Halogen-Bond-Promoted Photoactivation of Perfluoroalkyl Iodides: A Photochemical Protocol for Perfluoroalkylation Reactions

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Supporting Information

Content

1. Reagents

All commercial materials were used as received unless otherwise noted. Perfluoroalkyl iodides (CF_3I, C_3F_7I, C_4F_9I, $C_6F_{13}I$, $C_8F_{17}I$, $C_{10}F_{21}I$) and $BrCF_2COOCH_3$ were purchased from J&K Chemical, Energy Chemical or TCI. *N,N,N',N'*-tetraethylenediamine (TEEDA) was purchased from Energy Chemical. Dry solvents (THF (99.5%), 2-MeTHF (99.0%), THP (99.0%), dioxane (99.5%), Et_2O (99.0%), CH_2Cl_2 (99.0%), $ClCH_2CH_2Cl$ (98.9%), $CHCl_3$ (99.0%), MeCN (99.9%)) and deuterated solvents ($CDCl_3$, CD_3OD) were purchased from J&K Chemical. TLC were performed on silica gel Huanghai HSGF254 plates and visualization of the developed chromatogram was performed by fluorescence quenching (λ_{max} = 254 nm). Flash chromatography was performed using Silica gel (200-300 mesh) purchased from Qingdao Haiyang Chemical Co., China.

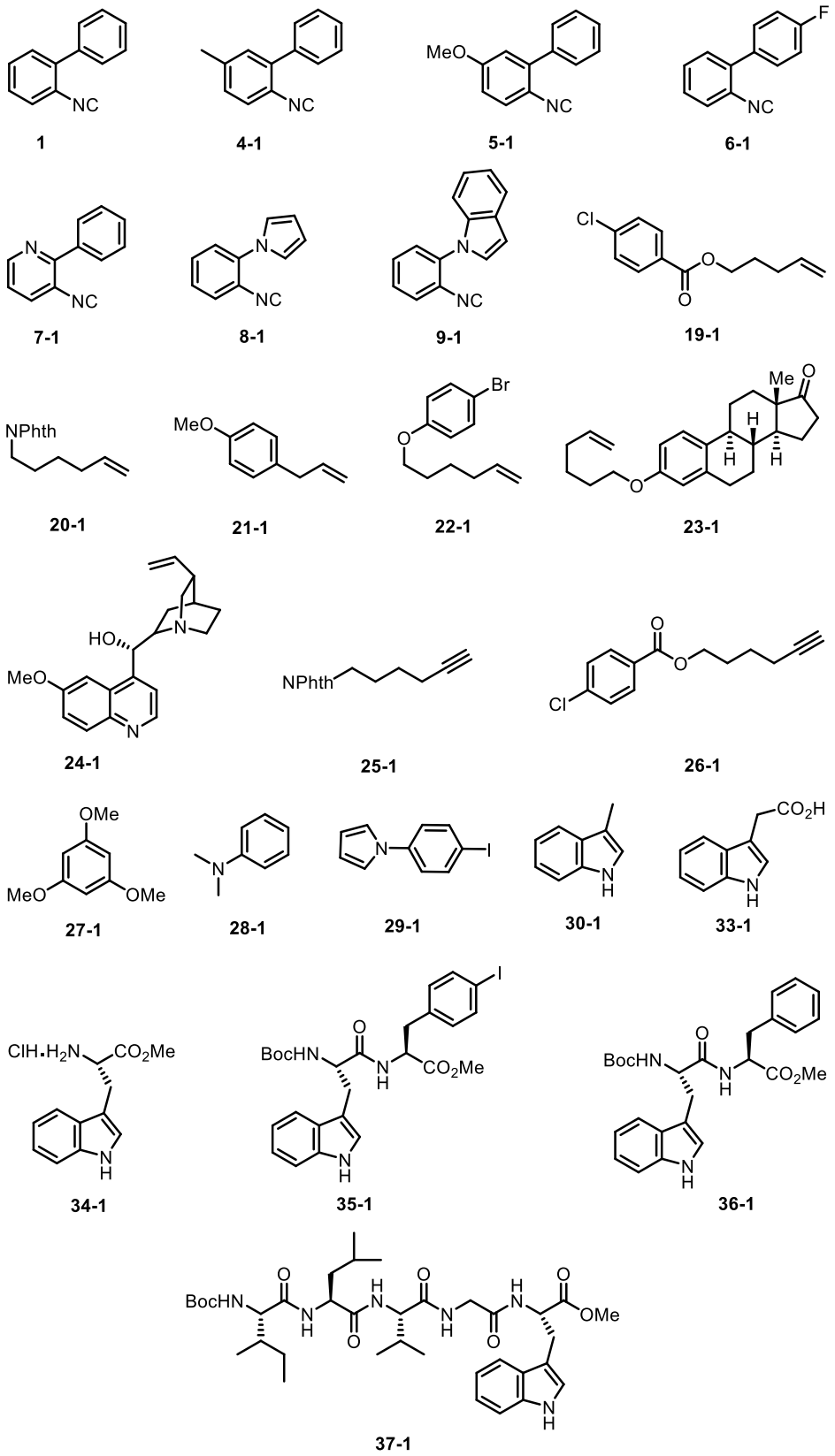
2. Instruments

NMR spectra were recorded on Bruker AVANCE AV 400 instruments and all NMR experiments were reported in units, parts per million (ppm), using residual solvent peaks ($CDCl_3$ (δ = 7.26 ppm) or CD_3OD (δ = 3.31 ppm) for ^{1}H NMR, chloroform (δ = 77.16 ppm) CD_3OD (δ = 49.00 ppm) for ^{13}C NMR) as internal reference. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet. HRMS were obtained on Varian 7.0T FTMS instrument. UV-vis data were recorded on a HITACHI U-3900 spectrophotometer.

All reactions were carried out in a 4 mL glass vial (Thermo SCIENTIFIC National B7999-2, made from superior quality 33 expansion borosilicate clear glass), sealed with PTEF cap on bench top.

Lights: PHILIPS TORNADO 25W CFL, Cnlight 220V/25W UV (254nm), Cnlight 220V/25W UV (365nm), Cnlight LED lights 25 W (red LED, yellow LED, green LED, blue LED, purple LED, white LED) were used in the perfluoroalkylation reactions

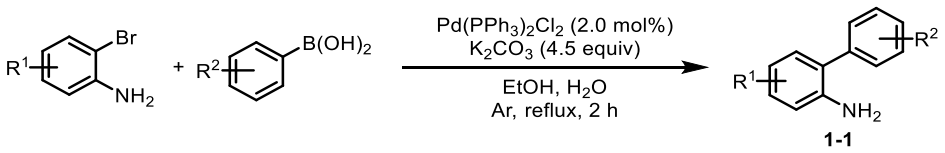
3. Synthesis of substrates



Scheme S1. List of all substrates used in this study

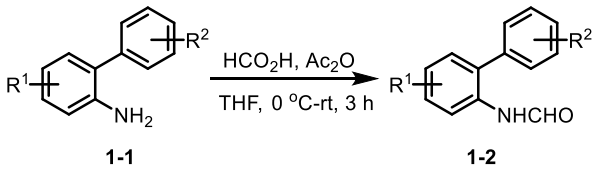
Compounds **21-1**, **24-1**, **27-1**, **28-1**, **29-1**, **30-1**, **33-1**, and **34-1** were commercial available and used as received. Compounds **1**[1], **4-1**[1], **5-1**[1], **6-1**[1], **7-1**[2], **8-1**[3], **9-1**[3], **19-1**[4], **20-1**[6], **25-1**[7], **26-1**[5] and **36-1**[8] were known compounds and were synthesized following the reported procedures. Compounds **22-1**, **23-1**, **35-1**, **37-1** were new compounds.

3.1 General procedure for synthesis of 2-Isocyanobiaryl substrates[1]



Scheme S2

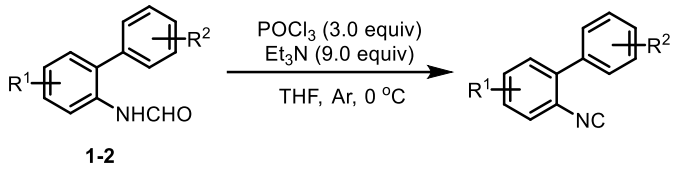
2-Bromoarylamine (10.0 mmol, 1.0 equiv), aryl boronic acid (12.0 mmol, 1.2 equiv), K_2CO_3 (6.2 g, 45.0 mmol, 4.5 equiv) and Pd $(PPh_3)_2Cl_2$ (140.4 mg, 0.2 mmol, 0.02 equiv) were added to a mixture of EtOH (20 mL) and water (20 mL) at room temperature. The mixture was heated to reflux for 2 h under Ar. After been cooled to room temperature, the mixture was extracted with EtOAc. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by chromatography on silica gel (eluted with hexane/acetone (v/v 40:1)) to afford compound **1-1**.



Scheme S3

Acetic formic anhydride (18.0 mmol, 6.0 equiv), which was newly prepared from the reaction of acetic anhydride (1.7 mL, 18.0 mmol) with formic acid (0.8 mL, 20.0 mmol) at 55 °C for 2 h, was added dropwise to a mixture of **1-1** (3.0 mmol, 1.0 equiv) in THF

(6.0 mL) at 0 °C. After the addition was completed, the mixture was warmed to room temperature and stirred for 3 h. Then, the reaction was quenched with Sat. $NaHCO_3$ and extracted with EtOAc. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to give compound **1-2**. These compound were used for the subsequent dehydration reaction without further purification.

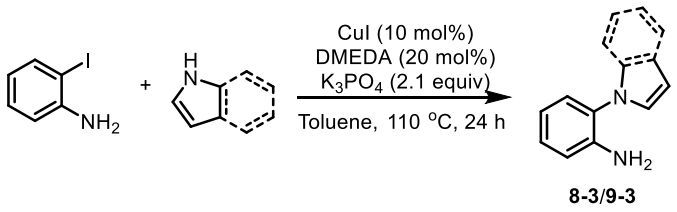


Scheme S4

$POCl_3$ (0.8 mL, 9.0 mmol, 3.0 equiv) was added via syring pump to a mixture of Et_3N (3.8 mL, 27.0 mmol, 9.0 equiv) and **1-2** (3.0 mmol, 1.0 equiv) in THF (6 mL) at 0 °C within 2 hours. After the addition was completed, the resulting mixture was stirred at 0 °C for another 2 hours. Then, the mixture was quenched with Sat. $NaHCO_3$ and extracted with $CHCl_3$. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by chromatography on silica gel (eluted with hexane/acetone (v/v 100:1)) to afford desired product.

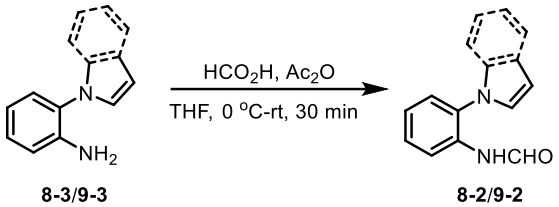
Compound **1** (0.46 g, 85% yield, 3 steps) [1], **4-1** (0.50 g, 86% yield, 3 steps) [1], **5-1** (0.47 g, 75% yield, 3 steps) [1], **6-1** (0.50 g, 85% yield, 3 steps) [1], and **7-1** (0.48 g, 88% yield, 3 steps) [2] were synthesized following the above procedure and spectra data are consistent with those reported in literature.

3.2 Synthesis of compound **8-1** and **9-1**[3]



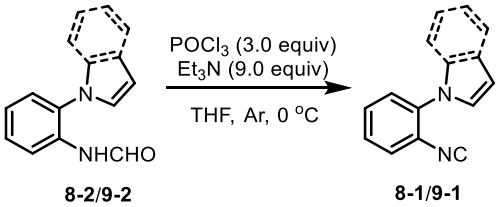
Scheme S5

Indole (702 mg, 6.0 mmol, 1.2 equiv) or pyrrole (403 mg, 6.0 mmol, 1.2 equiv) was added to a mixture of CuI (95 mg, 0.5 mmol, 0.1 equiv), K_3PO_4 (2.3 g, 10.5 mmol, 2.1 equiv), 2-iodoaniline (1.1 g, 5.0 mmol, 1.0 equiv) and *N*,*N*-dimethylethane-1,2-diamine (DMEDA) (88.1 mg, 1.0 mmol, 0.2 equiv) in toluene (5 mL) at room temperature. The reaction tube was purged with Argon and sealed with PTFE cap. After been heated at 110 °C for 24 h, the mixture was cooled to room temperature, diluted with ethyl acetate (50 mL) and filtered through a plug of celite. The filtrate was concentrated *in vacuo* and the resulting residue was purified by silica gel column chromatography to give the 2-heteroaryl aniline, which was subsequently subjected to the next step.



Scheme S6

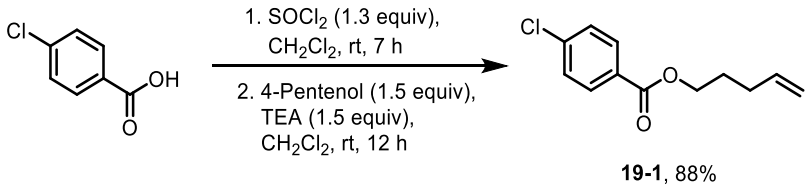
Acetic formic anhydride (18.0 mmol, 6.0 equiv), which was newly prepared from the reaction of acetic anhydride (1.7 mL, 18.0 mmol) with formic acid (0.8 mL, 20.0 mmol) at 55 °C for 2 h, was added dropwise to a mixture of **8-2** (475 mg, 3.0 mmol, 1.0 equiv) or **9-2** (625 mg, 3.0 mmol, 1.0 equiv) in THF (7 mL) at 0 °C. After the addition was completed, the mixture was warmed to room temperature and stirred for 30 mins. Then, the volatiles were removed *in vacuo* to afford (2-heteroaryl)-formanilide quantitatively. This product was directly used for the subsequent dehydration reaction without further purification.



Scheme S7

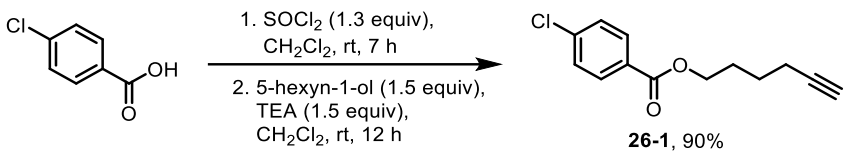
$POCl_3$ (0.8 mL, 9.0 mmol, 3.0 equiv) was added via syring pump to a mixture of Et_3N (3.8 mL, 27.0 mmol, 9.0 equiv) and (2-heteroaryl)-formanilide (3.0 mmol, 1.0 equiv) in THF (6 mL) at 0 °C within 2 hour. After the addition was completed, the resulting mixture was stirred at 0 °C for another 2 hour. Then, the mixture was quenched with Sat. $NaHCO_3$ and extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by chromatography on silica gel (eluted with hexane/acetone (v/v 100:1)) to give compound **8-1** (0.40 g, 78% yield, 3 steps)[3] and **9-1** (0.52 g, 80% yield, 3 steps)[3]. The spectra data are consistent with those reported in literature.

3.3 Synthesis of compound **19-1** and **26-1**



Scheme S8

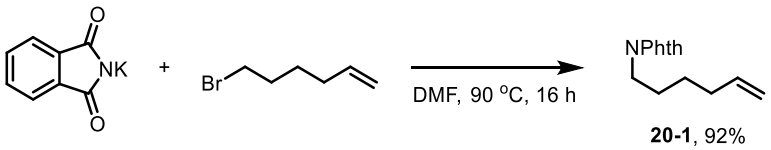
$SOCl_2$ (2.3 mL, 32.0 mmol, 1.3 equiv) was added dropwise to a solution of 4-chlorobenzoic acid (3.9 g, 25.0 mmol, 1.0 equiv) in dry CH_2Cl_2 (50 mL) at room temperature. The mixture was stirred for 7 h under N_2. DCM and excess of $SOCl_2$ were then removed under reduced pressure. The crude acyl chloride was dissolved in CH_2Cl_2 (50 mL), and 4-pentenol (3.2 g, 37.5 mmol, 1.5 equiv), TEA (4.9 mL, 37.5 mmol, 1.5 equiv) were added to this solution at 0 ^oC. The mixture was stirred at room temperature for 12 hour and then quenched with H_2O. The organic layer was seperated, washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (eluted with hexane) to afford compound **19-1** in 88% yield (4.93 g). The spectra data are consistent with those reported in literature.[4]



Scheme S9

To a solution of 4-chlorobenzoic acid (3.9 g, 25.0 mmol, 1.0 equiv) in dry CH_2Cl_2 (50 mL) was added $SOCl_2$ (2.3 mL, 32.0 mmol, 1.3 equiv). The mixture was stirred at room temperature for 7 h under N_2. DCM and excess of $SOCl_2$ were then removed under reduced pressure. The crude acyl chloride was dissolved in CH_2Cl_2 (50 mL), and 5-hexyn-1-ol (3.7 g, 37.5 mmol, 1.5 equiv), TEA (4.9 mL, 37.5 mmol, 1.5 equiv) were added to this solution at 0 ^{o}C. The mixture was stirred at room temperature for 12 hour and then quenched with H_2O. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (eluted with hexane) to afford compound **26-1** in 90% yield (5.31 g). The spectra data are consistent with those reported in literature.[5]

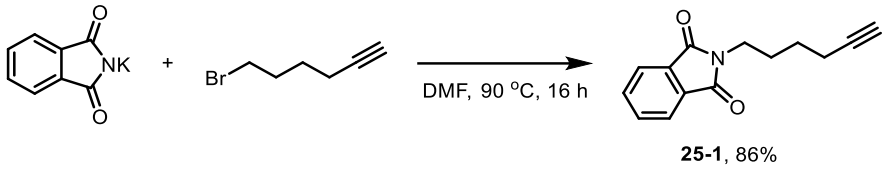
3.4 Synthesis of compound **20-1** and **25-1**



Scheme S10

Potassium phthalimide (3.9 g, 21.0 mmol, 1.1 equiv) was added to a solution of 6-bromohexene (3.2 g, 19.6 mmol, 1.0 equiv) in anhydrous DMF (23 mL) at room temperature. The mixture was heated to 90 °C for 16 h. After been cooled to room temperature, the reaction mixture was poured into water (75 mL) and extracted with CH_2Cl_2 (3 x 50 mL). The combined organic phase was washed with 100 mL of aq. KOH (0.2 M) and water. The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The resulting residue was purified by silica gel column

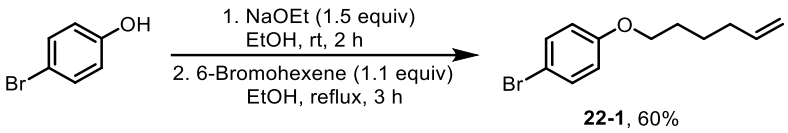
chromatography (eluted with hexane/acetone (v/v 5:1)) to afford the compound **20-1** in 92% yield (4.13 g). The spectra data are consistent with those reported in literature.[6]



Scheme S11

Potassium phthalimide (3.9 g, 21.0 mmol, 1.1 equiv) was added to a solution of 6-bromo-1-hexyne (3.1 g, 19.6 mmol, 1.0 equiv) in anhydrous DMF (23 mL) at room temperature. The mixture was heated to 90 °C for 16 h. After been cooled to room temperature, the reaction mixture was poured into water (75 mL) and extracted with CH_2Cl_2 (3 x 50 mL). The combined organic phase was washed with 100 mL of aq. KOH (0.2 M) and water. The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (eluted with hexane/acetone (v/v 5:1)) to afford compound **25-1** in 86% yield (3.83 g). The spectra data are consistent with those reported in literature.[7]

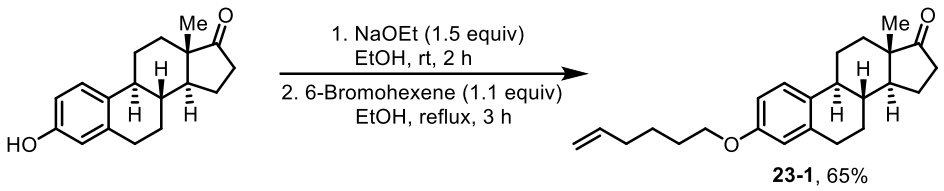
3.5 Synthesis of compound **22-1** and **23-1**



Scheme S12

A mixture of *p*-BrC_6H_4OH (0.5 g, 3.0 mmol, 1.0 equiv) and NaOEt (0.3 g, 4.5 mmol, 1.5 equiv) in EtOH (4 mL) was stirred at room temperature for 2 hour. Then 6-bromohexene (0.5 g, 3.3 mmol, 1.1 equiv) was added slowly. The resulting mixture was heated at reflux for 3 h. After been cooled to room temperature, the solvent was

removed under reduced pressure. The residue was dissolved in ethyl acetate and washed with water and brine. The organic phase was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (eluted with hexane) to afford compound **22-1** as a colorless oil in 60% yield (0.46 g, R_f = 0.7, hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 9.0 Hz, 2H), 6.77 (d, *J* = 9.0 Hz, 2H), 5.83 (m, 1H), 5.04 (dd, *J* = 17.1, 1.7 Hz, 1H), 4.99 (d, *J* = 8.0 Hz, 1H), 3.92 (t, *J* = 6.5 Hz, 2H), 2.13 (q, *J* = 7.2 Hz, 2H), 1.85-1.74 (m, 2H), 1.61-1.52 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.28, 138.52, 132.28, 116.35, 114.93, 112.68, 68.07, 33.51, 28.70, 25.36; **HRMS** Calcd for $C_{12}H_{15}BrO$ [M]: 254.0306, Found: 254.0302.

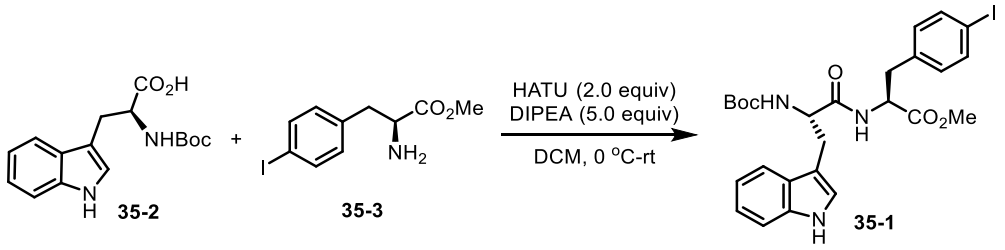


Scheme S13

A mixture of compound **23-2** (0.8 g, 3.0 mmol, 1.0 equiv) and NaOEt (0.3 g, 4.5 mmol, 1.5 equiv) in EtOH (4 mL) was stirred at room temperature for 2 hour. Then 6-bromohexene (0.5 g, 3.3 mmol, 1.1 equiv) was added to this solution. The resulting mixture was heated at reflux for 3 h. After been cooled to room temperature, the solvent was removed under reduced pressure. The residue was dissolved in ethyl acetate and washed with water and brine. The organic phase was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (eluted with hexane) to afford compound **23-1** as a white solid in 65% yield (0.69 g, R_f = 0.3, hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.6 Hz, 1H), 6.72 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.65 (d, *J* = 2.5 Hz, 1H), 5.89-5.79 (m, 1H), 5.04 (dd, *J* = 17.1, 1.7 Hz, 1H), 4.98 (dd, *J* = 10.2, 0.7 Hz, 1H), 3.94 (t, *J* = 6.4 Hz, 2H), 3.00-2.80 (m, 2H), 2.51 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.44-2.36 (m, 1H), 2.25 (dd, *J* = 13.6, 7.1 Hz, 1H), 2.18-1.93 (m, 6H), 1.86-1.73 (m, 2H), 1.69-1.53 (m, 5H), 1.52-1.38 (m, 3H), 0.92 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 220.95, 157.17, 138.63, 137.73, 131.91, 126.34,

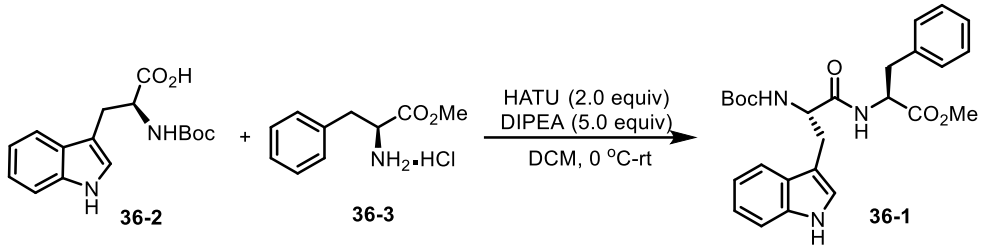
114.77, 114.58, 112.15, 67.70, 50.46, 48.06, 44.04, 38.45, 35.93, 33.51, 31.65, 29.72, 28.84, 26.64, 25.99, 25.41, 21.65, 13.92; **HRMS** Calcd for $C_{24}H_{32}O_2$ [M]: 352.2402; Found: 352.2401.

3.6 Synthesis of peptides **35-1** and **36-1**



Scheme S14

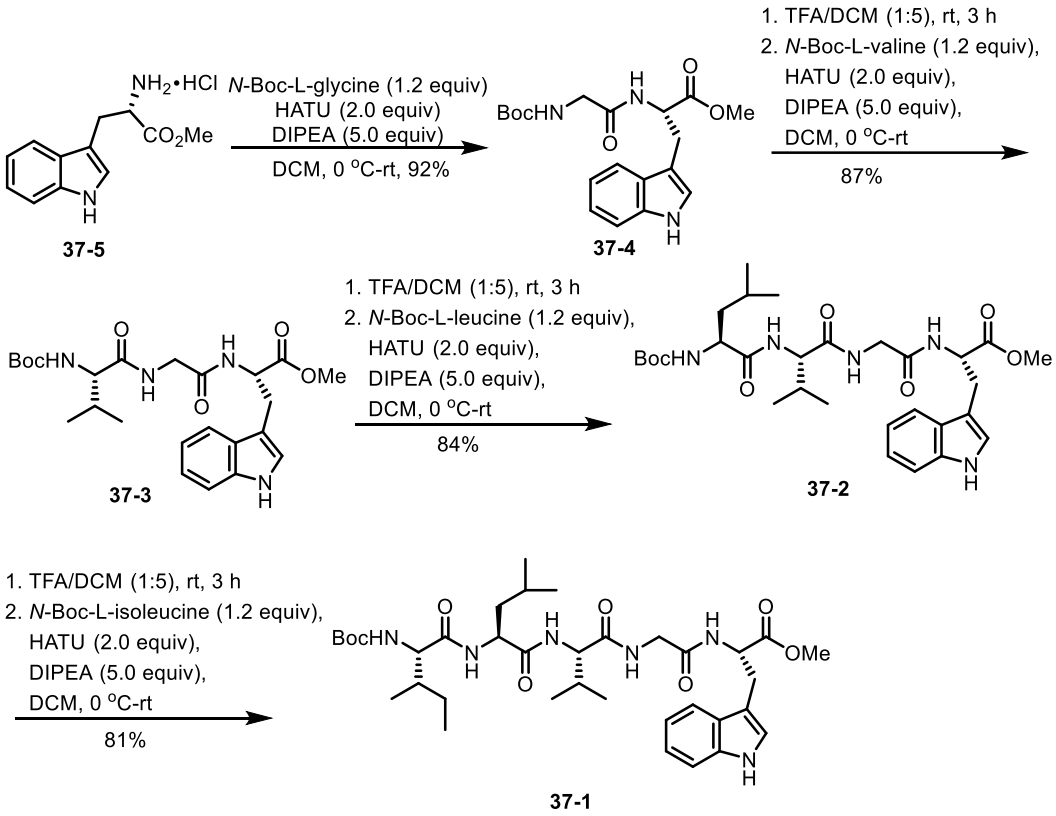
Compound **35-1** was prepared following the general amide coupling procedure: HATU (3.8 g, 10.0 mmol, 2.0 equiv) were added to a solution of compound **35-2** (1.5 g, 5.0 mmol, 1.0 equiv) and compound **35-3** (1.8 g, 6.0 mmol, 1.2 equiv) in dry DCM (25 mL) at 0 °C. After 10 min, DIPEA (4.1 mL, 25.0 mmol, 5.0 equiv) was added to the reaction mixture. The resulting solution was warmed to room temperature and stirred for 1 hour. Then the reaction mixture was washed with water and brine successively. The organic phase was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel flash chromatography (eluted with hexane/acetone (v/v 3:2)) to give the desired product **35-1** in 89% yield (2.63 g, R_f = 0.2, 20% acetone in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.00 (s, 1H), 6.51 (d, *J* = 7.8 Hz, 2H), 6.25 (s, 1H), 5.13 (s, 1H), 4.70 (s, 1H), 4.43 (s, 1H), 3.60 (s, 3H), 3.33 (d, *J* = 10.8 Hz, 1H), 3.11 (dd, *J* = 14.5, 7.2 Hz, 1H), 2.86 (d, *J* = 5.2 Hz, 2H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.53, 171.06, 155.46, 137.45, 136.34, 135.32, 131.19, 127.38, 123.45, 122.24, 119.70, 118.83, 111.38, 110.14, 92.57, 80.24, 55.18, 53.00, 52.31, 38.67, 37.28, 30.97, 28.32, 28.20; **HRMS** Calcd for $C_{26}H_{30}IN_3O_5Na$ [M+Na$^+$]: 614.1122, Found: 614.1126.



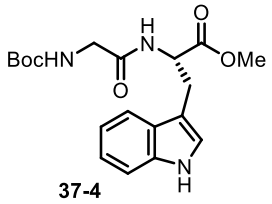
Scheme S15

Compound **36-1** was prepared following the same amide coupling procedure as compound **35-1** in 87% yield (2.02 g). The spectra data are consistent with those reported in literature.[8]

3.7 Synthesis of compound **37-1**

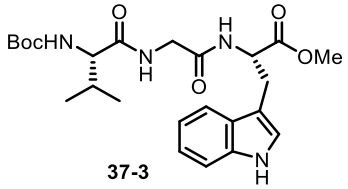


Scheme S16



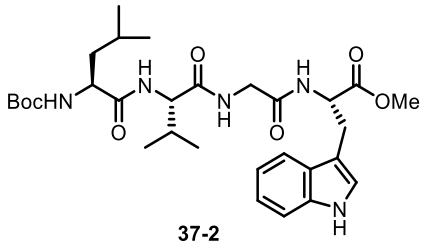
37-4

Compound **37-4** was synthesized by coupling **37-5** with *N*-Boc-L-glycine following the amide coupling procdure in 92% yield (1.72 g). The spectra data are consistent with those reported in literature.[9]



37-3

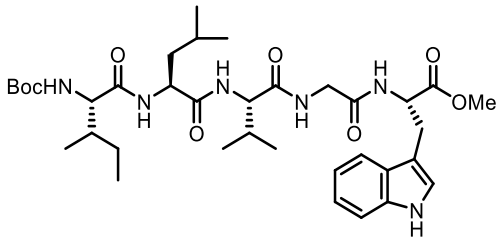
Trifluoroacetic acid (5.0 mL) was added to a solution of cmpound **37-4** (1.9 g, 5.0 mmol, 1.0 equiv) in dry dichloromethane (25 mL). The mixture was stirred for 3 hour at room temperature. Then the solvent was removed under reduced pressure and the residue was treated with *N*-Boc-L-valine (1.3 g, 6.0 mmol, 1.2 equiv), HATU (3.8 g, 10.0 mmol, 2.0 equiv) and DIPEA (4.1 mL, 25.0 mmol, 5.0 equiv) following the general amide coupling procedure to give **37-3** (R_f = 0.4, 60% acetone in hexane) in 87% yield (2.06 g). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 7.9 Hz, 1H), 7.16-6.98 (m, 4H), 6.94 (s, 1H), 5.43 (d, *J* = 8.6 Hz, 1H), 4.79 (d, *J* = 5.7 Hz, 1H), 4.07-3.94 (m, 1H), 3.77 (dd, *J* = 16.6, 5.0 Hz, 1H), 3.63 (s, 3H), 3.38-3.13 (m, 2H), 1.98 (d, *J* = 6.2 Hz, 1H), 1.43 (s, 9H), 1.28 (d, *J* = 6.1 Hz, 1H), 0.90 (d, *J* = 6.6 Hz, 3H), 0.82 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.57, 172.29, 168.92, 156.30, 136.28, 127.31, 123.84, 121.99, 119.37, 118.35, 111.63, 108.99, 80.16, 59.73, 52.48, 52.32, 42.88, 38.66, 31.23, 28.42, 27.33, 26.97, 19.33, 17.50; **HRMS** Calcd for $C_{24}H_{34}N_4O_6Na$ [M+Na$^+$]: 497.2371; Found: 497.2373.



37-2

Trifluoroacetic acid (5 mL) was added to a solution of cmpound **37-3** (2.06 g, 4.3 mmol,

1.0 equiv) in dry dichloromethane (25 mL). The mixture was stirred for 3 hour at room temperature. Then the solvent was removed under reduced pressure and the residue was treated with *N*-Boc-L-leucine (1.2 g, 5.2 mmol, 1.2 equiv), HATU (3.3 g, 8.6 mmol, 2.0 equiv) and DIPEA (3.5 mL, 21.5 mmol, 5.0 equiv) following the general amide coupling procedure to give **37-2** (R_f = 0.4, 5% CH_3OH in DCM) in 84% yield (2.12 g). **^{1}H NMR** (400 MHz, MeOD) δ 7.48 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.06 (t, *J* = 6.0 Hz, 2H), 6.99 (t, *J* = 7.0 Hz, 1H), 4.71 (t, *J* = 6.5 Hz, 1H), 4.16 (d, *J* = 6.8 Hz, 1H), 4.09 (q, *J* = 9.8, 1H), 3.85 (q, *J* = 16.8 Hz, 2H), 3.61 (s, 3H), 3.30-3.28 (m, 1H), 3.28-3.16 (m, 2H), 2.04 (m, 1H), 1.65-1.56 (m, 1H), 1.53-1.43 (m, 2H), 1.40 (s, 10H), 1.26 (s, 1H), 1.00-0.76 (m, 14H); **^{13}C NMR** (101 MHz, MeOD) δ 174.43, 172.55, 172.36, 169.71, 156.68, 136.57, 127.29, 123.23, 121.08, 118.50, 117.74, 111.01, 109.07, 79.32, 58.76, 54.40, 53.41, 53.14, 51.38, 41.88, 40.28, 30.60, 27.36, 27.09, 24.48, 22.15, 20.48, 18.38, 17.31, 17.18, 15.86; **HRMS** Calcd for $C_{24}H_{35}N_4O_6$ [M+H$^+$]: 587.3319; Found: 587.3320.



37-1

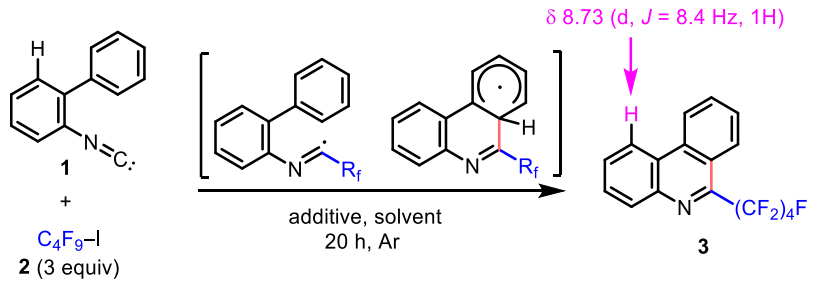
Trifluoroacetic acid (5.0 mL) was added to a solution of cmpound **37-2** (2.12 g, 3.6 mmol, 1.0 equiv) in dry dichloromethane (25 mL). The mixture was stirred for 3 h at room temperature. Then the solvent was removed under reduced pressure and the residue was treated with *N*-Boc-L-isoleucine (1.0 g, 4.3 mmol, 1.2 equiv), HATU (2.7 g, 7.2 mmol, 2.0 equiv) and DIPEA (3.0 mL, 18.0 mmol, 5.0 equiv) following the general amide coupling procedure to give **37-1** (R_f = 0.4, 5% CH_3OH in DCM) in 81% yield (2.04 g). **^{1}H NMR** (400 MHz, MeOD) δ 7.47 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.06 (t, 2H), 6.98 (t, *J* = 7.3 Hz, 1H), 4.73 (t, *J* = 6.4 Hz, 1H), 4.59 (m, 1H), 4.21 (d, *J* = 7.2 Hz, 1H), 3.94 (d, *J* = 7.6 Hz, 1H), 3.88 (d, *J* = 9.0 Hz, 2H), 3.58 (s, 3H), 3.29 (s, 1H), 3.26 (d, *J* = 5.8 Hz, 1H), 3.22 (d, *J* = 7.0 Hz, 1H), 2.02 (q, *J* = 4.0 Hz, 1H), 1.79-1.68 (m, 1H), 1.63 (m, 1H), 1.59-1.46 (m, 3H), 1.40 (s, 10H), 1.26 (s, 1H), 1.17-

1.04 (m, 1H), 0.88 (m, 21H); **^{13}C NMR** (101 MHz, MeOD) δ 174.46, 174.37, 173.87, 173.69, 170.94, 157.78, 137.88, 128.65, 124.55, 122.38, 119.81, 119.06, 112.33, 110.38, 80.39, 60.44, 60.32, 55.73, 54.81, 52.76, 52.68, 43.25, 41.80, 38.04, 31.86, 28.73, 28.52, 25.87, 25.66, 23.52, 22.17, 19.74, 18.96, 17.20, 16.09, 11.39; **HRMS** Calcd for $C_{24}H_{35}N_4O_6$ [M+H$^+$]: 701.4232; Found: 701.4235.

4. Evaluation of synthesis phenanthridine 3 from 2-isocyanobiphenyl and C_4F_9-I via a radical cascade process

All screening reactions were carried out at a 0.2 mmol scale in a 4 mL glass vial (Thermo Scientific, National B7999-2) sealed with PTEF cap and stirred on bench top. 2-Isocyanobiphenyl **1**, C_4F_9I and other specified reagents were dispersed in 2 mL of solvent and the resulting mixture was purged with Ar (if necessary) and vigorously stirred at specified temperature under light irradiation (laid 10 CM away from the vial, if necessary) for 20 hour. The solvent of the reaction mixture was removed under reduced pressure. The resulting residue was dissolved in 1 mL of $CDCl_3$ along with $Cl_2CHCHCl_2$ (20 μL) as an external standard for ^{1}H-NMR analysis. The composition of reaction mixture was based on the Ar-H at 8.73 ppm (d, J = 8.4 Hz, 1H) for compound **3**.

Table S1. Perfluoroalkylation reaction of 2-isocyanobiphenyl **1** with perfluorobutyl iodide **2**



Entry	Regents (equiv)/atmosphere[a]	Solvent	t (°C)	Time (h)	Yield (%)[b]
1	$NiCl_2$ (0.05), Cs_2CO_3 (1.5), Ar[c]	dioxane	100	20	62
2	Cs_2CO_3 (1.5), Ar[c]	dioxane	100	20	60

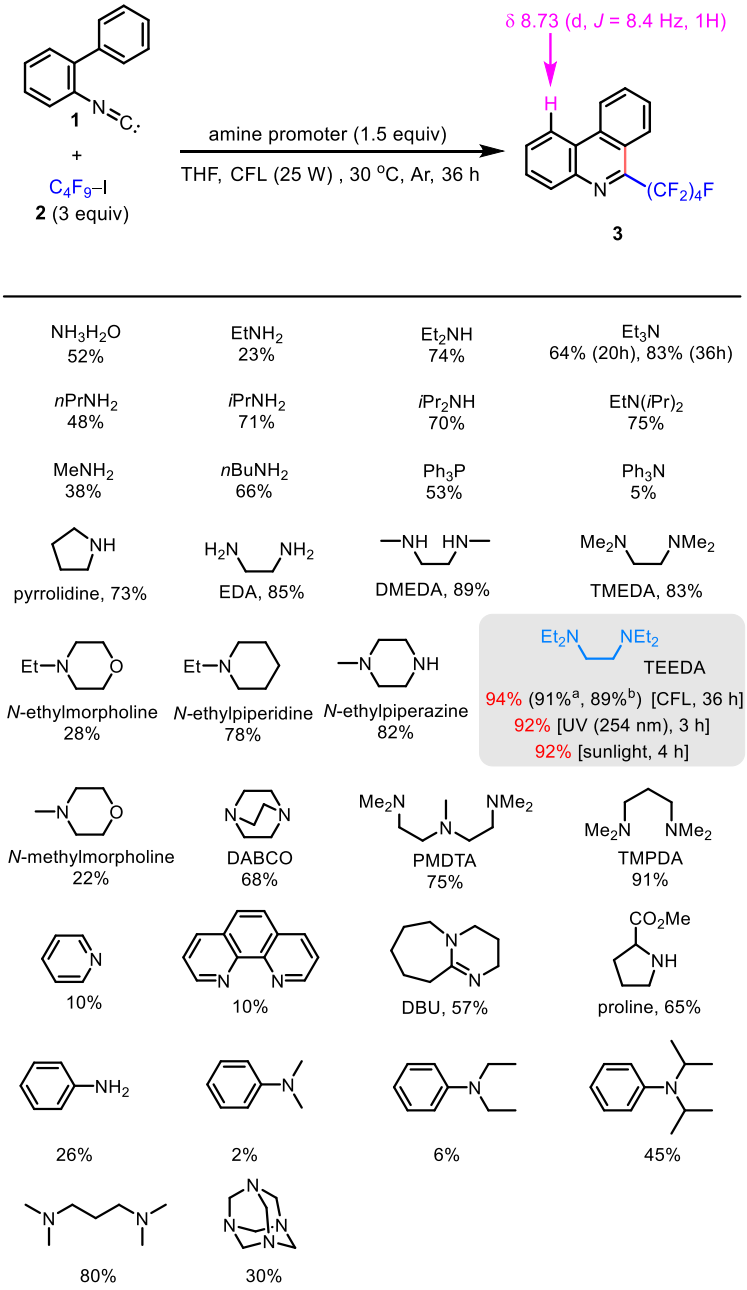
3	no additives, Ar[c]	dioxane	100	20	<2
4	Cs_2CO_3 (1.5), Ar[c]	dioxane	30	20	<2
5	no additives, CFL, Ar	dioxane	30	20	5
6	no additives, CFL, Ar	THF	30	20	10
7	no additives, CFL, Ar	THP	30	20	7
8	no additives, CFL, Ar	DCM	30	20	4
9	no additives, CFL, Ar	$CHCl_3$	30	20	5
10	no additives, CFL, Ar	CH_3CN	30	20	<2
11	no additives, CFL, Ar	DMF	30	20	<2
12	no additives, in dark, Ar	THF	30	20	<2
13	Cs_2CO_3 (1.5), CFL, Ar	THF	30	20	29
14	K_2CO_3 (1.5), CFL, Ar	THF	30	20	10
15	Na_2CO_3 (1.5), CFL, Ar	THF	30	20	7
16	NaOMe (1.5), CFL, Ar	THF	30	20	4
17	KO*t*-Bu (1.5), CFL, Ar	THF	30	20	20
18	Et_3N (1.5), CFL, Ar	THF	30	20	64
19	Et_3N (1.5), UV-Hg (254nm), Ar	THF	30	20	73
20	Et_3N (1.5), sunlight (direct irradiation), Ar	THF	30	4	76
21	UV-Hg (254nm), no Et_3N, Ar	THF	30	20	15
22	Et_3N (1.5), CFL, Ar	THP	30	20	57
23	Et_3N (1.5), CFL, Ar	2-MeTHF	30	20	52
24	Et_3N (1.5), CFL, Ar	Et_2O	30	20	28
25	Et_3N (1.5), CFL, Ar	MTBE	30	20	40
26	Et_3N (1.5), CFL, Ar	dioxane	30	20	38
27	Et_3N (1.5), CFL, Ar	$CHCl_3$	30	20	30
28	Et_3N (1.5), CFL, Ar	CH_3CN	30	20	46
29	Et_3N (1.5), CFL, Ar	H_2O	30	20	20
30	Et_3N (0.2), CFL, Ar	THF	30	20	16
31	Et_3N (0.2), K_2CO_3 (1.5), CFL, Ar	THF	30	20	32
32	Et_3N (1.5), in dark, Ar	THF	30	20	<2
33	Et_3N (1.5), CFL, O_2 (1 atm)	THF	30	20	4
34	Et_3N (1.5), CFL, air	THF	30	20	32
35	I_2 (0.1), CFL, Ar	THF	30	20	<2
36	I_2 (0.1), CFL, Ar	DCM	30	20	<2

a) CFL: household compact fluorescent lamp, 25W; UV (254 nm): low-pressure Hg-vapor lamp, 25W; b) Yield are based on ^{1}H-NMR analysis of crude reaction mixture on a 0.2 mmol scale; c) Conducted in the presence of ambient laboratory light.

5. Evaluation of amine promoters for synthesis of 3 under CFL irradiation

2-Isocyanobiphenyl **1** (36 mg, 0.2 mol, 1.0 equiv), C_4F_9I (208 mg, 0.6 mol, 3.0 equiv) and the specific amine (0.3 mol, 1.5 equiv) were dispersed in 2 mL of solvent. The

reaction vial was then purged with Ar for 1 min, sealed with PTEF cap. The reaction mixture was vigorously stirred at 30 °C under CFL (25W, laid 10 CM away from the vial) irradiation for 36 hour. Then THF was removed under reduced pressure. The resulting residue was dissolved in 1 mL of $CDCl_3$ along with $Cl_2CHCHCl_2$ (20 μL) as an external standard for ^{1}H-NMR analysis. The composition of reaction mixture was based on the Ar-H at 8.73 ppm (d, J = 8.4 Hz, 1H) for compound **3**.



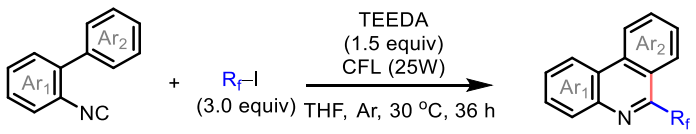
CFL: 25 W; UV (254 nm): low-pressure Hg-vapor lamp, 25 W; sunlight: direct irradiation for 4 h. Yields are based on ^{1}H-NMR analysis of crude reaction mixture on a 0.2 mmol scale performed

in 4 mL borosilicate glass vial under Ar. a) Isolated yield on 0.2 mmol scale. b) Isolated yield on 1 mmol scale.

Scheme S17

Procedure of phenanthridine synthesis in sunlight: 2-Isocyanobiphenyl **1** (36 mg, 0.2 mol, 1.0 equiv), C_4F_9I (208 mg, 0.6 mol, 3.0 equiv) and *N*,*N*,*N'*,*N'*-Tetraethylenediamine (TEEDA) (52 mg, 0.3 mmol, 1.5 equiv) were dispersed in 2 mL of THF. The reaction vial was then purged with Ar for 1 min and sealed with PTEF cap. The reaction mixture was vigorously stirred at 30 ^{o}C in sunlight for 4 hour. Then THF was removed under reduced pressure. The resulting residue was dissolved in 1 mL of $CDCl_3$ along with $Cl_2CHCHCl_2$ (20 μL) as an external standard for ^{1}H-NMR analysis.

6. General procedures and substrate scope of phenanthridine synthesis



Scheme S18

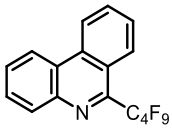
General procedure A for the synthesis of compound 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 and 15:

2-Isocyanobiaryl compound (0.2 mmol, 1.0 equiv), perfluoroalkyl iodide (0.6 mmol, 3.0 equiv) and *N*,*N*,*N'*,*N'*-Tetraethylenediamine (TEEDA) (0.3 mmol, 1.5 equiv) were dispersed in 2 mL of THF. The reaction vial was then purged with Ar for 1 min and sealed with PTEF cap. The reaction mixture was vigorously stirred at 30 ^{o}C under irradiation of CFL lamp (25W, laid 10 CM away from the vial) for 36 hour. Then the mixture was concentrated *in vacuo*, and the residue was purified by silica gel flash chromatography to give the desired product.

General procedure B for the synthesis of compound 16, 17and 18:

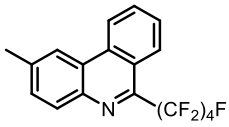
2-Isocyanobiaryl compound (0.2 mmol, 1.0 equiv), alkyl bromide (1.0 mmol, 5.0 equiv) and *N*,*N*,*N'*,*N'*-Tetraethylenediamine (TEEDA) (0.6 mmol, 3.0 equiv) were dispersed in 2 mL of THF. The reaction vial was then purged with Ar for 1 min and sealed with

PTEF cap. The reaction mixture was vigorously stirred at 30 ºC under irradiation of CFL lamp (25W, laid 10 CM away from the vial) for 36 h. Then the mixture was concentrated *in vacuo*, and the residue was purified by silica gel flash chromatography to give the desired product.



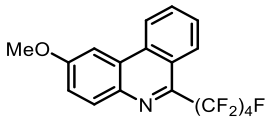
3 R_f = 0.5, 1% acetone in Hexane

Compound **3** was isolated in 91% yield (72 mg) following the general procedure **A**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 8.4 Hz, 1H), 8.67-8.58 (m, 1H), 8.47 (d, *J* = 8.4 Hz, 1H), 8.33-8.23 (m, 1H), 7.93 (t, *J* = 7.7 Hz, 1H), 7.86-7.72 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.79 (t, *J* = 24.1 Hz), 141.87, 134.13, 131.34, 131.32, 129.54, 129.44, 128.13, 126.36-126.22(m), 124.95, 123.08, 122.75, 122.16, 120-100 (m); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.97 (t, *J* = 10.6 Hz, 3F), -103.16 – -106.93 (m, 2F), -118.09 – -121.23 (m, 2F), -122.18 – -125.63 (m, 2F); **HRMS** Calcd for $C_{17}H_9F_9N$ [M+H$^+$]: 398.0586; Found: 398.0588.



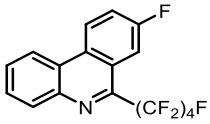
4 R_f = 0.5, 1% acetone in Hexane

Compound **4** was isolated in 85% yield (70 mg) following the general procedure **A**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.4 Hz, 1H), 8.44 (d, *J* = 8.4 Hz, 1H), 8.39 (s, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.89 (t, *J* = 7.3 Hz, 1H), 7.74 (t, *J* = 7.8 Hz, 1H), 7.63 (dd, *J* = 8.4, 1.4 Hz, 1H), 2.66 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.72 (t, *J* = 24.6 Hz), 140.24, 139.88, 133.77, 131.19, 131.00, 127.93, 126.23-126.09 (m), 124.80, 123.16, 122.67, 121.69, 120-100 (m), 22.32; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.98 (t, *J* = 10.6 Hz, 3F), -102.98 – -107.39 (m, 2F), -118.41 – -121.54 (m, 2F), -122.31 – -125.62 (m, 2F); **HRMS** Calcd for $C_{18}H_{11}F_9N$ [M+H$^+$]: 412.0742; Found: 412.0745.



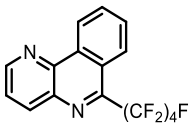
5 R_f = 0.6, 1% acetone in Hexane

Compound **5** was isolated in 71% yield (61 mg) following the general procedure **A**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.4 Hz, 1H), 8.44 (d, *J* = 8.4 Hz, 1H), 8.18 (d, *J* = 9.0 Hz, 1H), 7.95-7.84 (m, 2H), 7.75 (t, *J* = 7.8 Hz, 1H), 7.42 (dd, *J* = 9.0, 2.4 Hz, 1H), 4.04 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.41, 143.91(t, *J* = 24.9 Hz), 137.20, 133.35, 132.78, 130.68, 128.11, 126.35, 126.16-126.03 (m), 123.23, 122.64, 120-100 (m), 119.61, 102.60, 55.76; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.98 (t, *J* = 10.6 Hz, 3F), -113.62 – -106.12 (m, 2F), -118.72 – -121.21 (m, 2F), -122.31 – -125.62 (m, 2F); **HRMS** Calcd for $C_{18}H_{11}F_9NO$ [M+H$^+$]: 428.0691; Found: 428.0692.



6 R_f = 0.5, 1% acetone in Hexane

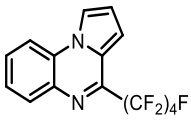
Compound **6** was isolated in 94% yield (78 mg) following the general procedure **A**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.72 (dd, *J* = 9.1, 5.4 Hz, 1H), 8.61-8.48 (m, 1H), 8.32-8.21 (m, 1H), 8.09 (d, *J* = 10.1 Hz, 1H), 7.81 (dd, *J* = 6.0, 3.4 Hz, 2H), 7.68 (t, *J* = 8.4 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.56 (d, *J* = 249.5 Hz), 145.91 (t, *J* = 24.6 Hz), 141.52, 131.40, 130.81, 129.97, 129.33, 125.25 (d, *J* = 8.8 Hz), 124.49, 124.06 (d, *J* = 8.9 Hz), 121.85, 120.90, 120.66, 120-100 (m), 111.12 (dt, *J* = 23.8, 7.1 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.97 (t, *J* = 10.7 Hz, 3F), -104.39 – -106.93 (m, 2F), -109.92 (s, 1F), -118.54 – -121.53 (m, 2F), -122.52 – -125.31 (m, 2F); **HRMS** Calcd for $C_{17}H_8F_{10}N$ [M+H$^+$]: 416.0492, Found: 416.0495.



7 R_f = 0.4, 1% acetone in Hexane

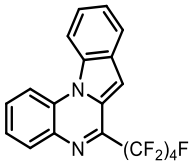
Compound **7** was isolated in 74% yield (59 mg) following the general procedure **A**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.37 (d, *J* = 7.7 Hz, 1H), 9.12 (dd, *J* = 4.3, 1.6 Hz, 1H), 8.55 (dd, *J* = 8.3, 1.7 Hz, 1H), 8.47 (d, *J* = 8.5 Hz, 1H), 8.07-7.97 (m, 1H), 7.88 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 1H), 7.76 (dd, *J* = 8.3, 4.3 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.90, δ 147.63 (t, *J* = 25.0 Hz), 141.46, 138.30, 136.75, 135.06, 131.84, 129.80, 125.73-125.55 (m), 125.20, 124.60, 124.42, 120-100 (m); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.95 (t, *J* = 10.4 Hz, 3F), -103.44 – -107.07 (m, 2F), -117.91 – -121.22 (m, 2F), -

122.63 – -125.32 (m, 2F); **HRMS** Calcd for $C_{16}H_8F_9N_2$ [M+H$^+$]: 399.0538, Found: 399.0536.



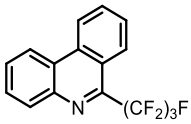
8 R_f = 0.3, 1% acetone in Hexane

Compound **8** was isolated in 59% yield (46 mg) following the general procedure **A**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09-8.05 (m, 2H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.17-7.10 (m, 1H), 7.03-6.93 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) 142.74 (t, *J* = 26.2 Hz), 134.25, 131.35, 130.16, 127.77, 125.91, 122.86, 120-100 (m), 115.50, 115.09, 113.90, 108.88; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -79.24 – 82.55 (m, 3F), -111.80 – -114.94 (m, 2F), -120.59 – -122.95 (m, 2F), -124.20 – -126.72 (m, 2F); **HRMS** Calcd for $C_{15}H_8F_9N_2$ [M+H$^+$]: 387.0538, Found: 387.0542.



9 R_f = 0.4, 1% acetone in Hexane

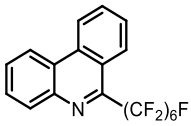
Compound **9** was isolated in 56% yield (49 mg) following the general procedure **A**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.4 Hz, 1H), 8.47 (d, *J* = 8.7 Hz, 1H), 8.11 (dd, *J* = 8.0, 1.4 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.73 (t, *J* = 7.9 Hz, 1H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.52-7.47 (m, 2H), 7.44 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.40 (t, *J* = 25.5 Hz), 134.17, 132.70, 131.86, 131.17, 130.95, 129.21, 125.72, 125.47, 124.69, 123.50, 123.43, 120-100 (m),114.90, 114.59, 102.33; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -78.78 – -82.87 (m, 3F), -111.17 – -114.63 (m, 2F), -119.64 – -122.95 (m, 2F), -123.59 – -127.19 (m, 2F); **HRMS** Calcd for $C_{19}H_{10}F_9N_2$ [M+H$^+$]: 437.0695, Found: 437.0698.



