supporting information for

Cross Dehydrogenative C–O Coupling Catalysed by a Catenane-Coordinated Copper(I)

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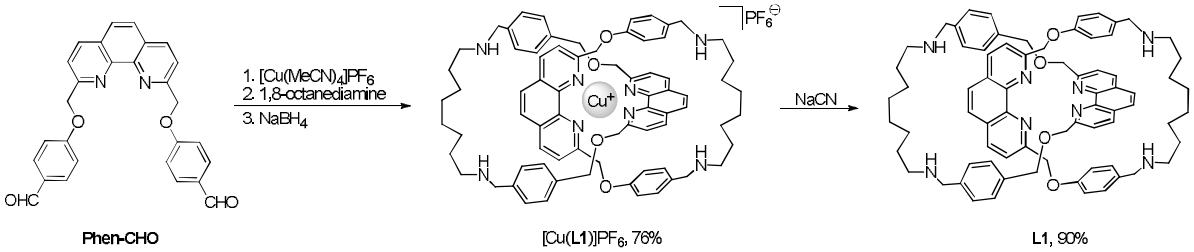
1. Synthesis of Catenane Ligands

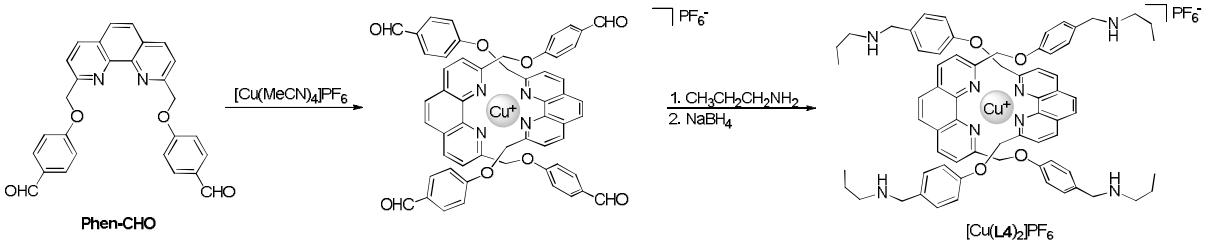
General: All reagents were purchased from commercial suppliers (Dkmchem, J & K, Aldrich and Energy) and used without further purification unless otherwise noted. All the solvents were of analytical grade (ACI Labscan and DUKSAN Pure Chemicals). MeCN were distilled over CaH_2 before use. Copper complexes [Cu(**L1**)]PF_6, [Cu(**L2**)]PF_6, [Cu(**L3**)]PF_6 and compound **3a'** were synthesised according to published procedures.[1,2] In the synthesis of **L1** in gram-scale, a MeCN/$CHCl_3$ mixture (v/v = 7:3) was further dried by activated 3Å molecular sieve. ESI-MS were carried out using a Waters-Acquity UPLC H-Class system coupled with a QDa MS detector. HRMS spectra were obtained from a Waters Micromass Q-ToF Premier quadrupole time-of-flight tandem mass spectrometer. NMR spectra were recorded on Bruker DPX spectrometers with working frequencies of 400 MHz or 500 MHz for ^1H, and 100 MHz or 125 MHz for ^{13}C, respectively. Chemical shifts are reported in ppm and referenced to solvent residues ($CDCl_3$: δ = 7.26 ppm for ^1H NMR and $CDCl_3$: δ = 77.16 ppm for ^{13}C NMR). Thin layer chromatography was performed on silica gel 60 F254 (Merck, Germany, Aluminium sheet) and column chromatography was carried out on silica gel 60F (Silicycle, Canada).



Scheme S1. Gram-scale synthesis of **L1**.

Gram-scale synthesis of L1. In a two-necked round bottom flask, a mixture of **Phen-CHO** (0.896 g, 2 mmol) and $[Cu(MeCN)_4]PF_6$ (372.7 mg, 1 mmol) in 200 mL of dried MeCN/$CHCl_3$ (v/v = 7:3) was stirred under argon for 30 min. After a clear red solution was obtained, 1,8-octanediamine (316.8 mg, 2.2 mmol) and piperidine (0.5 mL) were added. The reaction mixture was stirred for 4 hours and an additional amount of 1,8-octanediamine (72 mg, 0.5 mmol) was added. The reaction mixture was heated at 60°C for another 4 hours and the reaction progress was monitored by UPLC-MS. After the reaction has been completed, the reaction mixture was slowly cooled to 0°C in an ice bath. $NaBH_4$ (60 mg, 1.59 mmol) was added in 3 portions at a 10-min interval. MeOH (5 mL) was added and the reaction mixture was stirred at 0°C for 30 minutes. The resulting mixture was washed with saturated aq. $NaHCO_3$ (3 x 100 mL), water (100 mL) and brine (100 mL), and solvents were evaporated. The residue was re-dissolved in CH_2Cl_2 (50 mL), filtered through a Celite pad and concentrated. Ethyl acetate (50 mL) was added and the dark red suspension was stirred at room temperature for 30 min and filtered. The filtered solid was washed with Et_2O (200 mL) and dried under vacuum to afford [Cu(**L1**)]PF_6 as a brick-red powder. Yield = 1.01 g, 76%. ^1H NMR (400 MHz, 298 K, $CDCl_3$) δ 8.33 (d, *J* = 8.2 Hz, 4H), 7.84 (d, *J* = 8.2 Hz, 4H), 7.74 (s, 4H), 6.51 (d, *J* = 8.5 Hz, 8H), 5.88 (d, *J* = 8.5 Hz, 8H), 4.88 (s, 8H), 3.43 (s, 8H), 2.58 (t, *J* = 6.1 Hz, 8H), 1.53 (s, 24H). $^{13}C\{^1H\}$ NMR (101 MHz, 298 K, d_6-DMSO) δ 156.2, 154.4, 143.0, 138.0, 133.2, 128.7, 128.3, 126.7, 125.9, 112.7, 70.9, 52.8, 49.3, 30.4, 29.4, 27.1.

To extract the copper ion, [Cu(**L1**)]PF_6 (133 mg, 0.1 mmol) was dissolved in 2 mL MeCN and an aqueous solution of NaCN (100 mg, 2 mmol, 10 mL) was added (CAUTION! Special attention was paid during the handling of the highly toxic NaCN). The mixture was stirred for 2 hours and organic components were extracted by 10 mL $CHCl_3$. The organic phase was collected and solvents were evaporated. The residue was re-dissolved in 5 mL MeCN and 10 mg of tetrabutylammonium chloride was added. The mixture was stirred for 1 hour and the white precipitate was collected and washed with H_2O (10 mL) and Et_2O (10 mL) to afford **L1**. Yield = 100 mg, 90%. ^{1}H NMR (400 MHz, 298 K, d_6-DMSO) δ 8.52 (d, *J* = 8.2 Hz, 4H), 8.00 (s, 4H), 7.87 (d, *J* = 8.2 Hz, 4H), 6.92 (d, *J* = 8.5 Hz, 8H), 6.74 (d, *J* = 8.6 Hz, 8H), 5.30 (s, 8H), 3.41 (s, 8H), 2.06 (t, *J* = 7.6 Hz, 8H), 1.09 (s, 8H), 0.86 (s, 16H). ^{13}C{^{1}H} NMR (126 MHz, d_6-DMSO) δ 157.6, 157.4, 145.3, 137.6, 133.7, 129.3, 128.4, 126.9, 122.7, 114.9, 72.7, 52.8, 48.5, 30.6, 29.7, 27.2.



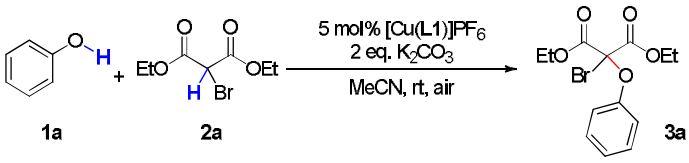
Scheme S2. Synthesis of [Cu(**L4**)$_2$]PF_6.

Synthesis of [Cu(L4)$_2$]PF$_6$. In a two-necked round bottom flask, a mixture of **Phen-CHO** (0.896 g, 2 mmol) and [Cu(MeCN)$_4$]PF_6 (372.7 mg, 1 mmol) in 200 mL of dried MeOH/MeCN/$CHCl_3$ (v/v = 2:3:5) was stirred under argon for 30 min. After a clear red solution was obtained, n-propylamine (590 mg, 10 mmol) and piperidine (0.5 mL) were added. The reaction mixture was heated at 60^{o}C for overnight and the reaction progress was monitored by UPLC-MS. After the reaction is completed, the reaction mixture was slowly cooled to 0^{o}C in an ice bath and $NaBH_4$ (190 mg, 5 mmol) was added. The reaction mixture is stirred at 0^{o}C for another 30 minutes. The resulting mixture was washed with saturated aq. $NaHCO_3$ (100 mL), water (100 mL) and brine (100 mL) and solvents were evaporated. The solid residue was recrystallized in MeCN and Et_2O to afford [Cu(**L4**)$_2$]PF_6 as a brick-red powder. Yield = 0.72 g, 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 8.2 Hz, 1H), 7.97 (t, *J* = 4.0 Hz, 2H), 6.80 (d, *J* = 7.8 Hz, 2H), 6.13 (d, *J* = 7.9 Hz, 2H), 4.93 (s, 2H), 3.57 (s, 2H), 2.54 (s, 2H), 1.65–1.43 (m, 2H), 0.92 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 156.3, 155.6, 142.9, 137.9, 129.1, 128.9, 126.8, 124.8, 113.4, 70.8, 53.1, 51.3, 23.0, 11.8. HRMS (ESI$^+$) calcd. for $C_{68}H_{76}CuN_8O_4$ [M]$^+$(*m/z*): 1131.5280, found: 1131.5271.

2. Screening of the CDC

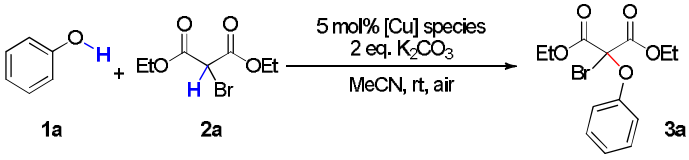
Screw-cap vials (10 mm inner diameter) and Synthware® Schlenk tubes were used to run the reactions under air and argon respectively. For a typical reaction, **1a** (0.1 mmol), **2a** (0.22 mmol), [Cu(**L1**)]PF_6 (5 mol%) and K_2CO_3 (0.2 mmol) in 0.5 mL MeCN was stirred in air for 24 hours unless otherwise stated. Yield of the coupling product was determined by ^1H NMR using the phenol resonance with 1,3,5-trimethoxybenzene as the internal standard. Thin layer chromatography (TLC) was performed on silica gel 60 F254 (Merck, Germany, Aluminium sheet) and column chromatography was carried out on silica gel 60F (Silicycle, Canada). Infrared Spectroscopy was conducted on PerkinElmer FT-IR Spectrometer Spectrum Two. ESI-MS were carried out using a Waters-Acquity UPLC H-Class system coupled with a QDa MS detector. HRMS spectra were obtained from a Waters Micromass Q-ToF Premier quadrupole time-of-flight tandem mass spectrometer. NMR spectra were recorded on Bruker DPX spectrometers with working frequencies of 400 MHz or 500 MHz for ^1H, and 100 MHz or 125 MHz for ^{13}C, respectively. Chemical shifts are reported in ppm and referenced to solvent residues.

Table S1. Effects of reaction conditions



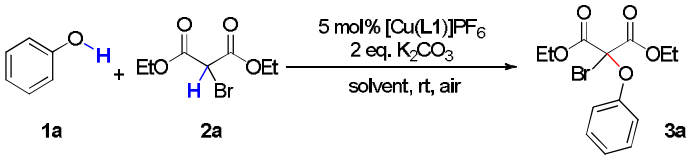
Entry	Condition Variations	Yield (%)
1	None	80
2	No [Cu(**L1**)]PF_6	12
3	No K_2CO_3	28
4	No K_2CO_3 with 2 eq. $PhCO_2H$	18
5	Under argon	77
6	Under oxygen	72
7	Shielded from light	78
8	No solvent	31

Table S2. Effects of copper catalyst



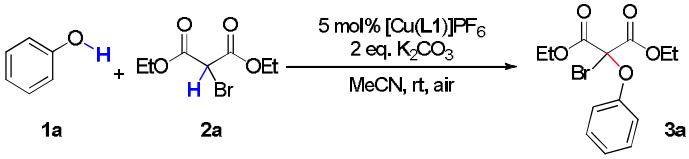
Entry	Copper	Yield (%)
1	[Cu(**L1**)]PF_6	80
2	$[Cu(MeCN)_4]PF_6$	44
3	[Cu(**L4**)$_2$]PF_6	42
4	CuBr	30
5	$Cu(OAc)_2$	41
6	$CuCl_2$	trace
7	$CuSO_4$	40
8	CuBr + 1 eq. **L4**	52
9	CuBr + 2 eq. **L4**	40

Table S3. Effects of solvent



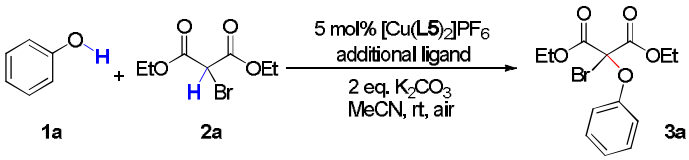
Entry	Solvent	Concentration	Yield (%)
1	MeCN	0.2 M	80
2	MeCN	0.1 M	79
3	MeCN	0.5 M	80
4	CH_2Cl_2	0.2 M	55
5	$CHCl_3$	0.2 M	48
6	THF	0.2 M	46
7	MeOH	0.2 M	complex mixture
8	EtOAc	0.2 M	71
9	Toluene	0.2 M	67
10	DMF	0.2 M	36
11	Et_2O	0.2 M	31
12	DMSO	0.2 M	complex mixture
13	H_2O	0.2 M	complex mixture

Table S4. Effects of equivalence of **2a**



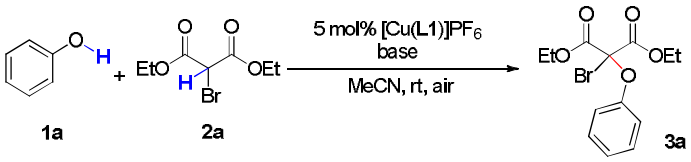
Entry	**2a**	Yield (%)
1	2.2 eq.	80
2	3 eq.	80
3	4 eq.	81
4	1.5 eq.	60
5	1.5 eq. under O_2	55

Table S5. Effects of additional ligand



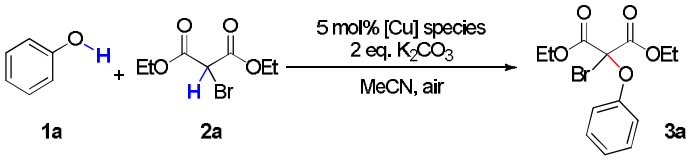
Entry	Additonal ligand	Yield (%)
1	None	46
2	2 mol% **L5**	51
3	10 mol% **L5**	50

Table S6. Effects of base



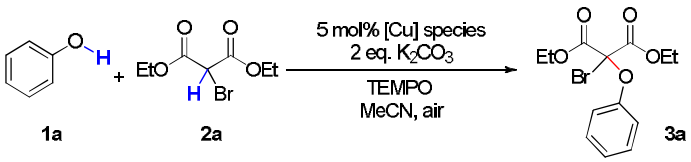
Entry	Base	Yield (%)
1	2 eq. K_2CO_3	80
2	4 eq. $NaHCO_3$	no reaction
3	2 eq. KOH	12
4	2 eq. NaOH	36
5	2 eq. Cs_2CO_3	56
6	2 eq. Et_3N	<10
7	4 eq. Et_3N	<10
8	3 eq. K_2CO_3	80
9	1 eq. K_2CO_3	68

Table S7. Effect of temperature



Entry	Copper complex	temp	Yield (%)
1	[Cu(**L1**)]PF_6	room temp	80
2	[Cu(**L1**)]PF_6	50°C	90
3	[Cu(**L1**)]PF_6	80°C	70
4	[Cu(**L1**)]PF_6	0 C	42
5	[Cu(MeCN)$_4$]PF_6	room temp	44
6	[Cu(MeCN)$_4$]PF_6	50°C	65
7	[Cu(MeCN)$_4$]PF_6	80°C	complex mixture
8	[Cu(MeCN)$_4$]PF_6	0°C	<10

Table S8. Effects of radical scavenger

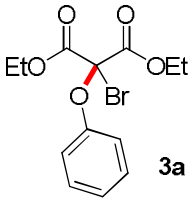


Entry	Copper complex	TEMPO	Yield (%)
1	[Cu(**L1**)]PF_6	0	80
2	[Cu(**L1**)]PF_6	0.5 eq.	55
3	[Cu(**L1**)]PF_6	1 eq.	26
4	[Cu(**L4**)]PF_6	0	42
5	[Cu(**L4**)]PF_6	0.5 eq.	60
6	[Cu(**L4**)]PF_6	1 eq.	70

General procedure for Cu-centered catenane catalysed CDC reaction:

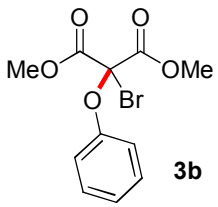
To a screw-cap vial (inner diameter = 10 mm) was added bromomalonate (2.2 equiv, 0.22 mmol), [Cu(**L1**)]PF_6 (1.33 mg, 0.001 mmol), K_2CO_3 (27,6 mg, 0.2 mmol) and 0.5 mL MeCN. The mixture was slightly stirred for 5 minutes and phenol (0.1 mmol) was added. The reaction tube was sealed carefully and heated to 50°C for 24 hours. After completion of the reaction, the mixture was concentrated in *vacuo* and purified by flash column chromatography or preparative TLC.

Characterization of new compounds:



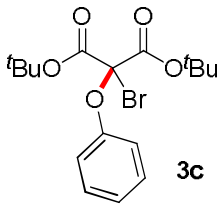
3a

Colorless oil. Yield = 90%. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.37–7.30 (m, 2H), 7.25–7.20 (m, 2H), 7.19–7.13 (m, 1H), 4.35 (dt, *J* = 7.1, 5.4 Hz, 4H), 1.27 (t, *J* = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$) δ 163.4, 153.5, 129.5, 124.7, 124.5, 118.9, 118.2, 88.1, 63.9, 13.7. IR (cm^{-1}): 2982, 2924, 1760, 1741, 1488, 1445, 1264, 1221, 1128, 1047, 912, 858, 753, 665. HRMS (EI$^+$) calcd. for $C_{13}H_{15}BrO_5$ [M]$^+$(*m/z*): 330.0103, found: 330.0099.



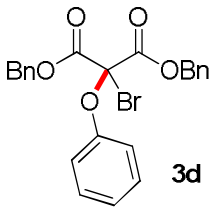
3b

Colorless oil. Yield = 91%. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.40–7.29 (m, 1H), 7.22–7.10 (m, 1H), 3.89 (d, *J* = 3.0 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$) δ 164.0, 153.3, 129.6, 124.8, 124.7, 118.9, 118.2, 87.3, 54.5, 54.4. IR (cm^{-1}): 2956, 1762, 1744, 1591, 1487, 1434, 1274, 1229, 1205, 1052, 982, 865, 753, 668. HRMS (EI$^+$) calcd. for $C_{11}H_{11}BrO_5$ [M]$^+$(*m/z*): 301.9790, found: 301.9795.



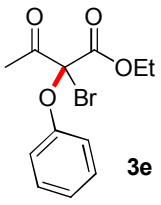
3c

Colorless oil. Yield = 90%. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.36–7.30 (m, 2H), 7.29–7.25 (m, 2H), 7.18–7.10 (m, 1H), 1.45 (s, 18H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$) δ 162.0, 153.9, 129.3, 124.2, 118.3, 84.9, 27.5. IR (cm^{-1}): 2979, 2933, 1757, 1737, 1492, 1369, 1242, 1144, 1128, 912, 843, 808, 689, 647. HRMS (EI$^+$) calcd. for $C_{17}H_{23}BrO_5$ [M]$^+$(*m/z*): 386.0729, found: 386.0730.



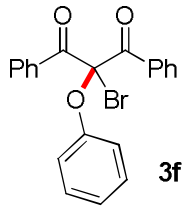
3d

Colorless oil. Yield = 85%. ^{1}H NMR (400 MHz, 298 K, CD_3CN) δ 7.42–7.33 (m, 9H), 7.29 (dd, *J* = 6.4, 3.2 Hz, 3H), 7.23 (dd, *J* = 10.6, 4.2 Hz, 1H), 7.12–7.07 (m, 2H), 5.27 (s, 4H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$) δ 163.1, 134.4, 129.9, 128.8, 128.6, 128.6, 128.5, 124.9, 118.1, 87.6, 69.5, 68.5. IR (cm^{-1}): 3033, 2922, 1757, 1739, 1495, 1455, 1265, 1214, 1132, 1001, 747, 695, 595. HRMS (EI$^+$) calcd. for $C_{23}H_{19}BrO_5$ [M]$^+$(*m/z*): 454.0416, found: 454.0424.



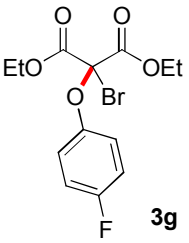
3e

Colorless oil. Yield = 81%. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.40–7.31 (m, 2H), 7.17 (ddd, *J* = 4.6, 2.8, 0.8 Hz, 3H), 4.29 (tdd, *J* = 7.2, 4.6, 2.7 Hz, 2H), 2.55 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$) δ 195.3, 153.2, 129.1, 124.4, 118.1, 117.7, 63.9, 23.6, 13.7. IR (cm^{-1}): 2923, 1764, 1734, 1590, 1488, 1253, 1195, 1118, 895, 753, 689. HRMS (EI$^+$) calcd. for $C_{12}H_{13}BrO_4$ [M]$^+$(*m/z*): 299.9997, found: 300.0003.



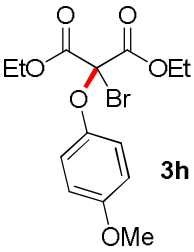
3f

Yellowish oil. Yield = 83%. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 8.16–8.11 (m, 4H), 7.64–7.56 (m, 2H), 7.45 (dd, *J* = 10.8, 4.8 Hz, 4H), 7.23 (ddd, *J* = 7.5, 5.8, 2.2 Hz, 2H), 7.16–7.11 (m, 2H), 7.06 (t, *J* = 7.3 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$) δ 188.6, 152.8, 134.0, 131.9, 130.7, 129.7, 128.6, 124.3, 117.9, 101.5. IR (cm^{-1}): 3062, 2923, 2852, 1708, 1676, 1594, 1490, 1447, 1230, 1200, 1183, 974, 796, 685, 634, 549. HRMS (EI^+) calcd. for $C_{21}H_{15}BrO_3$ $[M]^+$(*m/z*): 394.0205, found: 394.0221.



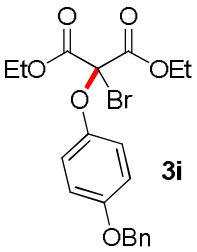
3g

Colorless oil. Yield = 86%. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.23–7.14 (m, 2H), 7.12–6.95 (m, 2H), 4.35 (dt, *J* = 7.1, 5.6 Hz, 4H), 1.29 (t, *J* = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$) δ 163.2, 120.3, 120.2, 116.2, 115.9, 64.0, 63.9, 29.7, 13.8, 13.8. IR (cm^{-1}): 2921, 2851, 1760, 1743, 1502, 1264, 1217, 1196, 1099, 1048, 1011, 833, 661. HRMS (EI^+) calcd. for $C_{13}H_{14}BrFO_5$ $[M]^+$(*m/z*): 348.0009, found: 348.0017.



