

Mild and Highly Regioselective Synthesis of Biaryl Acids via Rh(I)-Catalyzed Cross-Dehydrogenative Coupling of Benzoic Acids Using Sodium Chlorite as Oxidant

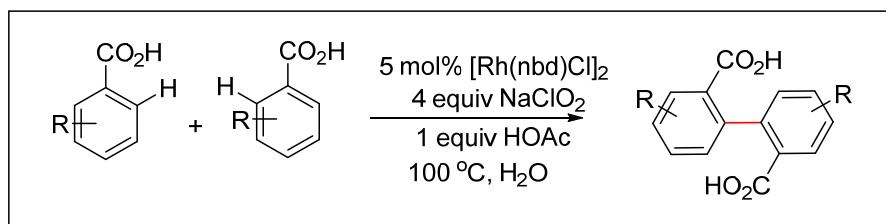
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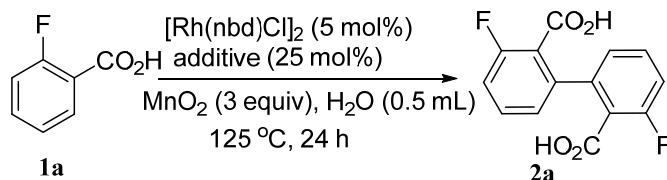
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1. Selected optimization results

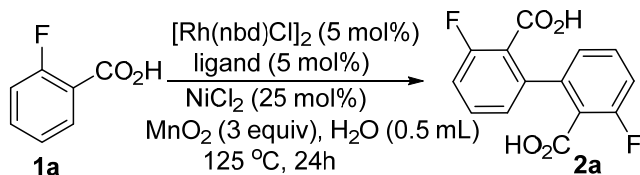
Table 1. Investigation of additives at 125 °C^a



Additive	Yield (%)	Additive	Yield (%) ^b
none	14	CuCl ₂	31
CoCl ₂	31	CuI	12
Co(acac) ₂	17	CuCl	25
CoI ₂	17	Cu(OAc) ₂	26
NiCl ₂	37	Ag ₂ CO ₃	14
NiCl ₂ (PPh ₃) ₂	37	Ag ₂ CO ₂ CF ₃	25
NiCl ₂ (bipyridyl)	NP ^c	AgOTf	22
NiBr ₂	25	AgOAc	25

^aReaction conditions: benzoic acid **1a** (0.2 mmol), [Rh(nbd)Cl]₂ (5 mol%), MnO₂ (0.6 mmol), additive (0.05 mmol), H₂O (0.5 mL), in sealed tube, 125 °C, 24 h. ^b NMR yields. ^c No product.

Table 2. Investigation of ligands at 125 °C^a



Ligand	Yield(%) ^b	Ligand	Yield(%) ^b
L-1	13	L-8	33
L-2	14	L-9	25
L-3	21	L-10	14
L-4	32	L-11	20
L-5	20	L-12	27
L-6	trace	L-13	0
L-7	trace		

^aReaction conditions: benzoic acid **1a** (0.2 mmol), Rh catalyst prepared by [Rh(nbd)Cl]₂ (5 mol%) and ligand (5 mol%), MnO₂ (0.6 mmol), NiCl₂ (25 mol%), H₂O (0.5 mL), in sealed tube, 125 °C, 24 h. ^b NMR yields.

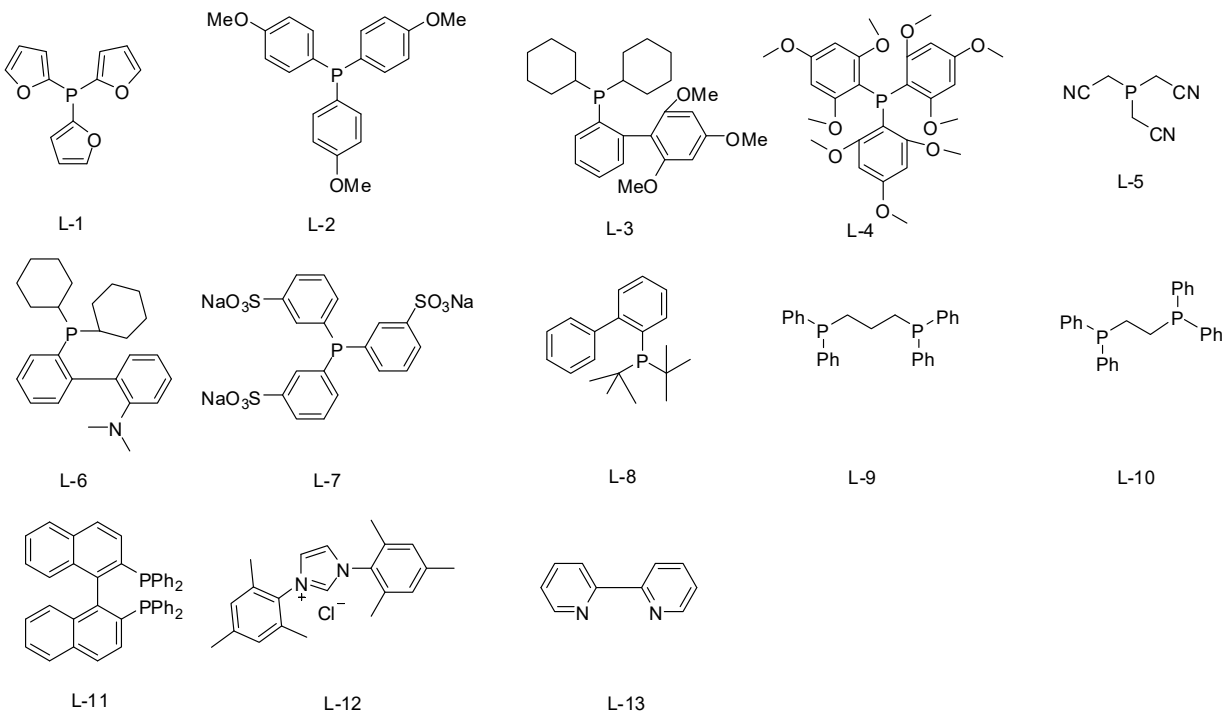
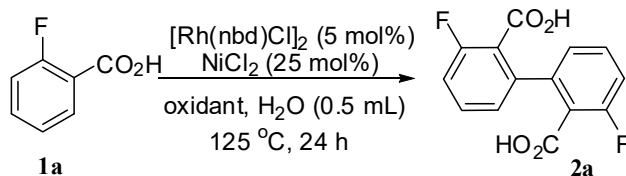


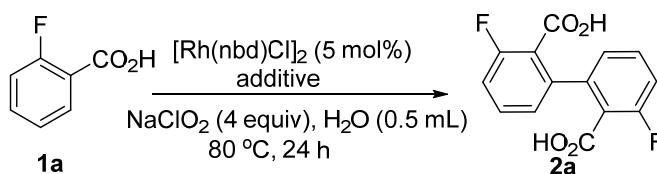
Table 3. Investigation of oxidants at 125 °C^a



Oxidant (equiv)	Yield (%) ^b	Oxidant (equiv)	Yield (%) ^b
NaCrO ₂ (3)	67	KIO ₄ (3)	0
KIO ₃ (3)	54	NaClO ₂ (3)	91
LiClO ₄ (3)	0	NaClO ₂ (4)	100

^aReaction conditions: benzoic acid **1a** (0.2 mmol), [Rh(nbd)Cl]₂ (5 mol%), NiCl₂ (25 mol%), oxidant, H₂O (0.5 mL), in sealed tube, 125 °C, 24 h. ^b NMR yields.

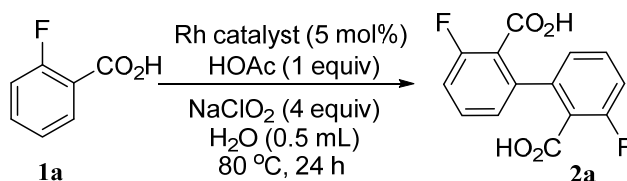
Table 4. Further investigation of additives at 80 °C^a



Additive (equiv)	Yield (%) ^b	Additive (equiv)	Yield (%) ^b
NiCl ₂ (0.25)	21	acetic acid (0.25)	38
CoCl ₂ (0.25)	20	1-adamantoic acid (0.25)	35
MgCl ₂ (0.25)	29	pivalic acid (0.25)	23
CaCl ₂ (0.25)	25	acetic acid (1)	48
NaNO ₂ (0.25)	32	acetic acid (1) ^c	45
formic acid (0.25)	36	acetic acid (1) ^d	96

^aReaction conditions: benzoic acid **1a** (0.2 mmol), [Rh(nbd)Cl]₂ (5 mol%), NaClO₂ (0.8 mmol), additive, H₂O (0.5 mL), in sealed tube, 80 °C, 24 h. ^bNMR yields. ^cAdding 0.25 equiv of NiCl₂. ^d Heating at 100 °C.

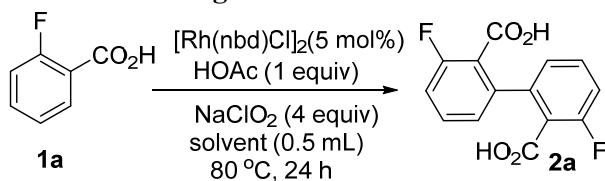
Table 5. Investigation of different rhodium catalyst at 80 °C^a



Catalyst (mol%)	Yield (%) ^b	Catalyst (mol%)	Yield (%) ^b
none	0	Rh ₂ (OAc) ₄ (5)	trace
RhCl ₃ •H ₂ O (10)	15	Rh(PPh ₃) ₂ (CO)Cl (10)	trace
Rh(CO) ₂ (acac) (10)	30		

^aReaction conditions: benzoic acid **1a** (0.2 mmol), rhodium catalyst, NaClO₂ (0.8 mmol), acetic acid (1 equiv), H₂O (0.5 mL), in sealed tube, 80 °C, 24 h. ^b NMR yields.

Table 6. Investigation of solvent effect at 80 °C^a



Solvent	Yield (%) ^b	Solvent	Yield (%) ^b
acetonitrile	0	dichloroethane	0
dioxane	0	1,2-dimethoxyethane	0

^aReaction conditions: benzoic acid **1a** (0.2 mmol), [Rh(nbd)Cl]₂ (5 mol%), NaClO₂ (0.8 mmol), HOAc (1 equiv), solvent (0.5 mL), in sealed tube, 80 °C, 24 h. ^b NMR yields.

Table 7. Turn-Over-Frequency (TOF) calculations^a

Product	TOF of catalyst (h ⁻¹)
2a	0.75
2b	0.65
2c	0.59
2d	0.61
2e	0.55
2f	0.63
2g	0.63
2h	0.57
2i	0.53
2j	0.48
2k	0.68
2l	0.69
2m, 2n	0.68
2o	0.73
2p	0.67
2q, 2r, 2s	0.73

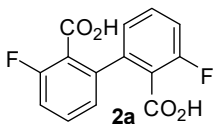
^a TOF of the catalyst = (mole of benzoic acid conversion) / (mole of catalyst × reaction time)

2. General synthetic procedure and characterization data for all products

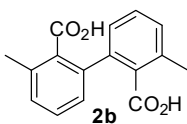
General procedure

The mixture of benzoic acid **1** (0.2 mmol), sodium chlorite (72 mg, 0.8 mmol), [Rh(nbd)Cl]₂ (4.6 mg, 0.01 mmol, 5 mol%), and acetic acid (12 mg, 0.2 mmol) was heated in water (0.5 mL) in a sealed tube at 100 °C for 24 h under an atmosphere of air. The reaction mixture was then cooled to room temperature and acidified by dilute HCl, and then water was evaporated *in vacuo*. The residue was purified by preparative thin-layer chromatography (TLC) on silica gel to give the desired product **2**.

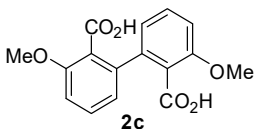
Characterization data for all products



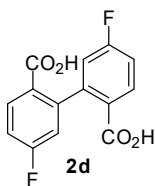
3,3'-Difluorobiphenyl-2,2'-dicarboxylic acid (2a) Colorless solid; Yield 90%; ^1H NMR (500 MHz, acetone-*d*₆) δ 7.12 (d, $J = 7.5$ Hz, 2H), 7.27 (t, $J = 8.5$ Hz, 2H), 7.50–7.54 (m, 2H); ^{13}C NMR (125 MHz, acetone-*d*₆) δ 165.4, 159.2 (d, $J = 250$ Hz), 139.7, 130.8 (d, $J = 9.0$ Hz), 125.7, 123.1 (d, $J = 15.6$ Hz), 115.3 (d, $J = 21.9$ Hz).



3,3'-Dimethylbiphenyl-2,2'-dicarboxylic acid (2b) Colorless solid; Yield 78%; ^1H NMR (500 MHz, acetone-*d*₆) δ 2.41 (s, 6H), 7.05 (d, $J = 7.0$ Hz, 2H), 7.28–7.33 (m, 4H); ^{13}C NMR (125 MHz, acetone-*d*₆) δ 170.5, 138.1, 134.9, 134.6, 129.5, 128.5, 127.0, 19.1; HRMS (ESI) m/z [M-H] calcd for $\text{C}_{16}\text{H}_{13}\text{O}_4$ 269.0814, found 269.0820.

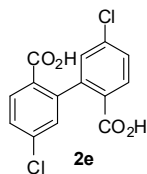


3,3'-Dimethoxybiphenyl-2,2'-dicarboxylic acid (2c) Colorless solid; Yield 71%; ^1H NMR (500 MHz, acetone-*d*₆) δ 3.88 (s, 6H), 6.87 (d, $J = 7.5$ Hz, 2H), 7.71 (d, $J = 8.5$ Hz, 2H), 7.38 (t, $J = 8.0$ Hz, 2H); ^{13}C NMR (125 MHz, acetone-*d*₆) δ 168.1, 156.0, 138.3, 129.7, 124.9, 121.6, 110.8, 55.4.

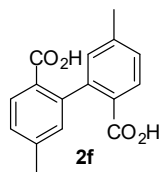


5,5'-Difluorobiphenyl-2,2'-dicarboxylic acid (2d) Colorless solid; Yield 73%; ^1H NMR (500 MHz,

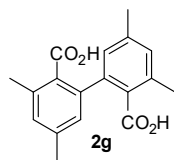
acetone-*d*6) δ 7.04 (dd, $J = 9.0, 2.5$ Hz, 2H), 7.26 (td, $J = 8.5, 2.5$ Hz, 2H), 8.13 (dd, $J = 8.5, 6.0$ Hz, 2H); ^{13}C NMR (125 MHz, acetone-*d*6) δ 165.8, 164.3 (d, $J = 250$ Hz), 145.8 (d, $J = 9.0$ Hz), 132.8 (d, $J = 10.0$ Hz), 126.0, 116.9 (d, $J = 22.5$ Hz), 114.0 (d, $J = 21.3$ Hz).



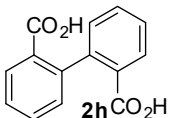
5,5'-Dichlorobiphenyl-2,2'-dicarboxylic acid (2e) Colorless solid; Yield 66%; ^1H NMR (500 MHz, CDCl_3) δ 7.31 (d, $J = 2.0$ Hz, 2H), 7.54 (dd, $J = 7.5, 2.0$ Hz, 2H), 8.06 (d, $J = 7.5$ Hz, 2H); ^{13}C NMR (125 MHz, acetone-*d*6) δ 166.0, 144.4, 136.8, 131.8, 129.9, 128.6, 127.4; HRMS (ESI) m/z [M-H] calcd for $\text{C}_{14}\text{H}_7\text{Cl}_2\text{O}_4$ 308.9721, found 308.9730.



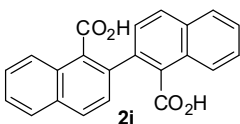
5,5'-Dimethylbiphenyl-2,2'-dicarboxylic acid (2f) Colorless solid; Yield 75%; ^1H NMR (400 MHz, acetone-*d*6) δ 2.40 (s, 6H), 6.99 (d, $J = 0.8$ Hz, 2H), 7.25 (ddd, $J = 8.0, 1.6, 0.4$ Hz, 2H), 7.90 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (125 MHz, acetone-*d*6) δ 167.3, 144.0, 141.3, 130.9, 130.0, 127.4, 127.3, 20.4; HRMS (ESI) m/z [M-H] calcd for $\text{C}_{16}\text{H}_{13}\text{O}_4$ 269.0814, found 269.0820.



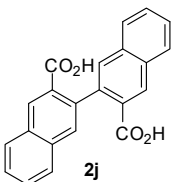
3,3',5,5'-Tetramethylbiphenyl-2,2'-dicarboxylic acid (2g) Colorless solid; Yield 76%; ^1H NMR (500 MHz, acetone-*d*6) δ 2.32 (s, 6H), 2.40 (s, 6H), 6.86 (s, 2H), 7.12 (s, 2H); ^{13}C NMR (125 MHz, acetone-*d*6) δ 170.5, 138.7, 138.6, 134.9, 131.4, 130.3, 127.6, 20.2, 19.1; HRMS (ESI) m/z [M-H] calcd for $\text{C}_{18}\text{H}_{17}\text{O}_4$ 297.1127, found 297.1132.