10 R_f = 0.5, 1% acetone in Hexane

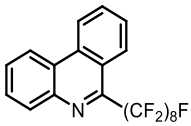
Compound **10** was isolated in 71% yield (49 mg) following the general procedure **A**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 8.3 Hz, 1H), 8.67-8.57 (m, 1H), 8.47 (d, *J* = 8.3 Hz, 1H), 8.34-8.22 (m, 1H), 7.92 (t, *J* = 7.6 Hz, 1H), 7.86-7.70 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.67 (t, *J* = 24.3 Hz), 141.94, 134.15, 131.38, 131.32, 129.53,

129.44, 128.12, 126.42-126.43 (m), 124.96, 123.13, 122.75, 122.16, 120-100 (m); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -79.05 (t, *J* = 10.2 Hz, 3F), -104.57 – -107.21 (m, 2F), -123.66 (t, *J* = 7.2 Hz, 2F); **HRMS** Calcd for $C_{16}H_9F_7N$ [M+H$^+$]: 348.0618, Found: 348.0620.



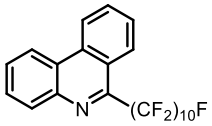
11 R_f = 0.5, 1% acetone in Hexane

Compound **11** was isolated in 93% yield (92 mg) following the general procedure **A**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 8.4 Hz, 1H), 8.66-8.58 (m, 1H), 8.47 (d, *J* = 8.4 Hz, 1H), 8.34-8.25 (m, 1H), 7.92 (t, *J* = 7.3 Hz, 1H), 7.86-7.70 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.77 (t, *J* = 24.9 Hz), 141.89, 134.09, 131.32, 131.25, 129.49, 129.40, 128.09, 126.28 (t, *J* = 6.9 Hz), 124.91, 123.13, 122.69, 122.10, 120-100 (m); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.82 (t, *J* = 11.6 Hz, 3F), -103.30 – -106.62 (m, 2F), -116.99 – -119.18 (m, 2F), -119.18 – -121.05 (m, 2F), -121.36 – -124.22 (m, 2F), -124.82 – -127.82 (m, 2F); **HRMS** Calcd for $C_{19}H_9F_{13}N$ [M+H$^+$]: 498.0522, Found: 498.0526.



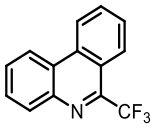
12 R_f = 0.6, 1% acetone in Hexane

Compound **12** was isolated in 93% yield (111 mg) following the general procedure **A**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 8.3 Hz, 1H), 8.66-8.58 (m, 1H), 8.47 (d, *J* = 8.4 Hz, 1H), 8.33-8.24 (m, 1H), 7.92 (t, *J* = 7.7 Hz, 1H), 7.86-7.70 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.80 (t, *J* = 24.9 Hz), 141.90, 134.11, 131.33, 131.25, 129.49, 129.40, 128.09, 126.29 (t, *J* = 6.8 Hz), 124.92, 123.15, 122.69, 122.11, 120-100 (m); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.63 – -81.09 (m, 3F), -104.82 – -105.07 (m, 2F), -118.50 – -119.29 (m, 2F), -119.75 (s, 2F), -121.13 – -122.26 (m, 4F), -122.76 (s, 2F), -125.73 – -126.59 (m, 2F); **HRMS** Calcd for $C_{21}H_9F_{17}N$ [M+H$^+$]: 598.0458, Found: 598.0462.



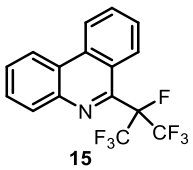
13 R_f = 0.7, 1% acetone in Hexane

Compound **13** was isolated in 94% yield (131 mg) following the general procedure **A**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 8.3 Hz, 1H), 8.66-8.54 (m, 1H), 8.47 (d, *J* = 8.3 Hz, 1H), 8.35-8.21 (m, 1H), 7.91 (t, *J* = 7.6 Hz, 1H), 7.86-7.65 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.81 (t, *J* = 24.7 Hz), 141.90, 134.10, 131.33, 131.23, 129.47, 129.38, 128.07, 126.29 (t, *J* = 6.8 Hz), 124.91, 123.15, 122.68, 122.09, 120-100 (m); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.82 (t, *J* = 10.6 Hz, 3F), -104.63 – -105.33 (m, 2F), -119.02 (s, 2F), -119.76 (s, 2F), -120.30 – -122.55 (m, 8F), -122.77 (s, 2F), -125.89 – -126.61 (m, 2F); **HRMS** Calcd for $C_{23}H_9F_{21}N$ [M+H$^+$]: 698.0394, Found: 698.0395.



14 R_f = 0.7, 1% acetone in Hexane

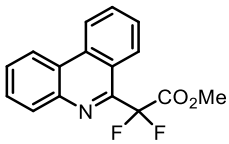
2-Isocyanobiphenyl **1** (36 mg, 0.2 mmol, 1.0 equiv) and *N,N,N',N'*-Tetraethylenediamine (TEEDA) (52 mg, 0.3 mmol, 1.5 equiv) were dispersed in 2 mL of THF. The reaction vial was then purged with CF_3I for 5 min and sealed with PTEF cap. The reaction mixture was stirred at 30 ^oC under irradiation of CFL lamp (25W, laid 10 CM away from the vial) for 36 h. Then the mixture was concentrated *in vacuo*, and the residue was purified by silica gel flash chromatography to give compound **14** in 66% yield (33 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 8.4 Hz, 1H), 8.60-8.52 (m, 1H), 8.42-8.33 (m, 1H), 8.31-8.24 (m, 1H), 7.89 (t, *J* = 7.7 Hz, 1H), 7.84-7.68 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.61 (q, *J* = 33.0 Hz), 141.84, 134.05, 131.48, 131.21, 129.44, 129.32, 128.16, 126.02 (q, *J* = 3.1 Hz), 125.21, 123.44, 122.63, 122.17; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.44 (s, 3F); **HRMS** Calcd for $C_{14}H_9F_3N$ [M+H$^+$]: 248.0682, Found: 248.0685.



15 R_f = 0.6, 1% acetone in Hexane

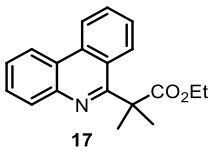
Compound **15** was isolated in 80% yield (56 mg) following the general procedure **A**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 8.3 Hz, 1H), 8.64-8.60 (m, 2H), 8.29-8.14 (m, 1H), 7.90 (t, *J* = 7.6 Hz, 1H), 7.84-7.66 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.90 (d, *J* = 23.9 Hz), 141.71 (d, *J* = 2.6 Hz), 134.25, 131.22, 131.15, 129.31 (d, *J* = 5.5 Hz), 128.05 (d, *J* = 3.3 Hz), 126.60, 126.39, 124.39, 124.25 (d, *J* = 4.0 Hz), 122.78, 122.07; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -72.48 (d, *J* = 6.9 Hz, 6F), -174.77 – -175.55 (m, 1F); **HRMS** Calcd for $C_{16}H_9F_7N$ [M+H$^+$]: 348.0618, Found: 348.0621.



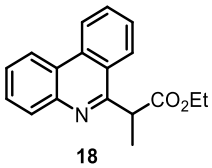
16 R_f = 0.6, 1% acetone in Hexane

Compound **16** was isolated in 66% yield (38 mg) following the general procedure **B**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 8.4 Hz, 1H), 8.64-8.53 (m, 2H), 8.14 (dt, *J* = 7.1, 3.7 Hz, 1H), 7.93 (t, *J* = 7.4 Hz, 1H), 7.82-7.71 (m, 3H), 4.08 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.19, 141.88, 134.07, 131.43, 131.20, 129.18, 129.11, 128.08, 126.41 (t, *J* = 4.8 Hz), 125.04, 122.69, 122.43, 122.19, 53.622; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -98.55 (s, 2F); **HRMS** Calcd for $C_{16}H_{12}F_2NO_2$ [M+H$^+$]: 288.0831, Found: 288.0835.



17 R_f = 0.6, Hexane

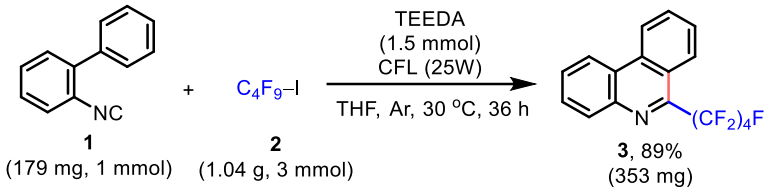
Compound **17** was isolated in 71% yield (42 mg) following the general procedure **B**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.3 Hz, 1H), 8.55 (d, *J* = 8.1 Hz, 1H), 8.17 (dd, *J* = 8.1, 0.9 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.78 (t, *J* = 7.7 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.67-7.55 (m, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 1.88 (s, 6H), 1.00 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.21, 161.34, 143.17, 133.61, 130.47, 129.83, 128.59, 126.96, 126.16, 124.41, 123.91, 122.95, 121.88, 100.07, 61.12, 50.05, 26.70, 14.00; **HRMS** Calcd for $C_{19}H_{20}NO_2$ [M+H$^+$]: 294.1489, Found: 294.1490.



18 R_f = 0.7, Hexane

Compound **18** was isolated in 94% yield (53 mg) following the general procedure **B**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 8.3 Hz, 1H), 8.54 (d, *J* = 8.1 Hz, 1H), 8.22 (d, *J* = 8.3 Hz, 1H), 8.16 (d, *J* = 8.1 Hz, 1H), 7.82 (t, *J* = 7.6 Hz, 1H), 7.76-7.59 (m, 3H), 4.75 (q, *J* = 7.1 Hz, 1H), 4.31-4.05 (m, 2H), 1.79 (d, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.83, 159.64, 143.60, 133.33, 130.44, 130.27, 128.68, 127.48, 126.92, 125.68, 124.72, 123.80, 122.76, 121.94, 61.06, 45.67, 16.55, 14.23; **HRMS** Calcd for $C_{18}H_{18}NO_2$ [M+H$^+$]: 280.1332, Found: 280.1335.

1 mmol scale reaction of 2-Isocyanobiphenyl 1 with perfluorobutyl iodide 2.

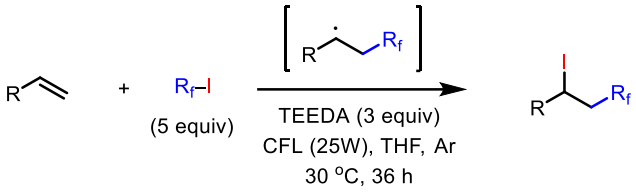


Scheme S19

In a 40 mL borosilicate glass vial, 2-isocyanobiphenyl **1** (179 mg, 1.0 mmol, 1.0 equiv), perfluorobutyl iodide **2** (1.04 g, 3.0 mmol, 3.0 equiv) and *N,N,N',N'*-tetraethylenediamine (TEEDA) (258 mg, 1.5 mmol, 1.5 equiv) were dispersed in 10 mL of THF. The reaction vial was then purged with Ar for 1 min and sealed with PTEF cap. The reaction mixture was vigorously stirred at 30 °C under irradiation of CFL lamp (25W, laid 10 CM away from the vial) and monitored by TLC analysis. After 36 hour, all the 2-Isocyanobiphenyl **1** was consumed. Then the mixture was concentrated *in vacuo*, and the residue was purified by silica gel flash chromatography to give compound **3** in 89% yield (353 mg).

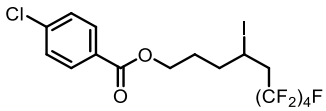
7. General procedures and substrate scope for addition of perfluorobutyl iodide to alkenes and alkynes

7.1 General procedure and substrate scope for addition of perfluorobutyl iodide to alkenes



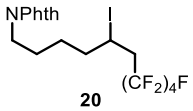
Scheme S20

General procedure C for the synthesis of compound 19, 20, 21, 22, 23, and 24: Alkene (0.2 mmol, 1.0 equiv), perfluoroalkyl iodide (1.0 mmol, 5.0 equiv) and *N,N,N',N'*-tetraethylenediamine (TEEDA) (0.6 mmol, 3.0 equiv) were dispersed in 2 mL of THF. The reaction vial was then purged with Ar for 1 min and sealed with PTEF cap. The reaction mixture was vigorously stirred at 30 °C under irradiation of CFL lamp (25W, laid 10 CM away from the vial) for 36 h. Then the mixture was concentrated *in vacuo*, and the residue was purified by silica gel flash chromatography to give the desired product.



19 R_f = 0.7, Hexane

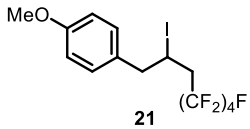
Compound **19** was isolated in 90% yield (103 mg) following the general procedure **C** (89% yield (102 mg) was obtained under the irradiation of UV (254nm) lamp for 20 hours; 74% yield (84 mg) was obtained after irradiated in sunlight for 4 hours). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 4.47-4.29 (m, 3H), 3.15-2.61 (m, 2H), 2.12-1.86 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.78, 139.67, 131.08, 128.91, 128.65, 63.93, 41.71 (t, *J* = 21.1 Hz), 36.91 (d, *J* = 2.9 Hz), 29.05, 19.52; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.11 – -81.80 (m, 3F), -109.86 – -112.76 (m, 1F), -113.86 – - 116.17 (m, 1F), -124.42 (s, 2F), -125.83 (q, *J* = 15.8 Hz, 2F); **HRMS** Calcd for $C_{16}H_{13}ClF_9IO_2Na$ [M+Na$^+$]: 592.9397, Found: 592.9400.



20 R_f = 0.6, Hexane

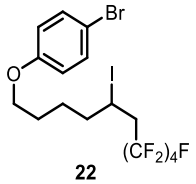
Compound **20** was isolated in 86% yield (99 mg) following the general procedure **C**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89-7.80 (m, 2H), 7.76-7.65 (m, 2H), 4.39-4.18 (m,

1H), 3.70 (t, *J* = 7.1 Hz, 2H), 3.04-2.59 (m, 2H), 1.90-1.63 (m, 5H), 1.54-1.36 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.53, 134.10, 132.23, 123.38, 41.72 (t, *J* = 20.9 Hz), 39.81, 37.66, 27.60, 27.09, 20.06; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -79.40 – -82.59 (m, 3F), -113.24 – -116.44 (m, 2F), -123.29 – -124.90 (m, 2F), -125.30 – -127.56 (m, 2F); **HRMS** Calcd for $C_{18}H_{15}F_9INO_2Na$ [M+Na$^+$]: 597.9896, Found: 597.9902.



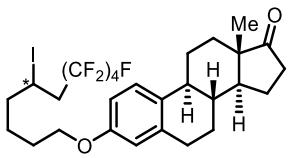
21 R_f = 0.8, Hexane

Compound **21** was isolated in 90% yield (89 mg) following the general procedure **C**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 4.46-4.38 (m, 1H), 3.81 (s, 3H), 3.25-3.11 (m, 2H), 3.02-2.72 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.95, 130.79, 130.18, 114.12, 100.13, 55.37, 46.37, 20.29; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -81.01 (s, 3F), -110.65 – -113.14 (m, 1F), -113.19 – -115.24 (m, 1F), -124.55 (s, 2F), -125.93 (s, 2F); **HRMS** Calcd for $C_{14}H_{12}F_9IONa$ [M+Na$^+$]: 516.9681, Found: 516.9680.



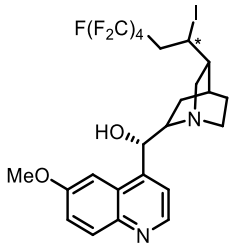
22 R_f = 0.8, Hexane

Compound **22** was isolated in 91% yield (109 mg) following the general procedure **C**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 9.0 Hz, 2H), 6.77 (d, *J* = 9.0 Hz, 2H), 4.38-4.32 (m, 1H), 3.95 (t, *J* = 6.1 Hz, 2H), 3.07-2.62 (m, 2H), 1.98-1.69 (m, 5H), 1.68-1.56 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.15, 132.38, 116.40, 112.95, 67.81, 41.69 (t, *J* = 20.9 Hz), 40.06, 28.23, 26.52, 20.34; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -81.19 (s, 3F), -110.63 – -113.25 (m, 1F), -114.02 – -116.26 (m, 1F), -124.73 (s, 2F), -126.10 (q, *J* = 14.8 Hz, 2F); **HRMS** Calcd for $C_{16}H_{15}BrF_9IONa$ [M+Na$^+$]: 622.9099, Found: 622.9096.



23 R_f = 0.7, 1% acetone in Hexane

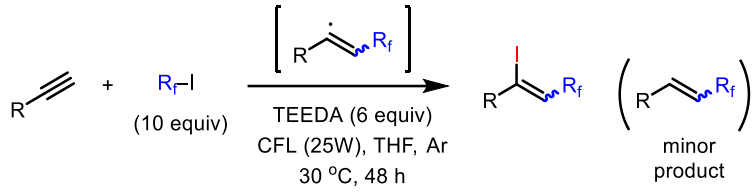
Compound **23** was isolated in 80% yield (112 mg) following the general procedure **C**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.6 Hz, 1H), 6.72 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.65 (d, *J* = 2.2 Hz, 1H), 4.44-4.22 (m, 1H), 3.96 (t, *J* = 6.0 Hz, 2H), 3.03-2.69 (m, 4H), 2.56- 2.36 (m, 2H), 2.25 (t, *J* = 10.3 Hz, 1H), 2.21-1.69 (m, 10H), 1.68-1.36 (m, 6H), 0.91 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 220.99, 157.07, 137.88, 132.20, 126.45, 114.70, 112.21, 67.50, 50.54, 48.13, 44.11, 41.69 (t, *J* = 20.8 Hz), 40.13, 38.50, 35.98, 31.71, 29.77, 28.36, 26.68, 26.61, 26.05, 21.70, 20.35, 13.96; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.82 (s, 3F), -109.99 – -112.70 (m, 1F), -113.59 – -116.17 (m, 1F), -124.36 (s, 2F), -125.71 (m, 2F); **HRMS** Calcd for $C_{28}H_{33}F_9IO_2$ [M+H$^+$]: 699.1376, Found: 699.1379.



24 R_f = 0.7, 5% CH_3OH in CH_2Cl_2

Compound **24** was isolated in 70% yield (94 mg) following the general procedure **C**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 3.8 Hz, 1H), 8.00 (d, *J* = 9.1 Hz, 1H), 7.54 (d, *J* = 3.8 Hz, 1H), 7.44-7.32 (m, 1H), 5.65 (s, 1H), 4.11-4.02 (m, 1H), 4.01-3.90 (m, 3H), 3.59 (s, 1H), 3.30-3.09 (m, 2H), 3.08-2.78 (m, 2H), 2.70 (d, *J* = 11.5 Hz, 1H), 2.59 (d, *J* = 10.1 Hz, 1H), 2.14 (s, 2H), 1.88 (s, 2H), 1.53 (s, 1H), 1.44-1.24 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.07, 147.54, 147.40, 144.15, 131.55, 126.54, 121.75, 118.46, 101.38, 71.33, 61.94, 60.12, 56.00, 44.24, 43.11, 39.05 (t, *J* = 20.8 Hz), 27.51, 26.58, 24.16, 20.03; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.96 (s, 3F), -110.95 – -116.63 (m, 2F), -123.23 – -125.12 (m, 2F), -125.28 – -126.74 (m, 2F); **HRMS** Calcd for $C_{24}H_{25}F_9IN_2O_2$ [M+H$^+$]: 671.0812, Found: 671.0815.

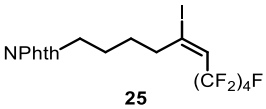
7.2 General procedure and substrate scope for addition of perfluorobutyl iodide to alkynes



Scheme S21

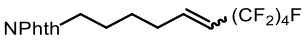
General procedure D for the synthesis of compound 25 and 26:

Alkynes (0.2 mmol, 1.0 equiv), perfluoroalkyl iodide (2.0 mmol, 10.0 equiv) and *N,N,N',N'*-tetraethylenediamine (TEEDA) (1.2 mmol, 6.0 equiv) were dispersed in 2 mL of THF. The reaction vial was purged with Ar for 1 min and then sealed with PTEF cap. The reaction mixture was vigorously stirred at 30 °C under irradiation of CFL lamp (25W, laid 10 CM away from the vial) for 36 h. After that, the mixture was concentrated *in vacuo*, and the residue was purified by silica gel flash chromatography to give the desired product.



25 R_f = 0.6, Hexane

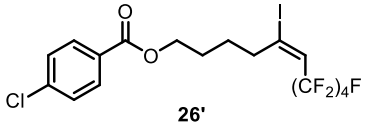
Compound **25**[5] was isolated in 72% yield (83 mg) following the general procedure **D**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85-7.82 (m, 2H), 7.75-7.66 (m, 2H), 6.33 (t, *J* = 14.4 Hz, 1H), 3.71 (t, *J* = 6.8 Hz, 2H), 2.67 (t, *J* = 6.6 Hz, 2H), 1.82-1.55 (m, 4H); **^{19}F NMR** (376 MHz, CDCl3) δ -81.58 (s, 3F), -106.10 (s, 2F), -124.75 (s, 2F), -126.39 (s, 2F); **HRMS** Calcd for $C_{18}H_{13}F_9INO_2Na$ [M+Na$^+$]: 595.9739, Found: 595.9846.



25' R_f = 0.6, Hexane

Compound **25'** was isolated in 19% yield (17 mg) following the general procedure **D**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90-7.80 (m, 2H), 7.76-7.67 (m, 2H), 6.41-6.34 (m, 0.7 H), 6.12-6.03 (m, 0.3 H), 5.75-5.37 (m, 1H), 3.80-3.57 (m, 2H), 2.43-2.12 (m, 2H), 1.78-1.61 (m, 2H), 1.54-1.46 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.54, 144.84, 142.60 (t, *J* = 8.8 Hz), 134.09, 132.26, 123.38, 117.45 (t, *J* = 22.9 Hz), 116.69 (t, *J* = 23.4 Hz), 37.79, 37.61, 31.60, 28.21, 28.08, 26.42, 25.38; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.10 – -81.73 (m, 3F), -106.45 – -107.38 (m, 0.6), -110.35 – -112.81 (m, 1.4), -

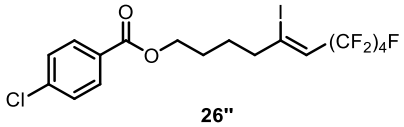
123.25 – -125.04 (m, 2F), -124.99 – -126.54 (m, 2F); **HRMS** Calcd for $C_{18}H_{14}F_9NO_2Na$ [M+Na$^+$]: 470.0773, Found: 470.0778.



26'

R_f = 0.7, Hexane

Compound **26'**[5] was isolated in 61% yield (71 mg) following the general procedure **D**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 6.37 (t, *J* = 14.4 Hz, 1H), 4.34 (t, *J* = 5.6 Hz, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 1.87-1.70 (m, 4H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -77.39 – -83.32 (m, 3F), -102.67 – -107.14 (m, 2F), -120.37 – -124.27 (m, 2F), -124.03 – -127.69 (m, 2F).

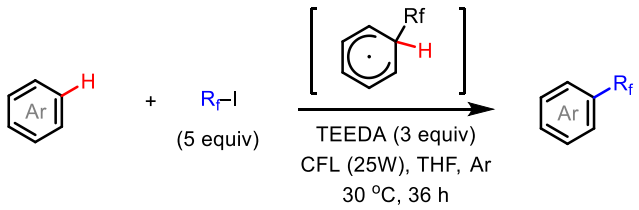


26"

R_f = 0.7, Hexane

Compound **26''**[5] was isolated in 11% yield (13 mg) following the general procedure **D**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 6.29 (t, *J* = 13.0 Hz, 2H), 4.34 (s, 3H), 2.74 (s, 2H), 1.77 (m, 4H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.46 (s, 3F), -108.33 (s, 2F), -123.34 (s, 2F), -125.29 (s, 2F).

8. General procedure and substrate scope for C-H perfluorobutylation of electron-rich arene and heteroarene

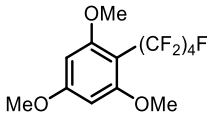


Scheme S22

General procedure E for the synthesis of compound 27-37:

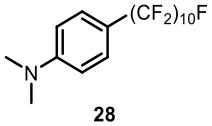
Electron-rich arene or heteroarene (0.2 mmol, 1.0 equiv), perfluoroalkyl iodide (1.0 mmol, 5.0 equiv) and *N*,*N*,*N'*,*N'*-tetraethylenediamine (TEEDA) (0.6 mmol, 3.0 equiv) were dispersed in 2 mL of THF. The reaction vial was purged with Ar for 1 min then sealed with PTEF cap. The reaction mixture was vigorously stirred at 30 °C under

irradiation of CFL lamp (25W, laid 10 CM away from the vial) for 36 h. After that, the mixture was concentrated *in vacuo*, and the residue was purified by silica gel flash chromatography to give the desired product.



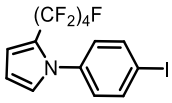
27 R_f = 0.4, Hexane

Compound **27** was isolated in 56% yield (43 mg; and 32% of starting material **27-1** was recovered) following the general procedure **E**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.14 (s, 2H), 3.84 (s, 3H), 3.80 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.98, 161.88 (t, *J* = 2.2 Hz), 98.60 (t, *J* = 21.8 Hz), 91.79, 56.44, 55.47; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.67 (t, *J* = 11.6 Hz, 3F), -101.07 – -104.45 (m, 2F), -122.76 – -123.27 (q, *J* = 9.6 Hz, 2F), -125.36 – -127.17 (m, 2F); **HRMS** Calcd for $C_{13}H_{12}F_9O_3$ [M+H$^+$]: 387.0637, Found: 387.0640.



28 R_f = 0.8, Hexane

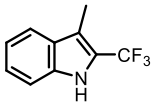
Compound **28** was isolated in 52% yield (67 mg; and 34% of starting material **28-1** was recovered) following the general procedure **E**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.8 Hz, 2H), 6.72 (d, *J* = 8.9 Hz, 2H), 3.02 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.53, 128.01 (t, *J* = 6.3 Hz), 115.43, 111.28, 40.18; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.06 – -81.37 (m, 3F), -108.23 – -110.06 (m, 2F), -118.80 – -124.76 (m, 14F), -125.57 – -127.21 (m, 2F); **HRMS** Calcd for $C_{18}H_{11}F_{21}N$ [M+H$^+$]: 640.0551, Found: 640.0557.



29 R_f = 0.7, Hexane

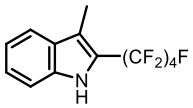
Compound **29** was isolated in 55% yield (54 mg; and 40% of starting material **29-1** was recovered) following the general procedure **E**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.84 (s, 1H), 6.74 (s, 1H), 6.33 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.48, 138.04, 129.28, 129.04, 120.13 (t, *J* = 29.9 Hz),

115.67, 109.27, 94.26; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.73 (t, *J* = 11.2 Hz, 3F), -99.87 – -101.89 (m, 2F), -121.16 (q, *J* = 9.5 Hz, 2F), -124.11 – -127.25 (m, 2F); **HRMS** Calcd for $C_{14}H_7F_9IN$ [M+H$^+$]: 486.9479, Found:486.9483.



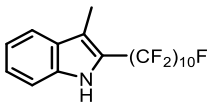
30 R_f = 0.4, 2% acetone in Hexane

3-Methyl indole **30-1** (0.2 mmol, 1.0 equiv) and *N*,*N*,*N'*,*N'*-tetraethylenediamine (TEEDA) (0.6 mmol, 3.0 equiv) were dispersed in 2 mL of THF. The reaction vial was purged with CF_3I for 5 min and then sealed with PTEF cap. The reaction mixture was stirred at 30 ^oC under the irradiation of CFL lamp (25W, laid 10 CM away from the vial) for 36 h. After that, the mixture was concentrated *in vacuo*, and the residue was purified by silica gel flash chromatography to give compound **30**[10] in 66% yield (26 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 2.44 (d, *J* = 1.7 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -58.10 (s, 3F).



31 R_f = 0.4, 2% acetone in Hexane

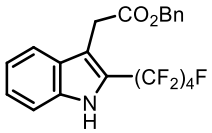
Compound **31** was isolated in 80% yield (56 mg) following the general procedure **E**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 2.46 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.07, 128.46, 125.09, 120.52, 120.22, 119.54 116.86 (t, *J* = 3.2 Hz), 111.65, 8.71; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -77.96 – -83.88 (m, 3F), -106.64 – -111.68 (m, 2F), -120.94 – -124.85 (m, 2F), -124.85 – -127.69 (m, 2F); **HRMS** Calcd for $C_{13}H_7F_9N$ [M-H$^+$]: 348.0440, Found: 348.0438.



32 R_f = 0.5, 2% acetone in Hexane

Compound **32** was isolated in 91% yield (118 mg) following the general procedure **E** (90% yield (117 mg) was obtained under the irradiation of UV lamp (254 nm, 25W) for

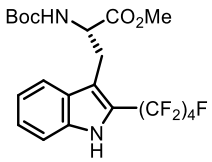
36 hours; 68% yield (88 mg) was obtained after irradiated in sunlight for 4 hours). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 2.44 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.08, 128.47, 125.08, 120.50, 120.22, 119.67 (t, *J* = 28.4 Hz), 116.84 (t, *J* = 3.3 H), 111.65, 8.65; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.42 – - 81.05 (m, 3F), -108.59 (s, 2F), -119.29 – -121.97 (m, 10F), -122.11 (m, 2F), -122.70 (m, 2F), -126.08 (m, 2F); **HRMS** Calcd for $C_{19}H_7F_{21}N$ [M-H$^+$]: 648.0248, Found: 648.0238.



33'

R_f = 0.4, 2% acetone in Hexane

Compound **33-1** (0.2 mmol, 1.0 equiv), perfluoroalkyl iodide **2** (1.0 mmol, 5.0 equiv) and *N,N,N',N'*-tetraethylenediamine (TEEDA) (0.6 mmol, 3.0 equiv) were dispersed in 2 mL of THF. The reaction vial was purged with Ar for 1 min and then sealded with PTEF cap. The reaction mixture was stirred at 30 ^oC under the irradiation of CFL lamp (25W, laid 10 CM away from the vial) for 36 h. After that, the mixture was concentrated *in vacuo*, and the residue was dissolved in actone (15 mL). BnBr (0.3 mmol, 1.5 equiv) was added, the resulting mixture was stirred at 30 ^oC for another 12 hour. Then the mixture was concentrated *in vacuo*, and the residue purified by silica gel flash chromatography to give compound **33'** in 67% yield (65 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.43-7.27 (m, 7H), 7.20 (t, *J* = 7.3 Hz, 1H), 5.16 (s, 2H), 3.98 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.60, 136.07, 135.82, 128.61, 128.33, 128.24, 127.73, 125.37, 121.17, 120.47, 113.09, 111.88, 66.96, 30.16; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.10 – -80.89 (m, 3F), -106.79 – -108.95 (m, 2F), -120.92 – -123.91 (m, 2F), -124.09 – -127.75 (m, 2F); **HRMS** Calcd for $C_{21}H_{18}F_9N_2O_2$ [M+NH$_4^+$]: 501.1219, Found: 501.1216.

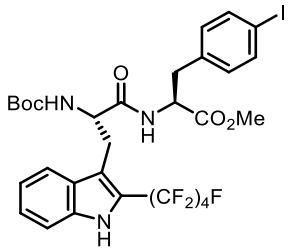


34'

R_f = 0.4, 4% acetone in Hexane

Compound **34-1** (0.2 mmol, 1.0 equiv), perfluoroalkyl iodide **2** (1.0 mmol, 5.0 equiv)

and *N,N,N',N'*-tetraethylenediamine (TEEDA) (0.6 mmol, 3.0 equiv) were dispersed in 2 mL of THF. The reaction vial was purged with Ar for 1 min and then sealded with PTEF cap. The reaction mixture was stirred at 30 ^{o}C under the irradiation of CFL lamp (25W, laid 10 CM away from the vial) for 36 hour. After that, the mixture was concentrated *in vacuo*, and the residue was dissolved in THF (2 mL). Boc_2O (2.0 mmol, 10.0 equiv), DIPEA (0.4 mmol, 2.0 equiv) were added, and the resulting mixture was stirred at 30 ^{o}C for another 12 hour. The reaction was quenched with 0.3 M HCl 20 mL and extracted with dichloromethane. Then organic phase was separated, washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by silica gel flash chromatography to give compound **34'** in 65% yield (70 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 5.15 (d, *J* = 8.3 Hz, 1H), 4.67 (q, *J* = 7.1 Hz, 1H), 3.64 (s, 3H), 3.40-3.24 (m, 2H), 1.36 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.60, 155.12, 136.27, 129.69, 127.66, 125.31, 121.03, 120.47, 115.47, 111.91, 80.03, 54.26, 52.37, 29.35, 28.29, 28.03; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.67 (t, *J* = 11.0 Hz, 3F), -105.25 – -109.24 (m, 2F), -121.92 – - 123.14 (m, 2F), -125.03 – -126.30 (m, 2F); **HRMS** Calcd for $C_{21}H_{21}F_9N_2O_4Na$ [M+Na^{+}]: 559.1250, Found: 559.1252

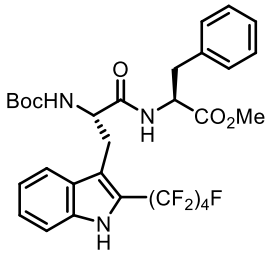


35

R_f = 0.3, 20% acetone in Hexane

Compound **35** was isolated in 68% yield (110 mg; and 23% of starting material **35-1** was recovered) following the general procedure **E**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 6.71 (d, *J* = 8.1 Hz, 2H), 6.08 (d, *J* = 6.7 Hz, 1H), 5.16 (s, 1H), 4.67 (q, *J* = 12.2, 1H), 4.50-4.30 (m, 1H), 3.58 (s, 3H), 3.28 (d, *J* = 5.2 Hz, 2H), 3.06-2.83 (m, 2H), 1.37 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.98,

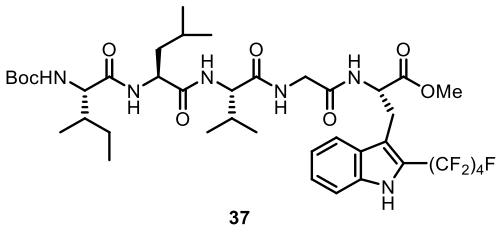
170.83, 155.28, 137.66, 136.31, 135.39, 131.36, 127.36, 125.54, 121.30, 120.93, 120.65, 120.36, 115.73, 111.88, 92.75, 80.26, 55.35, 53.17, 52.40, 37.70, 28.29; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -79.81 – - 81.92 (m, 3F), -105.42 – -109.99 (m, 2F), -122.70 (d, *J* = 10.3 Hz, 2F), -124.60 – -127.32 (m, 2F); **HRMS** Calcd for $C_{30}H_{29}F_9IN_3O_5Na$ [M+Na$^+$]: 832.0900, Found: 832.0905.



36

R_f = 0.3, 20% acetone in Hexane

Compound **36** was isolated in 65% yield (89 mg; and 20% of starting material **36-1** was recovered) following the general procedure **E**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.40 (s, 1H), 7.79 (d, *J* = 6.7 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.23-7.14 (m, 4H), 6.98 (s, 2H), 6.20 (d, *J* = 5.8 Hz, 1H), 5.16 (d, *J* = 6.1 Hz, 1H), 4.73 (q, *J* = 13.3, 5.9 Hz, 1H), 4.45 (d, *J* = 6.3 Hz, 1H), 3.58 (s, 3H), 3.37-3.15 (m, 2H), 3.07-2.94 (m, 2H), 2.81 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.24, 170.89, 165.95, 155.22, 136.58, 135.74, 129.33, 128.54, 127.37, 127.15, 125.16, 120.94, 120.45, 115.38, 112.05, 80.09, 55.45, 53.37, 52.20, 38.66, 38.18, 28.16; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -80.90 (s, 3F), -104.70 – -110.11 (m, 2F), -122.68 (s, 2F), -125.82 (s, 2F); **HRMS** Calcd for $C_{30}H_{30}F_9N_3O_5Na$ [M+Na$^+$]: 706.1934, Found: 706.1938.



37

R_f = 0.3, 5% CH_3OH in DCM

Compound **37-1** (0.1 mmol, 1.0 equiv), C_4F_9I (0.5 mmol, 5.0 equiv) and *N,N,N',N'*-tetraethylenediamine (TEEDA) (0.3 mmol, 3.0 equiv) were dispersed in 2 mL of THF. The reaction vial was purged with Ar for 1 min and the sealed with PTEF cap. The reaction mixture was stirred at 30 ^oC under the irradiation of CFL lamp (25W, laid 10 CM away from the vial). After 12 hour, C_4F_9I (0.5 mmol, 5.0 equiv) and *N,N,N',N'*-

tetraethylenediamine (TEEDA) (0.3 mmol, 3.0 equiv) were added and the resulting mixture was stirred at 30 ^{o}C under the irradiation of CFL lamp (25W, laid 10 CM away from the vial) for another 24 hour under Ar atmosphere. After that, the mixture was concentrated *in vacuo*, and the residue was purified by silica gel flash chromatography to give the compound **37** in 50% yield (46 mg; and 35% of the starting material compound **37-1** was recovered). **^{1}H NMR** (400 MHz, MeOD) δ 7.66 (d, *J* = 8.1 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 4.68 (t, *J* = 7.4 Hz, 1H), 4.50 (s, 1H), 4.10 (d, *J* = 7.1 Hz, 1H), 3.92-3.73 (m, 3H), 3.44 (s, 3H), 3.42-3.31 (m, 2H), 2.09-1.97 (m, 1H), 1.78-1.48 (m, 5H), 1.40 (s, 9H), 1.18-1.08 (m, 1H), 0.97-0.78 (m, 18H); **^{13}C NMR** (101 MHz, MeOD) δ 174.56, 173.90, 173.33, 170.89, 157.91, 138.19, 128.65, 125.69, 121.34, 120.93, 115.65, 113.14, 80.51, 60.54, 55.25, 52.87, 52.57, 43.20, 41.67, 38.07, 31.79, 28.70, 28.09, 25.89, 25.67, 23.46, 22.02, 19.71, 18.94, 16.06, 11.36; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -78.51 (s, 3F), -101.53 – -108.27 (m, 2F), -119.77 (s, 2F), -123.06 (s, 2F); **HRMS** Calcd for $C_{40}H_{55}F_9N_6O_8Na$ [M+Na^{+}]: 941.3830, Found: 941.3832.

9. Titration experiment of $C_{10}F_{21}I$ with TEEDA

^{19}F NMR spectra of eight samples of mixtures of $C_{10}F_{21}I$ and TEEDA in $CDCl_3$ were recorded at 298 K. The total volume of the mixture was 0.5 mL, the amount of $C_{10}F_{21}I$ was kept constant at 0.01 mmol (6.5 mg) while that of TEEDA was varied from 0 to 0.1 mmol. The molar ratios of $C_{10}F_{21}I$:TEEDA were 1:0, 1:1, 1:2, 1:3, 1:4, 1:5, 1:7, 1:10. Fluorobenzene ($\delta_{F\text{-}Ph}$ = -113.066) was used as internal standard.

The ^{19}F NMR signal of -CF_2I shifted upfield when the amount of TEEDA increased，indicating the formation of halogen bond between $C_{10}F_{21}I$ and TEEDA (Figure S1).

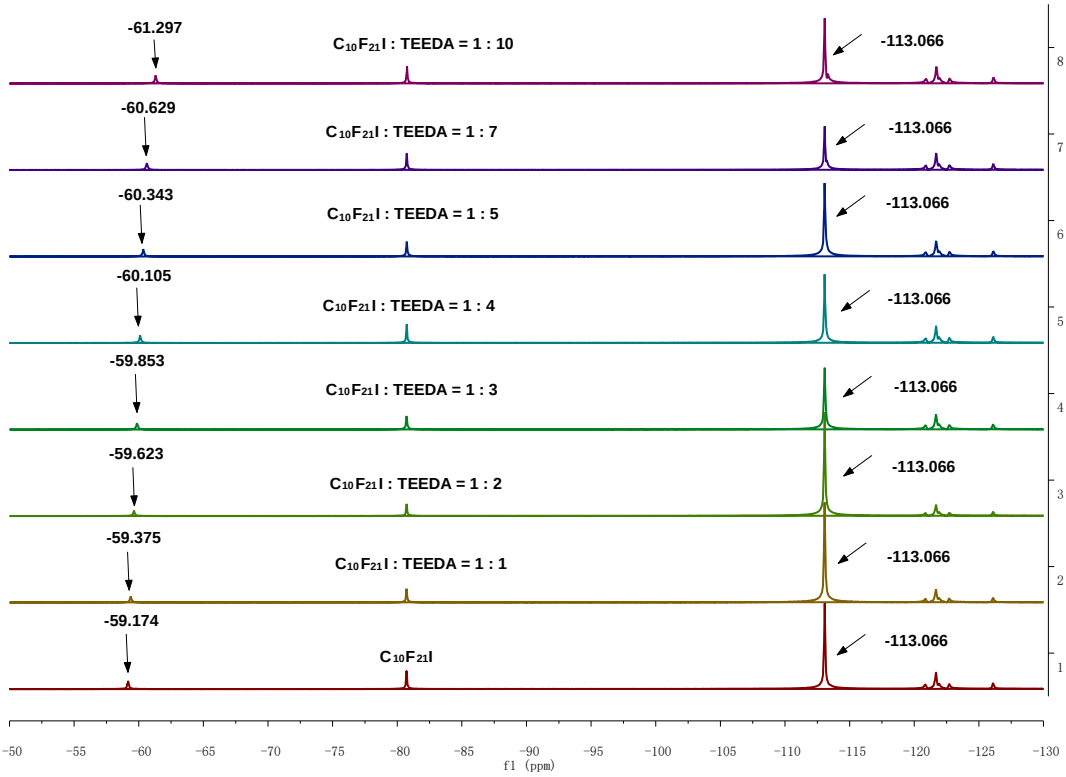


Figure S1. ^{19}F NMR shift of $C_{10}F_{21}I$ with TEEDA

10. Determination of binding stoichiometry of halogen bond complex[11]

The binding stoichiometry between $C_{10}F_{21}I$ and halogen bond acceptors (XB acceptor: TEEDA, TEA, THF, dioxane) were evaluated using Job's plot analysis[10]: ^{19}F NMR spectra of eleven samples of mixtures of $C_{10}F_{21}I$ and XB acceptor in $CDCl_3$ were recorded at 298 K. Fluorobenzene ($\delta_{F\text{-}Ph}$ = -113.066) was used as internal standard. The total volume of the mixture was 0.5 mL, and the total amount of $C_{10}F_{21}I$ and halogen bond acceptor was kept constant at 0.25 mmol (0.5 M), while the amount of $C_{10}F_{21}I$ was varied from 0 to 0.25 mmol (0-0.5 M). The molar ratios of $C_{10}F_{21}I$/ ($C_{10}F_{21}I$ + XB acceptor) were 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0. ^{19}F NMR for each sample was recorded and the chemical shifts differences ($\Delta\delta$) for $-CF_2I$ were used to draw the plot. The stoichiometry was determined by plotting ratios of $[C_{10}F_{21}I]\times\Delta\delta$ against ratios of $[C_{10}F_{21}I]$/ $[C_{10}F_{21}I$ + XB acceptor] to afford a maximum at

ratio $[C_{10}F_{21}I]/[C_{10}F_{21}I + XB\ acceptor] = 0.5$, which meant a 1:1 complex ratio between $C_{10}F_{21}I$ and XB acceptor.

10.1 Determination of binding stoichiometry of $C_{10}F_{21}I$ with TEEDA

	$[C_{10}F_{21}I]$ (M)	Δδ (ppm)	$[C_{10}F_{21}I]/[C_{10}F_{21}I + TEEDA]$	$[C_{10}F_{21}I]\times\Delta\delta$ (M.ppm)
1	0	0	0	0
2	0.05	4.117	0.1	0.2059
3	0.10	3.663	0.2	0.3663
4	0.15	3.215	0.3	0.4823
5	0.20	2.831	0.4	0.5662
6	0.25	2.144	0.5	0.5360
7	0.30	1.965	0.6	0.5895
8	0.35	1.384	0.7	0.4844
9	0.40	0.987	0.8	0.3948
10	0.45	0.458	0.9	0.2061
11	0.50	0	1.0	0

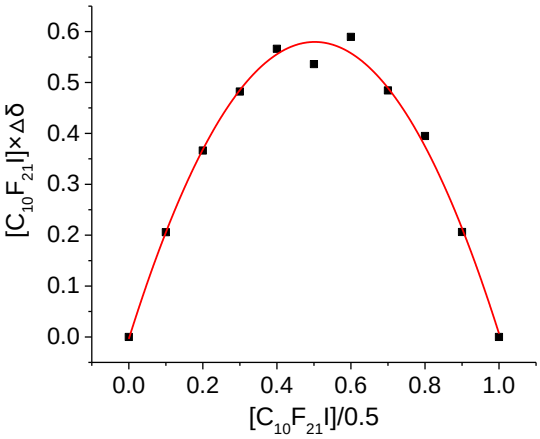


Figure S2

$y = -0.0039 + 2.3239x - 2.3135x^2$, $x_{max} = 2.3239/(-2\times(-2.3135)) = 0.50$

10.2 Determination of binding stoichiometry of $C_{10}F_{21}I$ with TEA

	$[C_{10}F_{21}I]$ (M)	Δδ (ppm)	$[C_{10}F_{21}I]/[C_{10}F_{21}I + TEA]$	$[C_{10}F_{21}I]\times\Delta\delta$ (M.ppm)
1	0	0	0	0
2	0.05	4.006	0.1	0.2003
3	0.10	3.493	0.2	0.3493
4	0.15	2.851	0.3	0.4277
5	0.20	2.505	0.4	0.5010
6	0.25	2.261	0.5	0.5653
7	0.30	1.758	0.6	0.5274

8	0.35	1.393	0.7	0.4876
9	0.40	0.975	0.8	0.3900
10	0.45	0.335	0.9	0.1507
11	0.50	0	1.0	0

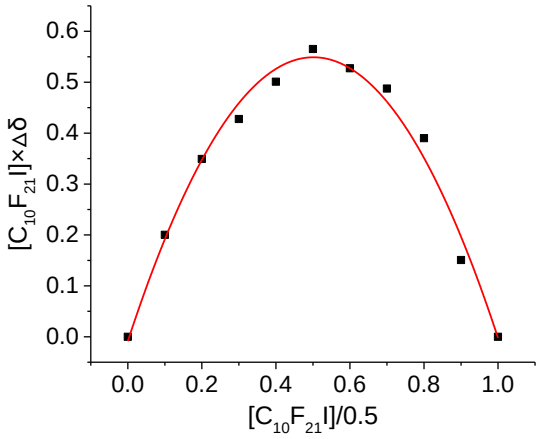


Figure S3

$y = -0.00872 + 2.22459x - 2.21822x^2$, $x_{max} = 2.22459/(-2\times(-2.21822)) = 0.50$

10.3 Determination of binding stoichiometry of $C_{10}F_{21}I$ with THF

	$[C_{10}F_{21}I]$ (M)	Δδ (ppm)	$[C_{10}F_{21}I]/[C_{10}F_{21}I + THF]$	$[C_{10}F_{21}I]\times\Delta\delta$ (M.ppm)
1	0	0	0	0
2	0.05	0.430	0.1	0.0215
3	0.10	0.325	0.2	0.0325
4	0.15	0.282	0.3	0.0423
5	0.20	0.254	0.4	0.0508
6	0.25	0.196	0.5	0.0490
7	0.30	0.165	0.6	0.0495
8	0.35	0.132	0.7	0.0462
9	0.40	0.097	0.8	0.0388
10	0.45	0.020	0.9	0.0090
11	0.50	0	1.0	0

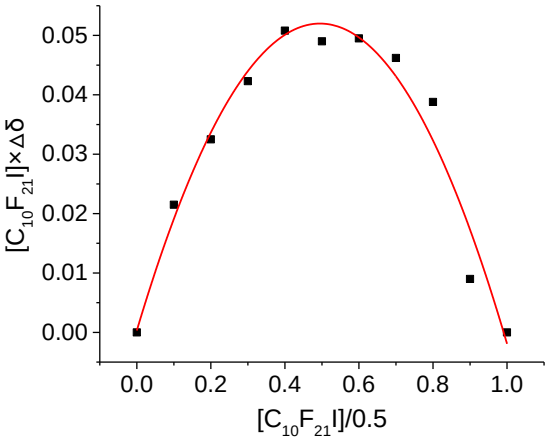


Figure S4

$y = 0.00031 + 0.20895x - 0.21119x^2$, $x_{max} = 0.20895/(-2\times(-0.21119)) = 0.50$

10.4 Determination of binding stoichiometry of $C_{10}F_{21}I$ with dioxane

	$[C_{10}F_{21}I]$ (M)	Δδ (ppm)	$[C_{10}F_{21}I]$/ $[C_{10}F_{21}I$ +Dioxane]	$[C_{10}F_{21}I]\times\Delta\delta$ (M.ppm)
1	0	0	0	0
2	0.05	0.392	0.1	0.0196
3	0.10	0.327	0.2	0.0327
4	0.15	0.302	0.3	0.0453
5	0.20	0.255	0.4	0.0510
6	0.25	0.198	0.5	0.0495
7	0.30	0.173	0.6	0.0519
8	0.35	0.153	0.7	0.0535
9	0.40	0.090	0.8	0.0360
10	0.45	0.047	0.9	0.0211
11	0.50	0	1.0	0

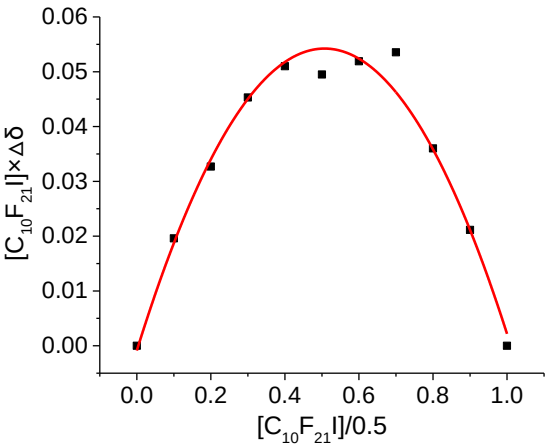


Figure S5

$y = 0.00087 + 0.21731x - 0.21427x^2$, $x_{max} = 0.21731/(-2\times(-0.21427)) = 0.50$

11. Determination of the association constant (K_a)

The association constant (K_a) was calculated using Hanna and Ashbaugh's[12-15] Graphical method: For ideal behaviour in an interaction between an halogen bond donor molecule **$C_{10}F_{21}I$** and an lewis base molecule **LB** to form a halogen bond complex **XB**, we may define an association constant ***K***, where

$$K = [XB]/[LB][\ C_{10}F_{21}I] \quad (1)$$

For 1:1 molecular complexes, when the concentration of lewis base molecule is in large excess we have

$$\delta_{obs} - \delta_0 = \frac{[XB]}{[XB]+[C_{10}F_{21}I]}(\delta_{XB} - \delta_0) \quad (2)$$

where δ_{obs} is the observed fluorine chemical shift of the -CF_2I group in the complexing medium, δ_0 is the fluorine chemical shift of the -CF_2I group in the uncomplexed state and δ_{XB} is the fluorine chemical shift of the -CF_2I group in the pure complex. If $\Delta = \delta_{obs} - \delta_0$ and $\Delta_0 = \delta_{XB} - \delta_0$, then substituting Eq. (1) into Eq. (2), we obtain Eq. (3) as follows:

$$\Delta = \frac{[LB]K}{1+[LB]K}\Delta_0 \quad (3)$$

This assumes that δ_{obs} is the result of molecular complexing between halogen bond donor molecule **$C_{10}F_{21}I$** and lewis base molecule **LB**, and that there are no significant solvent effects on chemical shifts of the various species.

To obtain *K* from a series of measurements of Δ for various values of [LB], the Eq. (3) may be rewritten as:

$$\frac{1}{\Delta} = \frac{1}{K\Delta_0}\ \frac{1}{[LB]} + \frac{1}{\Delta_0} \quad (4)$$

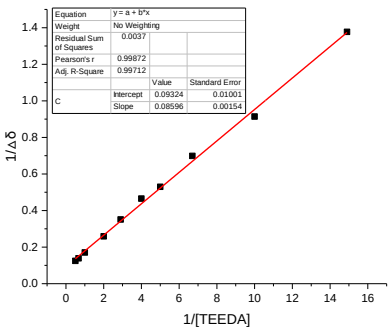
Plots of $1/\Delta$against 1/[LB] should be a straight line, *K* may be obtained from the gradient using the value of $1/\Delta_0$ from the intercept of the line with the ordinate:

$$K = \left(\frac{1}{\Delta_0}\right) / \left(\frac{1}{K\Delta_0}\right) = \text{intercept / gradient} \quad (5)$$

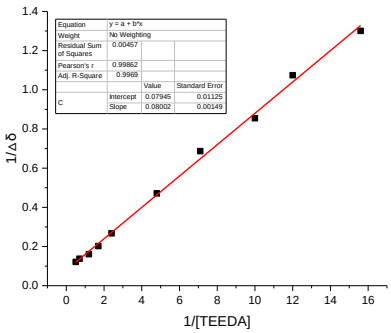
11.1 Determination of the association constant of $C_{10}F_{21}I$ with TEEDA (K_{TEEDA})

^{19}F NMR spectra of ten samples of mixtures of $C_{10}F_{21}I$ and TEEDA in $CDCl_3$ were recorded at 298 K (Fluorobenzene ($\delta_{F\text{-}Ph}$ = -113.066) was used as internal standard). The total volume of the mixture was 0.6 mL, the amount of $C_{10}F_{21}I$ was kept constant at 0.03 mmol (19.4 mg), while that of TEEDA was varied from 0.03 to 1.2 mmol. ^{19}F NMR for each sample was recorded and the chemical shifts differences ($\Delta\delta$) for $-CF_2I$ were used to draw the plot.

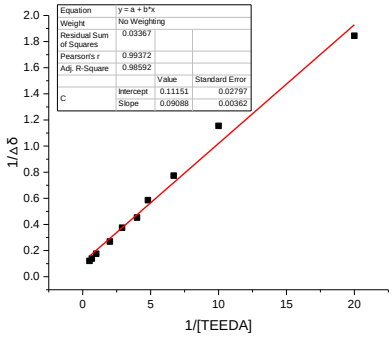
	trial 1				trial 2				trial 3			
	TEEDA (mol/L)	$\frac{1}{[TEEDA]}$ (L/mol)	$\Delta\delta$ (ppm)	$1/\Delta\delta$ (ppm^{-1})	TEEDA (mol/L)	$\frac{1}{[TEEDA]}$ (L/mol)	$\Delta\delta$ (ppm)	$1/\Delta\delta$ (ppm^{-1})	TEEDA (mol/L)	$\frac{1}{[TEEDA]}$ (L/mol)	$\Delta\delta$ (ppm)	$1/\Delta\delta$ (ppm^{-1})
1	2.00	0.5	8.006	0.1249	2.00	0.5	8.237	0.1214	2.00	0.5	8.264	0.1210
2	1.49	0.67	7.199	0.1389	1.43	0.7	7.278	0.1374	1.49	0.67	7.194	0.1390
3	1.00	1.0	5.865	0.1705	0.83	1.2	6.211	0.1610	1.00	1.0	5.682	0.1760
4	0.50	2.0	3.860	0.2591	0.59	1.7	4.950	0.2020	0.50	2.0	3.717	0.2690
5	0.34	2.9	2.849	0.3510	0.42	2.4	3.745	0.2670	0.34	2.9	2.667	0.3750
6	0.25	4.0	2.148	0.4655	0.21	4.8	2.123	0.4710	0.25	4	2.208	0.4529
7	0.20	5.0	1.888	0.5297	0.14	7.1	1.456	0.6868	0.21	4.8	1.706	0.5862
8	0.15	6.7	1.431	0.6988	0.10	10.0	1.170	0.8547	0.15	6.7	1.292	0.7740
9	0.10	10.0	1.094	0.9141	0.083	12.0	0.931	1.0741	0.10	10	0.866	1.1547
10	0.067	14.9	0.726	1.3774	0.064	15.6	0.769	1.3004	0.05	20	0.542	1.8450
	K_{TEEDA} = 0.09324/0.08596 = 1.0847				K_{TEEDA} = 0.07945/0.08002 = 0.9929				K_{TEEDA} = 0.11151/0.09088 = 1.2270			



Trial 1



Trial 2



Trial 3

Figure S6

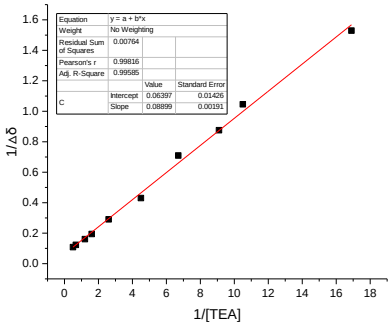
The association constant of $C_{10}F_{21}I$ and TEEDA (K_{TEEDA}) was calculated (average of three experiments) to be 1.1 (K_{TEEDA} = *1.1* M^{-1}).