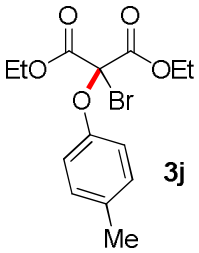
3h

Colorless oil. Yield = 92%. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.21–7.09 (m, 2H), 6.89–6.77 (m, 2H), 4.34 (q, *J* = 7.1 Hz, 4H), 3.79 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$) δ 163.5, 156.7, 147.2, 120.1, 114.4, 89.6, 63.9, 55.6, 13.8. IR (cm^{-1}): 2982, 2838, 1759, 1741, 1504, 1220, 1197, 1108, 1015, 828, 658, 568. HRMS (EI^+) calcd. for $C_{14}H_{17}BrO_6$ $[M]^+$(*m/z*): 360.0209, found: 360.0201.



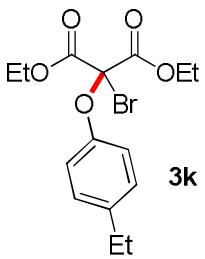
3i

Colorless oil. Yield = 81% yield. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.50–7.32 (m, 5H), 7.21–7.12 (m, 2H), 7.03–6.86 (m, 2H), 5.04 (s, 2H), 4.35 (q, *J* = 7.1 Hz, 4H), 1.29 (dd, *J* = 9.1, 5.1 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$) δ 163.5, 155.9, 147.4, 136.7, 128.6, 128.1, 127.5, 120.1, 115.4, 89.5, 70.4, 63.9, 13.8. IR (cm^{-1}): 2982, 2924, 1759, 1740, 1502, 1220, 1192, 1108, 1047, 1010, 911, 826, 740, 697. HRMS (EI^+) calcd. for $C_{20}H_{21}BrO_6$ $[M]^+$(*m/z*): 436.0522, found: 436.0510.



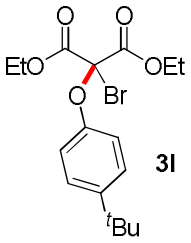
3j

Colorless oil. Yield = 96%. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.20–7.05 (m, 4H), 4.35 (dd, *J* = 14.3, 7.2 Hz, 4H), 2.32 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$) δ 163.5, 151.3, 134.3, 129.9, 118.3, 88.6, 63.9, 20.7, 13.8. IR (cm^{-1}): 2982, 2923, 1760, 1741, 1506, 1262, 1221, 1129, 1047, 1015, 911, 815, 659, 640. HRMS (EI^+) calcd. for $C_{14}H_{17}BrO_5$ $[M]^+$(*m/z*): 344.0259, found: 344.0262.



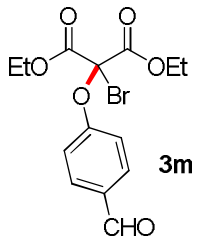
3k

Colorless oil. Yield = 94%. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.19–7.09 (m, 4H), 4.35 (q, *J* = 7.1 Hz, 4H), 2.63 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 6H), 1.23 (t, *J* = 7.6 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$) δ 163.5, 151.4, 140.6, 128.7, 119.0, 118.3, 63.9, 28.1, 15.5, 13.7. IR (cm^{-1}): 2961, 2923, 1761, 1742, 1507, 1263, 1222, 1129, 1049, 1015, 912, 831, 659. HRMS (EI^+) calcd. for $C_{15}H_{19}BrO_5$ $[M]^+$(*m/z*): 358.0416, found: 358.0406.



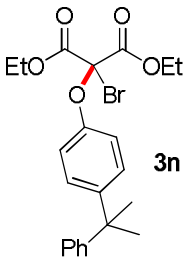
3l

Colorless oil. Yield = 88%. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.39–7.30 (m, 2H), 7.24–7.06 (m, 2H), 4.34 (dd, *J* = 11.2, 4.0 Hz, 4H), 1.31 (s, 9H), 1.27 (t, *J* = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$) δ 163.5, 151.2, 147.5, 126.3, 117.8, 88.5, 63.9, 34.4, 31.4, 13.7. IR (cm^{-1}): 2962, 1761, 1742, 1509, 1297, 1264, 1225, 1187, 1103, 1048, 1014, 913, 832, 672. HRMS (EI^{+}) calcd. for $C_{17}H_{23}BrO_5$ [M]$^{+}$(*m/z*): 386.0729, found: 386.0740.



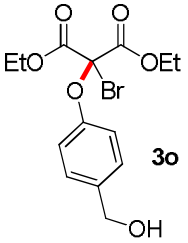
3m

Colorless oil. Yield = 78%. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 9.98 (s, 1H), 7.90 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 8.8 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 4H), 1.29 (t, *J* = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$) δ 190.7, 163.0, 157.9, 132.5, 131.5, 118.2, 86.1, 64.3, 29.7, 13.7. IR (cm^{-1}): 2924, 2852, 1760, 1744, 1698, 1599, 1504, 1264, 1225, 1163, 1110, 1046, 852, 831, 664. HRMS (EI^{+}) calcd. for $C_{15}H_{15}BrO_6$ [M]$^{+}$(*m/z*): 358.0052, found: 358.0039.



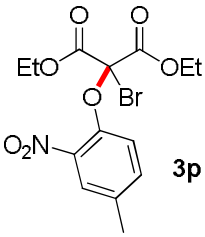
3n

Colorless oil. Yield = 80%. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.28 (dd, *J* = 10.5, 4.4 Hz, 1H), 7.23–7.18 (m, 1H), 7.15–7.07 (m, 1H), 4.39–4.27 (m, 2H), 1.68 (s, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$) δ 163.5, 151.4, 150.3, 147.0, 128.0, 127.8, 126.7, 125.7, 117.7, 88.4, 63.9, 42.6, 30.8, 13.7. IR (cm^{-1}): 2969, 2932, 1761, 1742, 1504, 1262, 1223, 1186, 1132, 1048, 913, 832, 764, 700. HRMS (EI^{+}) calcd. for $C_{22}H_{25}BrO_5$ [M]$^{+}$(*m/z*): 448.0885, found: 448.0901.



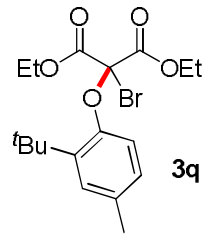
3o

Colorless oil. Yield = 85%. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.34 (dd, *J* = 8.0, 5.4 Hz, 2H), 7.25–7.15 (m, 2H), 4.68 (s, 2H), 4.43–4.29 (m, 4H), 1.29 (t, *J* = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$) δ 163.4, 152.9, 137.1, 128.2, 118.4, 87.9, 64.7, 64.0, 29.7, 13.8. IR (cm^{-1}): 3302, 2923, 1759, 1506, 1266, 1224, 1128, 1048, 1012, 914, 818, 662. HRMS (EI^{+}) calcd. for $C_{14}H_{17}BrO_6$ [M]$^{+}$(*m/z*): 360.0209, found: 360.0201.



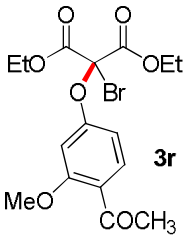
3p

Colorless oil. Yield = 90%. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.86 (d, *J* = 2.6 Hz, 1H), 7.39 (dd, *J* = 8.5, 2.7 Hz, 1H), 7.33 (d, *J* = 8.6 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 4H), 2.58 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$) δ 163.0, 151.6, 149.1, 133.6, 129.8, 123.4, 115.1, 86.9, 64.4, 19.9, 13.8. IR (cm^{-1}): 2983, 2923, 1760, 1743, 1529, 1264, 1229, 1125, 1048, 1013, 911, 811, 731. HRMS (EI^{+}) calcd. for $C_{14}H_{16}BrNO_7$ [M]$^{+}$(*m/z*): 389.0110, found: 389.0101.

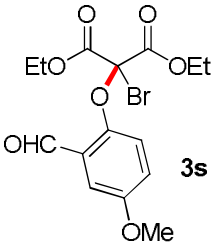


3q

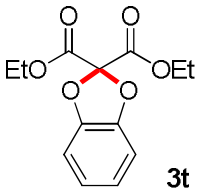
Colorless oil. Yield = 72%. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.17 (d, *J* = 1.9 Hz, 1H), 7.09 (d, *J* = 8.3 Hz, 1H), 6.96 (dd, *J* = 8.4, 1.6 Hz, 1H), 4.41–4.23 (m, 4H), 2.31 (s, 3H), 1.45 (s, 9H), 1.26 (t, *J* = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$) δ 163.7, 150.0, 139.5, 132.7, 128.4, 126.8, 114.4, 87.3, 63.9, 34.7, 29.8, 29.7, 20.9, 13.7. IR (cm^{-1}): 2983, 2922, 2869, 1763, 1744, 1494, 1262, 1222, 1134, 1048, 918, 810, 661. HRMS (EI^{+}) calcd. for $C_{18}H_{25}BrO_5$ [M]$^{+}$(*m/z*): 400.0885, found: 400.0896.



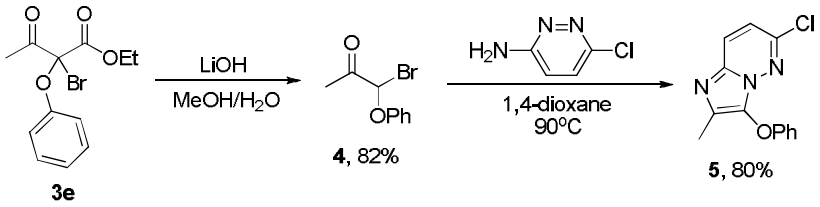
Colorless oil. Yield = 92%. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.57 (d, *J* = 1.9 Hz, 1H), 7.51 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.27 (d, *J* = 8.3 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 4H), 3.93 (s, 3H), 2.58 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$) δ 196.8, 163.2, 150.6, 146.8, 133.8, 121.8, 116.7, 111.6, 86.7, 64.2, 56.3, 26.4, 13.7. IR (cm^{-1}): 2982, 2937, 1759, 1742, 1681, 1593, 1504, 1413, 1266, 1217, 1174, 1151, 1029, 914, 856, 661. HRMS (EI^{+}) calcd. for $C_{16}H_{19}BrO_7$ [M]$^{+}$(*m/z*): 402.0314, found: 402.0325.



Colorless oil. Yield = 88%. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 9.92 (s, 1H), 7.48 (d, *J* = 1.8 Hz, 1H), 7.43 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 4H), 3.95 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$) δ 190.9, 163.1, 151.1, 147.7, 133.1, 124.8, 117.0, 110.6, 86.4, 64.3, 56.3, 13.7. IR (cm^{-1}): 2982, 2923, 2851, 1760, 1689, 1593, 1502, 1464, 1263, 1225, 1136, 1030, 914, 859, 734. HRMS (EI^{+}) calcd. for $C_{15}H_{17}BrO_7$ [M]$^{+}$(*m/z*): 388.0158, found: 388.0166.



Yellowish oil. Yield = 75%. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.00–6.87 (m, 4H), 4.39 (q, J = 7.1 Hz, 4H), 1.36 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, 298 K, $CDCl_3$) δ 163.6, 145.9, 122.7, 109.3, 105.2, 63.3, 13.9. IR (cm^{-1}): 2984, 2923, 1761, 1481, 1370, 1310, 1224, 1126, 1050, 854, 802, 738. HRMS (EI^{+}) calcd. for $C_{13}H_{14}O_6$ [M]$^{+}$(*m/z*): 266.0790, found: 266.0793.



Scheme S3. Conversion of **3e** to a functionalizable chloroimidazo[1,2-*b*]pyridazine.

Conversion of 3e to 5. To a solution of **3e** (300 mg, 1 mmol) in MeOH (20 mL) and H_2O (10 mL) under argon was added LiOH (48 mg, 2 mmol) at 0 °C. The reaction was stirred at room temperature for 72 hours. After the reaction is completed, CH_2Cl_2 (30 mL) was added. The organic phase was separated, washed with brine and dried over through Na_2SO_4. The solvents were evaporated to give **4** (187 mg, 82%) as a yellowish oil, which could be used directly in next step without further purification. To a solution of **4** (187 mg, 0.82 mmol) in 1,4-dioxane (10 mL) was added 3-amino-6-chloropyridazine (106 mg, 0.82 mmol). The reaction mixture was stirred at 95 °C for 7 hours. After cooling, the reaction mixture was diluted with ethyl acetate (30 mL) and washed with saturated $NaHCO_3$ solution. The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The crude solid was purified by column chromatography to give **5** (170 mg, 80%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 9.4 Hz, 1H), 7.32 (dd, *J* = 8.6, 7.5 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.99 (d, *J* = 9.4 Hz, 1H), 6.93 (d, *J* = 7.9 Hz, 2H), 2.38 (s, 3H). The ^{1}H NMR spectrum was checked with a previously report spectrum and is consistent.[3]

3. ESI-MS Analysis of the Reaction Mixture

For the reaction between **1a** and **2a** catalyzed by [Cu(**L1**)]PF_6, the mixture was analyzed by FIA-ESI-MS using a Waters-Acquity UPLC H-Class system coupled with a QDa MS detector. The ESI-MS (+ve) spectrum showed peaks at *m/z* = 395.3, *m/z* = 592.1 and *m/z* = 1184.1, which are assigned to $[Cu(\mathbf{L1})+2H]^{3+}$, $[Cu(\mathbf{L1})+H]^{2+}$ and $[Cu(\mathbf{L1})]^{+}$ (Figure S1), showing that the catenane copper complex as the only detectable copper-containing species in the system.

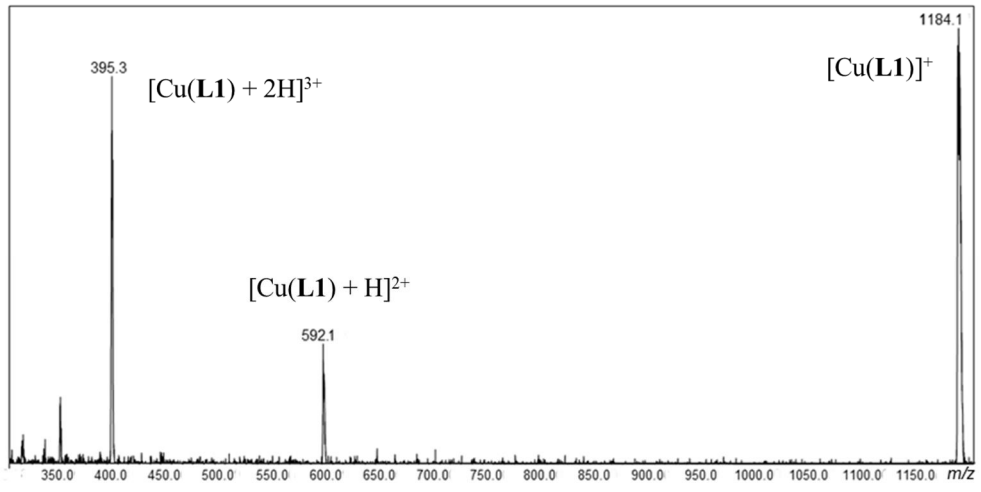


Figure S1.

To analyse the possible formation of copper-TEMPO complex with [Cu(**L1**)]PF_6, a 20 mM solution of [Cu(**L1**)]PF_6 in the presence of 50 eq. TEMPO in CD_3CN was analysed by FIA-ESI-MS. No copper-TEMPO complex was identified and only peaks due to $[Cu(\mathbf{L1})]^{+}$ (*m/z* = 1183.9), $[Cu(\mathbf{L1})+H]^{2+}$ (*m/z* = 592.3), $[Cu(\mathbf{L1})+2H]^{3+}$ (*m/z* = 395.2), and $[Cu(\mathbf{L1})+3H]^{4+}$ (*m/z* = 296.7) were observed.

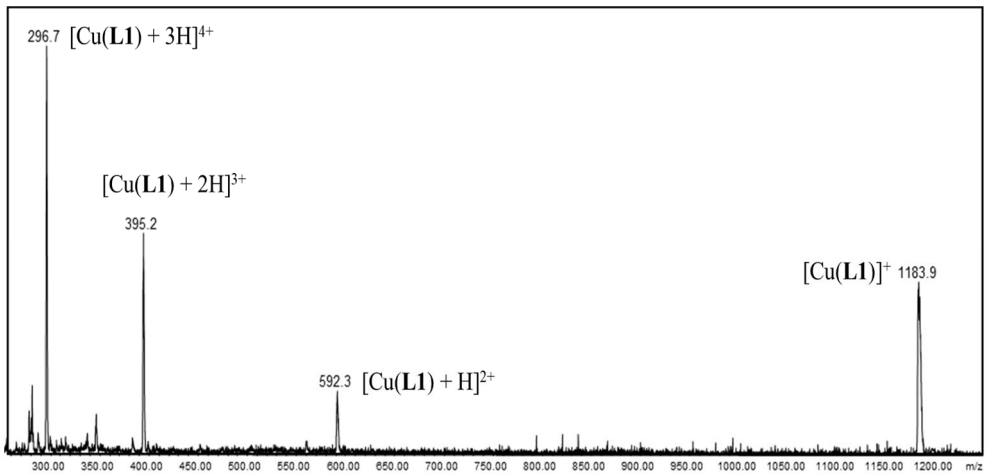


Figure S2.

For the reaction between **1a** and **2a** catalyzed by $[Cu(\mathbf{L5})_2]PF_6$, the reaction mixture was analyzed by FIA-ESI-MS. The ESI-MS (+ve) spectrum showed peaks at *m/z* = 352.3, *m/z* = 649.2 and *m/z* = 703.4, and are assigned as $[\{Cu(\mathbf{L5})(MeCN)\}_2Br+H]^{2+}$, $[\{Cu(\mathbf{L5})(HCOO)\}_2(OH)]^{+}$ and $[\{Cu(\mathbf{L5})(MeCN)\}_2\ Br]^{+}$, suggesting dinuclear copper species are involved in the reaction.

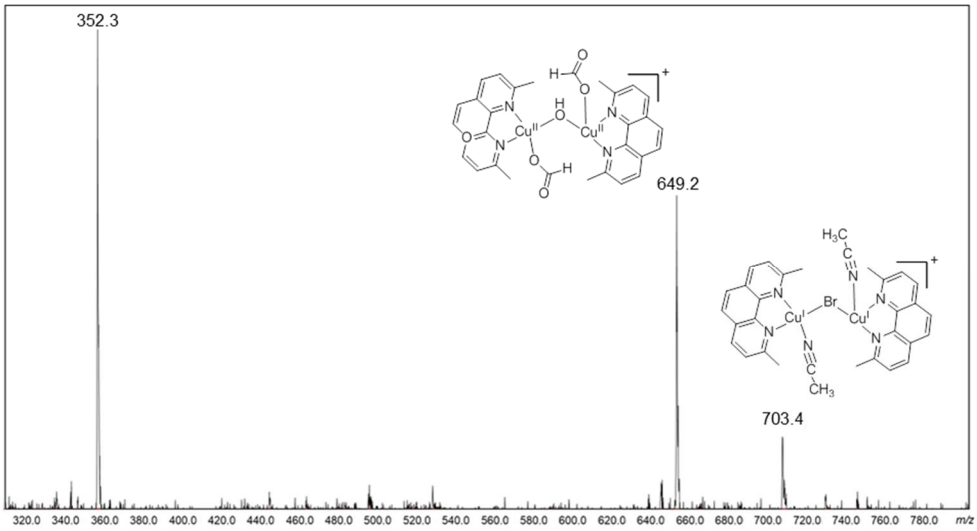
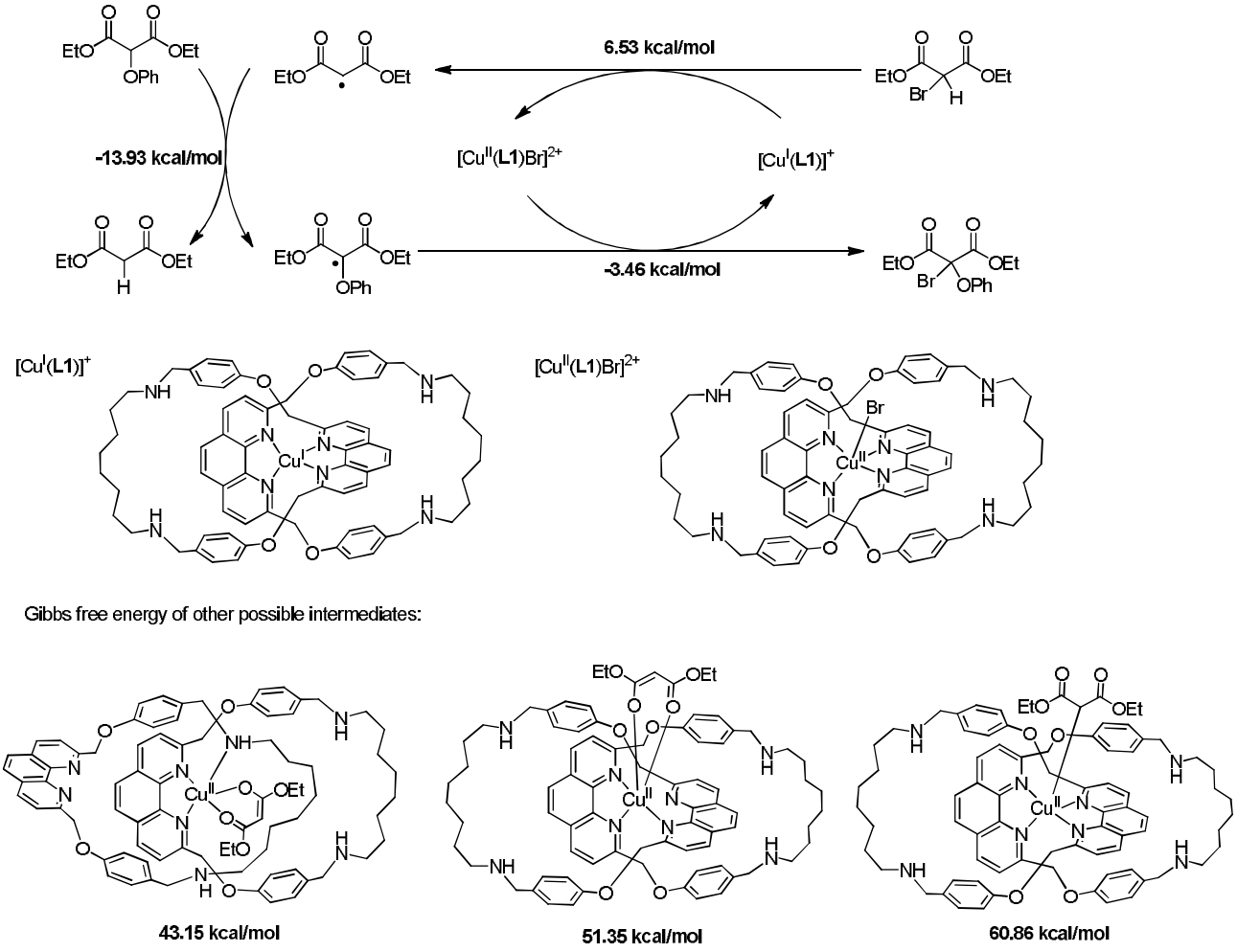


Figure S3.

