Electrochemical Aerobic Wacker-type Oxygenation of

Triaryl Substituted Alkenes to 1,2,2-Triarylethanones

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Supporting Information

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1. General Information

All reactions that required anhydrous conditions were carried out using standard procedures under an argon atmosphere. Unless otherwise noted, materials were purchased from commercial suppliers and used without any additional purification. The solvents were dried by distillation using the appropriate drying reagents. Other chemicals were obtained from commercial sources and were used without any additional purification.

Column chromatography was typically conducted using silica gel (300-400 mesh), and the reactions were monitored using thin-layer chromatography (TLC) with 210 nm/254 nm UV light to observe the reaction progress.

¹H NMR (400 MHz), ¹³C NMR (100 MHz), and ¹⁹F NMR (376 MHz) spectra were acquired using a 400 MHz spectrometer in CDCl₃. The chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as the internal standard. The NMR signals are described as singlet (s), doublet (d), or multilet (m), and the coupling constants are given in hertz (Hz). Highresolution mass spectra (HRMS) were acquired using an electrospray ionization (ESI) and electron ionization (EI) source, coupled with a time-of-flight (TOF) detector mass spectrometer. The melting points were measured using a digital melting point detector.

Cyclic voltammetric (CV) curves were recorded using a three-electrode setup. The working electrode was a platinum plate, and a platinum wire served as counter electrode. Saturated calomel electrode (SCE) was used as the reference electrode. The working electrode was polished before recording each cyclic voltammetry (CV) measurements.

entry	electricity	solvent	atmosphere	Yield (%)
1	LiClO ₄	CH ₃ CN	O ₂	67
2	LiClO ₄	THF	O_2	N.R.
3	LiClO ₄	CH_2Cl_2	O_2	N.R.
4	LiClO ₄	EA	O_2	N.R.
5	LiClO ₄	DMSO	O_2	< 5
6	LiClO ₄	DMF	O_2	N.R.
7	LiClO ₄	CHCl ₃	O_2	N.R.
8	LiClO ₄	EtOH	O_2	N.R.

2. The condition optimization of solvent and electrochemical oxidation of other olefins Table S1: the condition optimization of solvent^a

[a] Undivided cell, graphite felt cathode (2 cm x 1 cm x 0.5 cm), **1a** (0.2 mmol), anhydrous solvent (5 mL), constant voltage at 5 V, room temperature, 1.5 h.

Table S2: electrochemical oxidation of other olefins^a

entry	olefins	Yield ^b (%)
1	styrene	trace
2	(Z)-1,2-diphenylethene	N.R.
3	trans-stilbene	N.R.
4	ethene-1,1-diyldibenzene	trace
5	1,1,2,2-tetraphenylethene	trace
6	1-(4-bromophenyl)-1,2,2-triphenylethylene	N.R.

[a] Undivided cell, graphite felt cathode (2 cm x 1 cm x 0.5 cm), **1a** (0.2 mmol), anhydrous solvent (5 mL), constant voltage at 5 V, room temperature, 1.5 h. [b] Unseparated yield, The result was determined by LC-MS.

3. X-ray data of 2-(4-fluorophenyl)-1,2-diphenylethan-1-one (2b):

Single crystals of $C_{20}H_{15}FO$ (2b) were figure S1. A suitable crystal was selected and on a CCD area detector diffractometer. The crystal was kept at 100.15 K during data collection. Using Olex₂ ^[1], the structure was solved with the XT ^[2] structure solution program using Intrinsic Phasing and refined with the XL ^[3]refinement package using Least Squares minimisation. Further information on the crystal structure determinations have been deposited with the Cambridge Crystallographic Data Center [2b(1 a): CCDC 2323256]. Figure S1 shows the X-ray data of 2b.

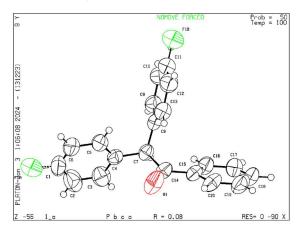


Fig S1: X-ray data of 2-(4-fluorophenyl)-1,2-diphenylethan-1-one (2b)

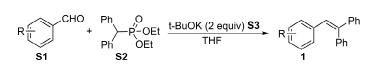
Item	Date
Identification code	2b(1_a)
Empirical formula	$C_{20}H_{15}FO$
Formula weight	290.32
Temperature (K)	100.15
Crystal system	orthorhombic
Space group	Pbca
A (Å)	16.4099(16)
b (Å)	10.0684(10)
c (Å)	18.6788(16)
α (°)	90
β(°)	90
γ (°)	90
Volume (Å ³⁾	3086.1(5)
Ζ	8
$ ho_{calc} \left(g/cm^3\right)$	1.250
μ (mm ⁻¹)	0.677
F (000)	1216.0
Crystal size (mm ³)	$0.22 \times 0.2 \times 0.18$
Radiation	$CuK\alpha$ ($\lambda = 1.54178$)
2θ range for data collection (°)	9.47 to 133.512
Index ranges	$-19 \leqslant h \leqslant 16, -11 \leqslant k \leqslant 8,$
	$-22 \leq 1 \leq 21$
Reflections collected	15338
Independent reflections	2713 [$R_{int} = 0.0779, R_{sigma} = 0.0650$]
Data/restraints/parameters	2713/2/203
Goodness-of-fit on F ²	1.081
Final R indexes [I>=2 σ (I)]	$R_1 = 0.0822, wR_2 = 0.2170$
Final R indexes [all data]	$R_1 = 0.0998, wR_2 = 0.2324$
Largest diff. peak/hole (e Å ⁻³)	0.30/-0.31

Table S3: Crystallographic data and structural refinement for compound 2b

4. General procedure

4.1 General procedure for the substrates

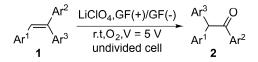
Substrates 1 were synthesized according to the reported literature^[4].



The potassium t-butoxide (**t-BuOK**) (1.12 g, 10 mmol, 2 equiv) was added dropwise to a solution of diethyl benzhydrylphosphonate (**S2**) (3.04 g, 10 mmol, 2 equiv) in tetrahydrofuran (THF, 50 mL) under argon atmosphere at -78 °C. Subsequently, the mixture was stirred for 30 minutes at -78 °C.

Then, ArCHO **S1** (5 mmol, 1 equiv) was added, and stirring was continued until the reaction mixture slowly warmed to room temperature overnight. After the reaction was completed, the mixture was concentrated under reduced pressure. The residue was then extracted with ethyl acetate (EtOAc, $3 \times 20 \text{ mL}$), and the combined organic layer was washed with water and brine. It was then dried over anhydrous magnesium sulfate (MgSO₄), filtered, and concentrated. The residue was purified by flash chromatography using silica gel, resulting in the desired product.

4.2 General procedure of electrochemical oxidation



A 10 mL two-necked heart-shaped flask was equipped with a stir bar. Substrate 1 (0.2 mmol) and LiClO₄ (0.1mmol) were added to the flask, followed by 5 mL of CH₃CN solvent. The reaction flask was equipped with graphite felt (2 cm \times 1 cm \times 0.5 cm) as the anode and cathode. Two electrodes were separated by a Teflon film, which served as a spacer between the anode and cathode. The entire cell was undivided. The graphite felt anode was attached to a platinum wire, and cathode was attached to a silver wire. A Teflon wire was tied around two electrodes. The solution was stirred and electrolyzed at a constant voltage of 5 V for 1.5 hours at room temperature without a reference electrode, in the presence of oxygen. When the reaction was completed, as monitored with TLC and GC-MS analysis, the mixture was extracted with ethyl acetate (3 \times 15 mL). The combined organic layer was combined, washed with brine (10 mL), and then dried over MgSO₄. It was filtered, and concentrated under reduced pressure. Purified product **2** was obtained after column chromatography using silica gel.

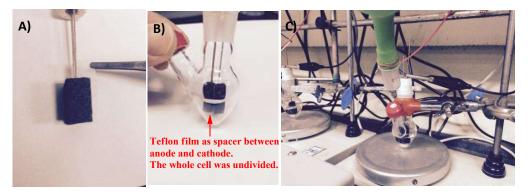
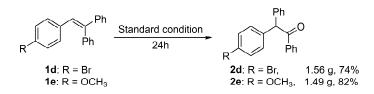


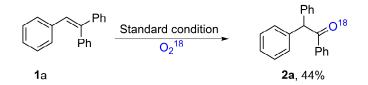
Figure S2. Graphical guide for the 0.2 mmol reaction setup. A) A Teflon film was put between the anode and cathode (made of graphite felts) to act as an isolated film and a spacer; B) The isolated anode and cathode were put inside the two-necked heart-shaped flask for the electrochemical reaction; C) An overall view of the electrochemical reaction setup

5. Scale-up transformation of 2d/2e



In an undivided flask (100 mL) equipped with a stir bar, 1d/1e (6 mmol), LiClO₄ (3 mmol), and CH₃CN (V = 90 mL) were added. The reaction flask was equipped with graphite felt as both the anode and cathode, with dimensions of 3.6 cm × 1.8 cm × 0.5 cm for each electrode. The solution was stirred and electrolyzed at a constant voltage of 5 V without a reference electrode for 45 hours at room temperature in the presence of oxygen. After completing the reaction, the mixture was quenched with water (200 mL) and extracted with ethyl acetate (3 × 50 mL). The combined organic layer was combined, washed with brine (50 mL), and then dried over MgSO₄. It was filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether (PE) and ethyl acetate (EA) as the eluent. This process yielded the desired product 2d/2e in solid form.

6. Isotope labeling experiment6.1 O₂¹⁸ labeling experiment



The isotope labeling experiment was designed to rationalize the reaction pathway. A 10 mL twonecked heart-shaped flask was equipped with a stir bar. 1a (0.2 mmol), LiClO₄ (0.1 mmol), and 5 mL of CH₃CN solvent were added. The reaction flask was equipped with graphite felt ($2 \text{ cm} \times 1 \text{ cm}$ \times 0.5 cm) as the anode and cathode. Two electrodes were separated by a Teflon film, which acted as an isolated film and a spacer between the anode and cathode. The entire cell was undivided. The graphite felt anode is attached to a platinum wire, and the cathode was attached to a silver wire. A Teflon wire was tied around two electrodes. The reaction was degassed and backfilled with argon three times. After that, the flask was vacuumed, and then 10 mL of O218 was added to the flask using a syringe. The solution was stirred and electrolyzed at a constant voltage of 5 V without a reference electrode for 1.5 hours at room temperature. When the reaction was completed, as monitored with TLC and GC-MS analysis, the mixture was extracted with ethyl acetate (3×15 mL). The organic layer was combined, washed with brine (10 mL), and then dried over MgSO4. It was filtered and concentrated under reduced pressure. Purified O18 labeled 2a was obtained after column chromatography using silica gel. The purified product was detected using a high-resolution mass spectrometer, and the resulting picture is shown in the following figure. HRMS $(ESI)([M + H]^+)$ Calcd For C₂₀H₁₇O¹⁸: 275.1317, found: 275.1322.