11.2 Determination of the association constant of $C_{10}F_{21}I$ and TEA (K_{TEA})

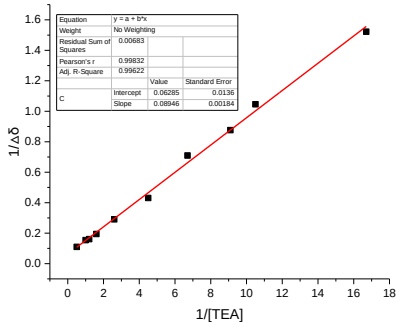
^{19}F NMR spectra of ten samples of mixtures of $C_{10}F_{21}I$ and TEA in $CDCl_3$ were recorded at 298 K (Fluorobenzene ($\delta_{F\text{-}Ph}$ = -113.066) was used as internal standard). The total volume of the mixture was 0.6 mL, the amount of $C_{10}F_{21}I$ was kept constant at 0.03 mmol (19.4 mg), while that of TEA was varied from 0.036 to 1.2 mmol. ^{19}F NMR for each sample was recorded and the chemical shifts differences ($\Delta\delta$) for $-CF_2I$ were used to draw the plot.

	trial 1				trial 2				trial 3			
	TEA (mol/L)	$\frac{1}{[TEA]}$ (L/mol)	$\Delta\delta$ (ppm)	$1/\Delta\delta$ (ppm^{-1})	TEA (mol/L)	$\frac{1}{[TEA]}$ (L/mol)	$\Delta\delta$ (ppm)	$1/\Delta\delta$ (ppm^{-1})	TEA (mol/L)	$\frac{1}{[TEA]}$ (L/mol)	$\Delta\delta$ (ppm)	$1/\Delta\delta$ (ppm^{-1})
1	2.00	0.5	9.225	0.1084	2.00	0.5	9.115	0.1097	2.00	0.5	9.311	0.1074
2	1.49	0.67	8.104	0.1234	1.00	1.0	6.493	0.1540	1.49	0.67	8.032	0.1245
3	0.83	1.2	6.215	0.1609	0.83	1.2	6.215	0.1609	1.0	1.0	6.510	0.1536
4	0.63	1.6	5.141	0.1945	0.63	1.6	5.141	0.1945	0.53	1.9	4.290	0.2331
5	0.38	2.6	3.439	0.2908	0.38	2.6	3.438	0.2909	0.34	2.9	2.946	0.3394
6	0.22	4.5	2.323	0.4305	0.22	4.5	2.321	0.4308	0.26	3.8	2.381	0.4200

7	0.15	6.7	1.409	0.7097	0.15	6.7	1.409	0.7097	0.21	4.8	2.036	0.4912
8	0.11	9.1	1.142	0.8757	0.11	9.1	1.141	0.8764	0.16	6.3	1.601	0.6246
9	0.095	10.5	0.956	1.0460	0.095	10.5	0.956	1.0460	0.11	9.1	1.156	0.8651
10	0.059	16.9	0.654	1.5291	0.06	16.7	0.657	1.5221	0.06	16.7	0.637	1.5700
	K_{TEA} = 0.06397/0.08899 = 0.7188				K_{TEA} = 0.06285/0.08946 = 0.7025				K_{TEA} = 0.06554/0.08965 = 0.7311			



Trial 1



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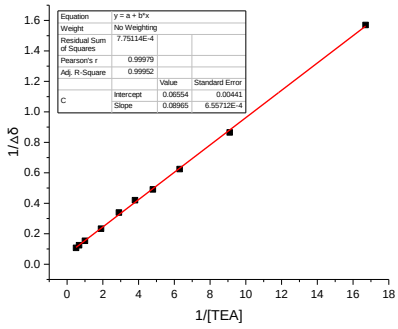


Trial 3

Figure S7

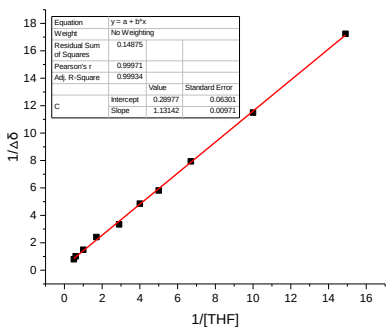
The association constant of $C_{10}F_{21}I$ and TEA (K_{TEA}) was calculated (average of three experiments) to be 0.72 ($K_{TEA} = 0.72\ M^{-1}$).

11.3 Determination of the association constant of $C_{10}F_{21}I$ and THF (K_{THF})

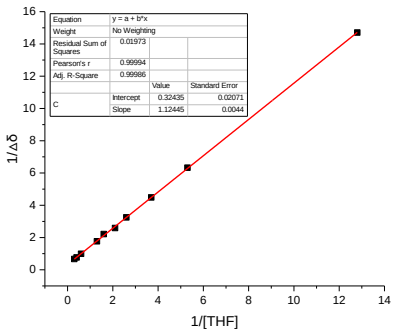
^{19}F NMR spectra of ten samples of mixtures of $C_{10}F_{21}I$ and THF in $CDCl_3$ were recorded at 298 K (Fluorobenzene ($\delta_{F\text{-}Ph}$ = -113.066) was used as internal standard). The total volume of the mixture was 0.6 mL, the amount of $C_{10}F_{21}I$ was kept constant

at 0.03 mmol (19.4 mg), while that of THF was varied from 0.04 to 2.0 mmol. ^{19}F NMR for each sample was recorded and the chemical shifts differences (Δδ) for -CF_2I were used to draw the plot.

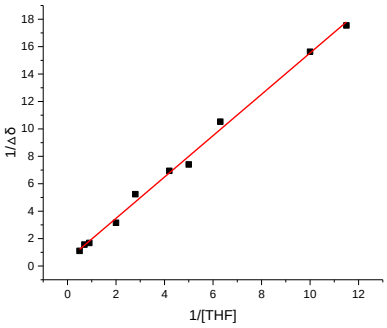
	trial 1				trial 2				trial 3			
	THF (mol/L)	$\frac{1}{[THF]}$ (L/mol)	Δδ (ppm)	1/Δδ (ppm^{-1})	THF (mol/L)	$\frac{1}{[THF]}$ (L/mol)	Δδ (ppm)	1/Δδ (ppm^{-1})	THF (mol/L)	$\frac{1}{[THF]}$ (L/mol)	Δδ (ppm)	1/Δδ (ppm^{-1})
1	2.00	0.5	1.247	0.8019	3.33	0.3	1.488	0.6720	2.00	0.5	0.906	1.1037
2	1.67	0.6	0.985	1.0152	2.50	0.4	1.305	0.7662	1.43	0.7	0.640	1.5625
3	1.00	1.0	0.671	1.4903	1.67	0.6	1.010	0.9900	1.11	0.9	0.594	1.6835
4	0.59	1.7	0.413	2.4213	0.77	1.3	0.566	1.7668	0.50	2.0	0.317	3.1546
5	0.34	2.9	0.299	3.3444	0.63	1.6	0.452	2.2124	0.36	2.8	0.191	5.2356
6	0.25	4.0	0.206	4.8544	0.48	2.1	0.386	2.5907	0.24	4.2	0.144	6.9444
7	0.20	5.0	0.172	5.8140	0.38	2.6	0.308	3.2468	0.20	5.0	0.135	7.4074
8	0.15	6.7	0.126	7.9365	0.27	3.7	0.223	4.4843	0.16	6.3	0.095	10.5263
9	0.10	10.0	0.087	11.4943	0.19	5.3	0.158	6.3291	0.10	10.0	0.064	15.6250
10	0.067	14.9	0.058	17.2414	0.078	12.8	0.068	14.7059	0.087	11.5	0.057	17.5439
	K_{THF} = 0.28977/1.13142 = 0.2561				K_{THF} = 0.32435/1.12445 = 0.2885				K_{THF} = 0.46041/1.50758 = 0.3054			



Trial 1



Trial 2



Trial 3

Figure S8

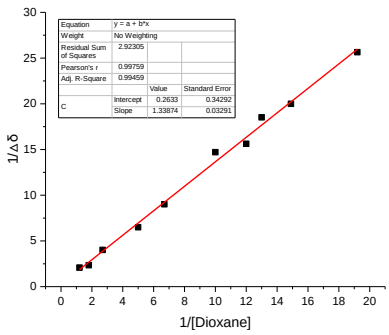
The association constant of $C_{10}F_{21}I$ and TEEDA (K_{THF}) was calculated (average of three experiments) to be 0.28 ($K_{THF} = 0.28\ M^{-1}$).

11.4 Determination of the association constant of $C_{10}F_{21}I$ and dioxane ($K_{Dioxane}$)

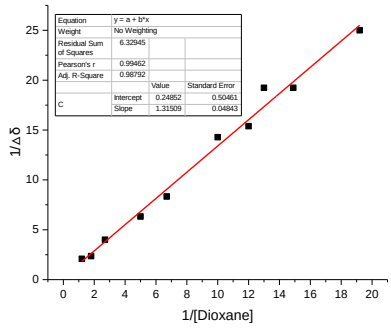
^{19}F NMR spectra of ten samples of mixtures of $C_{10}F_{21}I$ and dioxane in $CDCl_3$ were recorded at 298 K (Fluorobenzene ($\delta_{F\text{-}Ph}$ = -113.066) was used as internal standard). The total volume of the mixture was 0.6 mL, the amount of $C_{10}F_{21}I$ was kept constant at 0.03 mmol (19.4 mg), while that of dioxane was varied from 0.03 to 0.05 mmol. ^{19}F NMR for each sample was recorded and the chemical shifts differences ($\Delta\delta$) for $-CF_2I$ were used to draw the plot.

	trial 1				trial 2				trial 3			
	Dioxane (mol/L)	$\frac{1}{[Dioxane]}$ (L/mol)	Δδ (ppm)	1/Δδ (ppm^{-1})	Dioxane (mol/L)	$\frac{1}{[Dioxane]}$ (L/mol)	Δδ (ppm)	1/Δδ (ppm^{-1})	Dioxane (mol/L)	$\frac{1}{[Dioxane]}$ (L/mol)	Δδ (ppm)	1/Δδ (ppm^{-1})
1	0.83	1.2	0.480	2.0833	0.83	1.2	0.479	2.0877	0.83	1.2	0.464	2.1552
2	0.56	1.8	0.427	2.3419	0.56	1.8	0.424	2.3585	0.56	1.8	0.420	2.3810
3	0.37	2.7	0.249	4.0161	0.37	2.7	0.250	4.000	0.37	2.7	0.250	4.000
4	0.20	5.0	0.154	6.4935	0.20	5.0	0.158	6.3291	0.20	5.0	0.151	6.6225
5	0.15	6.7	0.111	9.0090	0.15	6.7	0.120	8.3333	0.15	6.7	0.110	9.0909

6	0.10	10.0	0.068	14.7059	0.10	10.0	0.070	14.2857	0.10	10.0	0.065	15.3846
7	0.083	12.0	0.064	15.6250	0.083	12.0	0.065	15.3846	0.083	12.0	0.060	16.6667
8	0.077	13.0	0.054	18.5185	0.077	13.0	0.052	19.2308	0.077	13.0	0.055	18.1818
9	0.067	14.9	0.050	20.0000	0.067	14.9	0.052	19.2308	0.067	14.9	0.050	20.0000
10	0.052	19.2	0.039	25.6410	0.052	19.2	0.040	25.0000	0.052	19.2	0.037	27.0270
	$K_{Dioxane}$ = 0.2633/1.33874 = 0.1967				$K_{Dioxane}$ = 0.24852/1.31509 = 0.1890				$K_{Dioxane}$ = 0.15474/1.38685 = 0.1116			



Trial 1



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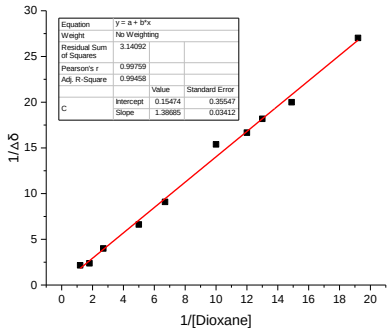


Trial 3

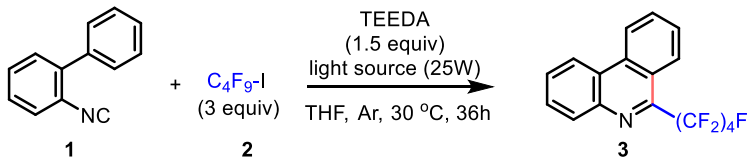
Figure S9

The association constant of $C_{10}F_{21}I$ and TEEDA ($K_{Dioxane}$) was calculated (average of three experiments) to be 0.17 ($K_{Dioxane} = 0.17\ M^{-1}$).

12. Evaluation of different light source

2-Isocyanobiphenyl **1** (35.8 mg, 0.2 mol, 1.0 equiv), C_4F_9I (207.5 mg, 0.6 mol, 3.0 equiv) and TEEDA (0.3 mol, 1.5 equiv) were dispersed in 2 mL of THF. The reaction

vial was then purged with Ar for 1 min, sealed with PTEF cap. The reaction mixture was vigorously stirred at 30 °C under the irradiation of differnet light source (25W, laid 10 CM away from the vial) for 36 h. Then THF was removed under reduced pressure. The resulting residue was dissolved in 1 mL of $CDCl_3$ along with $Cl_2CHCHCl_2$ (20 μL) as an external standard for ^{1}H-NMR analysis. The composition of reaction mixture was based on the Ar-H at 8.73 ppm (d, J = 8.4 Hz, 1H) for compound **3**.



	yield
LED red (620-625 nm)	<2%
LED yellow (585-590 nm)	<2%
LED green (520-525 nm)	<2%
LED blue (460-465 nm)	21%
LED purple (400-405 nm)	57%
CFL white	94%
UV 365 nm	86%
UV 254 nm	92%
sunlight	91%

Scheme S23

As shown in Scheme S23, the source of light clearly has an impact to the reaction of **1** and **2** for synthesis of **3**. Irradiation by LED lamp of red, yellow and green colors (25W) gave little product **3**; the blue LED lamp with relatively shorter emission wavelength (25W) gave 21% yield, the purple LED lamp with relatively shorter emission wavelength (25W) gave 57% yield. The irradiation of UV lamp (254 or 360nm), CFL of the same power intensity or sunlight gave excellent yields. It is known that CFL emit small amount of UV light. These results suggest that the low-intensity irradiation in the UV region is responsible for the XB-promoted photochemical activation of Rf-I.

13. References

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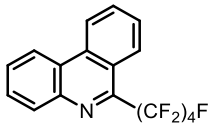
14. Spectra



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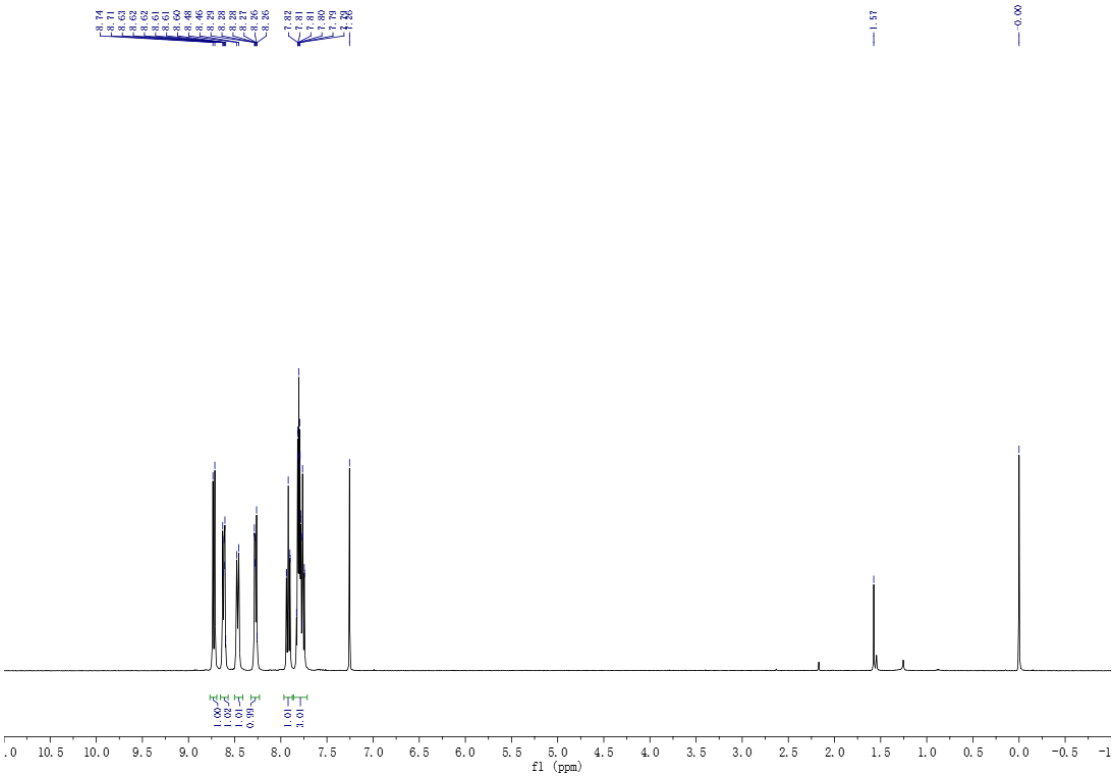
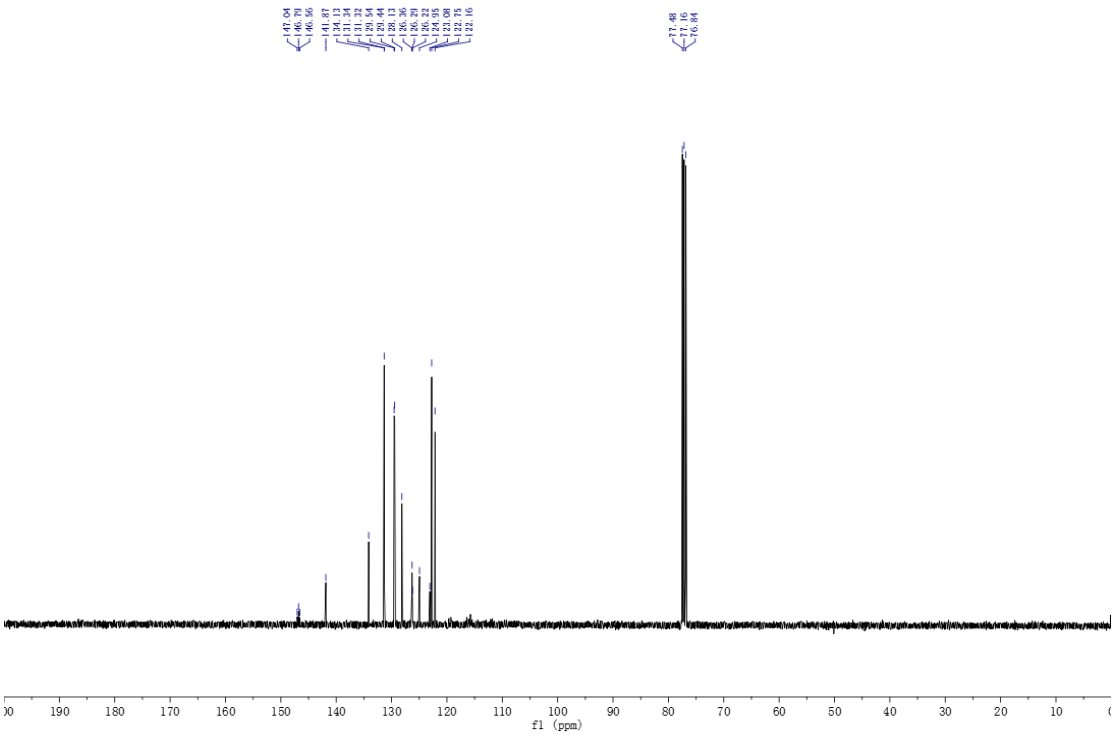
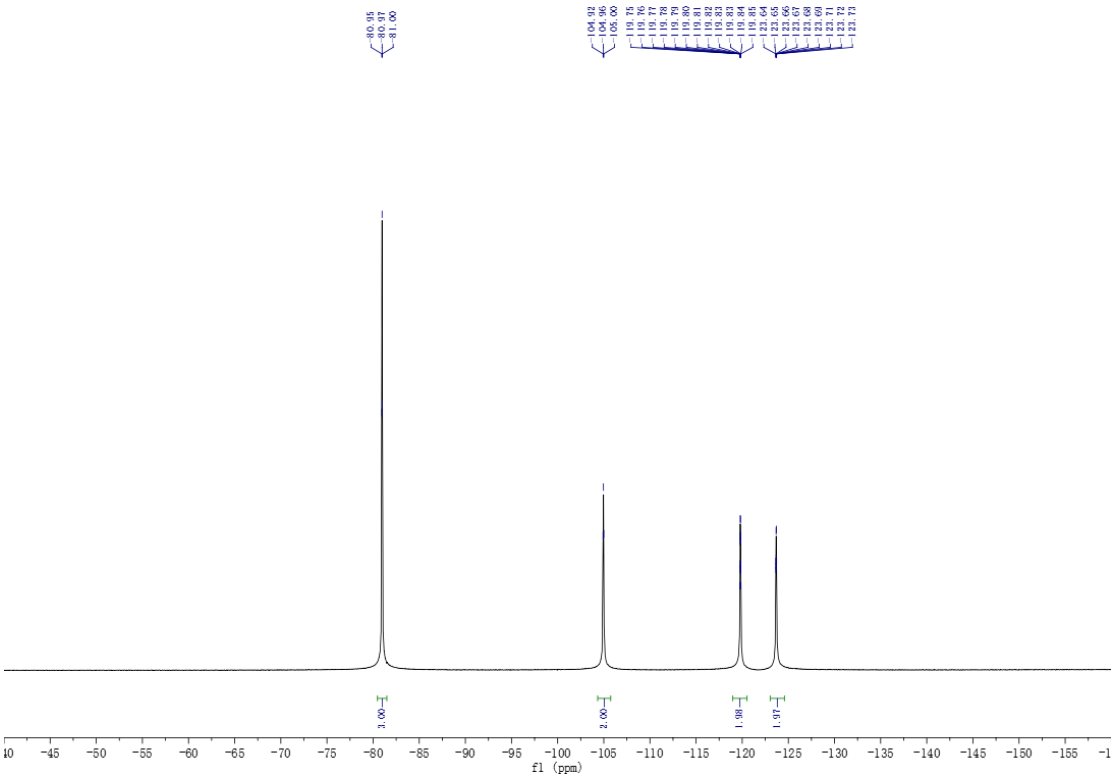


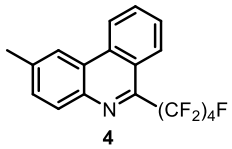
^{1}H NMR of compound **3**

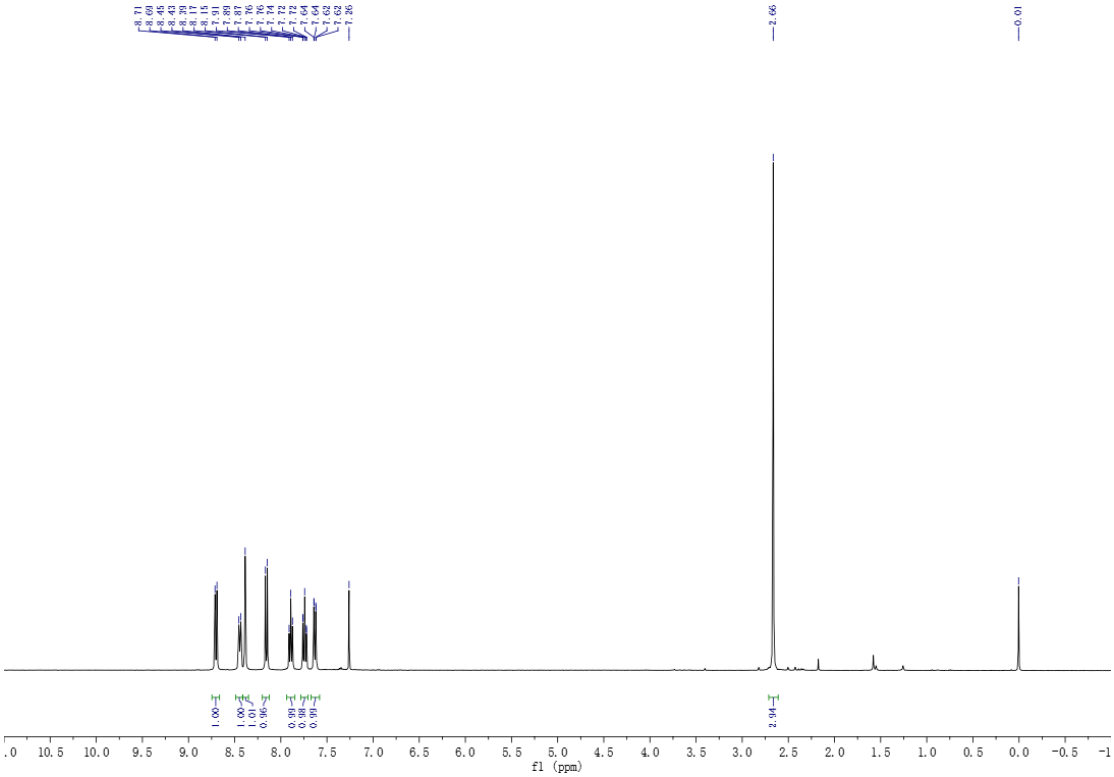


^{13}C NMR of compound **3**

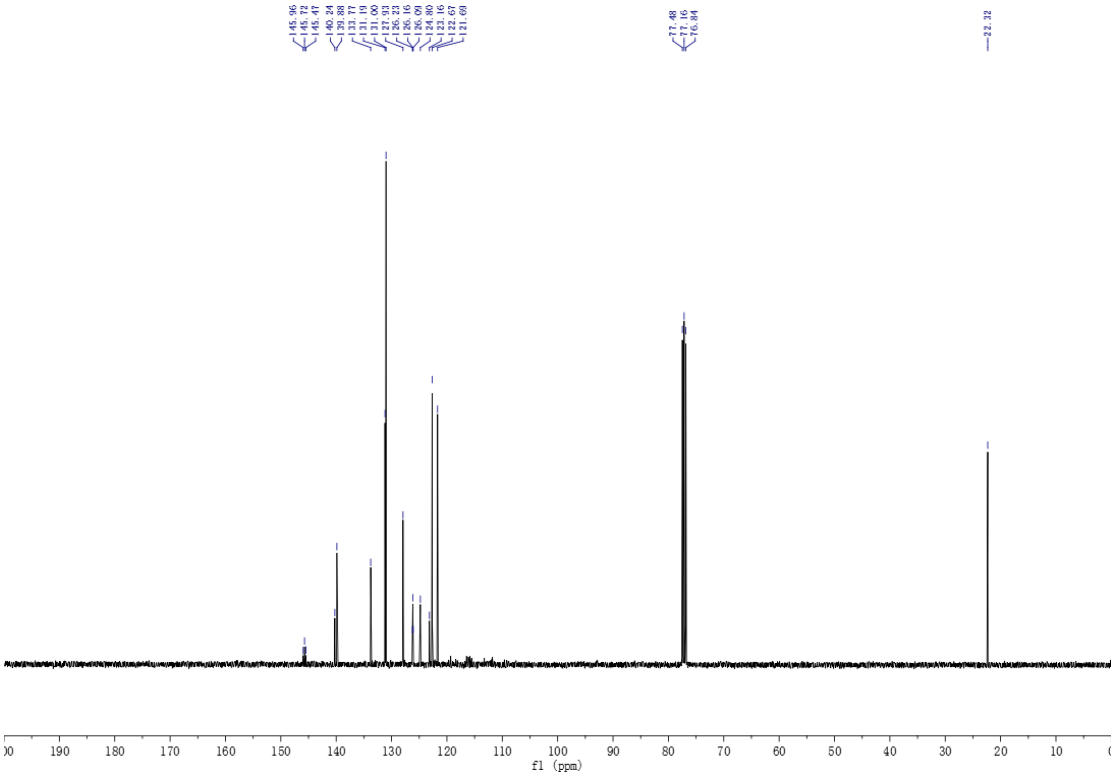


^{19}F NMR of compound **3**





^{1}H NMR of compound **4**



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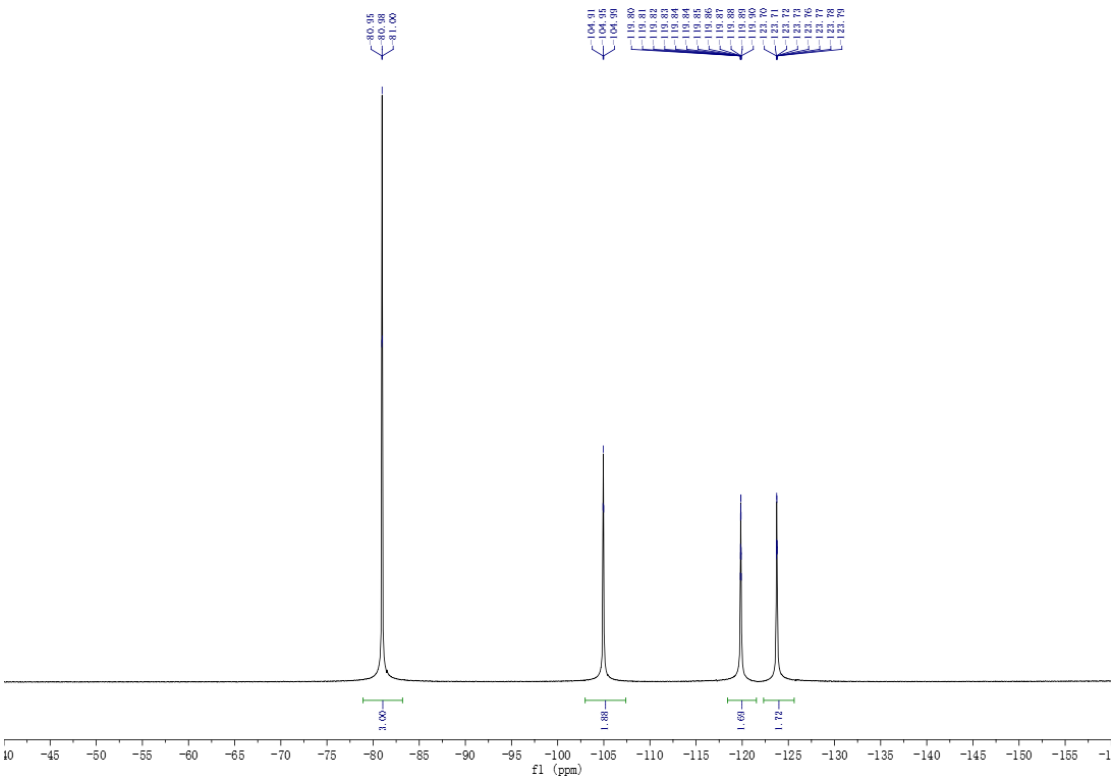

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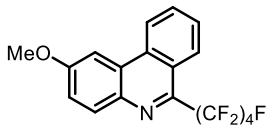

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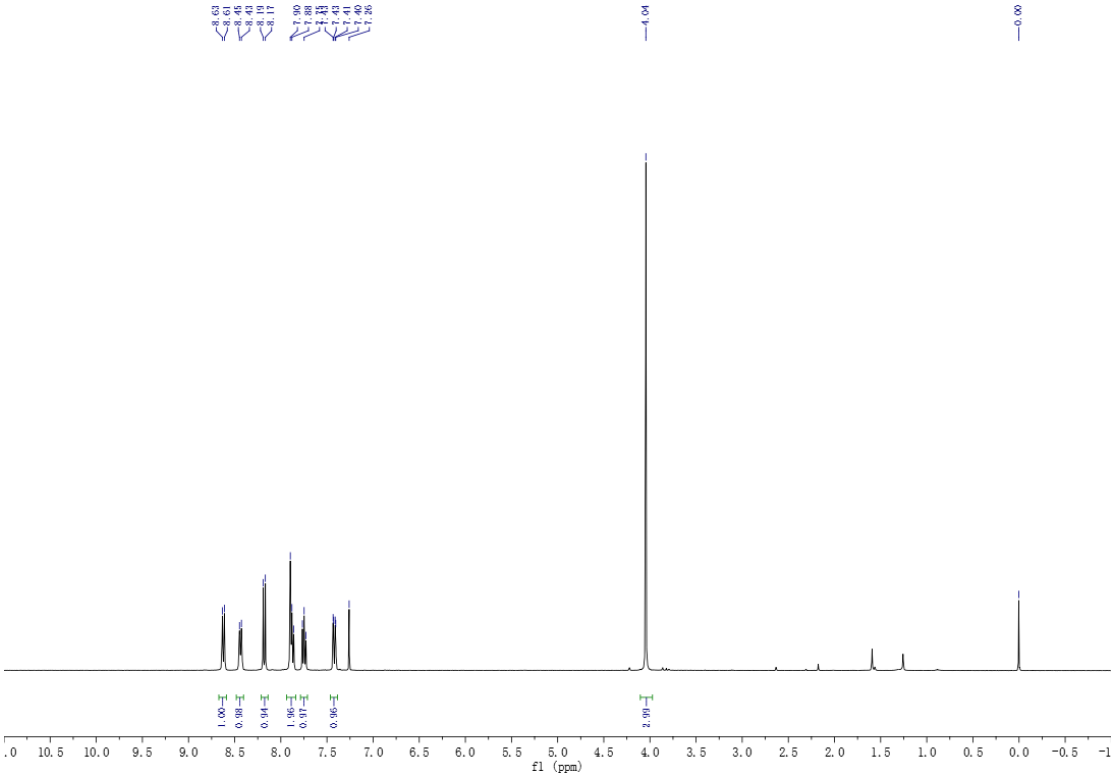
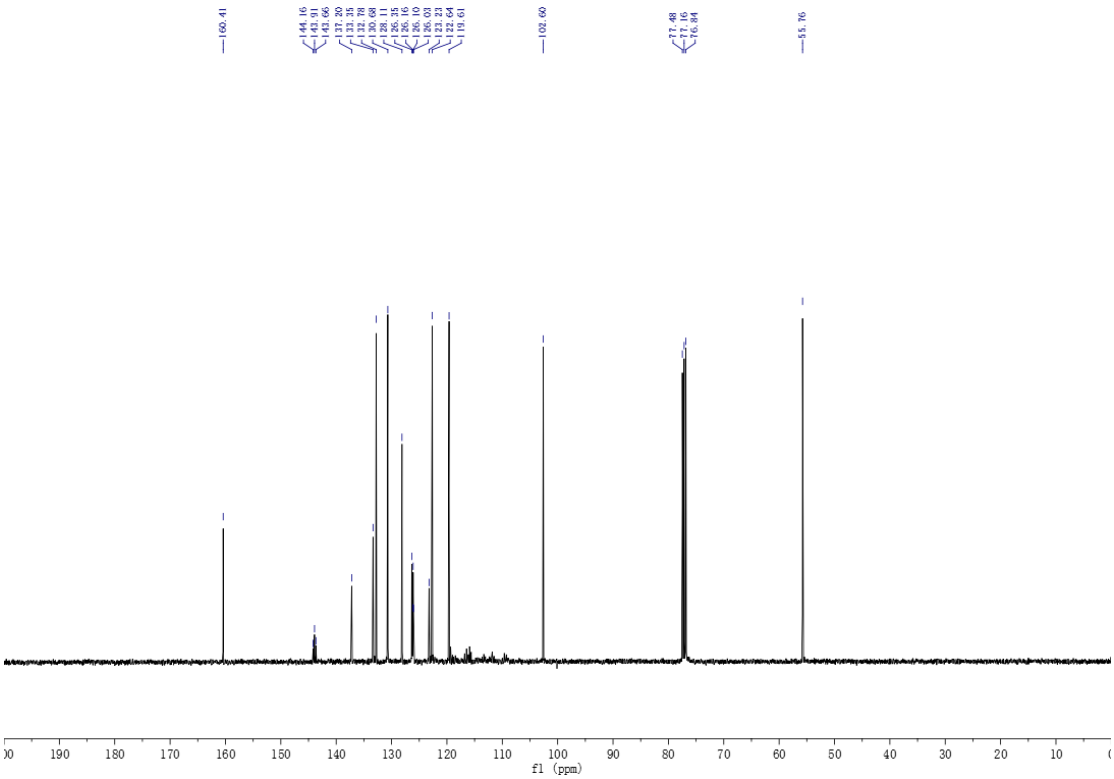


^{1}H NMR of compound **5**



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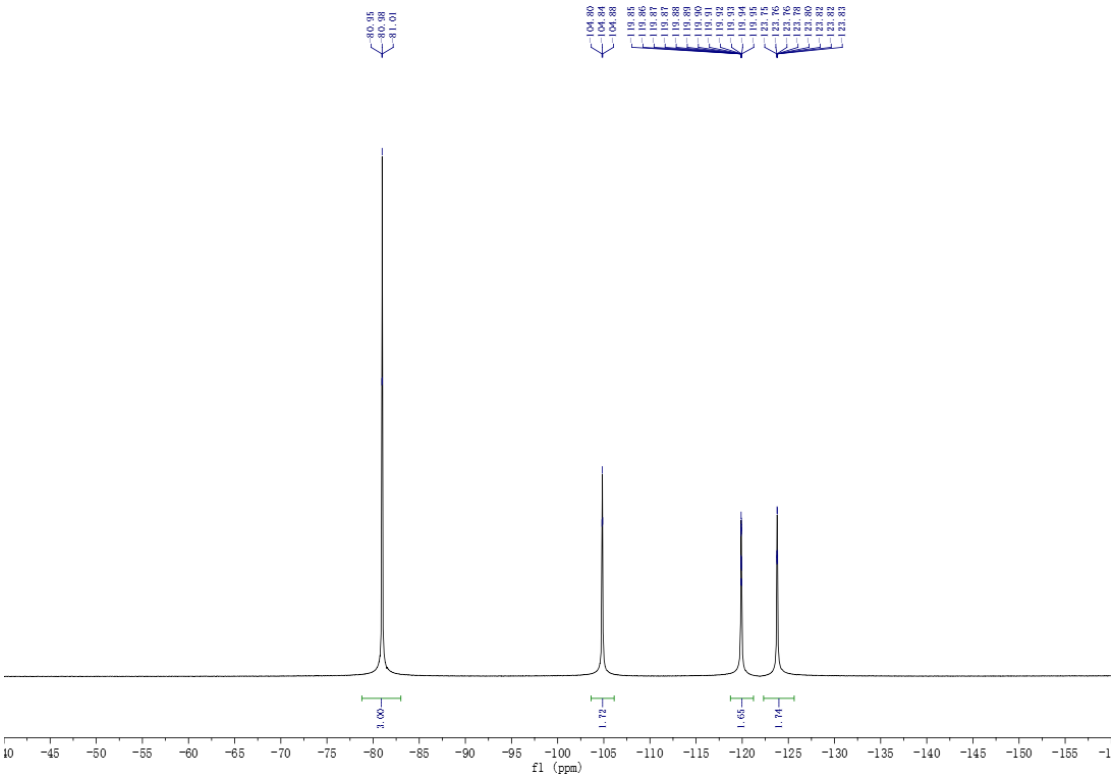

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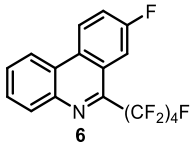
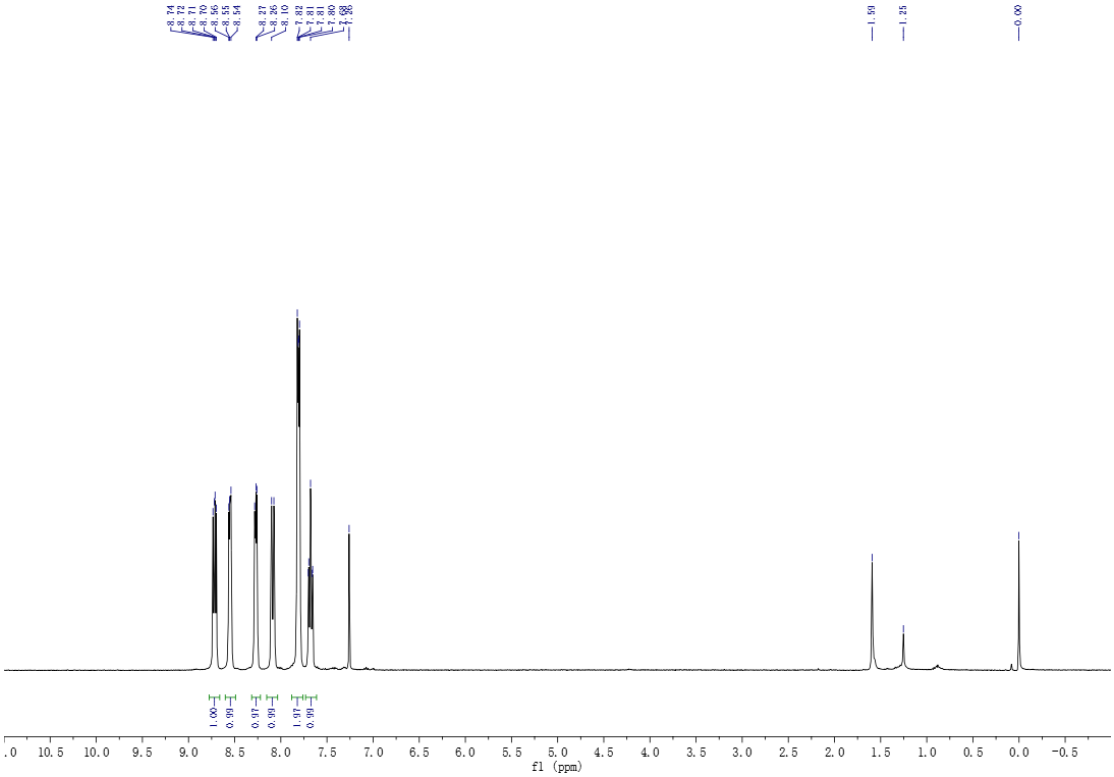
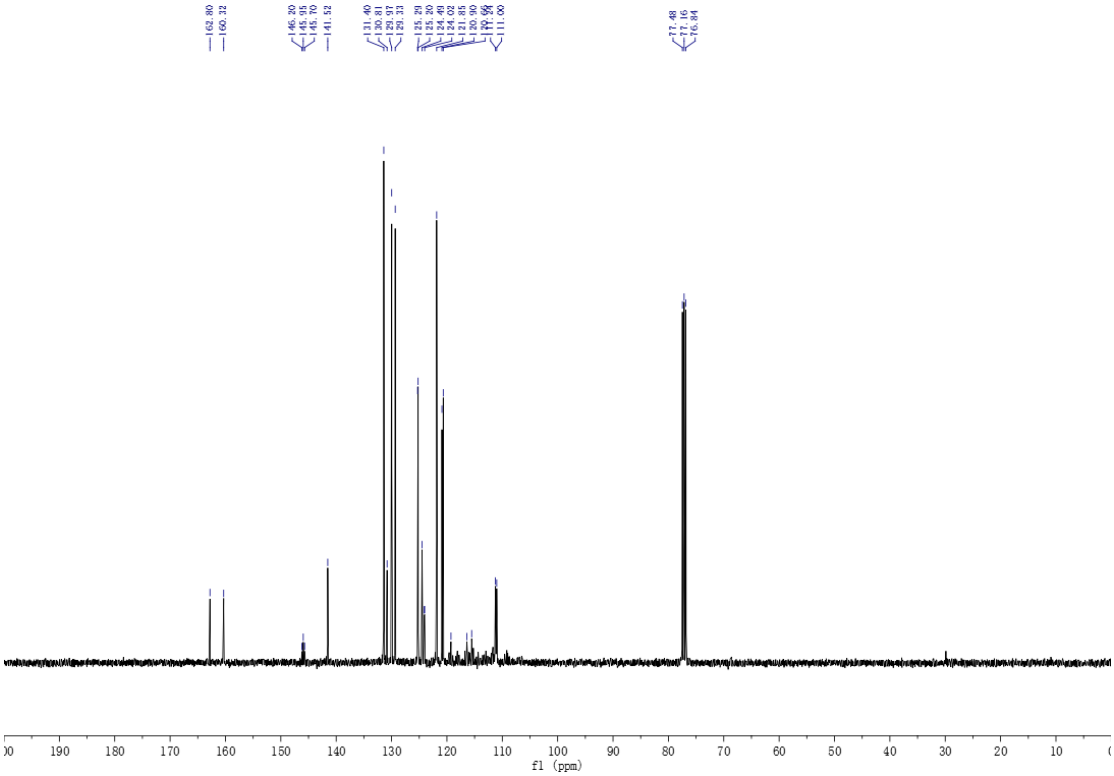




^{1}H NMR of compound **6**



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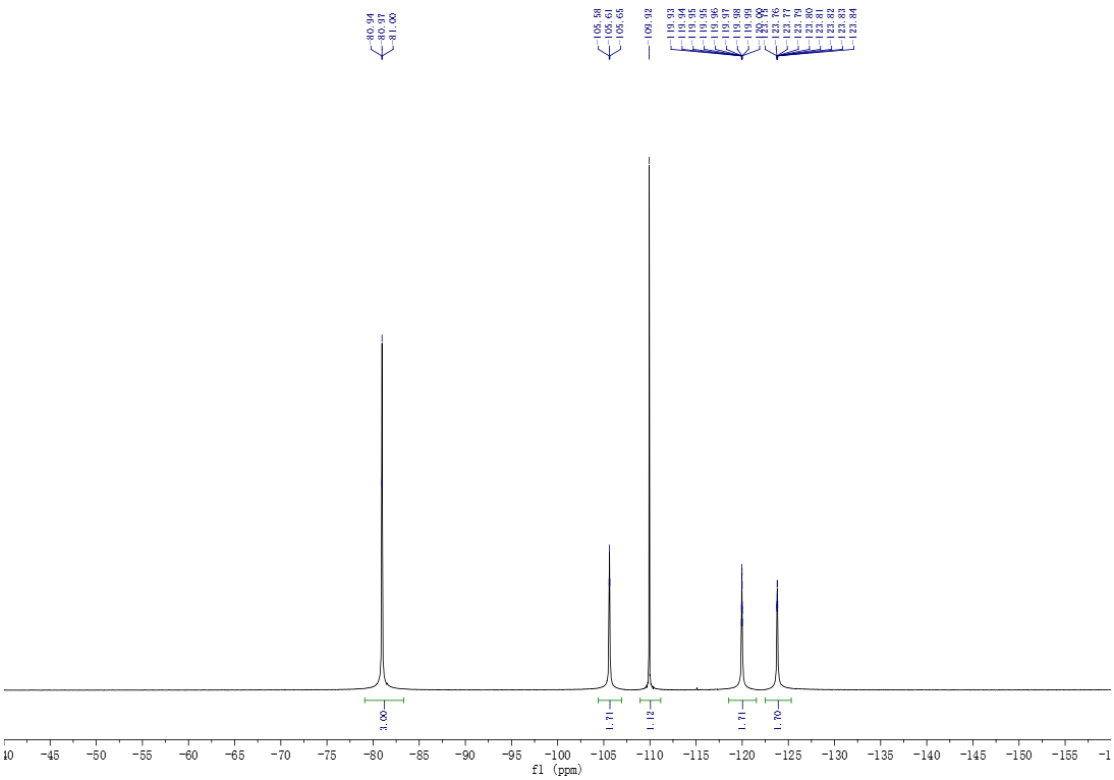

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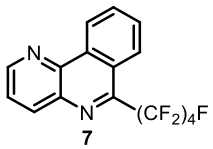

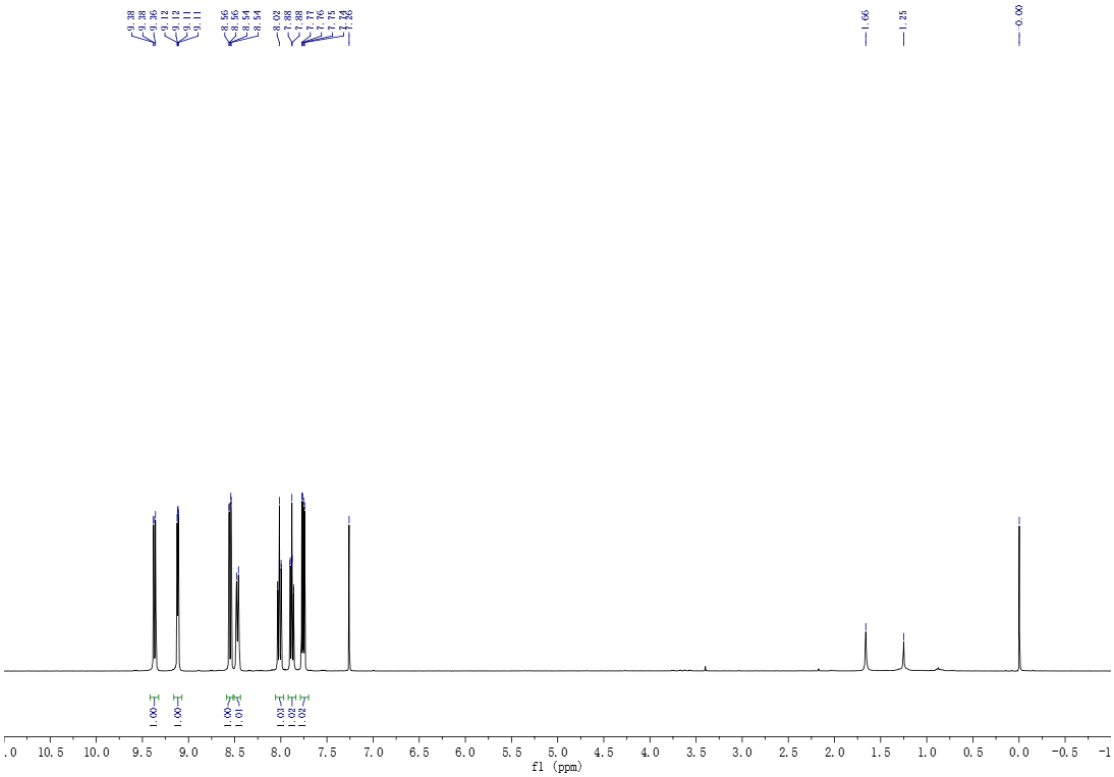

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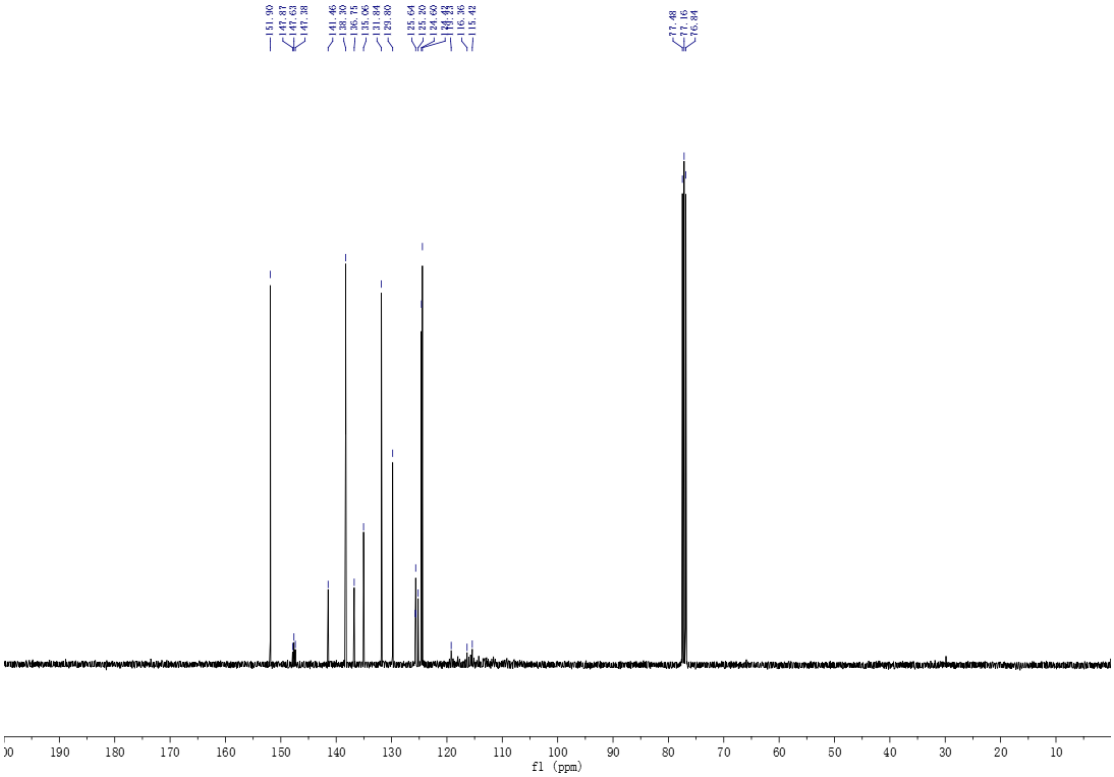

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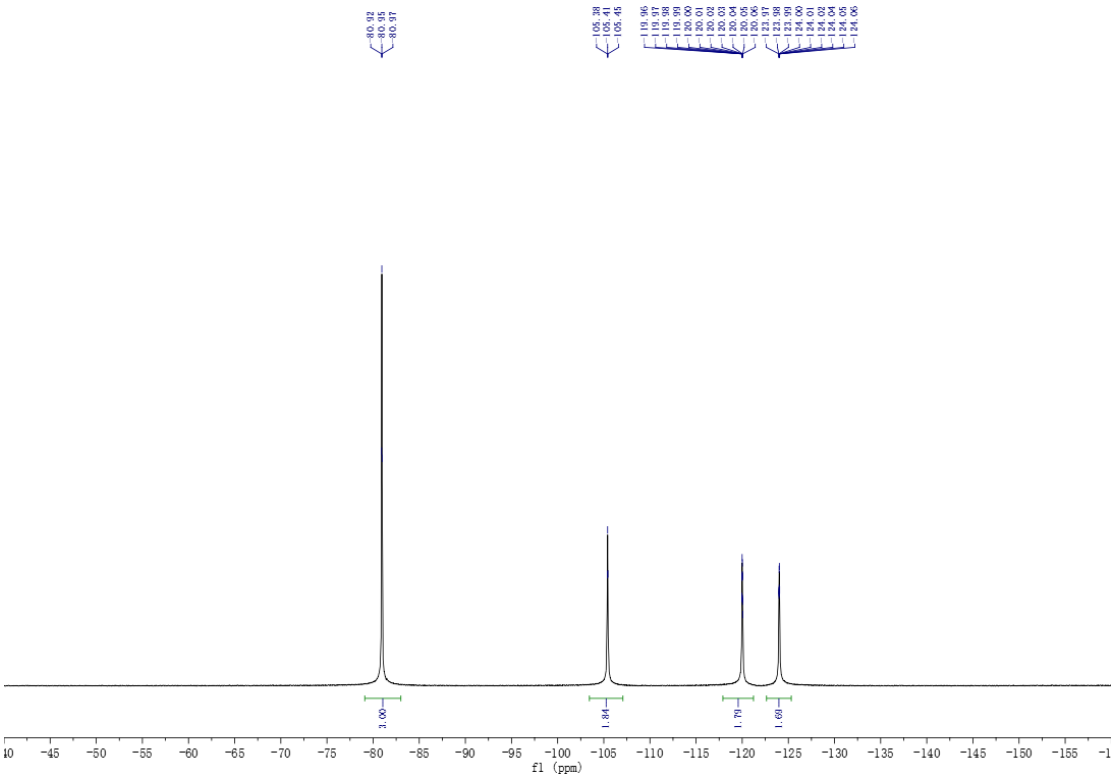

