051	5.135811	-0.225611
C	-3.157509	-0.222678	0.169778
C	-2.085492	-0.943854	0.556737
H	-2.127867	-2.027040	0.508912
C	-4.403957	-0.947494	-0.202441
C	-4.799804	-2.110198	0.478845
C	-5.207132	-0.477806	-1.255120
C	-5.953895	-2.795217	0.104684
H	-4.213349	-2.459205	1.322700
C	-6.356288	-1.168480	-1.633166
H	-4.918686	0.424001	-1.784157
C	-6.733750	-2.329400	-0.955481
H	-6.250468	-3.686570	0.649403
H	-6.958486	-0.798636	-2.457602
H	-7.634570	-2.862088	-1.245072

HI

B3LYP-D3BJ/BSI SCF energy:

-12.014282

G_{corr} at B3LYP-D3BJ/BSI level:

-0.015058

B3LYP-D3BJ/BSII SCF energy:

-12.019327

I 0.000000 0.000000 0.030017

H 0.000000 0.000000 -1.590904

12_Alk•

B3LYP-D3BJ/BSI SCF energy:

-1914.861082

G_{corr} at B3LYP-D3BJ/BSI level:

0.206529

B3LYP-D3BJ/BSII SCF energy:

-1915.461481

C 3.689824 -2.006913 0.321147

C 3.203482 -0.665846 -0.283817

C 1.751670 -0.287431 0.112062

C 1.412357 1.208920 -0.156317

C -0.116333 1.478613 -0.207802

C -0.529005 2.962708 -0.037257

F 4.842628 -2.354886 -0.261676

F 3.891224 -1.882905 1.636330

F 2.784647 -2.970525 0.102431

F 4.047647 0.305170 0.135411

F 3.271436 -0.769130 -1.628112

F 0.907899 -1.076140 -0.596328

F 1.581623 -0.534651 1.430715

F 1.968241 1.944671 0.831047

F 1.953950 1.571567 -1.342020

F -0.567131 1.026945 -1.406678

F -0.702631 0.747361 0.778258

F 0.359328 3.708625 -0.766516

F -0.351230 3.280201 1.276284

C -2.979396 -1.902038 -0.015624

C -3.191700 -3.174571 -0.543358

C -4.485881 -3.695032 -0.623242

C -5.563689 -2.932612 -0.172243

C -5.347498 -1.658193 0.356149

C -4.055724 -1.127377 0.443333

H -1.970955 -1.500373 0.040266

H -2.346518 -3.762713 -0.889835

H -4.651208 -4.687545 -1.032076

H -6.573350 -3.329695 -0.228641

H -6.190216 -1.068873 0.709225

C -3.808825 0.265458 0.971525

C -3.610978 1.289707 -0.173649

H -2.912206 0.264074 1.597236

H -4.641556 0.586708 1.606751

C -3.025585 2.583582 0.283783

H -2.971270 0.845689 -0.943206

H -4.587737 1.449098 -0.661544

C -1.955582 3.292704 -0.480820

H -3.324090 2.992084 1.245269

H -2.014241 3.074841 -1.551788

H -2.028157 4.379919 -0.357202

12HI

B3LYP-D3BJ/BSI SCF energy:

-1914.286994

G_{corr} at B3LYP-D3BJ/BSI level:

0.195413

B3LYP-D3BJ/BSII SCF energy:

-1914.892681

C	-5.298710	1.328512	0.328176
C	-4.375153	0.231164	-0.258440
C	-2.871643	0.437002	0.067322
C	-2.010444	-0.836973	-0.164798
C	-0.489183	-0.539757	-0.265470
C	0.439628	-1.768829	-0.080500
F	-6.517640	1.206025	-0.209925
F	-5.397690	1.198834	1.654716
F	-4.817682	2.545422	0.039232
F	-4.784844	-0.959121	0.238205
F	-4.530655	0.233453	-1.599538
F	-2.410156	1.439529	-0.715436
F	-2.755778	0.800995	1.365847
F	-2.241552	-1.685083	0.862233
F	-2.409026	-1.420754	-1.319771
F	-0.257710	-0.007023	-1.492178
F	-0.161196	0.379987	0.677410
F	-0.083927	-2.780160	-0.845213
F	0.347747	-2.142908	1.228083
C	6.448118	1.412241	-0.890013
C	7.784105	1.659189	-1.207972
C	8.798201	1.238678	-0.345837
C	8.466798	0.571487	0.834971
C	7.129696	0.327103	1.148798
C	6.103051	0.744543	0.291836
H	5.661466	1.744593	-1.562966
H	8.032707	2.183073	-2.126533
H	9.838439	1.432681	-0.590051
H	9.249412	0.244882	1.513824
H	6.876663	-0.189515	2.071552
C	4.659646	0.433407	0.609072
C	4.237648	-0.955491	0.072437
H	4.004706	1.194289	0.171150
H	4.499543	0.460467	1.693191
C	2.816705	-1.275801	0.414854
H	4.389249	-0.991951	-1.011476
H	4.897931	-1.712611	0.515530
C	1.850686	-1.488051	-0.479682
H	2.568380	-1.318712	1.474013
H	2.027601	-1.440502	-1.549751