4. DFT Calculations

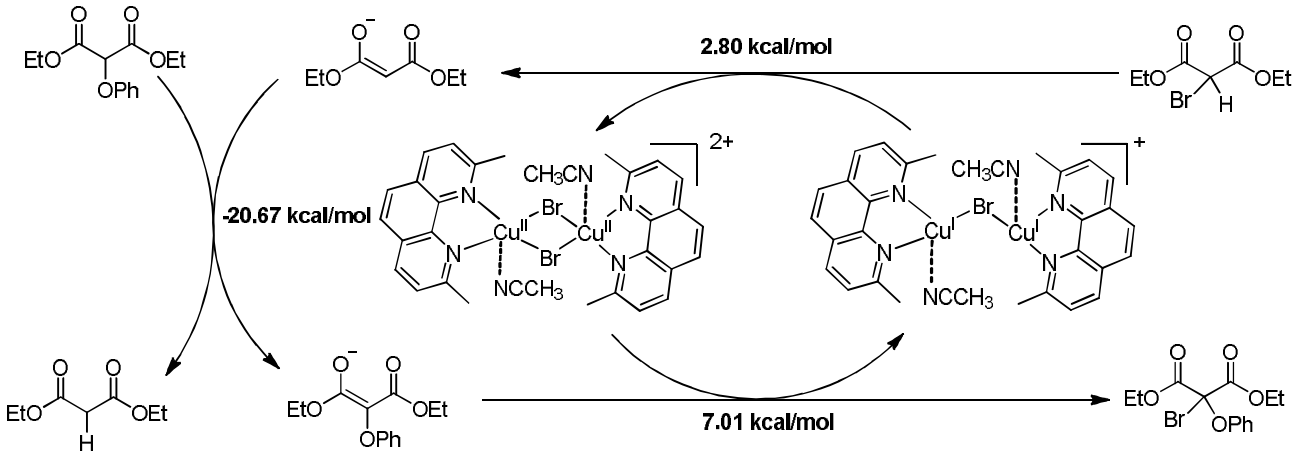
All molecular structures were optimized at the unrestricted DFT/B3LYP[4] level of theory in solvent environment using the quantum chemistry program package Gaussian 16 Revision B.01.[5] Dispersion correction was performed using DFT-D3 model.[6] The Gibbs free energies corresponding to 298.15 K were computed for making thermal correction to all structures. Each optimized geometry was confirmed as minimum electronic energy. LanL2DZ pseudopotential and basis for Cu[7] and 6-31G(d,p) basis for other atoms were used for geometry optimization.[8-10] All-electron 6-31G(d,p) basis was used for single point energy calculation of optimized geometry and further thermal correction. The Solvation Model based on Density (SMD) was employed to account for the Gibbs free energy change of the solvated structures in the acetonitrile solvent.[11] Due to the large molecular size of the catenane ligand, only a few possible intermediate molecules were hypothesized and optimized, as shown in Schemes S4 and S5.

For the CDC catalysed by [Cu(**L1**)]PF_6, Gibbs free energies of the reactants, products and assumed possible intermediates were computed (Scheme S4). A few radical addition products of the copper catenane were proposed and calculated. The corresponding Cu(II) bromide was found as an accessible intermediate in the reaction pathway of a low free energy barrier.



Scheme S4.

For the CDC catalysed by [Cu(**L5**)$_2$]PF_6, a binuclear reduction mechanism involving the dicopper complexes [{Cu^{I}(**L5**)(MeCN)}$_2$Br]$^+$ and [{Cu^{II}(**L5**)(MeCN)Br}$_2$]$^+$ was studied (Scheme S5), because a similar mechanism has been previously reported and the dicopper complexes have been observed in the ESI-MS analysis of the corresponding reaction mixture.



Scheme S5.

5. Time-dependent Studies

To study the possible intermediate involved in the CDC between **1a** (0.1 mmol) and **2a** (0.22 mmol) catalysed by 1 mol% [Cu(**L1**)]PF_6 at 50°C in MeCN, a time-dependent ^{1}H NMR study was performed using 1,3,5-trimethoxybenzene as the internal standard. In addition to **3a** (δ = 7.20 ppm), diethyl phenoxymalonate **3a′** (δ = 5.23 ppm) and diethyl malonate (δ = 3.39 ppm) were identified (see Figure S6). The reaction was monitored for 24 hours.

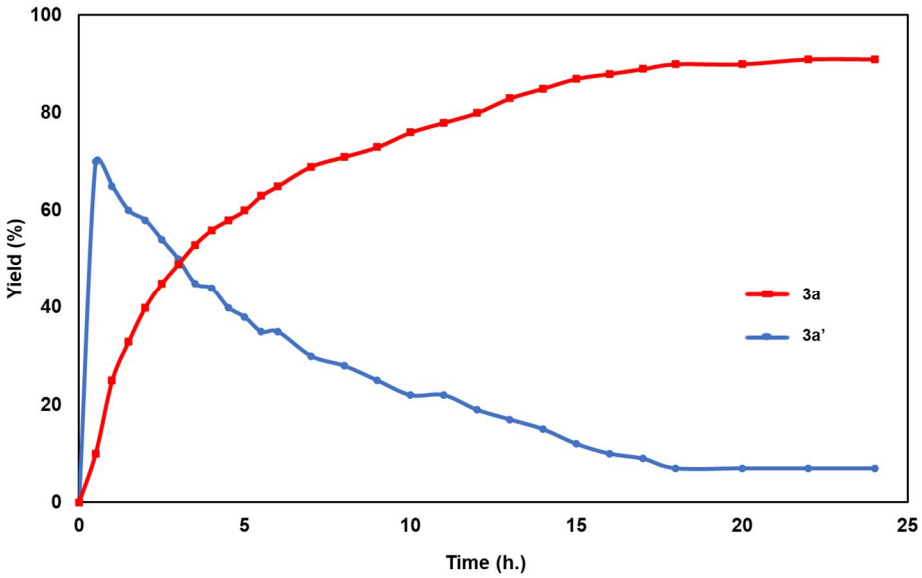


Figure S4. Time-dependent distribution of **3a** (red)) and **3a′** (blue).

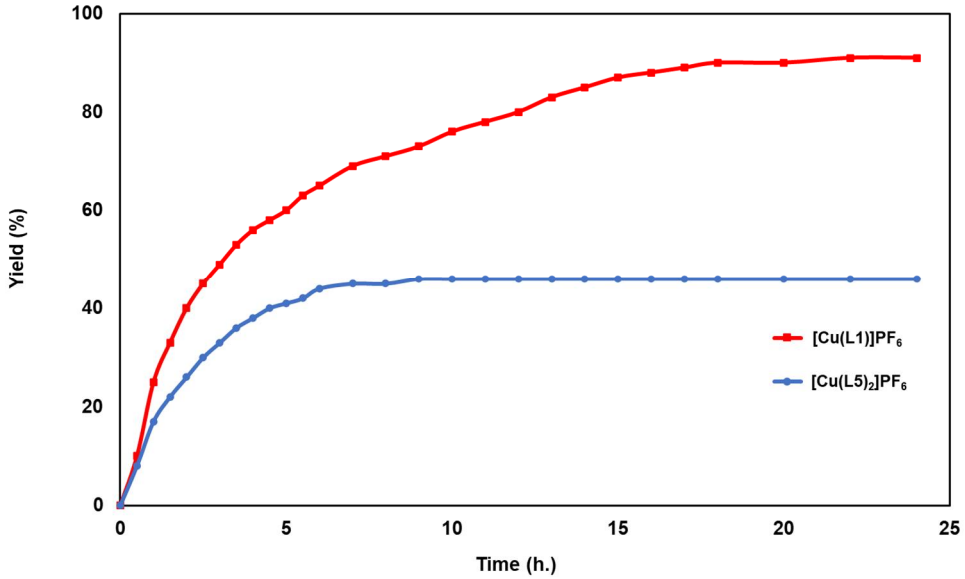


Figure S5. Time-dependent formation of **3a** catalysed by [Cu(**L1**)]PF_6 (red) and [Cu(**L5**)$_2$]PF_6 (blue).

6. NMR Spectra

A crude mixture of the coupling between **1a** and **2a** catalysed by [Cu(**L1**)]PF_6 was studied by ^{1}H NMR using a Bruker 400 MHz DPX spectrometer. After the reaction is completed, the reaction mixture was passed through a short pad of silica gel and the solvents were evaporated. The ^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of the residue showed a peak at 3.39 ppm which was assigned to diethyl malonate,[12] and the peaks at 6.99 ppm and 5.23 ppm were assigned to diethyl phenoxymalonate **3a′**.[13]

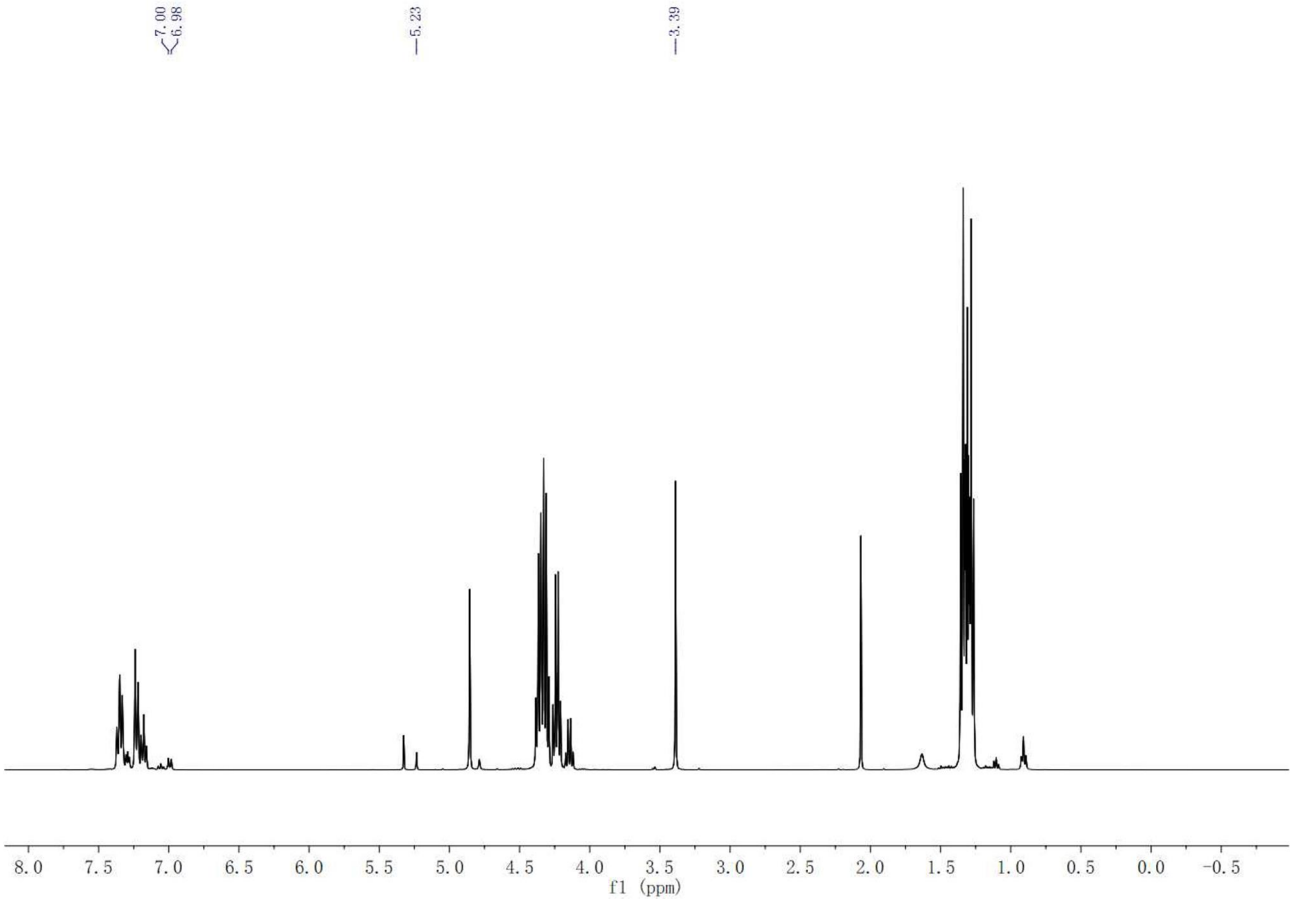


Figure S6. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of a crude coupling product mixture **1a** and **2a** catalysed by [Cu(**L1**)]PF_6.

To analyse the possible formation of copper-TEMPO complex with [Cu(**L1**)]PF_6, a ^{1}H NMR spectrum of a 20 mM solution of [Cu(**L1**)]PF_6 in the presence of 50 eq. TEMPO in CD_3CN was obtained. Apart from the peaks due to TEMPO at 15.1 ppm, -16.0 ppm and -28.8 ppm, no other paramagnetically shifted signal due to any possible TEMPO complex of [Cu(**L1**)]$^+$ was observed. Peak broadening of the signals from [Cu(**L1**)]$^+$ due to the presence of TEMPO was observed.

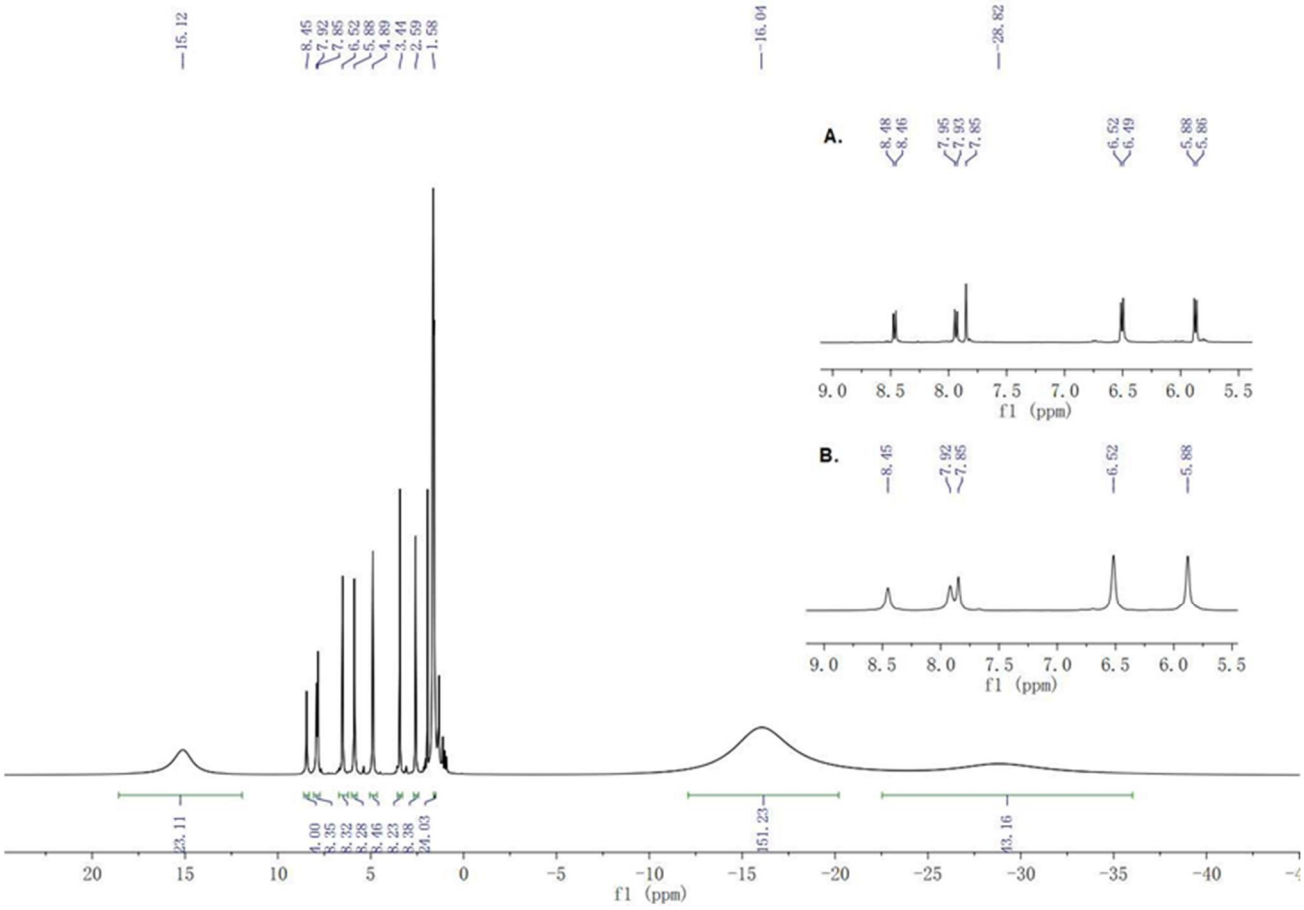


Figure S7. ^{1}H NMR (400 MHz, 298 K, CD_3CN) spectrum of [Cu(**L1**)]PF_6 in the presence of 50 eq. TEMPO. Shown in the inset are the expanded region of the ^{1}H spectrum of (A) a solution of [Cu(**L1**)]PF_6 only; and (B) a mixture of [Cu(**L1**)]PF_6 and 50 eq. TEMPO for comparison.

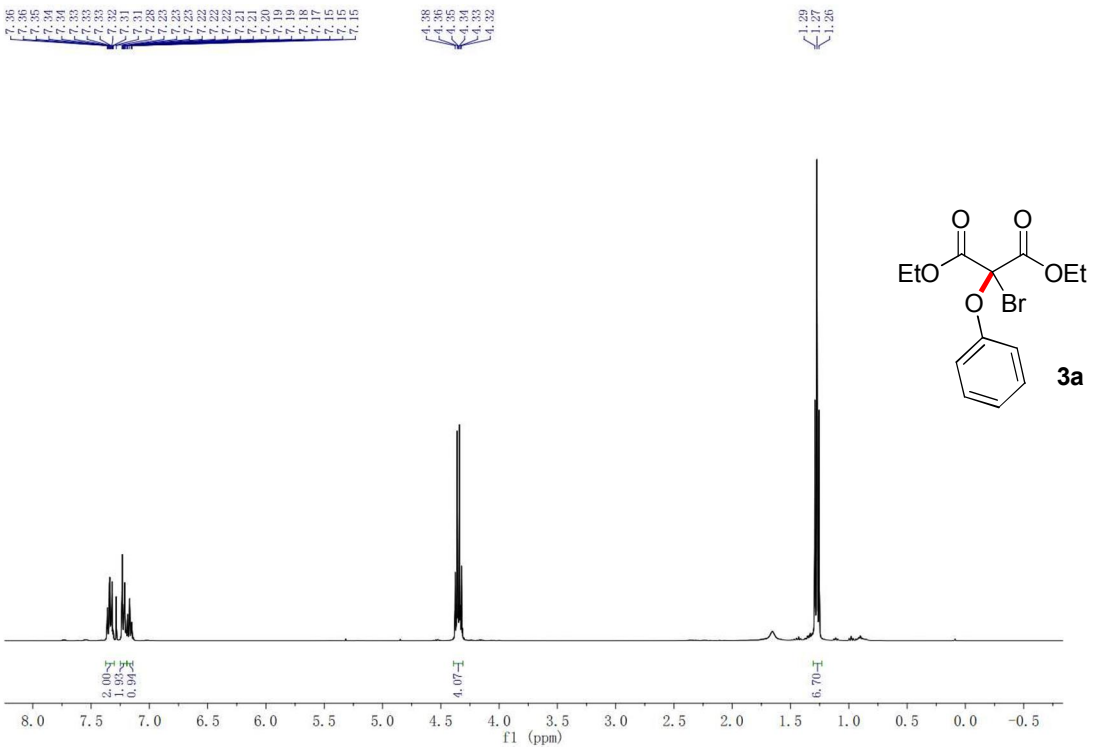


Figure S8 ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of **3a**.

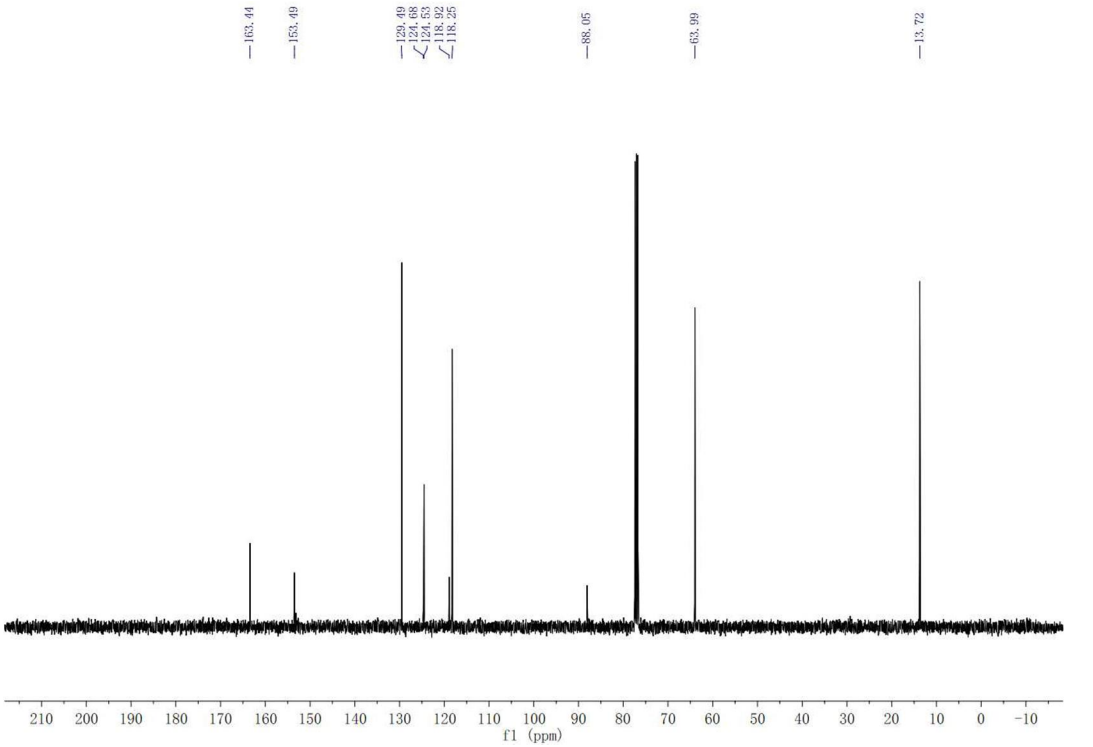


Figure S9. $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of **3a**.