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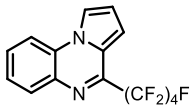

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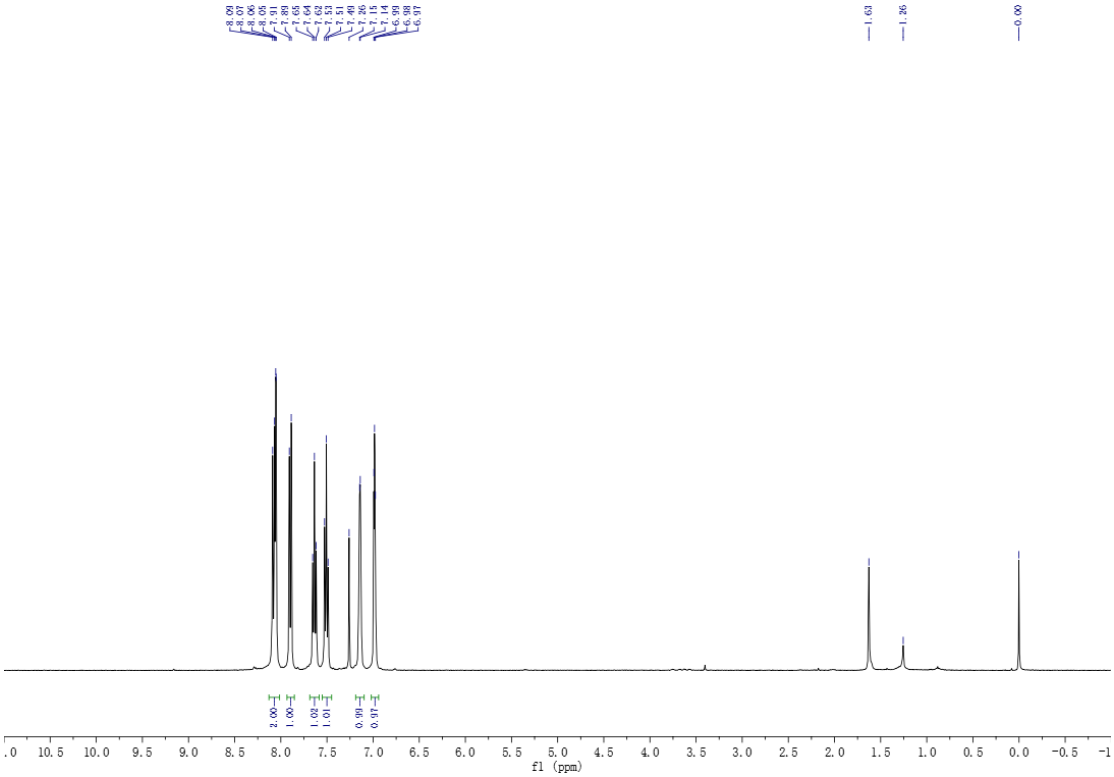

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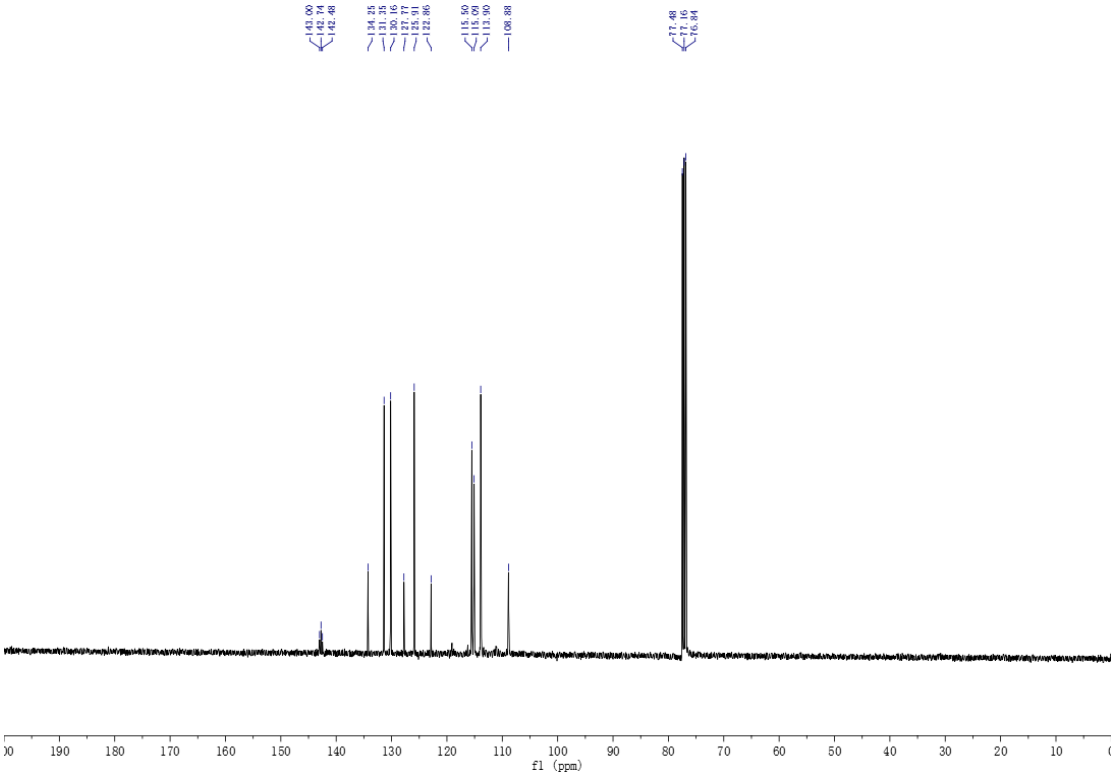

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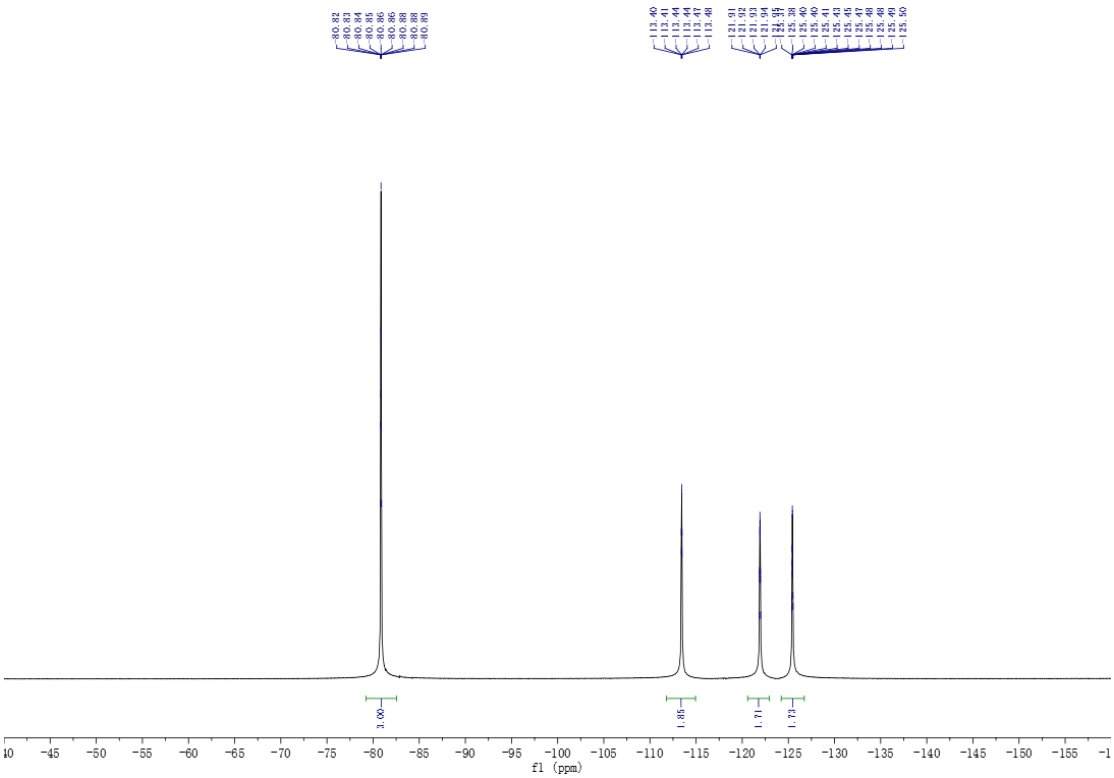

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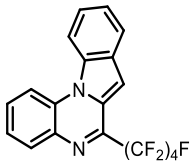

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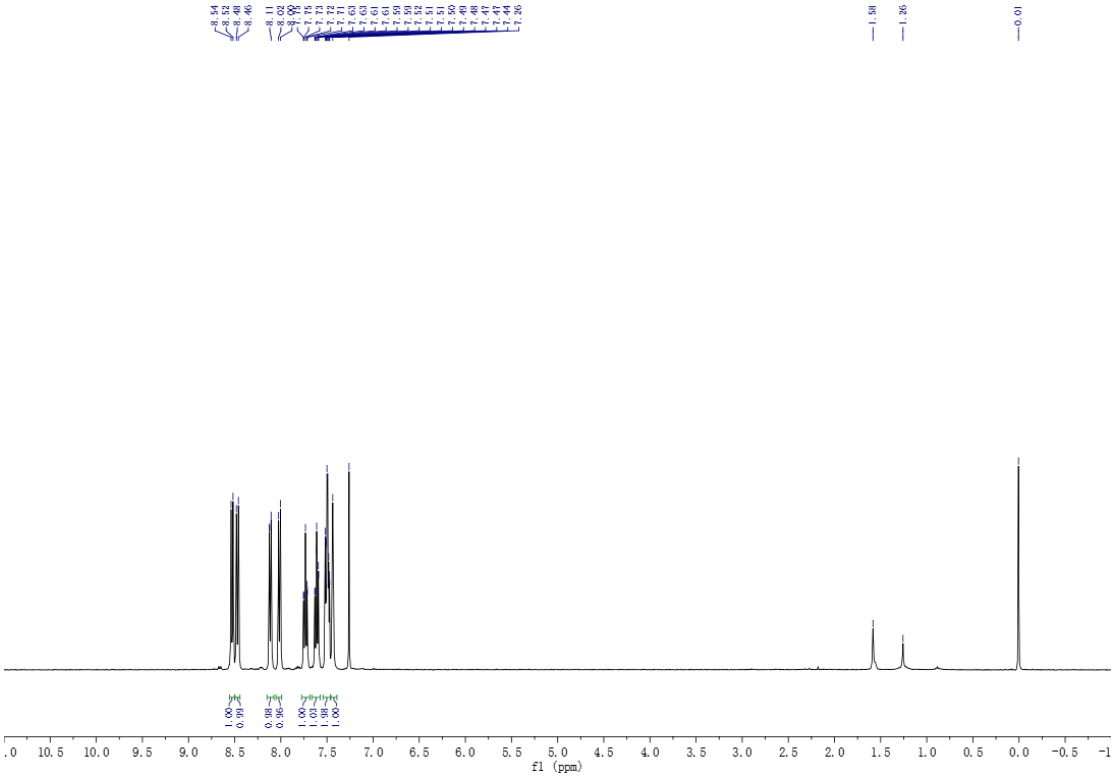
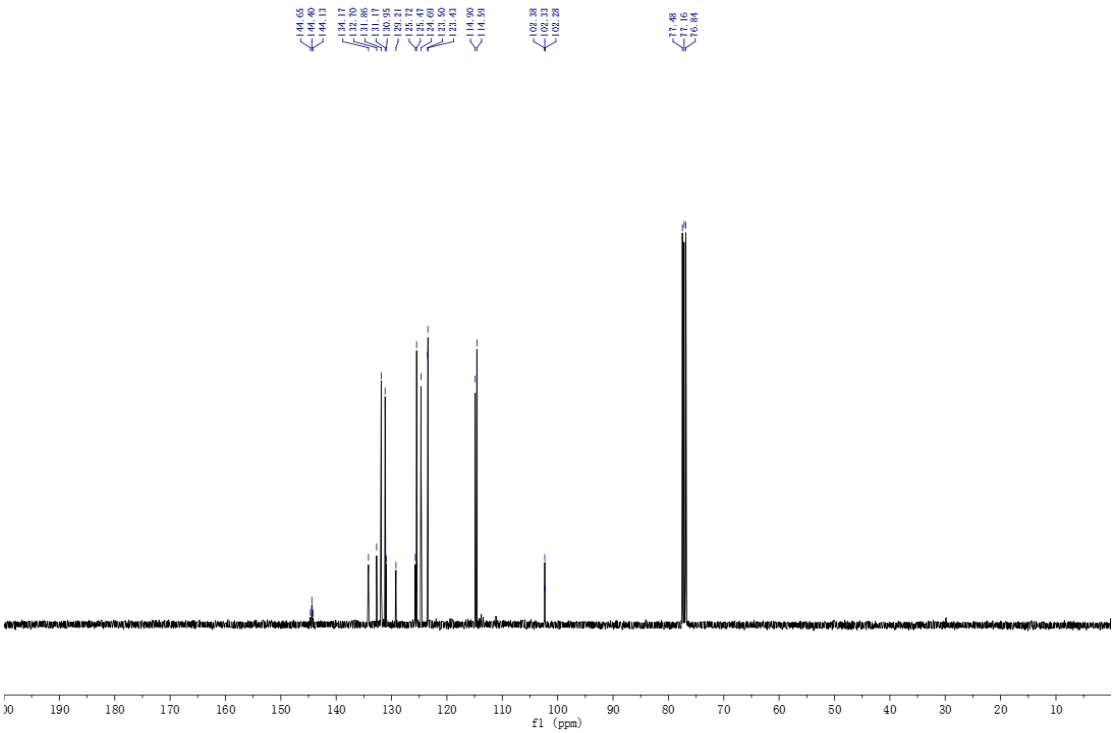
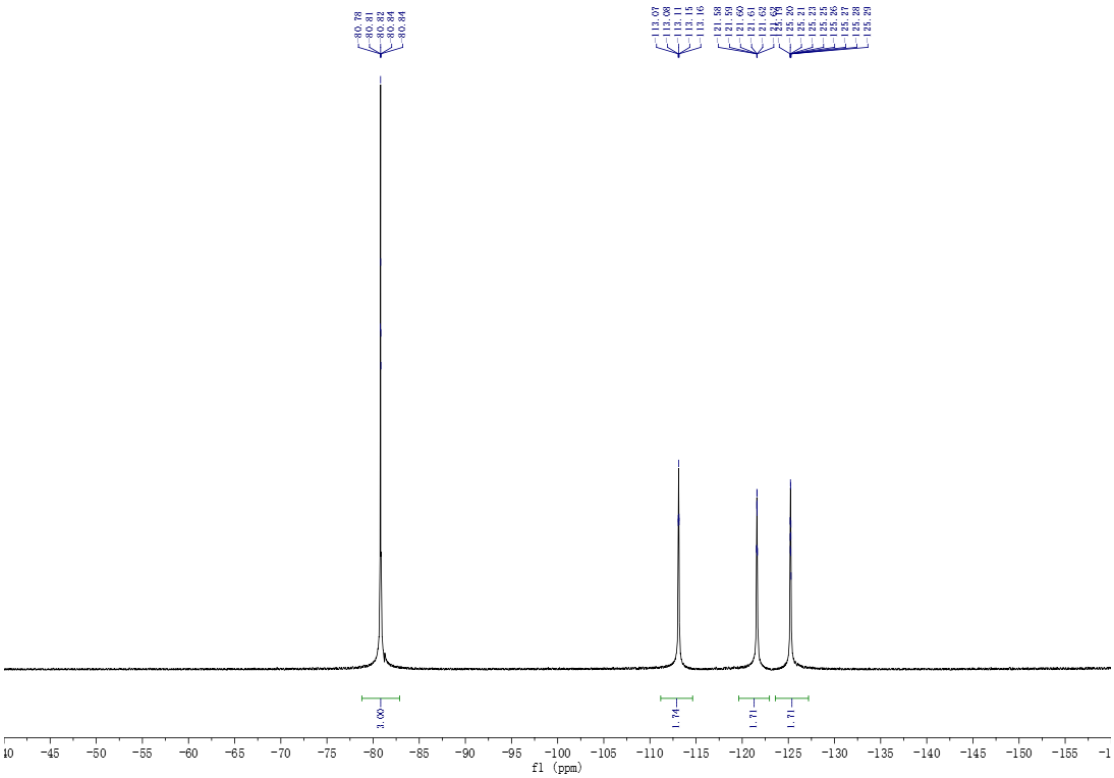


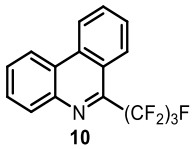
^{1}H NMR of compound **9**



^{13}C NMR of compound **9**



^{19}F NMR of compound **9**



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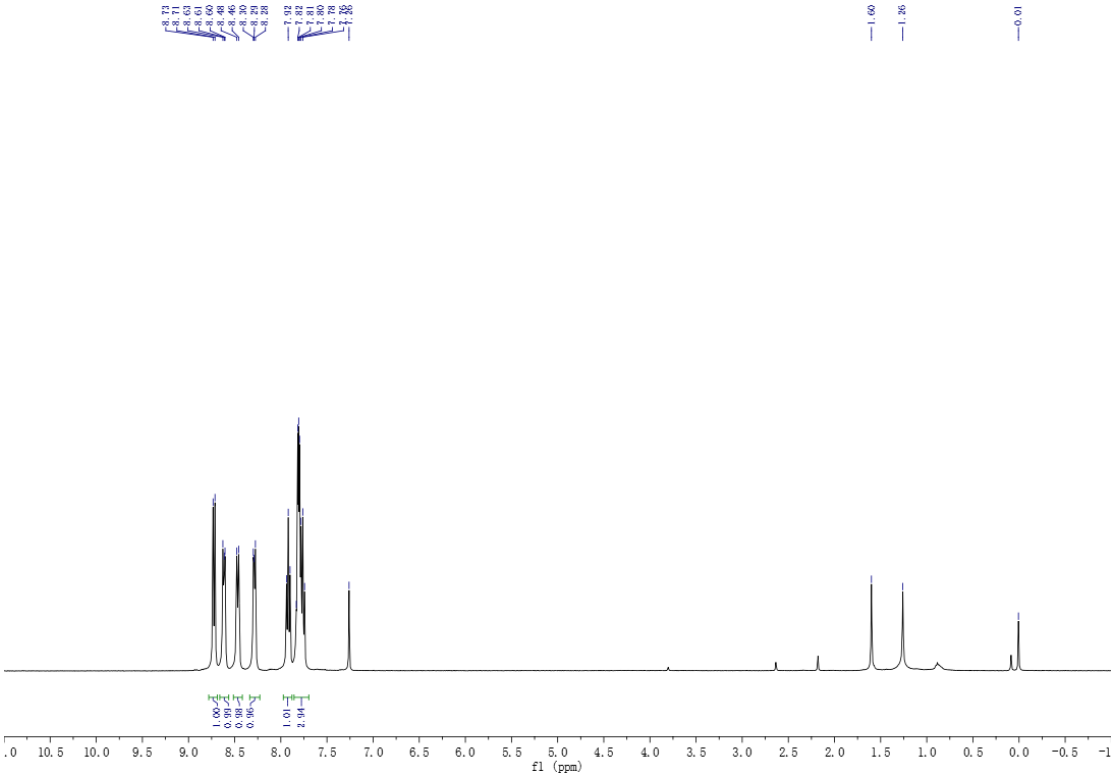

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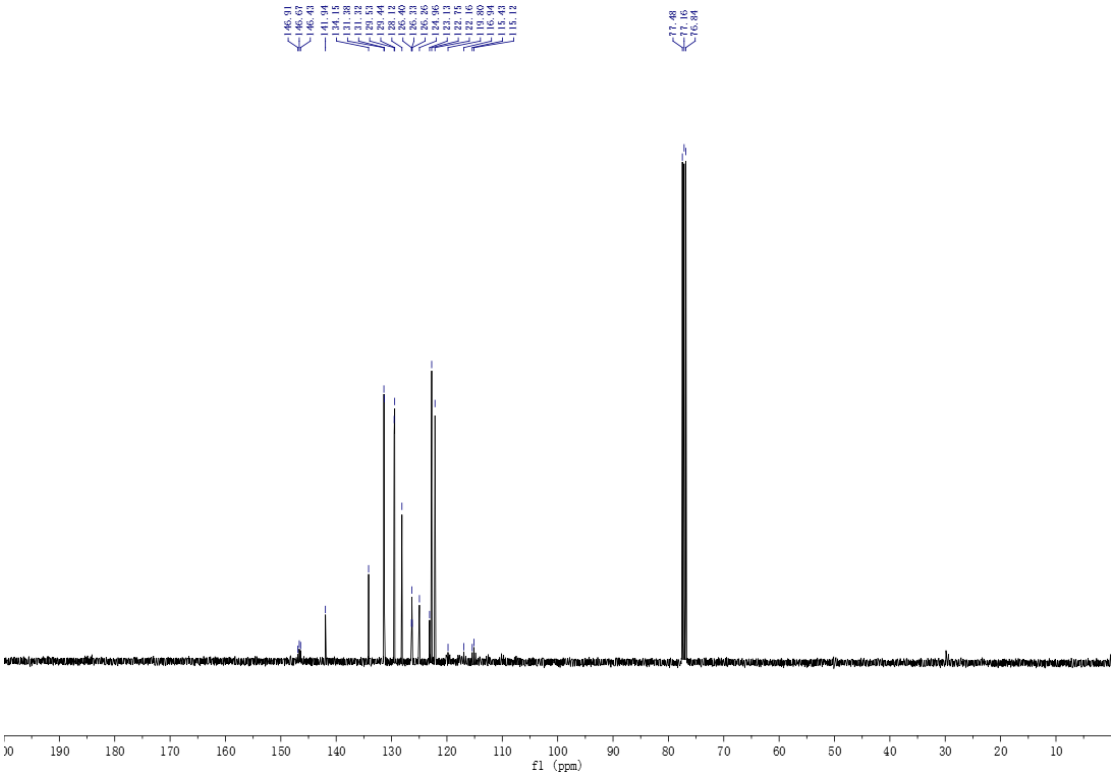

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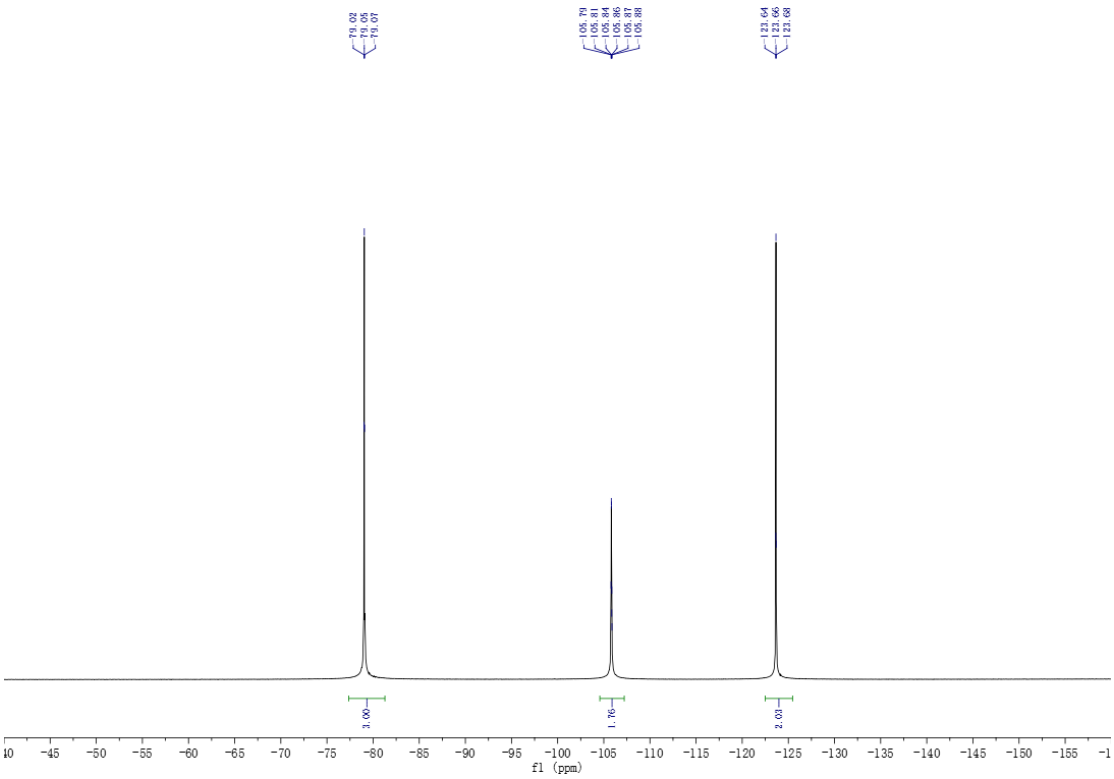

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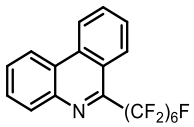

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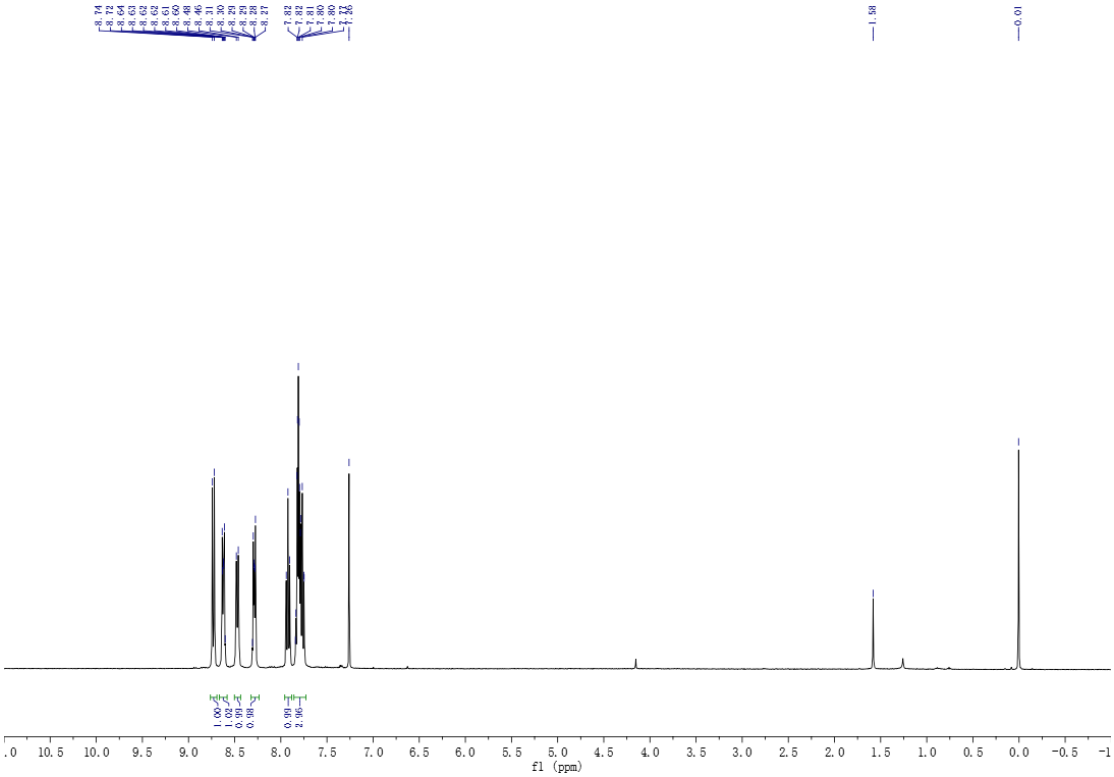

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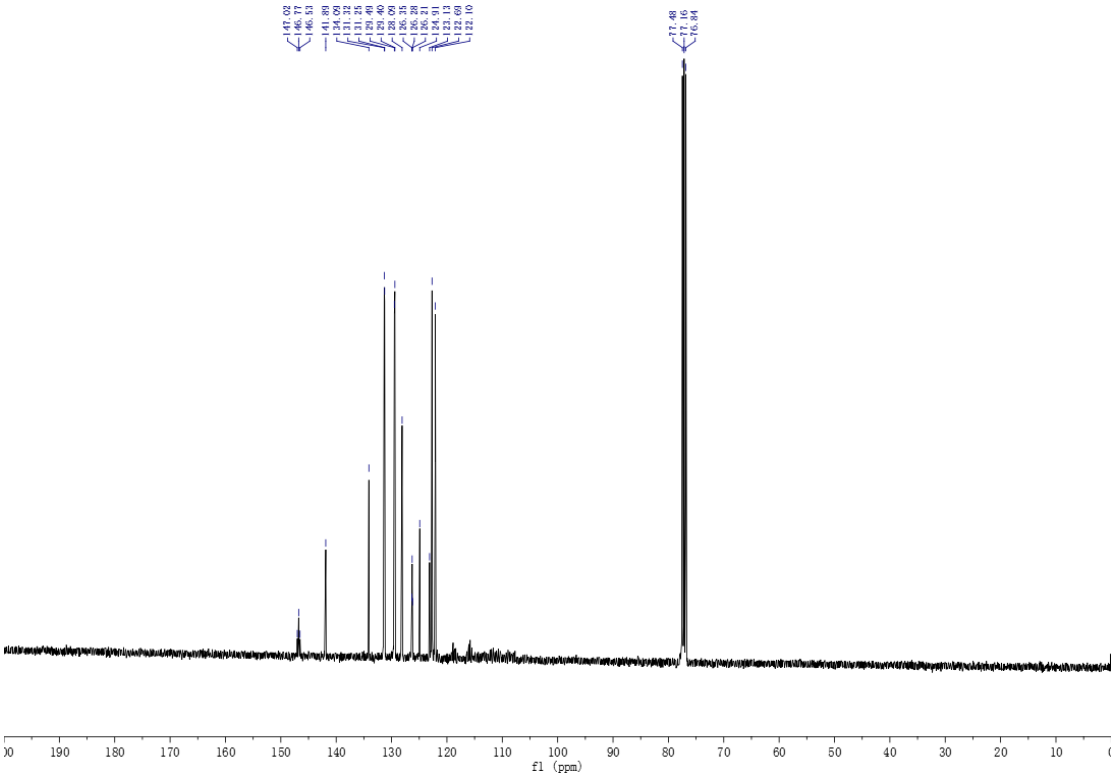

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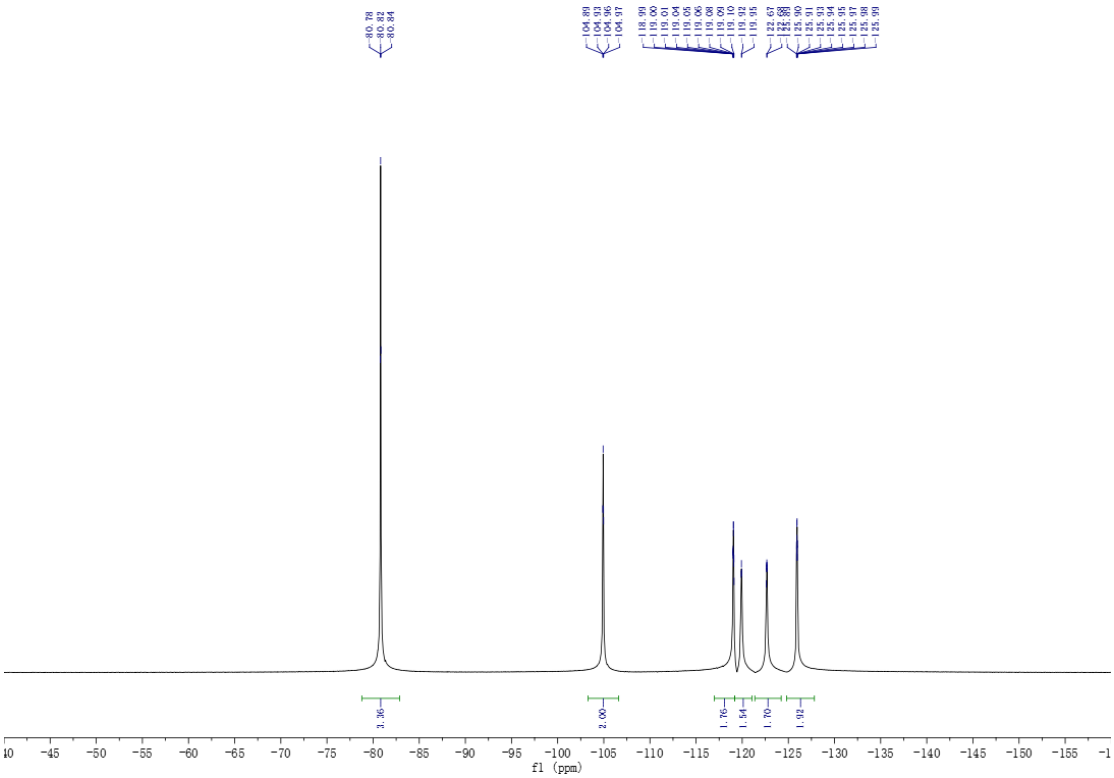

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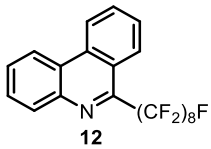

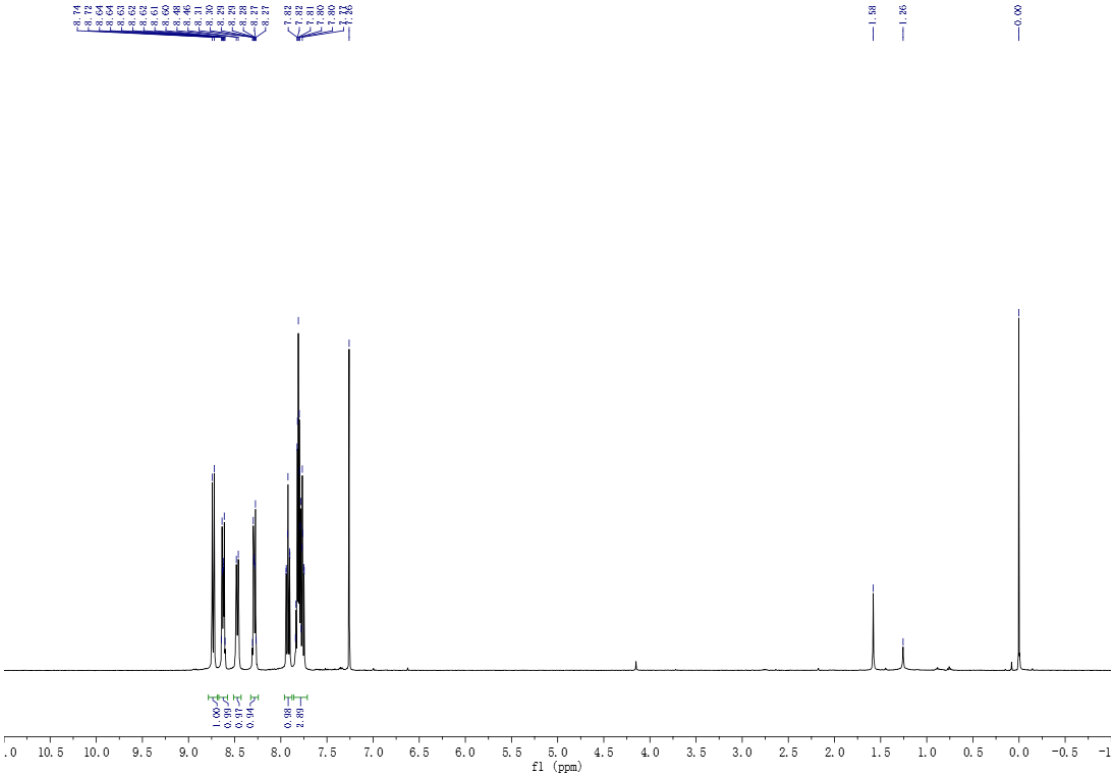

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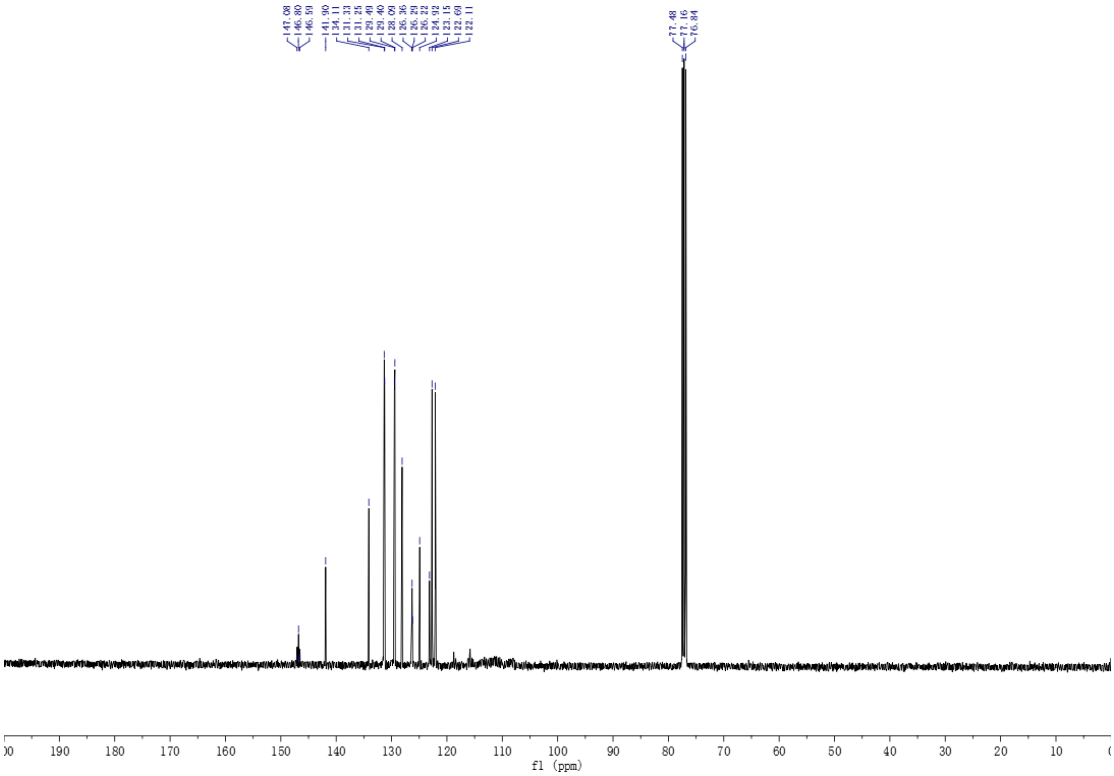

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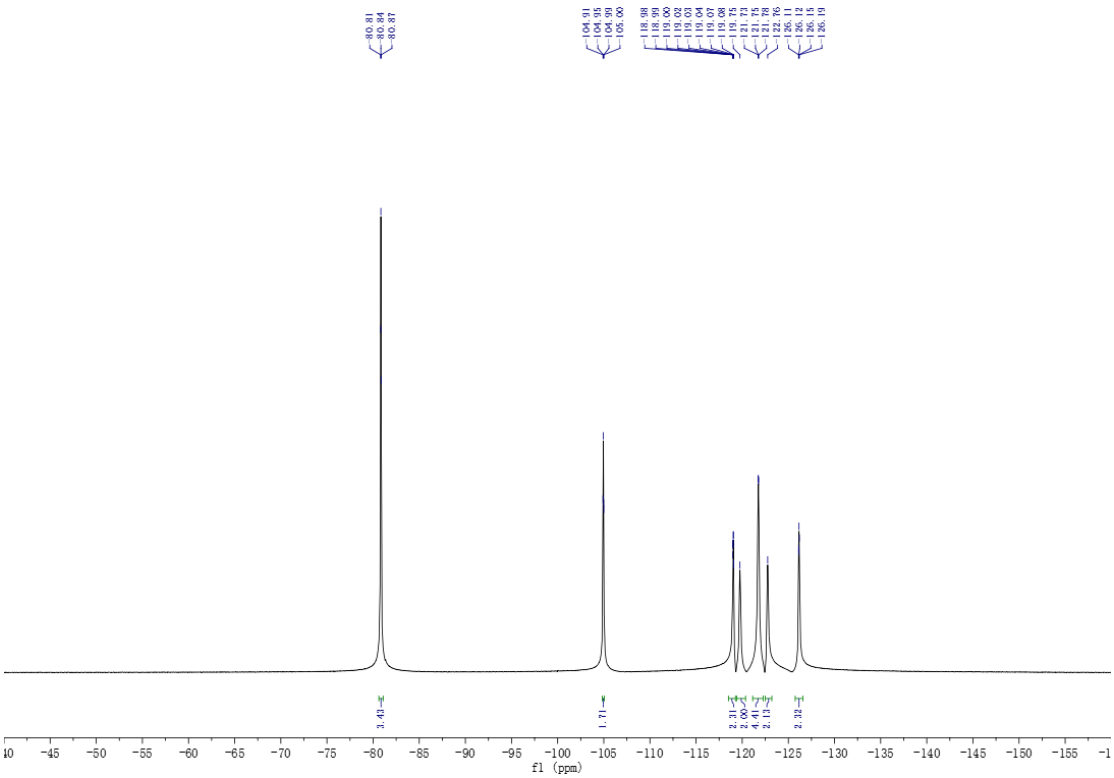

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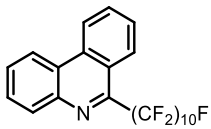

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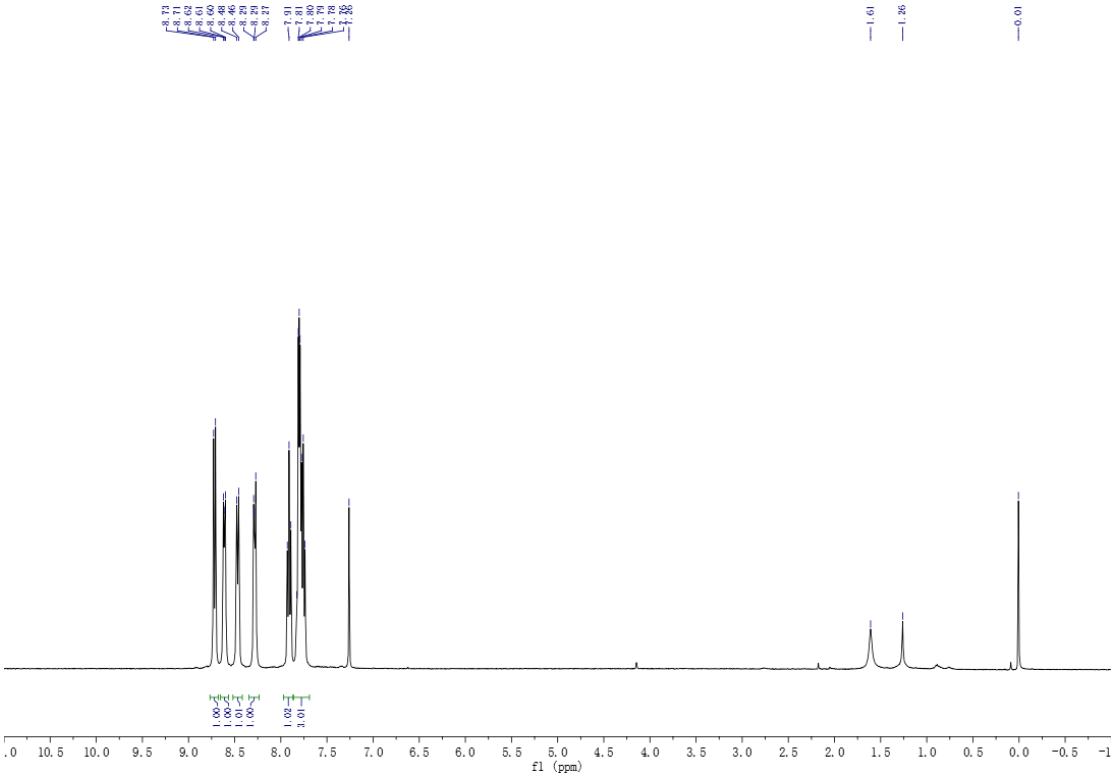

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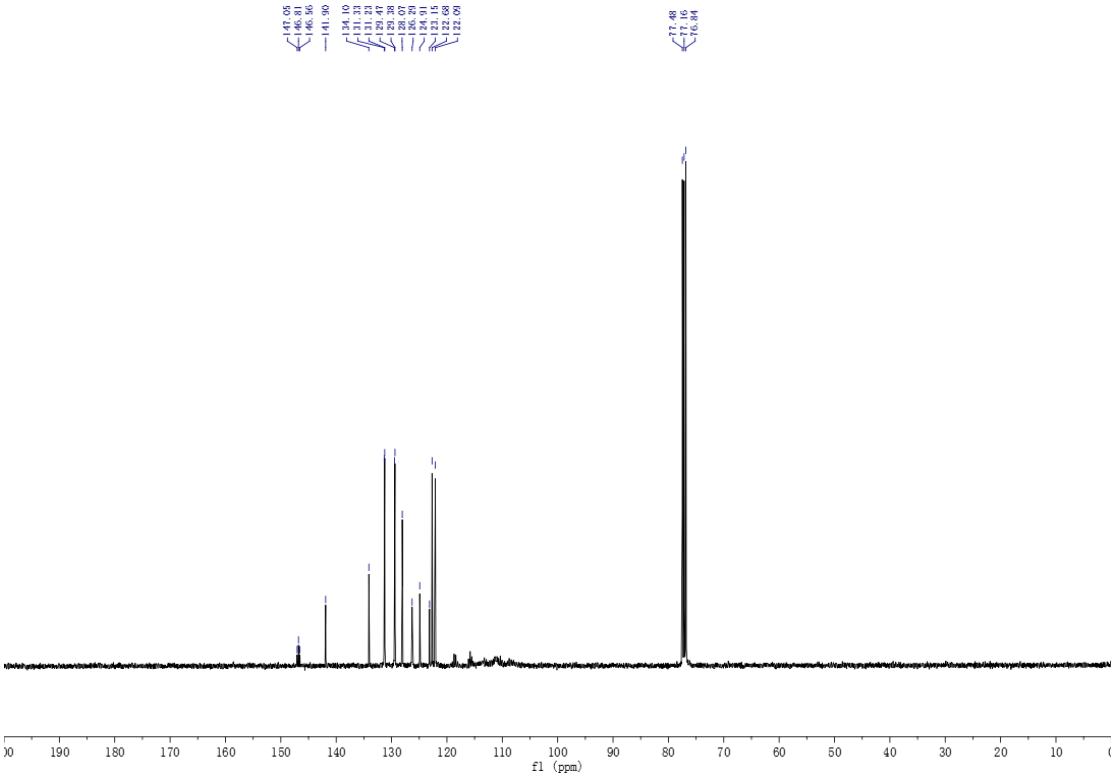

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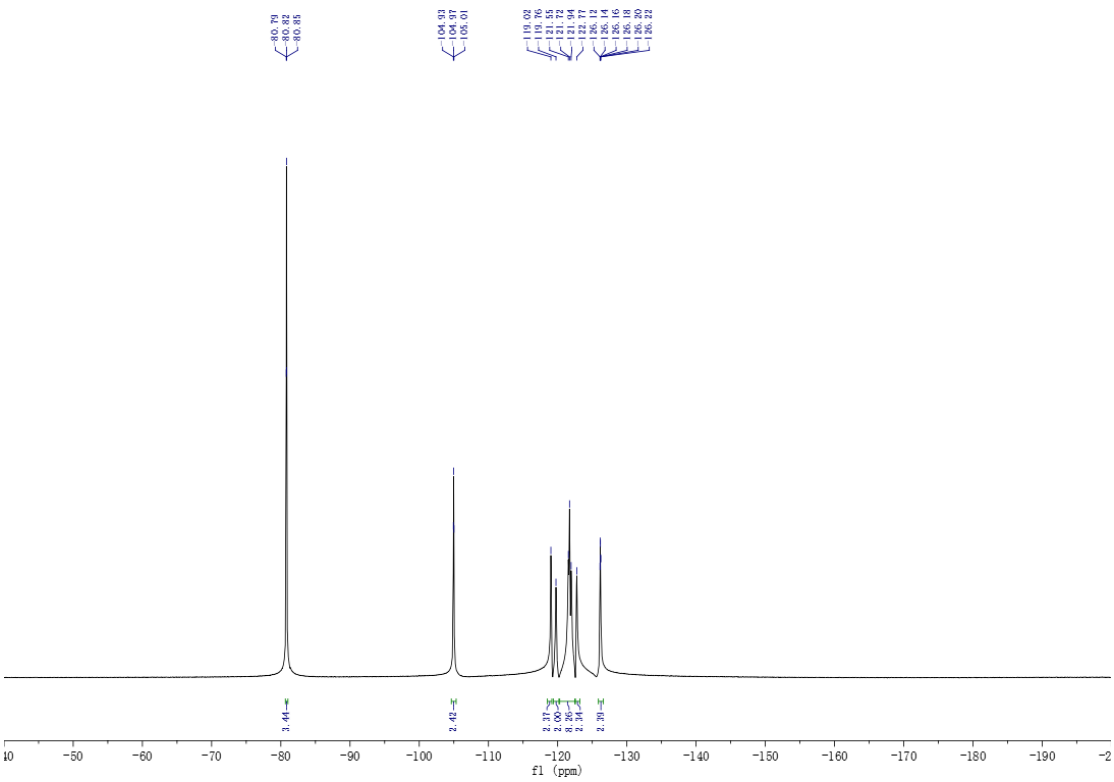

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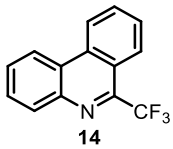

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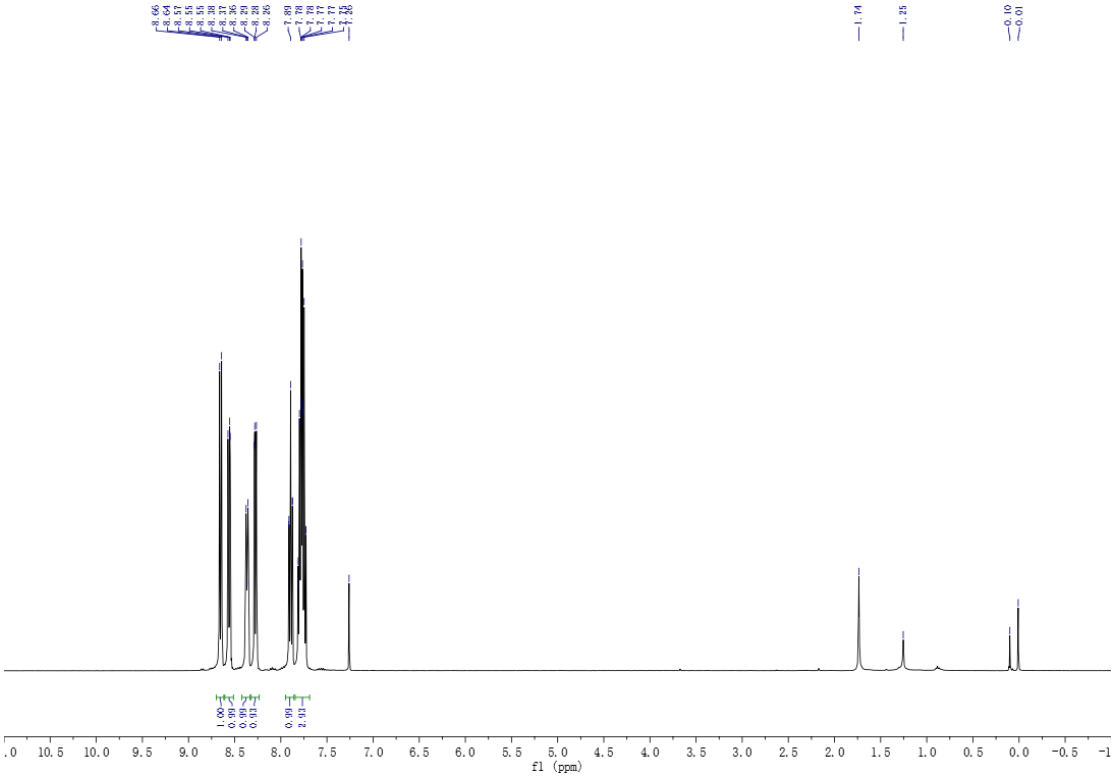

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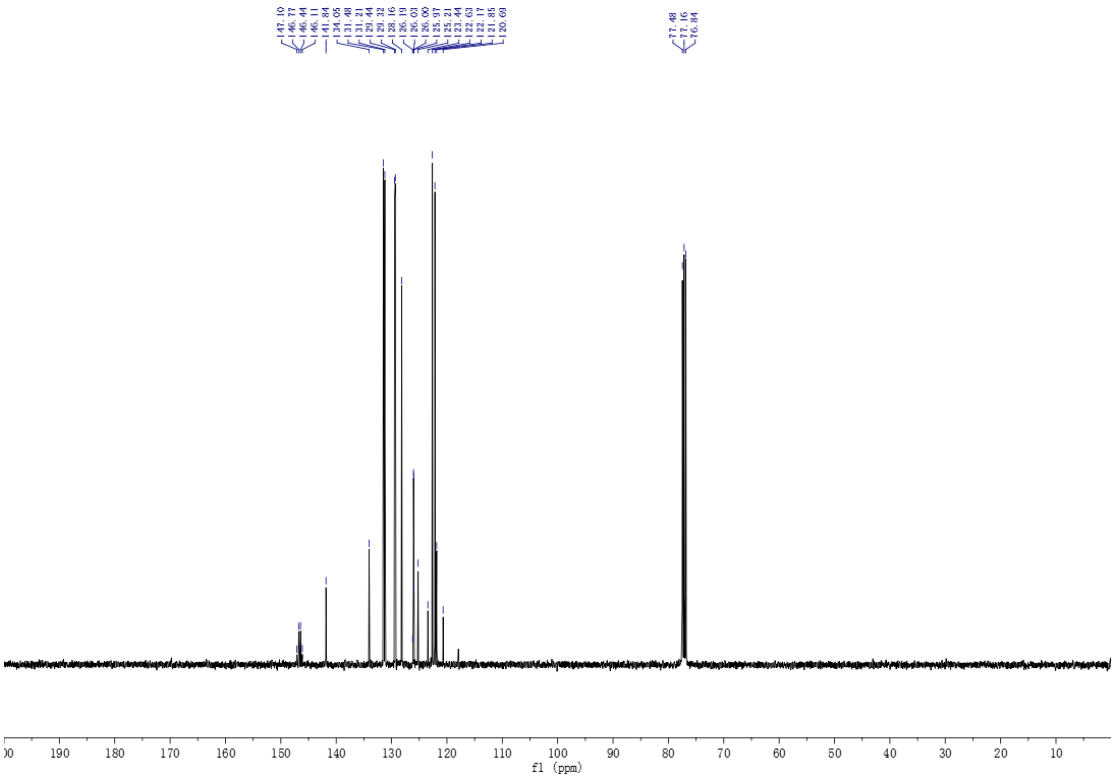