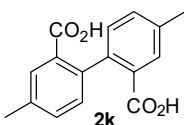
Biphenyl-2,2'-dicarboxylic acid (2h) Colorless solid; Yield 68%; ^1H NMR (500 MHz, acetone-*d*₆) δ 7.21 (dd, $J = 7.5, 1.0$ Hz, 2H), 7.46 (td, $J = 7.5, 1.5$ Hz, 2H), 7.56 (td, $J = 7.5, 1.5$ Hz, 2H), 8.00 (dd, $J = 7.5, 1.0$ Hz, 2H). ^{13}C NMR (125 MHz, acetone-*d*₆) δ 167.3, 143.6, 131.0, 130.3, 130.1, 129.8, 126.9.



2,2'-Binaphthyl-1,1'-dicarboxylic acid (2i) Colorless solid; Yield 63%; ^1H NMR (500 MHz, acetone-*d*₆) δ 7.48 (d, $J = 7.5$ Hz, 2H), 7.61–7.66 (m, 4H), 8.02–8.05 (m, 4H), 8.14–8.16 (m, 2H). ^{13}C NMR (125 MHz, acetone-*d*₆) δ 169.8, 136.3, 132.9, 132.3, 129.5, 128.9, 128.2, 127.3, 127.2, 126.5, 125.7; HRMS (ESI) m/z [M-H] calcd for C₂₂H₁₃O₄ 341.0814, found 341.0814.

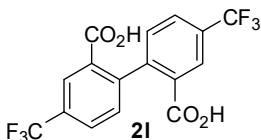


2,2'-Binaphthyl-3,3'-dicarboxylic acid (2j) Colorless solid; Yield 57%; ^1H NMR (500 MHz, acetone-*d*₆) δ 7.62–7.70 (m, 4H), 7.84 (s, 2H), 7.99 (d, $J = 8.0$ Hz, 2H), 8.13 (d, $J = 8.0$ Hz, 2H), 8.67 (s, 2H); ^{13}C NMR (125 MHz, acetone-*d*₆) δ 167.1, 140.3, 134.7, 131.8, 130.8, 129.4, 128.9, 128.7, 128.2, 127.6, 126.5.

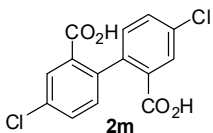


4,4'-Dimethylbiphenyl-2,2'-dicarboxylic acid (2k) Colorless solid; Yield 82%; ^1H NMR (500 MHz, acetone-*d*₆) δ 2.43 (s, 6H), 7.08 (dd, $J = 7.6$ Hz, 2H), 7.36 (dd, $J = 8.0, 1.2$ Hz, 2H), 7.80 (s, 2H); ^{13}C

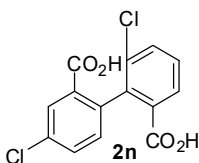
NMR (125 MHz, acetone-*d*₆) δ 167.6, 140.7, 136.3, 131.6, 130.5, 130.2, 130.1, 20.1; HRMS (ESI) m/z [M-H] calcd for C₁₆H₁₃O₄ 269.0814, found 269.0819.



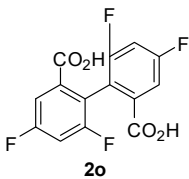
4,4'-Bis(trifluoromethyl)biphenyl-2,2'-dicarboxylic acid (2l) Colorless solid; Yield 83%; ¹H NMR (500 MHz, acetone-*d*₆) δ 7.53 (d, J = 8.0 Hz, 2H), 7.98 (dd, J = 8.0, 1.0 Hz, 2H), 8.34 (d, J = 1.0 Hz, 2H); ¹³C NMR (125 MHz, acetone-*d*₆) δ 165.6, 146.5, 131.1, 130.8, 129.2 (q, J = 32.5 Hz), 127.3 (dd, J = 163, 3.8 Hz), 125.1, 123.0; HRMS (ESI) m/z [M-H] calcd for C₁₆H₇F₆O₄ 377.0249, found 377.0253.



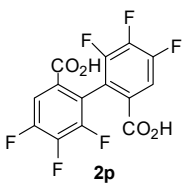
4,4'-Dichlorobiphenyl-2,2'-dicarboxylic acid (2m) Colorless solid; Yield 63%; ¹H NMR (500 MHz, acetone-*d*₆) δ 7.28 (d, J = 8.5 Hz, 2H), 7.63 (dd, J = 8.0, 2.0 Hz, 2H), 8.01 (d, J = 2.0 Hz, 2H); ¹³C NMR (125 MHz, acetone-*d*₆) δ 165.7, 141.3, 132.6, 132.1, 131.7, 131.2, 129.6.



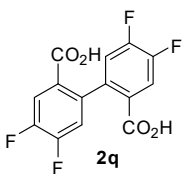
4,6'-Dichlorobiphenyl-2,2'-dicarboxylic acid (2n) Colorless solid; Yield 18%; ¹H NMR (500 MHz, acetone-*d*₆) δ 7.20 (d, J = 8.5 Hz, 1H), 7.51 (t, J = 8.0 Hz, 1H), 7.65 (dd, J = 8.0, 2.5 Hz, 1H), 7.69 (dd, J = 8.0, 1.0 Hz, 1H), 7.98 (dd, J = 8.0, 1.0 Hz, 1H), 8.07 (d, J = 2.0 Hz, 1H); ¹³C NMR (125 MHz, acetone-*d*₆) δ 170.5, 140.7, 139.2, 133.8, 132.9, 132.2, 132.0, 131.5, 129.8, 128.7, 128.5.



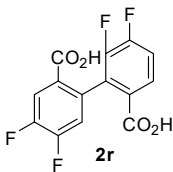
4,4',6,6'-Tetrafluorobiphenyl-2,2'-dicarboxylic acid (2o) Colorless solid; Yield 88%; ^1H NMR (500 MHz, acetone-*d*6): δ 7.39–7.43 (m, 2H), 7.69–7.72 (m, 2H); ^{13}C NMR (125 MHz, acetone-*d*6) δ 164.7, 162.2 (dd, $J = 250, 12.5$ Hz), 160.1 (dd, $J = 250, 12.5$ Hz), 133.6, 119.5 (dd, $J = 18.8, 3.8$ Hz), 113.2 (dd, $J = 23.8, 3.3$ Hz), 107.2 (t, $J = 26.3$ Hz); HRMS (ESI) m/z [M-H] calcd for $\text{C}_{14}\text{H}_5\text{F}_4\text{O}_4$ 313.0124, found 313.0131.



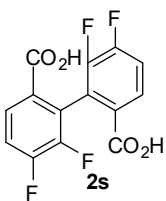
4,4',5,5',6,6'-Hexafluorobiphenyl-2,2'-dicarboxylic acid (2p) Colorless solid; Yield 80%; ^1H NMR (500 MHz, acetone-*d*6) δ 7.95–7.99 (m, 2H); ^{13}C NMR (125 MHz, acetone-*d*6) δ 163.9, 150.3 (ddd, $J = 250, 10, 3.8$ Hz), 148.7 (ddd, $J = 250, 10, 3.8$ Hz), 142.0 (dt, $J = 250, 12.5$ Hz), 126.5, 120.4 (d, $J = 16.3$ Hz), 115.0 (dd, $J = 18.8, 3.8$ Hz); HRMS (ESI) m/z [M-H] calcd for $\text{C}_{14}\text{H}_3\text{F}_6\text{O}_4$ 348.9936, found 348.9941.



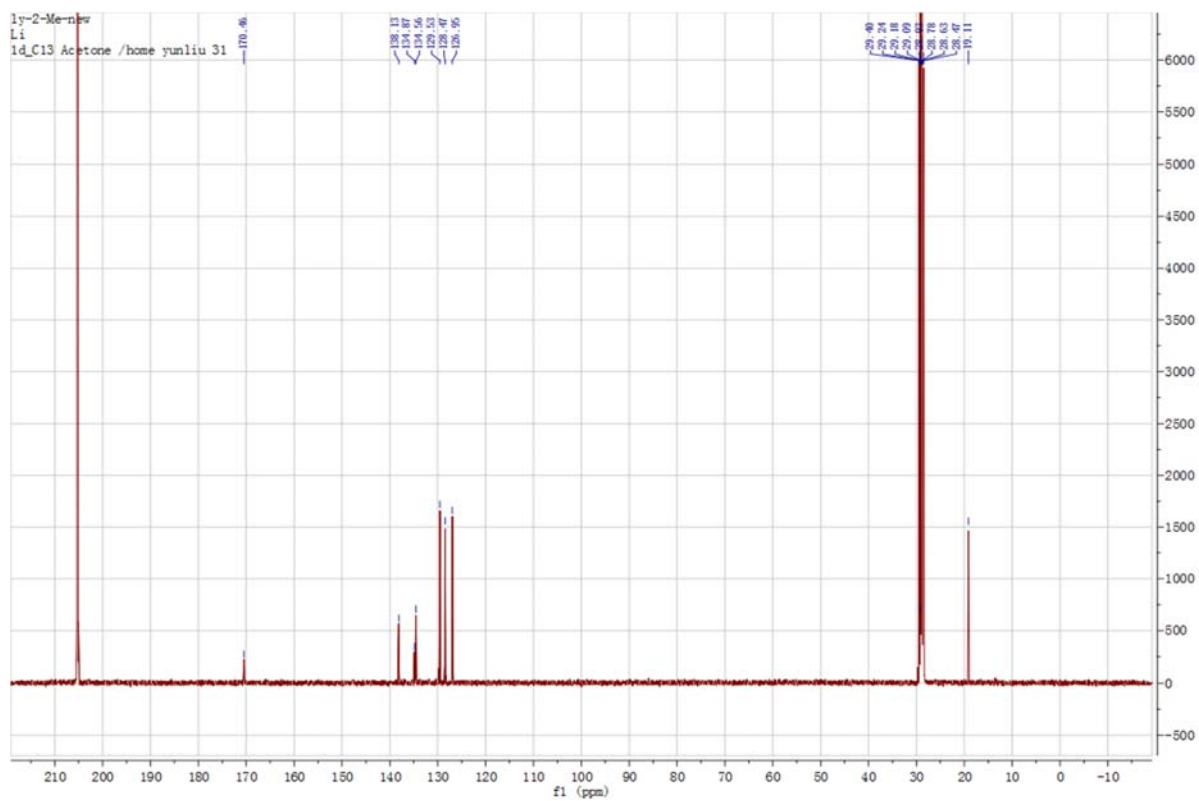
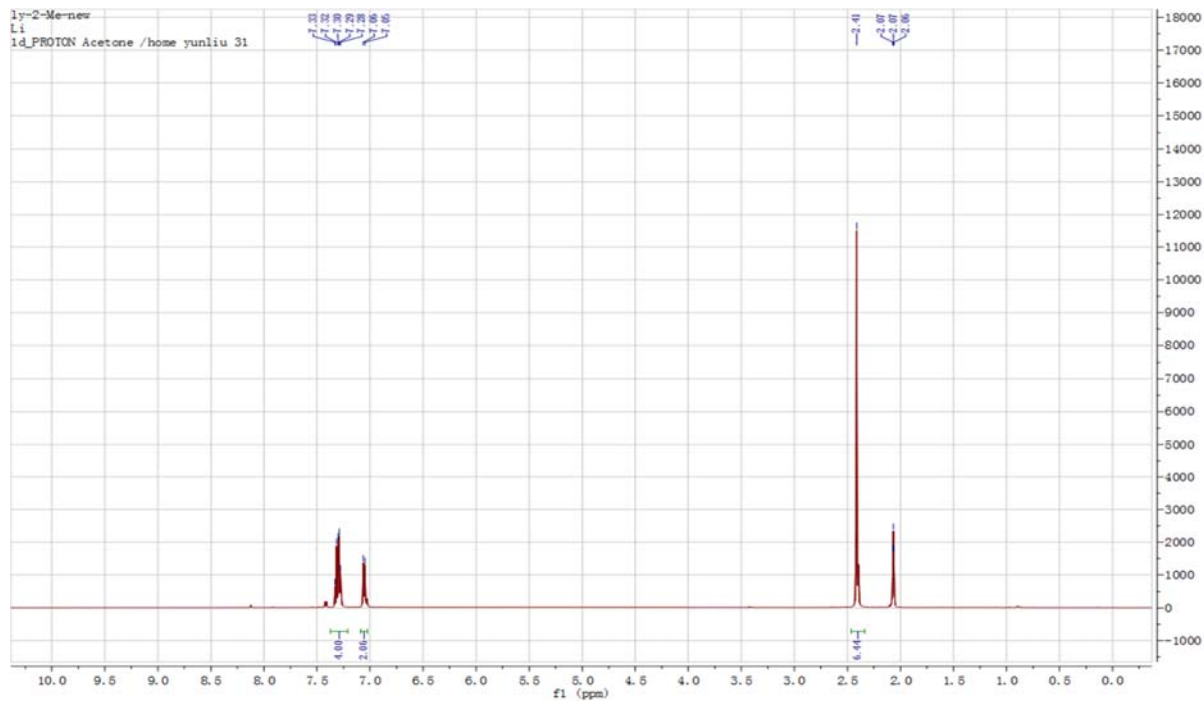
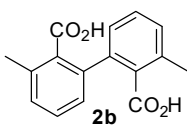
4,4',5,5'-Tetrafluorobiphenyl-2,2'-dicarboxylic acid (2q) Colorless solid; Yield 34%; ^1H NMR (500 MHz, acetone-*d*6) δ 7.29–7.33 (m, 2H), 7.94–7.98 (m, 2H); ^{13}C NMR (125 MHz, acetone-*d*6) δ 164.8, 151.5 (dd, $J = 250, 12.5$ Hz), 148.8 (dd, $J = 250, 12.5$ Hz), 139.7, 126.9, 119.4 (d, $J = 18.8$ Hz), 119.2 (d, $J = 18.8$ Hz); HRMS (ESI) m/z [M-H] calcd for $\text{C}_{14}\text{H}_5\text{F}_4\text{O}_4$ 313.0124, found 313.0132.

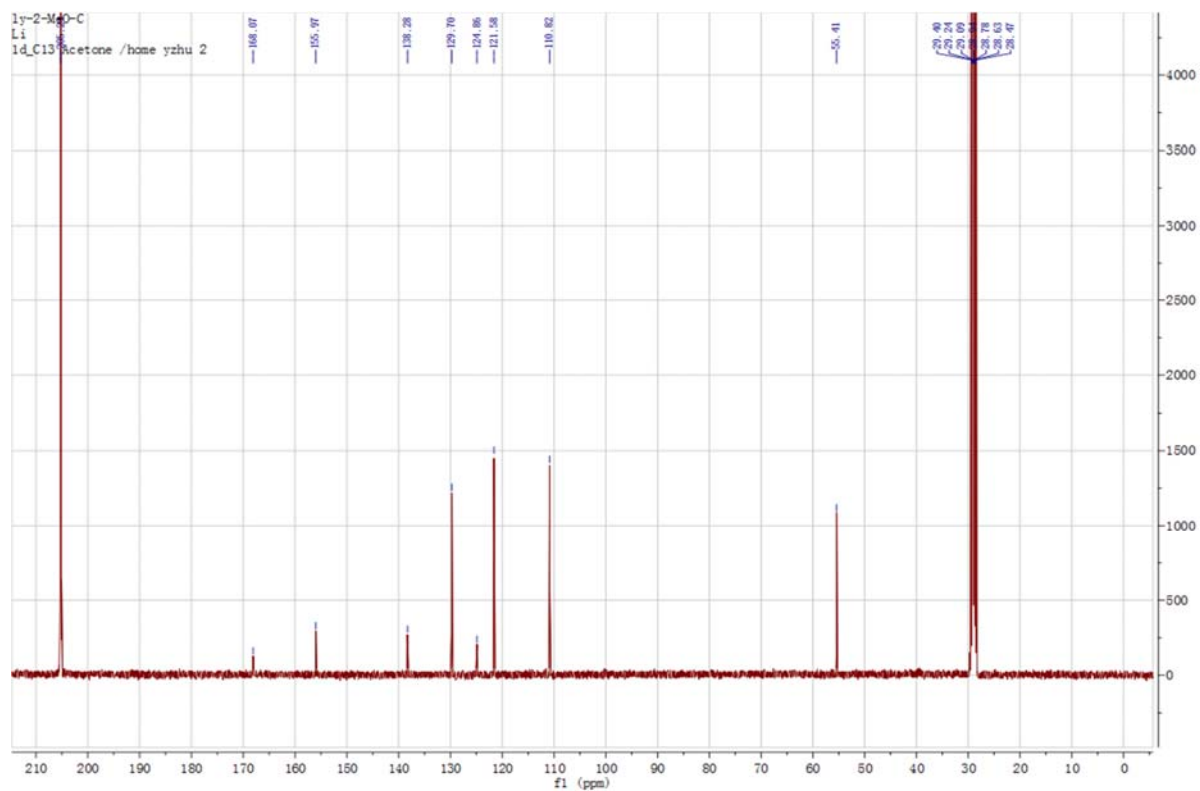
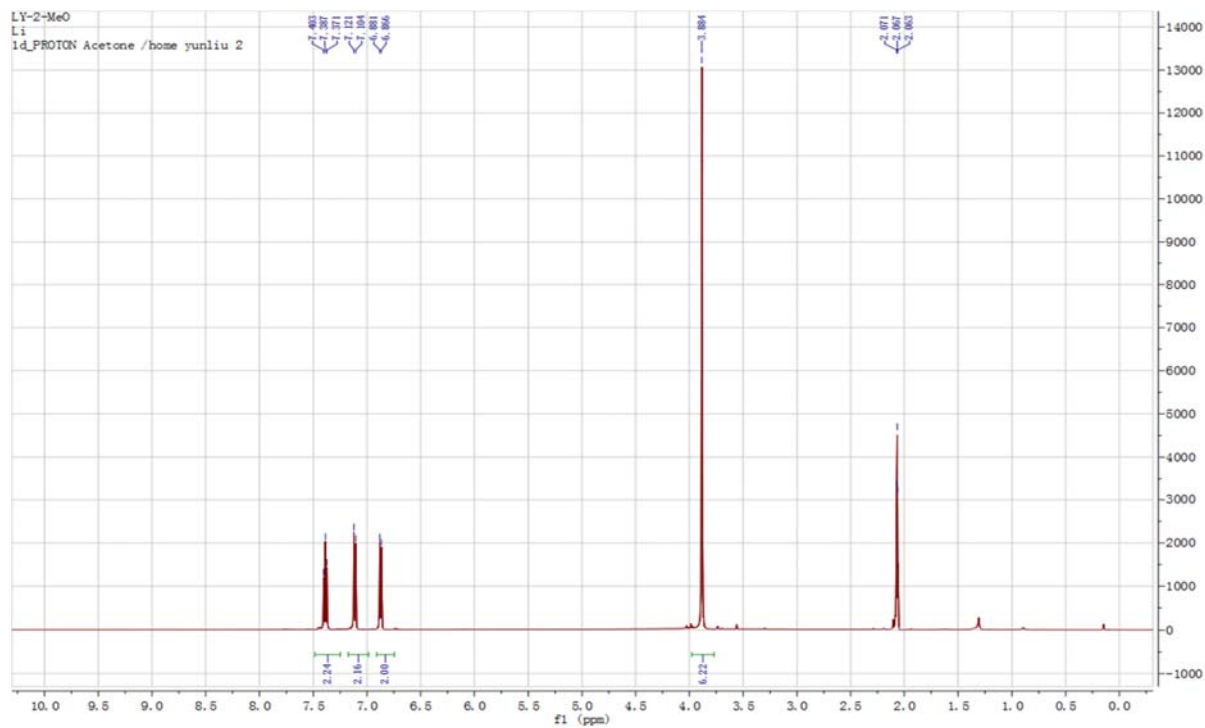
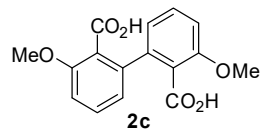