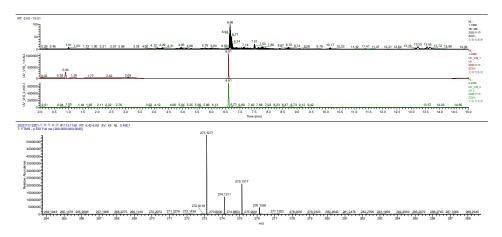


Figure S3 High resolution mass spectrum of O¹⁸ labeled product 2a when using O₂¹⁸.

6.2 H₂O¹⁸ labeling experiment

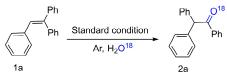


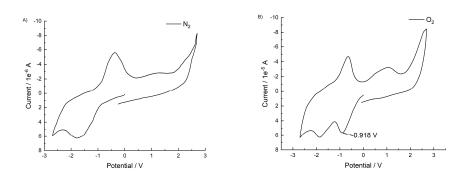
Table S4 Results of H₂O¹⁸ labeling experiment.

	1		
solvent	additive	equivalent	yield
CH ₃ CN	H ₂ O	0.5	N.R.
CH ₃ CN	H ₂ O	1.0	N.R.
CH ₃ CN	H ₂ O	2.0	N.R.
CH ₃ CN	H_2O^{18}	0.5	N.R.
CH ₃ CN	H_2O^{18}	1.0	N.R.
CH ₃ CN	H_2O^{18}	2.0	N.R.
CH ₃ CN	H_2O	$CH_3CN/H_2O = 4:1^a$	N.R.

[a] The reaction solvent used here consisted of a mixture of CH_3CN and H_2O in a ratio of 4:1.

An argon atmosphere was employed instead of an oxygen atmosphere under standard conditions. Different equivalents of water (H_2O^{18}) were added to the electrochemical reaction tank to observe the reaction phenomenon. The data in the above table were obtained after monitoring through TLC and LC-MS.

7. Cyclic voltammetry experiment



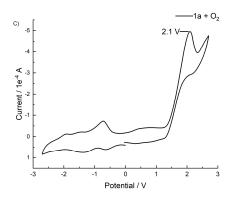
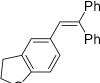


Figure S3. A) Cyclic voltammetry experiment of N_2 : a solution of LiClO₄ (0.1 mmol) in 5 mL anhydrous CH₃CN was subject to cyclic voltammetry experiment under N_2 atmosphere. B) Cyclic voltammetry experiment of O_2 : a solution of LiClO₄ (0.1 mmol) in 5 mL anhydrous CH₃CN was subject to cyclic voltammetry experiment under O_2 atmosphere. C) A solution of substrate **1a** (0.2 mmol), LiClO₄ (0.1 mmol) in 5 mL anhydrous CH₃CN was subject to cyclic voltammetry experiment under O_2 atmosphere. For all experiments, cyclic voltammetry (CV) curves were recorded using a three-electrode setup. The working electrode was a platinum plate, and a platinum wire served as counter electrode. A saturated calomel electrode (SCE) was used as the reference electrode. The working electrode was polished before recording each cyclic voltammetry (CV) curve.

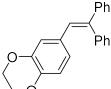
8. Spectroscopic data for the substrates

5-(2,2-diphenylvinyl)-2,3-dihydrobenzofuran 1k:



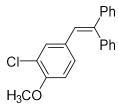
^O 2.32 g, yield: 78%, chromatography on silica gel (n-Hexane:EtOAc = 98:2, v/v, $R_f = 0.4$). ¹H NMR (400 MHz, Chloroform-*d*) $\delta = 8.06 - 8.00$ (m, 2H), 7.56 - 7.51 (m, 1H), 7.46 - 7.41 (m, 2H), 7.37 - 7.32 (m, 2H), 7.30 - 7.27 (m, 3H), 7.14 (s, 1H), 7.03 (dd, J = 8.2, 1.6 Hz, 1H), 6.75 (d, J = 8.2 Hz, 1H), 5.99 (s, 1H), 4.56 (t, J = 8.7 Hz, 2H), 3.19 (t, J = 8.7 Hz, 2H). ¹³C NMR (100 MHz, Chloroform-*d*) $\delta = 198.54$, 159.26, 139.62, 136.87, 132.87, 130.91, 128.96, 128.86, 128.81, 128.59, 128.51, 127.56, 126.93, 125.57, 109.25, 71.25, 58.73, 29.65. HRMS (ESI) ([M + Na]⁺) Calcd For C₂₂H₁₈ONa: 321.1250, found: 321.1244.

6-(2,2-diphenylvinyl)-2,3-dihydrobenzo[b][1,4]dioxine 11:



 $\begin{array}{c} \label{eq:constraint} $$ -O$ 2.36 g, yield: 75\%, chromatography on silica gel (n-Hexane:EtOAc = 98:2, v/v, R_f = 0.38). ^1H NMR (400 MHz, Chloroform-$ *d* $) <math>\delta$ = 7.41 – 7.24 (m, 10H), 6.88 (s, 1H), 6.66 – 6.64 (m, 1H), 6.56 – 6.54 (m, 2H), 4.23 – 4.20 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ = 143.46, 142.89, 142.57, 141.06, 140.45, 131.00, 130.29, 128.71, 128.14, 127.47, 127.38, 127.36, 127.23, 123.15, 118.18, 116.66, 64.41, 64.22. HRMS (ESI) ([M+H]^+) Calcd For C_{22}H_{19}O_2: 315.1380, found: 315.1388. \\ \end{array}

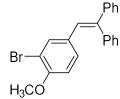
(2-(3-chloro-4-methoxyphenyl)ethene-1,1-diyl)dibenzene 1m:



2.37 g, yield: 74%, chromatography on silica gel (n-Hexane:EtOAc = 98:2, v/v,

 R_f = 0.4).¹H NMR (400 MHz, Chloroform-*d*) δ = 7.41 – 7.31 (m, 8H), 7.25 – 7.21 (m, 2H), 7.05 (d, *J* = 2.0 Hz, 1H), 6.90 – 6.86 (m, 2H), 6.70 (d, *J* = 8.7 Hz, 1H), 3.86 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ = 153.66, 143.10, 142.08, 140.10, 131.28, 131.05, 130.25, 128.84, 128.79, 128.21, 127.55, 127.49, 127.42, 126.22, 121.87, 111.44, 56.05. HRMS (EI) ([M]⁺) Calcd For C₂₁H₁₇ClO: 320.0962, found: 320.0957.

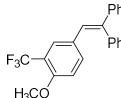
(2-(3-bromo-4-methoxyphenyl)ethene-1,1-diyl)dibenzene 1n:



2.67 g, yield: 73%, chromatography on silica gel (n-Hexane:EtOAc = 98:2, v/v,

R_f = 0.35). ¹H NMR (400 MHz, Chloroform-*d*) δ = 7.36 (m, 3H), 7.33 – 7.27 (m, 5H), 7.21 – 7.19 (m, 3H), 6.89 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.85 (s, 1H), 6.65 (d, *J* = 8.6 Hz, 1H), 3.83 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ = 154.53, 143.07, 142.09, 140.09, 134.44, 131.54, 130.26, 129.51, 128.78, 128.21, 127.54, 127.49, 127.42, 126.08, 111.25, 111.08, 56.14. HRMS (EI) ([M]⁺) Calcd For C₂₁H₁₇BrO:364.0457, found: 364.0456.

(2-(4-methoxy-3-(trifluoromethyl)phenyl)ethene-1,1-diyl)dibenzene 1o:



2.5 g, yield: 71%, chromatography on silica gel (n-Hexane:EtOAc = 98:2, v/v,

R_f = 0.4). ¹H NMR (400 MHz, Chloroform-*d*) δ = 7.51 – 7.39 (m, 9H), 7.37 – 7.32 (m, 2H), 7.24 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.05 (s, 1H), 6.84 (d, *J* = 8.7 Hz, 1H), 3.91 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ = 156.13 (q, *J*_{C-F} = 1.8 Hz), 143.04, 142.50, 140.14, 134.13, 130.29, 129.76, 129.04, 128.49 (q, *J* = 5.4 Hz), 128.40, 127.76 (q, *J* = 5.1 Hz), 127.53, 126.24, 123.64 (q, *J* = 272.6 Hz), 118.33 (q, *J* = 30.7 Hz), 111.66, 55.89. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ = -62.38. HRMS (EI) ([M]⁺) Calcd For C₂₂H₁₇OF₃:354.1226, found: 354.1222.

9. Spectroscopic data of the products

1,2,2-triphenylethan-1-one 2a:



32 mg, yield: 58.7%, chromatography on silica gel (n-Hexane:EtOAc = 98:2, v/v, $R_f = 0.4$). ¹H NMR (400 MHz, Chloroform-*d*) $\delta = 8.09 - 8.02$ (m, 2H), 7.57 - 7.53 (m, 1H), 7.467 - 7.43 (m, 2H), 7.39 - 7.27 (m, 100H), 6.09 (s, 1H). ¹³C NMR (100 MHz, Chloroform-*d*) $\delta = 198.14$, 139.06, 136.82, 132.98, 129.11, 128.92, 128.68, 128.57, 127.10, 59.40. HRMS (ESI) ([M + H]⁺) Calcd For C₂₀H₁₇O⁺: 273.1274, found: 273.1276. HRMS (ESI) ([M + H]⁺) Calcd For C₂₀H₁₇O⁻: 273.1276.

2-(4-fluorophenyl)-1,2-diphenylethan-1-one 2b:



F 49 mg, yield: 84%, chromatography on silica gel (n-Hexane:EtOAc = 98:2, v/v, R_f = 0.45). ¹H NMR (400 MHz, Chloroform-*d*) δ = 8.08 – 8.00 (m, 2H), 7.58 – 7.52 (m, 1H), 7.49 – 7.42 (m, 2H), 7.39 – 7.34 (m, 2H), 7.33 – 7.25 (m, 5H), 7.09 – 7.00 (m, 2H), 6.06 (s, 1H). ¹³C NMR (100 MHz, Chloroform-*d*) δ = 198.03, 161.93 (d, *J* = 245.9 Hz), 138.9, 136.66, 134.90 (d, *J* = 3.3 Hz), 133.12, 130.70 (d, *J* = 8.0 Hz), 128.96, 128.90, 128.85, 128.63, 127.27, 115.49 (d, *J* = 21.4 Hz), 58.51. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ = -115.59. HRMS (ESI) ([M + H]⁺) Calcd For C₂₀H₁₆FO: 291.1180, found: 291.1183.

2-(4-chlorophenyl)-1,2-diphenylethan-1-one 2c:



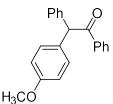
Cl 50 mg, yield: 82%, chromatography on silica gel (n-Hexane:EtOAc = 98:2, v/v, R_f = 0.45). ¹H NMR (400 MHz, Chloroform-*d*) δ = 8.00 – 7.98 (m, 2H), 7.55 – 7.51 (m, 1H), 7.45 – 7.39 (m, 2H), 7.36 – 7.25 (m, 7H), 7.23 – 7.18 (m, 2H), 6.01 (s, 1H). ¹³C NMR (100 MHz, Chloroform-*d*) δ = 197.79, 138.61, 137.68, 136.60, 133.19, 133.11, 130.50, 128.98, 128.92, 128.90, 128.79, 128.67, 127.36, 58.68. HRMS (ESI) ([M + H]⁺) Calcd For C₂₀H₁₆ClO: 307.0884, found: 307.0889.