TS

B3LYP-D3BJ/BSI SCF energy:

-1926.281229

G_{corr} at B3LYP-D3BJ/BSI level:

0.197108

B3LYP-D3BJ/BSII SCF energy:

-1926.880711

C	-6.582284	0.949475	-0.004547
C	-5.289117	1.514454	-0.644673
C	-3.989632	0.838978	-0.130109

C	-2.758383	1.104382	-1.041785
C	-1.403781	0.818542	-0.334146
C	-0.202511	0.651356	-1.296305
F	-7.607678	1.751148	-0.313917
F	-6.837175	-0.277146	-0.468586
F	-6.455466	0.900488	1.328088
F	-5.381763	1.345100	-1.984275
F	-5.228270	2.833537	-0.364412
F	-3.731572	1.315776	1.109014
F	-4.188596	-0.496230	-0.061213
F	-2.864153	0.318882	-2.136194
F	-2.770012	2.402801	-1.423988
F	-1.137027	1.860166	0.494568
F	-1.511159	-0.310679	0.400146
F	-0.265314	1.650432	-2.226795
F	-0.337213	-0.532894	-1.947542
C	6.135278	2.615010	-0.135207
C	7.521846	2.740925	-0.041263
C	8.278348	1.722819	0.541722
C	7.641766	0.580793	1.031411
C	6.255448	0.457407	0.937342
C	5.488618	1.474063	0.353538
H	5.549022	3.412643	-0.585271
H	8.010120	3.634645	-0.418658
H	9.357058	1.821014	0.618182
H	8.223270	-0.212435	1.491730
H	5.759940	-0.429123	1.324956
C	3.993561	1.307328	0.213462
C	3.646380	0.556565	-1.081815
H	3.501546	2.285352	0.221754
H	3.602006	0.730387	1.057002
C	2.251759	0.196763	-1.318658
H	3.903681	1.176272	-1.968626
H	4.269879	-0.336102	-1.216342
C	1.137147	0.704763	-0.580367
H	2.047913	-0.526127	-2.107180
H	1.303584	1.645345	-0.056385
H	1.128256	-0.112501	0.253793
I	1.918154	-2.118248	1.206551

12

B3LYP-D3BJ/BSI SCF energy:

-1926.341405

G_{corr} at B3LYP-D3BJ/BSI level:

0.205074

B3LYP-D3BJ/BSII SCF energy:

-1926.943615

C	-6.376134	0.605213	0.504705
C	-5.120581	0.601936	-0.403022
C	-3.786394	0.434367	0.372518
C	-2.593984	0.023104	-0.537783
C	-1.208164	0.284309	0.116622
C	-0.026070	-0.478037	-0.533319
F	-7.433573	0.995101	-0.216171
F	-6.609399	-0.619144	0.986376
F	-6.209100	1.456589	1.525921
F	-5.256153	-0.411934	-1.288666

F	-5.087183	1.775857	-1.068971
F	-3.504010	1.611905	0.976249
F	-3.948279	-0.519595	1.318045
F	-2.723319	-1.290179	-0.824865
F	-2.658705	0.736459	-1.686834
F	-0.965807	1.618137	0.038558
F	-1.262084	-0.068860	1.426369
F	-0.138353	-0.329222	-1.891237
F	-0.196202	-1.797368	-0.253726
C	5.468151	2.963967	0.196361
C	6.630834	3.708516	-0.007169
C	7.872681	3.072208	-0.037407
C	7.943442	1.688726	0.138084
C	6.778807	0.948653	0.341413
C	5.526741	1.576442	0.373789
H	4.503455	3.464999	0.222649
H	6.566962	4.784890	-0.138673
H	8.778937	3.649978	-0.193000
H	8.906255	1.186210	0.120660
H	6.838075	-0.127980	0.481304
C	4.266764	0.760969	0.546000
C	3.762154	0.219551	-0.801375
H	3.491104	1.376463	1.014119
H	4.458177	-0.080683	1.219662
C	2.511107	-0.648314	-0.748616
H	3.516723	1.068084	-1.456568
H	4.563949	-0.332633	-1.299472
C	1.326249	0.031019	-0.066585
H	2.244217	-0.977365	-1.751399
H	1.361171	1.094448	-0.325774
H	1.375854	-0.036115	1.021795
I	3.008887	-2.608411	0.245094

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