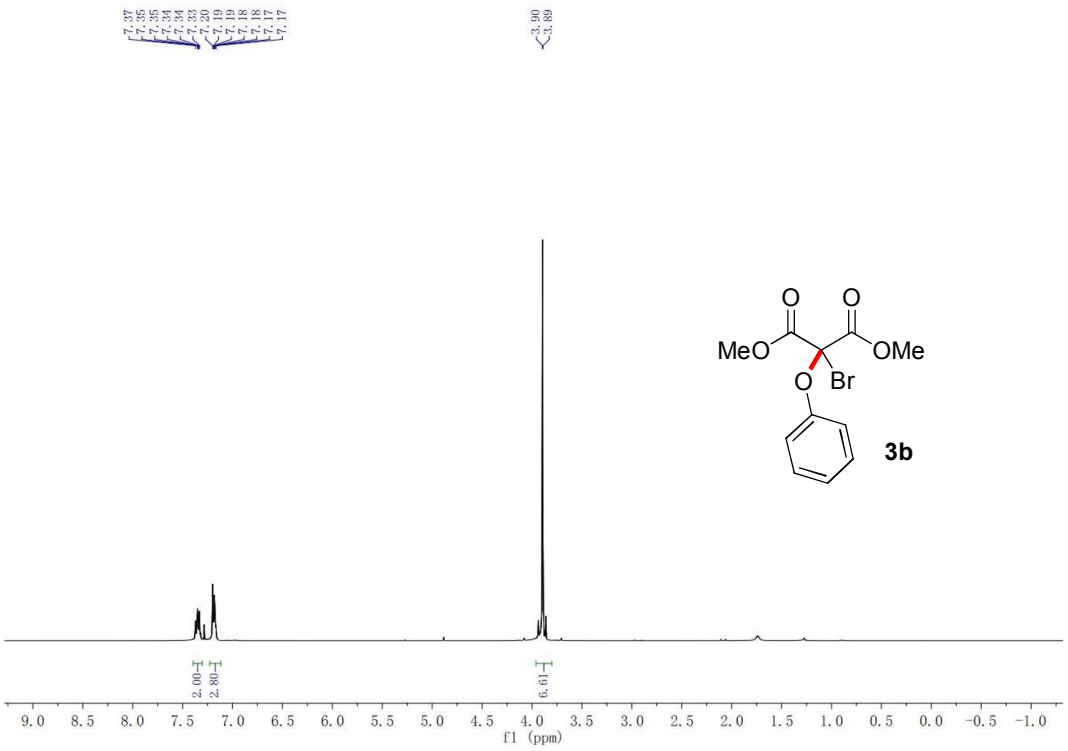


Figure S10. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of **3b**.

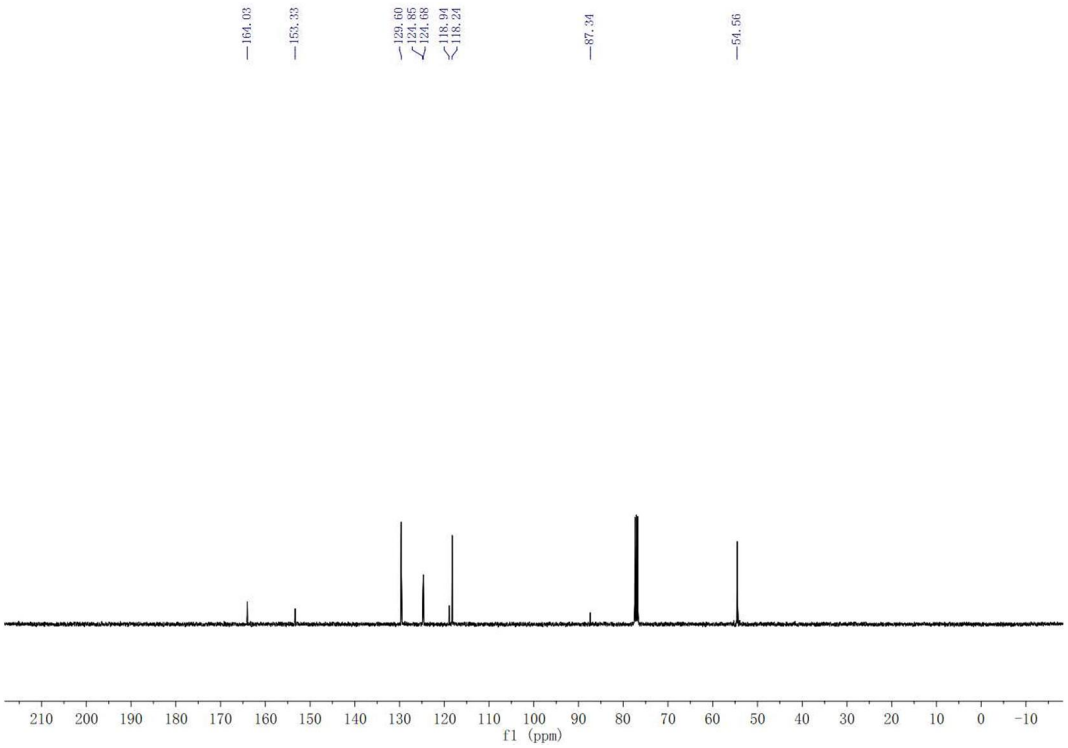


Figure S11. $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of **3b**.

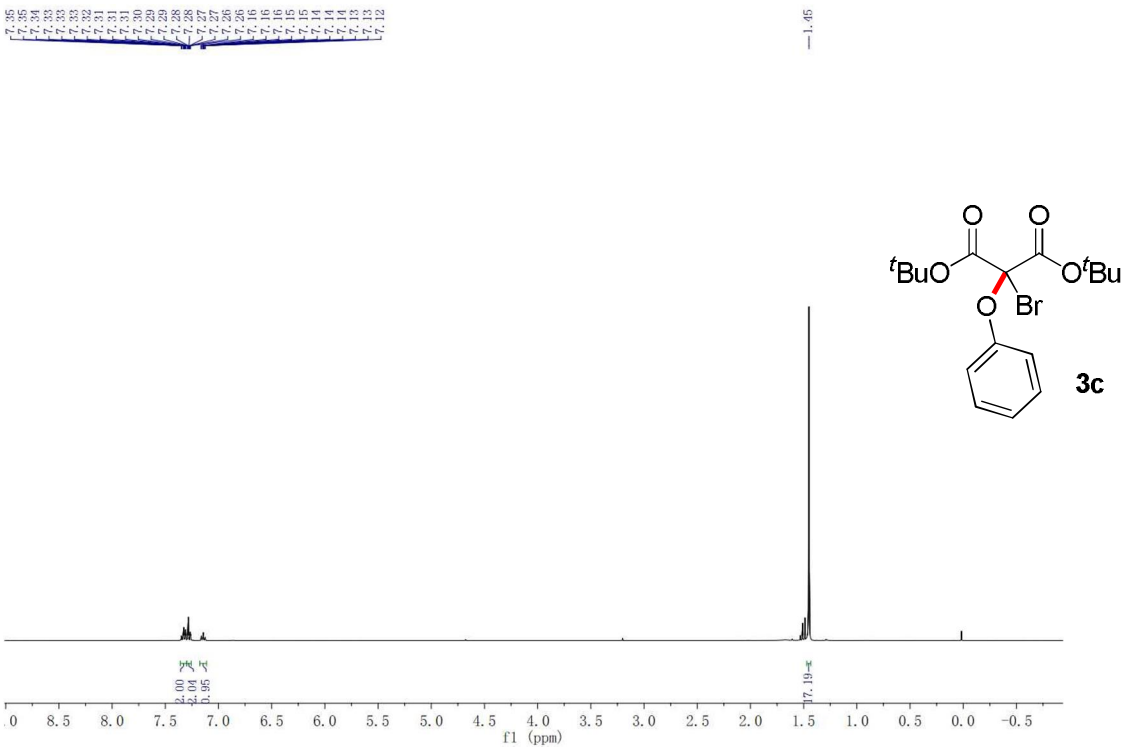


Figure S12. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of **3c**.

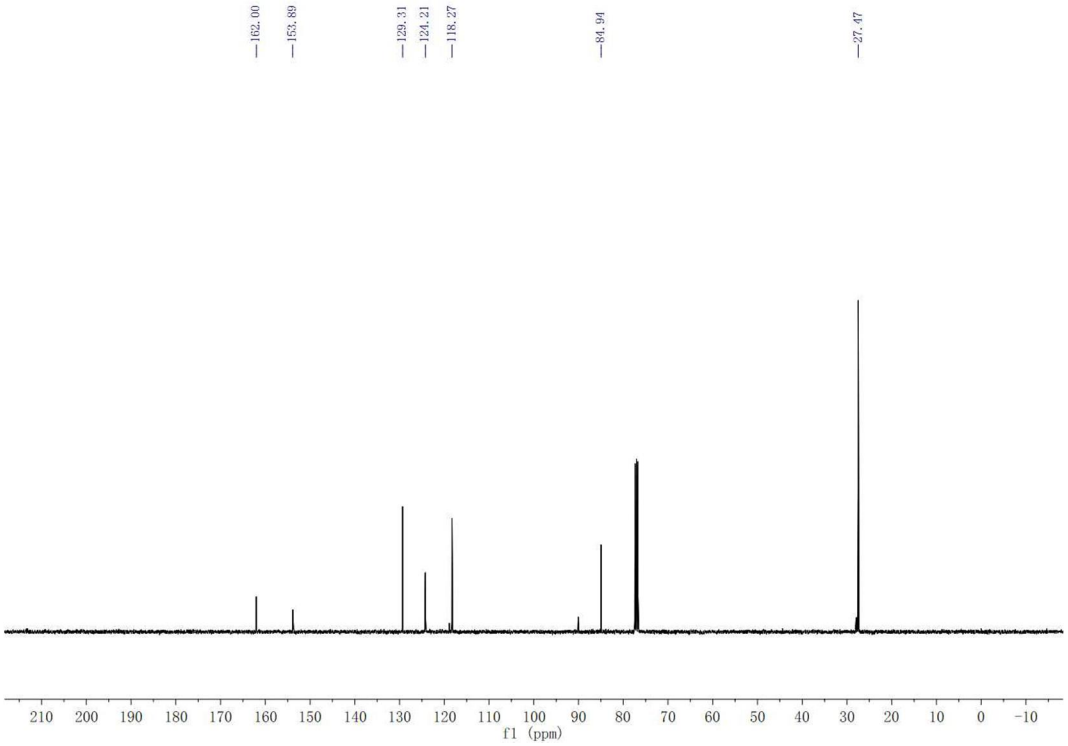


Figure S13. $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of **3c**.

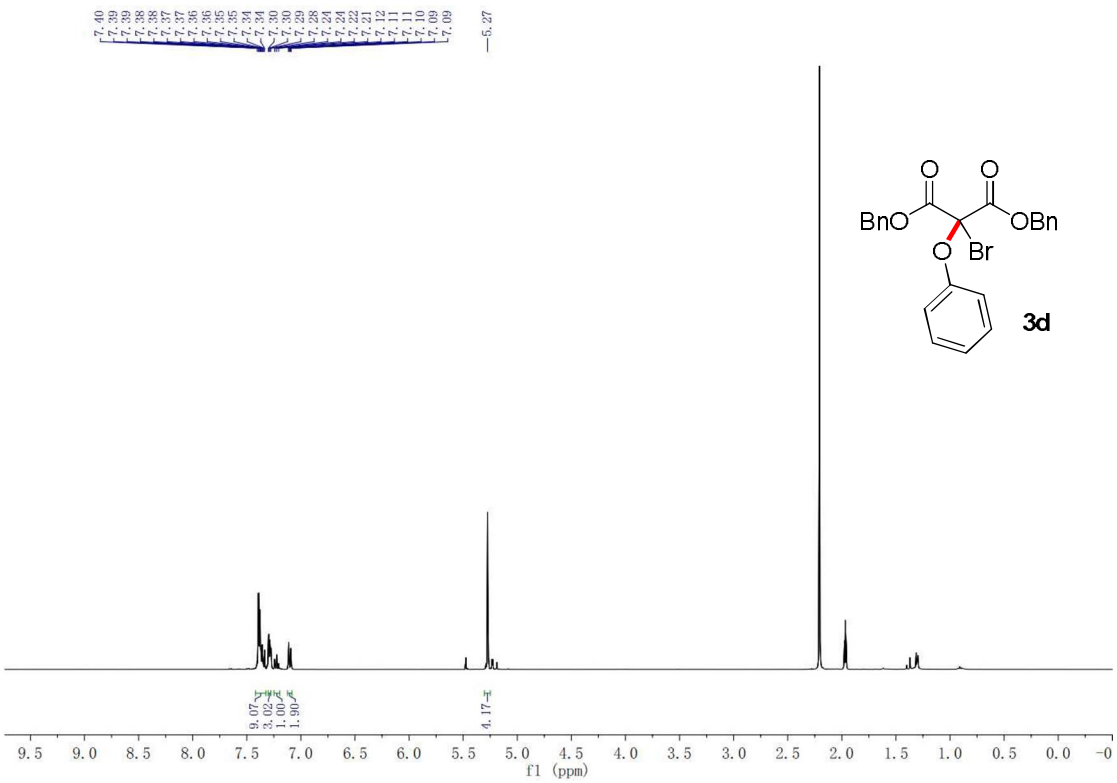


Figure S14. ^{1}H NMR (400 MHz, 298 K, CD_3CN) spectrum of **3d**.

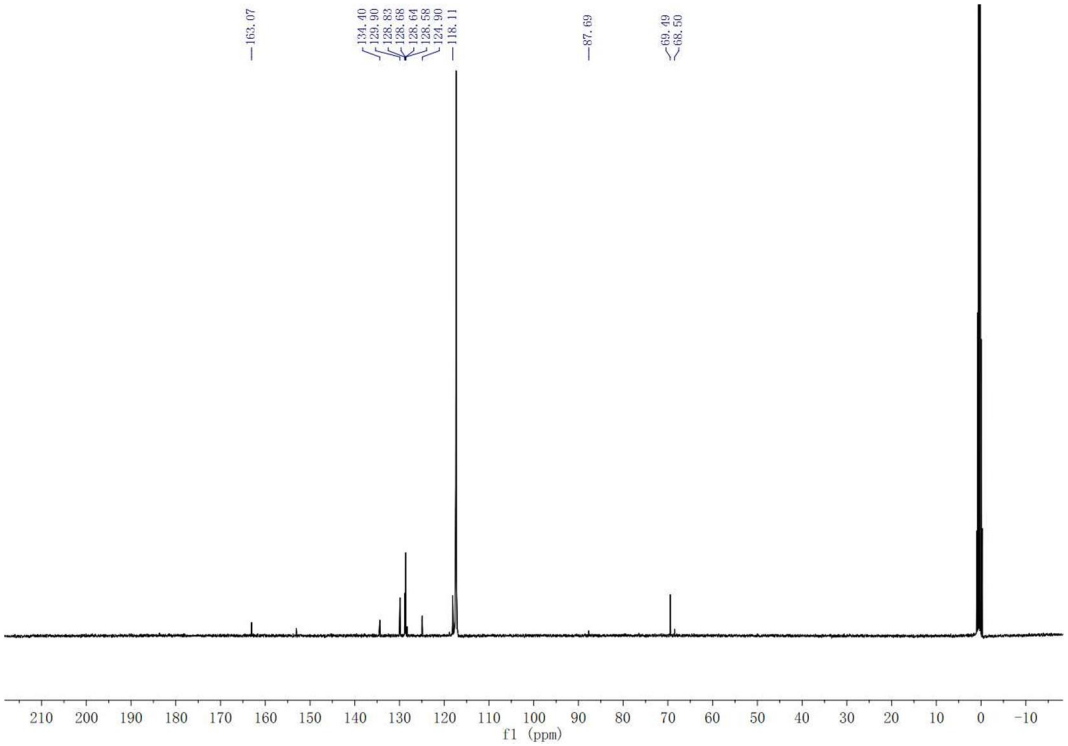


Figure S15. $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, CD_3CN) spectrum of **3d**.

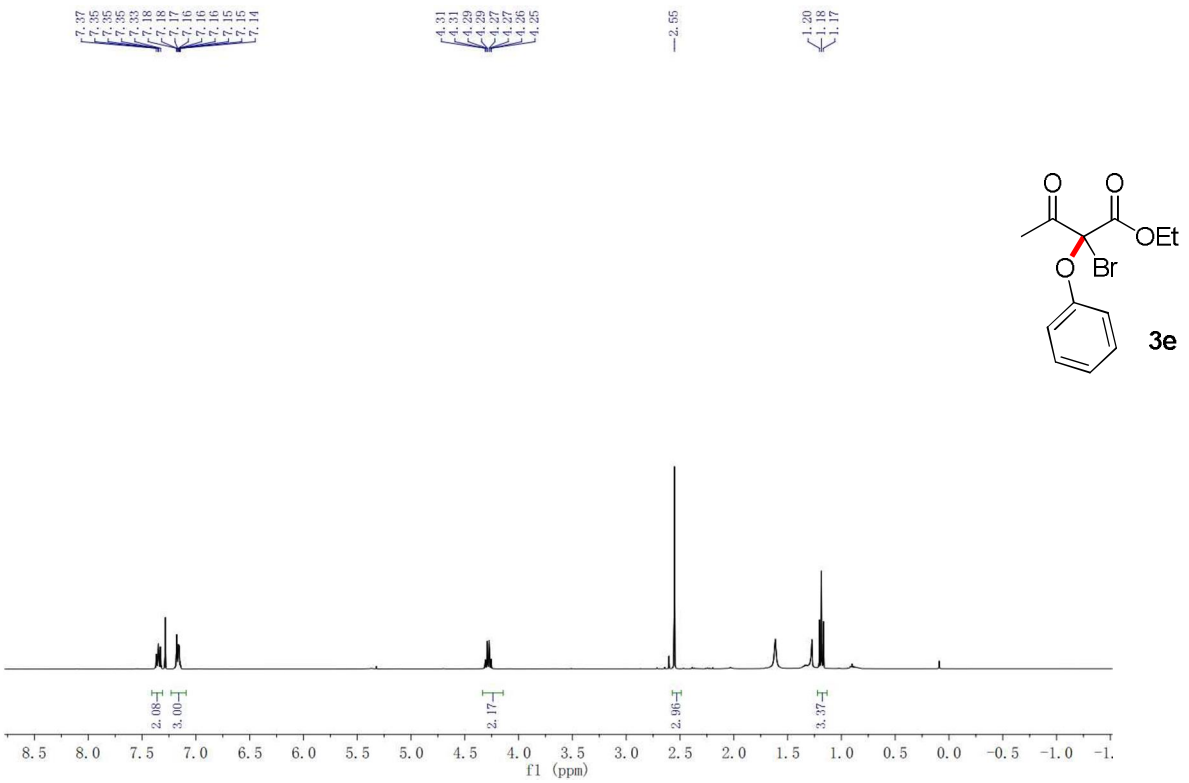


Figure S16. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of **3e**.

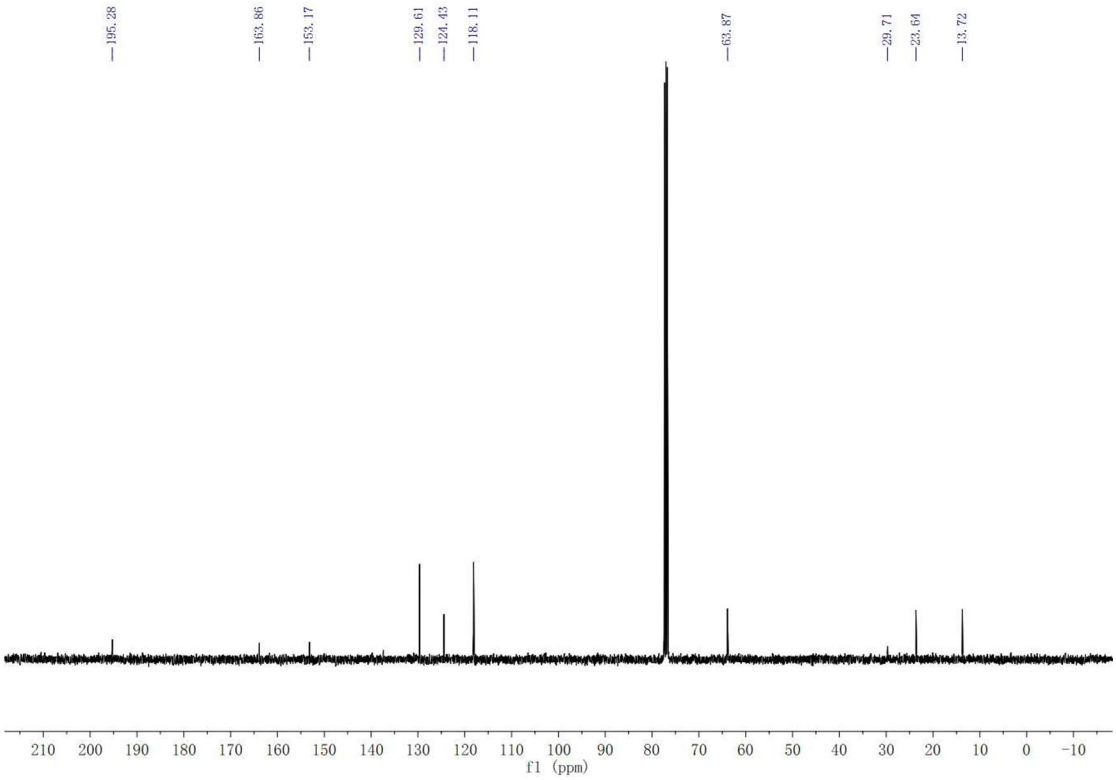


Figure S17. $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of **3e**.

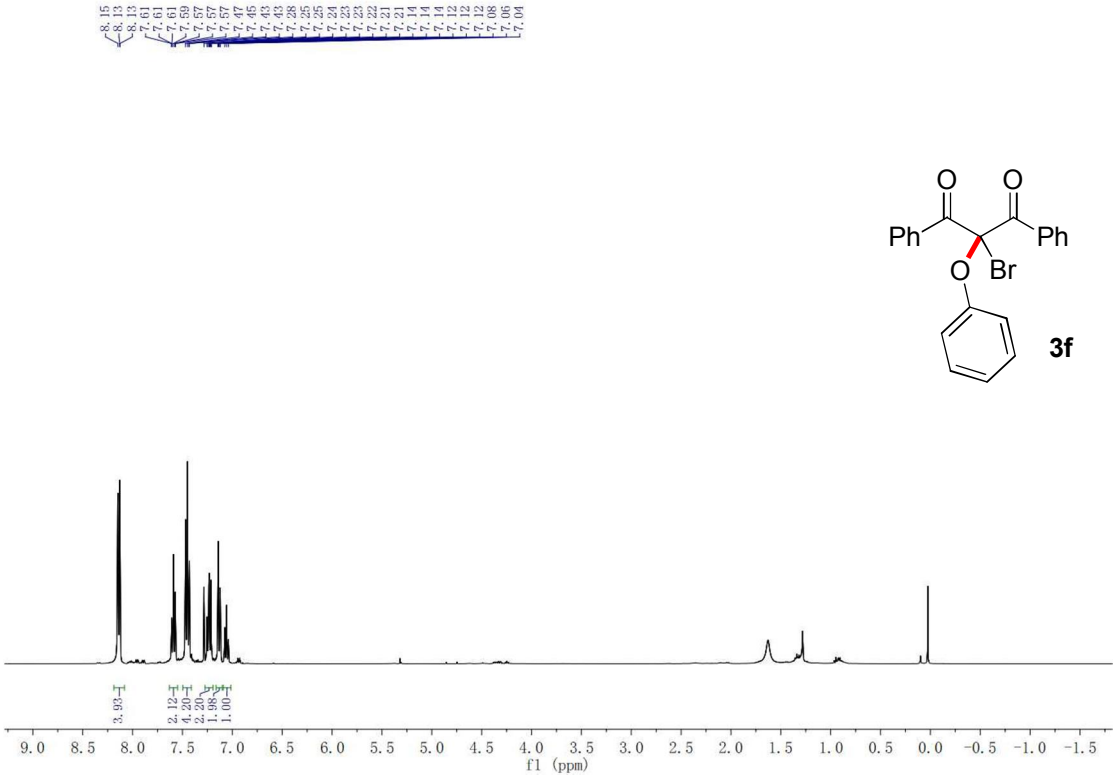


Figure S18. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of **3f**.