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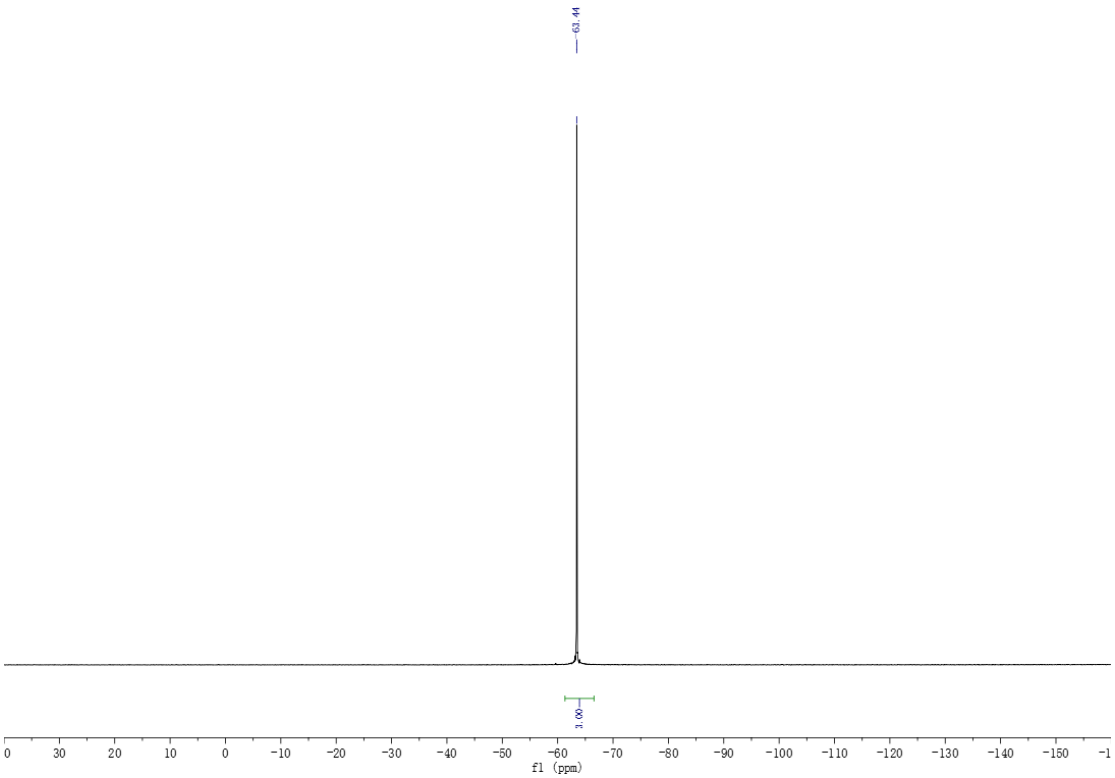

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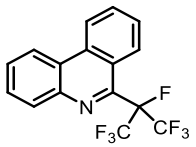

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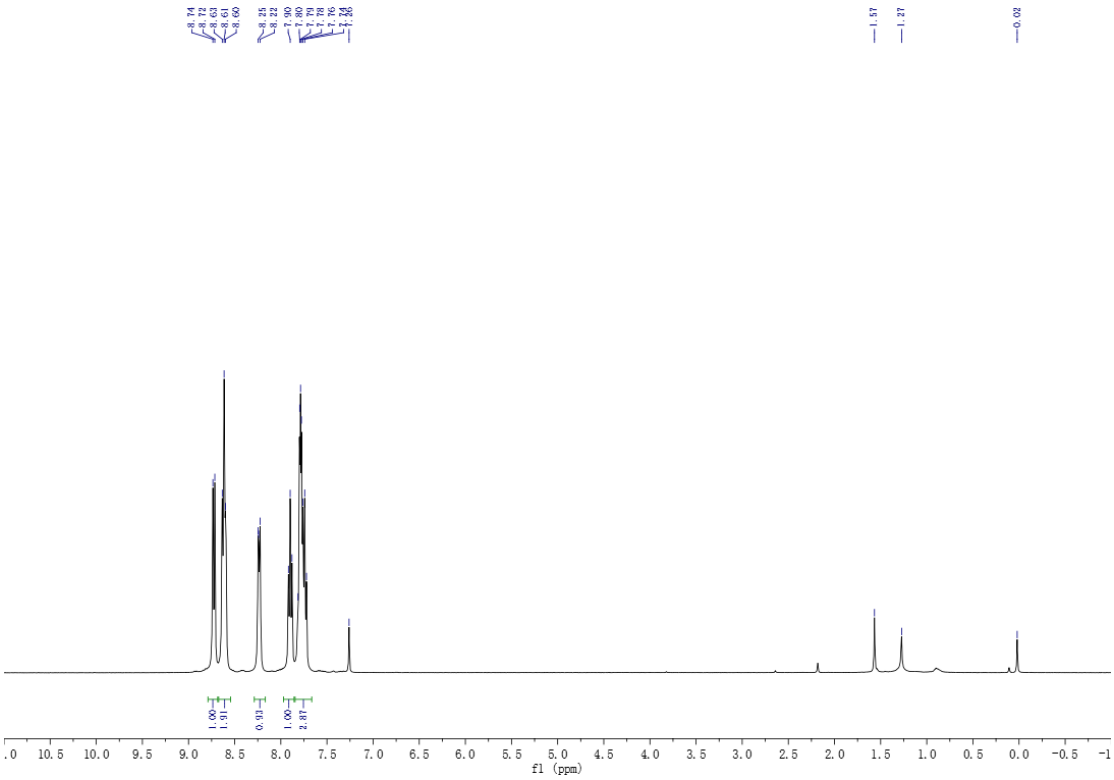

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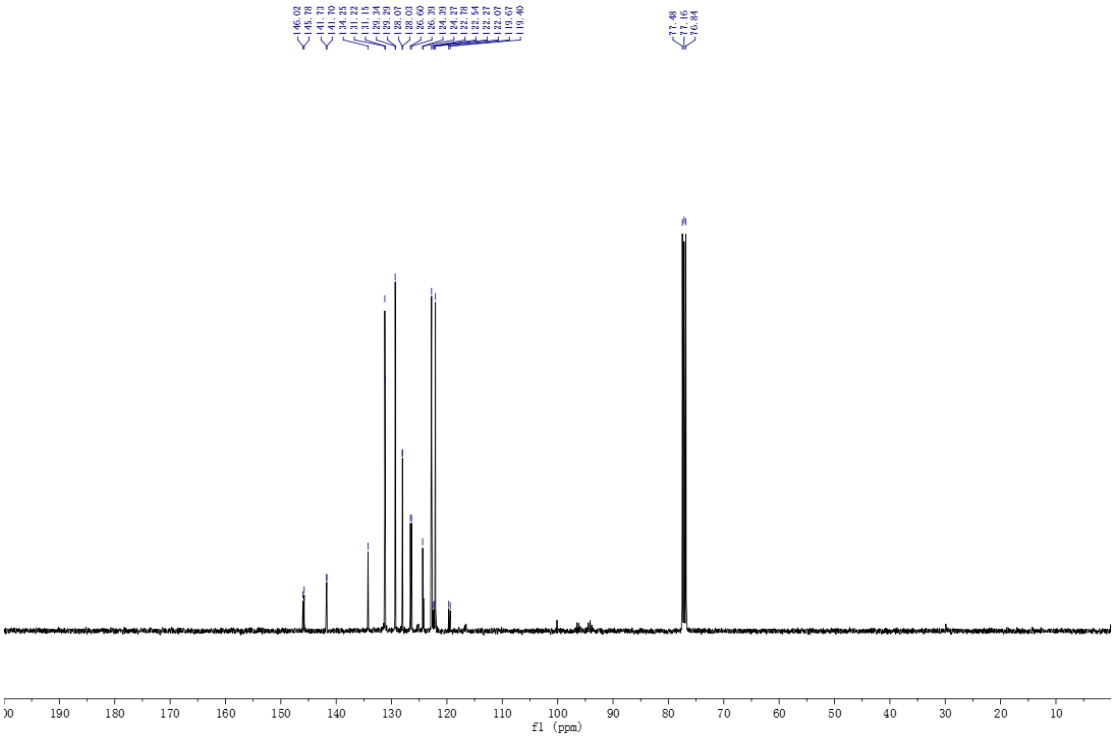

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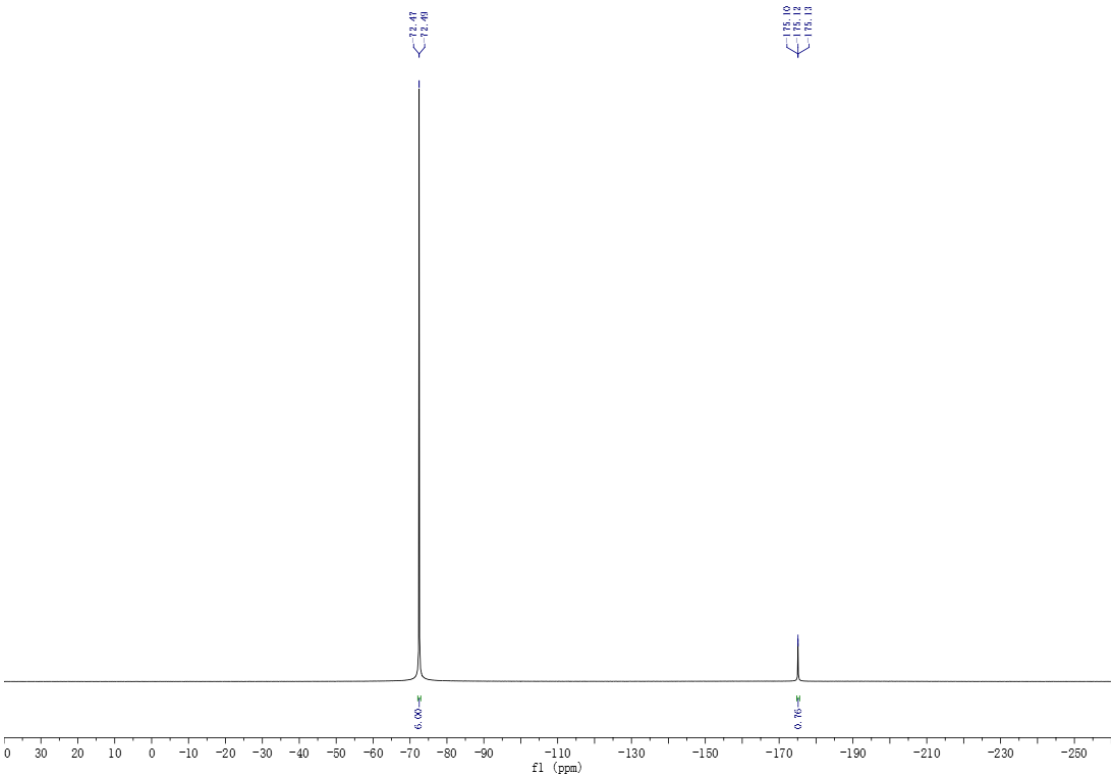

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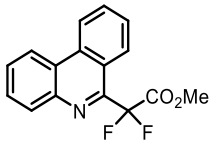

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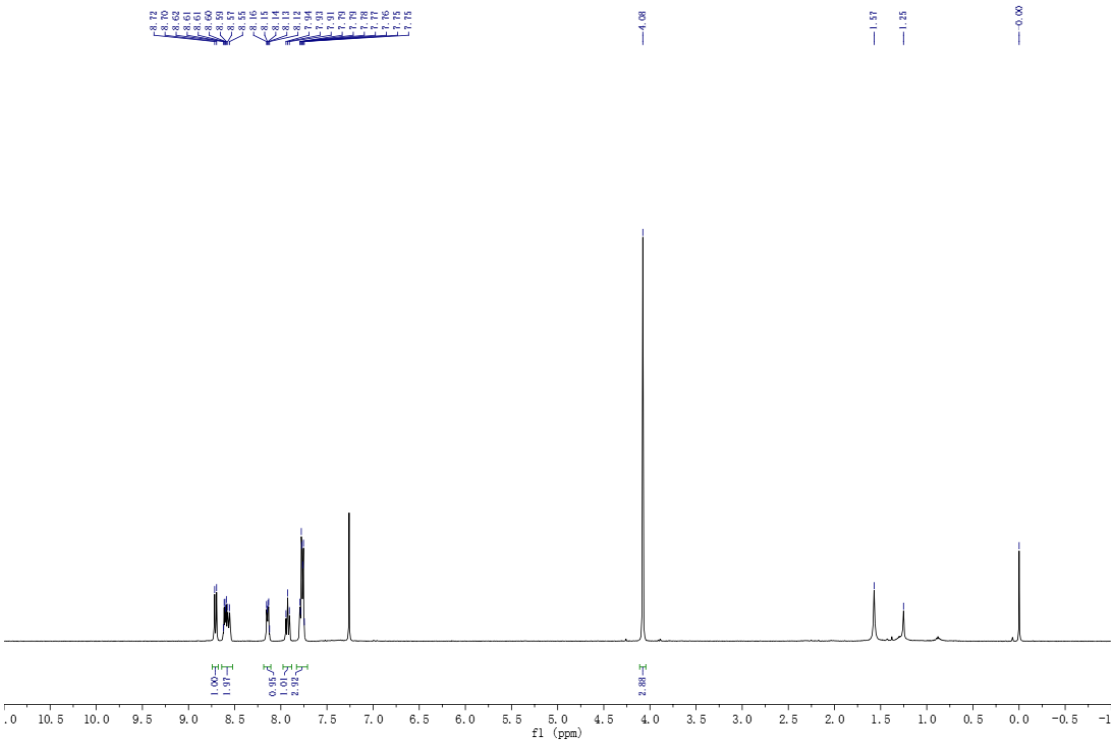

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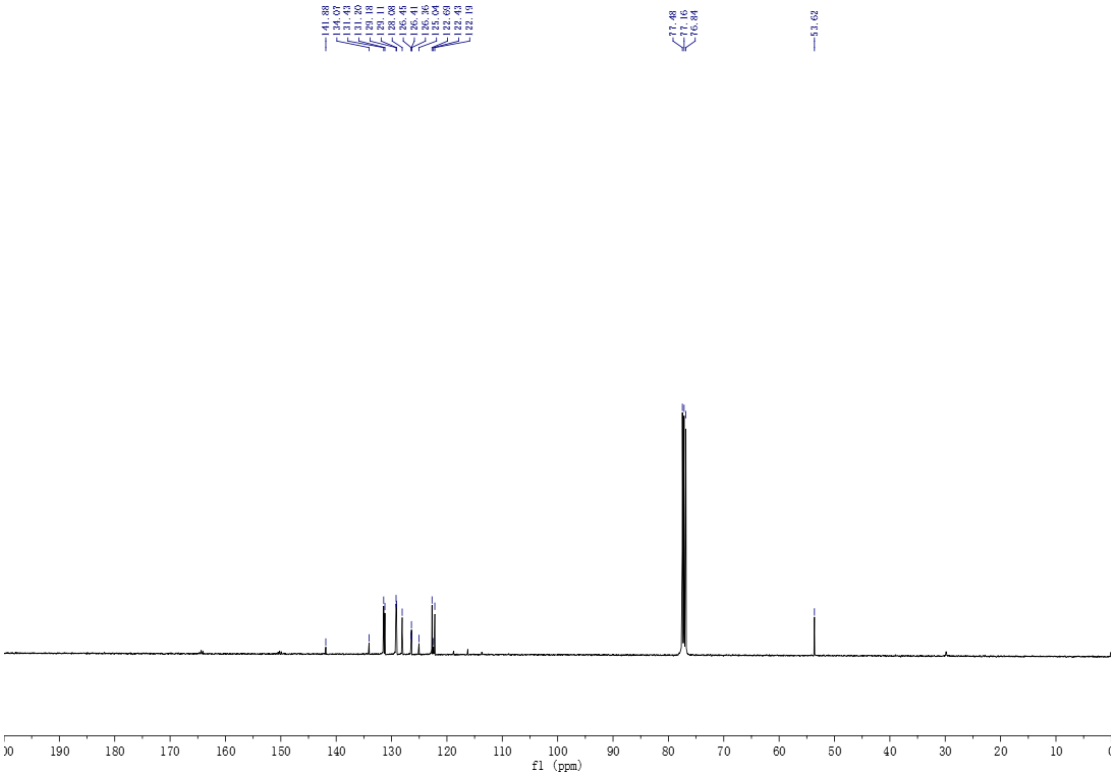

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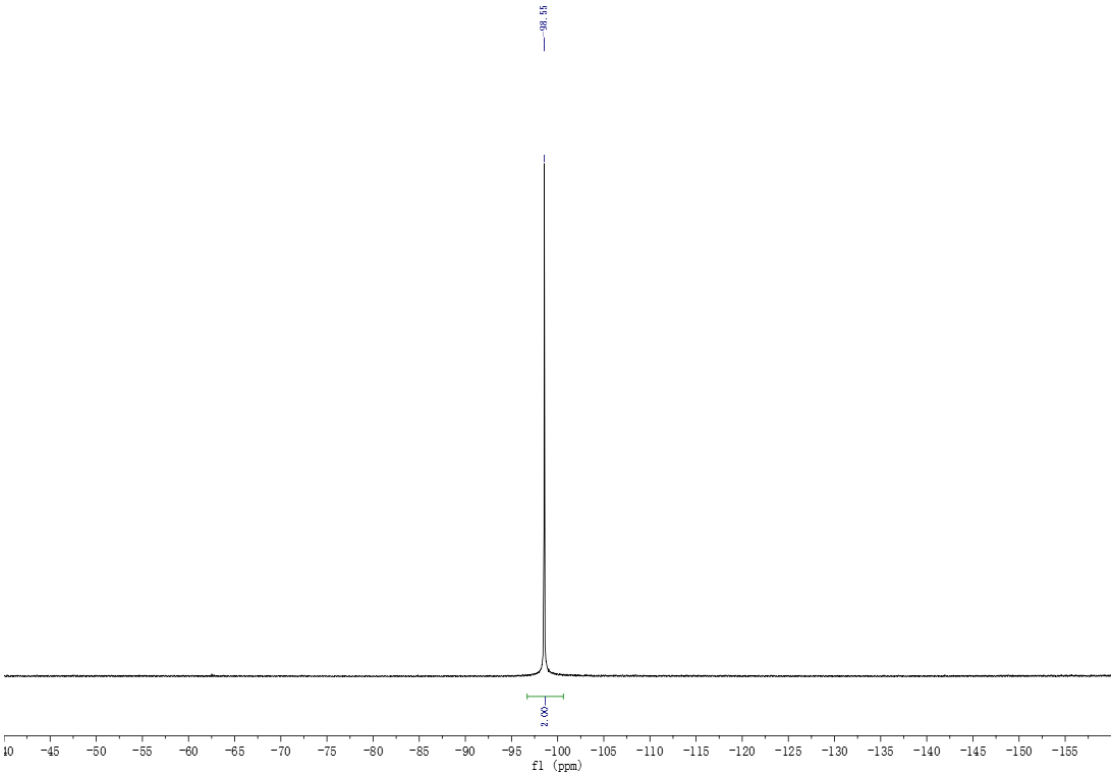

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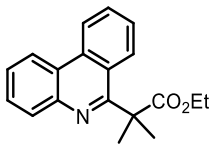

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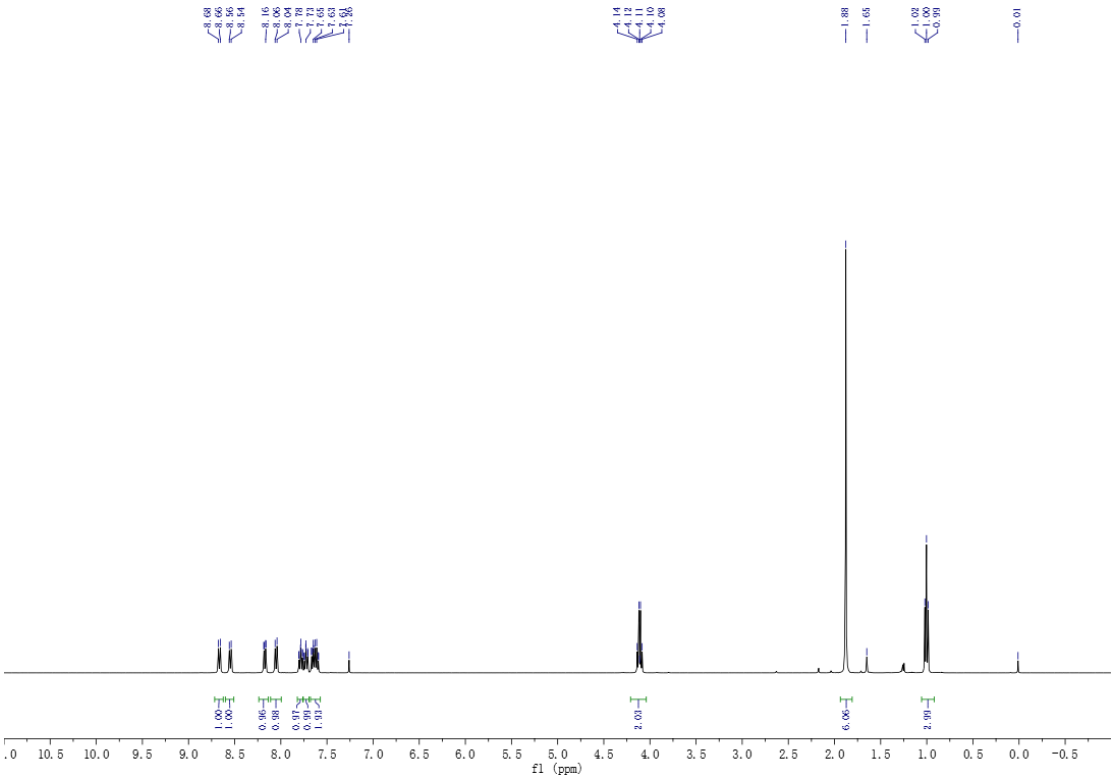

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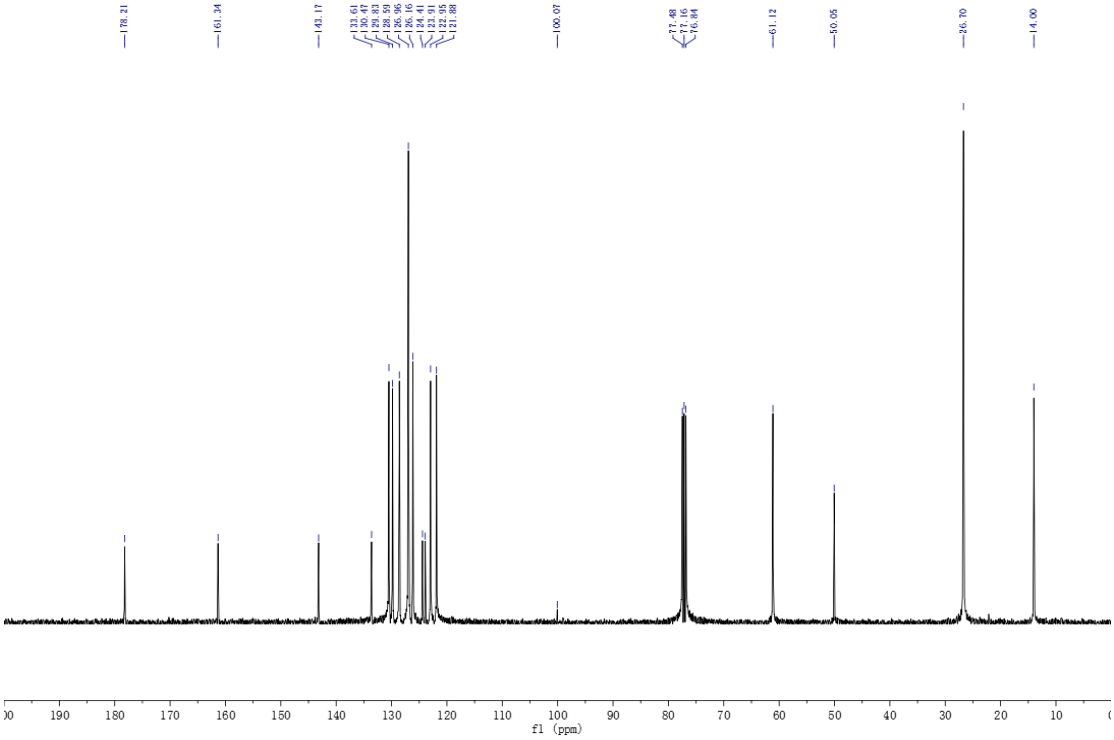

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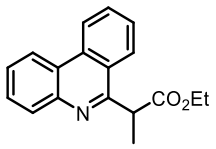

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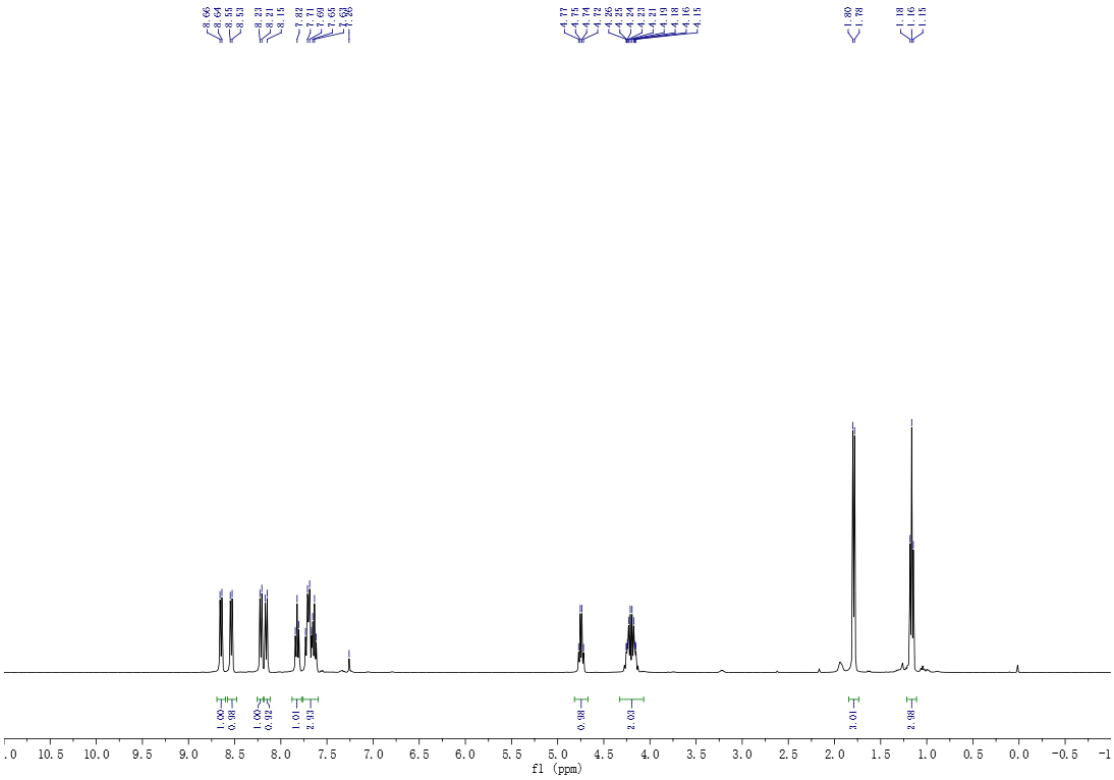

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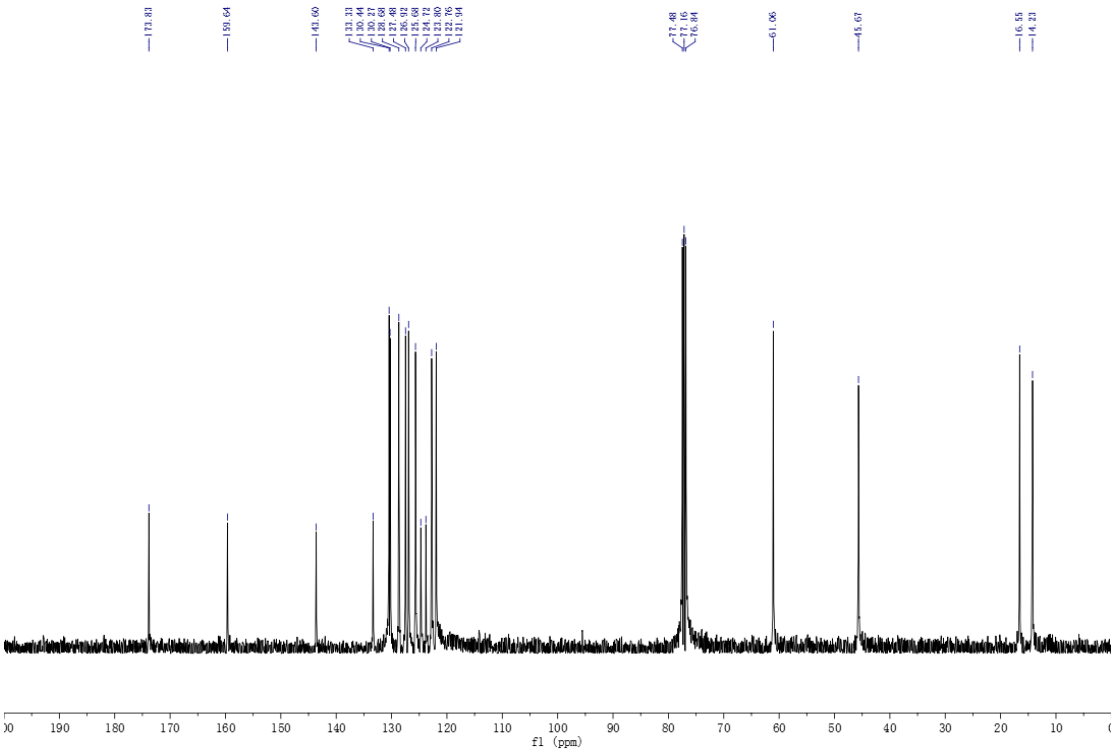

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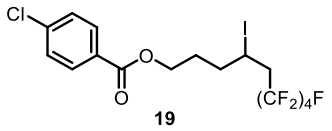

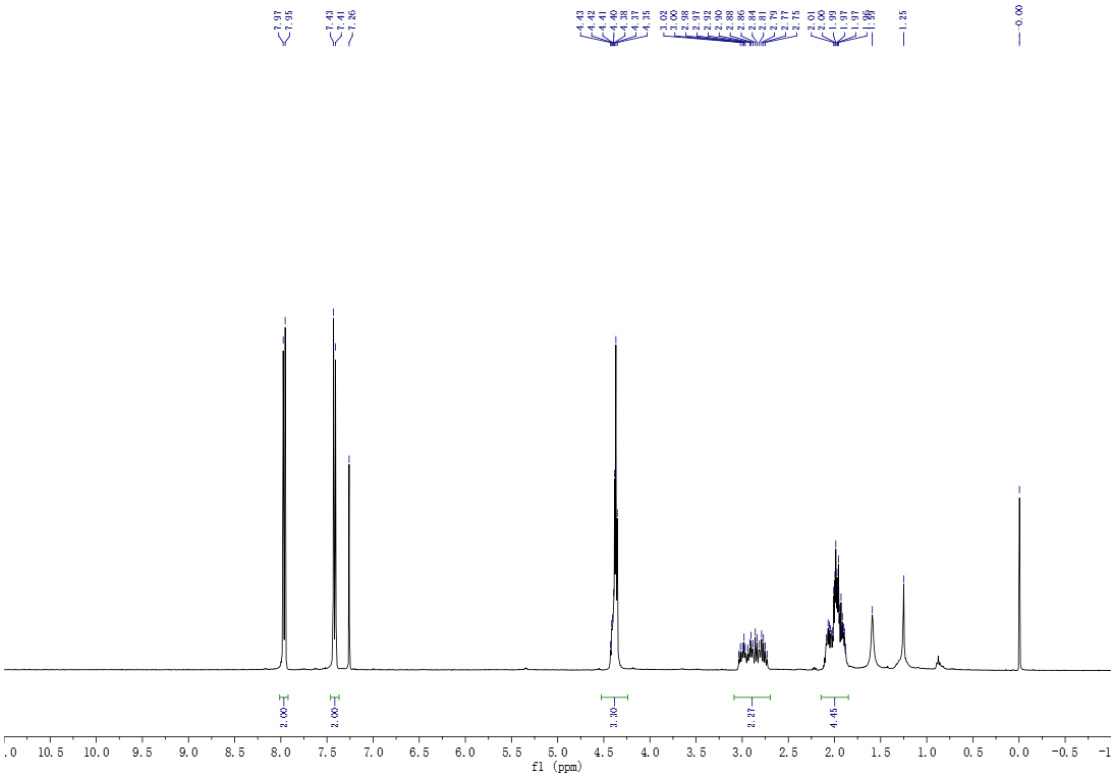

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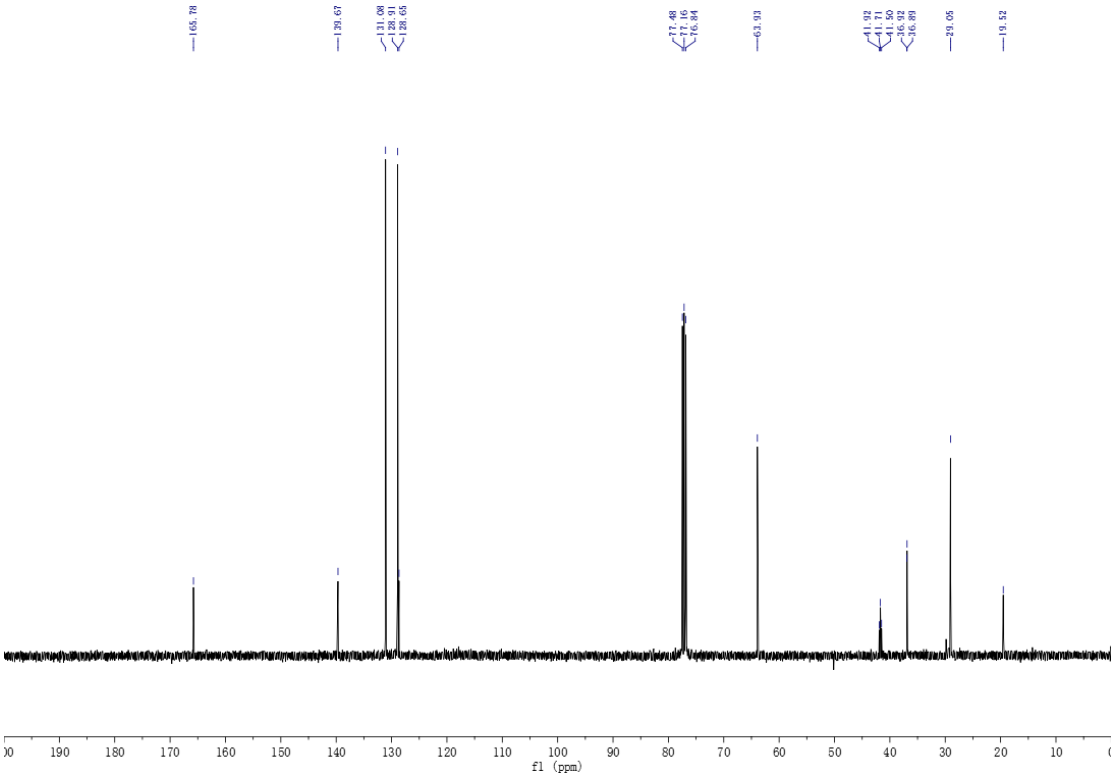

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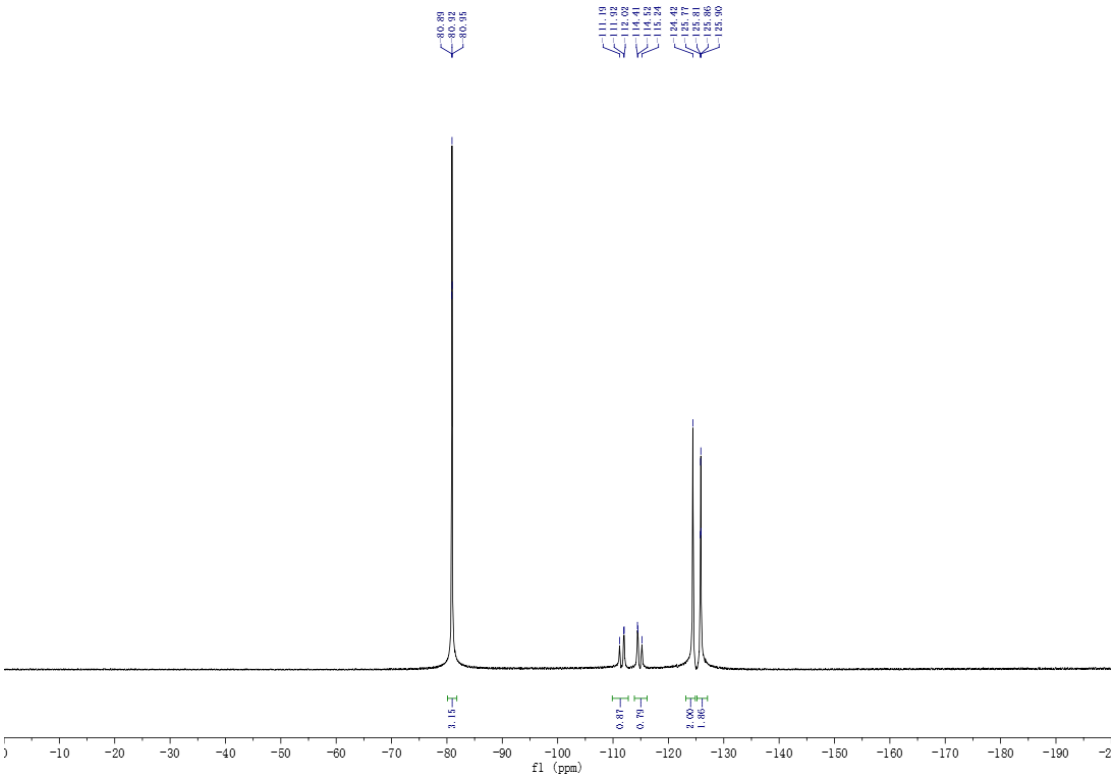

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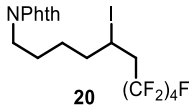

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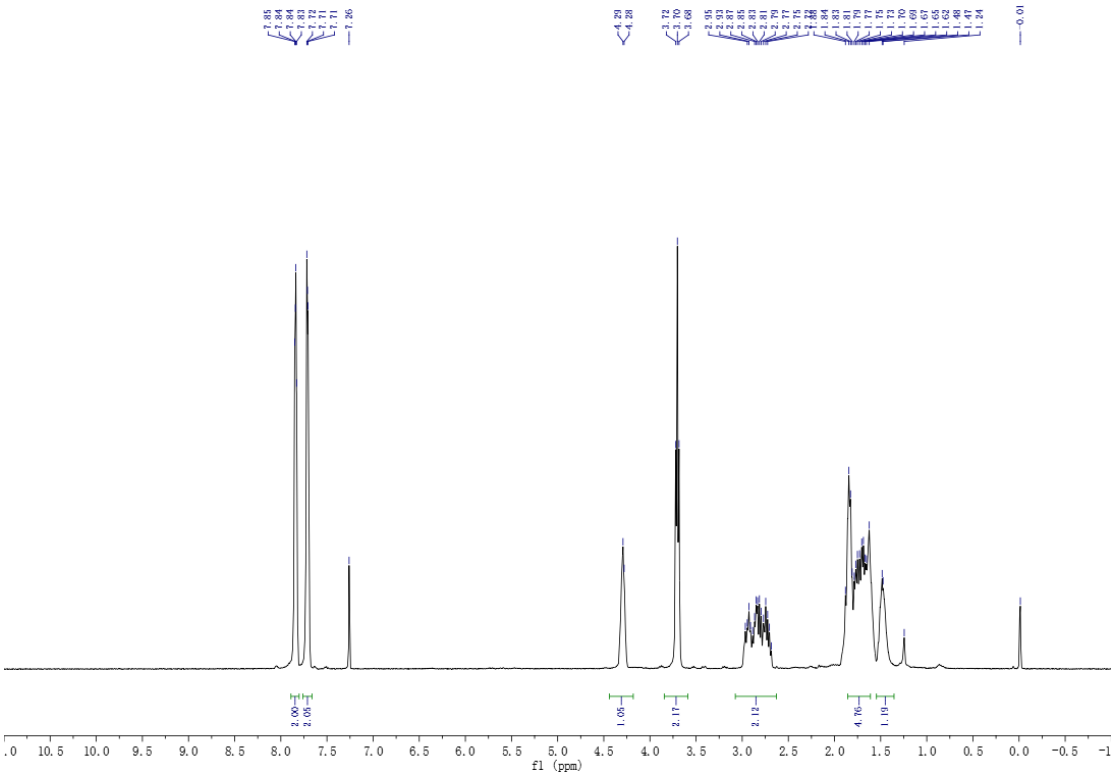

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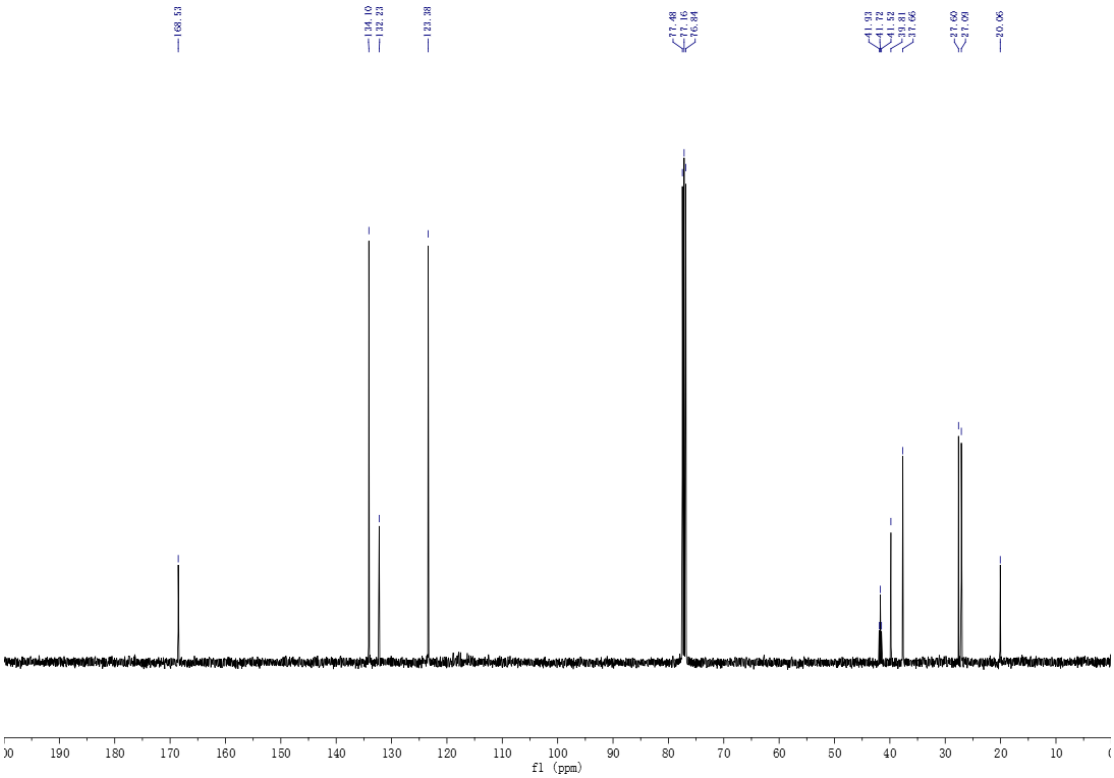

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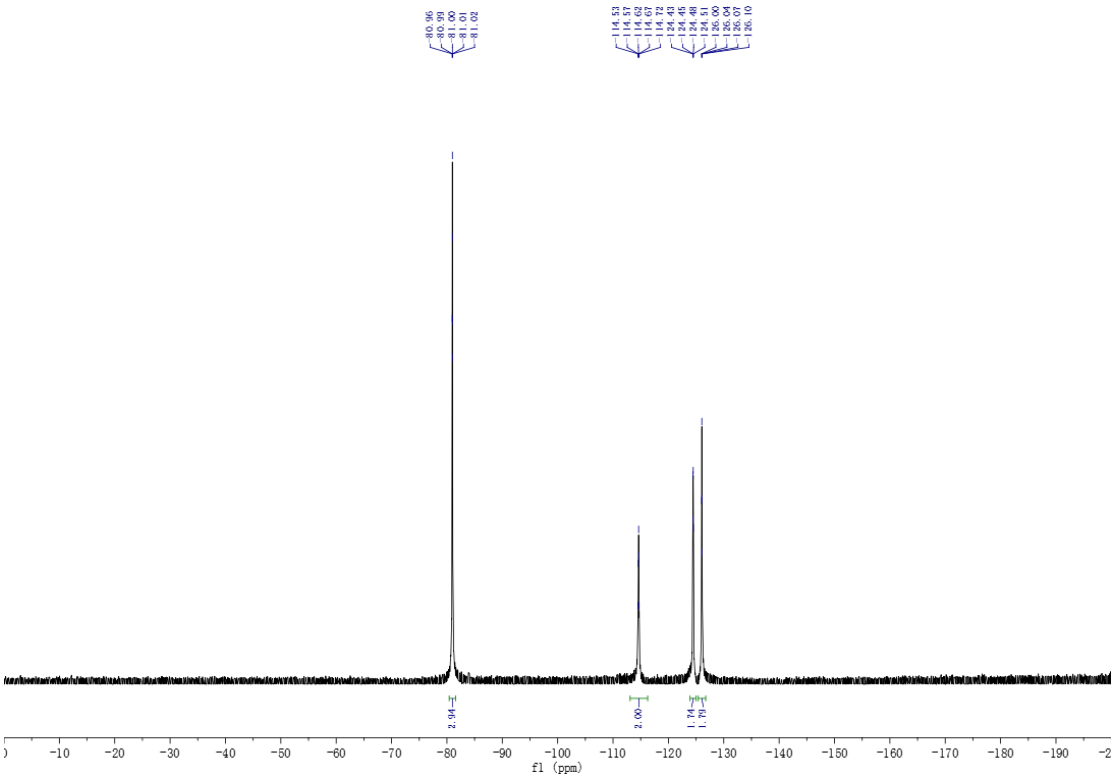

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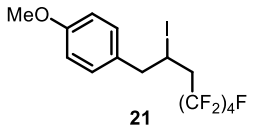

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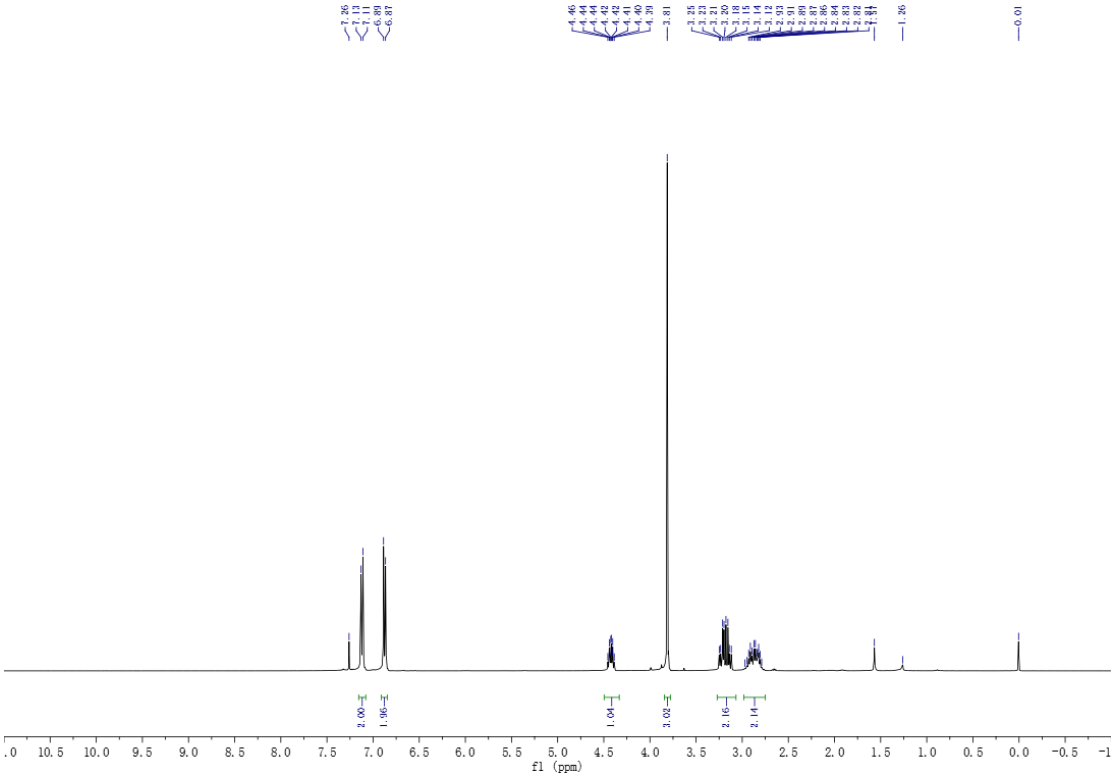

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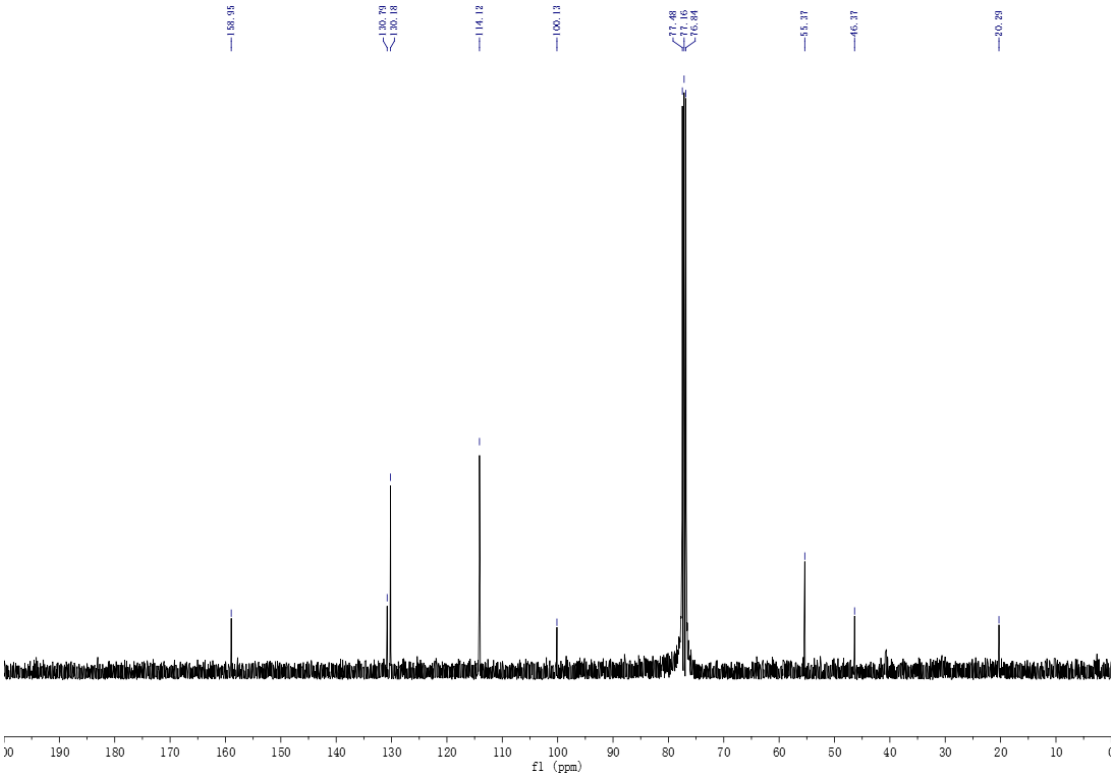

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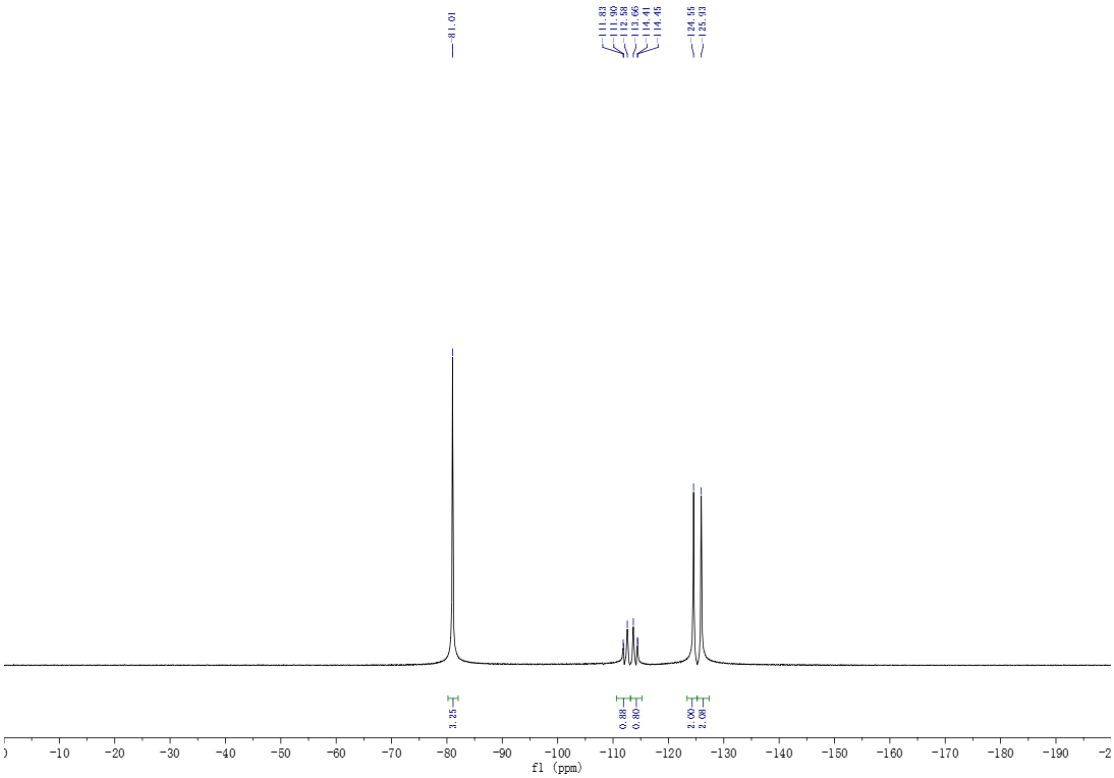

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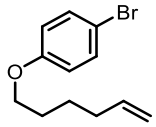
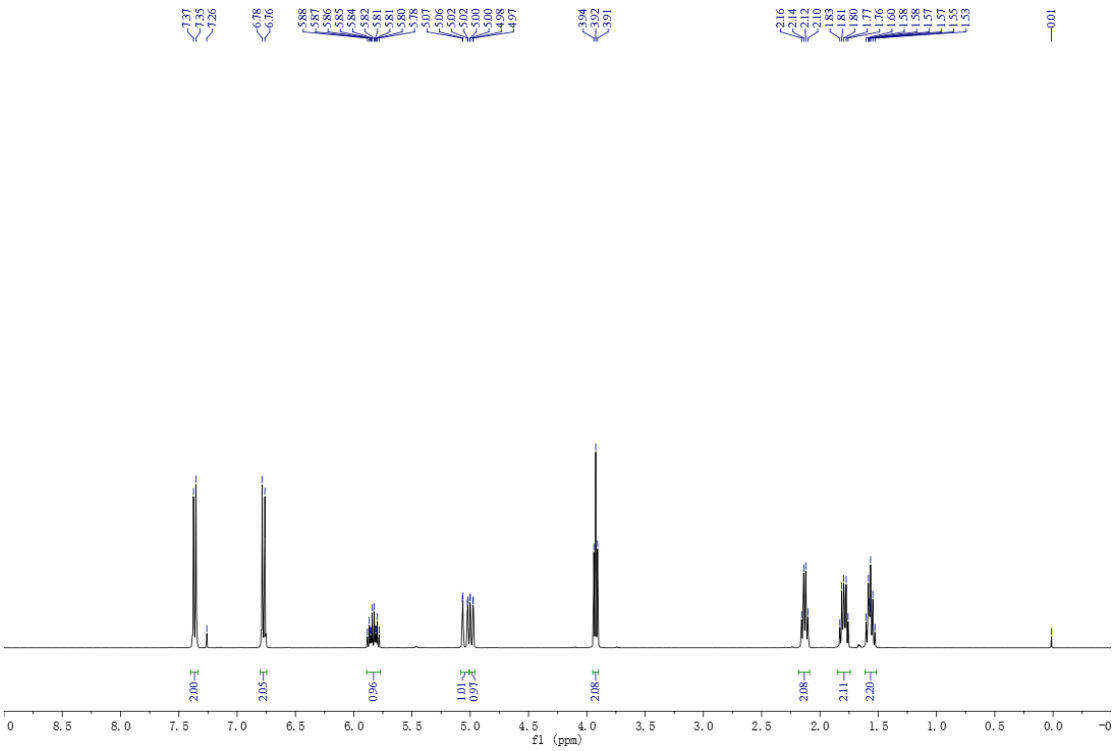