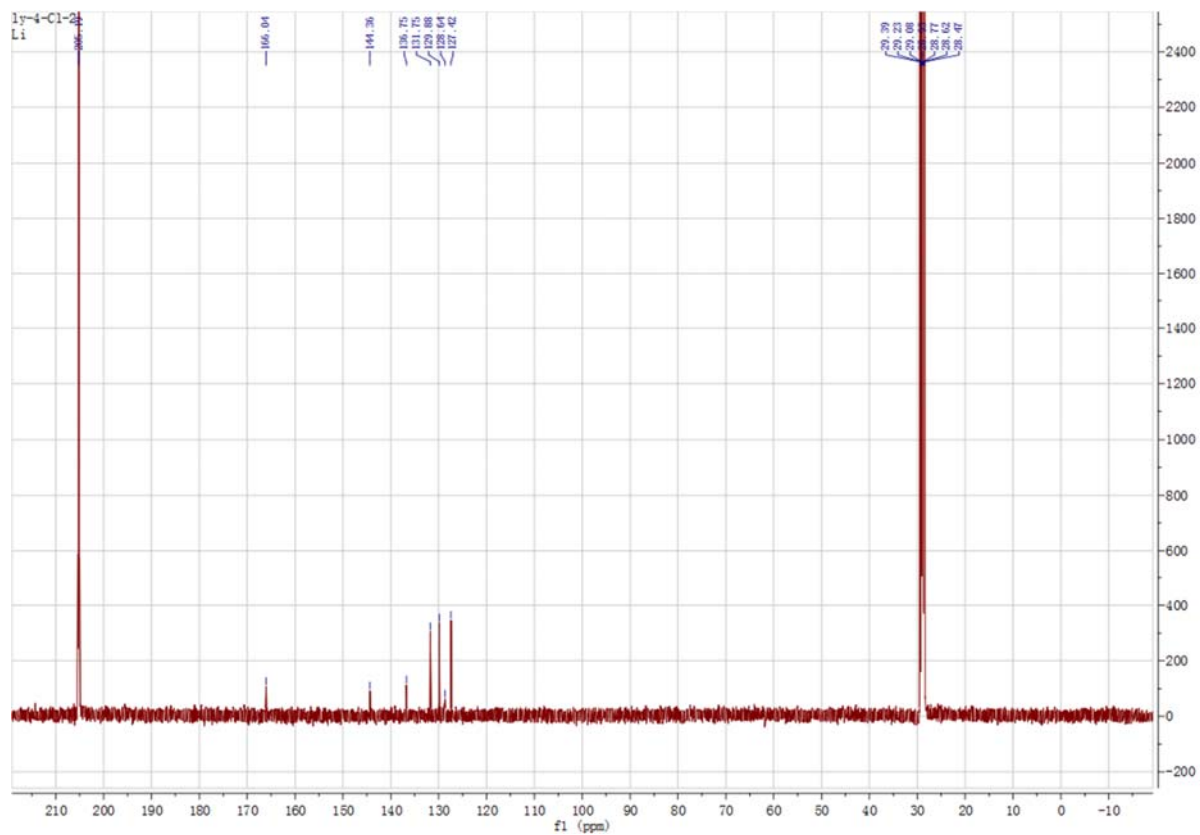
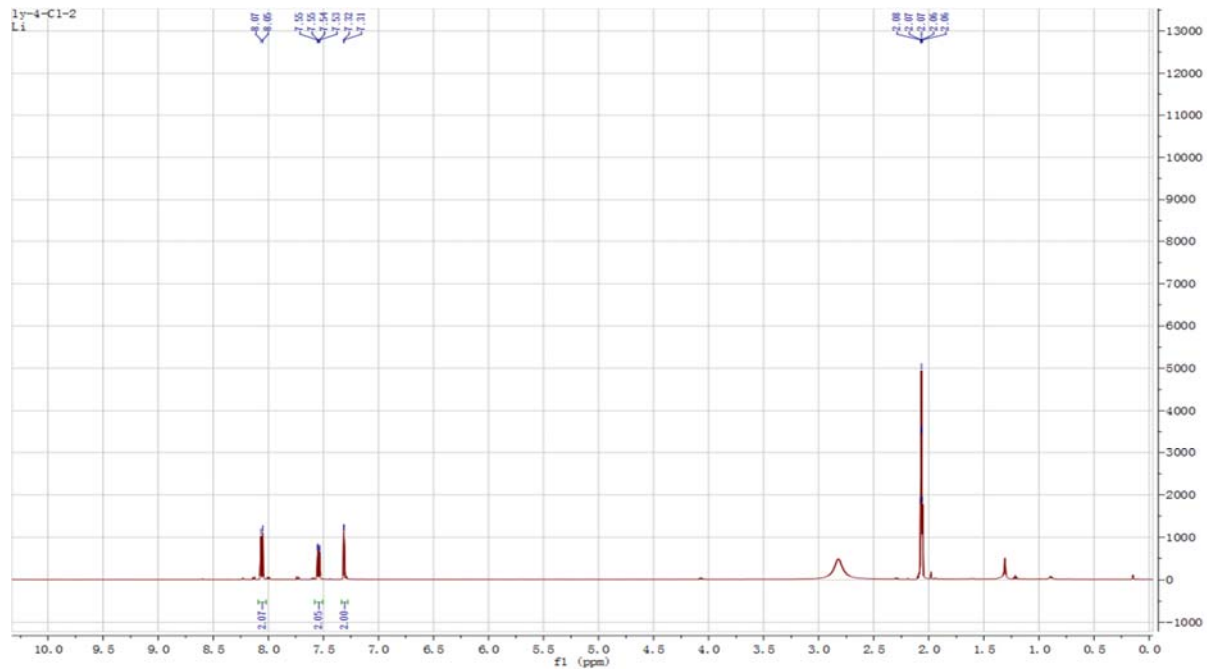
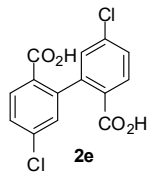
4,5,5',6'-Tetrafluorobiphenyl-2,2'-dicarboxylic acid (2r) Colorless solid; Yield 31%; ^1H NMR (500 MHz, acetone-*d*6) δ 7.39–7.42 (m, 1H), 7.47–7.52 (m, 1H), 7.95–7.99 (m, 1H), 8.03–8.07 (m, 1H); ^{13}C NMR (125 MHz, acetone-*d*6) δ 165.1, 164.6, 152.5 (dd, $J = 250, 12.5$ Hz), 151.8 (d, $J = 250, 12.5$ Hz), 149.1 (d, $J = 250, 12.5$ Hz), 147.4 (d, $J = 250, 12.5$ Hz), 133.3, 132.0 (d, $J = 12.5$ Hz), 127.4, 127.1 (q, $J = 4.0$ Hz), 126.9, 119.8 (d, $J = 18.8$ Hz), 119.6 (d, $J = 18.8$ Hz), 116.1 (d, $J = 17.5$ Hz); HRMS (ESI) m/z [M-H] calcd for $\text{C}_{14}\text{H}_5\text{F}_4\text{O}_4$ 313.0124, found 313.0131.

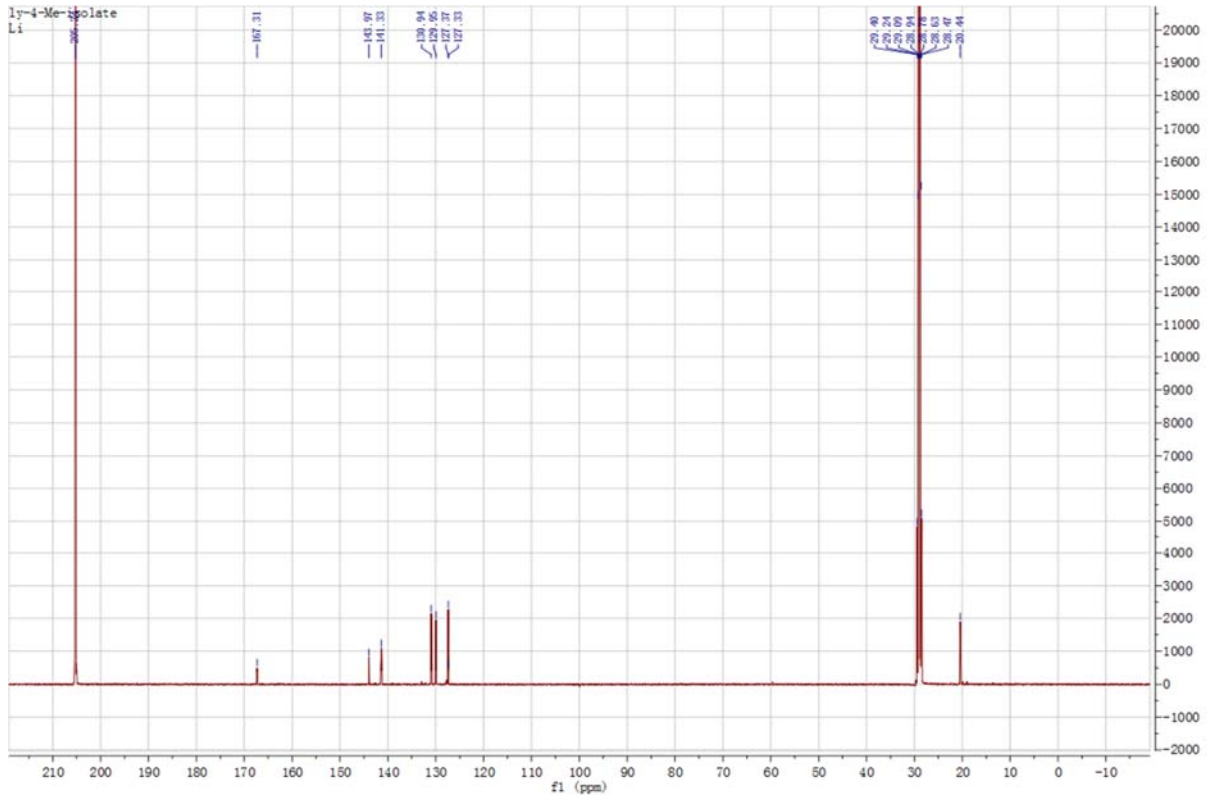
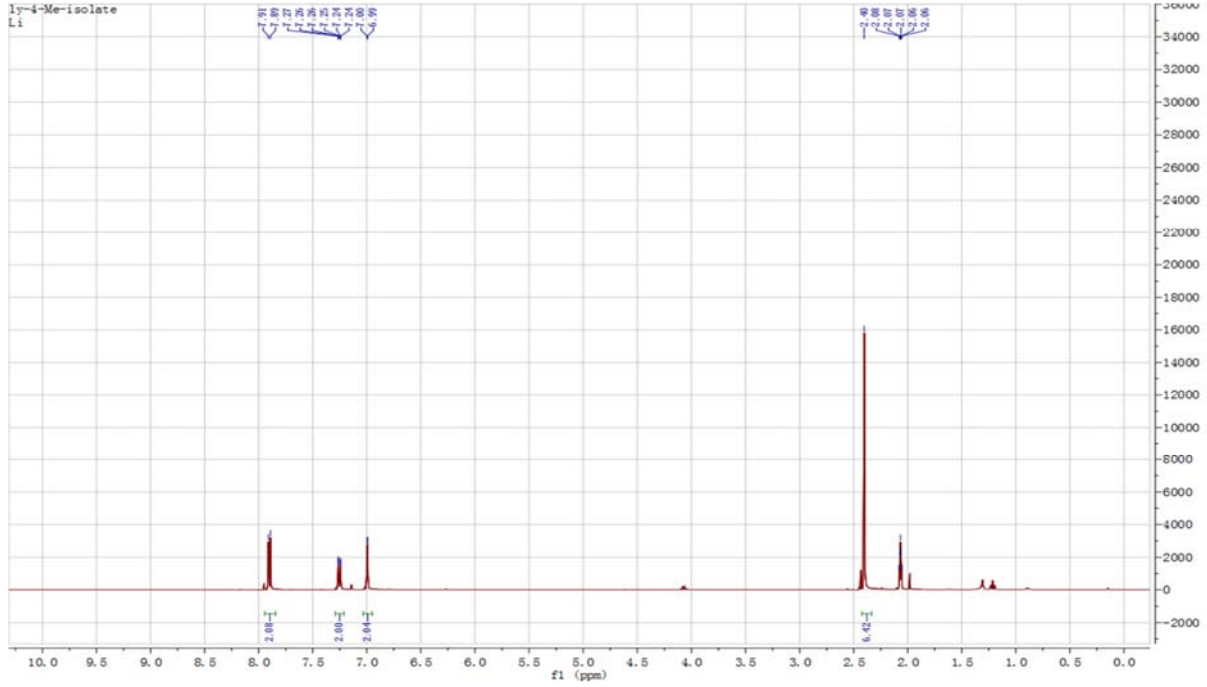
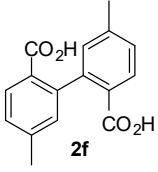