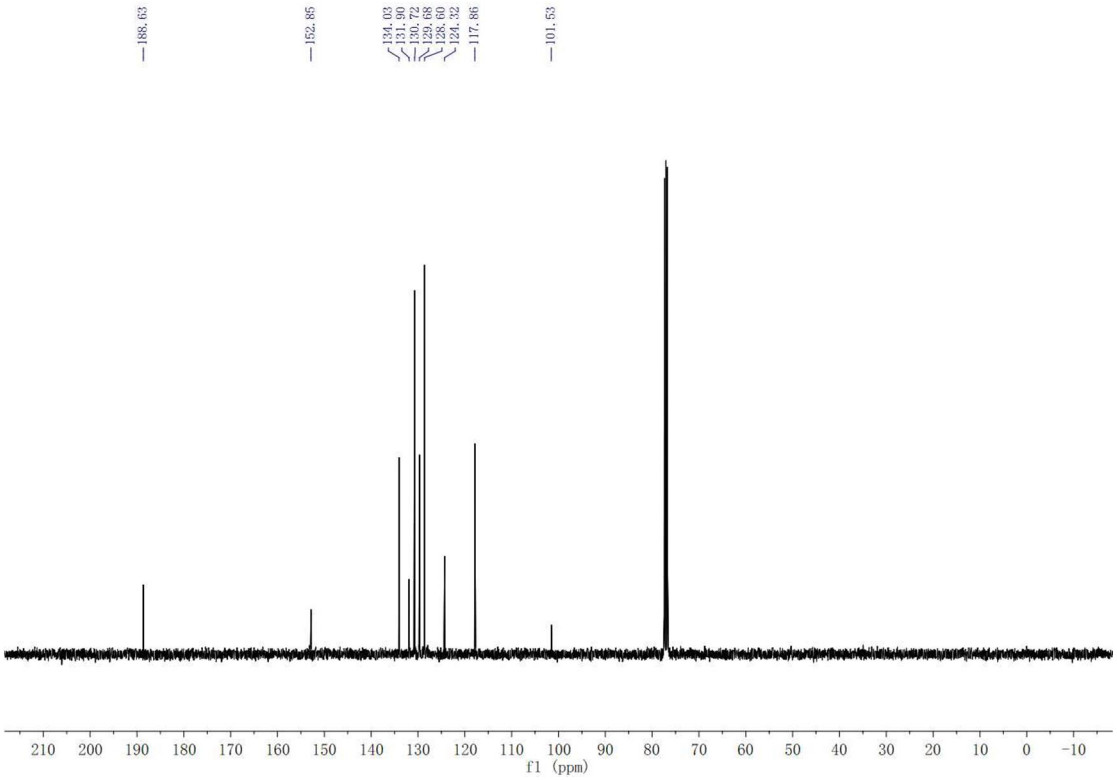


Figure S19. $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of **3f**.

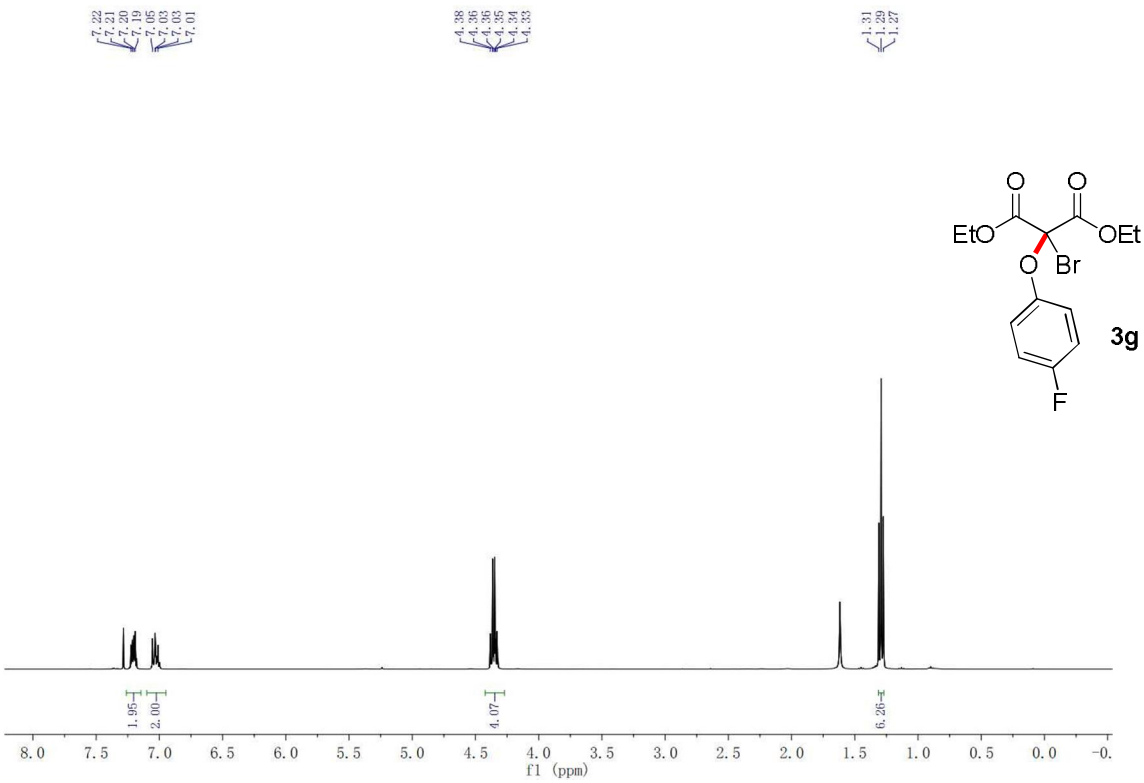


Figure S20. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of **3g**.

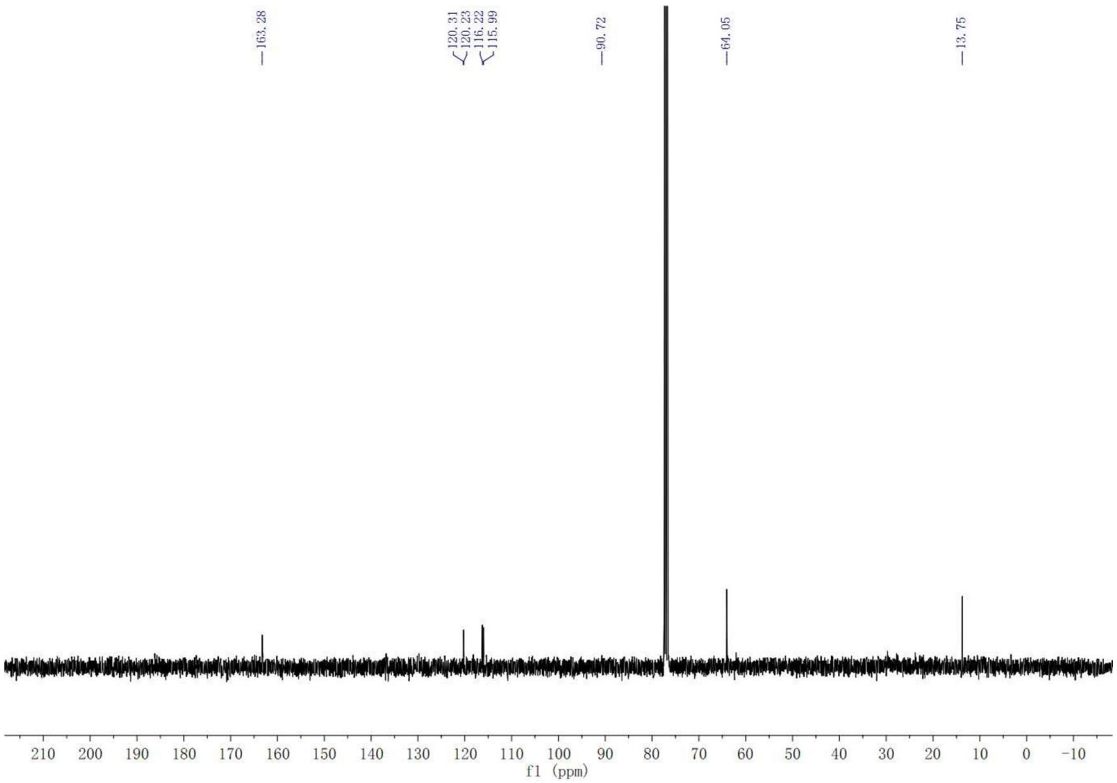


Figure S21. $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of **3g**.

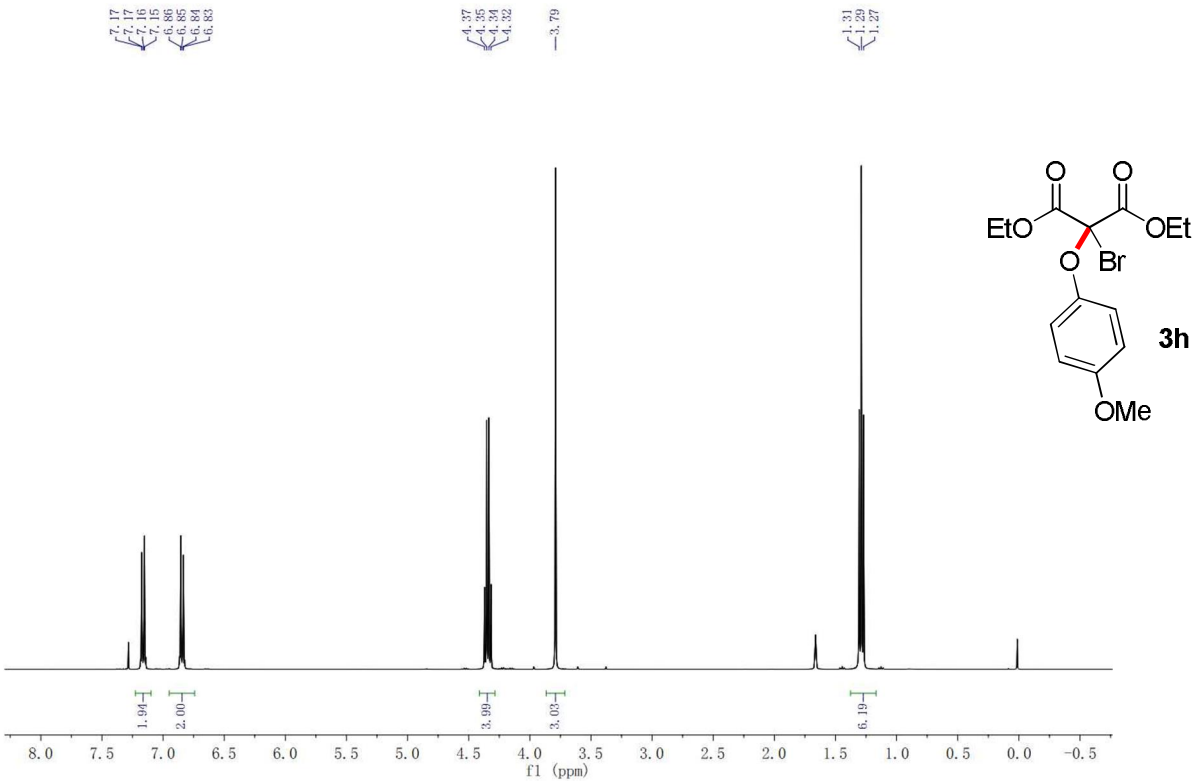


Figure S22. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of **3h**.

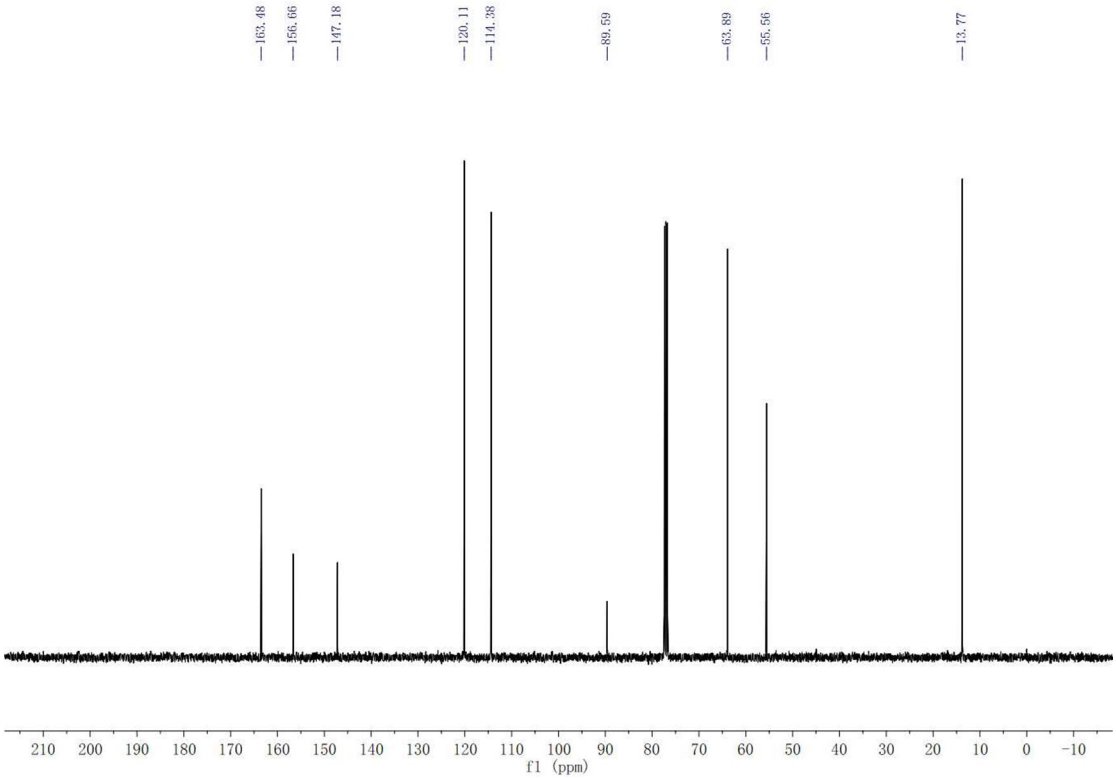


Figure S23. $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of **3h**.

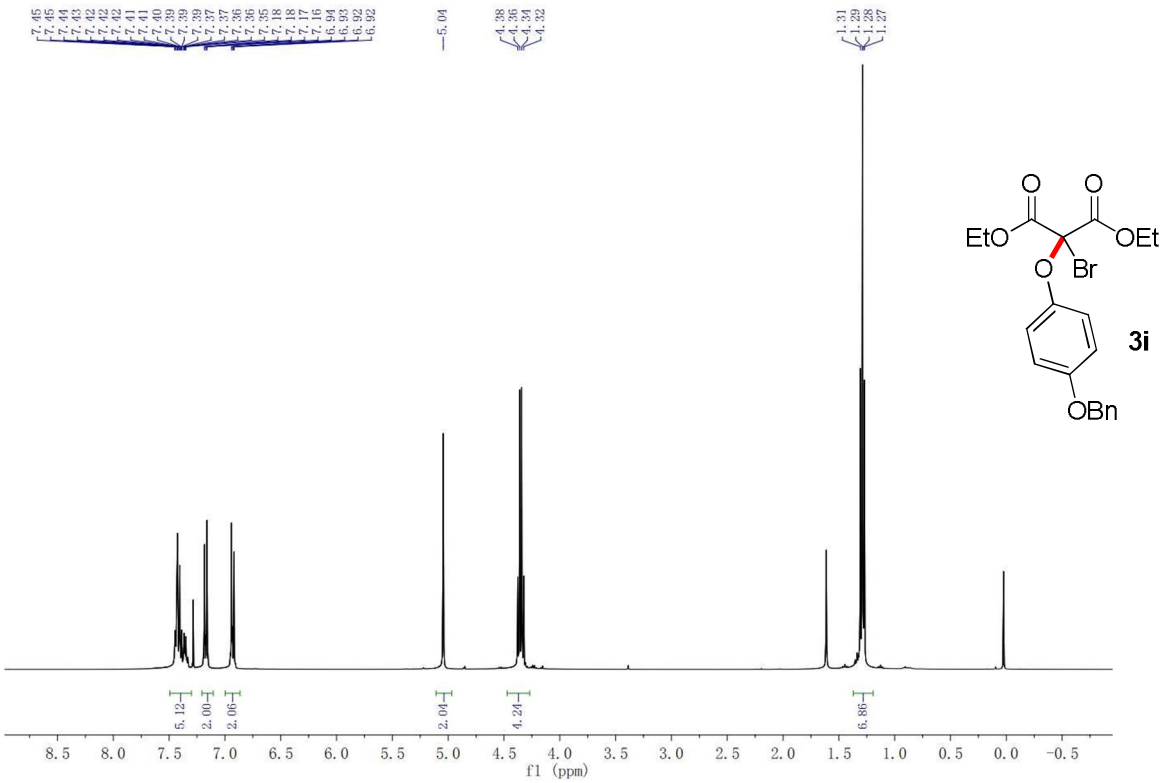


Figure S24. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of **3i**.

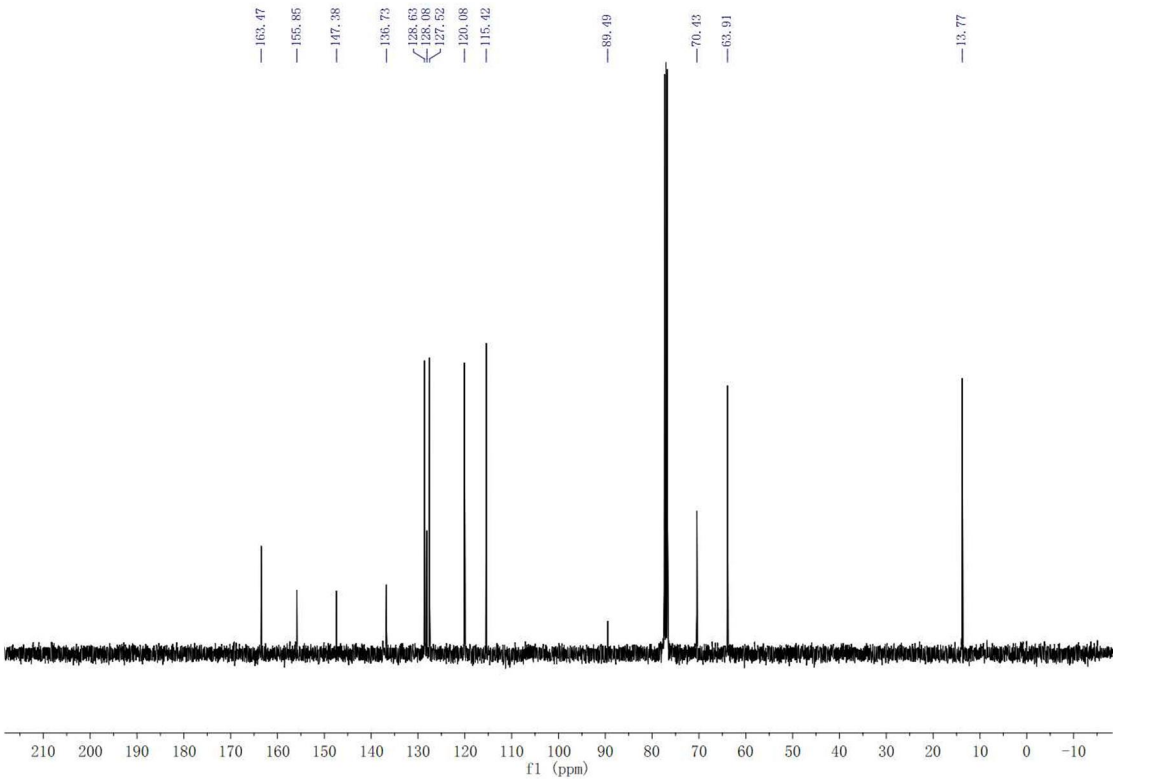


Figure S25. $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of **3i**.

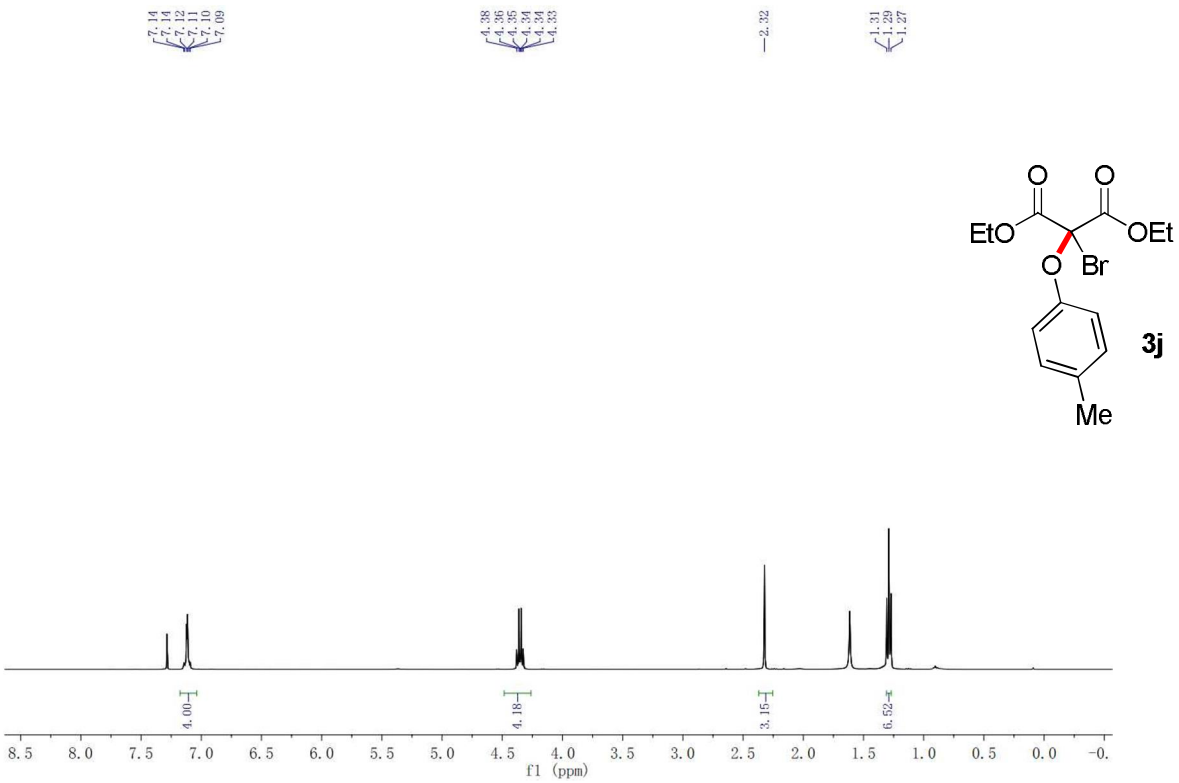


Figure S26. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of **3j**.