2-(4-bromophenyl)-1,2-diphenylethan-1-one 2d:



Br 53 mg, yield: 80%, chromatography on silica gel (n-Hexane:EtOAc = 98:2, v/v, R_f = 0.3). ¹H NMR (400 MHz, Chloroform-*d*) δ = 8.05 – 8.00 (m, 2H), 7.58 – 7.53 (m, 1H), 7.50 – 7.42 (m, 4H), 7.39 – 7.33 (m, 2H), 7.31 – 7.28 (m, 3H), 7.20 – 7.16 (m, 2H), 6.03 (s, 1H). ¹³C NMR (100 MHz, Chloroform-*d*) δ = 197.66, 138.49, 138.19, 136.53, 133.18, 131.70, 130.85, 128.94, 128.88, 128.64, 127.34, 121.22, 58.70. HRMS (ESI) ([M + H]⁺) Calcd For C₂₀H₁₆BrO: 351.0379, found: 351.0385.

2-(4-methoxyphenyl)-1,2-diphenylethan-1-one 2e:



51 mg, yield: 84%, chromatography on silica gel (n-Hexane:EtOAc = 98:2, v/v,

R_f = 0.32). ¹H NMR (400 MHz, Chloroform-*d*) δ = 8.03 (d, *J* = 7.5 Hz, 2H), 7.55 – 7.52 (m, 1H), 7.45 – 7.41 (m, 2H), 7.36 – 7.21 (m, 7H), 6.89 (d, *J* = 8.6 Hz, 2H), 6.02 (s, 1H), 3.80 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ = 198.42, 158.68, 139.48, 136.89, 132.91, 131.13, 130.14, 129.02, 128.90, 128.64, 128.55, 127.00, 114.16, 58.58, 55.19. HRMS (ESI) ([M + H]⁺) Calcd For C₂₁H₁₉O₂: 303.1380, found: 303.1382.

2-(4-(methylthio)phenyl)-1,2-diphenylethan-1-one 2f:

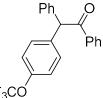


H₃CS

39 mg, yield: 61%, chromatography on silica gel (n-Hexane:EtOAc = 98:2, v/v,

$$\begin{split} &R_{\rm f} = 0.36). \ ^{1}\text{H NMR} \ (400 \ \text{MHz}, \ \text{Chloroform-}d) \ \delta = 8.05 - 8.00 \ (m, \ 2\text{H}), \ 7.56 - 7.52 \ (m, \ 1\text{H}), \ 7.46 \\ &- 7.42 \ (m, \ 2\text{H}), \ 7.38 - 7.33 \ (m, \ 2\text{H}), \ 7.32 - 7.28 \ (m, \ 3\text{H}), \ 7.24 \ (s, \ 4\text{H}), \ 6.03 \ (s, \ 1\text{H}), \ 2.48 \ (s, \ 3\text{H}). \\ &^{13}\text{C NMR} \ (100 \ \text{MHz}, \ \text{Chloroform-}d) \ \delta = 198.06, \ 139.00, \ 137.34, \ 136.76, \ 135.93, \ 133.03, \ 129.57, \\ &129.02, \ 128.90, \ 128.72, \ 128.60, \ 127.15, \ 126.88, \ 58.84, \ 15.77. \ \text{HRMS} \ (\text{ESI}) \ ([\text{M} + \text{Na}]^+) \ \text{Calcd For} \\ &C_{21}\text{H}_{18}\text{OSNa: } 341.0971, \ \text{found: } 341.0969. \end{split}$$

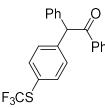
1,2-diphenyl-2-(4-(trifluoromethoxy)phenyl)ethan-1-one 2g:



63 mg, yield: 89%, chromatography on silica gel (n-Hexane:EtOAc = 98:2, v/v,

R_f = 0.32). ¹H NMR (400 MHz, Chloroform-*d*) δ = 8.08 – 8.00 (m, 2H), 7.57 – 7.52 (m, 1H), 7.46 – 7.42 (m, 2H), 7.39 – 7.27 (m, 7H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.09 (s, 1H). ¹³C NMR (100 MHz, Chloroform-*d*) δ = 197.75, 148.26 (q, *J* = 1.8 Hz), 138.52, 137.89, 136.56, 133.22, 130.54, 128.97, 128.94, 128.90, 128.67, 127.42, 120.93, 120.45 (q, *J* = 257.1 Hz), 58.56. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ = -57.76. HRMS (EI) ([M]⁺) Calcd For C₂₁H₁₅F₃O₂: 356.1019, found: 356.1025.

1,2-diphenyl-2-(4-((trifluoromethyl)thio)phenyl)ethan-1-one 2h:



60 mg, yield: 81%, chromatography on silica gel (n-Hexane:EtOAc = 98:2, v/v,

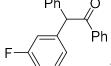
R_f = 0.3). ¹H NMR (400 MHz, Chloroform-*d*) δ = 8.05 – 7.98 (m, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.56 – 7.52 (m, 1H), 7.45 – 7.41 (m, 2H), 7.39 – 7.27 (m, 7H), 6.08 (s, 1H). ¹³C NMR (100 MHz, Chloroform-*d*) δ = 197.48, 142.42, 138.15, 136.54, 136.39, 133.34, 130.35, 129.57 (d, *J* = 308.2 Hz), 129.09, 129.03, 128.96, 128.74, 127.58, 123.07 (d, *J* = 2.0 Hz), 58.98. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ = -42.57. HRMS (EI) ([M]⁺) Calcd For C₂₁H₁₅F₃OS: 372.0790, found: 372.0795.

2-(2-fluorophenyl)-1,2-diphenylethan-1-one 2i:



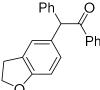
39 mg, yield: 41%, chromatography on silica gel (n-Hexane:EtOAc = 98:2, v/v, R_f = 0.39). ¹H NMR (400 MHz, Chloroform-*d*) δ = 8.07 – 8.02 (m, 2H), 7.56 – 7.52 (m, 1H), 7.46 – 7.28 (m, 8H), 7.14 – 7.07 (m, 3H), 6.35 (s, 1H). ¹³C NMR (100 MHz, Chloroform-*d*) δ = 197.27, 160.16 (d, *J* = 245.8 Hz), 136.78 (d, *J* = 73.5 Hz), 133.07, 130.62 (d, *J* = 3.5 Hz), 129.39, 128.93, 128.88, 128.80, 128.60, 127.45, 126.80 (d, *J* = 14.9 Hz), 124.14 (d, *J* = 3.5 Hz), 115.21 (d, *J* = 22.2 Hz), 51.96 (d, *J* = 2.5 Hz). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ = -116.82. HRMS (ESI) ([M + H]⁺) Calcd For C₂₀H₁₆FO: 291.1180, found: 291.1181.

2-(3-fluorophenyl)-1,2-diphenylethan-1-one 2j:



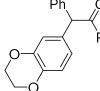
24 mg, yield: 41%, chromatography on silica gel (n-Hexane:EtOAc = 98:2, v/v, R_f = 0.28). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, J = 7.4 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.8 Hz, 2H), 7.36 – 7.27 (m, 6H), 7.06 (d, J = 7.7 Hz, 1H), 7.02 – 6.93 (m, 2H), 6.03 (s, 1H). ¹³C NMR (100 MHz, Chloroform-*d*) δ = 197.59, 162.93 (d, J = 246.2 Hz), 141.60 (d, J = 7.3 Hz), 138.37, 136.63, 133.20, 129.99 (d, J = 8.3 Hz), 129.03, 128.92, 128.67, 127.42, 124.79 (d, J = 2.9 Hz), 116.29 (d, J = 22.1 Hz), 114.10 (d, J = 21.2 Hz), 58.95. ¹⁹F NMR (376 MHz, Chloroformd) δ = -112.67. HRMS (ESI) ([M + H]⁺) Calcd For C₂₀H₁₆FO: 291.1180, found: 291.1182.

2-(3-fluorophenyl)-1,2-diphenylethan-1-one 2k:

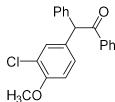


^O 48 mg, yield: 76%, chromatography on silica gel (n-Hexane:EtOAc = 98:2, v/v, $R_f = 0.29$). ¹H NMR (400 MHz, Chloroform-*d*) $\delta = 8.06 - 8.00$ (m, 2H), 7.56 - 7.51 (m, 1H), 7.46 - 7.41 (m, 2H), 7.37 - 7.32 (m, 2H), 7.30 - 7.26 (m, 3H), 7.14 (s, 1H), 7.03 (dd, J = 8.2, 1.7 Hz, 1H), 6.75 (d, J = 8.2 Hz, 1H), 6.00 (s, 1H), 4.56 (t, J = 8.7 Hz, 2H), 3.19 (t, J = 8.7 Hz, 2H). ¹³C NMR (100 MHz, Chloroform-*d*) $\delta = 198.54, 159.26, 139.62, 136.87, 132.87, 130.91, 128.96, 128.86, 128.81, 128.59, 128.51, 127.56, 126.93, 125.57, 109.25, 71.25, 58.73, 29.65. HRMS (ESI) ([M + Na]⁺) Calcd For C₂₂H₁₈O₂Na: 337.1199, found: 337.1197.$

2-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-1,2-diphenylethan-1-one 2l:



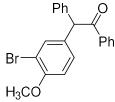
2-(3-chloro-4-methoxyphenyl)-1,2-diphenylethan-1-one 2m:



55 mg, yield: 82%, chromatography on silica gel (n-Hexane:EtOAc = 98:2, v/v,

R_f = 0.36). ¹H NMR (400 MHz, Chloroform-*d*) δ = 8.03 (d, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.38 – 7.28 (m, 6H), 7.16 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.90 (d, *J* = 8.5 Hz, 1H), 6.00 (s, 1H), 3.88 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ = 197.84, 154.08, 138.73, 136.58, 133.11, 132.24, 130.85, 128.89, 128.87, 128.84, 128.62, 128.33, 127.27, 122.57, 112.11, 58.12, 56.08. HRMS (ESI) ([M + H]⁺) Calcd For C₂₁H₁₈ClO₂: 337.0990, found: 337.0994.

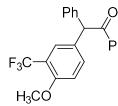
2-(3-bromo-4-methoxyphenyl)-1,2-diphenylethan-1-one 2n:



64 mg, yield: 84%, chromatography on silica gel (n-Hexane:EtOAc = 98:2, v/v,

 R_f = 0.37). ¹H NMR (400 MHz, Chloroform-*d*) δ = 8.04 – 8.01 (m, 2H), 7.58 – 7.50 (m, 2H), 7.47 – 7.41 (m, 2H), 7.39 – 7.33 (m, 2H), 7.31 – 7.28 (m, 3H), 7.21 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 1H), 5.99 (s, 1H), 3.88 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ = 197.83, 154.96, 138.75, 136.57, 133.84, 133.12, 132.68, 129.10, 128.89, 128.87, 128.84, 128.62, 127.27, 111.93, 111.82, 58.04, 56.18. HRMS (ESI) ([M + H]⁺) Calcd For C₂₁H₁₈BrO₂: 381.0485, found: 381.0487.

