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Supporting Information

Base-promoted [1,4]-Wittig Rearrangement of Chalcone-derived Allylic Ethers Leading to Aromatic *β*-Benzyl Ketones

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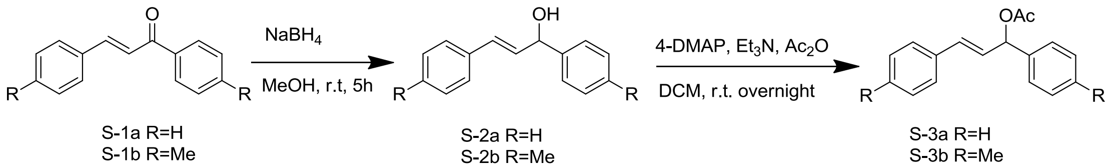
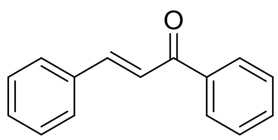
1. General Information

Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by thin layer chromatography using silica gel. ^{1}HNMR and ^{13}CNMR (400 and 100MHz, respectively) spectra were recorded in $CDCl_3$, ^{1}H NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$ at 7.26 ppm). ^{13}CNMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard).

2. General Procedure for Synthesis of α,β-Unsaturated Ketones

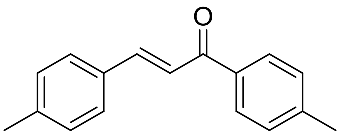
To a solution of NaOH (2.2 g, 55 mmol, 1.3 equiv) in H_2O (20 mL) and phenyl ketone (43 mmol, 1.0 equiv) in 12 mL ethanol at 0 ℃ was added gradually phenyl aldehyde (43 mmol, 1.0 equiv). The mixture was then allowed to warm to room temperature and stirred for 4h after which a precipitate of the product formed. The product was collected by suction filtration on a Buchner funnel and washed repeatedly with cold water. Recrystallization from ethanol afforded *α,β*-unsaturated ketones S-1a and S-1b.





S-1a

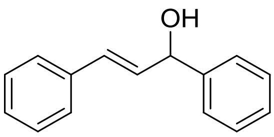
(E)-chalcone: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 7.5 Hz, 2H), 7.83 (d, J = 15.7 Hz, 1H), 7.64 (d, J = 4.6 Hz, 2H), 7.60-7.47 (m, 4H), 7.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.27, 142.60, 136.02, 132.69, 130.60, 128.36, 126.78, 126.44, 126.32, 126.27, 119.89.


S-1b

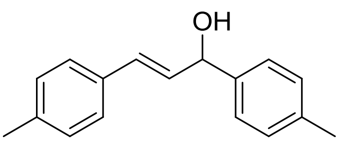
(E)-1,3-di-p-tolylprop-2-en-1-one: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.6 Hz, 2H), 7.78 (d, J = 15.6 Hz, 1H), 7.59-7.43 (m, 5H), 7.28 (d, J = 7.6 Hz, 1H), 7.20 (d, J = 7.6 Hz, 1H), 2.41 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.07, 144.48, 143.50, 140.94, 135.80, 132.30, 129.71, 129.32, 128.65, 128.47, 121.10, 21.68, 21.54.

3. General Procedure for Synthesis of allylic alcohols

To a cooled solution (0 ℃) of *α,β*-Unsaturated Ketones 1a (9.5 g, 45.9mmol)/ 1b (10.9g, 45.9mmol) in methanol, sodium borohydride (3.5g, 91.4mmol, 2equiv.) was added portion wise at 0 ℃ , and stirred for about 6 h hour until 1a/1b was completely consumed. The reaction was quenched with H_2O, and extracted with DCM. The combined extracts were washed with brine, and dried over Na_2SO_4. The solvent was removed in vacuo.S-1a. White solid, Yield: 94%. S-2a. White solid, Yield: 91%.


S-2a

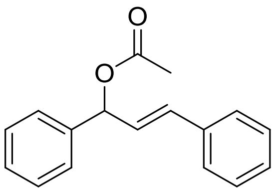
^{1}H NMR (400 MHz, CDCl3) δ 7.33 (d, J = 7.3 Hz, 2H), 7.28 (d, J = 7.4 Hz, 4H), 7.25 (d, J = 4.5 Hz, 1H), 7.21 (dd, J = 9.3, 5.6 Hz, 3H), 7.15 (d, J = 7.4 Hz, 1H), 6.58 (d, J = 15.8 Hz, 1H), 6.28 (dd, J = 15.8, 6.5 Hz, 1H), 5.27 (d, J = 6.4 Hz, 1H), 2.16 (s, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 142.85, 136.59, 131.61, 130.58, 128.66, 128.61, 127.82, 126.67, 75.29.