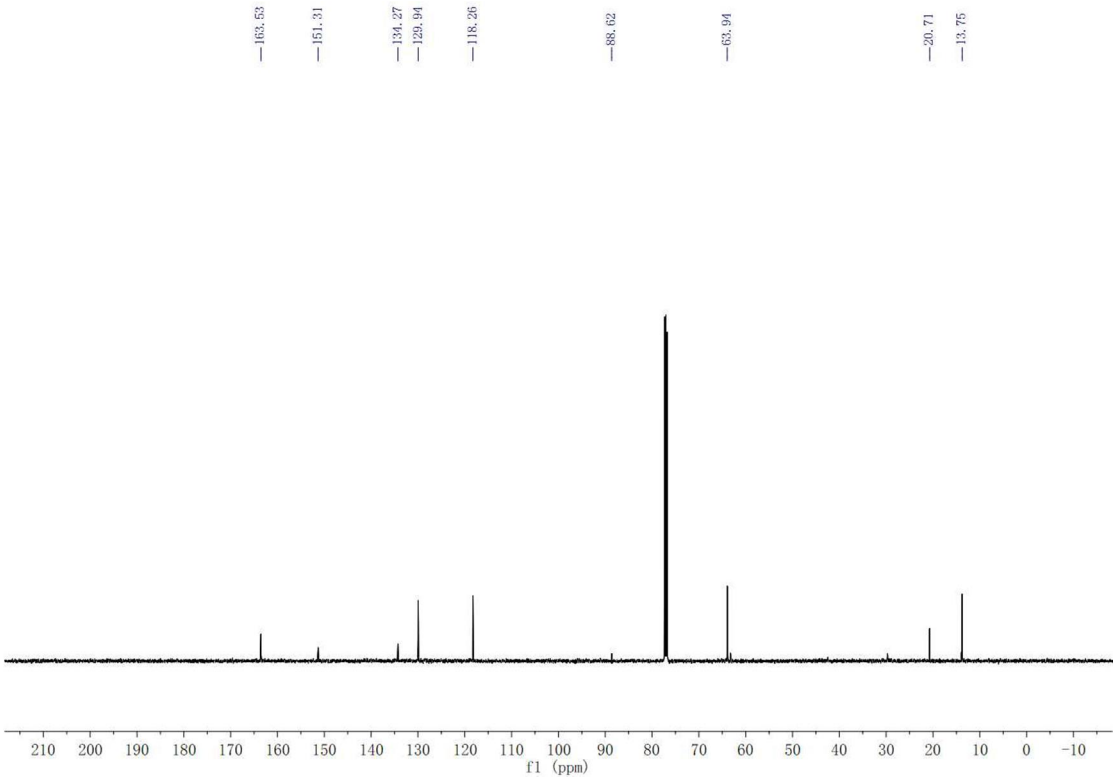


Figure S27. $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of **3j**.

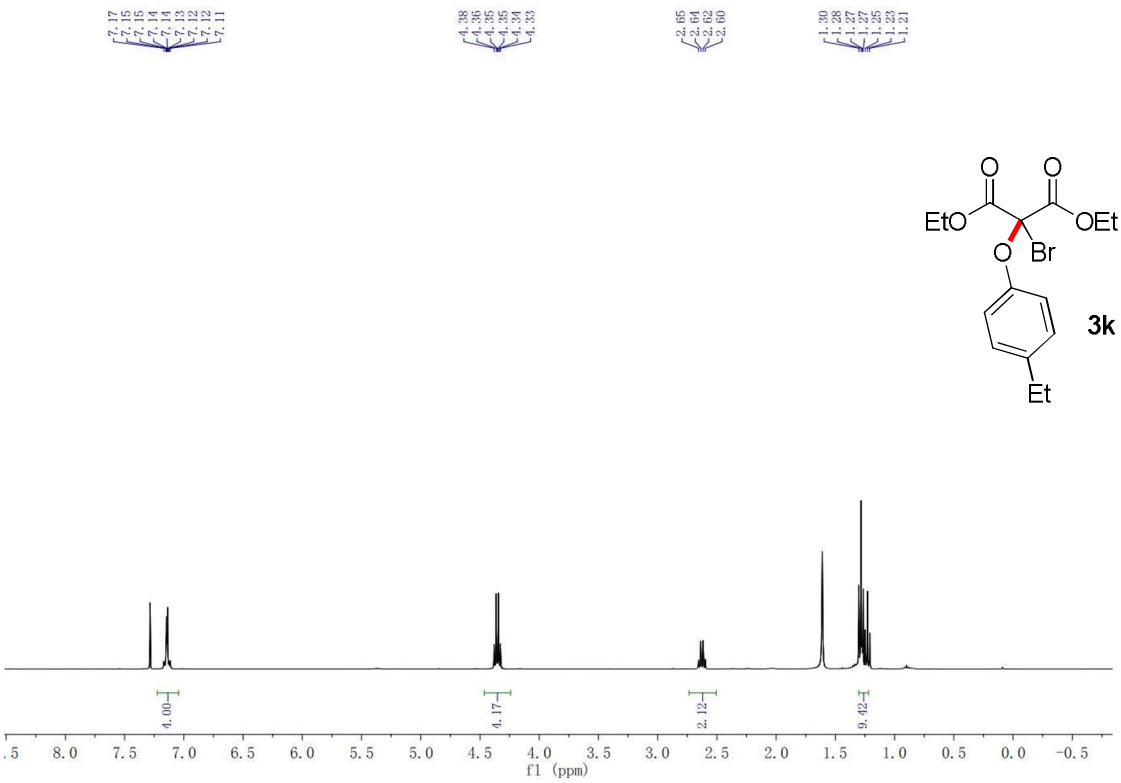


Figure S28. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of **3k**.

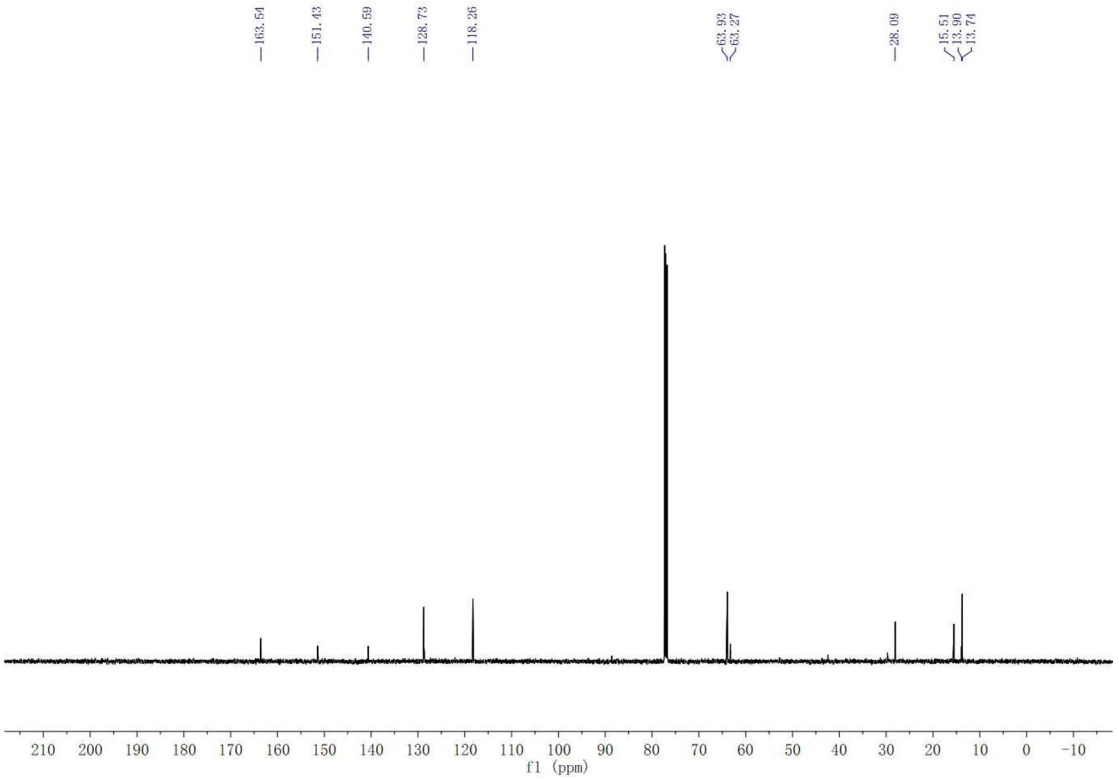


Figure S29. $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of **3k**.

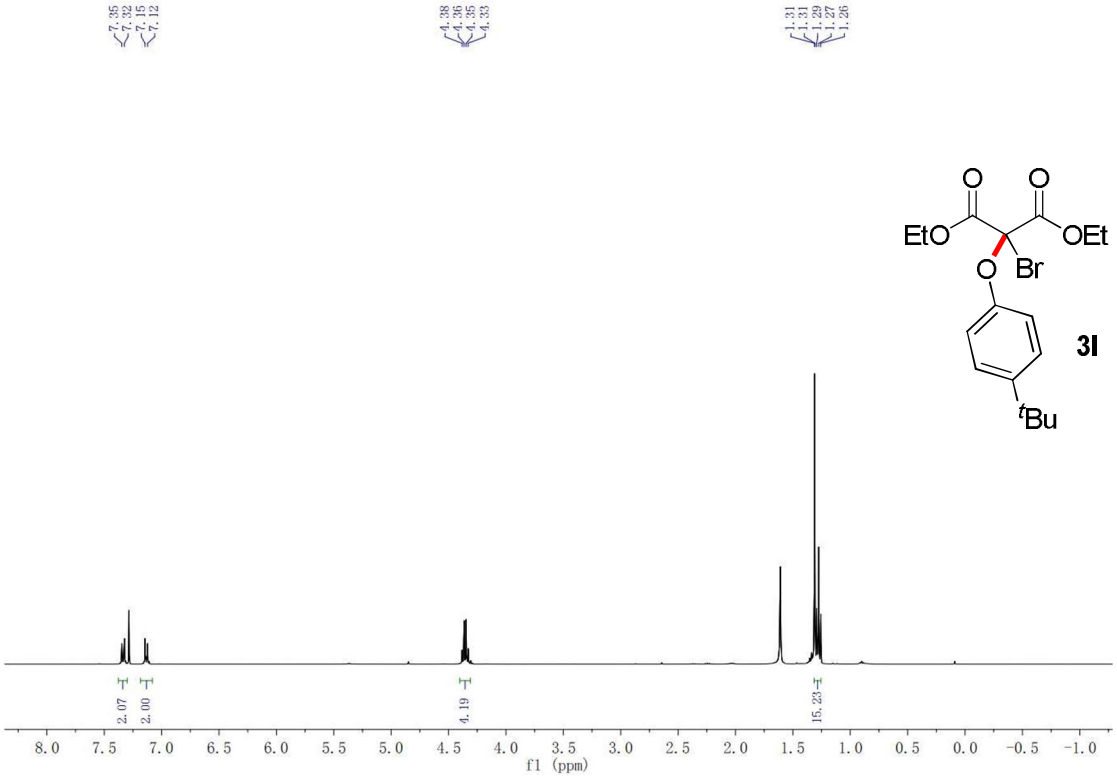


Figure S30. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of **3l**.

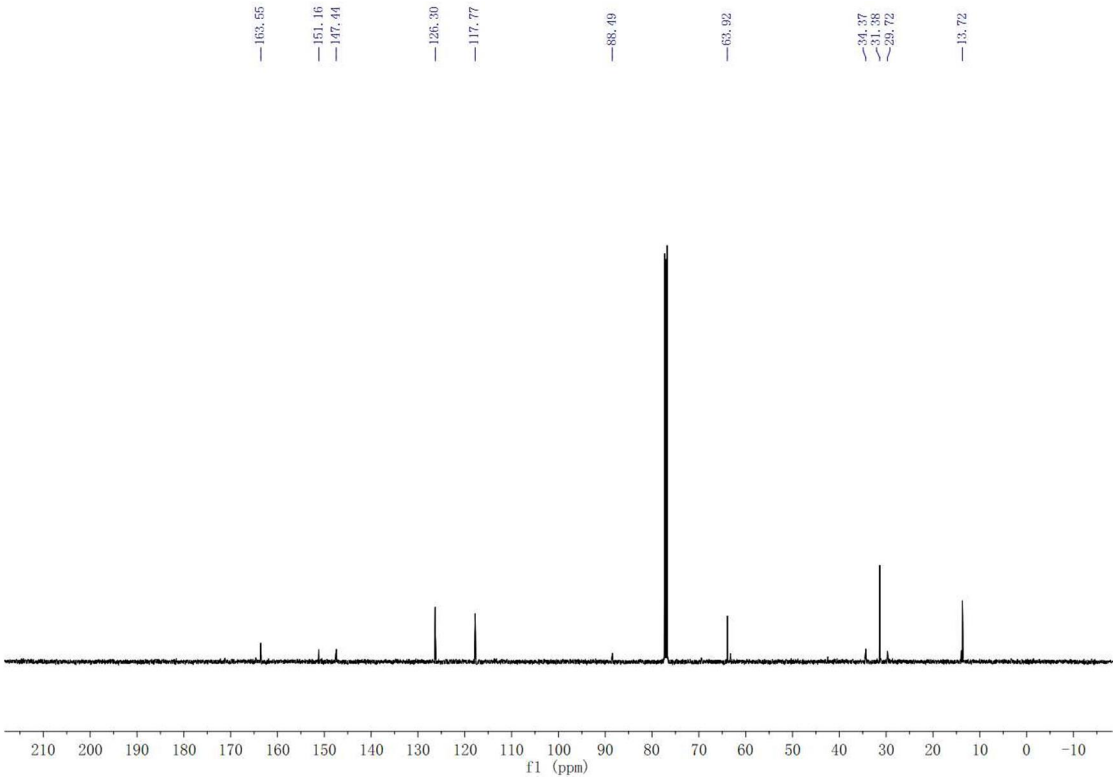


Figure S31. $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of **3l**.

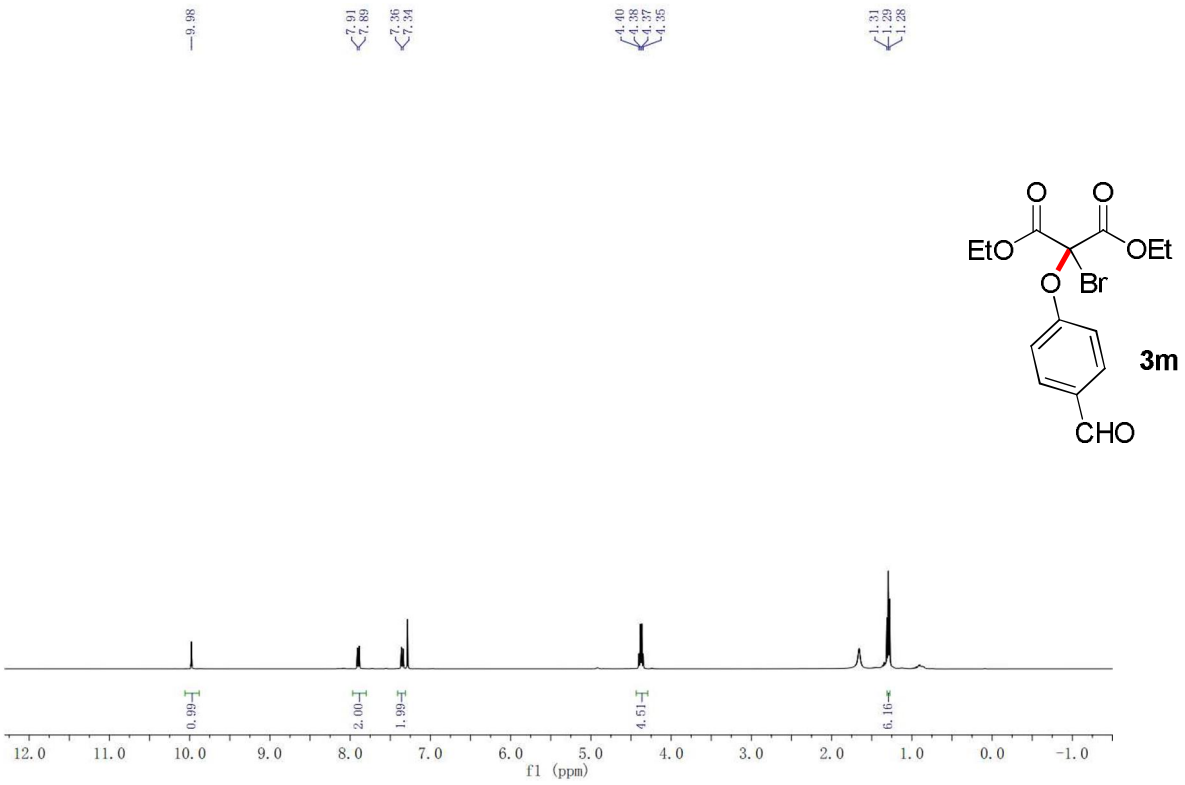


Figure S32. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of **3m**.

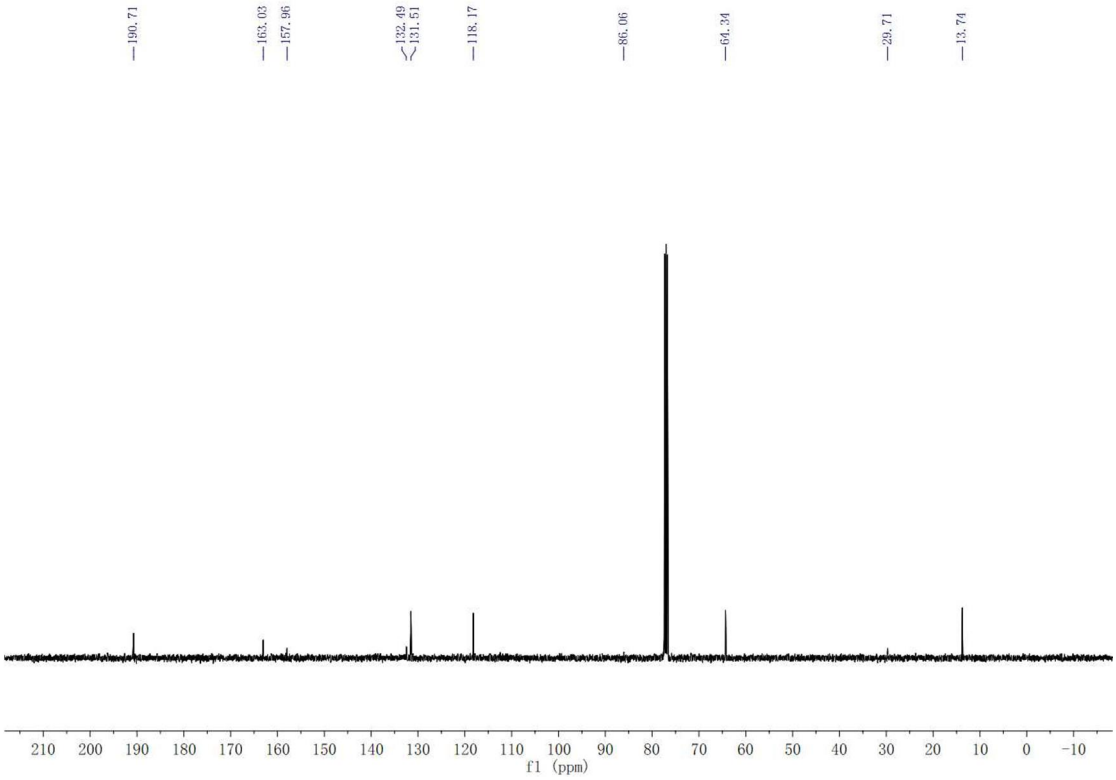


Figure S33. $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of **3m**.

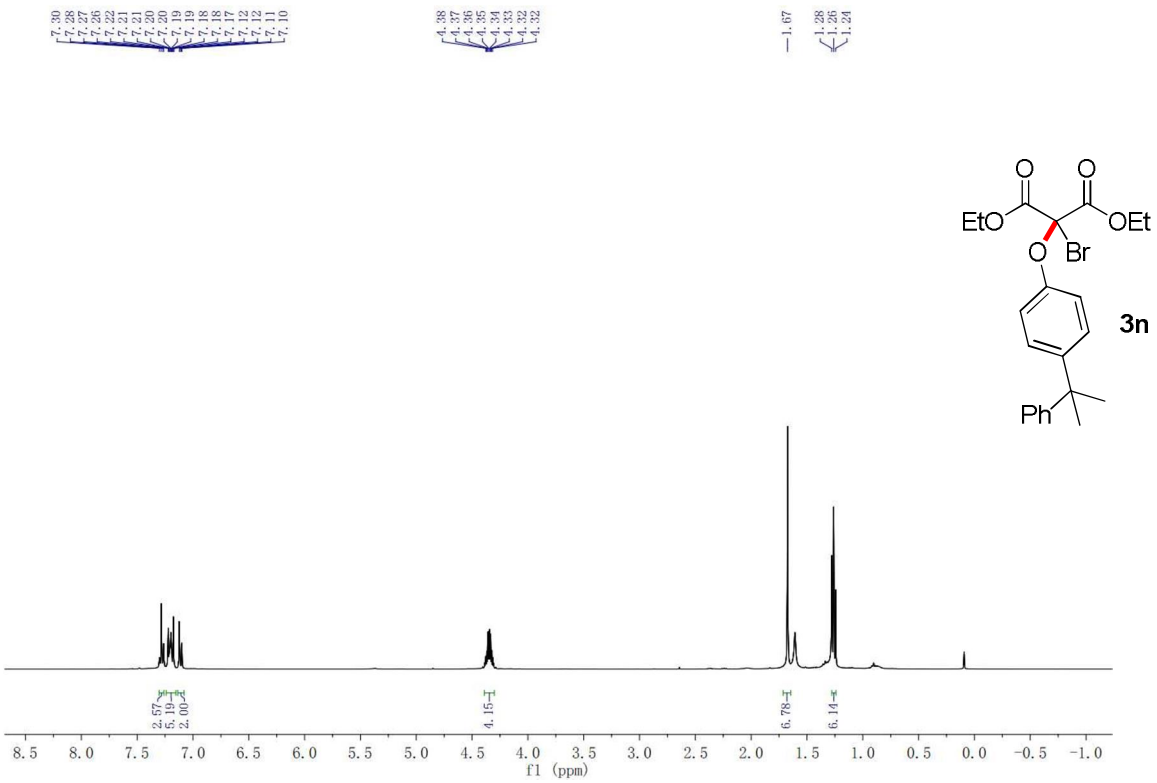


Figure S34. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of **3n**.

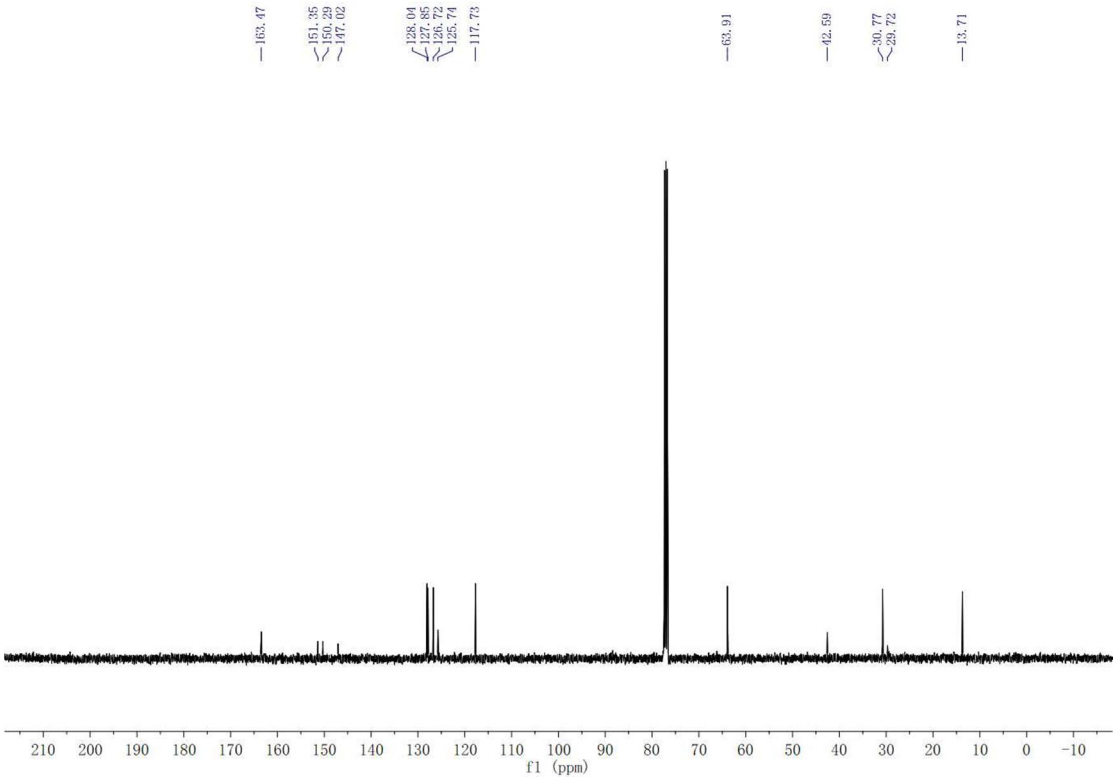


Figure S35. $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of **3n**.