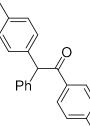
2-(4-methoxy-3-(trifluoromethyl)phenyl)-1,2-diphenylethan-1-one 20:



60 mg, yield: 81%, chromatography on silica gel (n-Hexane:EtOAc = 98:2,

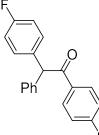
v/v, $R_f = 0.34$). ¹H NMR (400 MHz, Chloroform-*d*) $\delta = 8.05$ (d, J = 7.8 Hz, 2H), 7.58 – 7.54 (m, 2H), 7.46 (t, J = 7.7 Hz, 3H), 7.41 – 7.35 (m, 2H), 7.33 – 7.29 (m, 3H), 6.99 (d, J = 8.6 Hz, 1H), 6.07 (s, 1H), 3.89 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) $\delta = 197.83$, 156.55, 138.65, 136.47, 133.91, 133.21, 130.96, 128.98, 128.89, 128.82, 128.66, 127.76 (q, J = 5.2 Hz), 127.38, 123.52 (q, J = 272.5 Hz), 118.70 (q, J = 30.8 Hz), 112.21, 58.22, 55.91. ¹⁹F NMR (376 MHz, Chloroform-*d*) $\delta = -62.25$. HRMS (ESI) ([M + Na]⁺) Calcd For C₂₂H₁₇F₃O₂Na: 393.1073, found: 393.1072.

2-phenyl-1,2-di-p-tolylethan-1-one 2p:



36 mg, yield: 60%, chromatography on silica gel (n-Hexane:EtOAc = 98:2, v/v, R_f = 0.37). ¹H NMR (400 MHz, Chloroform-*d*) δ = 7.95 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.15 (m, 11H), 6.02 (s, 1H), 2.40 (s, 3H), 2.34 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ = 197.91, 143.74, 139.51, 136.67, 136.23, 134.39, 129.39, 129.25, 129.09, 129.06, 128.97, 128.59, 126.94, 58.92, 21.57, 21.01. HRMS (ESI) ([M + H]⁺) Calcd For C₂₂H₂₁O₂: 301.1587, found: 301.1584.

1,2-bis(4-fluorophenyl)-2-phenylethan-1-one 2q:

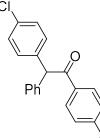


F 38 mg, yield: 61%, chromatography on silica gel (n-Hexane:EtOAc = 98:2, v/v,

 $R_f = 0.34$). ¹H NMR (400 MHz, Chloroform-*d*) $\delta = 8.08 - 8.03$ (m, 2H), 7.40 - 7.34 (m, 2H), 7.32 - 7.23 (m, 5H), 7.15 - 7.08 (m, 2H), 7.07 - 7.02 (m, 2H), 6.00 (s, 1H). ¹³C NMR (100 MHz, 2H), 7.07 - 7.02 (m, 2H), 6.00 (s, 1H).

Chloroform-*d*) δ = 196.44, 165.63 (d, *J* = 255.6 Hz), 161.96 (d, *J* = 246.2 Hz), 138.70, 134.69 (d, *J* = 3.3 Hz), 132.97 (d, *J* = 3.0 Hz), 131.58 (d, *J* = 9.3 Hz), 130.66 (d, *J* = 8.1 Hz), 128.92, 128.90, 127.38, 115.65 (d, *J* = 43.8 Hz), 115.65, 58.56. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ = -104.70, -115.39. HRMS (EI) ([M]⁺) Calcd For C₂₀H₁₄F₂O: 308.1007, found: 308.1010.

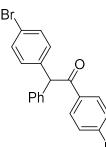
1,2-bis(4-chlorophenyl)-2-phenylethan-1-one 2r:



Cl 38 mg, yield: 56%, chromatography on silica gel (n-Hexane:EtOAc = 98:2,

v/v, $R_f = 0.46$). ¹H NMR (400 MHz, Chloroform-*d*) $\delta = 7.95$ (d, J = 8.6 Hz, 2H), 7.43 – 7.26 (m, 9H), 7.21 (d, J = 8.5 Hz, 2H), 5.97 (s, 1H). ¹³C NMR (100 MHz, Chloroform-*d*) $\delta = 196.57$, 139.69, 138.25, 137.32, 134.80, 133.24, 130.45, 130.32, 128.99, 128.90, 128.84, 127.50, 58.77. HRMS (ESI) ([M + H]⁺) Calcd For C₂₀H₁₅Cl₂O: 341.0494, found: 341.0498.

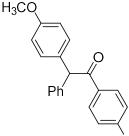
1,2-bis(4-bromophenyl)-2-phenylethan-1-one 2s:



Br 34 mg, yield: 40%, chromatography on silica gel (n-Hexane:EtOAc = 98:2,

v/v, $R_f = 0.27$). ¹H NMR (400 MHz, Chloroform-*d*) $\delta = 7.90 - 7.83$ (m, 2H), 7.61 - 7.55 (m, 2H), 7.51 - 7.44 (m, 2H), 7.39 - 7.33 (m, 2H), 7.32 - 7.25 (m, 3H), 7.17 - 7.12 (m, 2H), 5.94 (s, 1H). ¹³C NMR (100 MHz, Chloroform-*d*) $\delta = 196.66$, 138.12, 137.80, 135.18, 131.99, 131.79, 130.80, 130.41, 129.00, 128.89, 128.46, 127.52, 121.40, 58.82. HRMS (ESI) ([M + H]⁺) Calcd For C₂₀H₁₅Br₂O: 428.9484, found: 428.9494.

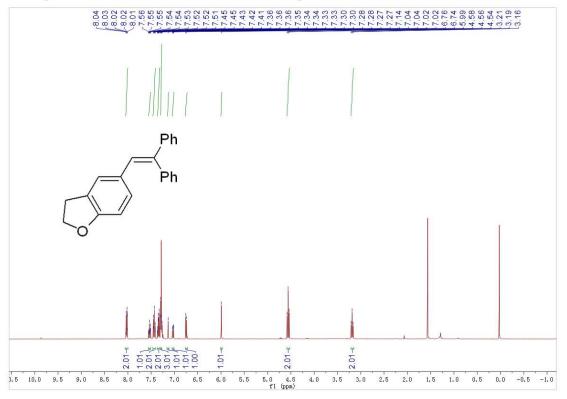
1-(4-fluorophenyl)-2-(4-methoxyphenyl)-2-phenylethan-1-one 2t:



F 41 mg, yield: 64%, chromatography on silica gel (n-Hexane:EtOAc = 98:2,

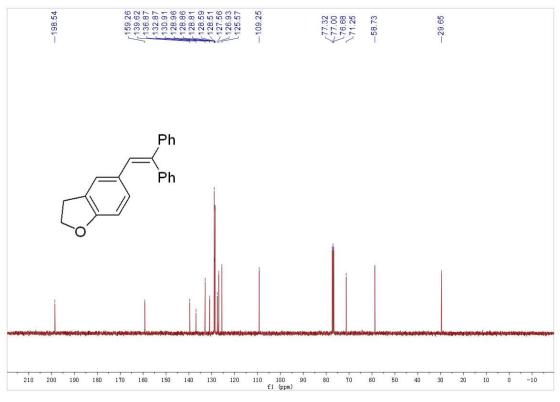
v/v, $R_f = 0.46$). ¹H NMR (400 MHz, Chloroform-d) δ 8.01 (m, J = 8.4, 5.3, 2.5 Hz, 2H), 7.31 (d, J

= 7.1 Hz, 2H), 7.26 – 7.22 (m, 3H), 7.17 (d, J = 8.7 Hz, 2H), 7.07 (t, J = 8.6 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 5.92 (s, 1H), 3.78 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ = 196.91, 165.14 (d, J = 253.0 Hz), 158.76, 139.27, 131.63 (d, J = 1.0 Hz), 130.92, 130.14, 128.88 (d, J = 250 Hz), 127.16, 115.72 (d, J = 21.0 Hz), 114.23, 58.67, 55.25. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ = -105.16. HRMS (ESI) ([M + H]⁺) Calcd For C₂₁H₁₈FO₂: 321.1285, found: 321.1287.