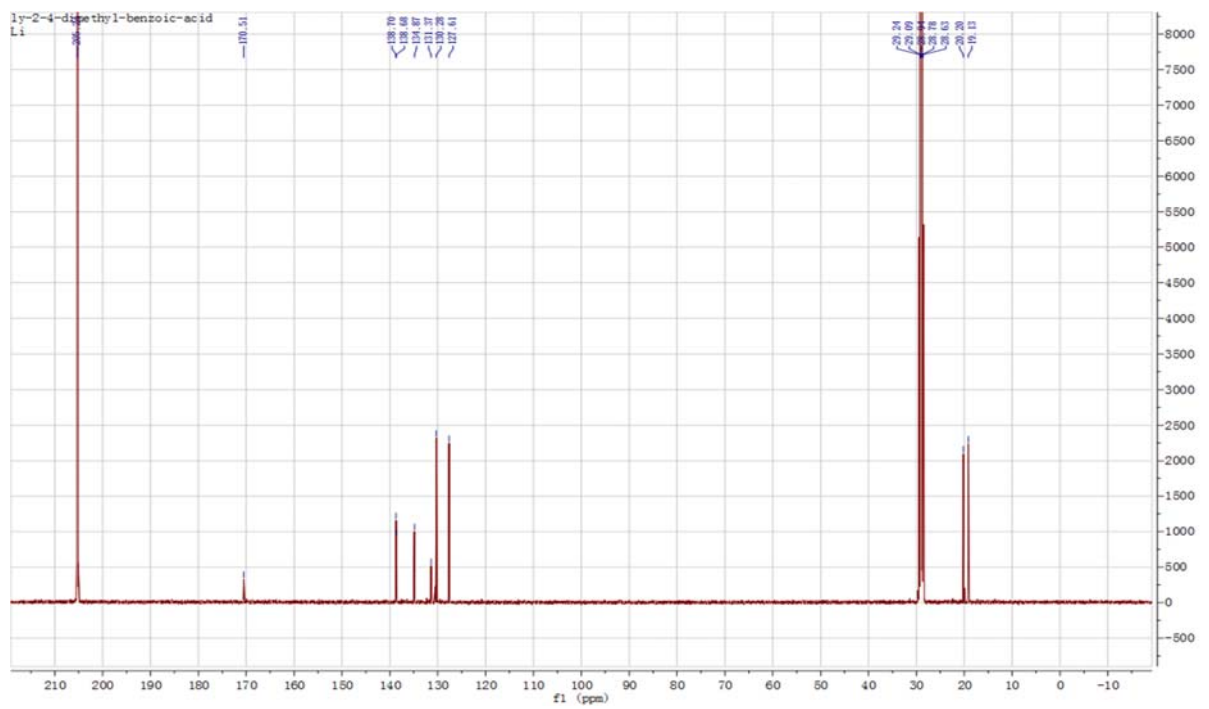
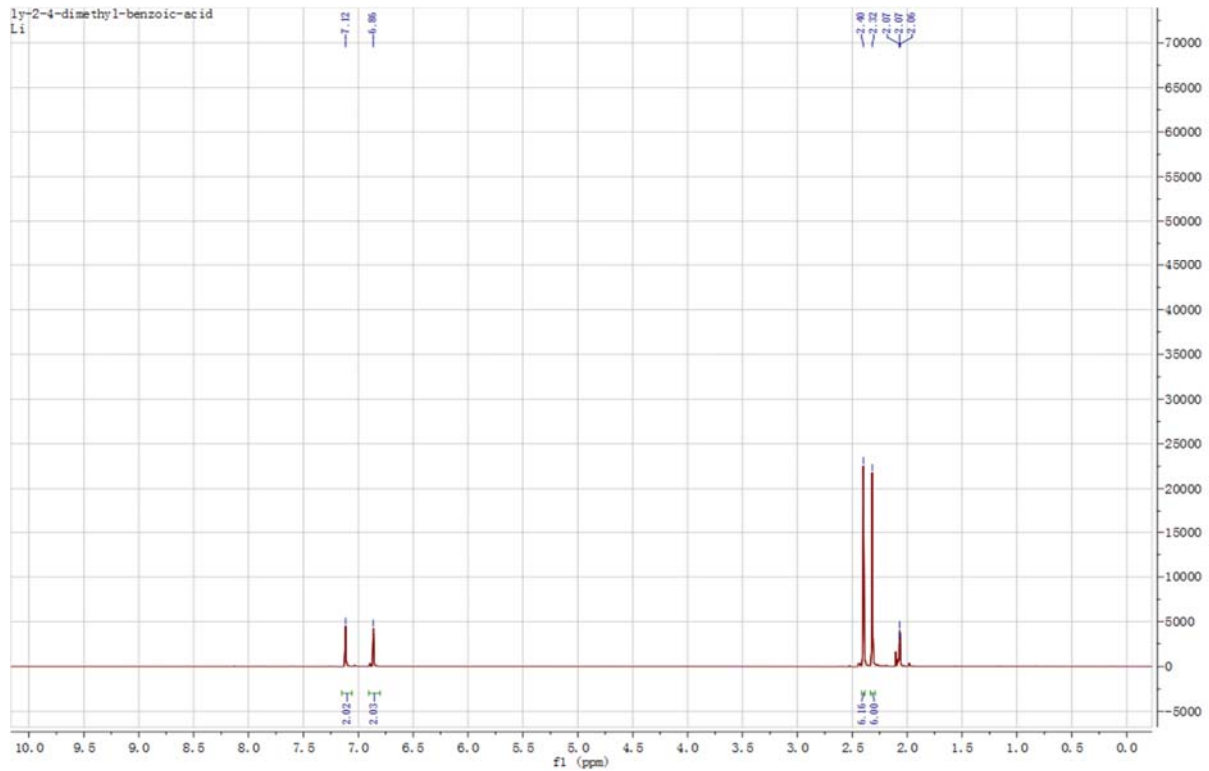
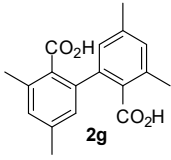
5,5',6,6'-Tetrafluorobiphenyl-2,2'-dicarboxylic acid (2s) Colorless solid; Yield 22%; ^1H NMR (500 MHz, acetone-*d*6) δ 7.54–7.59 (m, 2H), 8.02–8.05 (m, 2H); ^{13}C NMR (125 MHz, acetone-*d*6) δ 165.0, 152.5 (dd, $J = 250, 13.8$ Hz), 147.4 (d, $J = 250, 13.8$ Hz), 127.5, 127.3, 125.5 (d, $J = 15.0$ Hz), 116.9 (d, $J = 17.5$ Hz); HRMS (ESI) m/z [M-H] calcd for $\text{C}_{14}\text{H}_5\text{F}_4\text{O}_4$ 313.0124, found 313.0132.

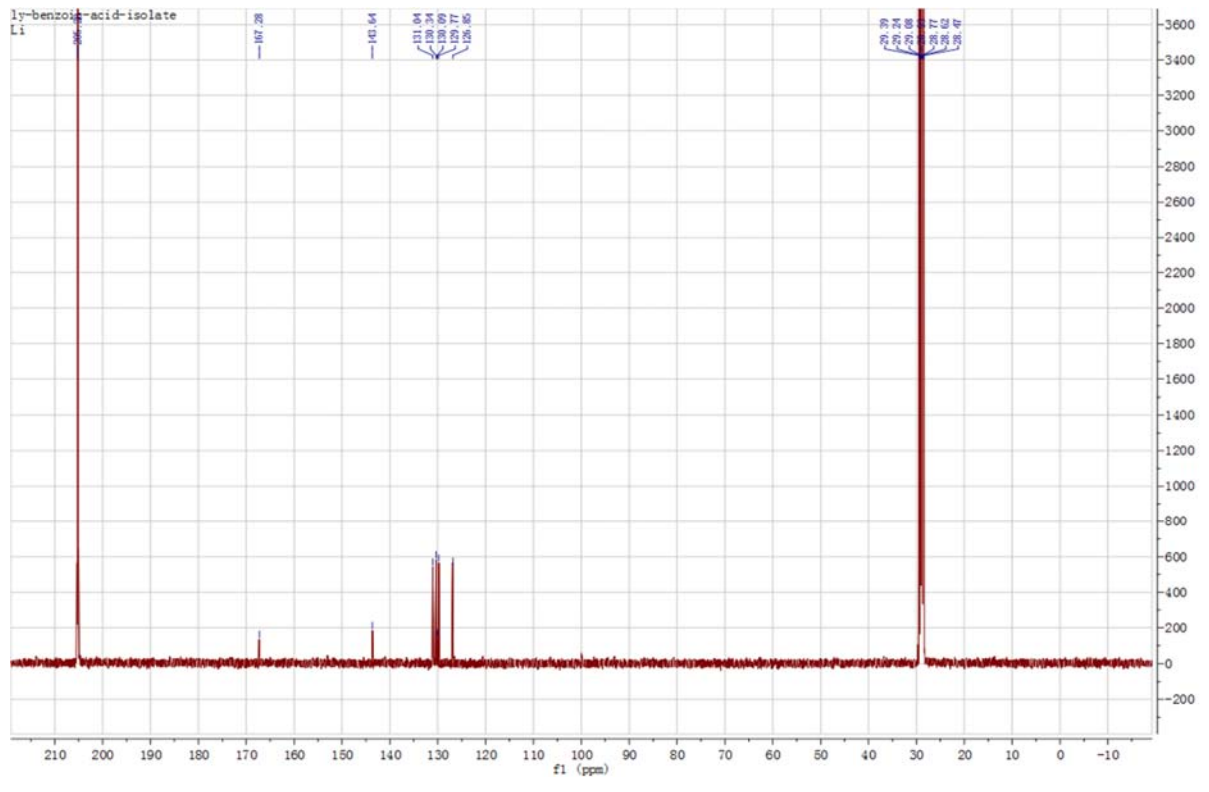
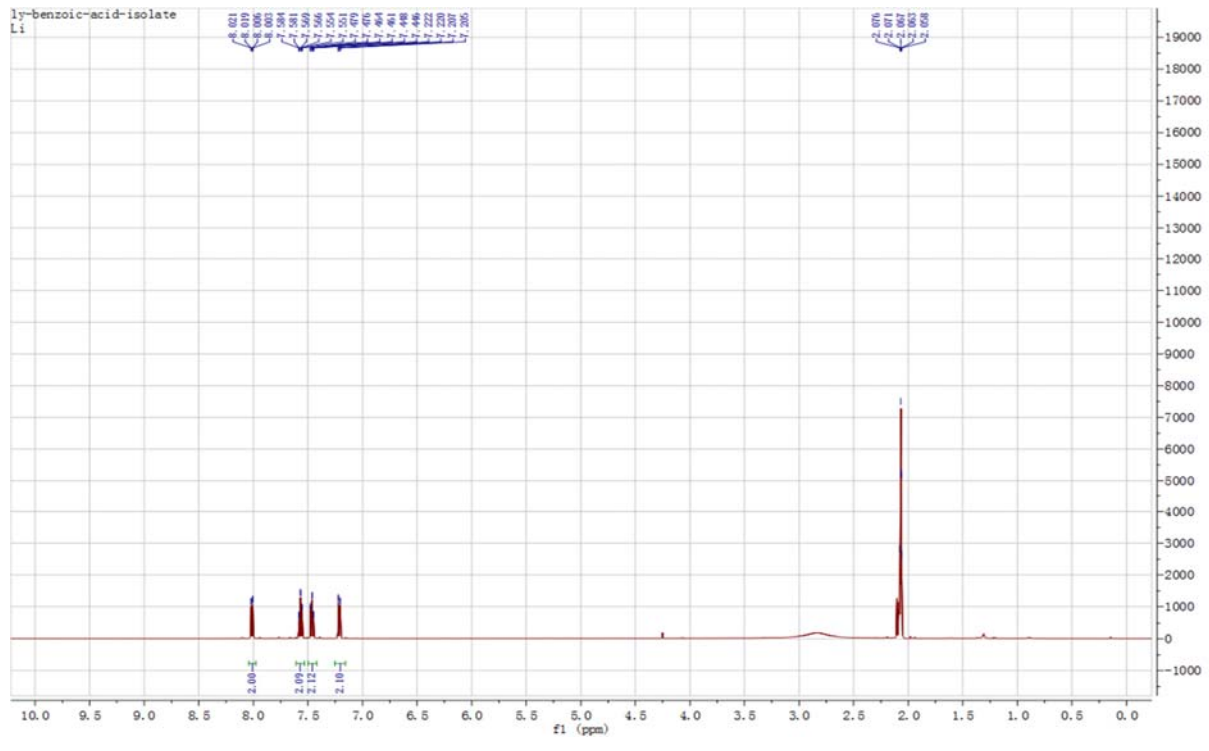
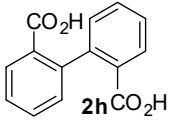


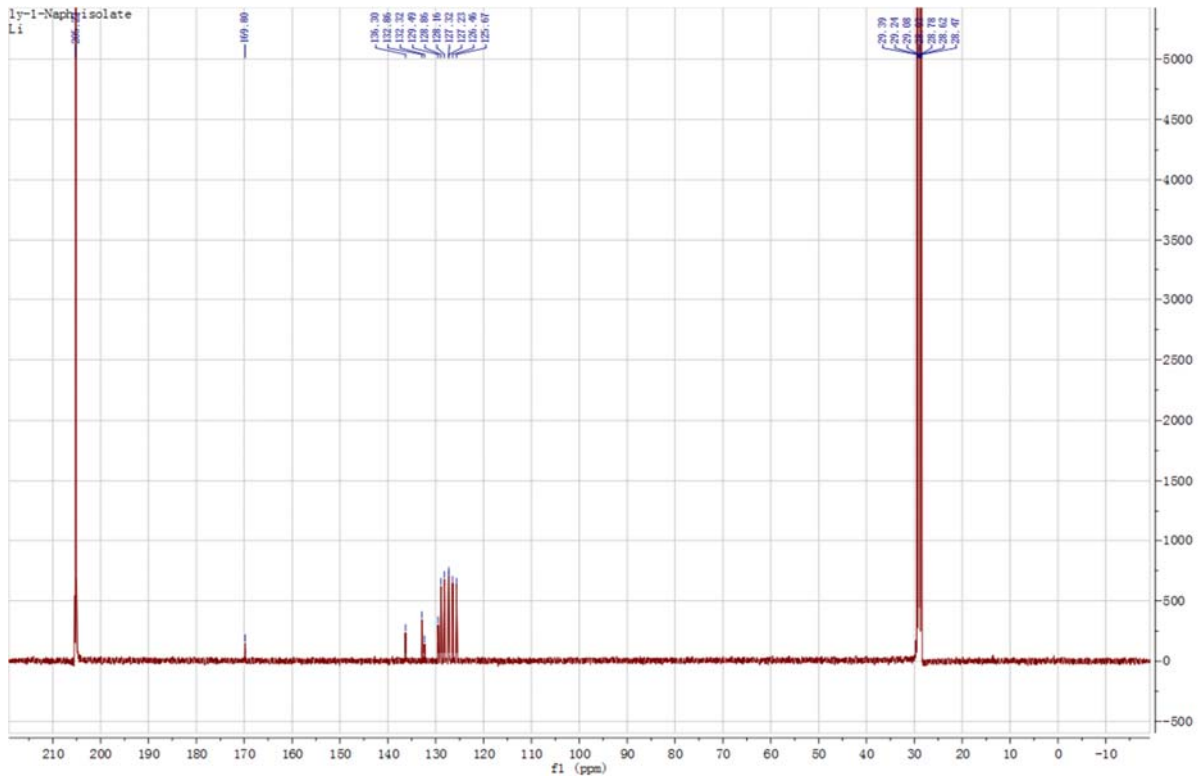
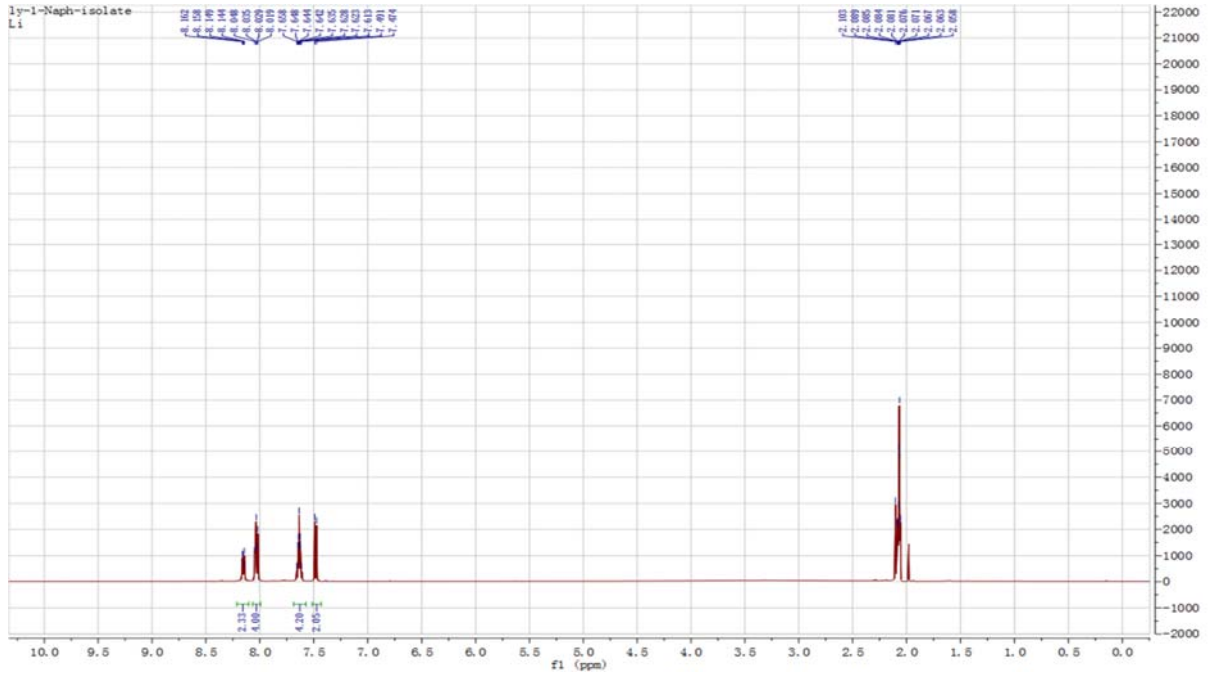
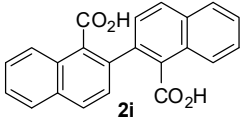