22-1



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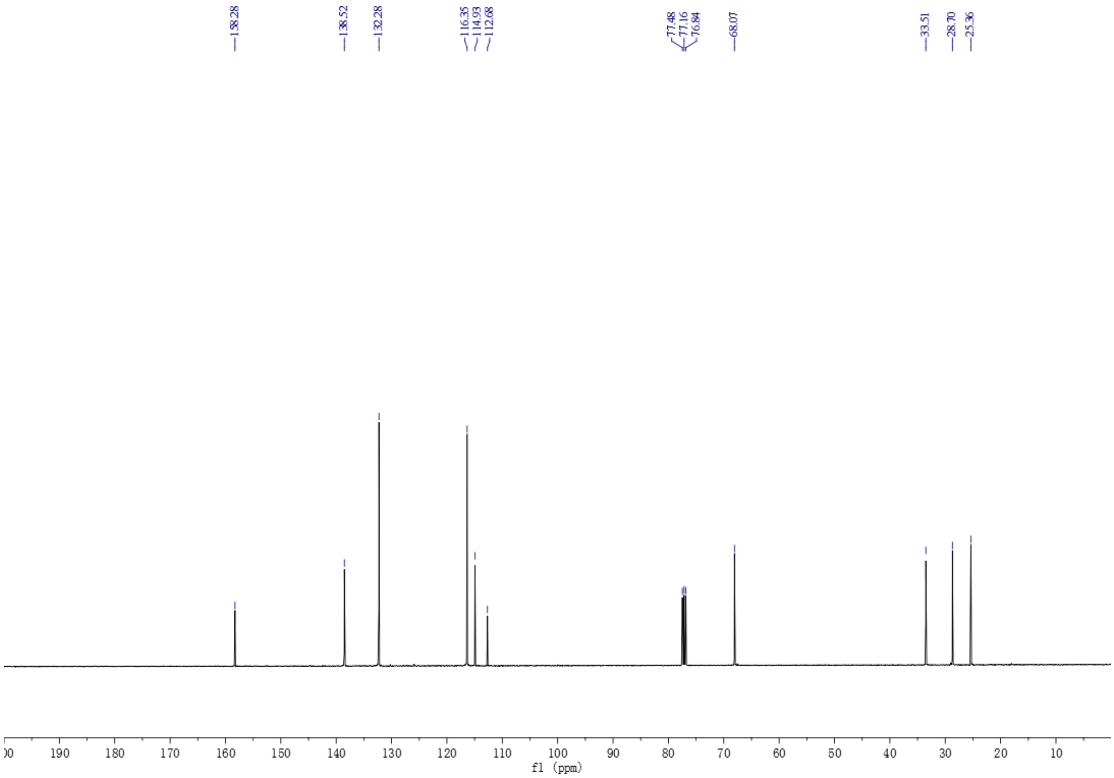

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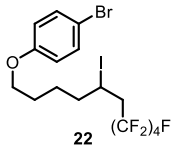

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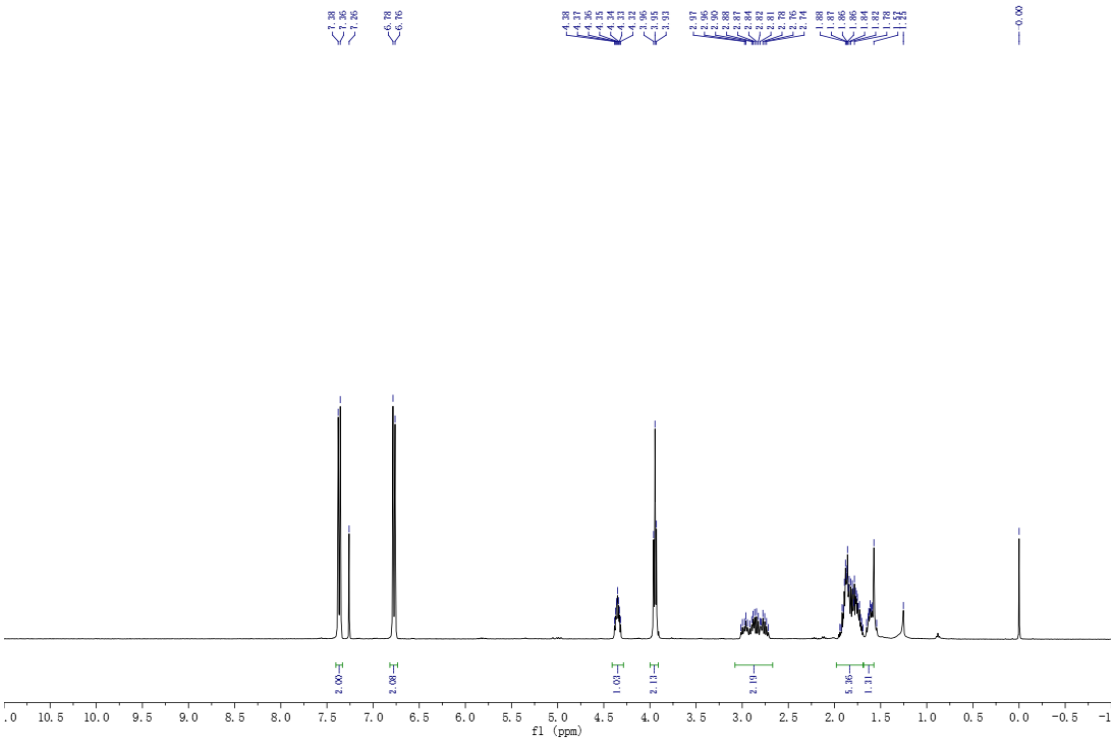

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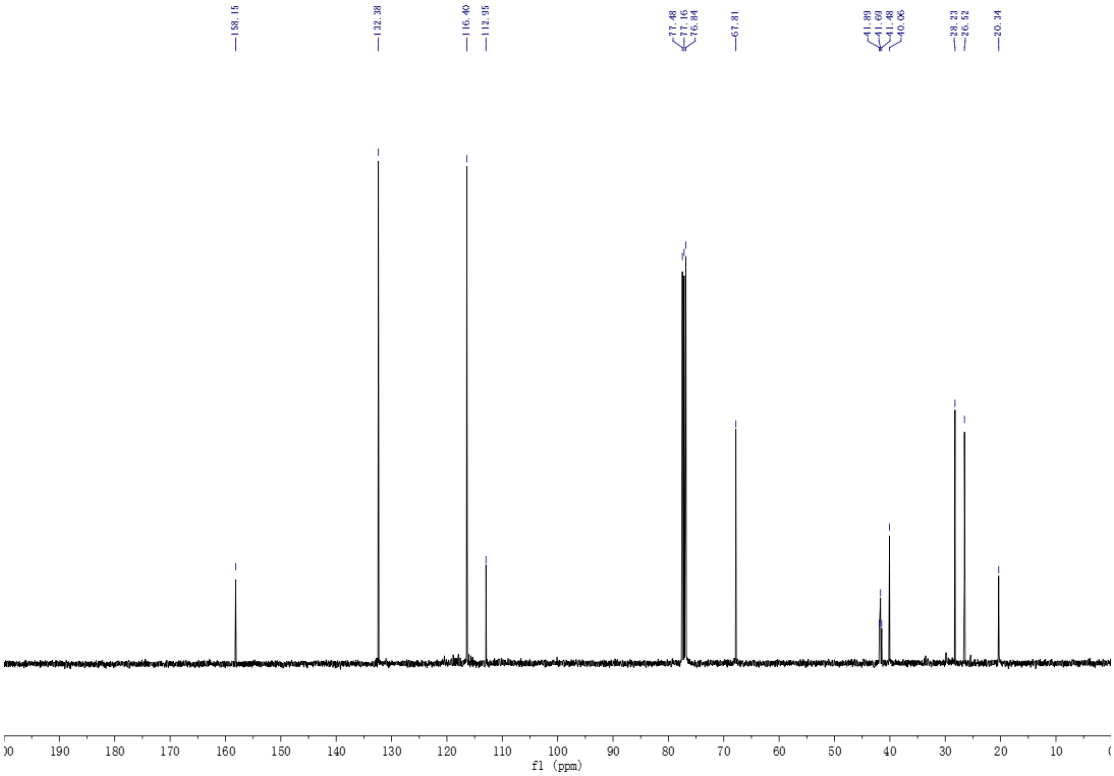

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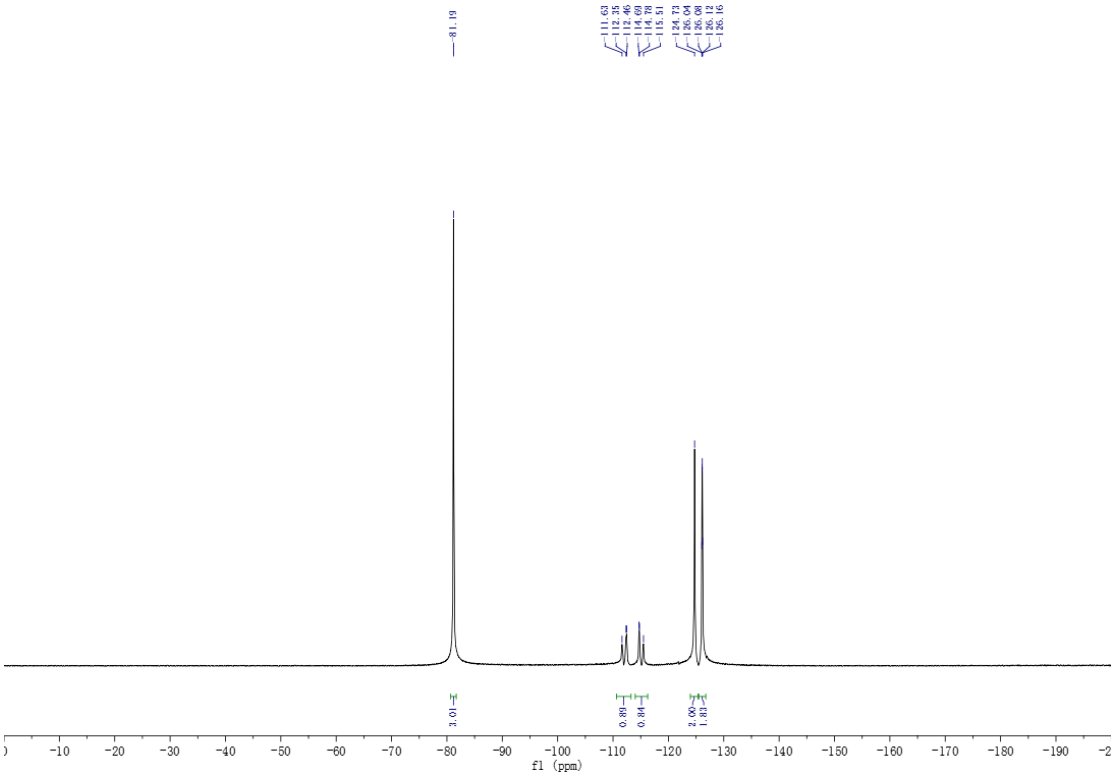

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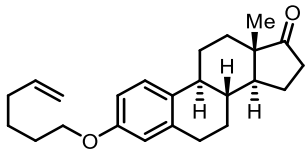
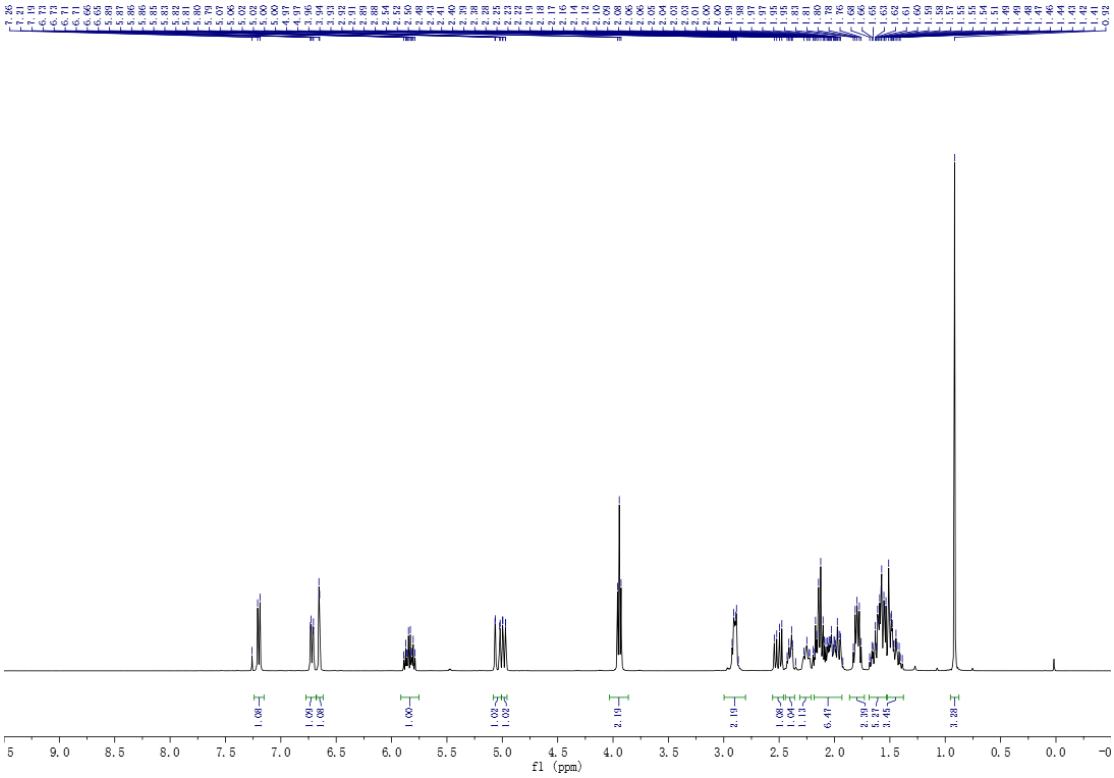


23-1



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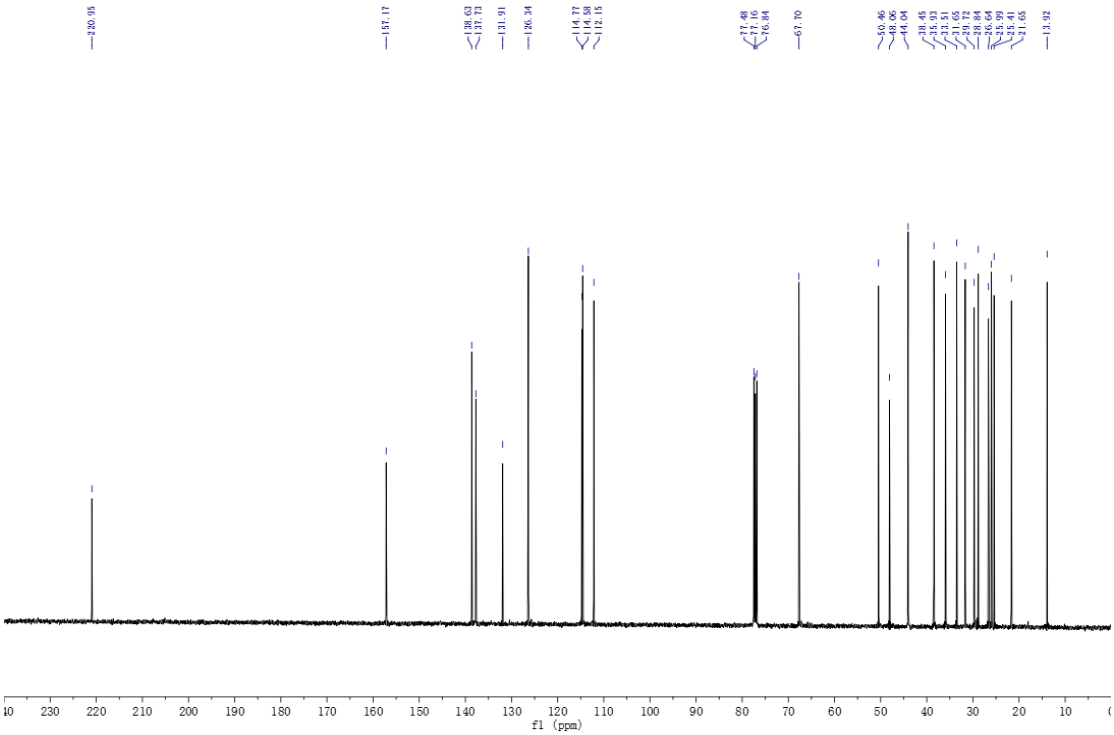
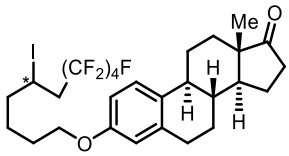
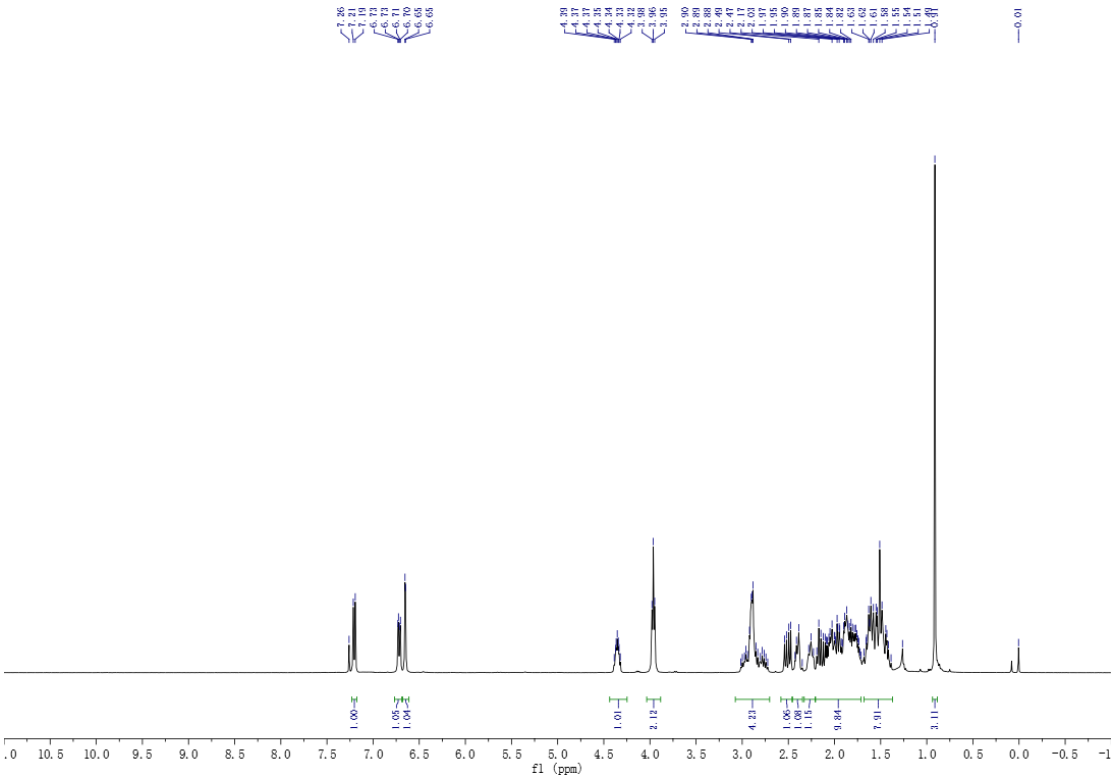


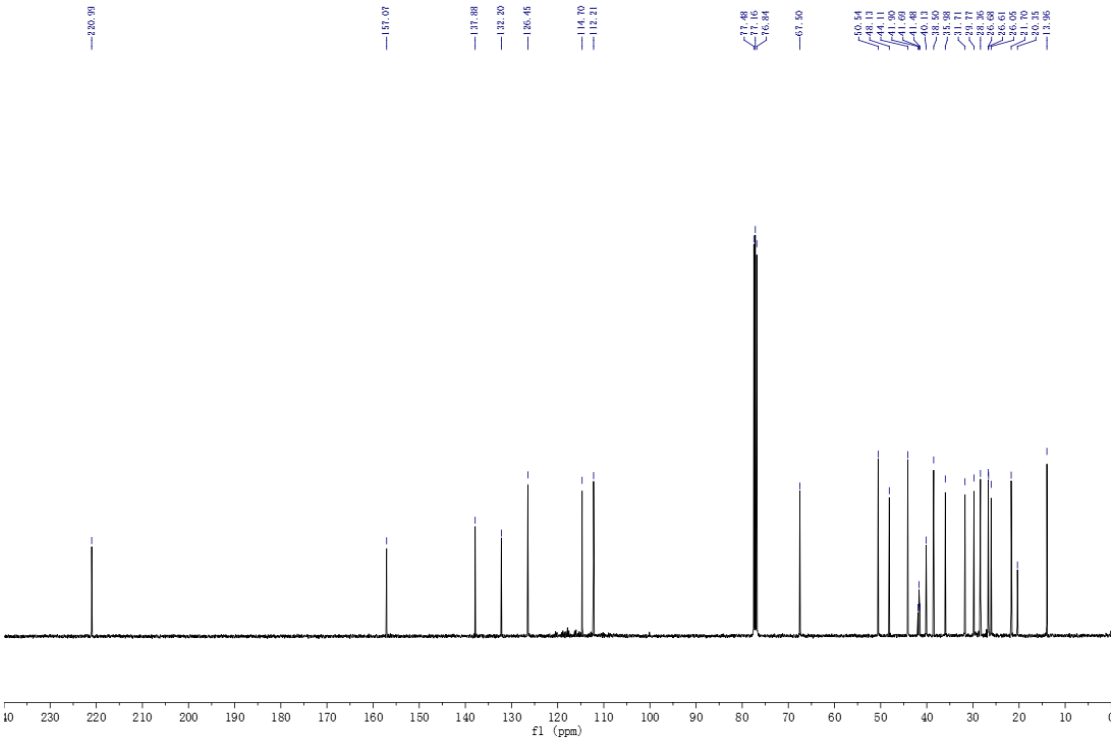
^{13}C NMR of compound **23-1**



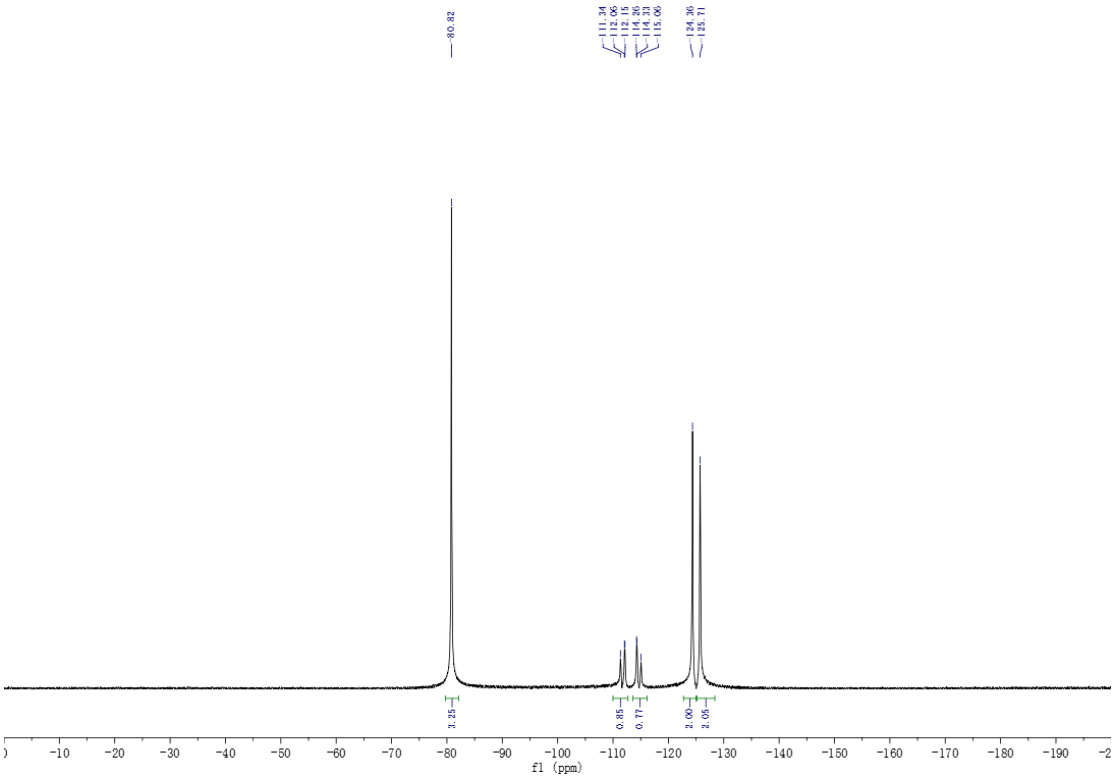
23



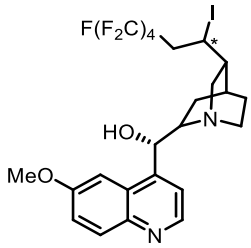
^{1}H NMR of compound **23**



^{13}C NMR of compound **23**



^{19}F NMR of compound **23**



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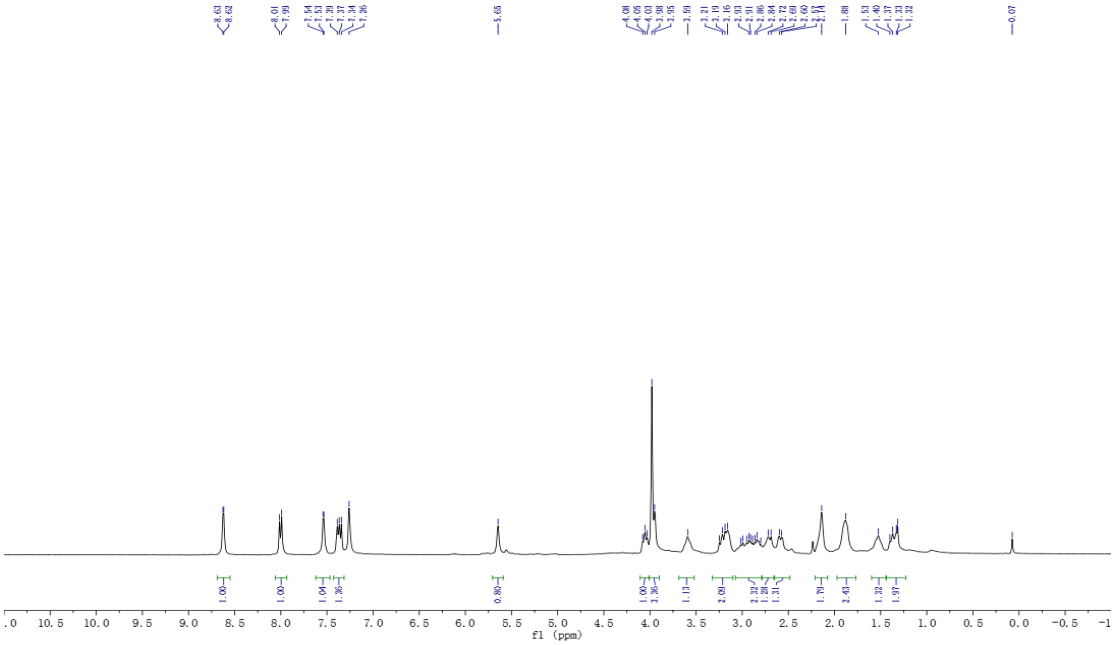
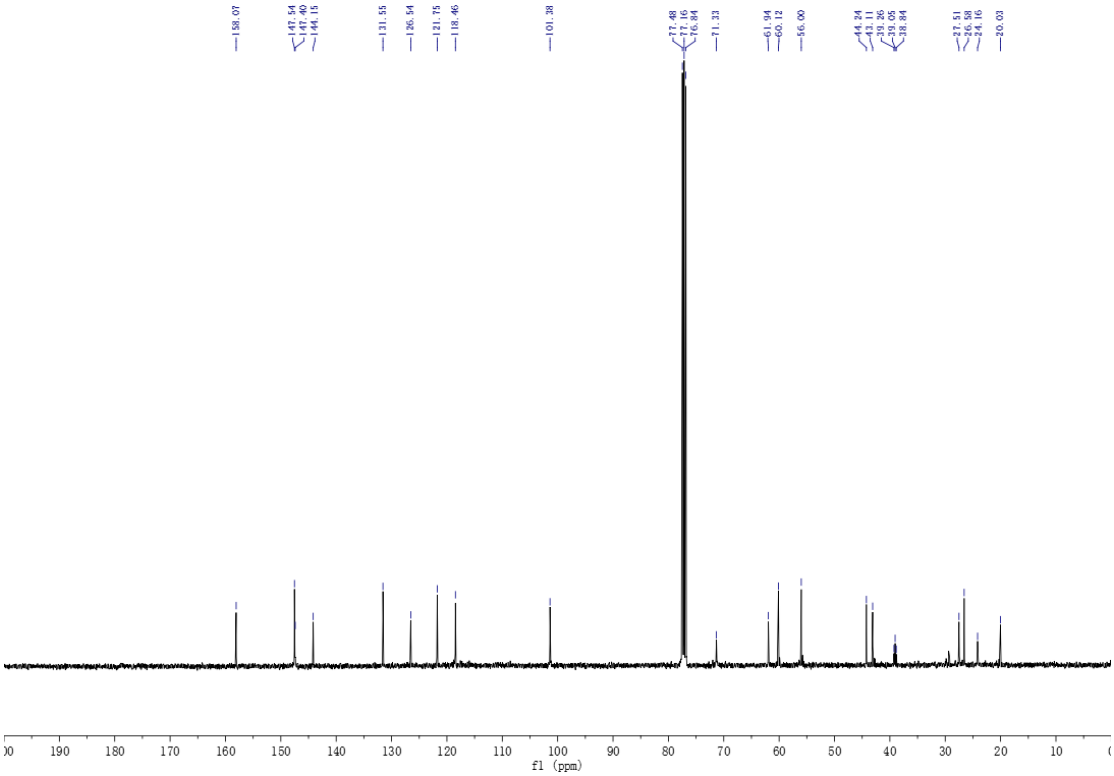
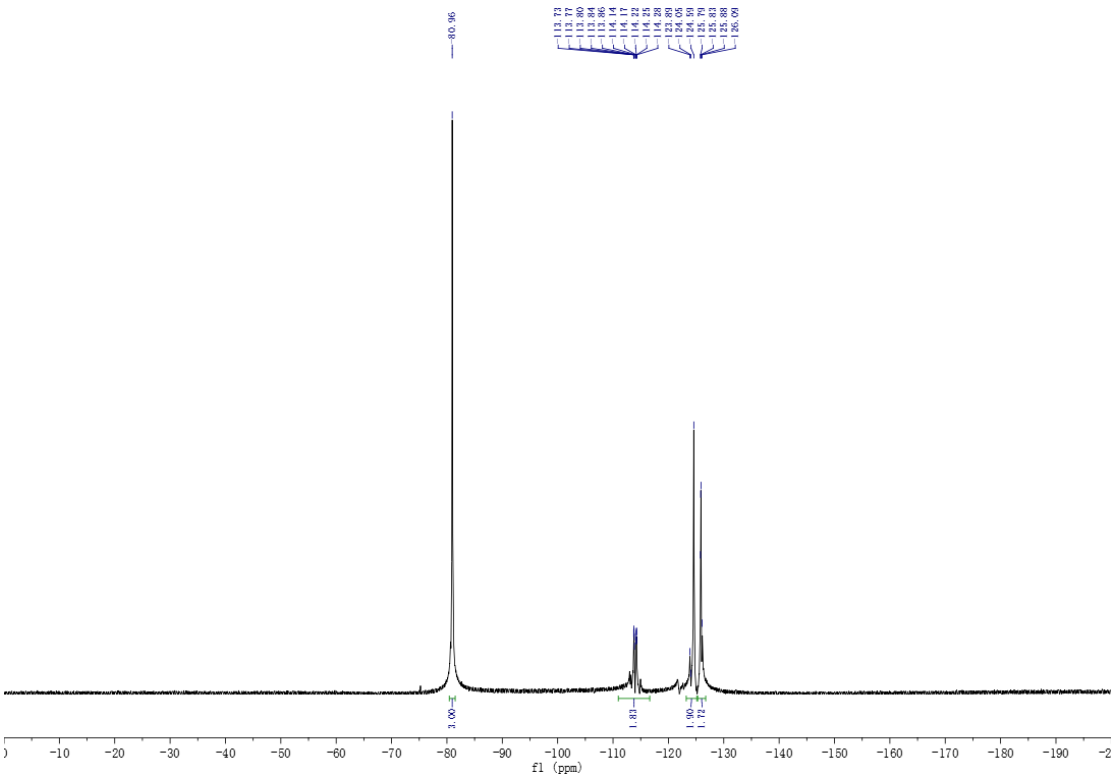


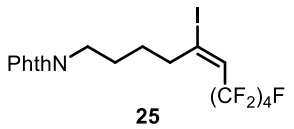
^{1}H NMR of compound **24**



^{13}C NMR of compound **24**



^{19}F NMR of compound **24**



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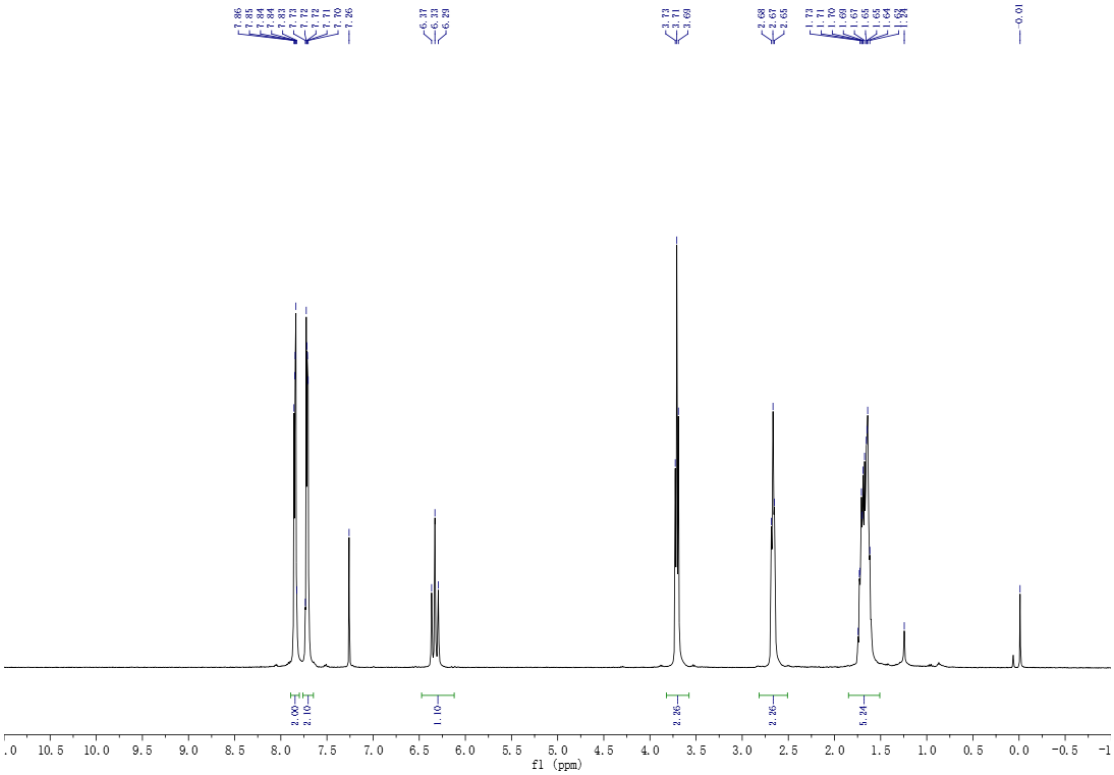
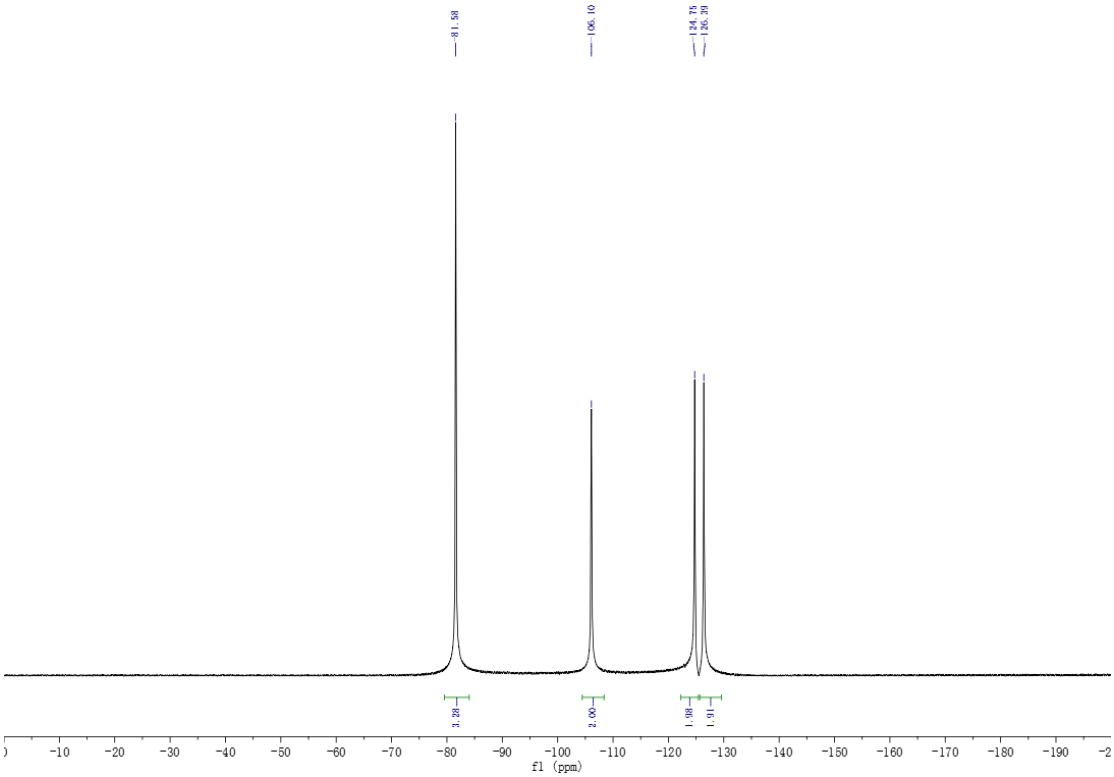
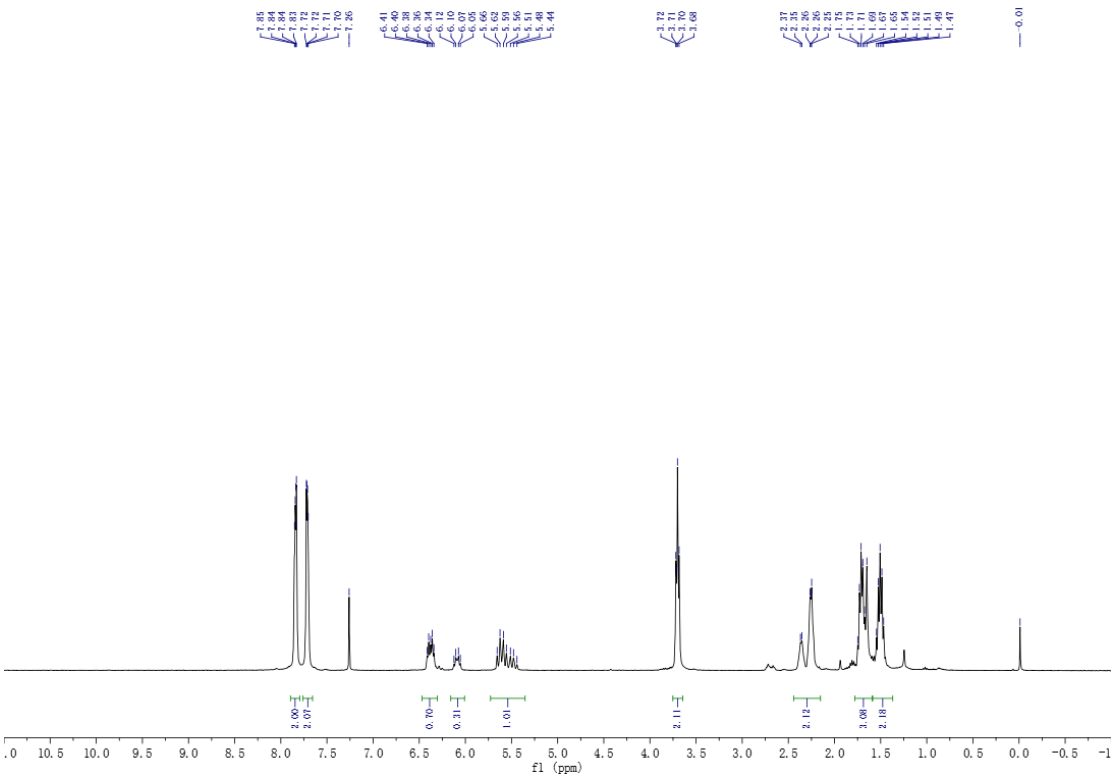


^{1}H NMR of compound **25**

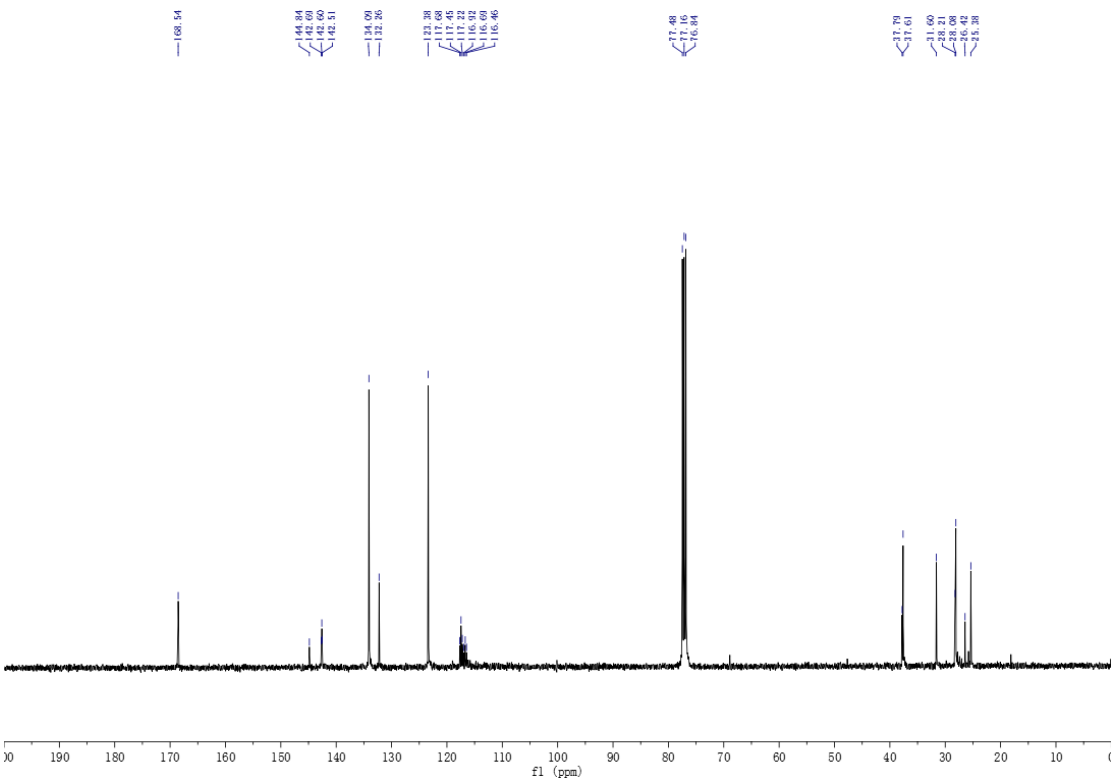


^{19}F NMR of compound **25**

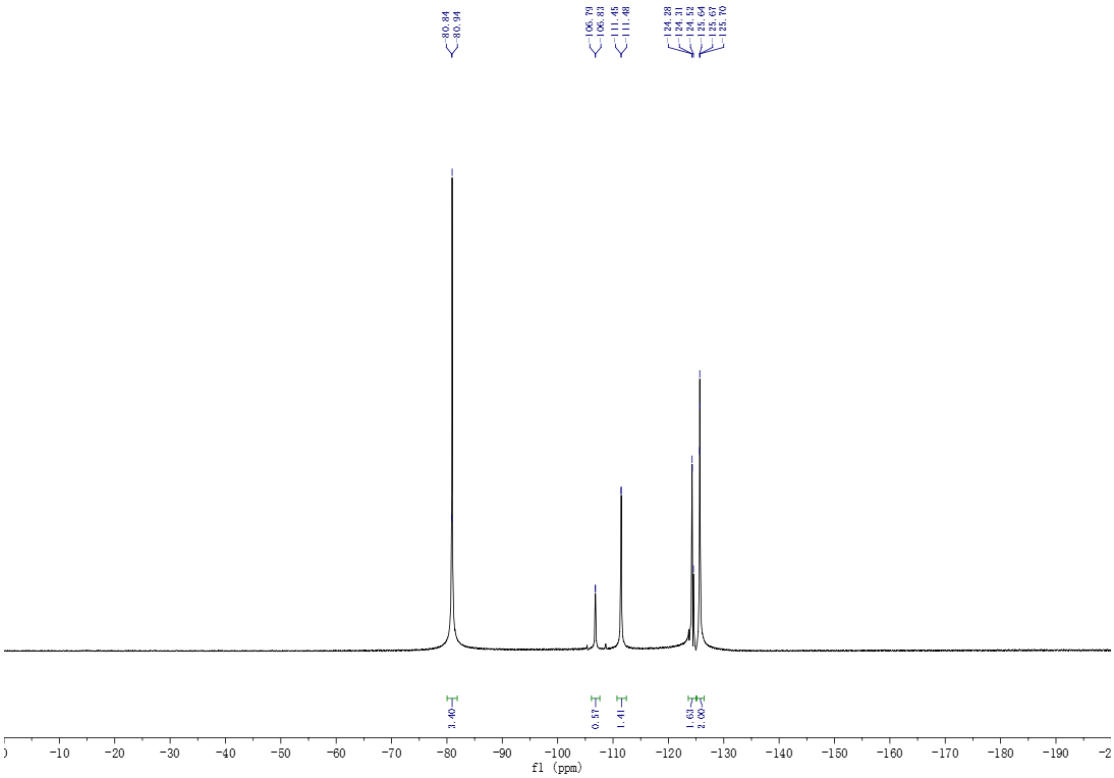
25'



^{1}H NMR of compound **25'**



^{13}C NMR of compound **25'**



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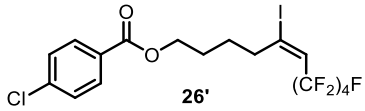
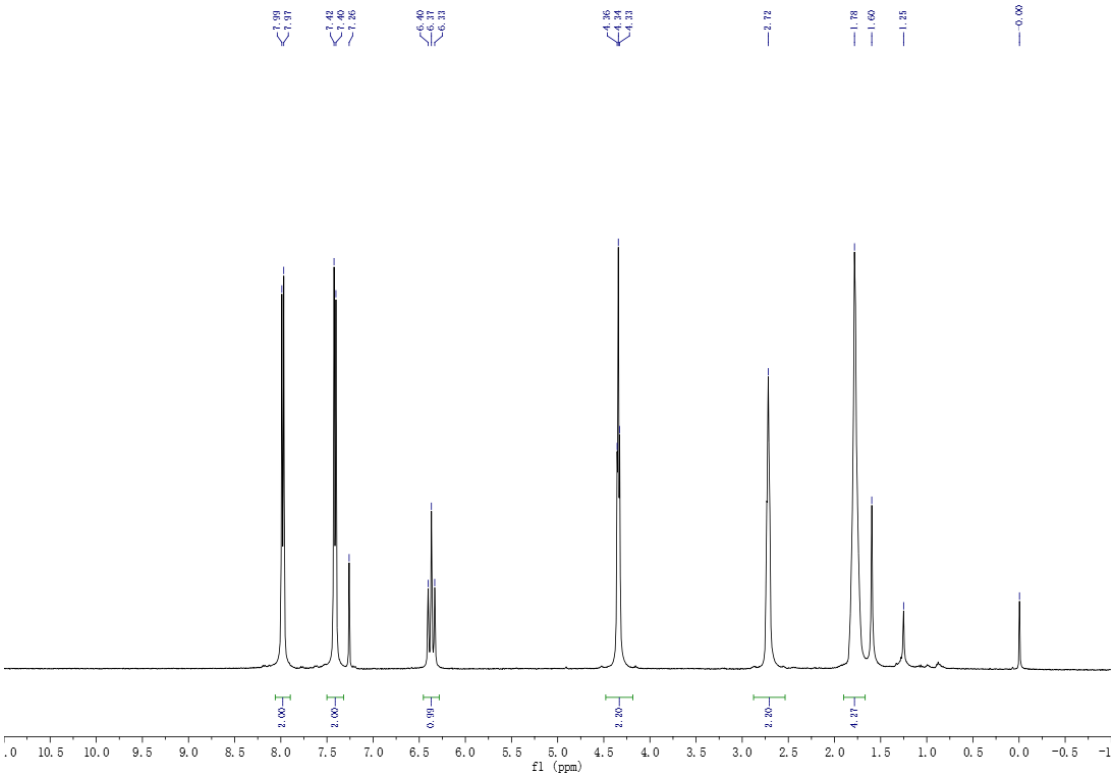
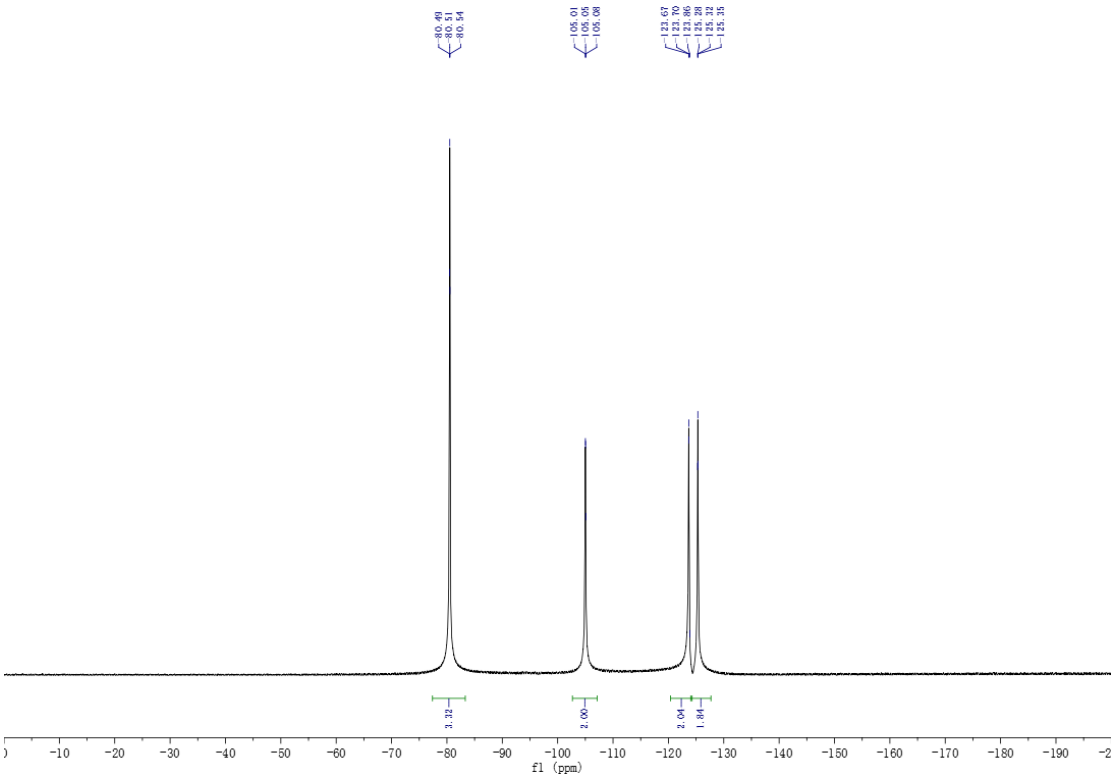


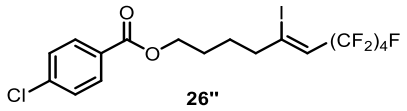
26'