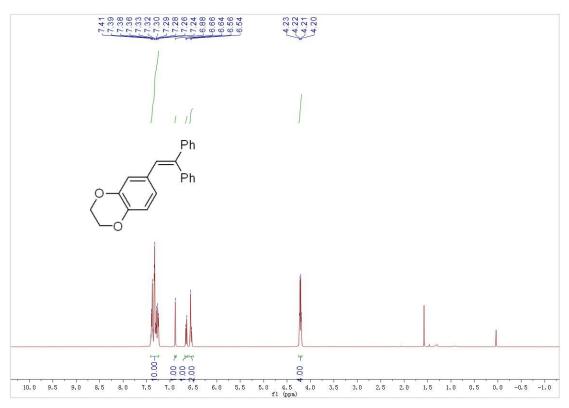


10. Copies of ¹H NMR, ¹³C NMR and ¹⁹F NMR Spectra

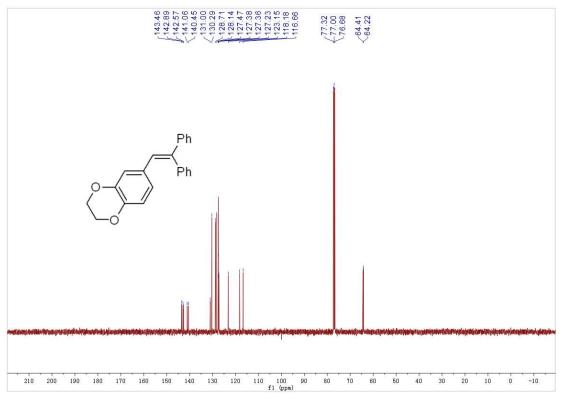
¹H NMR Spectrum of Compound 1k



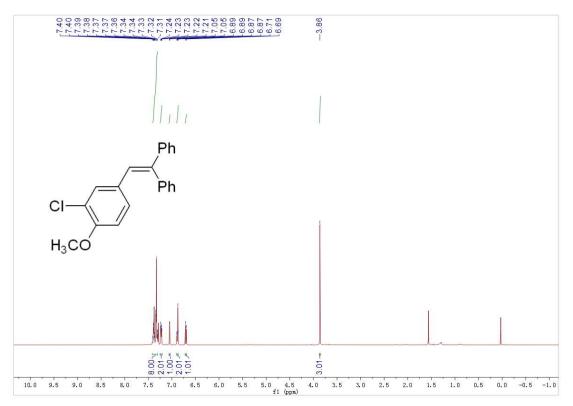
¹³C NMR Spectrum of Compound 1k



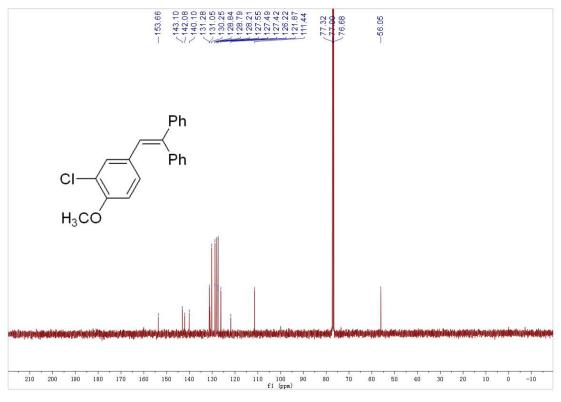
¹H NMR Spectrum of Compound 11



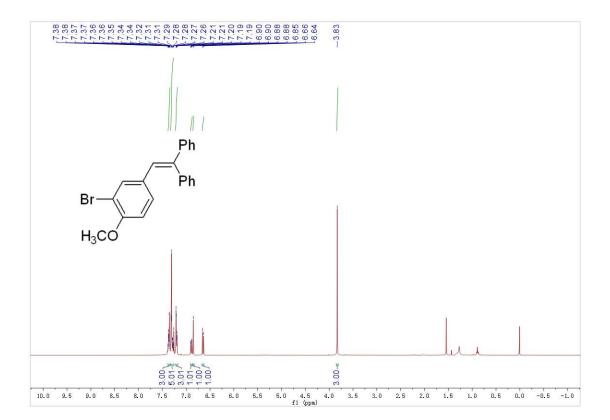
¹³C NMR Spectrum of Compound 11



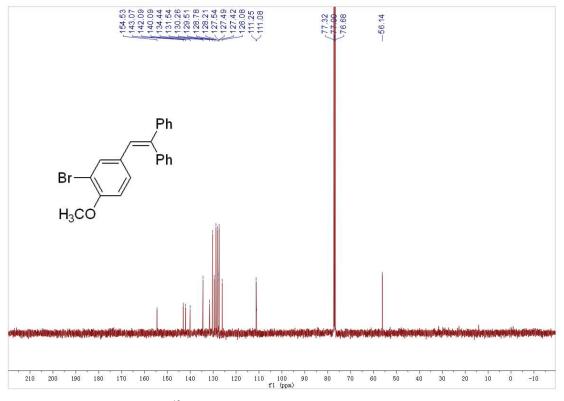
¹H NMR Spectrum of Compound 1m



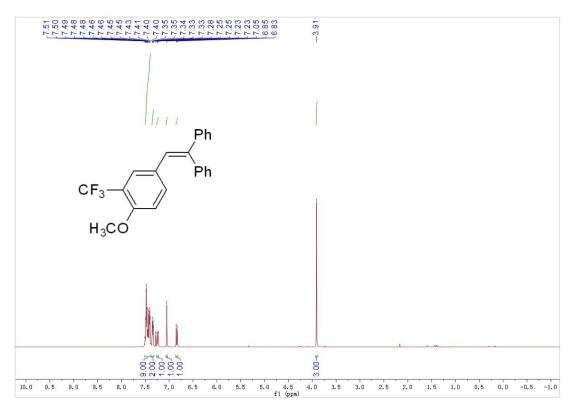
¹³C NMR Spectrum of Compound 1m



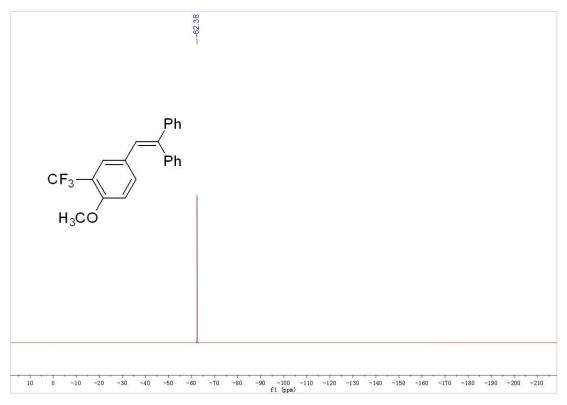
¹H NMR Spectrum of Compound 1n



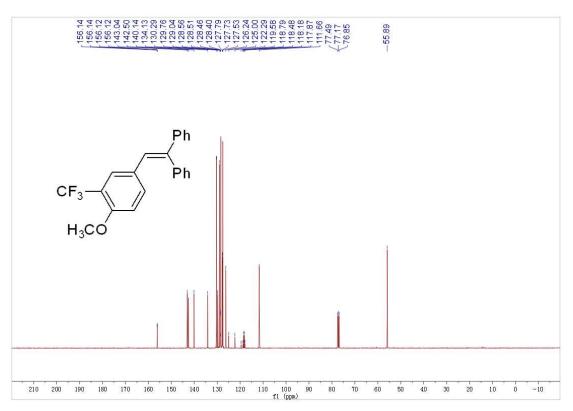
¹³C NMR Spectrum of Compound 1n



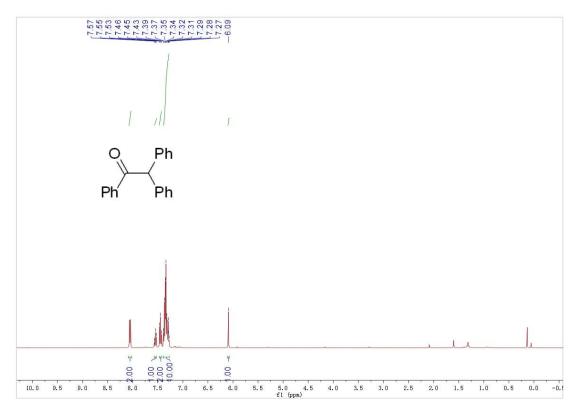
¹H NMR Spectrum of Compound 10



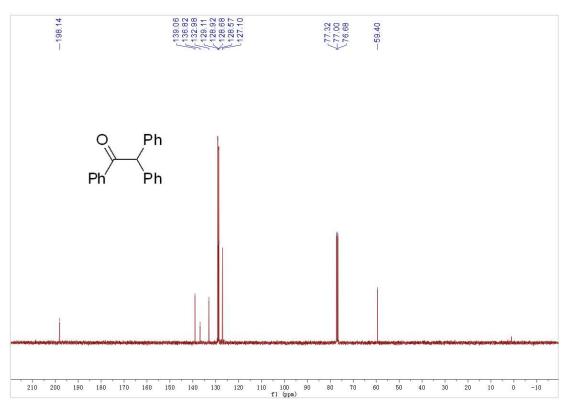
¹⁹F NMR Spectrum of Compound 10



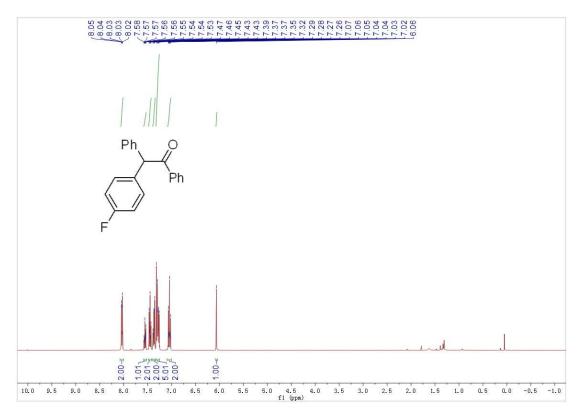
¹³C NMR Spectrum of Compound 10



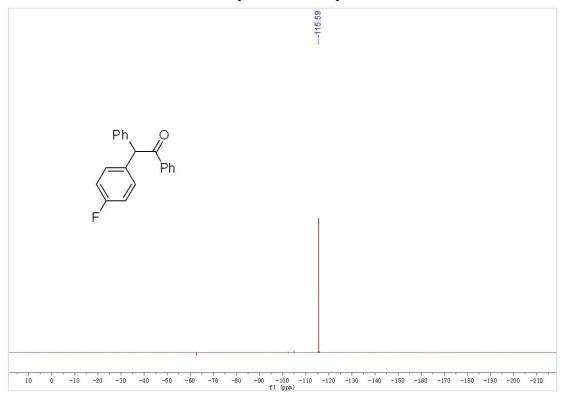
¹H NMR Spectrum of Compound 2a



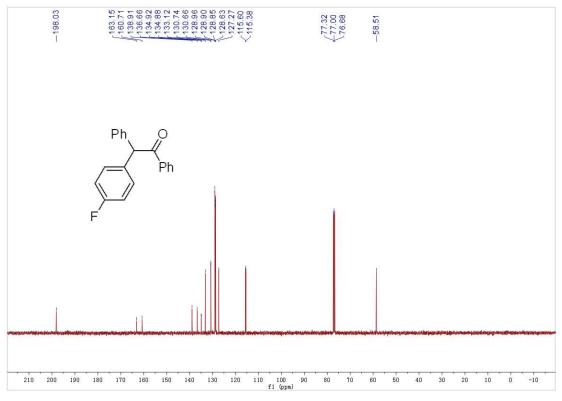
¹³C NMR Spectrum of Compound 2a



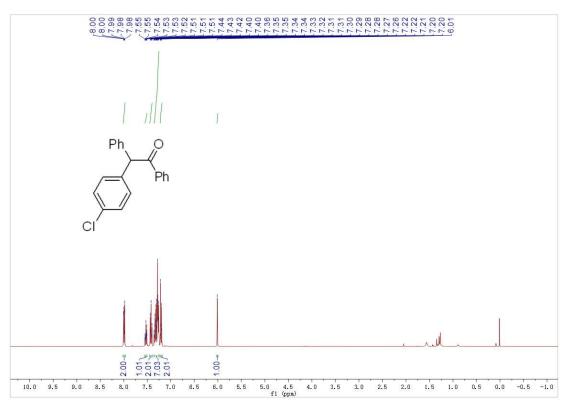