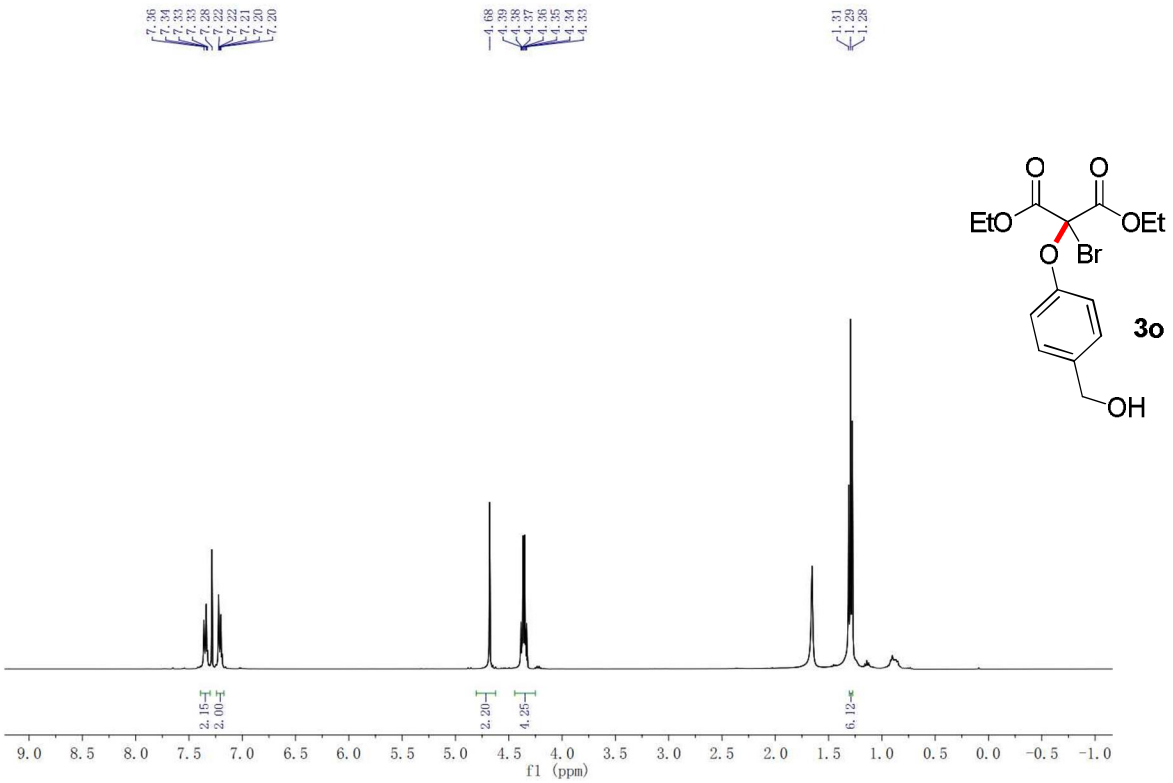


Figure S36. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of **3o**.

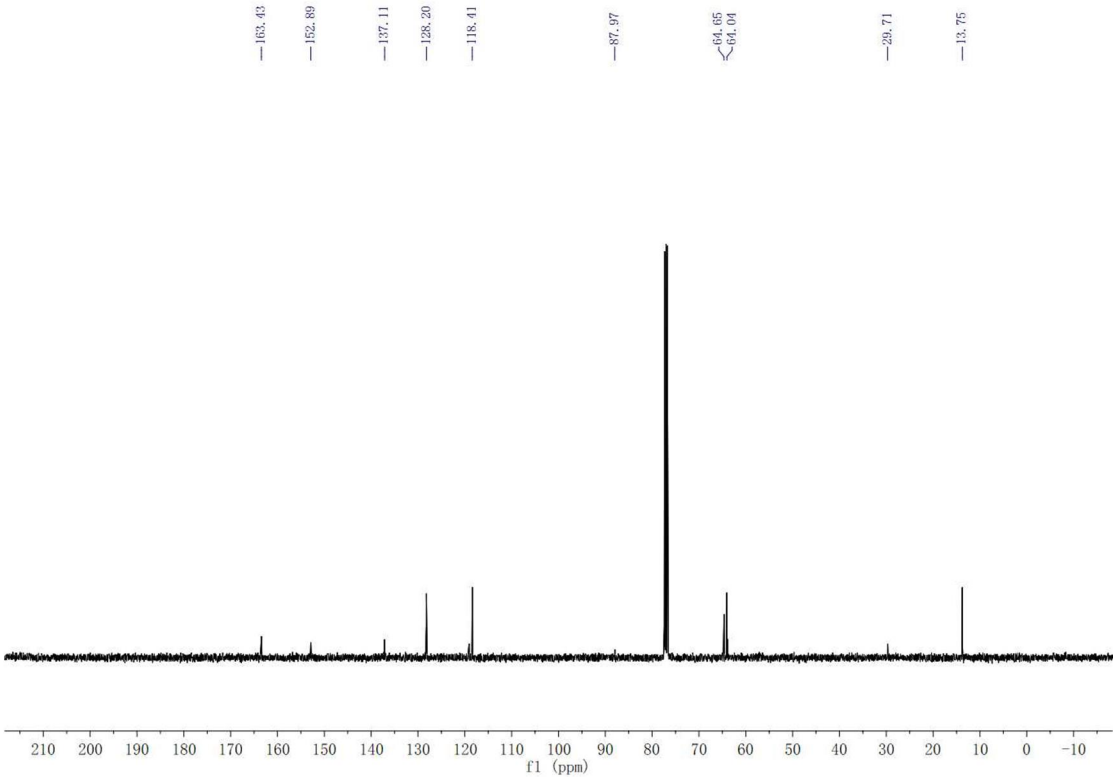


Figure S37. $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of **3o**.

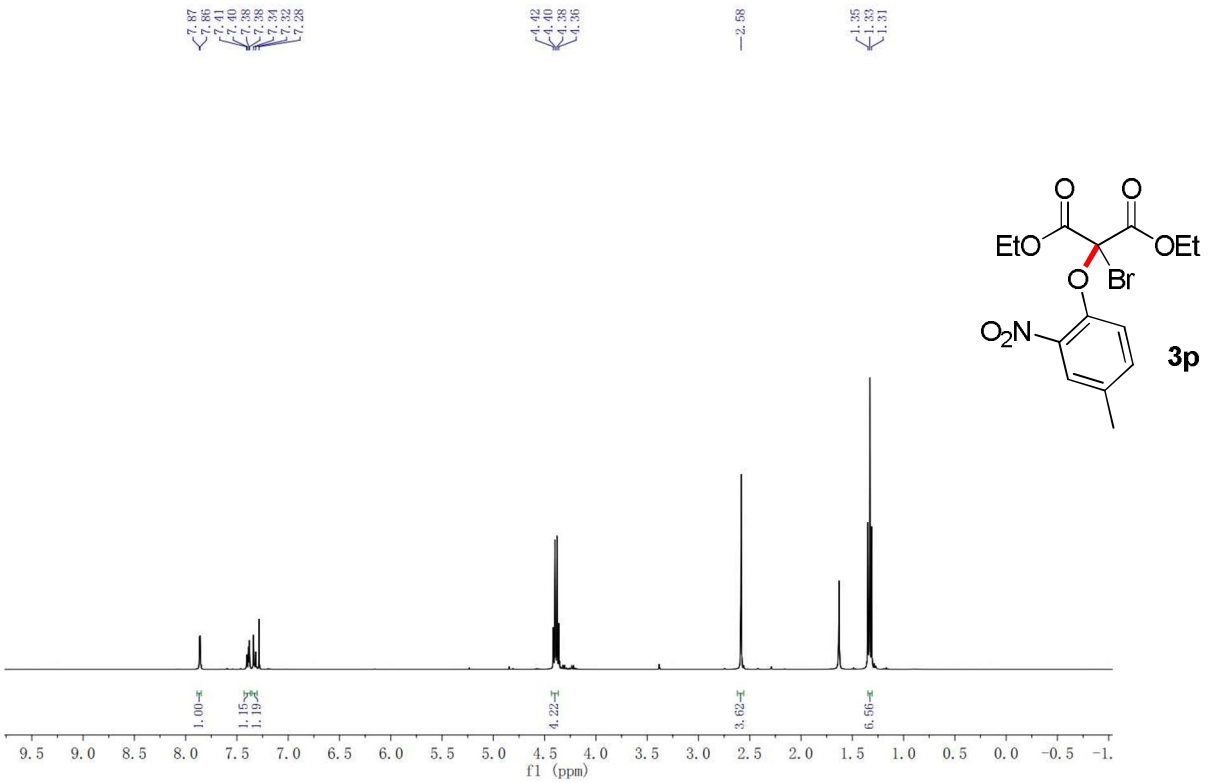


Figure S38. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of **3p**.

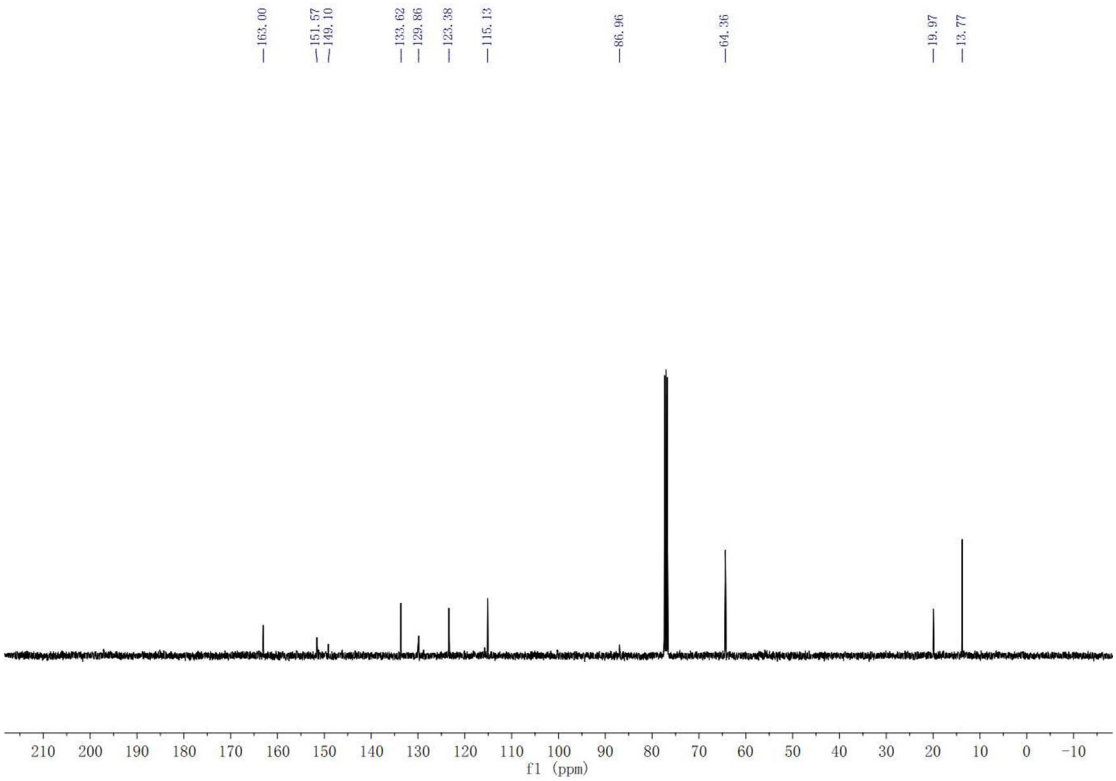


Figure S39. $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of **3p**.

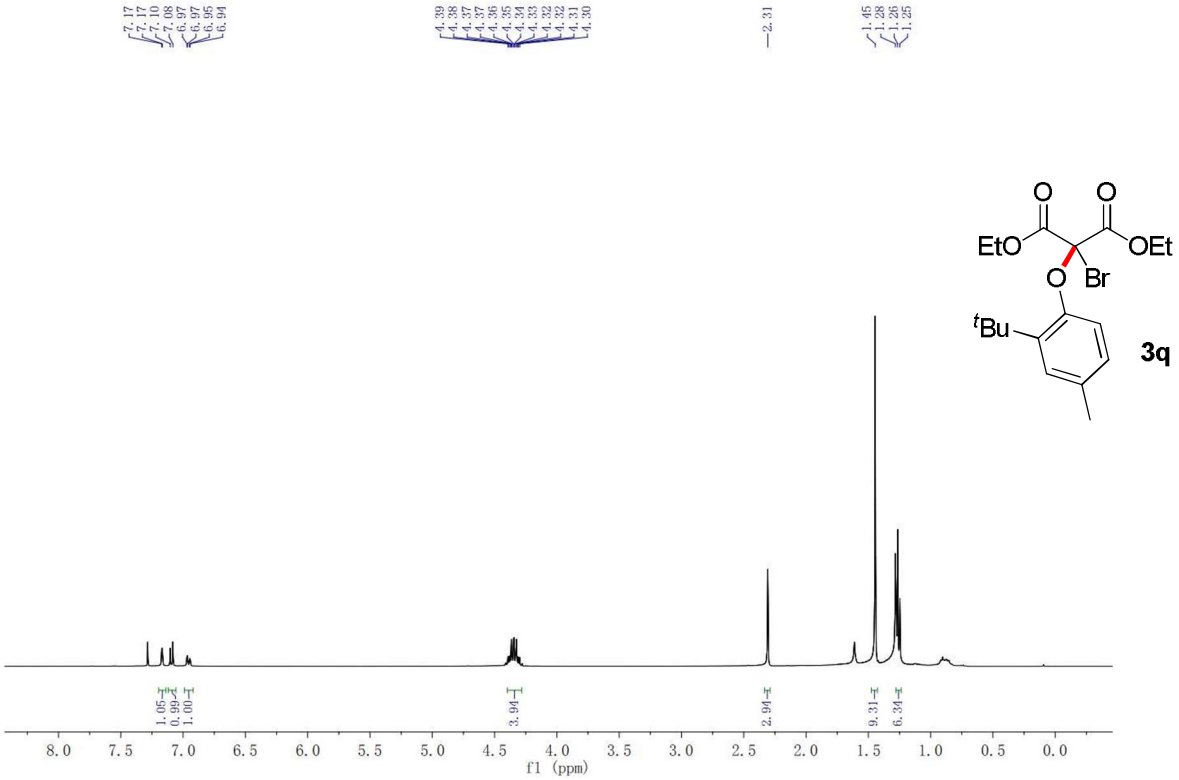


Figure S40. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of **3q**.

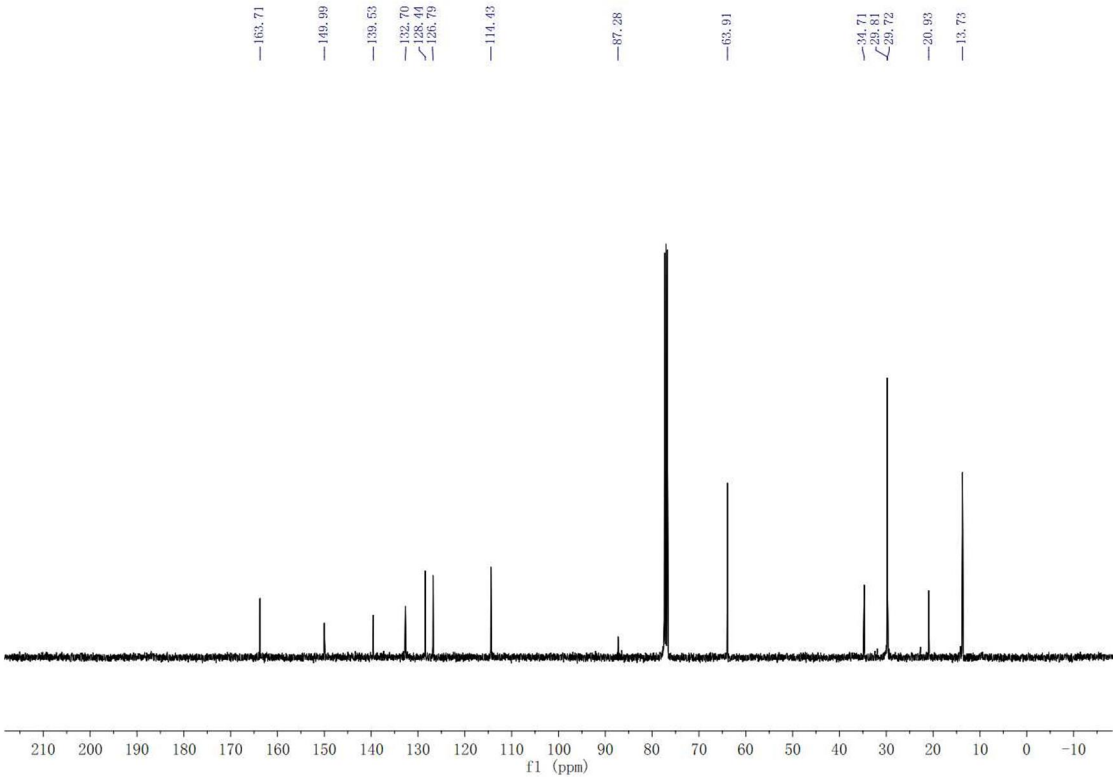


Figure S41. $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of **3q**.

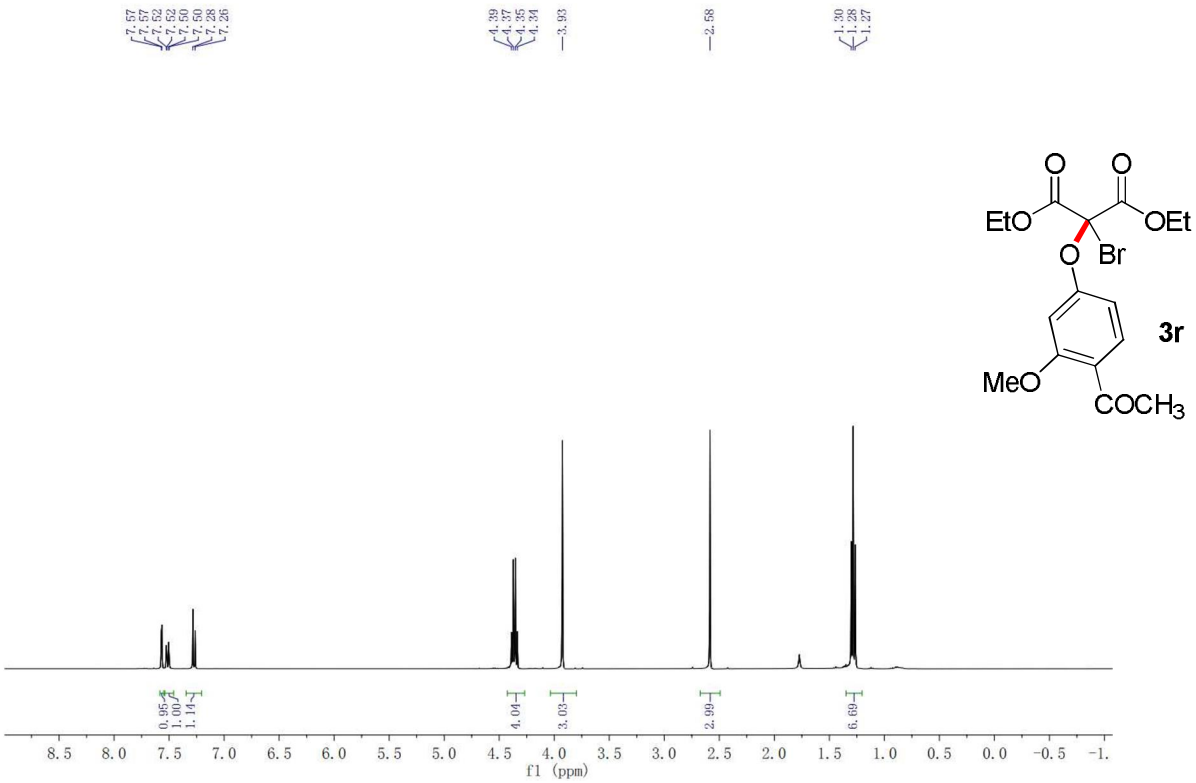


Figure S42. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of **3r**.

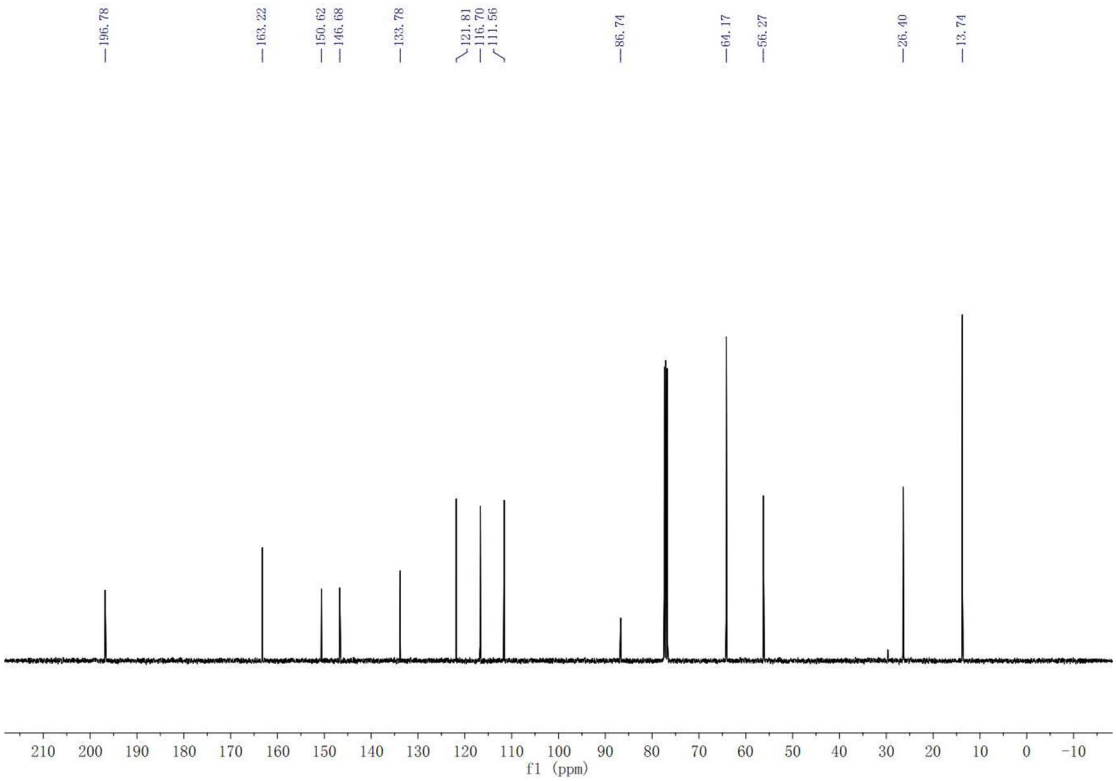


Figure S43. $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of **3r**.