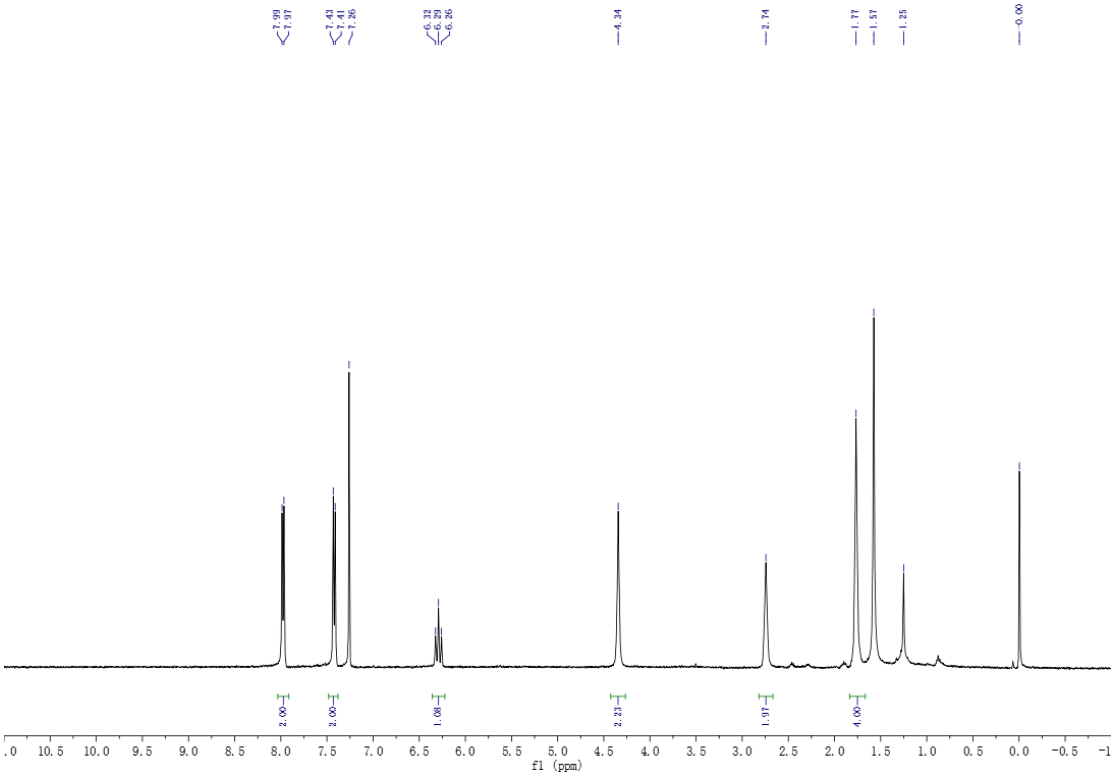


^{1}H NMR of compound **26'**

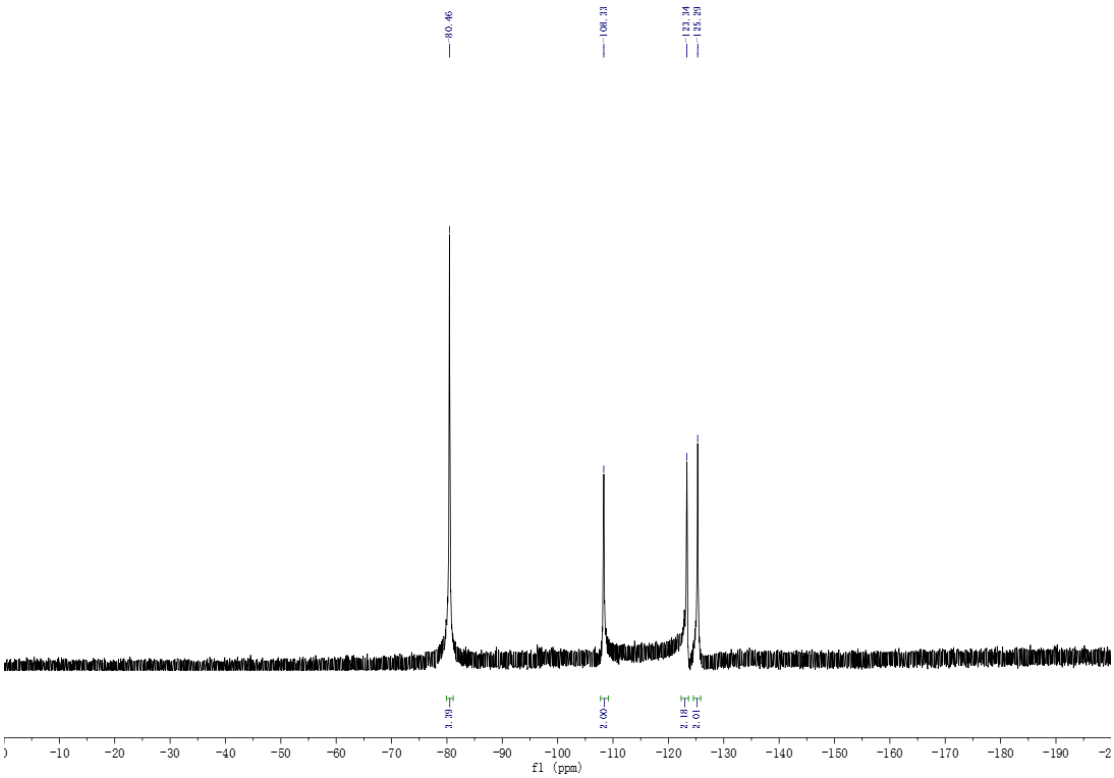


^{19}F NMR of compound **26'**

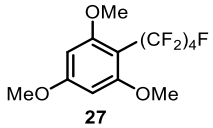




^{1}H NMR of compound **26''**



^{19}F NMR of compound **26”**



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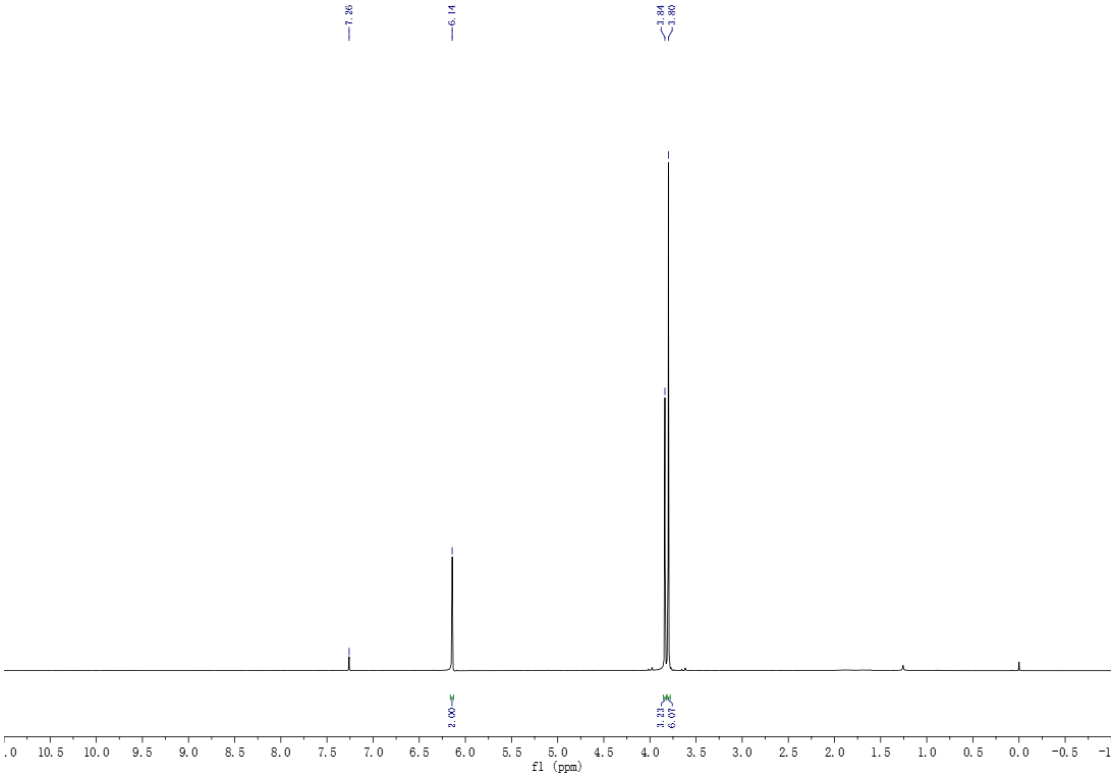
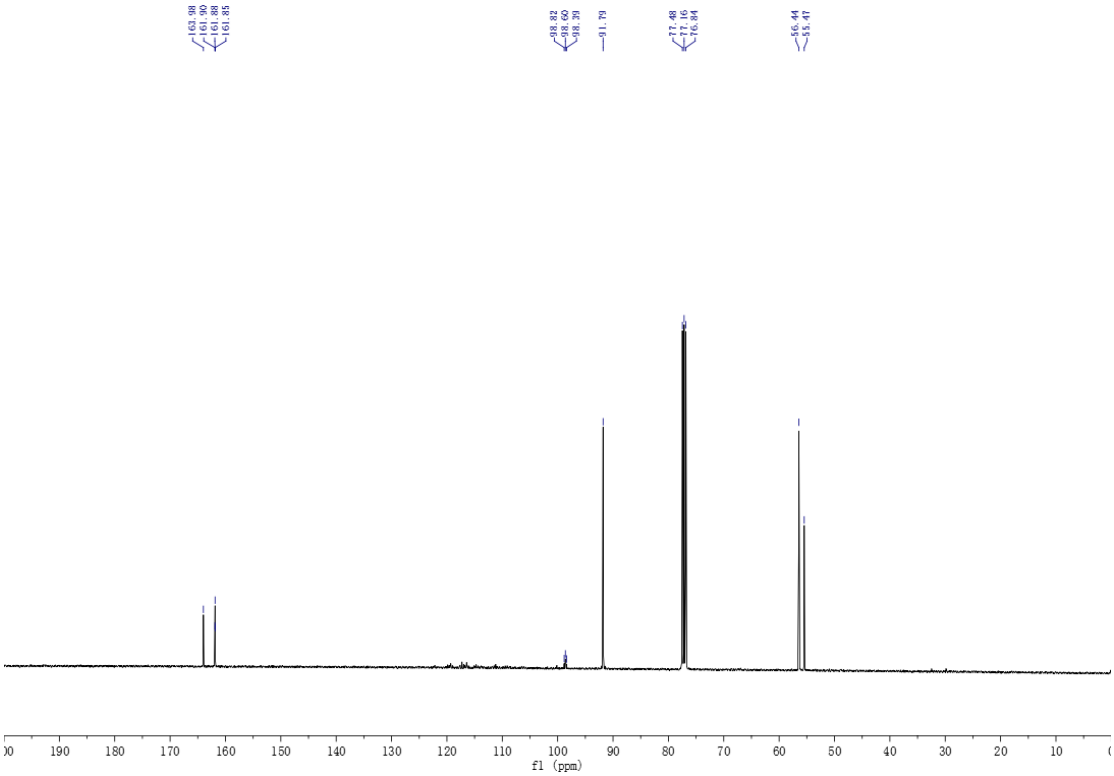
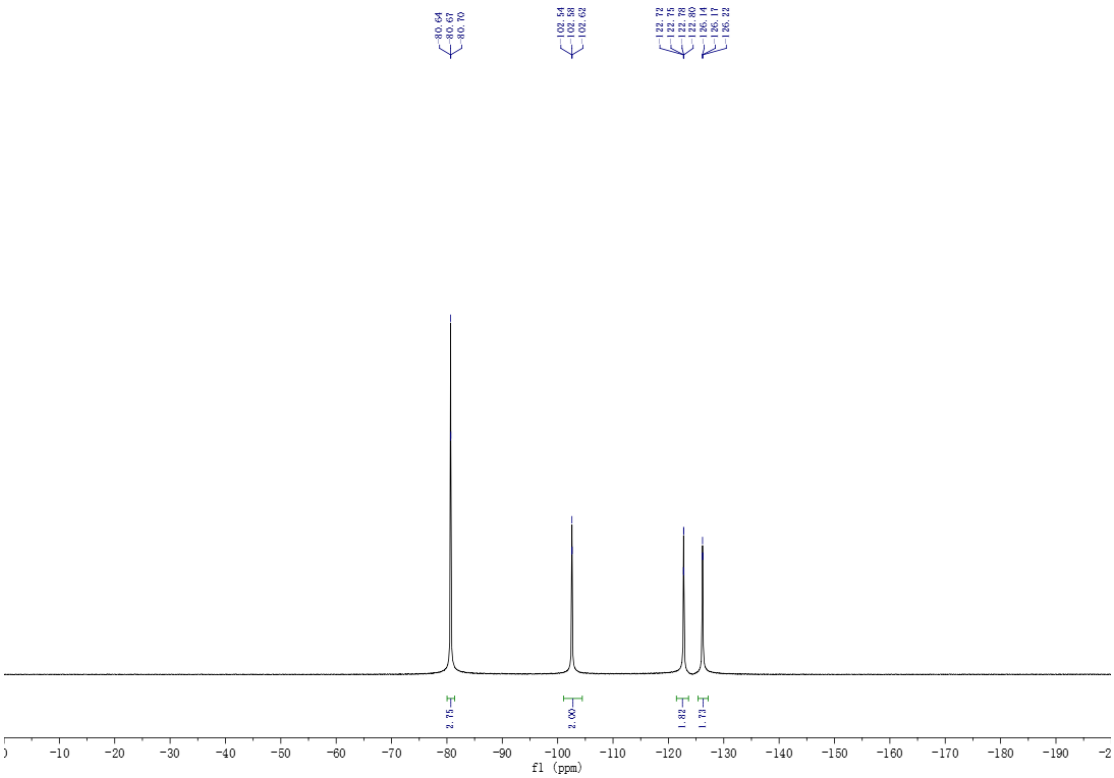


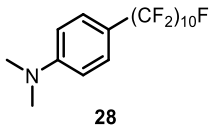
^{1}H NMR of compound **27**



^{13}C NMR of compound **27**



^{19}F NMR of compound **27**



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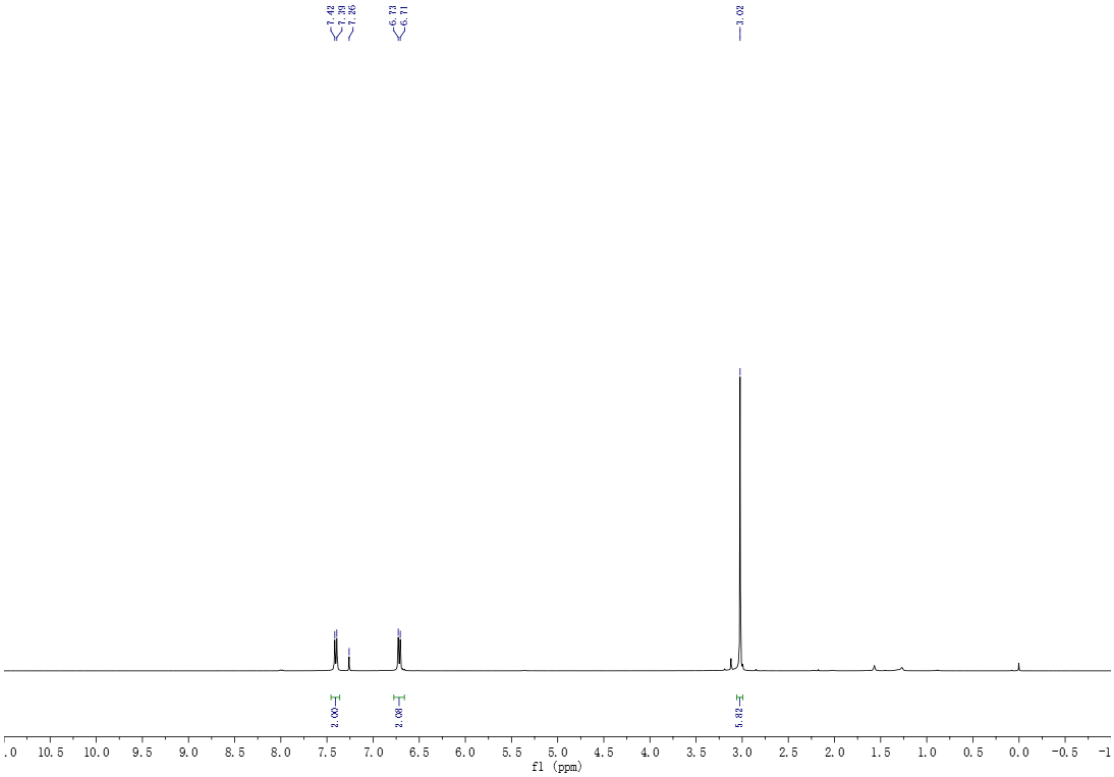

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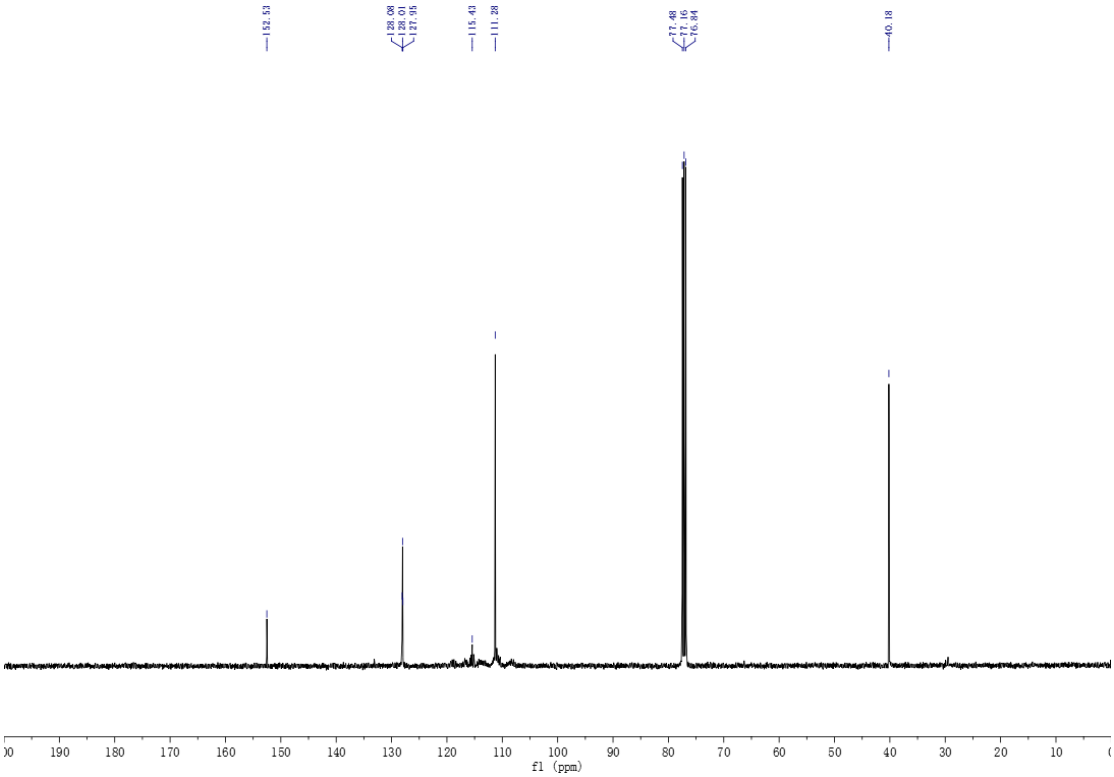
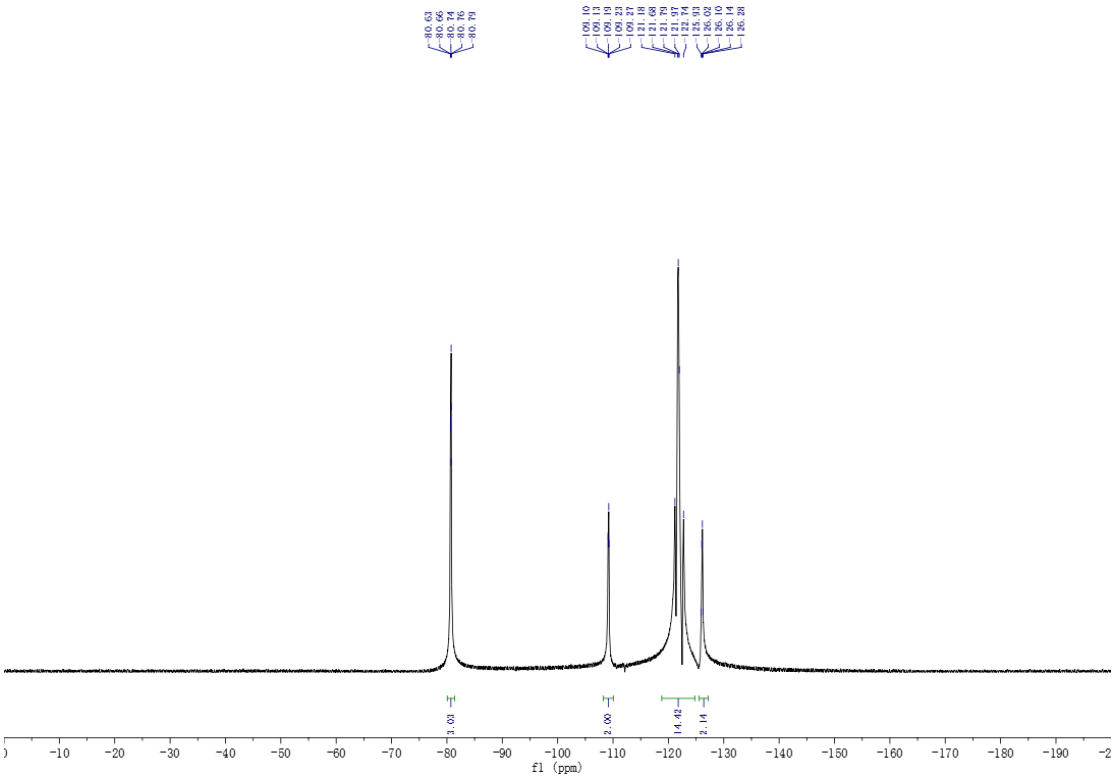
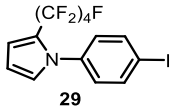
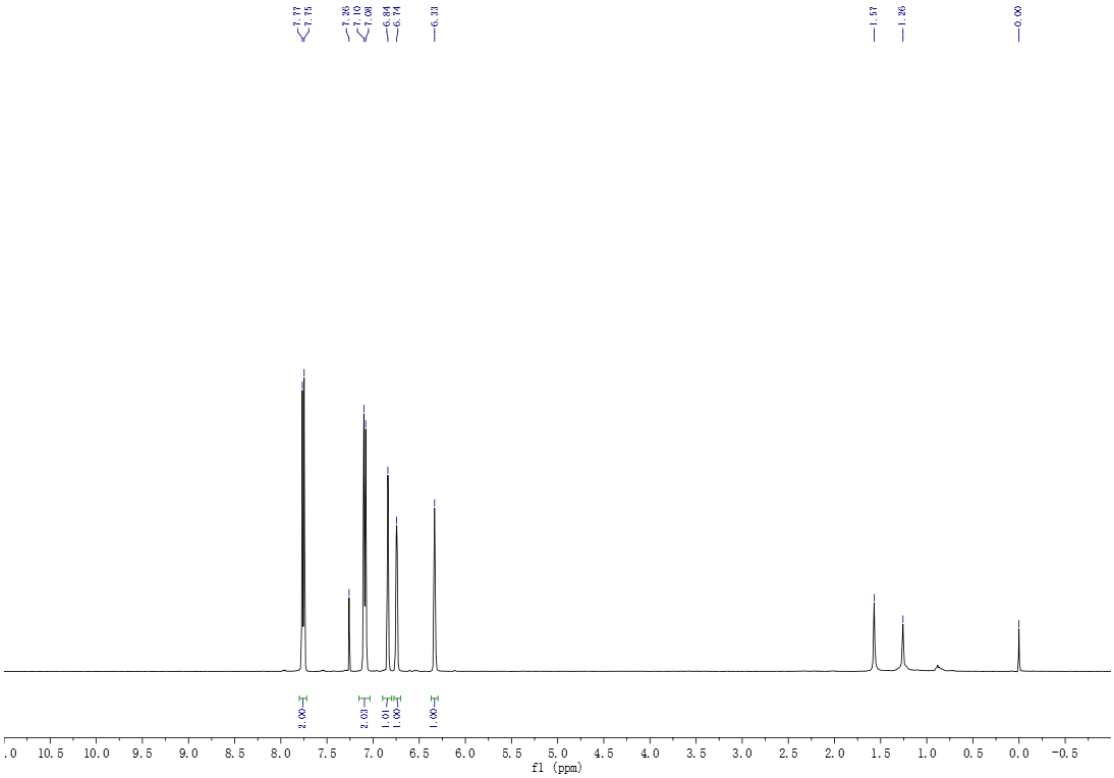


^{13}C NMR of compound **28**

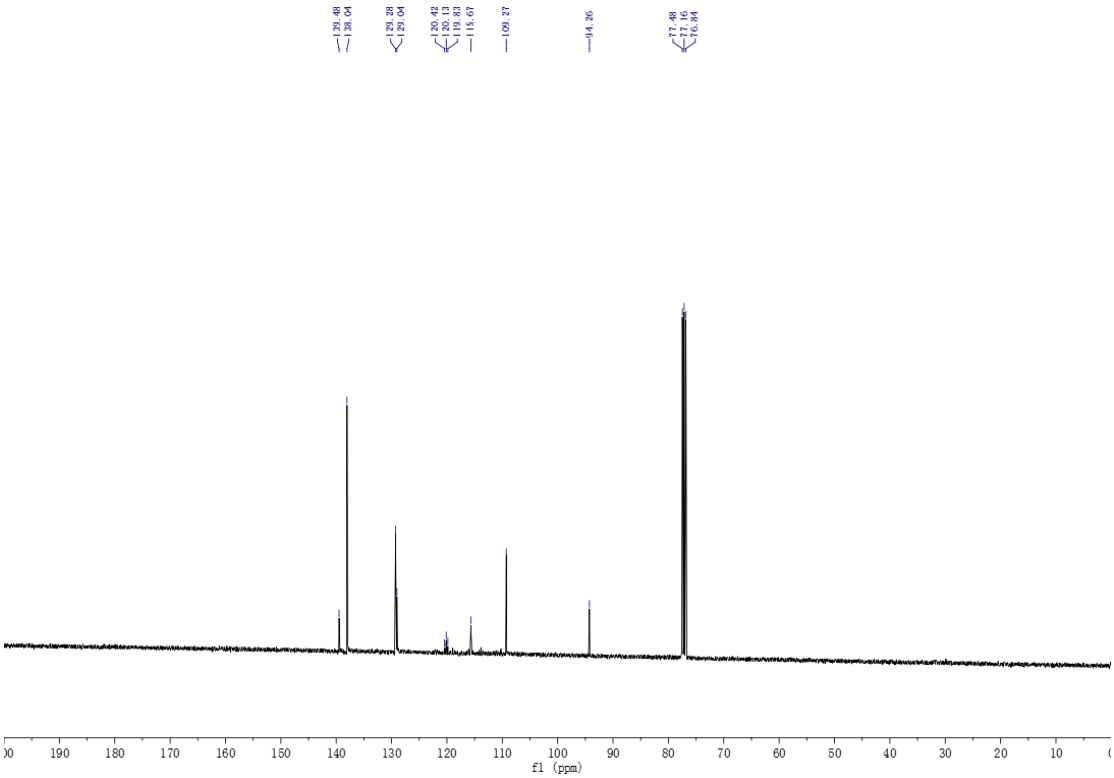


^{19}F NMR of compound **28**

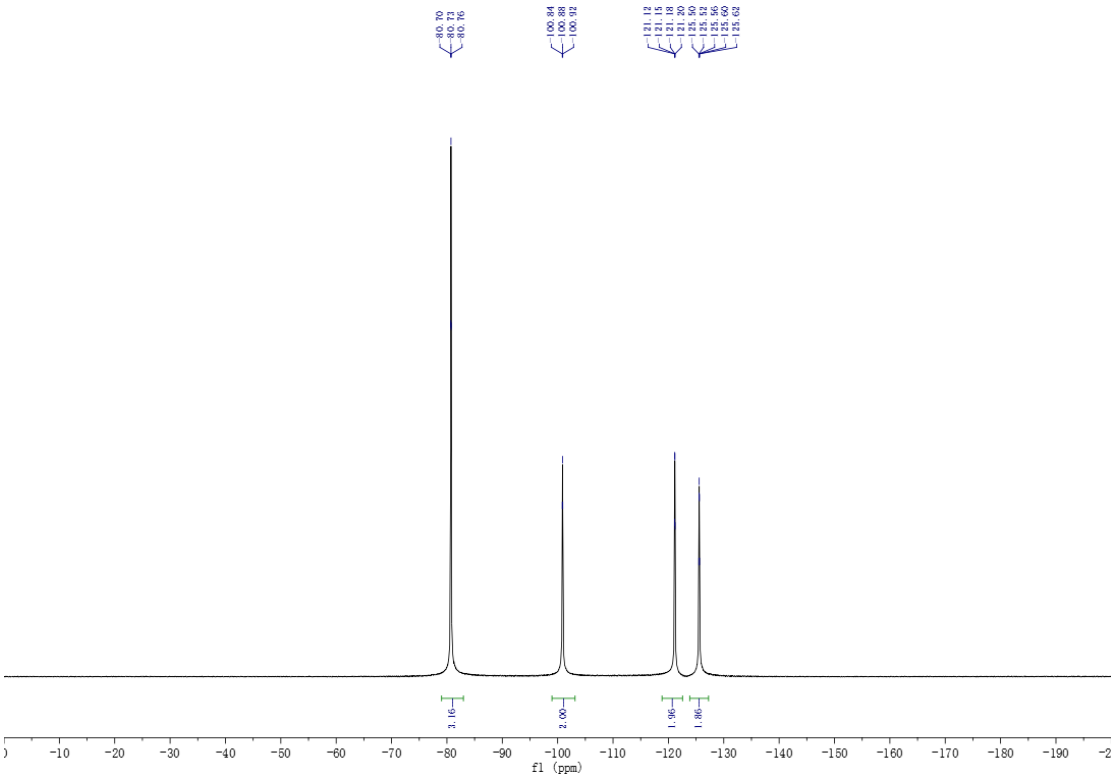




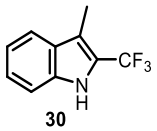
^{1}H NMR of compound **29**



^{13}C NMR of compound **29**



^{19}F NMR of compound **29**



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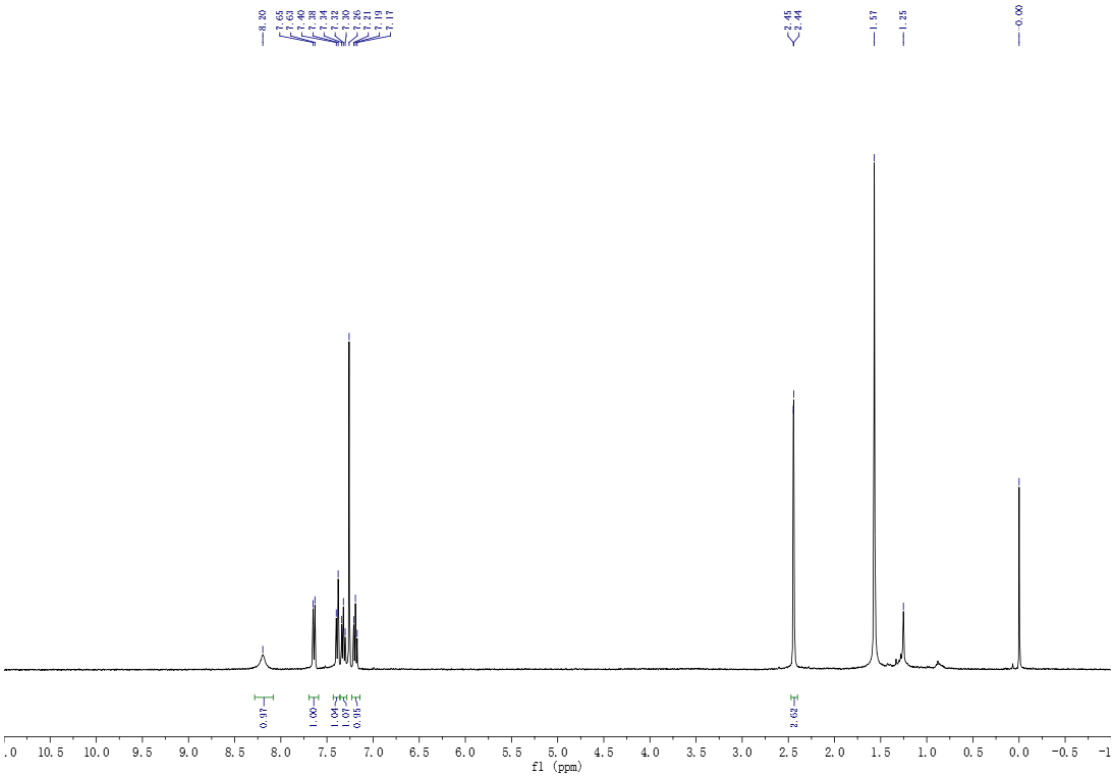

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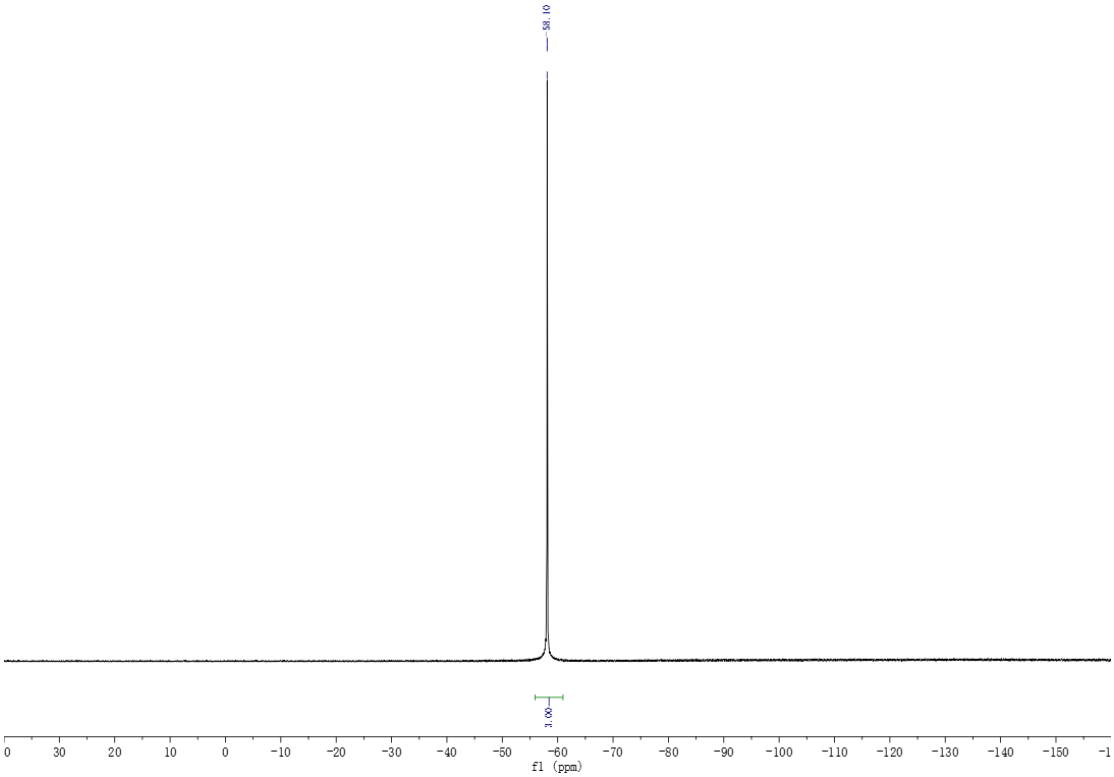

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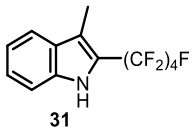

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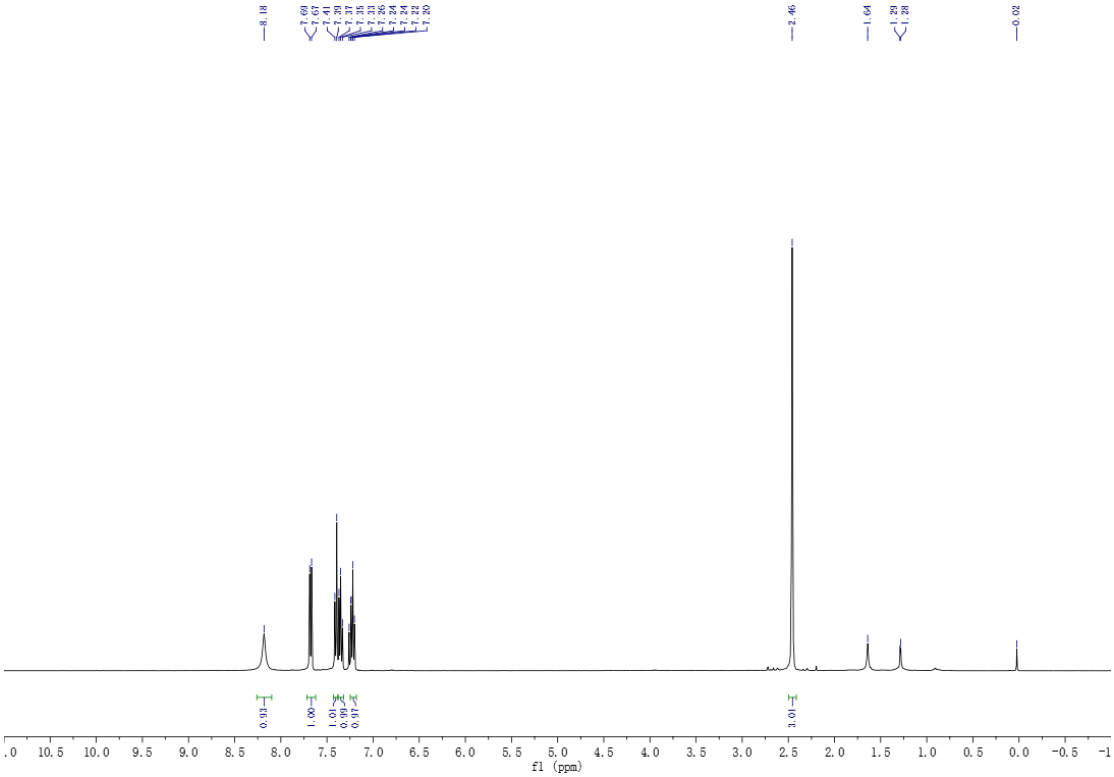
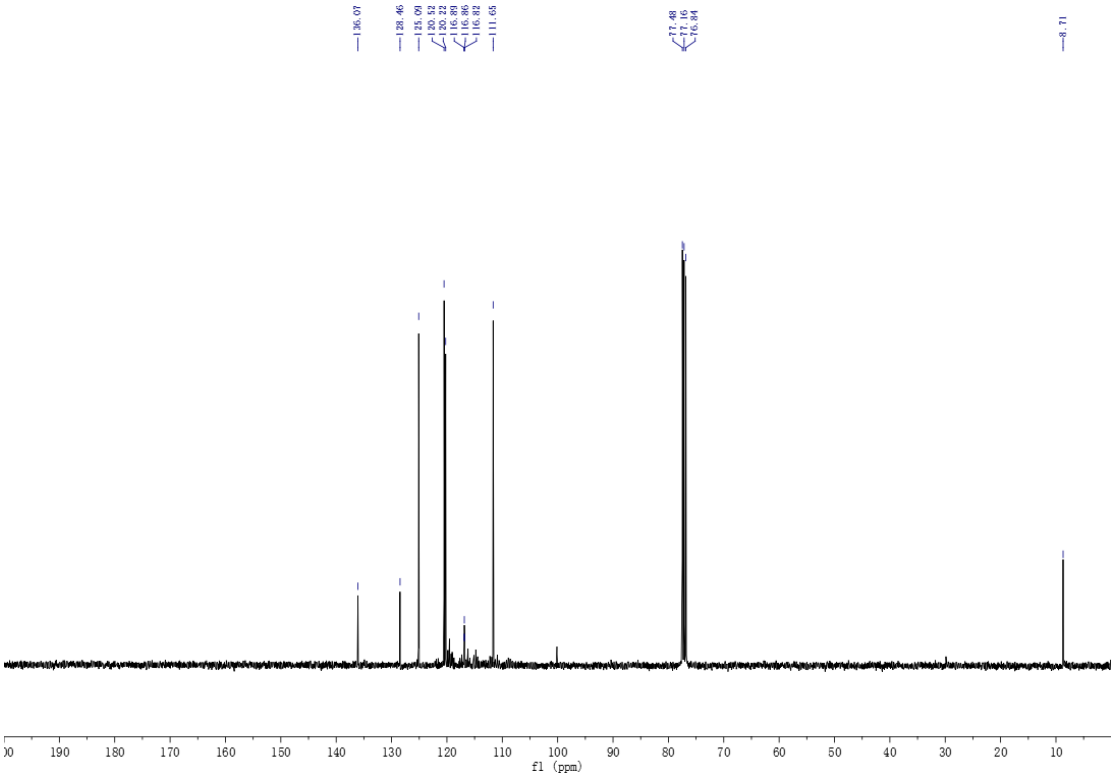
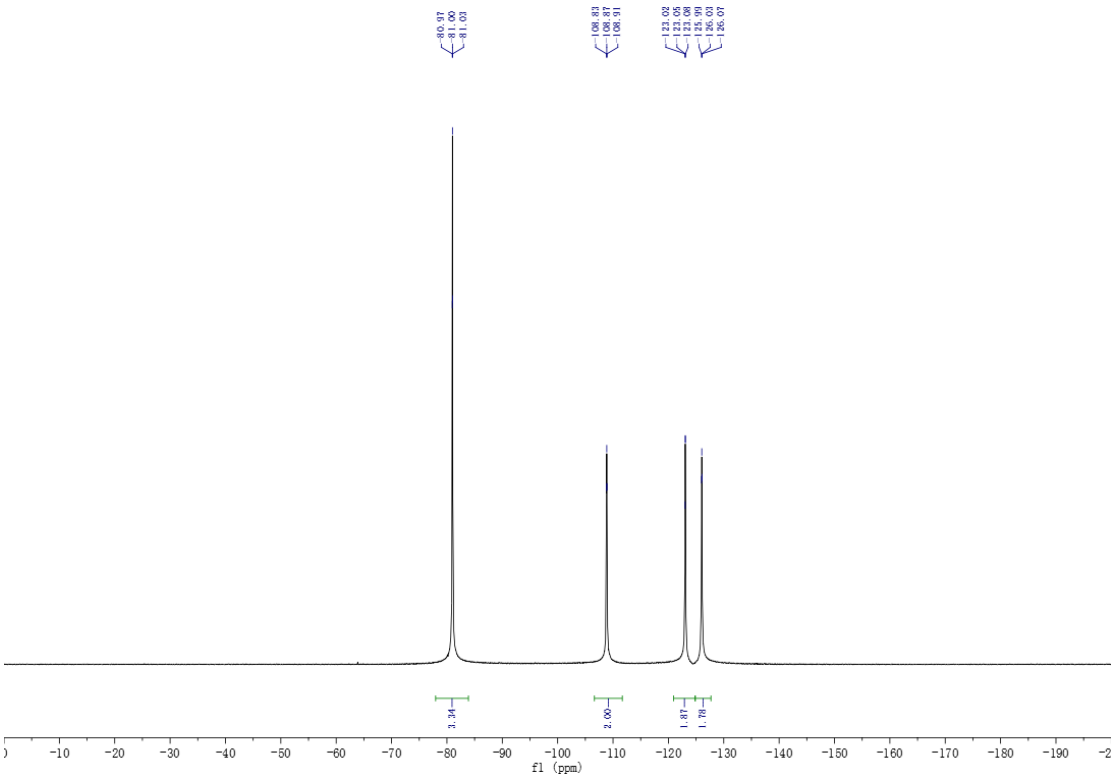


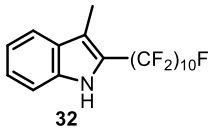
^{1}H NMR of compound **31**



^{13}C NMR of compound **31**



^{19}F NMR of compound **31**



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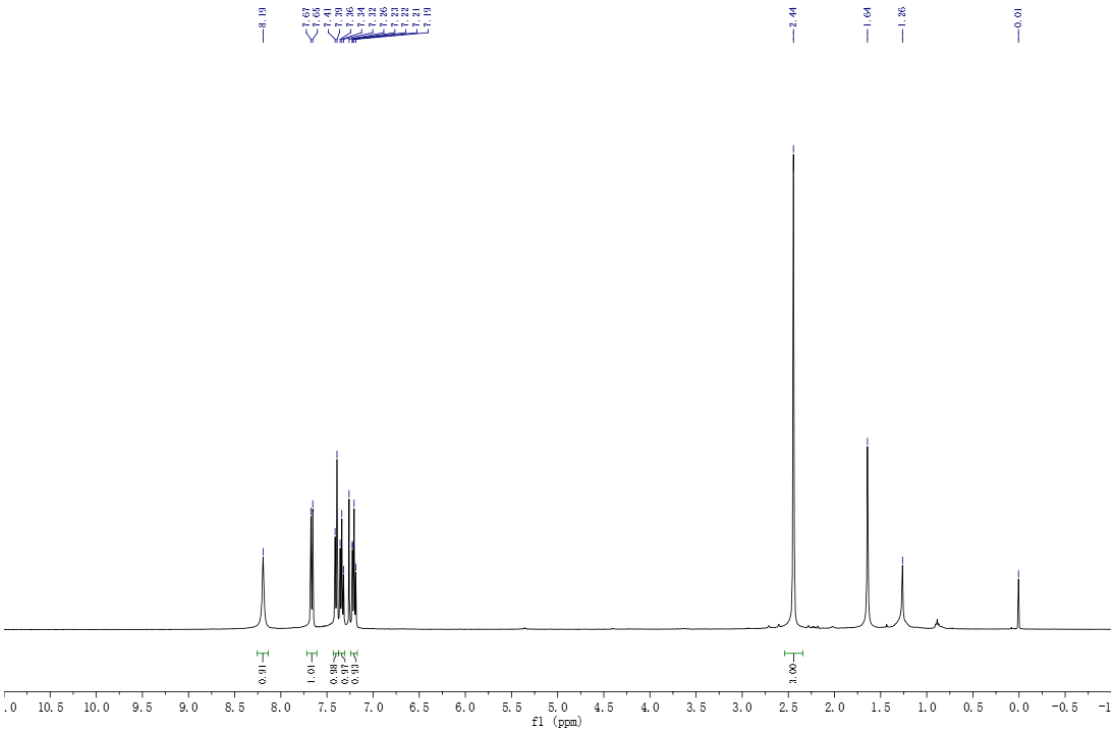
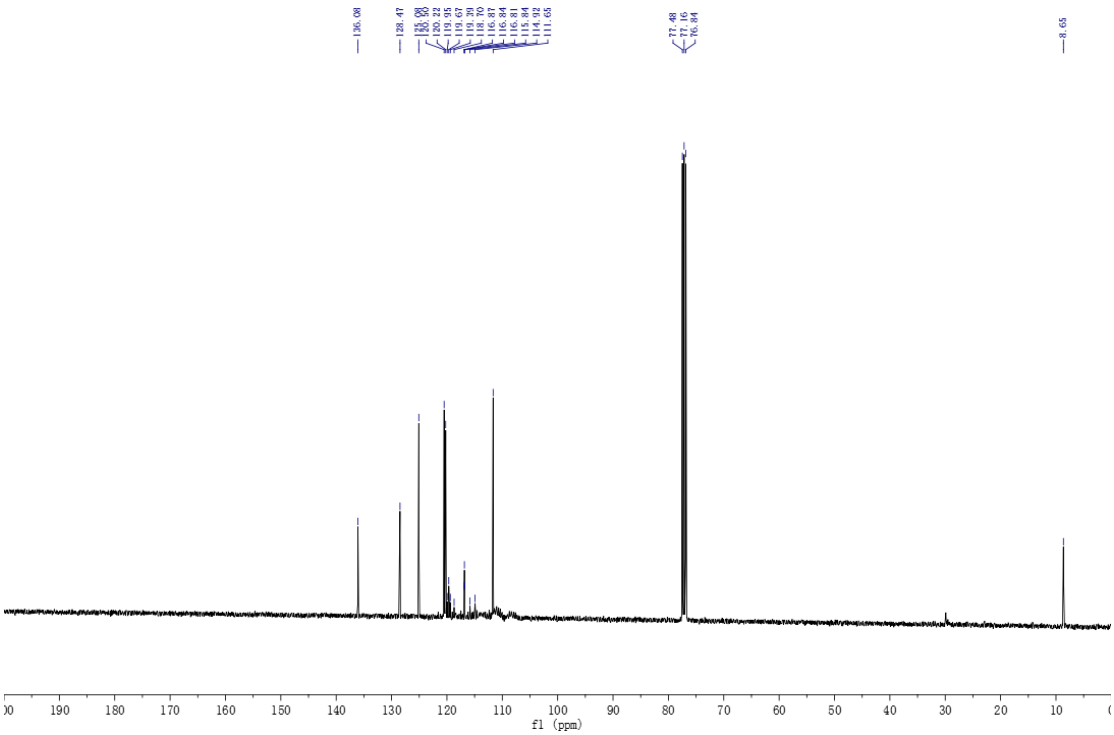
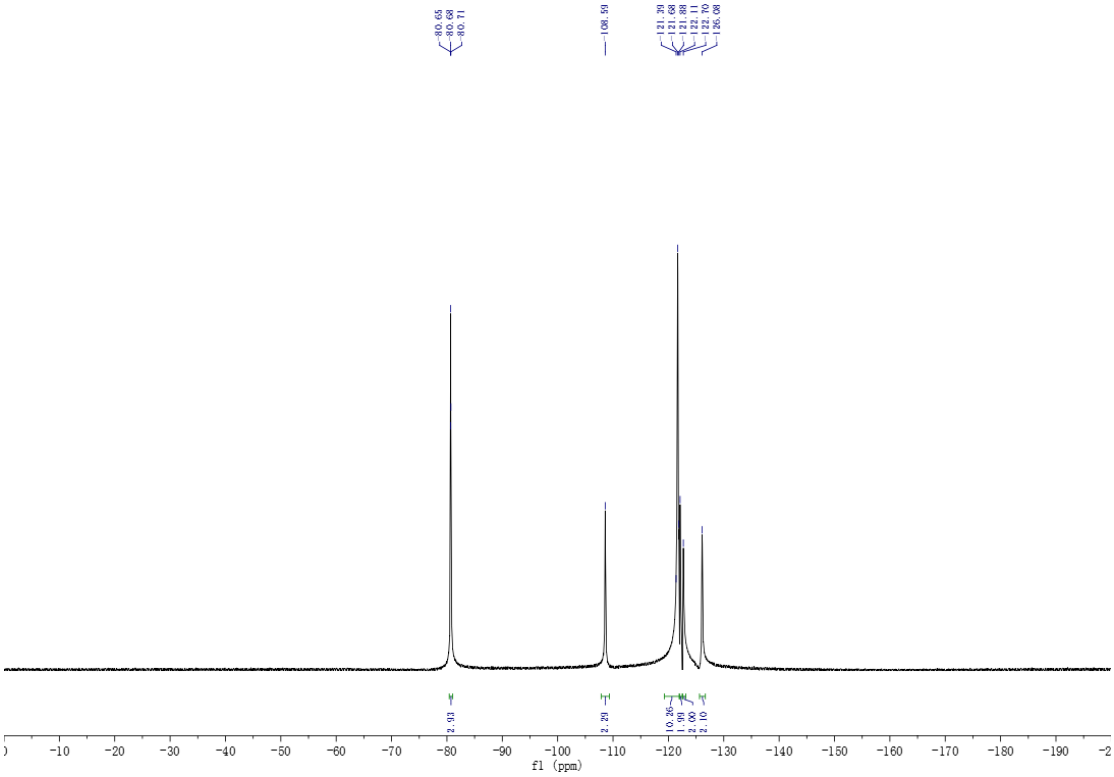


^{1}H NMR of compound **32**



^{13}C NMR of compound **32**



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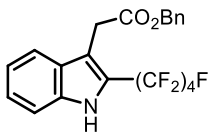
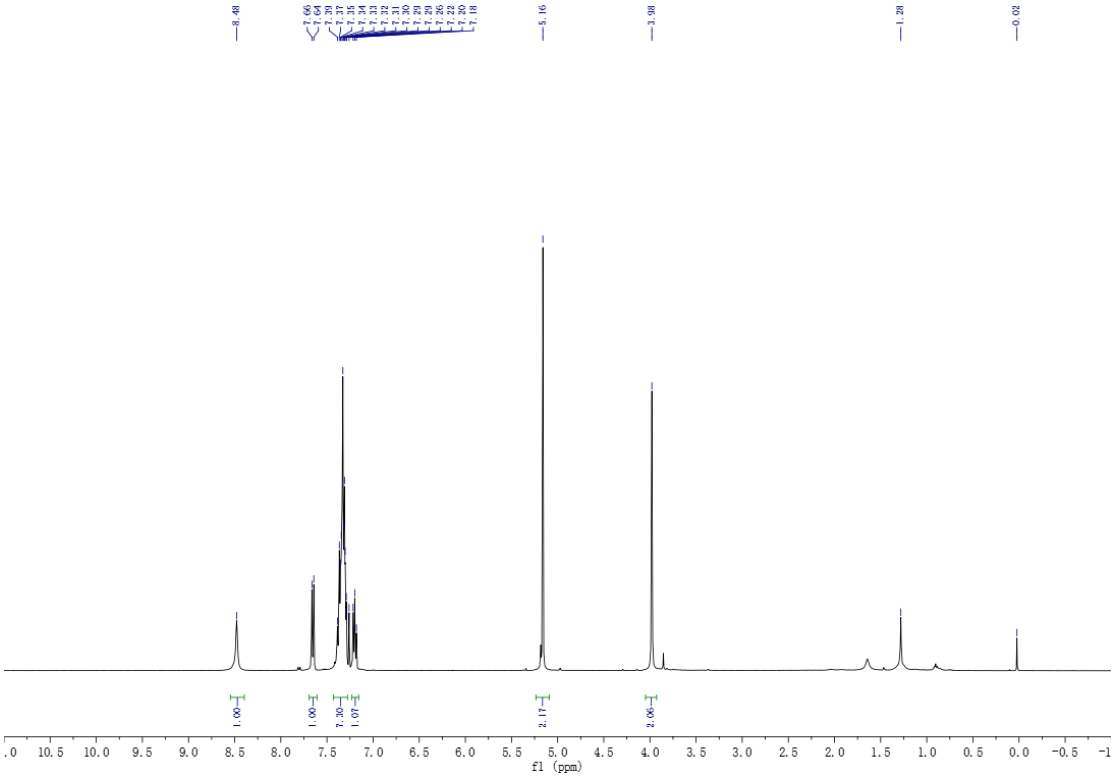
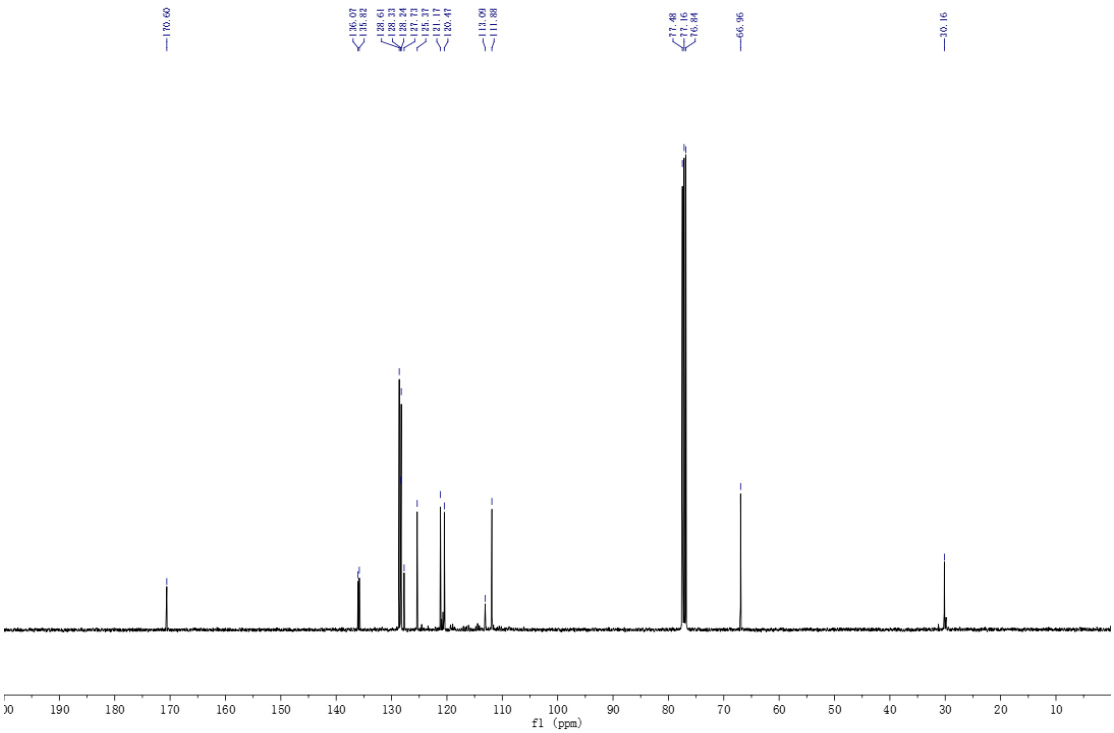