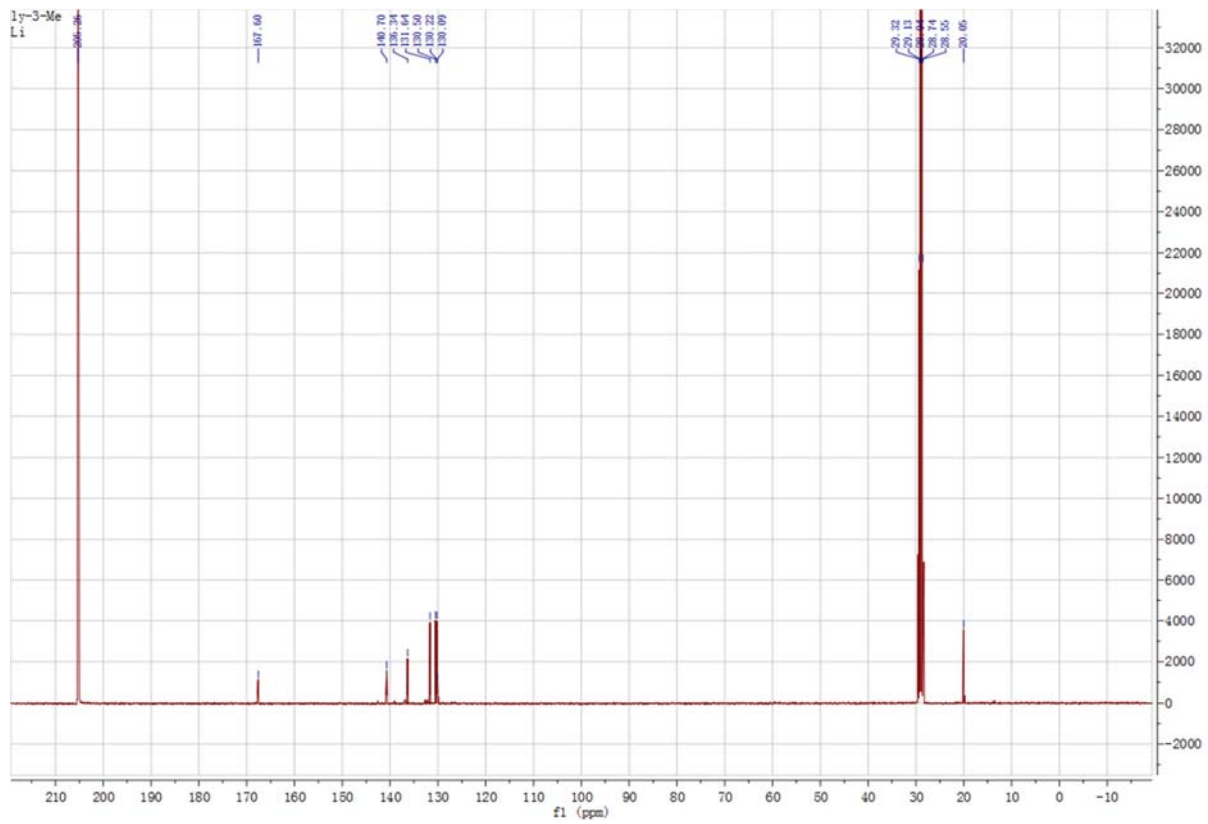
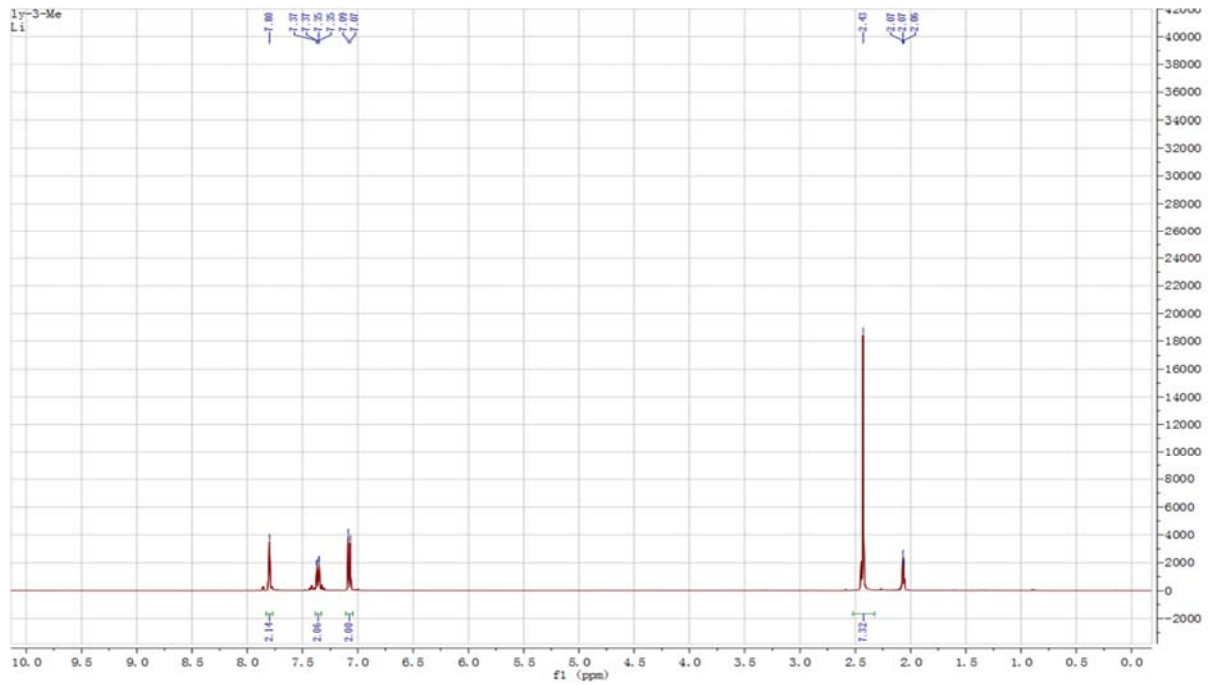
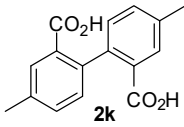


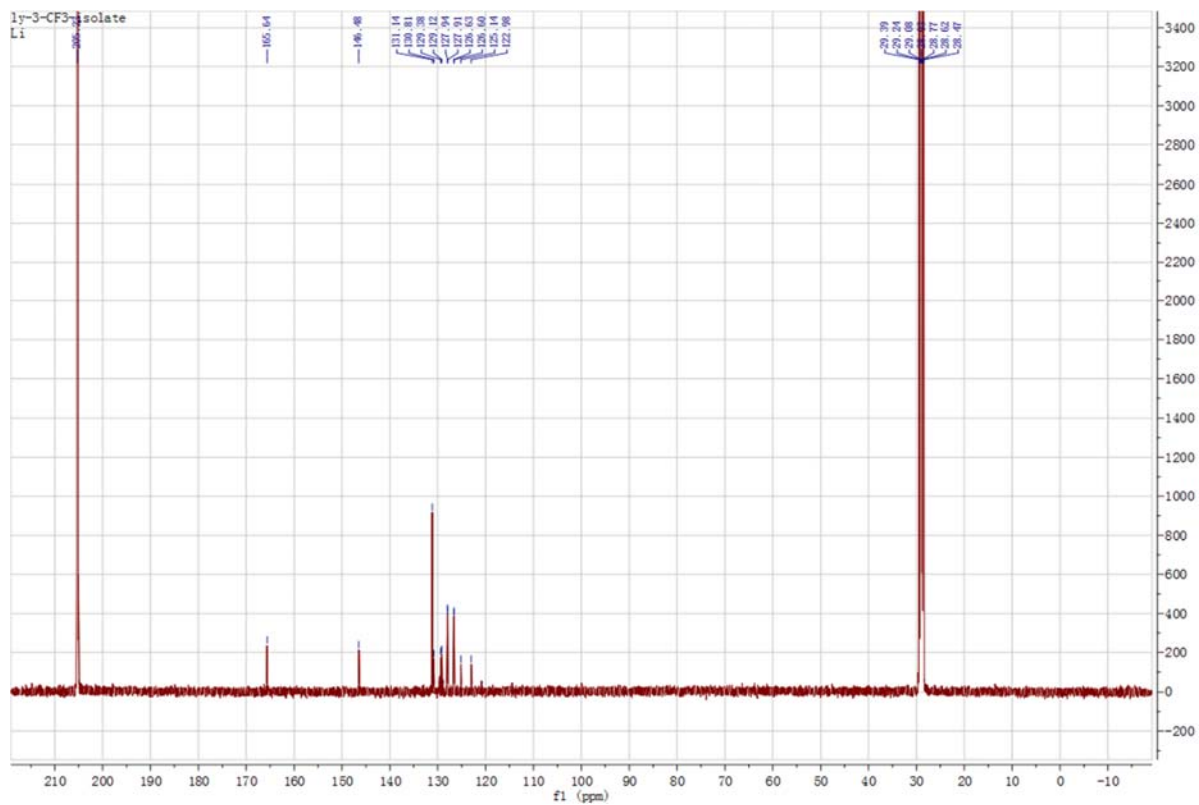
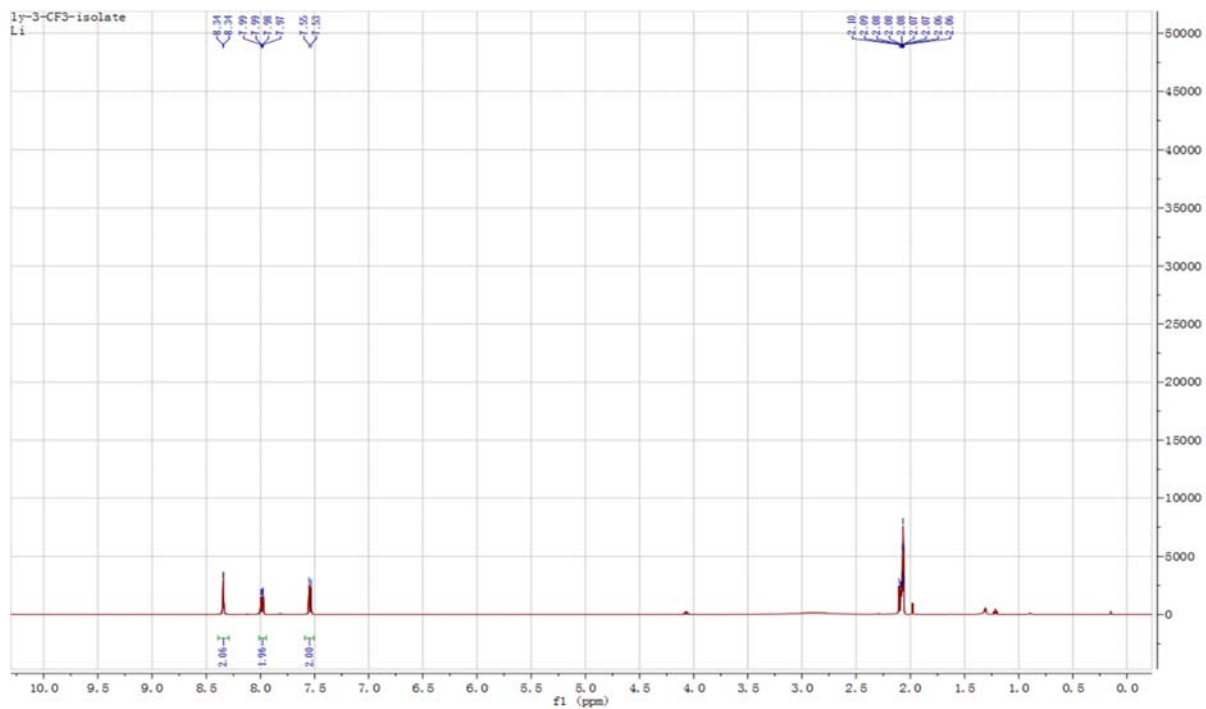
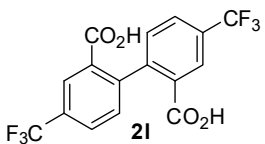


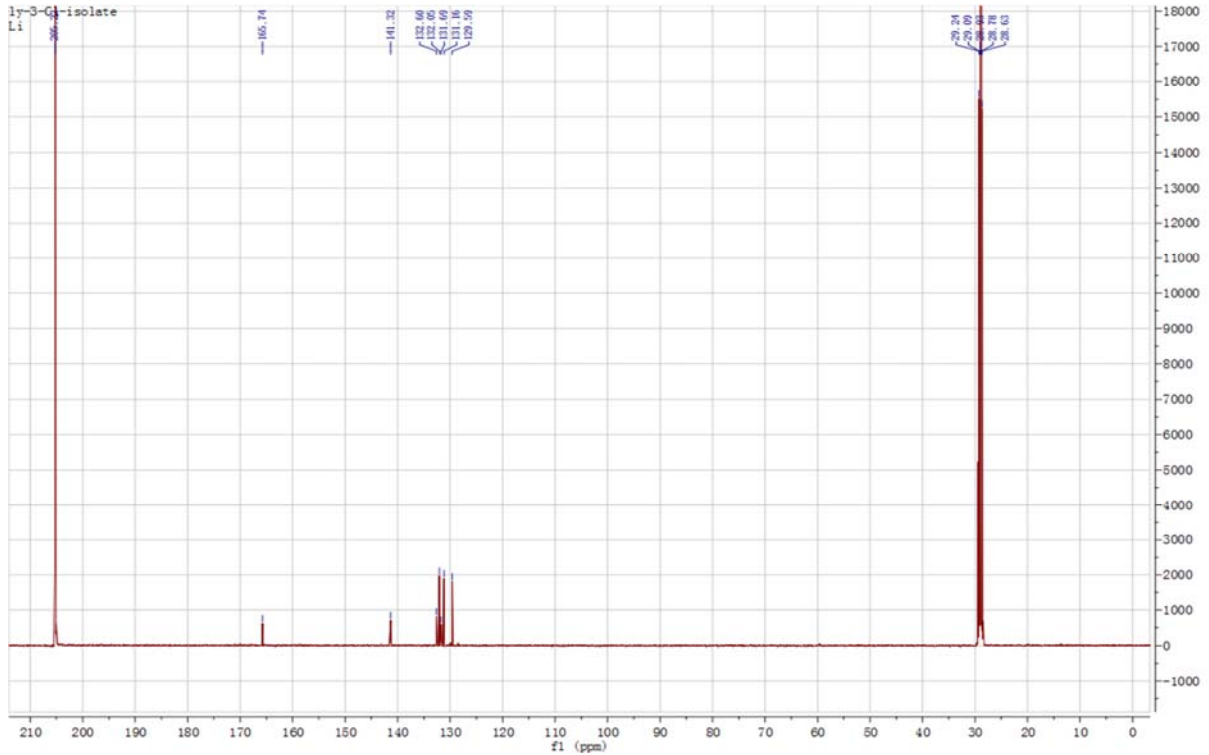
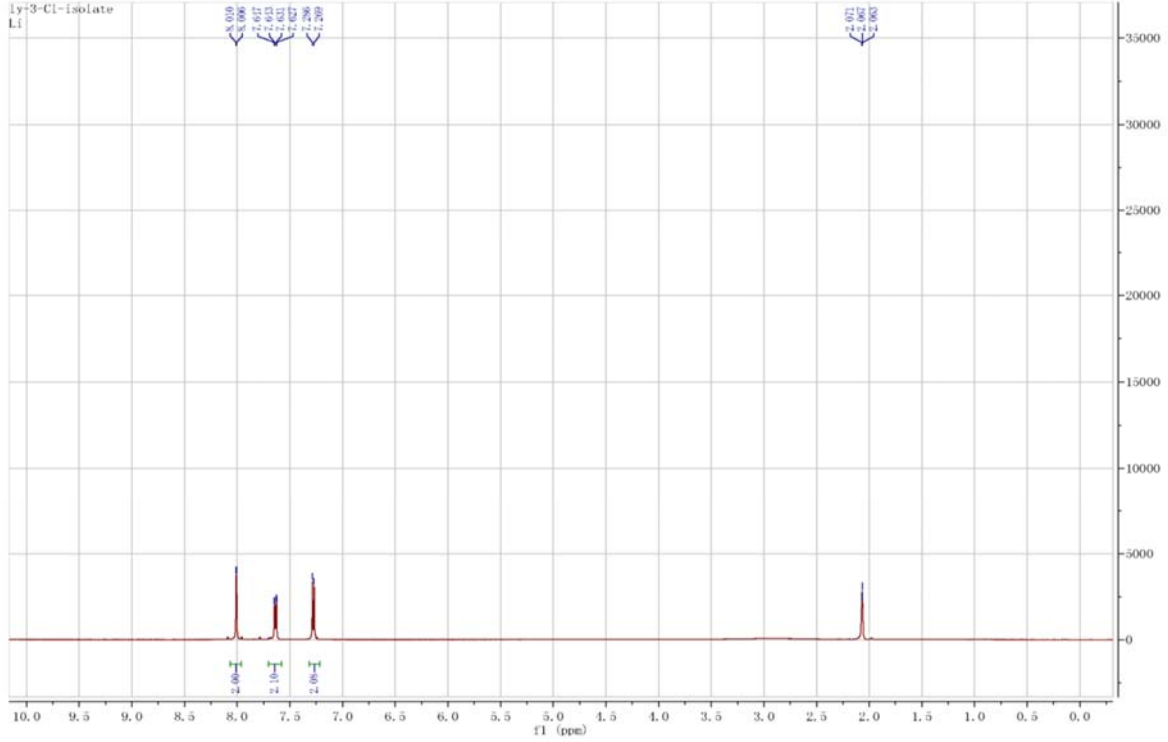
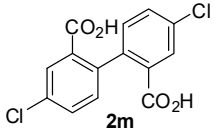