¹H NMR Spectrum of Compound 2b



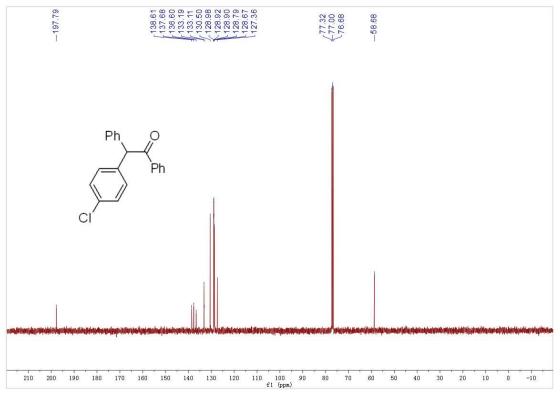
¹⁹F NMR Spectrum of Compound 2b



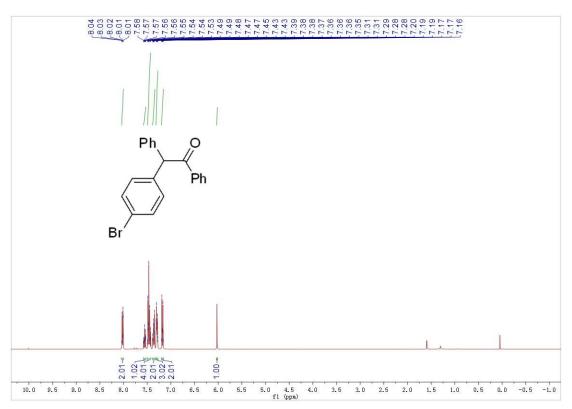
¹³C NMR Spectrum of Compound 2b



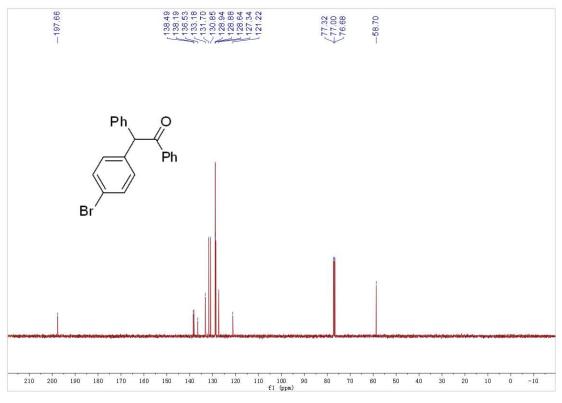
¹H NMR Spectrum of Compound 2c



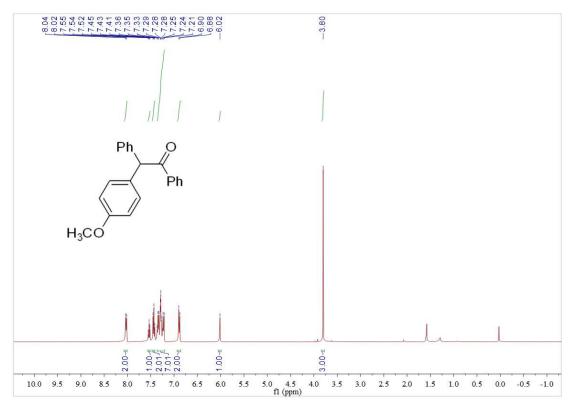
¹³C NMR Spectrum of Compound 2c



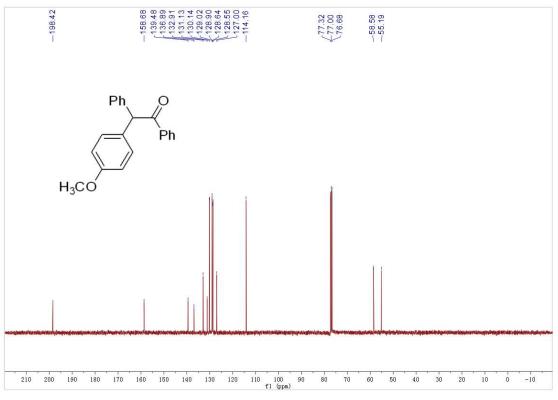
¹H NMR Spectrum of Compound 2d



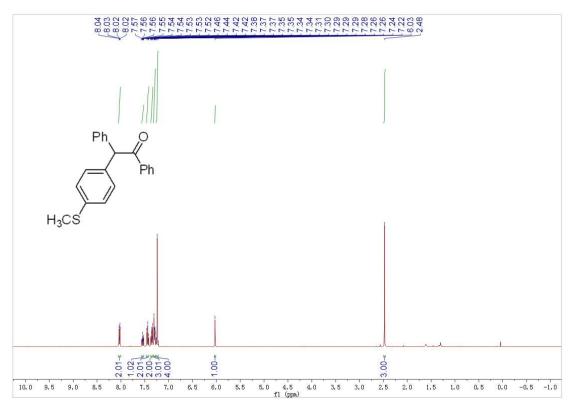
¹³C NMR Spectrum of Compound 2d



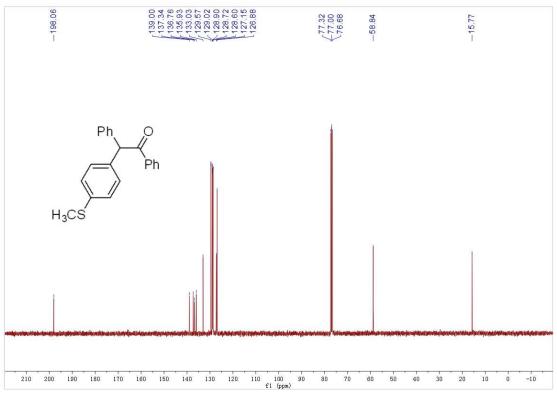
¹H NMR Spectrum of Compound 2e



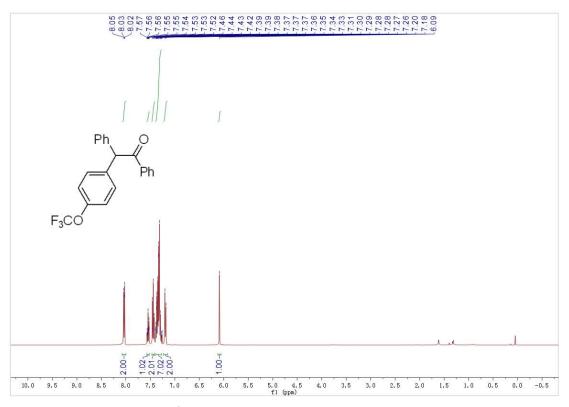
¹³C NMR Spectrum of Compound 2e



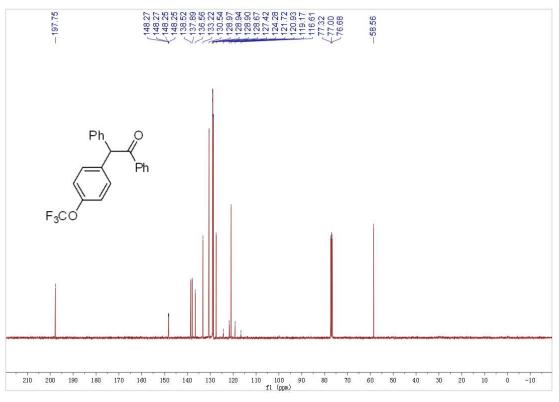
¹H NMR Spectrum of Compound 2f



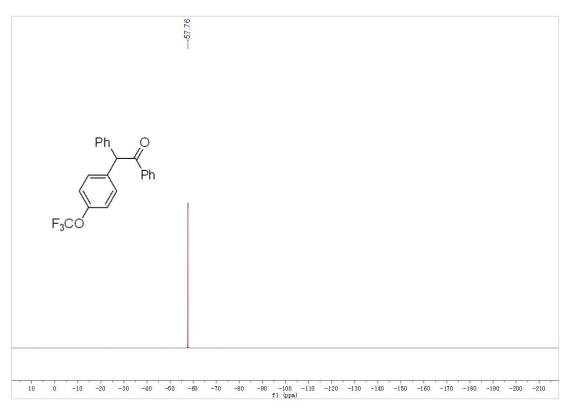
¹³C NMR Spectrum of Compound 2f



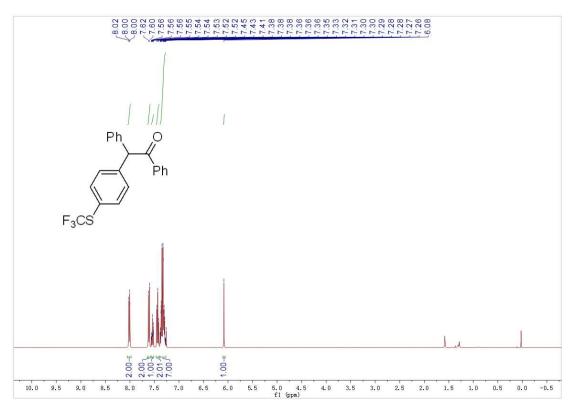
¹H NMR Spectrum of Compound 2g



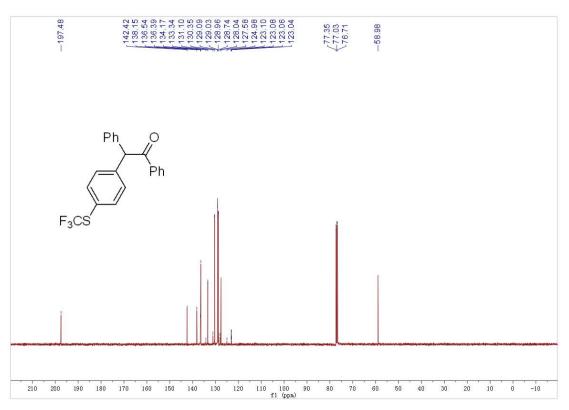
¹³C NMR Spectrum of Compound 2g



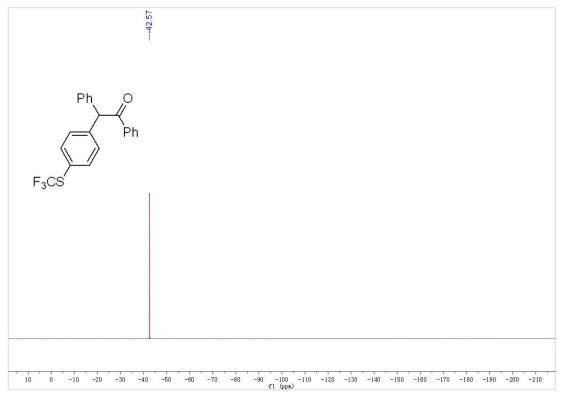
¹⁹F NMR Spectrum of Compound 2g



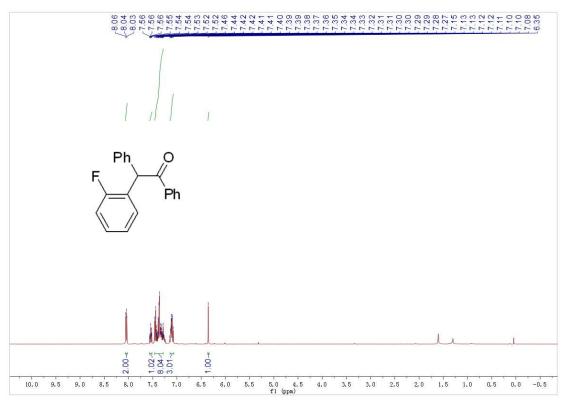
¹H NMR Spectrum of Compound 2h