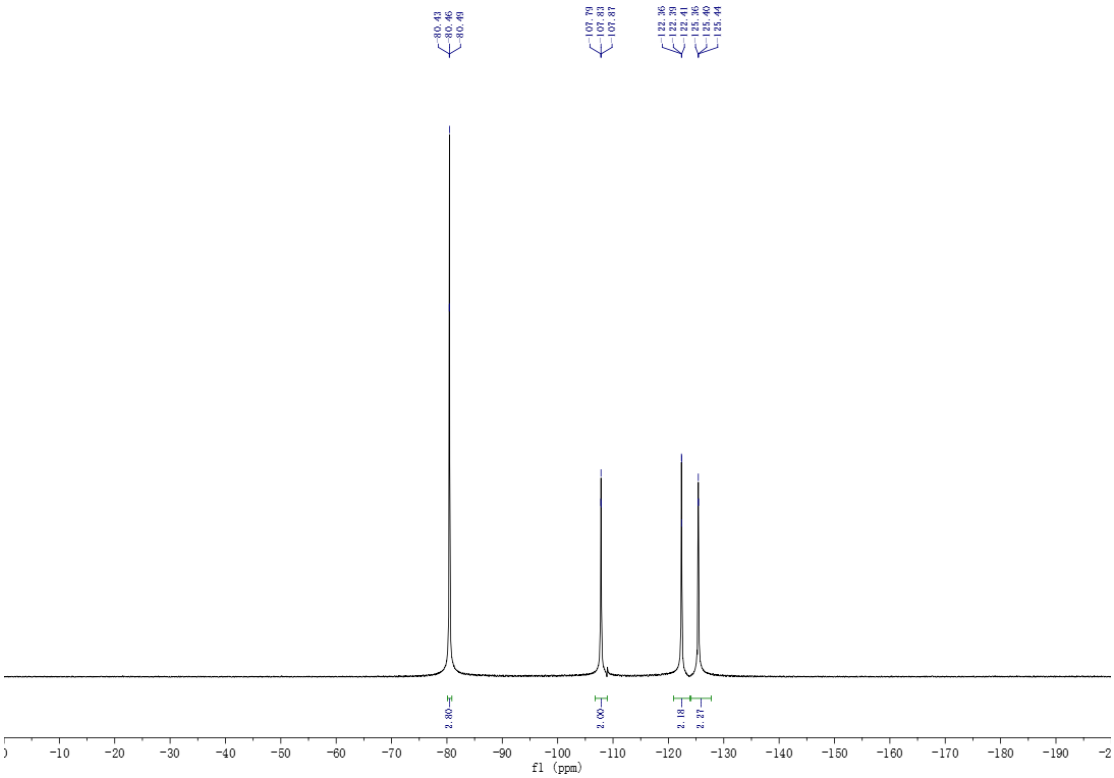
33'



^{1}H NMR of compound **33'**



^{13}C NMR of compound **33'**



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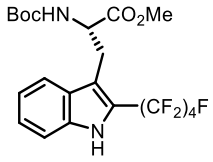
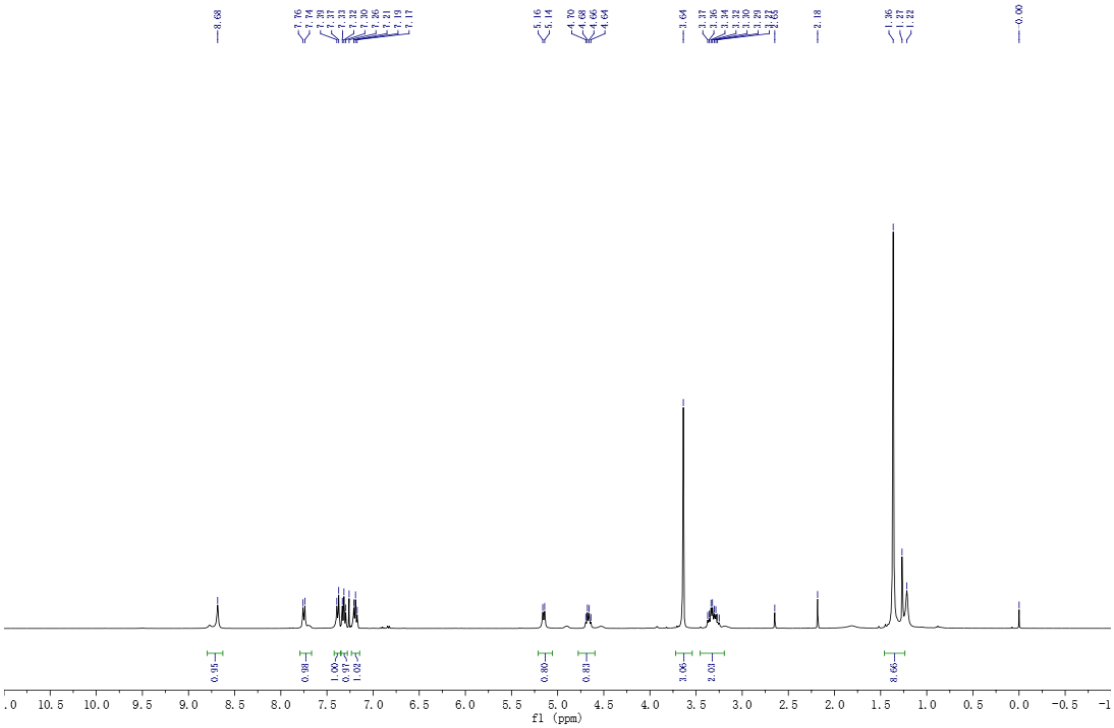
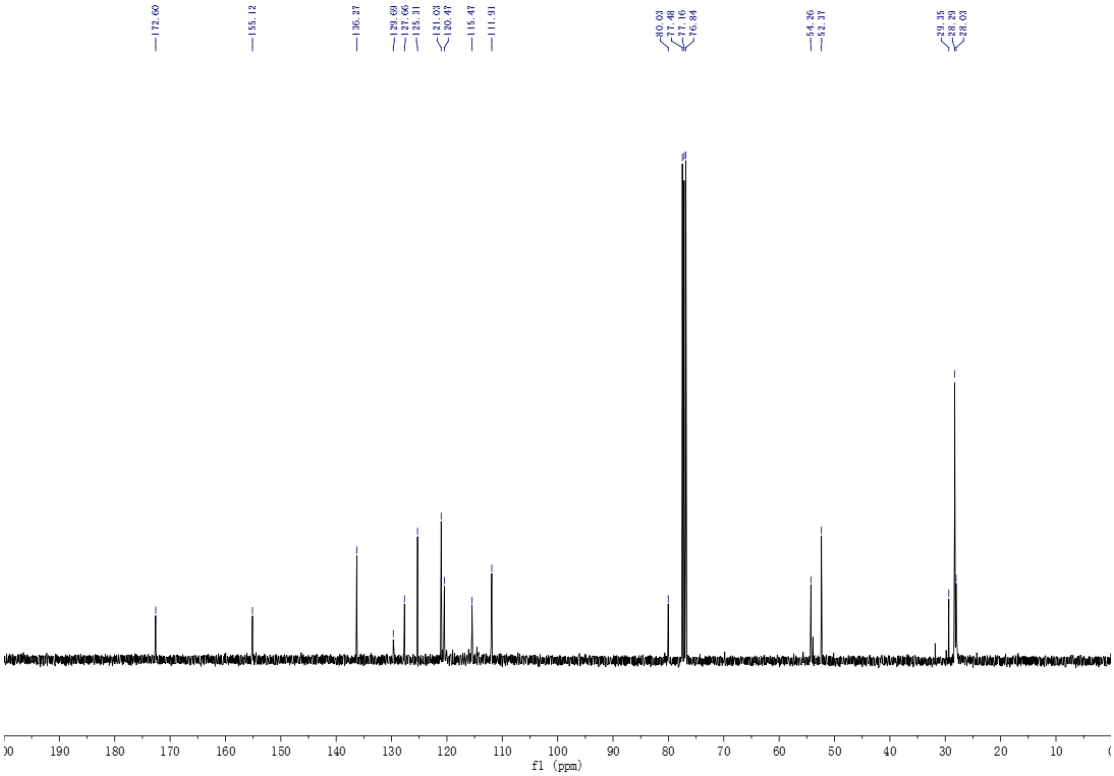


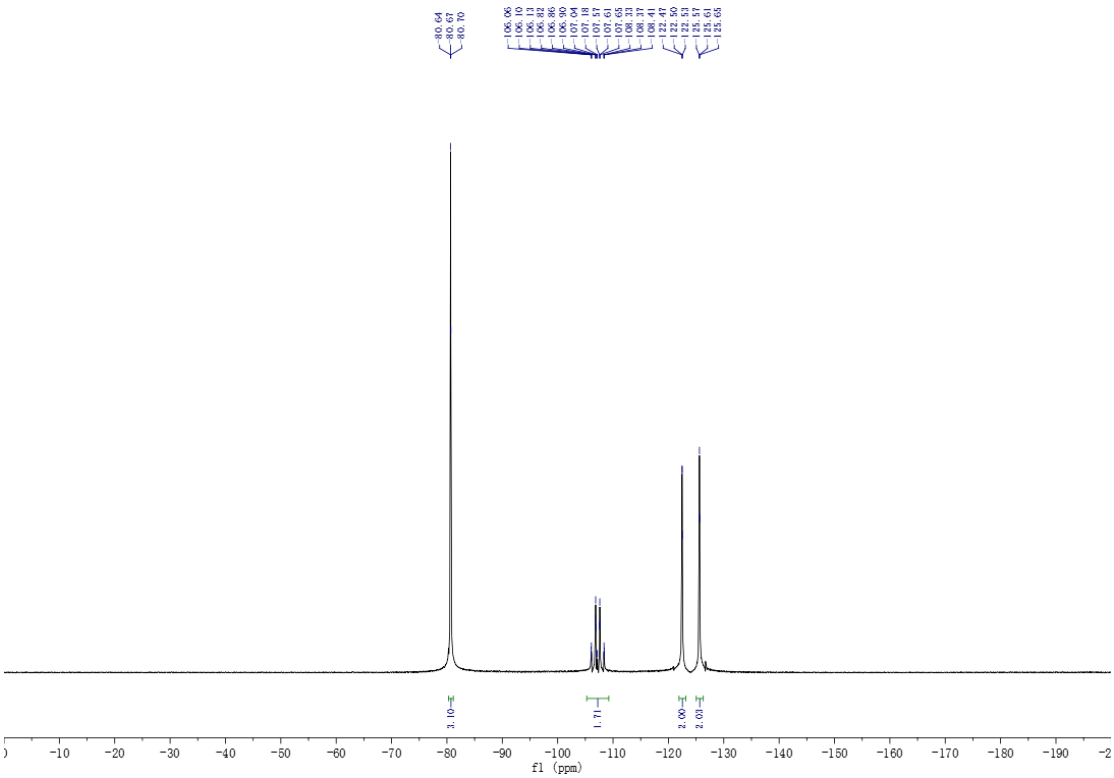
34'



^{1}H NMR of compound **34'**



^{13}C NMR of compound **34'**



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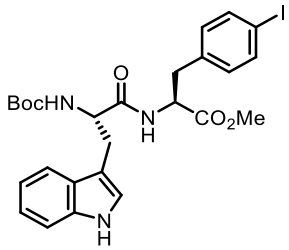
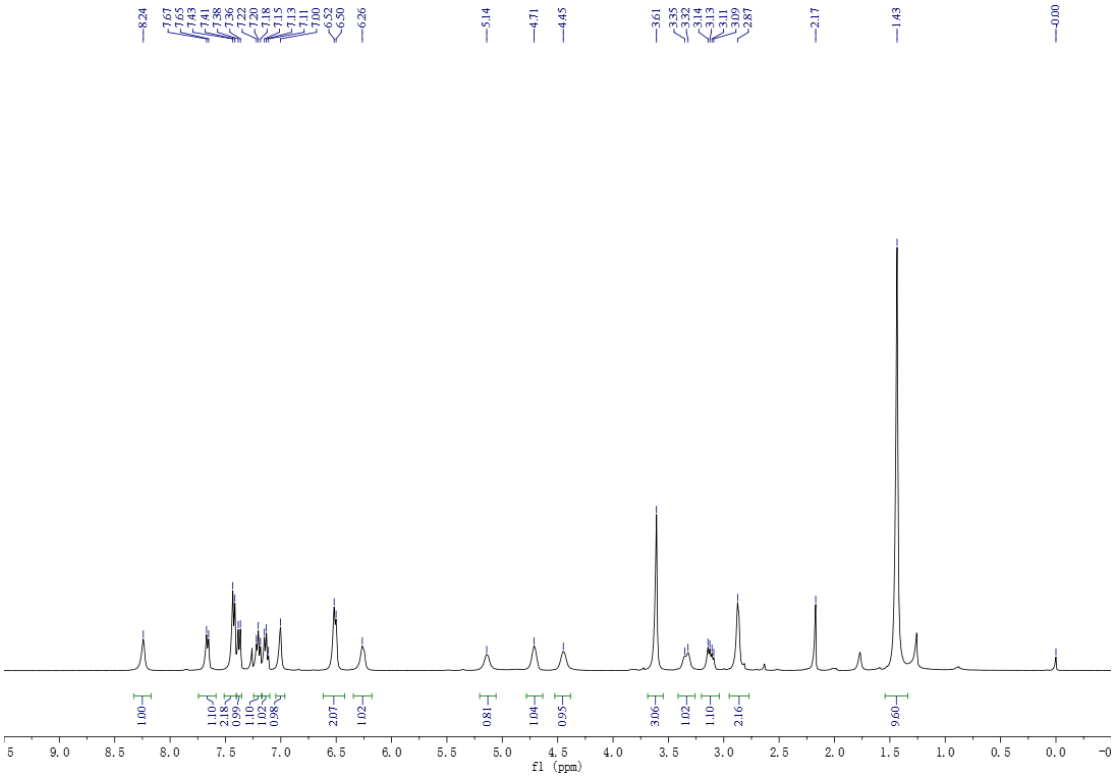
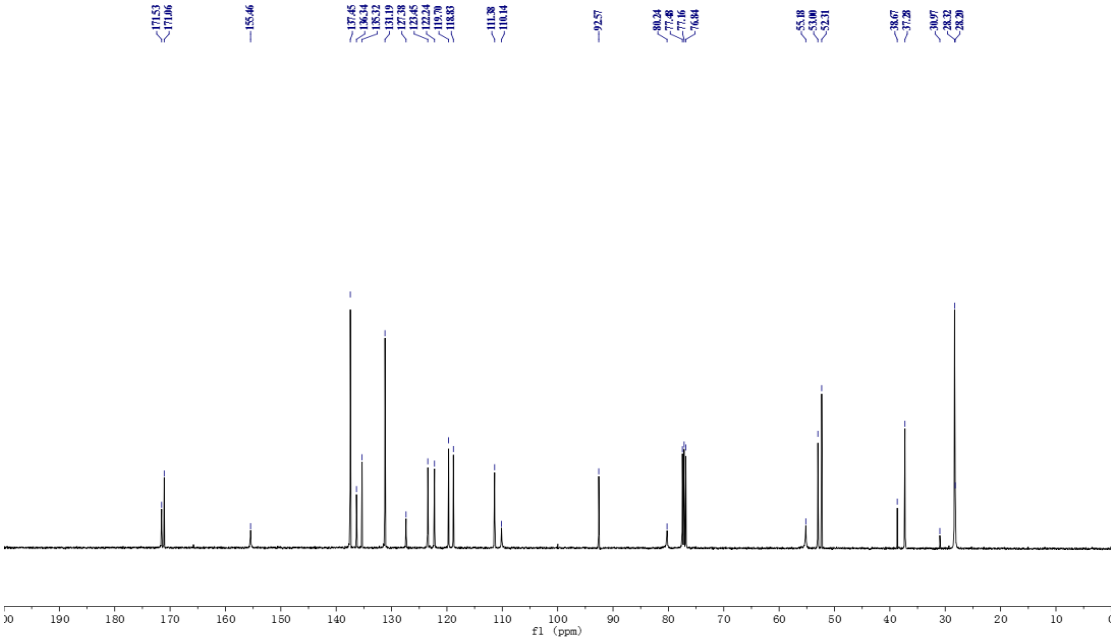


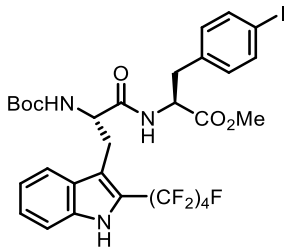
35-1



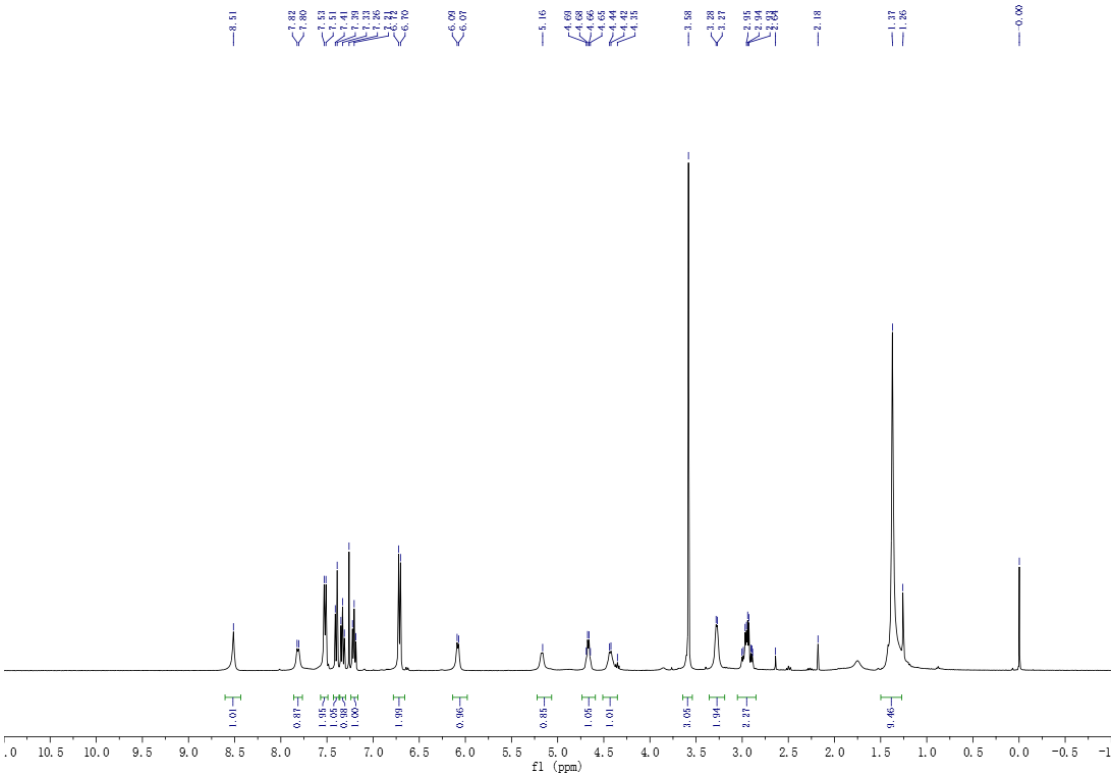
^{1}H NMR of compound **35-1**



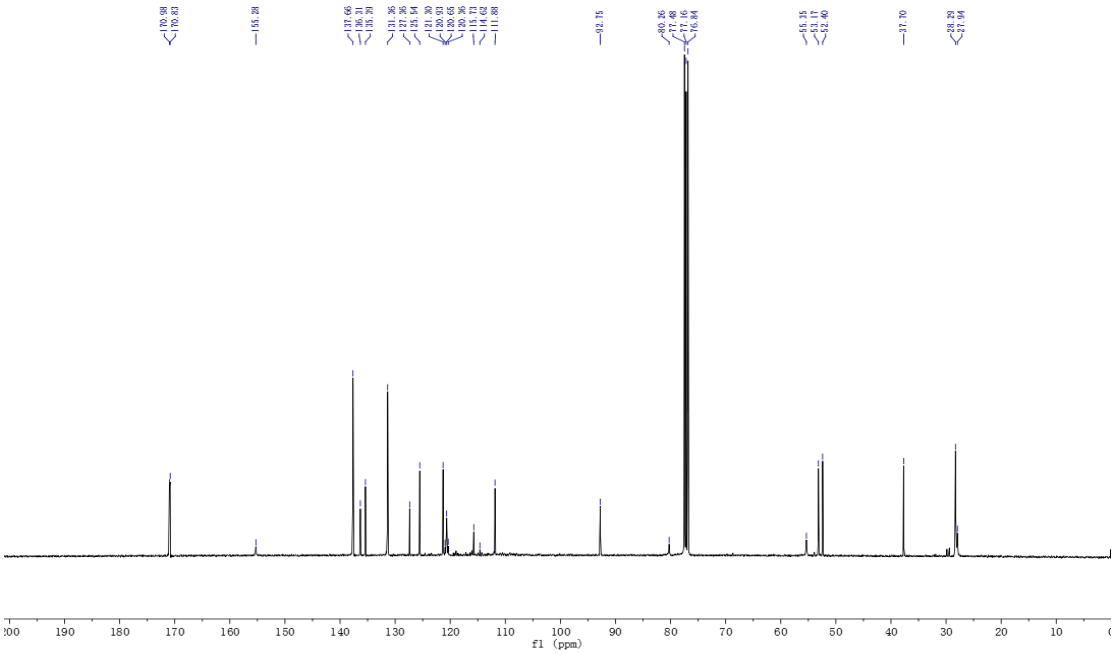
^{13}C NMR of compound **35-1**



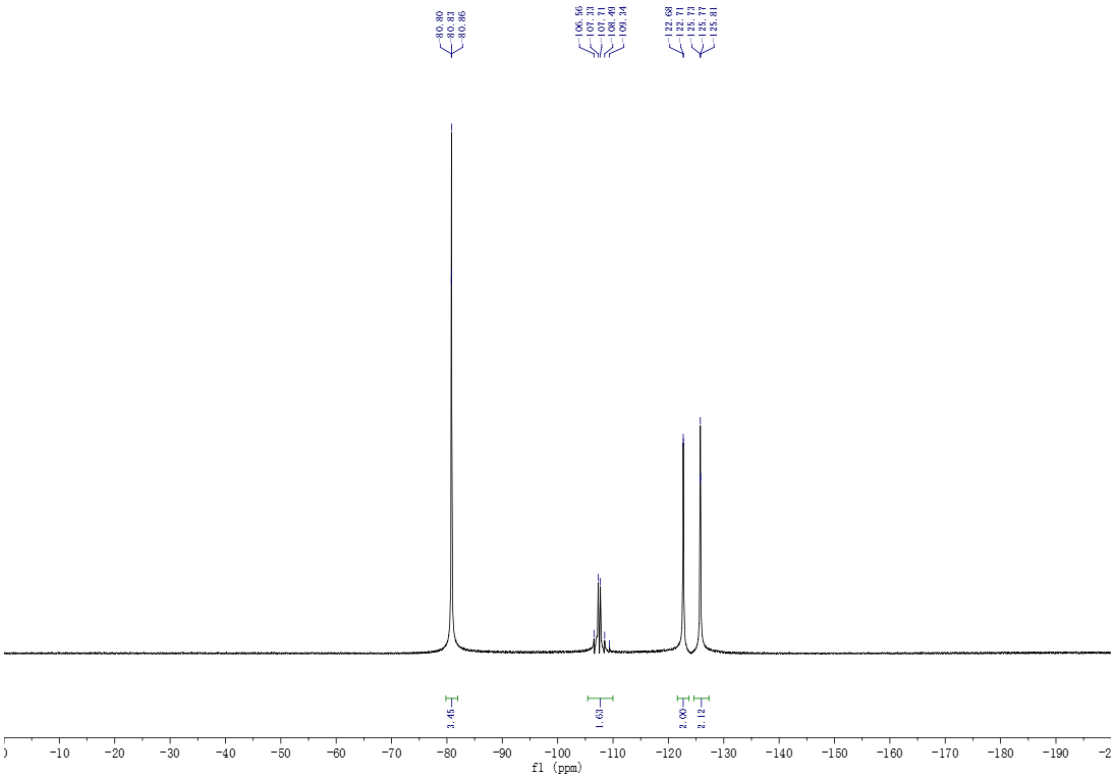
35



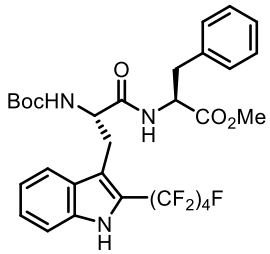
^{1}H NMR of compound **35**



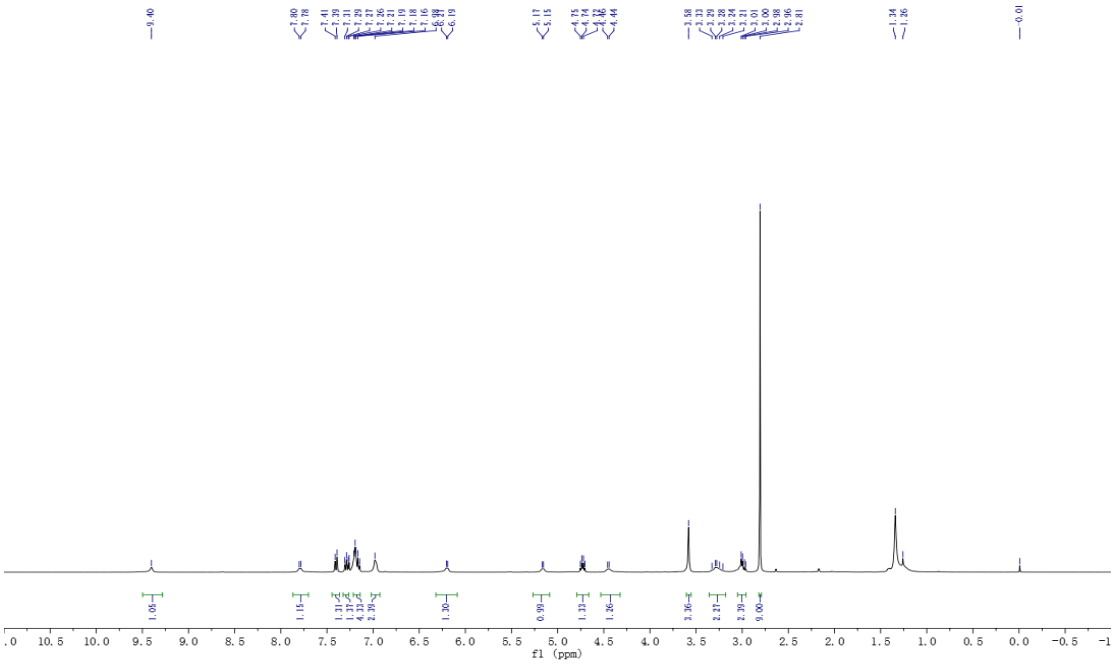
^{13}C NMR of compound **35**



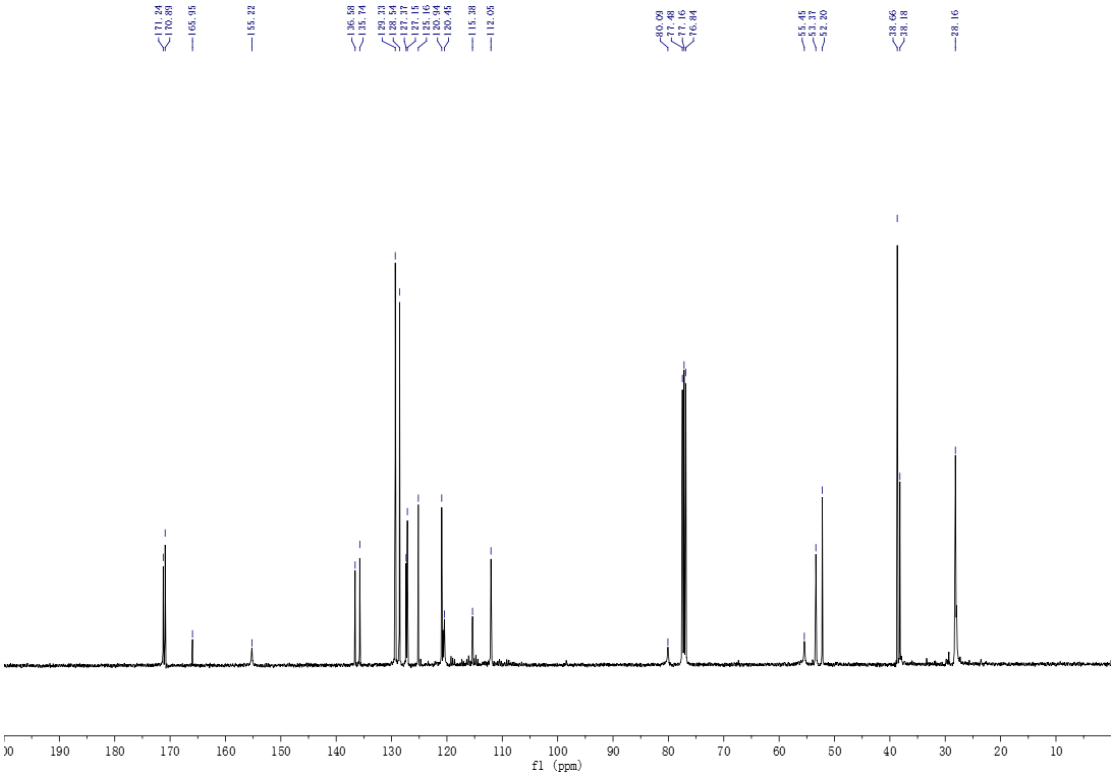
^{19}F NMR of compound **35**



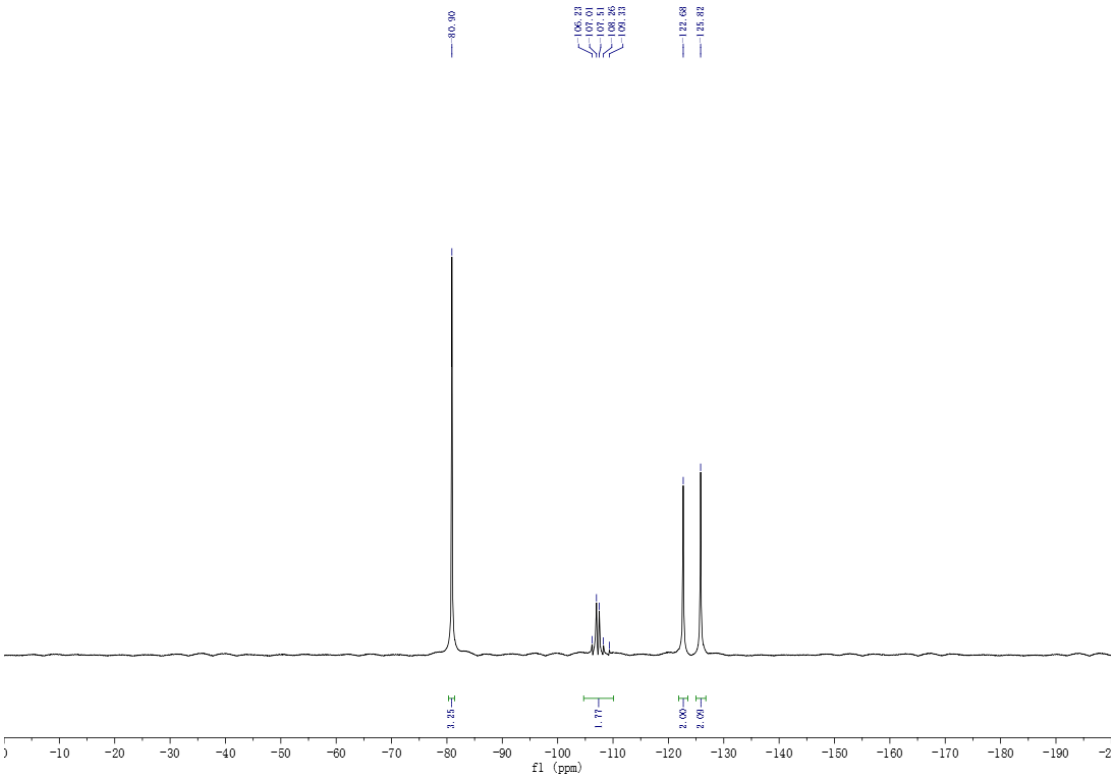
36



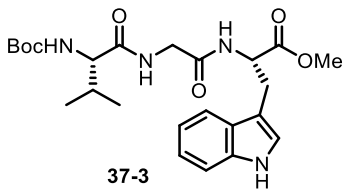
^{1}H NMR of compound **36**



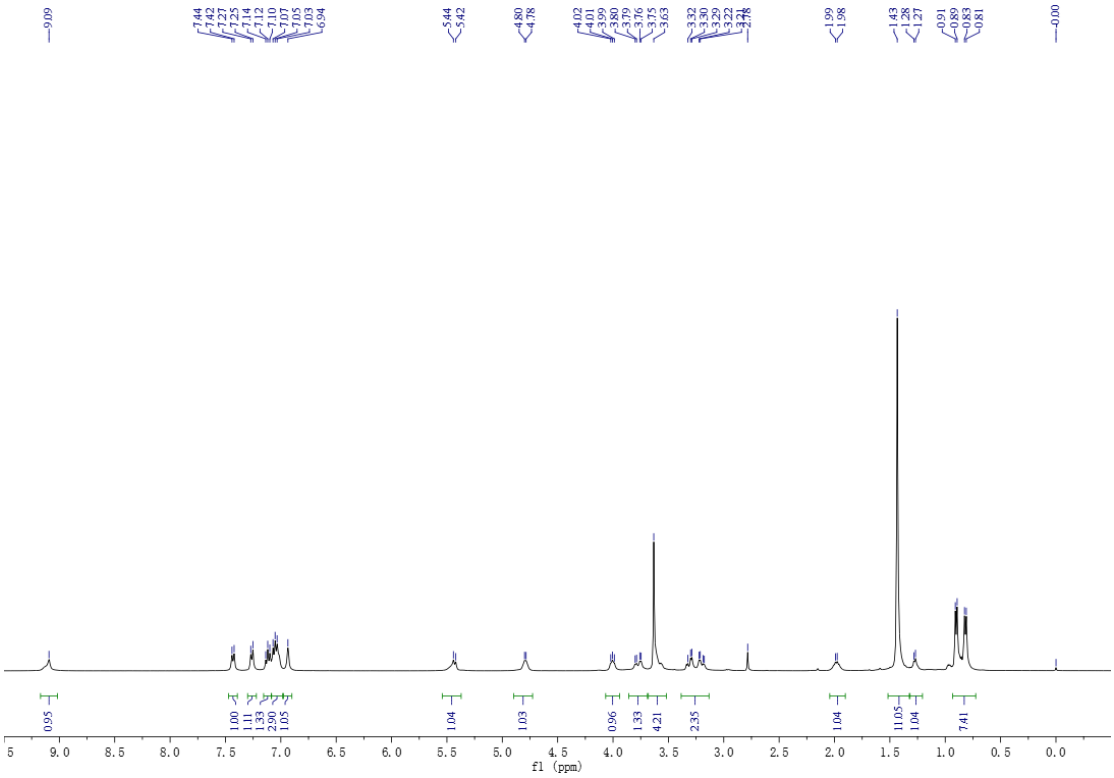
^{13}C NMR of compound **36**



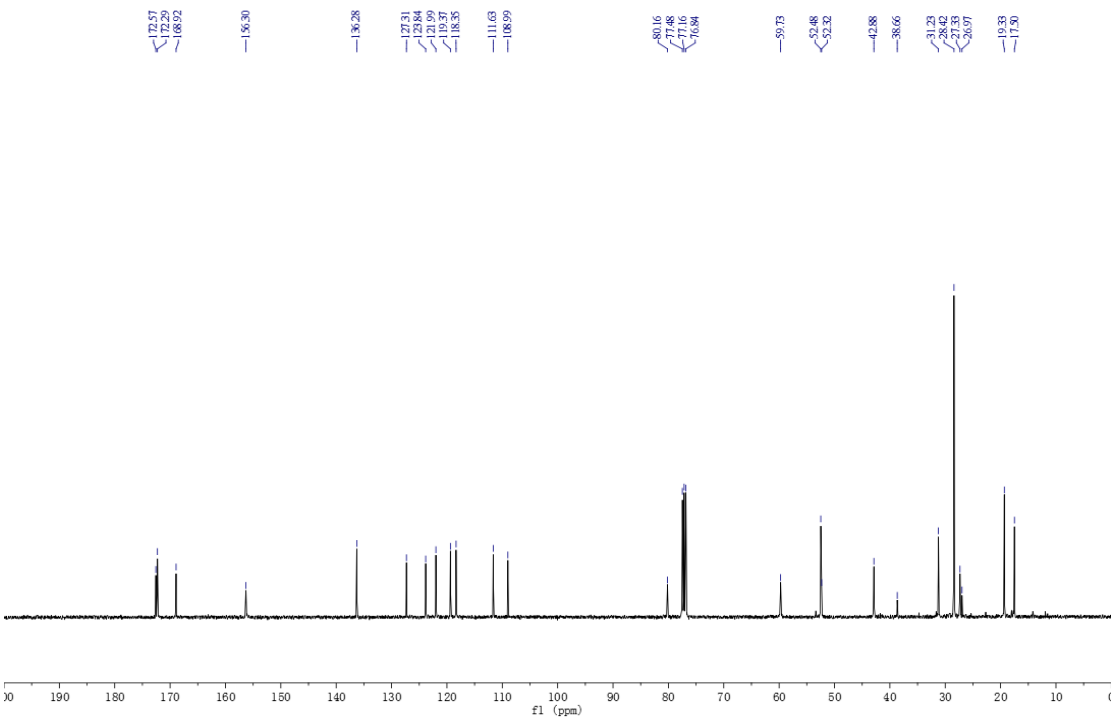
^{19}F NMR of compound **36**



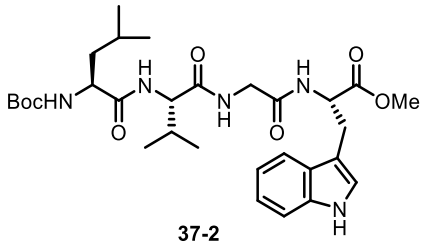
37-3

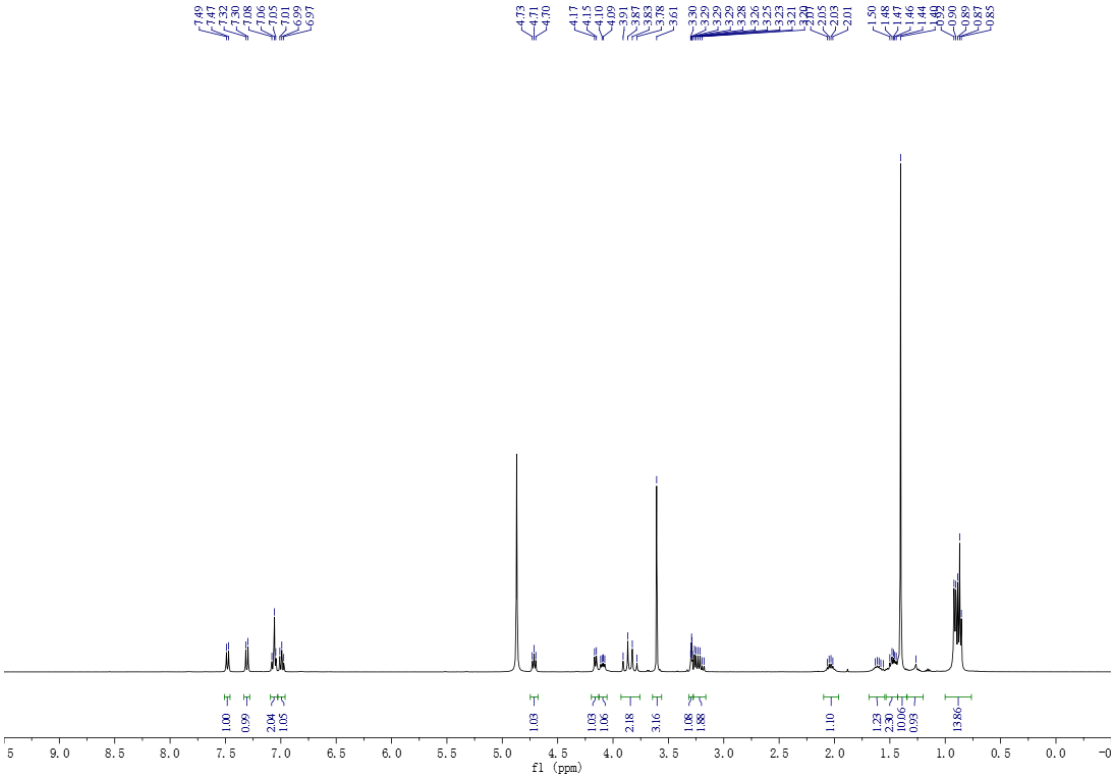


^{1}H NMR of compound **37-3**

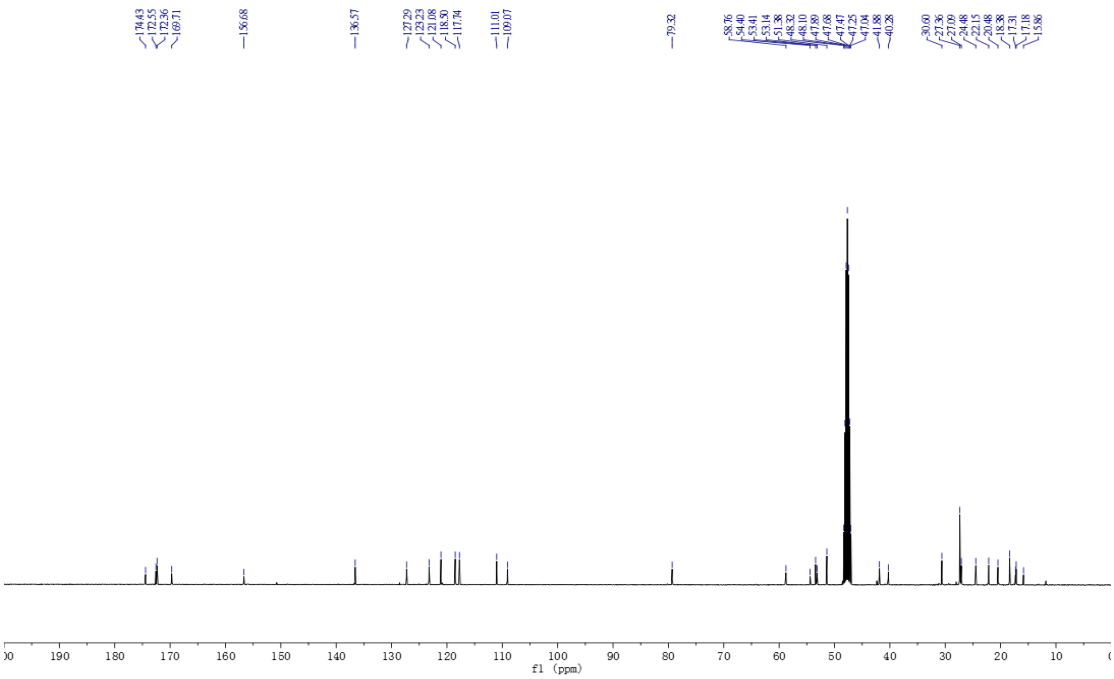


^{13}C NMR of compound **37-3**

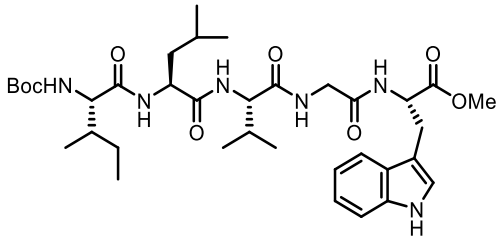


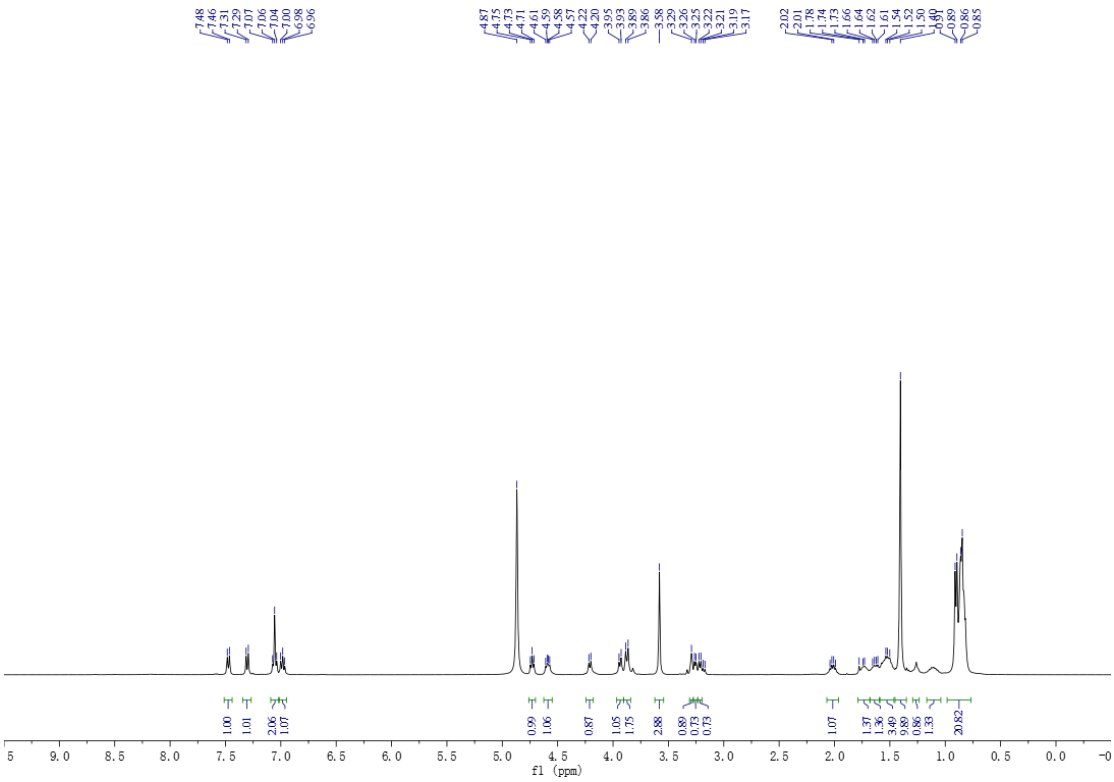


^{1}H NMR of compound **37-2**

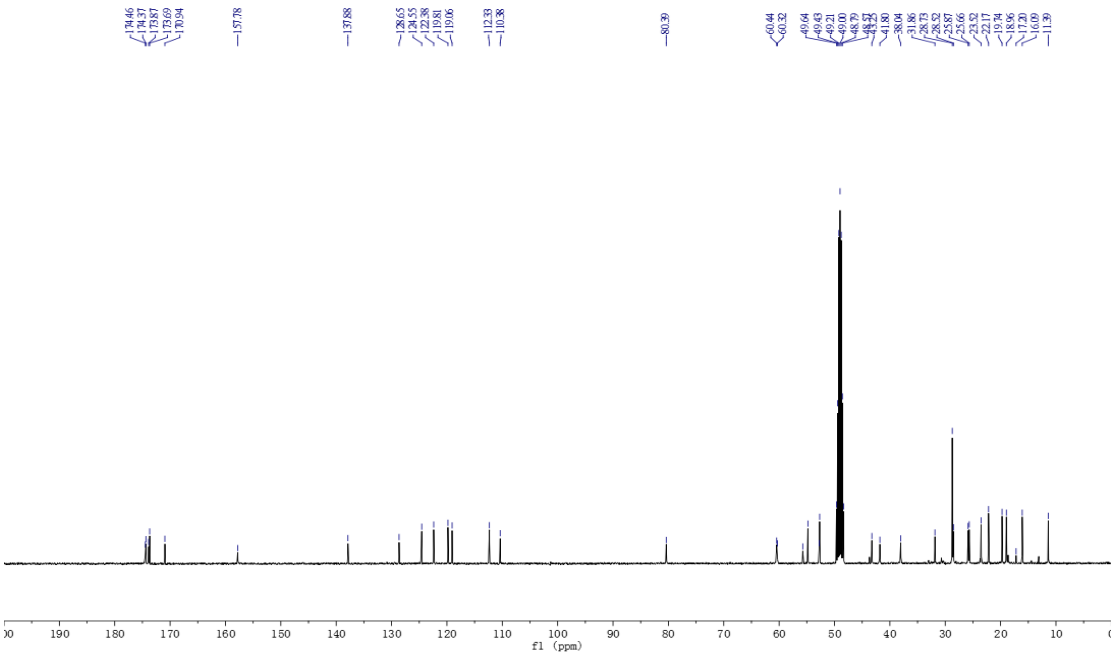


^{13}C NMR of compound **37-2**

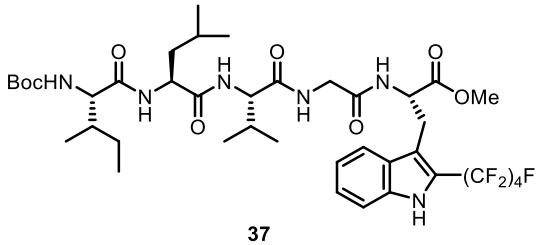




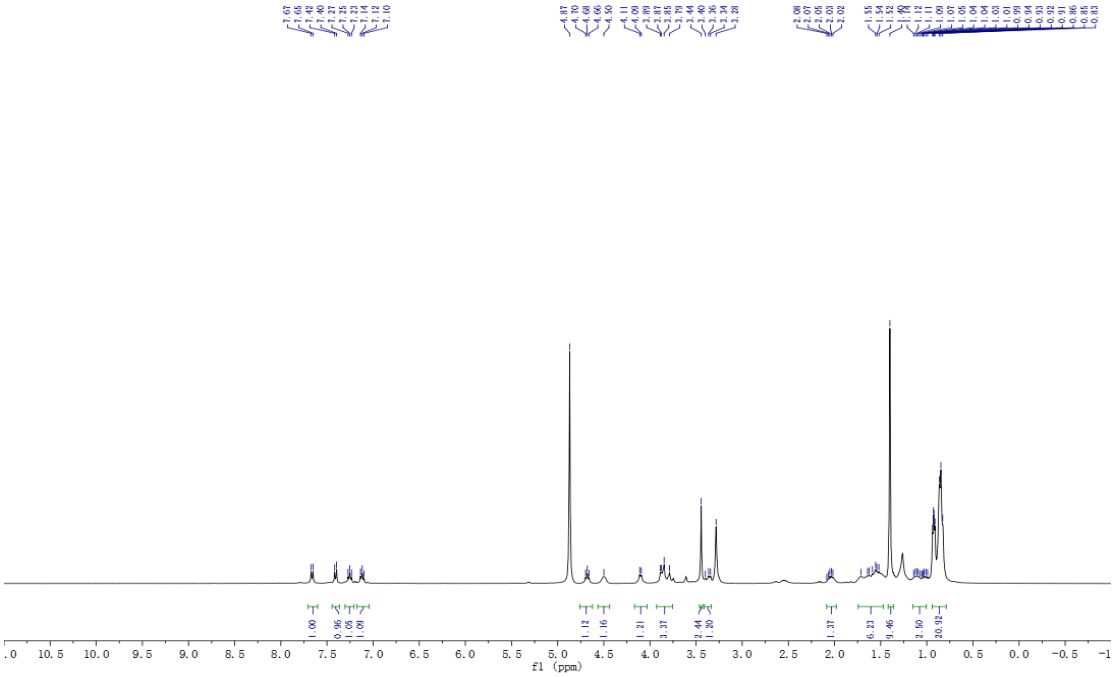
^{1}H NMR of compound **37-1**



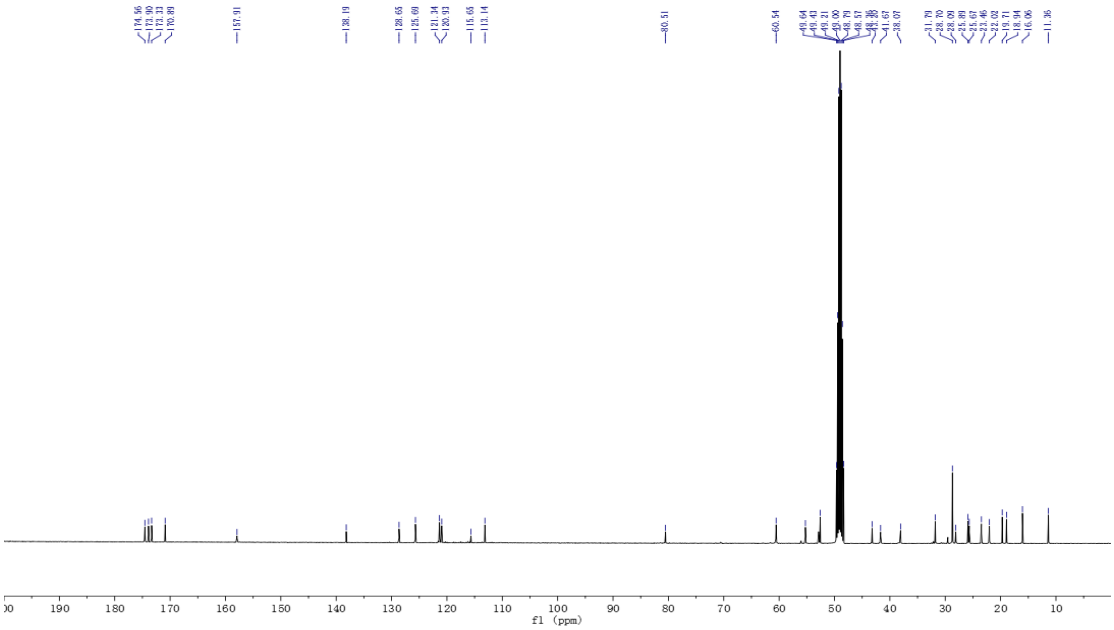
^{13}C NMR of compound **37-1**



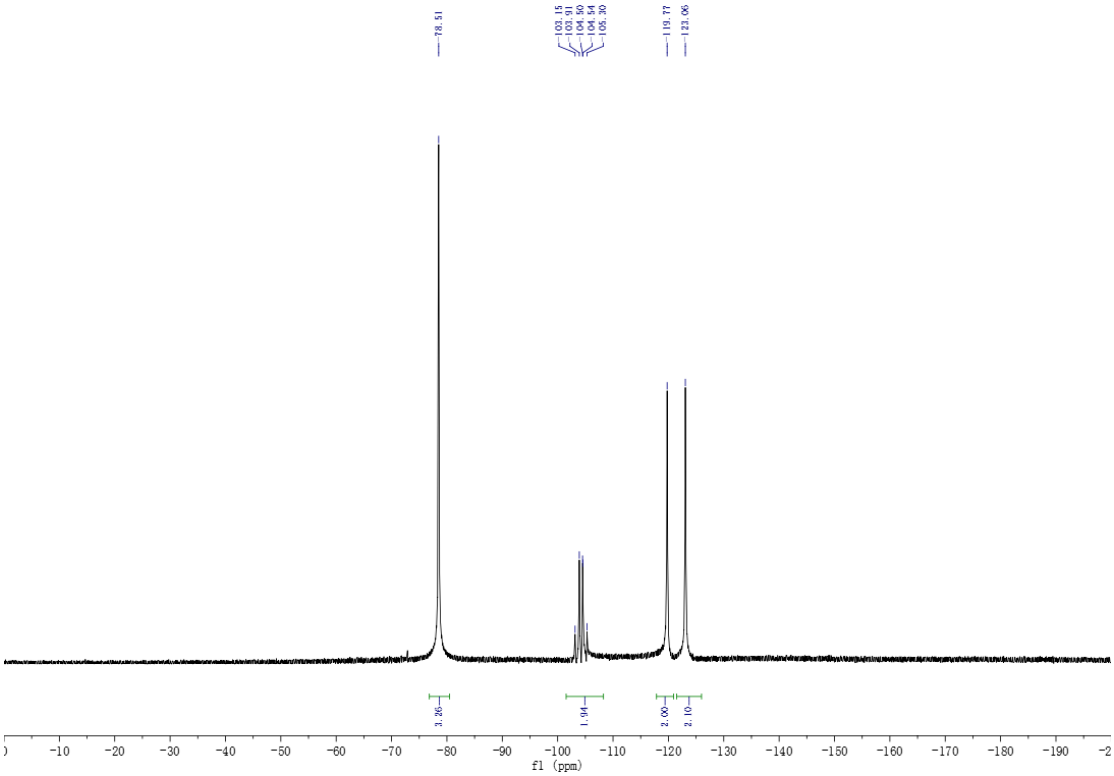
37



^{1}H NMR of compound **37**



^{13}C NMR of compound **37**



^{19}F NMR of compound **37**