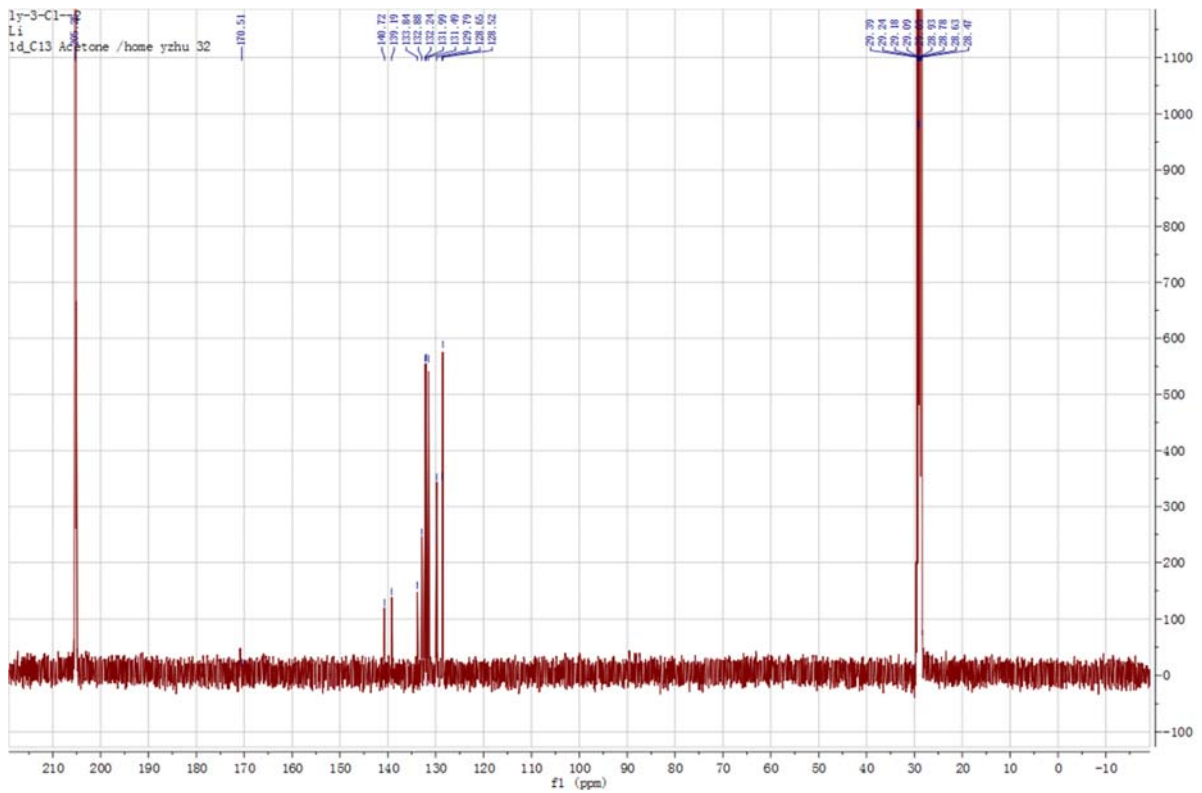
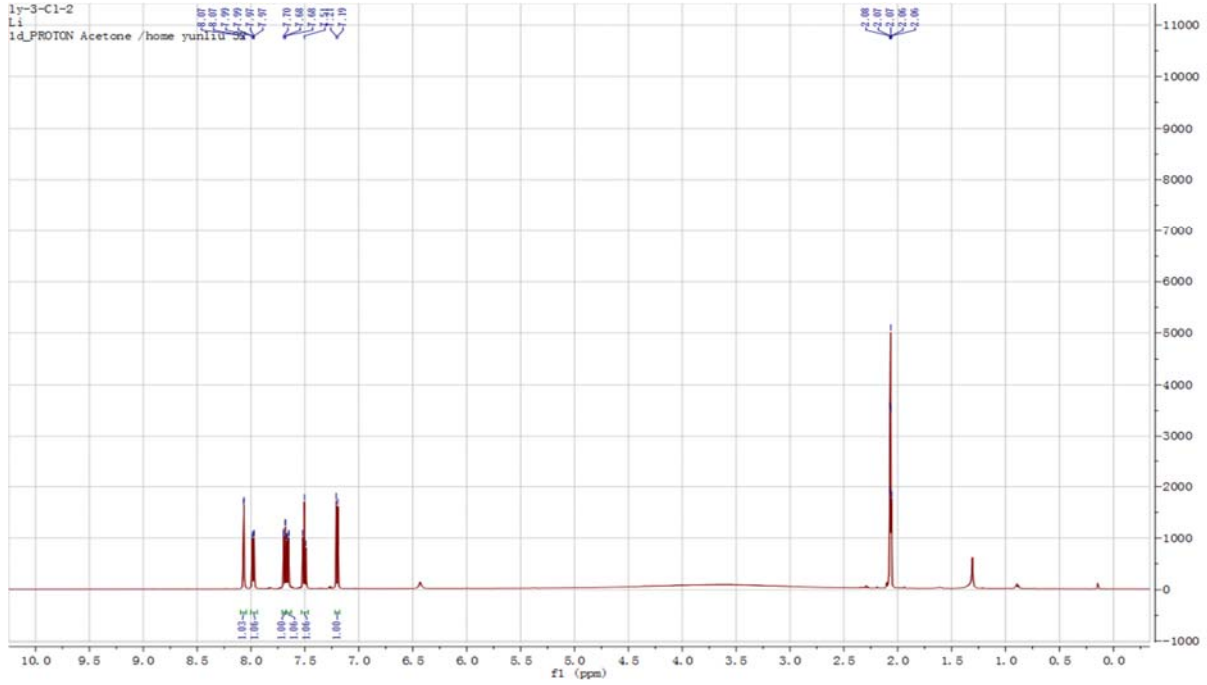
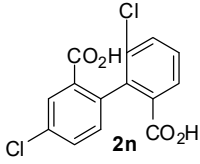


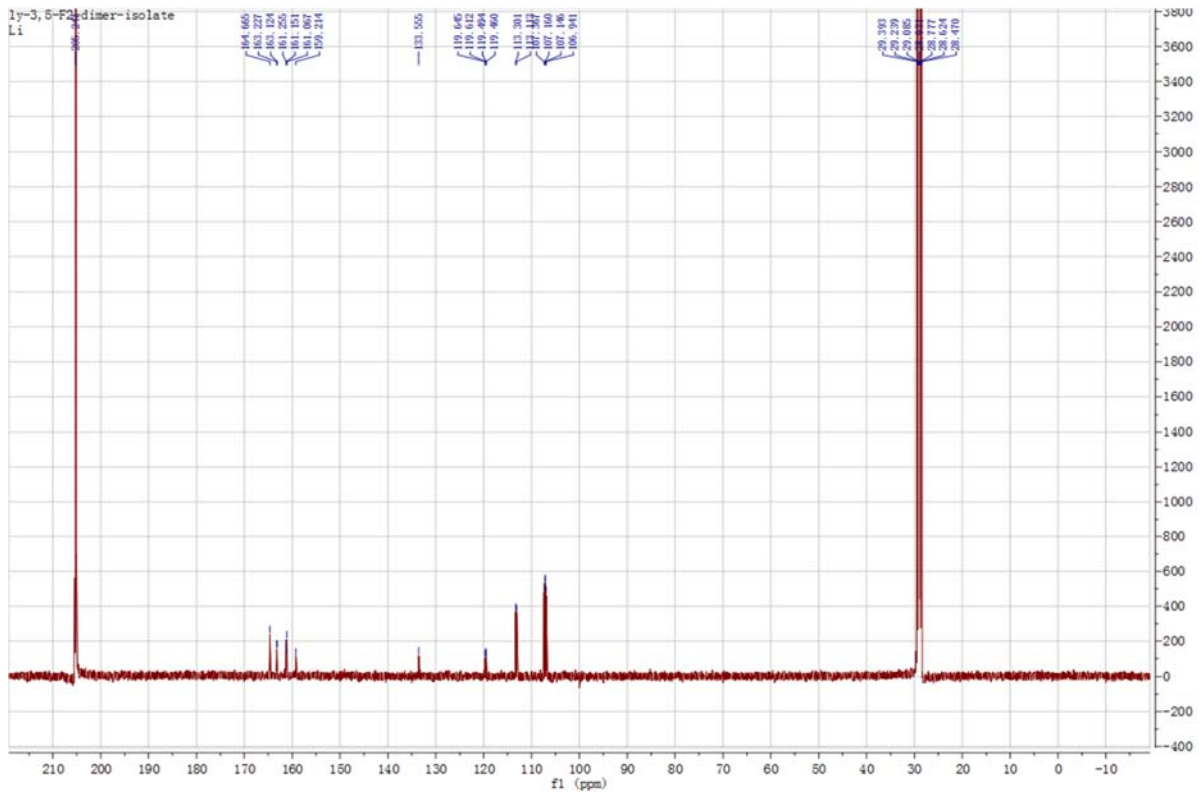
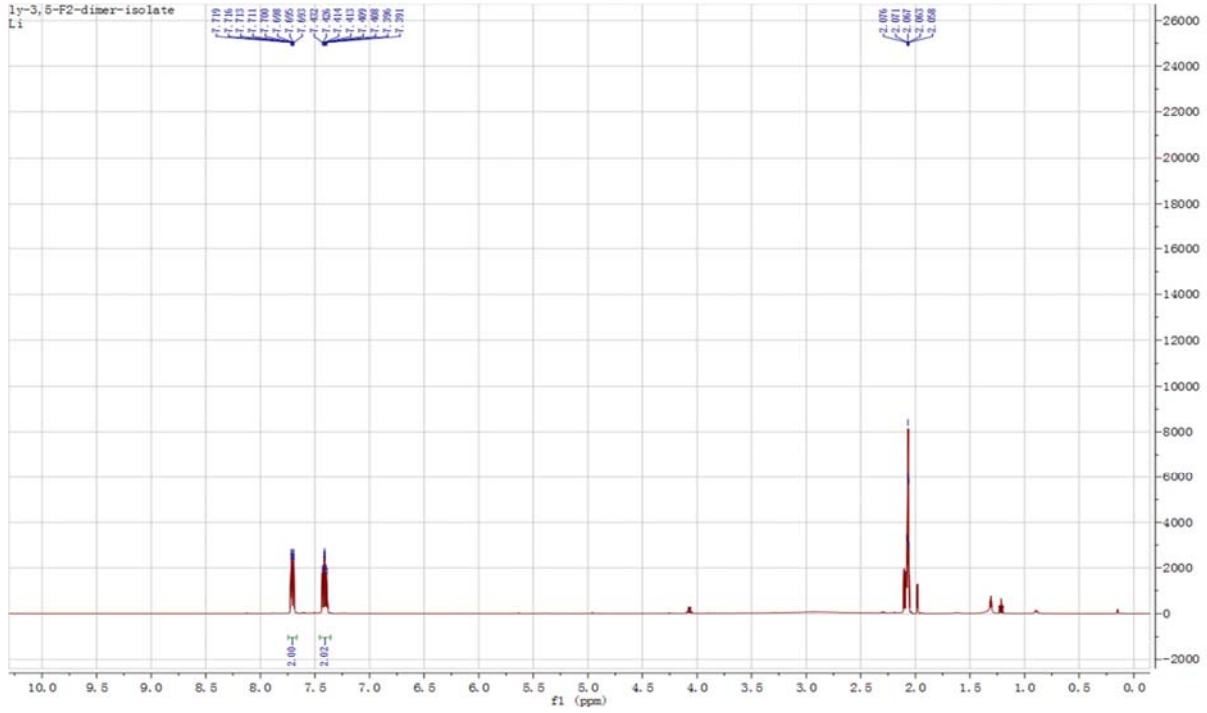
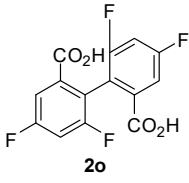


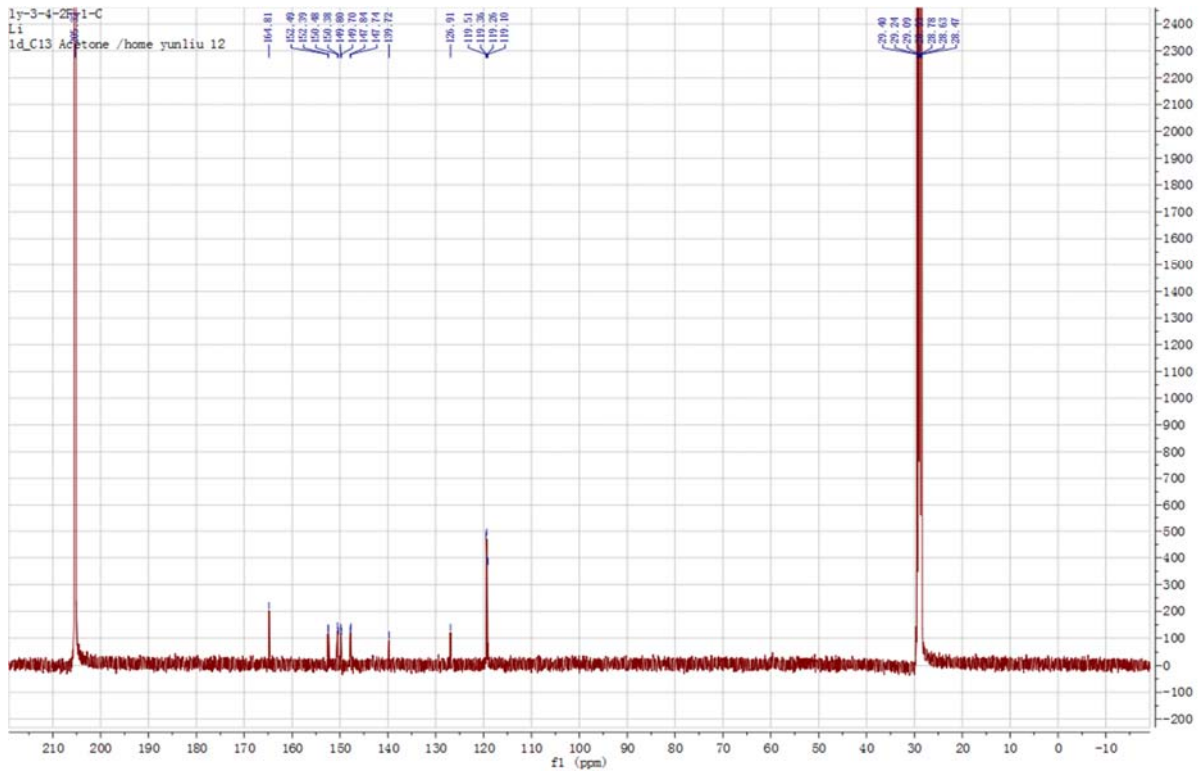
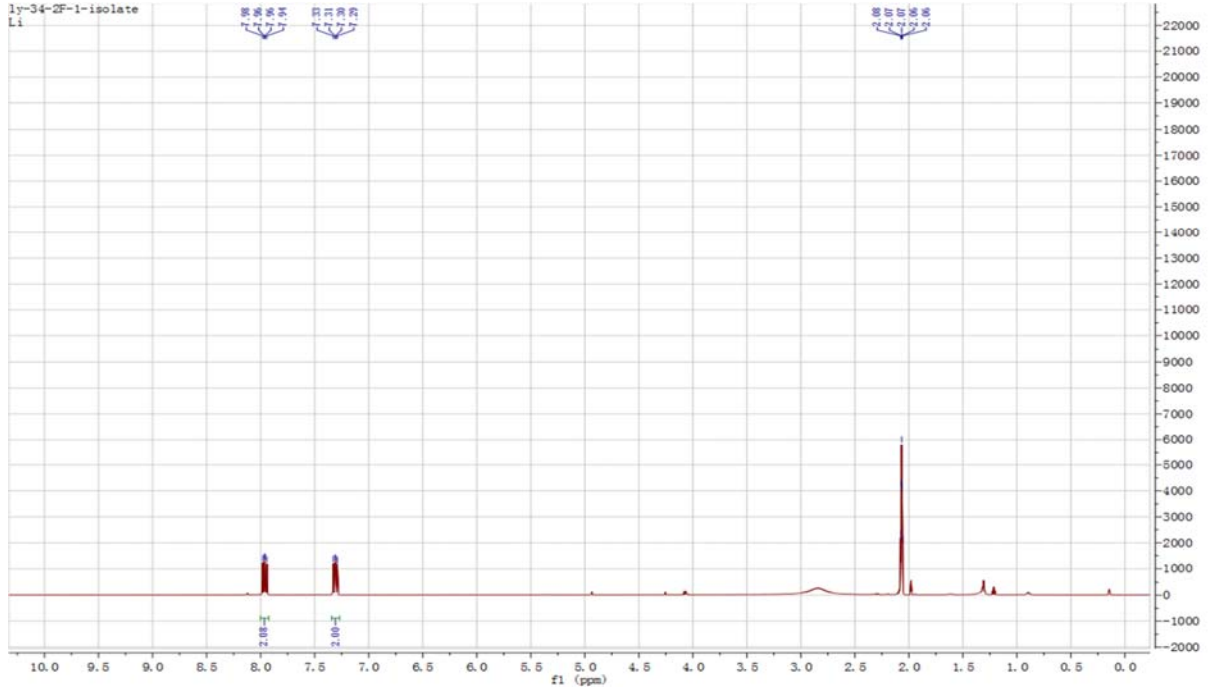
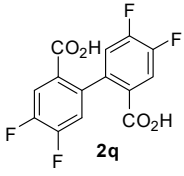