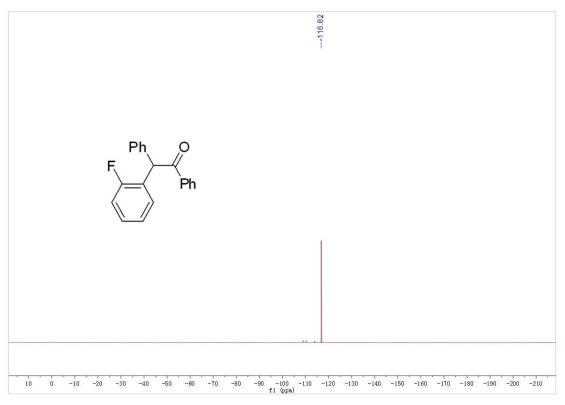
¹³C NMR Spectrum of Compound 2h



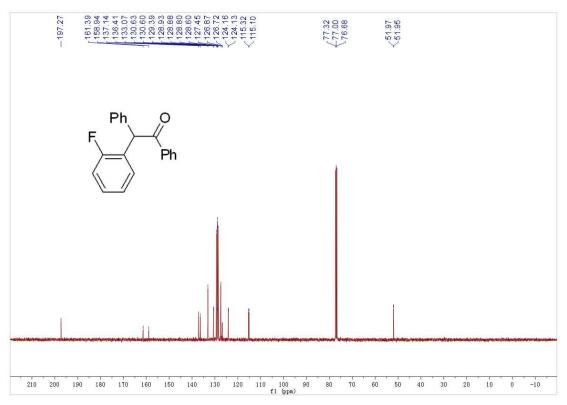
¹⁹F NMR Spectrum of Compound 2h



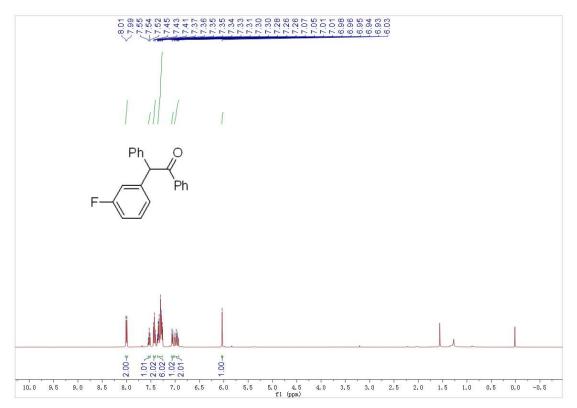
¹H NMR Spectrum of Compound 2i



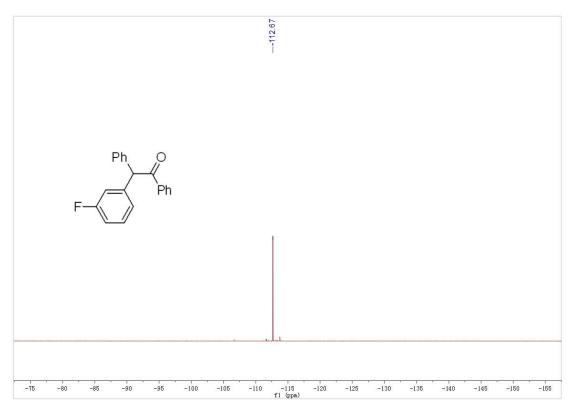
¹⁹F NMR Spectrum of Compound 2i



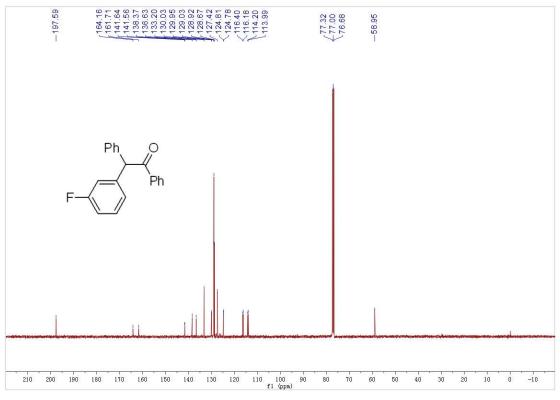
¹³C NMR Spectrum of Compound 2i



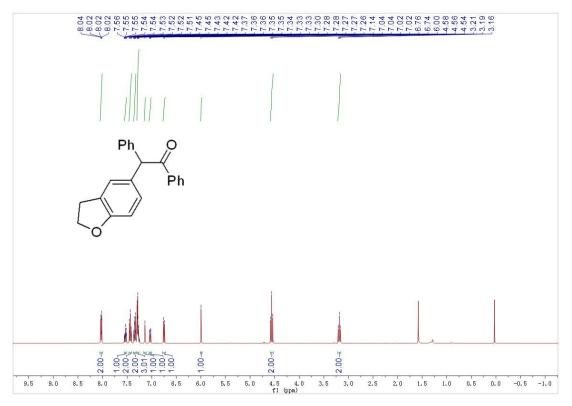
¹H NMR Spectrum of Compound 2j



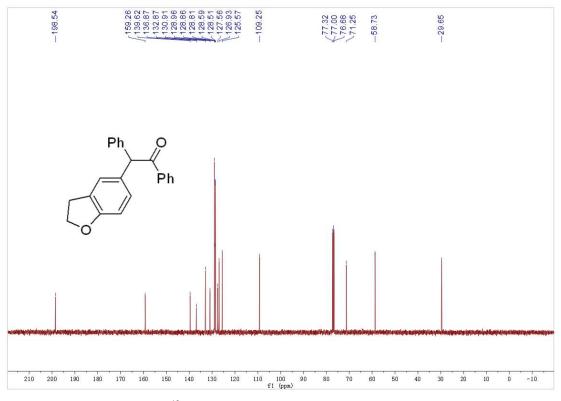
¹⁹F NMR Spectrum of Compound 2j



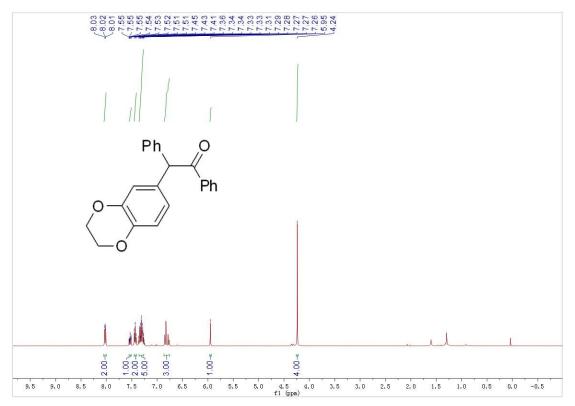
¹³C NMR Spectrum of Compound 2j



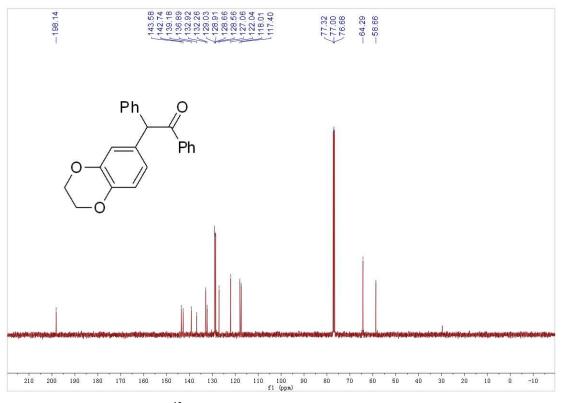
¹H NMR Spectrum of Compound 2k



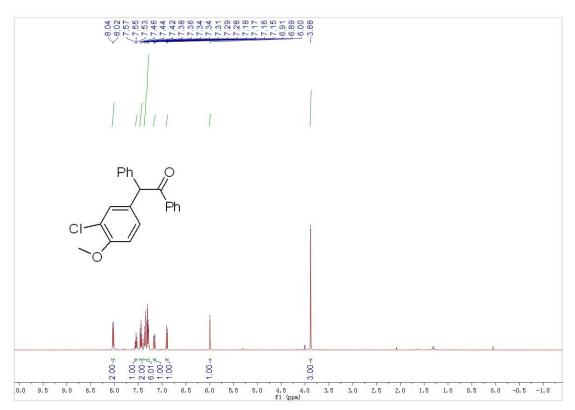
¹³C NMR Spectrum of Compound 2k



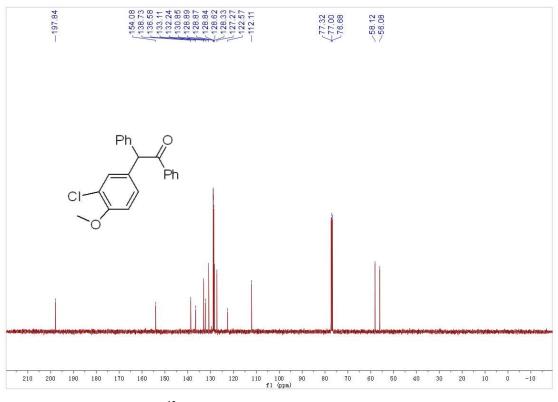
¹H NMR Spectrum of Compound 21



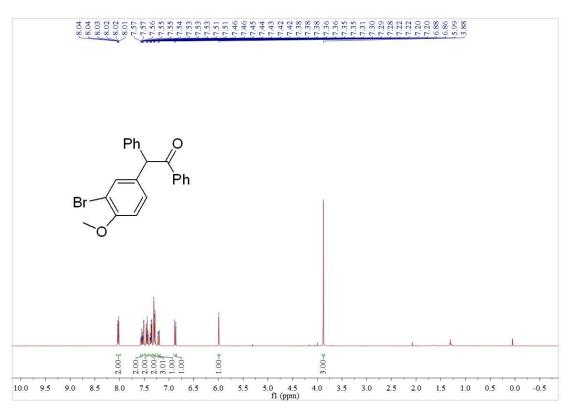
¹³C NMR Spectrum of Compound 21



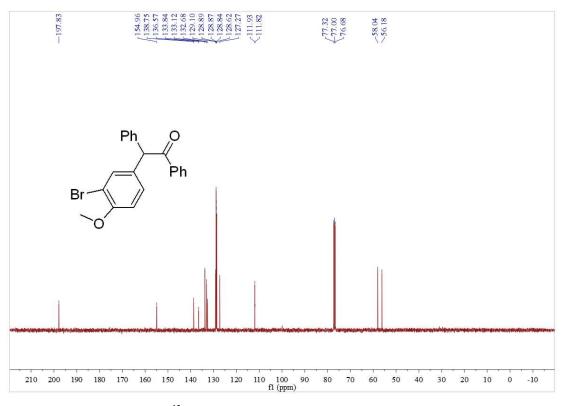
¹H NMR Spectrum of Compound 2m



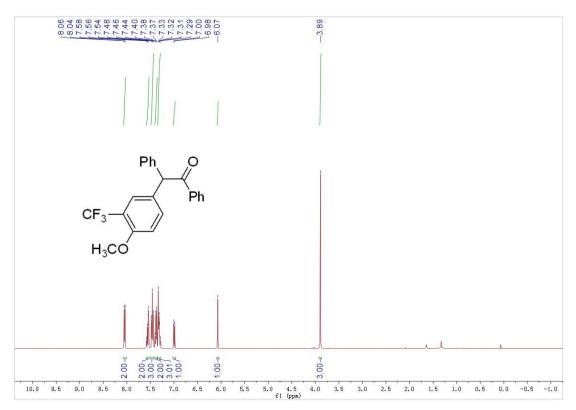
¹³C NMR Spectrum of Compound 2m



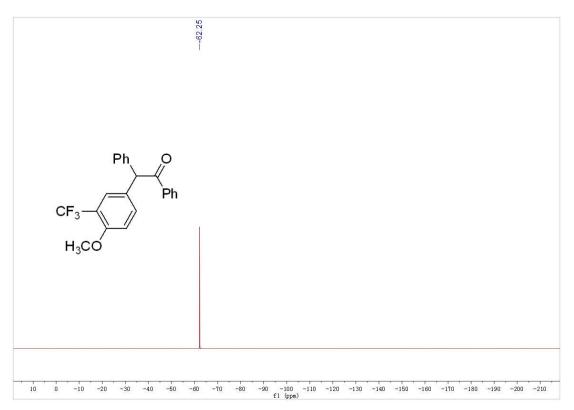