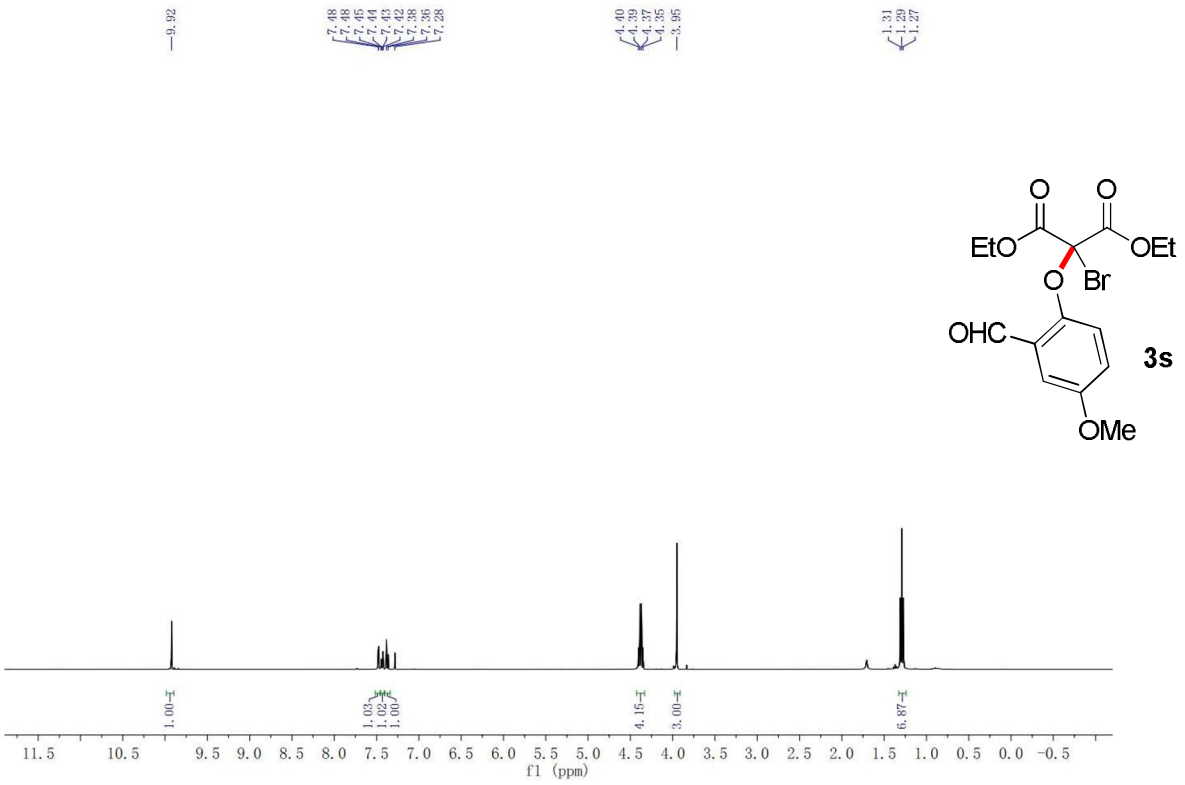


Figure S44. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of **3s**.

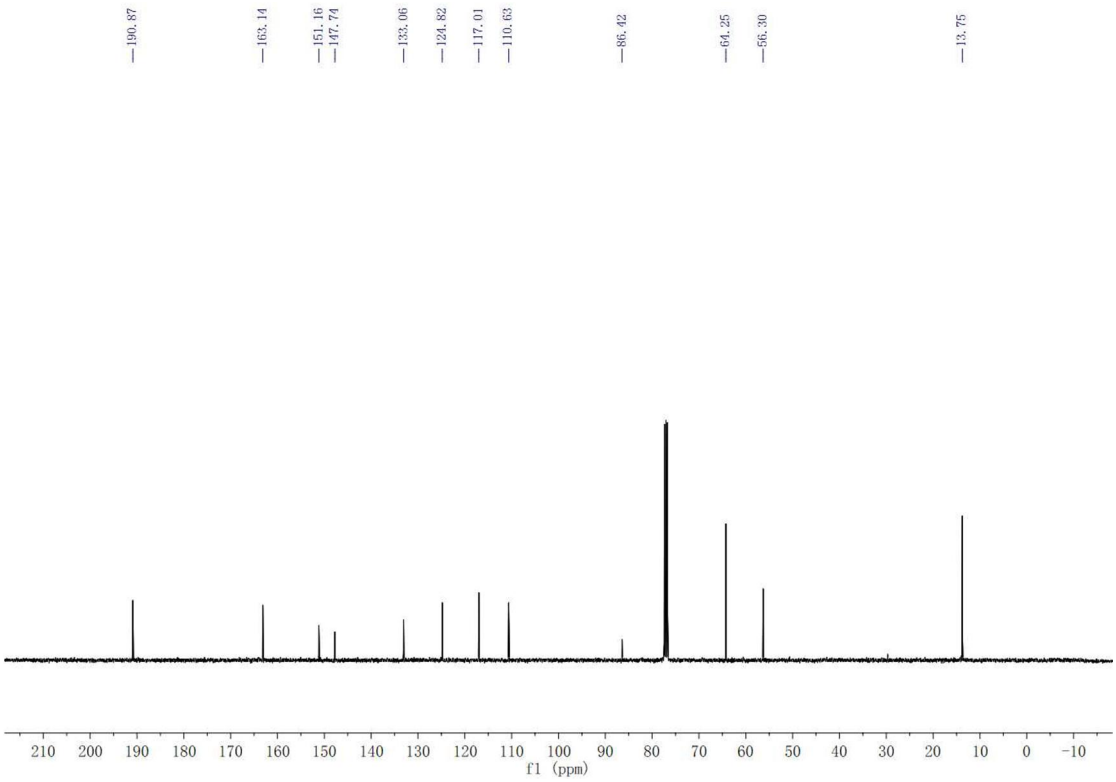


Figure S45. $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of **3s**.

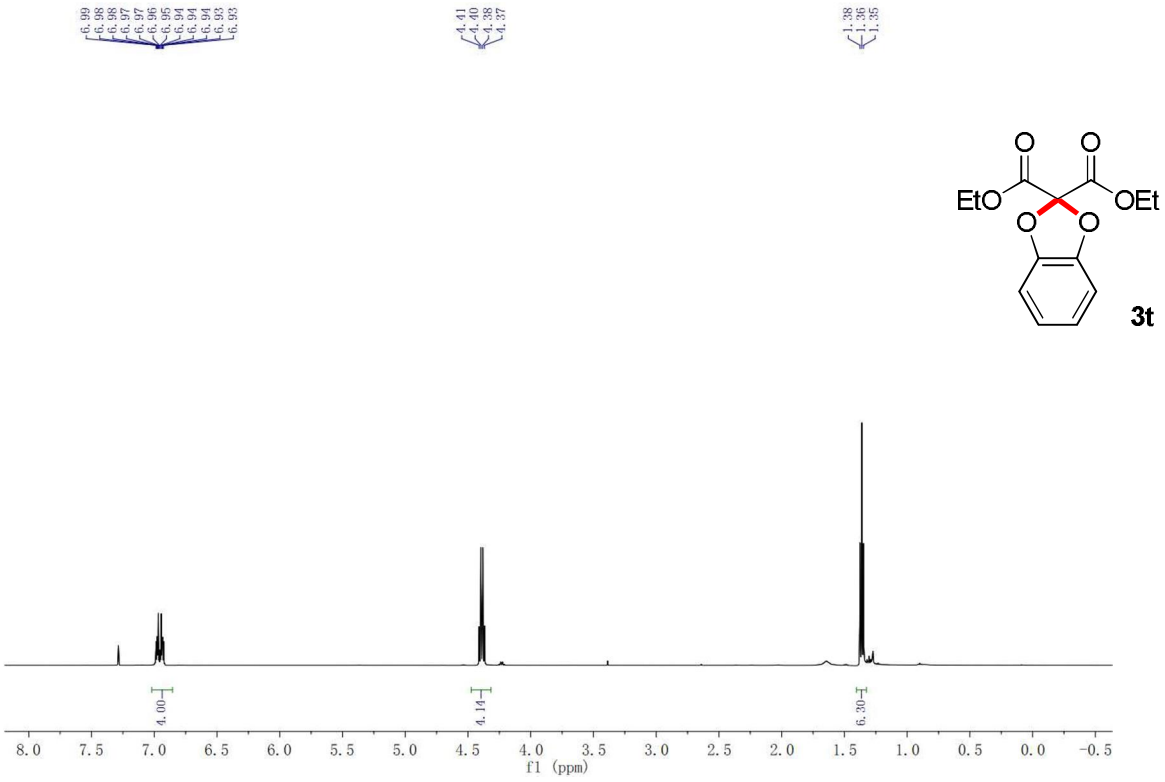


Figure S46. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of **3t**.

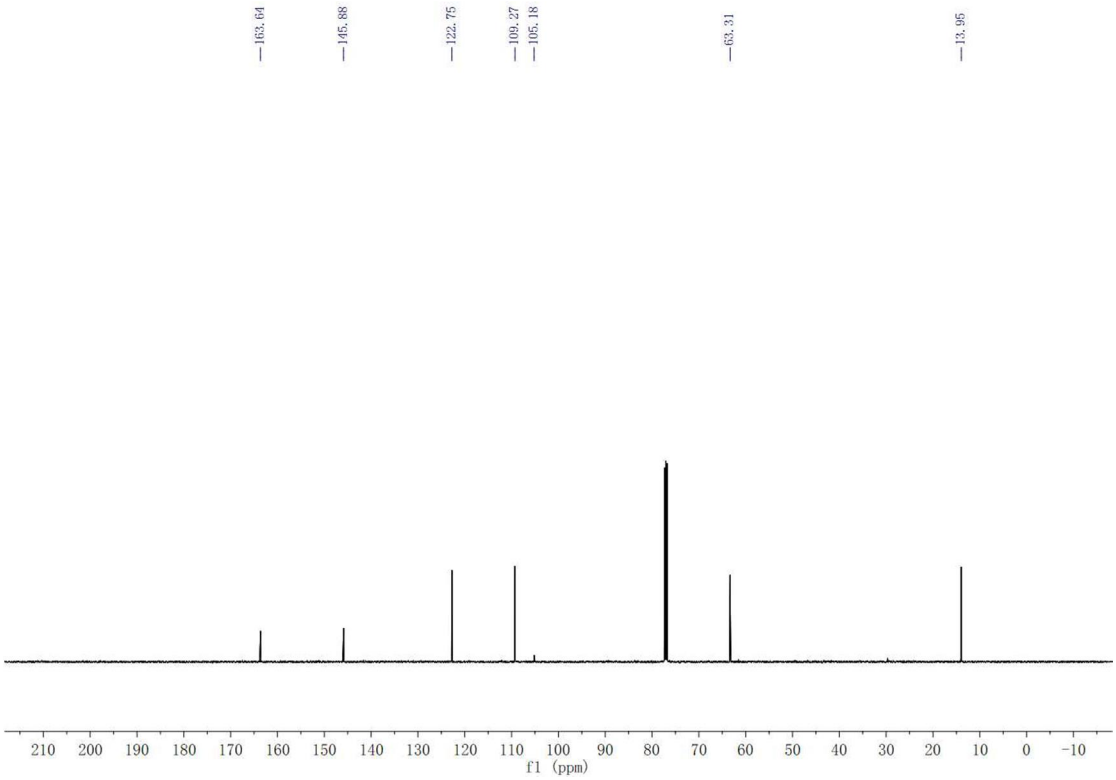


Figure S47. $^{13}C\{^{1}H\}$ NMR (101 MHz, 298 K, $CDCl_3$) spectrum of **3t**.

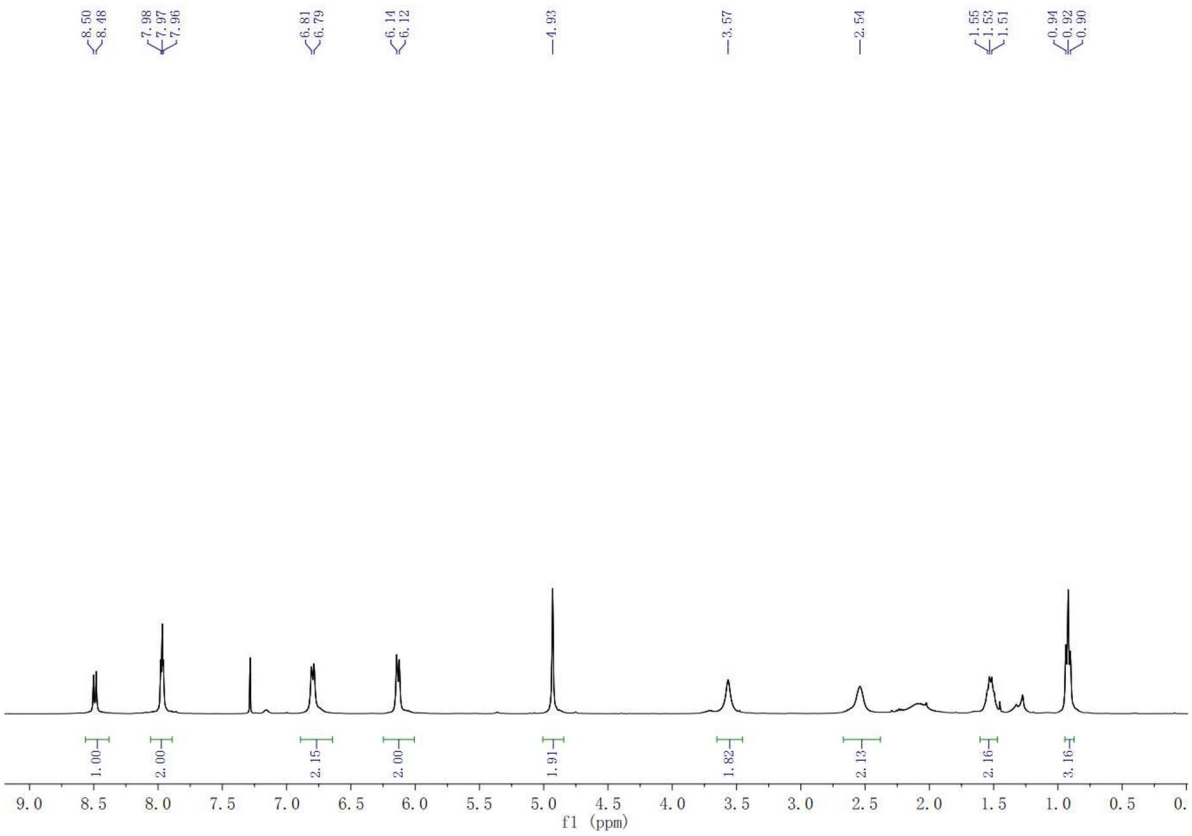


Figure S48. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of [Cu(**L4**)$_2$]PF_6.

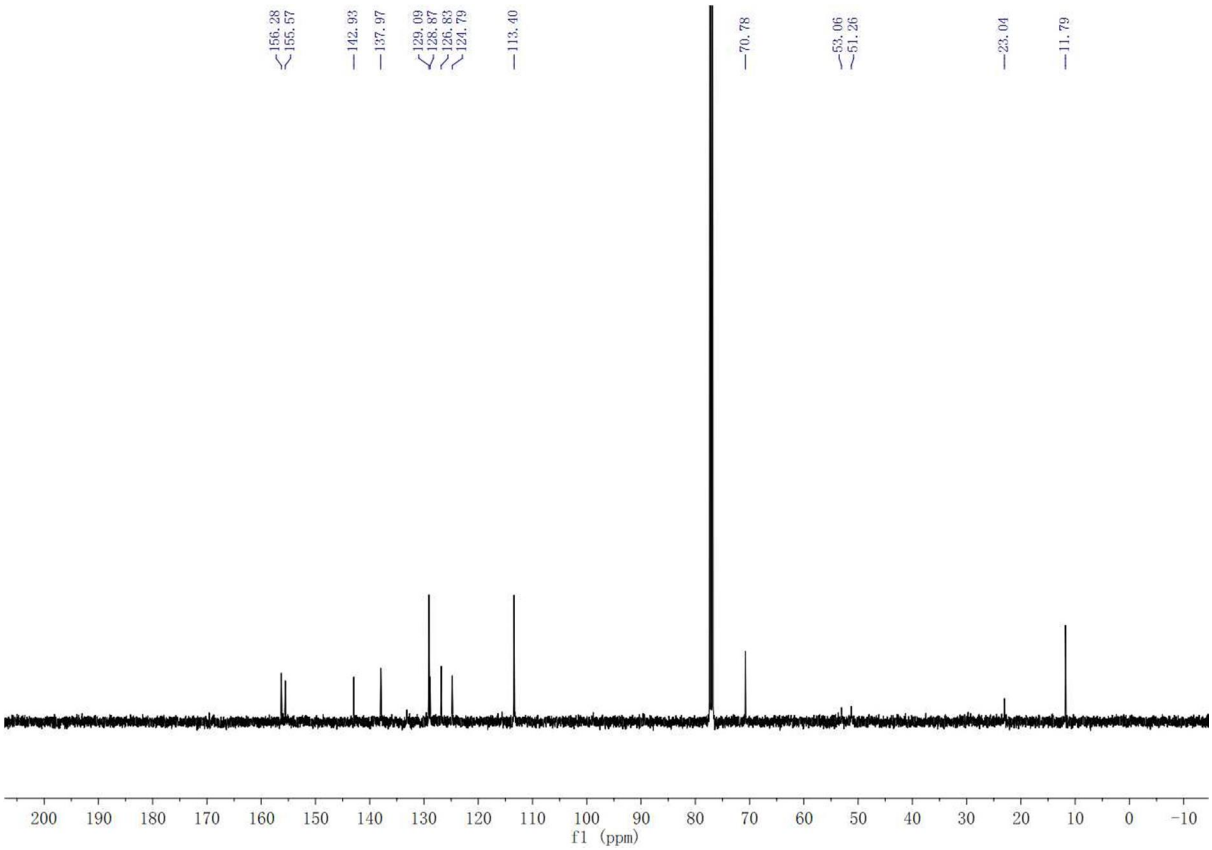


Figure S49. $^{13}C\{^{1}H\}$ NMR (126 MHz, 298 K, $CDCl_3$) spectrum of [Cu(**L4**)$_2$]PF_6.

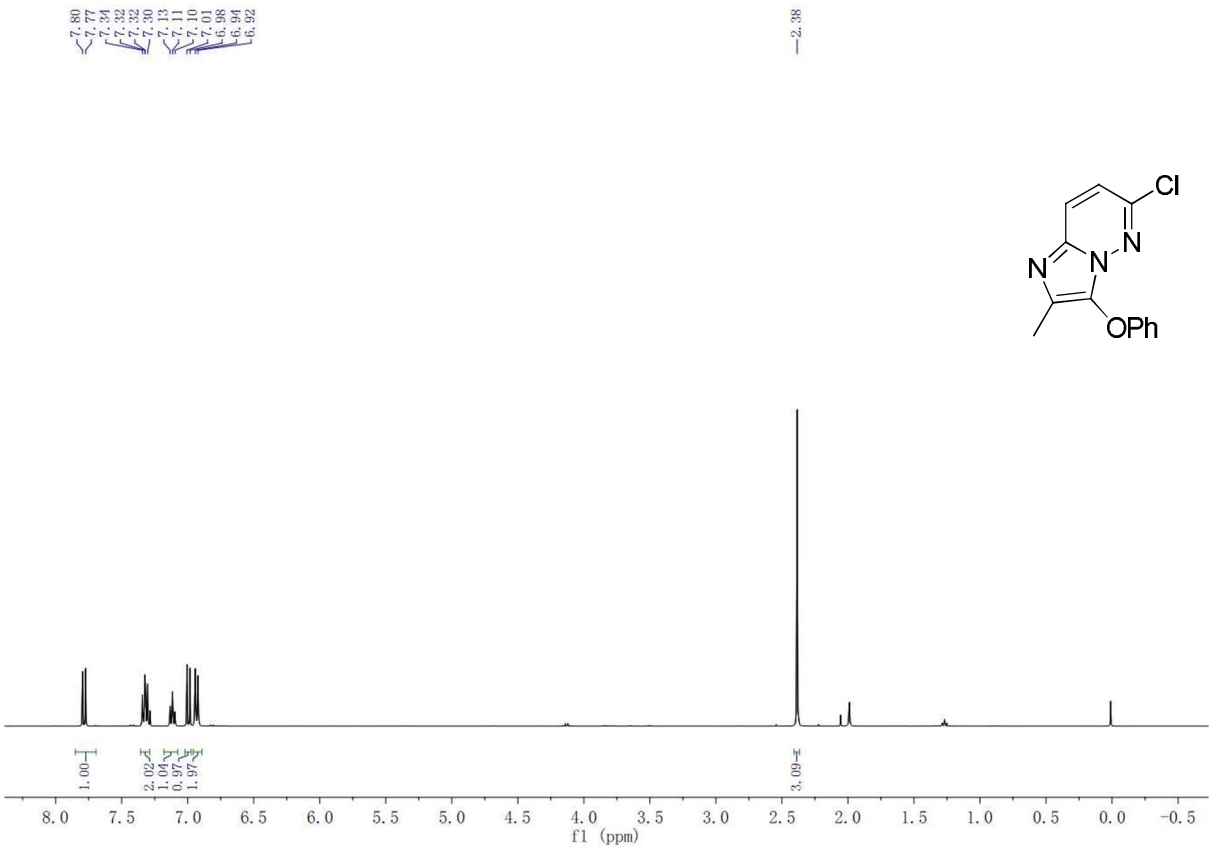


Figure S50. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of **5**.

7. References

1. Yee, C.-C.; Ng, A. W. H.; Au-Yeung, H. Y. *Chem. Commun.* **2019**, 55, 6169.
2. Robins, A. H. Comp. Incorp. *US5192785*, **1993**, A.
3. Ali, M. H.; Brookings, D. C.; Brown, J. A.; Hutchings, M. C.; Jackson, V. E.; Kroeplien, B.; Porter, J. R.; Quincey, J. R. *U.S. Patent* **2015**, 9, 703.
4. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, 37, 785.
5. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R; Li, X. et. al. *Gaussian 16. Revision B*, 01. **2016**.
6. Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, 82, 270.
7. Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, 28, 213.
8. Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, 56, 2257.
9. Rassolov, V. A.; Ratner, M. A.; Pople, J. A.; Redfern, P. C.; Curtiss, L. A. *J. Comput. Chem.* **2001**, 22, 976
10. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, 113, 6378.
11. Patil, Y. P.; Nethaji, M. *RSC Adv.* **2014**, 4, 44938.
12 Paul, N. D.; Chirila, A.; Lu, H.; Zhang, X. P.; de Bruin, B. Chem. Eur. J. **2013**, *19*, 12953.
13. Takemura, K. H.; Pulickal, S. M.; Hoff, F. O. *J. Org. Chem.* **1971**, *36*, 3646.