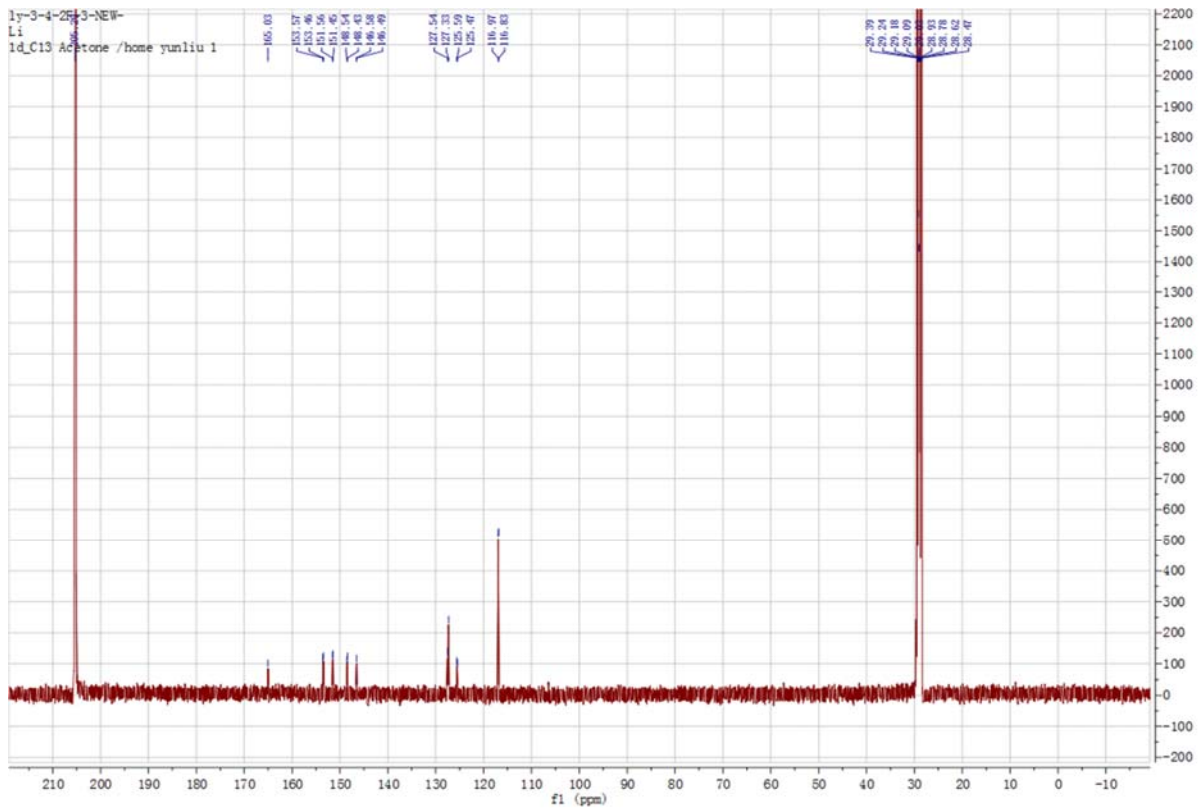
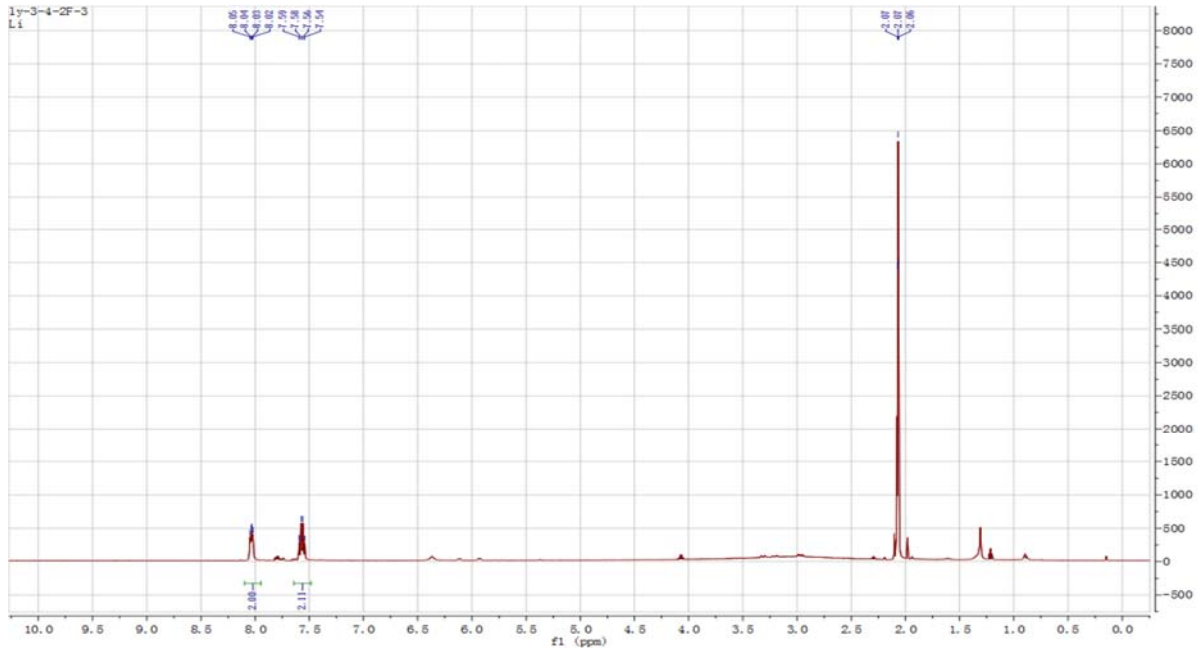
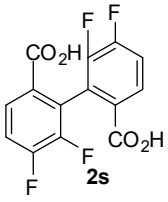






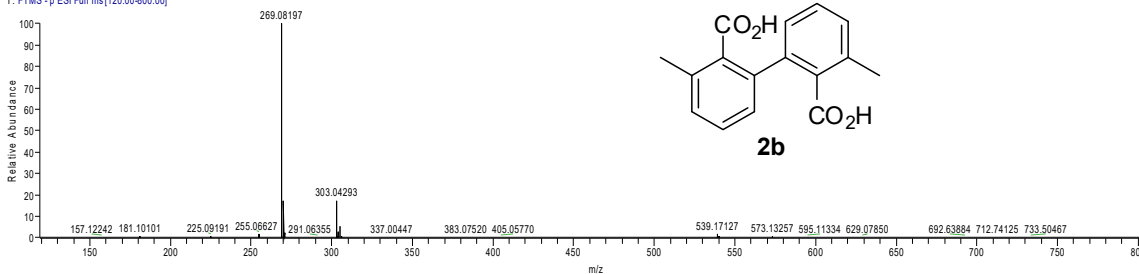




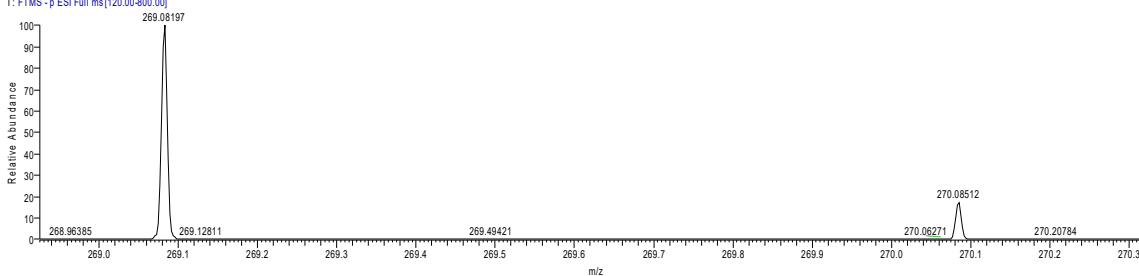


4. Copies of HRMS for all new products

160118-01ESIHR-Li-Yun Liu-LY-4_160118113450 #410-423 RT: 1.00-1.00 AV: 2 NL: 2.47E9
T: FTMS - p ESI Full ms [120.00-800.00]



160118-01ESIHR-Li-Yun Liu-LY-4_160118113450 #410-423 RT: 1.00-1.00 AV: 2 NL: 2.47E9
T: FTMS - p ESI Full ms [120.00-800.00]



160118-01ESIHR-Li-Yun Liu-LY-4_160118113450 #422-423 RT: 1.00-1.00 AV: 2

T: FTMS - p ESI Full ms [120.00-800.00]

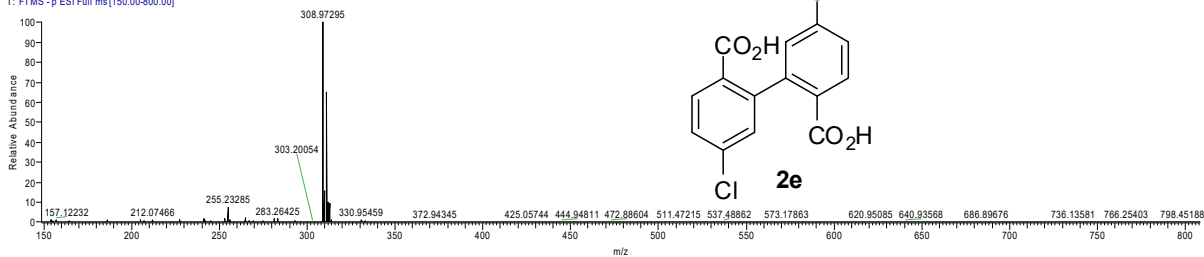
m/z = 269.06852-269.09483

m/z	Intensity	Relative Resolution	Charge	Theo. Mass	Delta (mmu)	RDB equiv.	Composition
269.08197	2503531008.0	100.00	33264.18	1.00	269.08193	0.15	10.5 C ₁₆ H ₁₃ O ₄

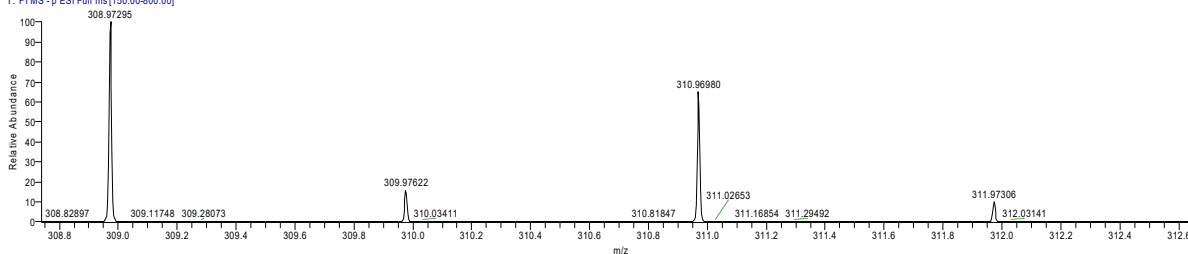
160121-17ESIHR-Li-Yun Liu-LY-1-Ly-5

1/21/2016 2:40:43 PM

160121-17ESIHR-Li-Yun Liu-LY-1-Ly-5 #361-371 RT: 0.86-0.88 AV: 11 NL: 7.59E8
T: FTMS - p ESI Full ms [150.00-800.00]



160121-17ESIHR-Li-Yun Liu-LY-1-Ly-5 #361-371 RT: 0.86-0.88 AV: 11 NL: 7.59E8
T: FTMS - p ESI Full ms [150.00-800.00]



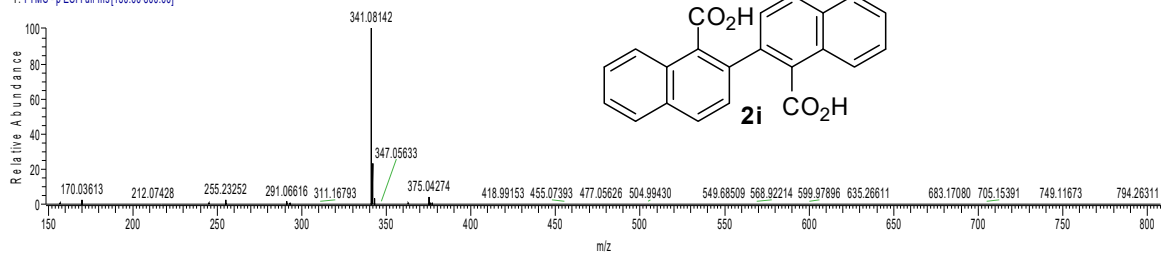
160121-17ESIHR-Li-Yun Liu-LY-1-Ly-5 #361-371 RT: 0.86-0.88 AV: 11

T: FTMS - p ESI Full ms [150.00-800.00]

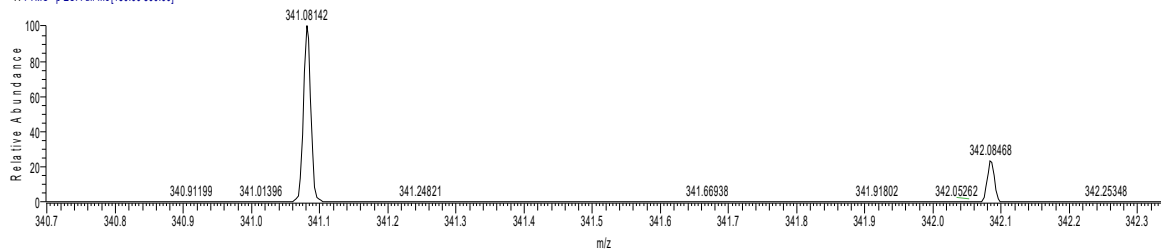
m/z = 308.95603-308.98552

m/z	Intensity	Relative Resolution	Charge	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
308.97295	776963520.0	100.00	30710.02	1.00	308.97269	0.84	10.5 C ₁₄ H ₇ O ₄ Cl ₂

160122-06ESIHR-Li-Yun Liu-LY-2 #351-362 RT: 0.82-0.84 AV: 12 NL: 8.84E8
T: FTMS - p ESI Full ms [150.00-800.00]

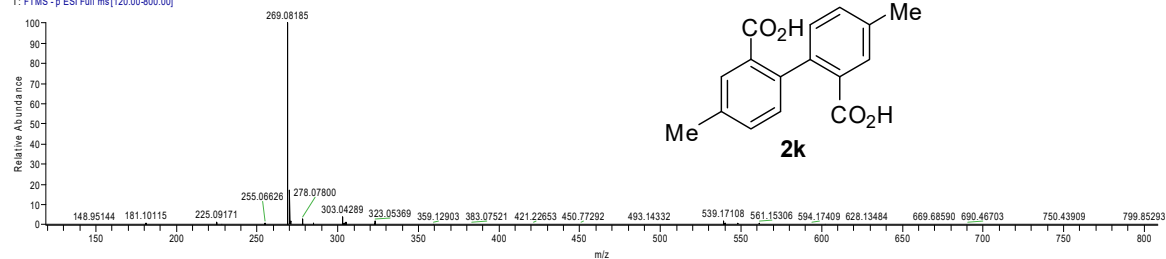


160122-06ESIHR-Li-Yun Liu-LY-2 #351-362 RT: 0.82-0.84 AV: 12 NL: 8.84E8
T: FTMS - p ESI Full ms [150.00-800.00]

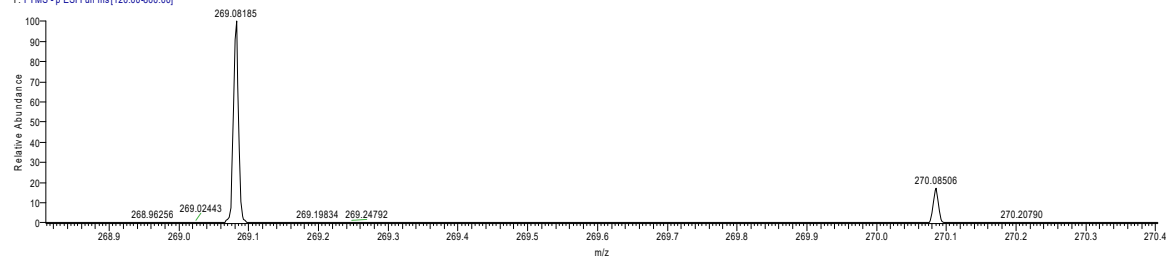


m/z	Intensity	Relative Resolution	Charge	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
341.08142	895902592.0	100.00	28556.94	1.00	341.08063	2.31	9.5 C ₁₇ H ₁₃ O ₃ F ₄

160118-01ESIHR-Li-Yun Liu-LY-4 #300-307 RT: 0.71-0.72 AV: 8 NL: 3.69E9
T: FTMS - p ESI Full ms [120.00-800.00]



160118-01ESIHR-Li-Yun Liu-LY-4 #300-307 RT: 0.71-0.72 AV: 8 NL: 3.69E9
T: FTMS - p ESI Full ms [120.00-800.00]