¹H NMR Spectrum of Compound 2n



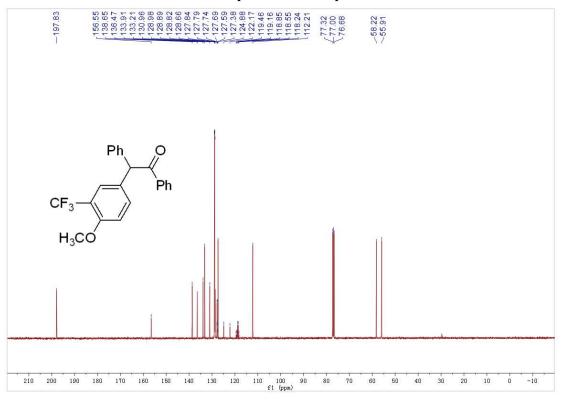
¹³C NMR Spectrum of Compound 2n



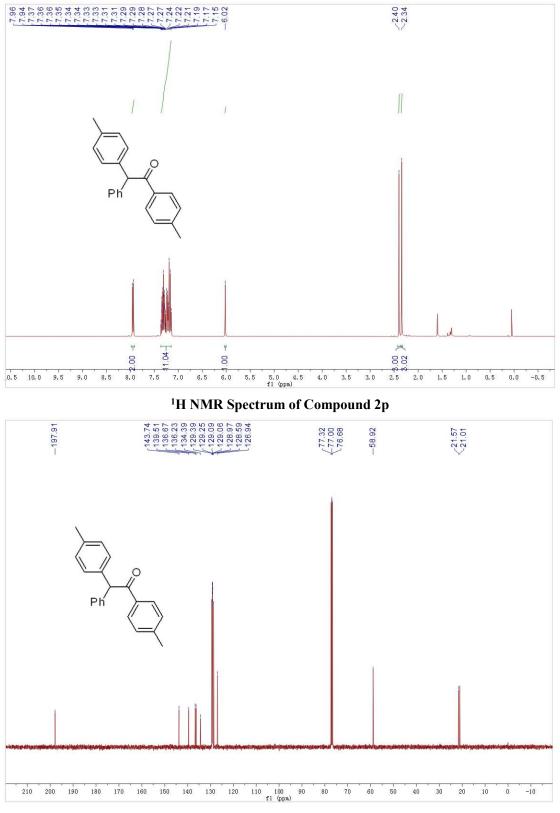
¹H NMR Spectrum of Compound 20



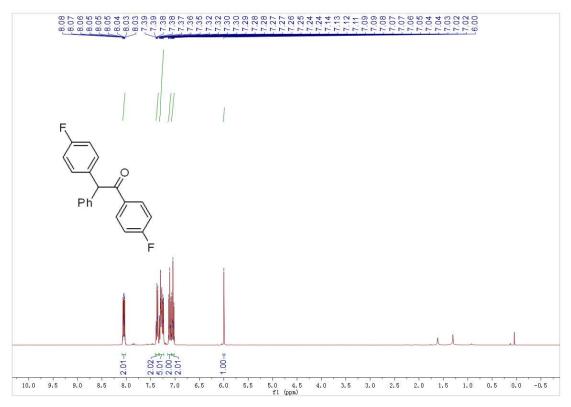
¹⁹F NMR Spectrum of Compound 20



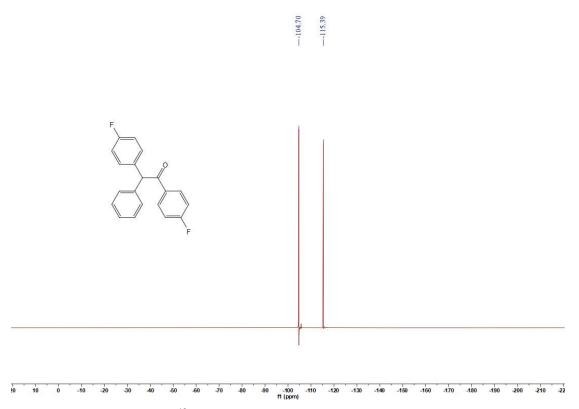
¹³C NMR Spectrum of Compound 20



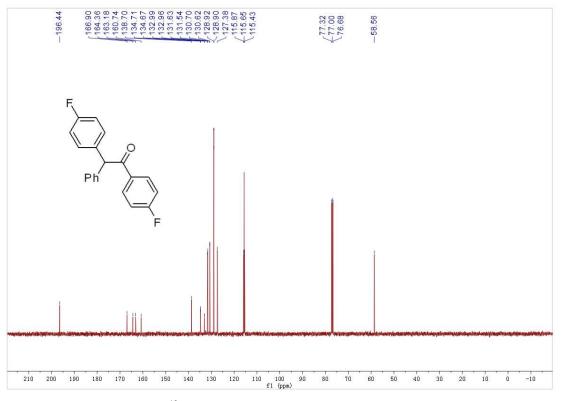
¹³C NMR Spectrum of Compound 2p



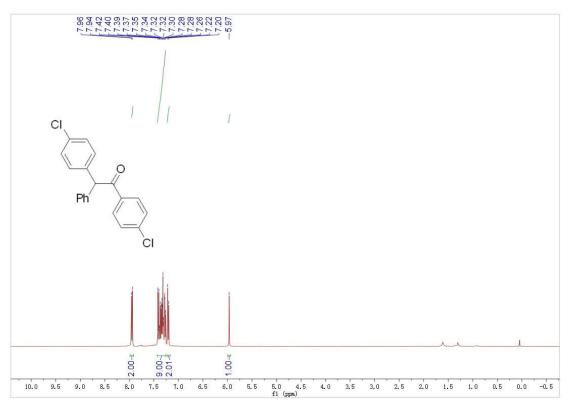
¹H NMR Spectrum of Compound 2q



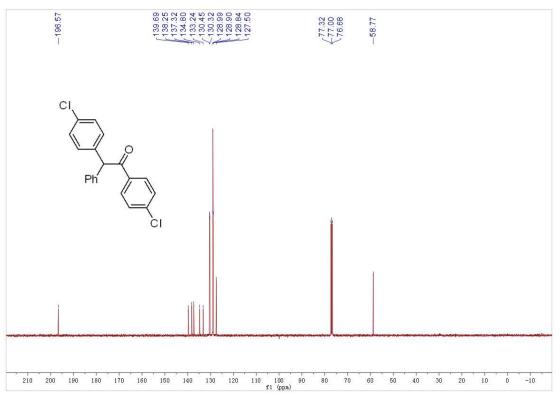




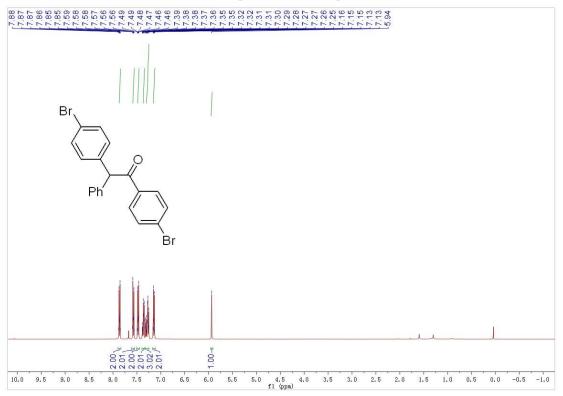
¹³C NMR Spectrum of Compound 2p



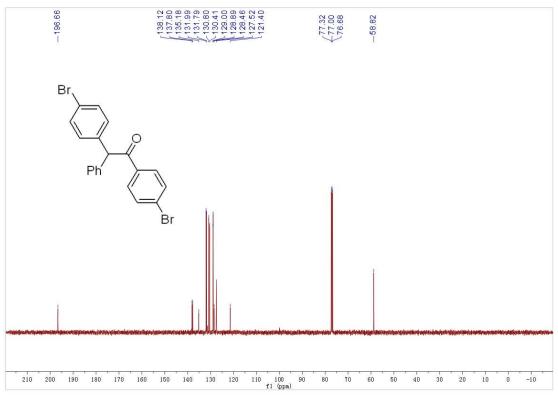
¹H NMR Spectrum of Compound 2r



¹³C NMR Spectrum of Compound 2r



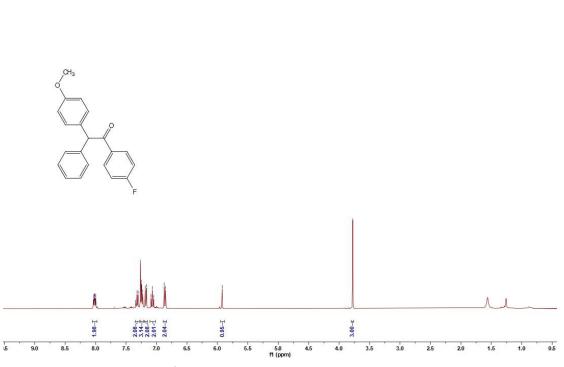
¹H NMR Spectrum of Compound 2s



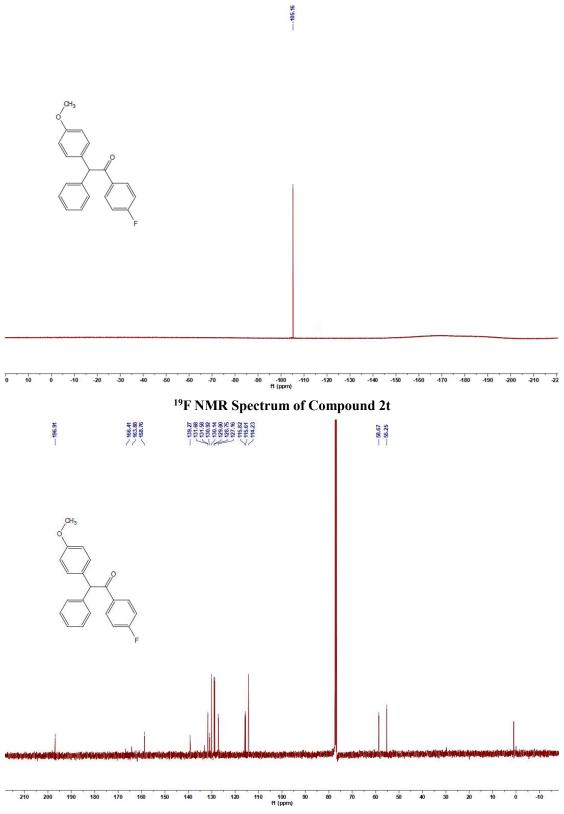
¹³C NMR Spectrum of Compound 2s

-5.92

88.8 --3.78







¹³C NMR Spectrum of Compound 2t

11. References

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[2] G. Sheldrick, Acta Crystallographica Section C 2015, 71, 3-8.

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