160118-01ESIHR-Li-Yun Liu-LY-4#300-307 RT: 0.71-0.72 AV: 8

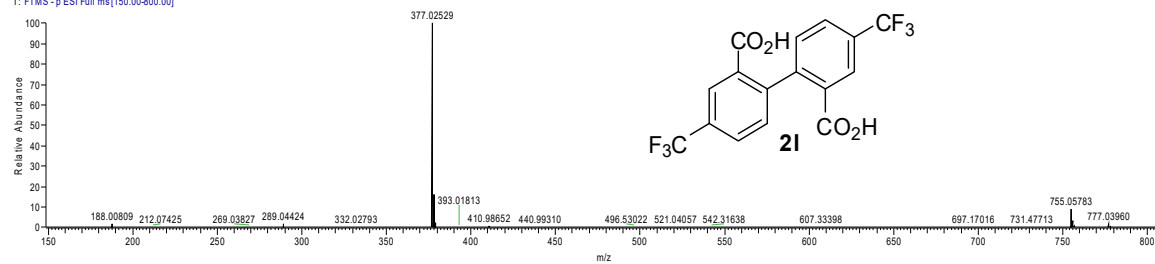
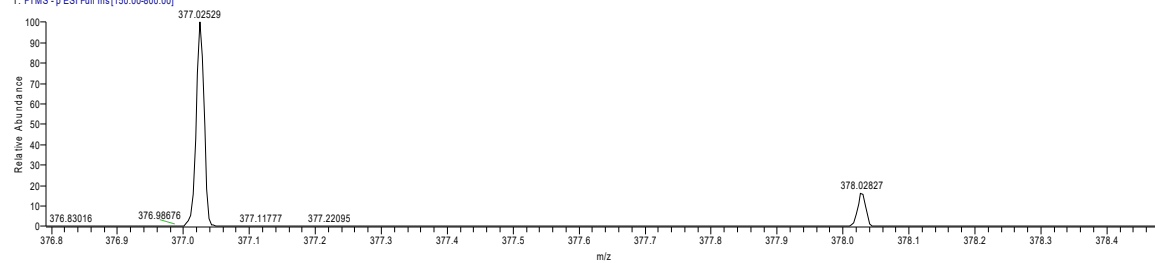
T: FTMS - p ESI Full ms [120.00-800.00]

m/z = 269.06782-269.09172

m/z	Intensity	Relative Resolution	Charge	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
269.08185	3747176704.0	100.00	33882.58	1.00	269.08193	-0.29	10.5 C ₁₆ H ₁₃ O ₄
					269.08221	-1.32	12.0 C ₁₇ H ₁₂ ONNa
					269.08086	3.67	12.5 C ₁₅ H ₁₀ N ₄ Na
					269.08059	4.70	11.0 C ₁₄ H ₁₁ O ₃ N ₃

160121-21ESIHR-Li-Yun Liu-LY-1-Ly-4

1/21/2016 3:25:04 PM

160121-21ESIHR-Li-Yun Liu-LY-1-Ly-4 #227-236 RT: 0.54-0.56 AV: 10 NL: 3.85E9
T: FTMS - p ESI Full ms [150.00-800.00]160121-21ESIHR-Li-Yun Liu-LY-1-Ly-4 #227-236 RT: 0.54-0.56 AV: 10 NL: 3.85E9
T: FTMS - p ESI Full ms [150.00-800.00]

160121-21ESIHR-Li-Yun Liu-LY-1-Ly-4#227-236 RT: 0.54-0.56 AV: 10

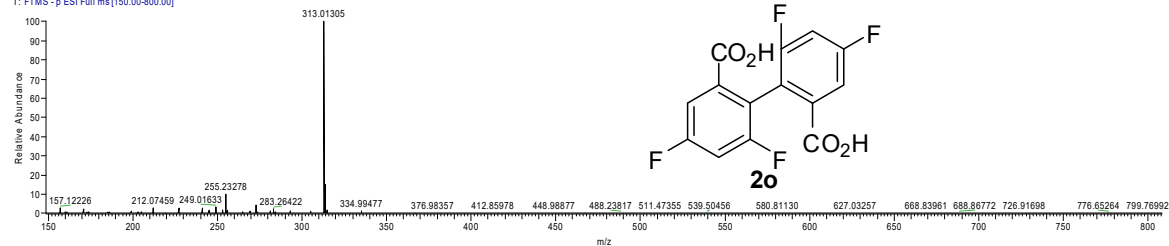
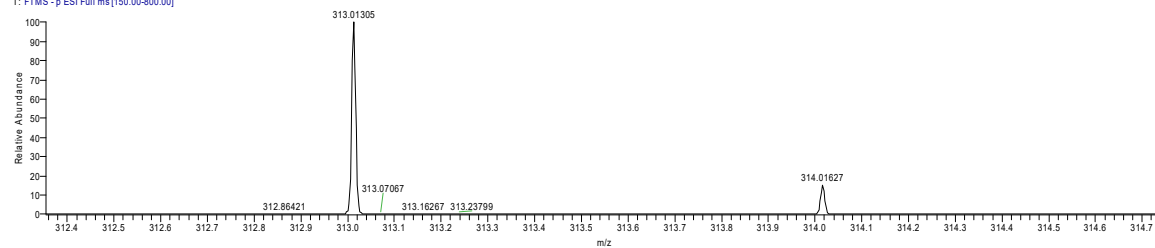
T: FTMS - p ESI Full ms [150.00-800.00]

m/z = 377.00906-377.04456

m/z	Intensity	Relative Resolution	Charge	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
377.02529	3856136960.0	100.00	28894.84	1.00	377.02540	-0.30	10.5 C ₁₆ H ₇ O ₄ F ₆
					377.02654	-3.33	6.5 C ₁₃ H ₆ O ₅ F ₇

160122-05ESIHR-Li-Yun Liu-LY-1

1/22/2016 12:56:44 PM

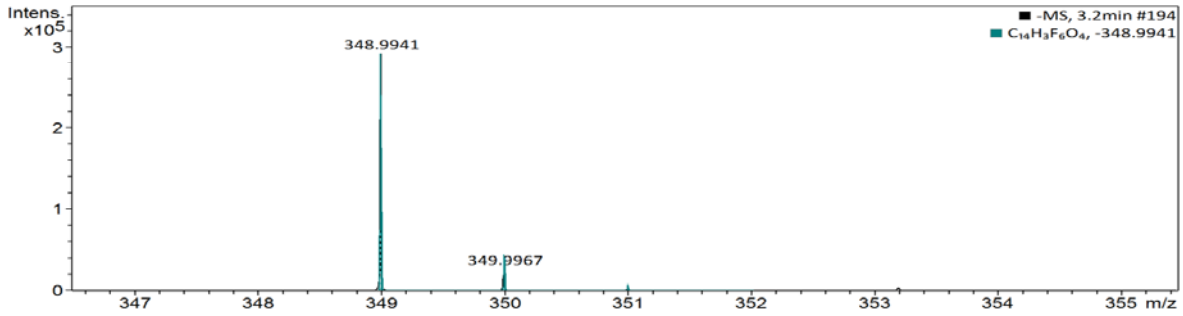
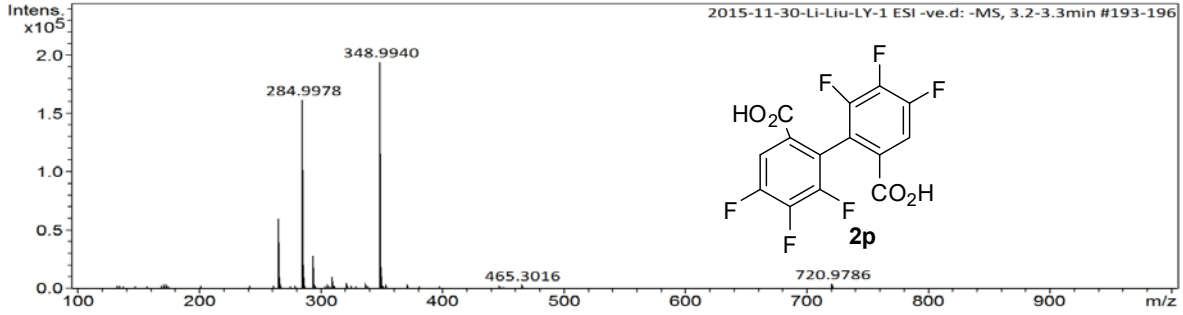
160122-05ESIHR-Li-Yun Liu-LY-1 #473-483 RT: 1.13-1.16 AV: 11 NL: 3.30E8
T: FTMS - p ESI Full ms [150.00-800.00]160122-05ESIHR-Li-Yun Liu-LY-1 #473-483 RT: 1.13-1.16 AV: 11 NL: 3.30E8
T: FTMS - p ESI Full ms [150.00-800.00]

160122-05ESIHR-Li-Yun Liu-LY-1#473-483 RT: 1.13-1.16 AV: 11

T: FTMS - p ESI Full ms [150.00-800.00]

m/z = 313.00044-313.02389

m/z	Intensity	Relative Resolution	Charge	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
313.01305	330436960.0	100.00	31511.27	1.00	313.01294	0.35	10.5 C ₁₄ H ₅ O ₄ F ₄
					313.01180	4.00	14.5 C ₁₇ H ₄ O ₃ F ₃

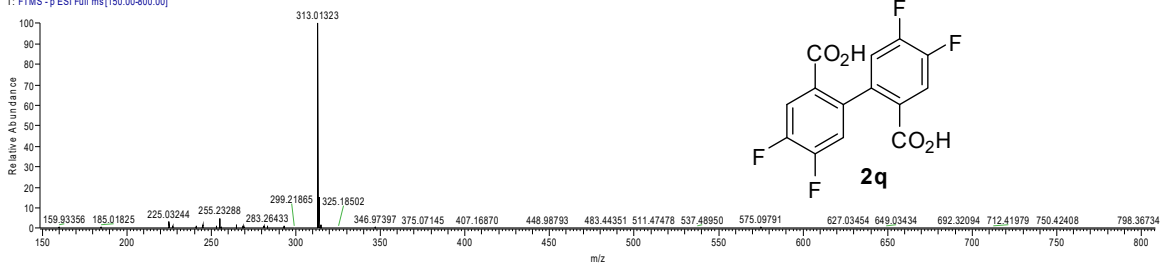


Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e ⁻ Conf	N-Rule
284.9978	1	C7H4F3N2O7	284.9976	-0.7	7.0	1	100.00	5.5	even	ok
	2	C5HN8O7	284.9974	-1.5	7.1	2	89.67	9.5	even	ok
	3	C13H2F5O2	284.9980	0.9	32.2	3	57.09	10.5	even	ok
	4	C21HO2	284.9982	1.4	82.9	4	9.96	21.5	even	ok
348.9941	1	C14H3F6O4	348.9941	0.1	38.4	1	100.00	10.5	even	ok

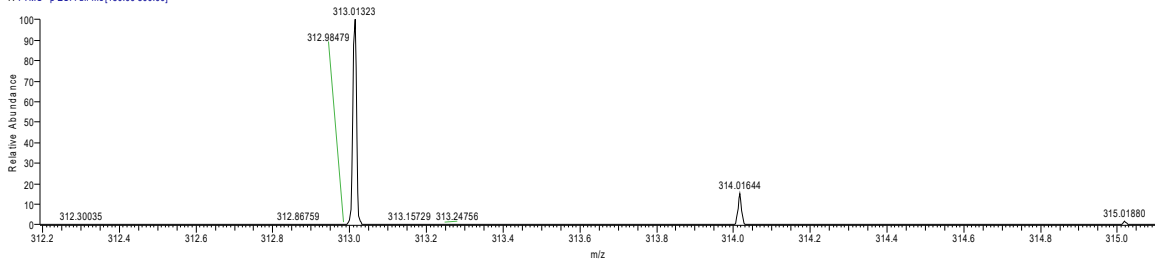
160121-18ESIHR-Li-Yun Liu-LY-1-Ly-1

1/21/2016 2:57:19 PM

160121-18ESIHR-Li-Yun Liu-LY-1-Ly-1 #305-317 RT: 0.72-0.75 AV: 13 SB: 11 0.80-0.82 NL: 3.10E8
T: FTMS - p ESI Full ms [150.00-800.00]



160121-18ESIHR-Li-Yun Liu-LY-1-Ly-1 #305-317 RT: 0.72-0.75 AV: 13 SB: 11 0.80-0.82 NL: 3.10E8
T: FTMS - p ESI Full ms [150.00-800.00]



160121-18ESIHR-Li-Yun Liu-LY-1-Ly-1 #305-317 RT: 0.72-0.75 AV: 13

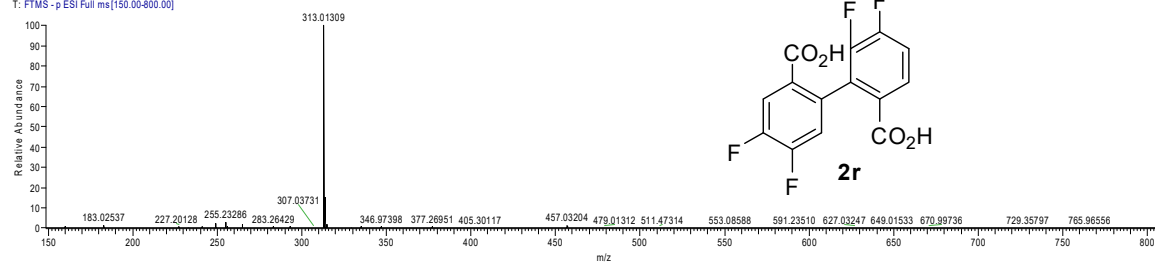
SB: 11 0.80-0.82

T: FTMS - p ESI Full ms [150.00-800.00]

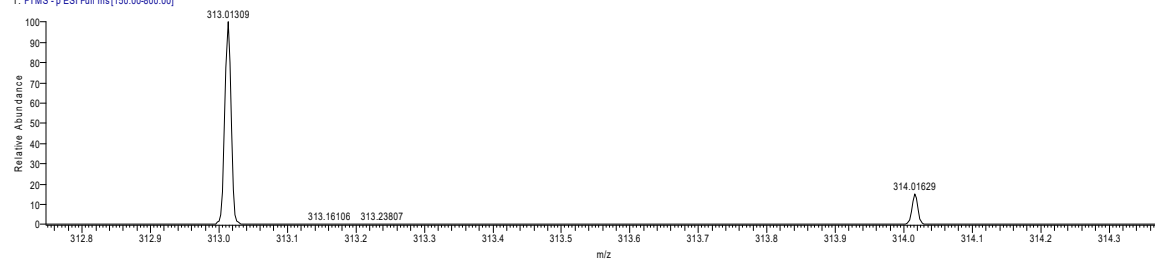
m/z = 312.99839-313.02889

m/z	Intensity	Relative	Resolution	Charge	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
313.01323	311698400.0	100.00	30122.56	1.00	313.01294	0.92	10.5	C ₁₄ H ₅ O ₄ F ₄

160121-19ESIHR-Li-Yun Liu-LY-1-Ly-2 #266-271 RT: 0.63-0.64 AV: 6 NL: 1.13E9
T: FTMS - p ESI Full ms [150.00-800.00]



160121-19ESIHR-Li-Yun Liu-LY-1-Ly-2 #266-271 RT: 0.63-0.64 AV: 6 NL: 1.13E9
T: FTMS - p ESI Full ms [150.00-800.00]



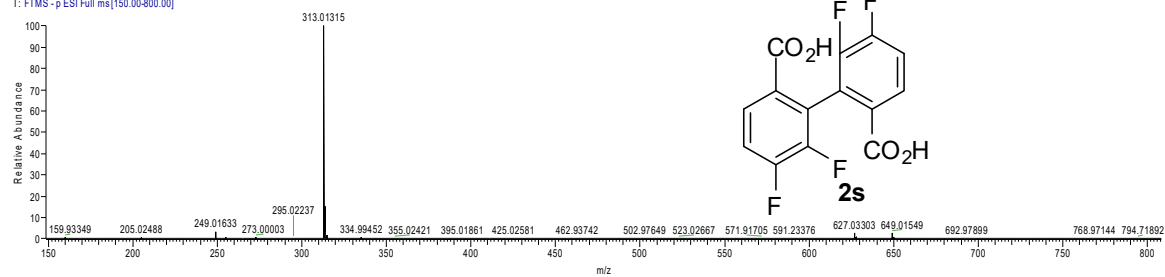
160121-19ESIHR-Li-Yun Liu-LY-1-Ly-2 #266-271 RT: 0.63-0.64 AV: 6

T: FTMS - p ESI Full ms [150.00-800.00]

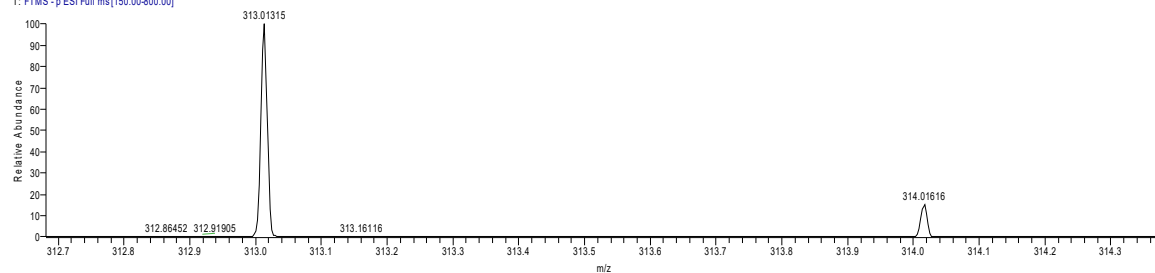
m/z = 312.99948-313.02146

m/z	Intensity	Relative	Resolution	Charge	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
313.01309	1135117440.0	100.00	31677.71	1.00	313.01294	0.46	10.5	C ₁₄ H ₅ O ₄ F ₄

160121-20ESIHR-Li-Yun Liu-LY-1-Ly-3 #334-341 RT: 0.79-0.80 AV: 8 NL: 3.22E9
T: FTMS - p ESI Full ms [150.00-800.00]



160121-20ESIHR-Li-Yun Liu-LY-1-Ly-3 #334-341 RT: 0.79-0.80 AV: 8 NL: 3.22E9
T: FTMS - p ESI Full ms [150.00-800.00]



160121-20ESIHR-Li-Yun Liu-LY-1-Ly-3 #334-341 RT: 0.79-0.80 AV: 8

T: FTMS - p ESI Full ms [150.00-800.00]

m/z = 312.99722-313.02900

m/z	Intensity	Relative	Resolution	Charge	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
313.01315	3245085184.0	100.00	30443.77	1.00	313.01294	0.64	10.5	C ₁₄ H ₅ O ₄ F ₄