S-2b

^{1}H NMR (400 MHz, CDCl3) δ 7.23 (d, J = 7.5 Hz, 2H), 7.19 (d, J = 7.6 Hz, 2H), 7.09 (d, J = 7.7 Hz, 2H), 7.04 (d, J = 7.8 Hz, 2H), 6.51 (d, J = 15.8 Hz, 1H), 6.23 (dd, J = 15.8, 6.5 Hz, 1H), 5.19 (s, 1H), 2.93 (s, 1H), 2.29 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.29, 137.56, 137.35, 134.08, 131.01, 130.31, 129.39, 126.71, 126.54, 75.01, 21.35, 21.29.

4. General Procedure for Synthesis of (E)-1, 3-diphenylallyl acetate

DMAP (5.8 mg, 0.048 mmol) was added to a 3 mL DCM solution of 1a (100 mg, 0.48 mmol), Et_3N (1 mL, 1.2 mmol), and acetic anhydride (1 mL, 1.2 mmol). The reaction mixture was stirred at room temperature until B had disappeared as monitored by TLC. Ethyl acetate (30 mL) was added and the mixture was washed with water (3 × 30 mL). The organic layer was dried over $MgSO_4$, filtered, concentrated, and purified by column chromatography on silica gel with ethyl acetate and petroleum (v/v = 1:5) as eluent to give S-3a as colourless oil (110 mg, 91%).



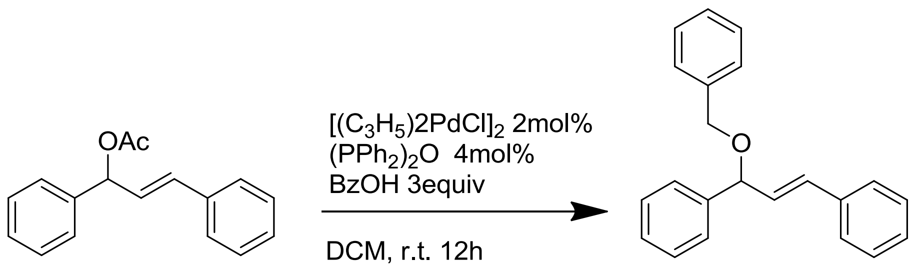
S-3a

^{1}H NMR (400 MHz, CDCl3) δ 7.34 (d, J = 7.8 Hz, 2H), 7.31 (d, J = 7.1 Hz, 4H), 7.24 (dd, J = 13.3, 6.9 Hz, 3H), 7.17 (d, J = 4.4 Hz, 1H), 6.56 (d, J = 15.7 Hz, 1H), 6.37 (d, J = 6.9 Hz, 1H), 6.28 (dd, J = 15.7, 6.8 Hz, 1H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.07, 139.24, 136.17, 132.60, 128.65, 128.59, 128.20, 128.08, 127.50, 127.06, 126.71, 76.16, 21.18.

5. General procedure for the Pd-catalyzed allylic etherification of (E)-1,3-di-phenylallyl acetate 3 with benzyl alcohol

A solution of $[(C_3H_5)PdCl]_2$ (0.0019 g, 0.005 mmol) and phosphine ligand (0.01 mmol) was stirred for 30 min. (*E*)-1,3-diphenylallyl acetate (0.05 ml, 0.25 mmol) was added and the solution stirred for 15 min, then benzyl alcohol (0.08 ml, 0.75 mmol) and anhydrous Cs_2CO_3 (0.245 g, 0.75 mmol) were added and the reaction mixture stirred overnight. The resulting solution was quenched with EtOAc (1.5 ml) and saturated aqueous NH_4Cl solution (3 ml). The mixture was then extracted with EtOAc (2 x 2 ml), dried over anhydrous Na_2SO_4, evaporated at reduced pressure, the residue was purified by flash chromatography on a short pad of silica gel (10 cm, EtOAc/ Petroleum ether 1/10) and dried in vacuum for 2 h gave the desired product 3a as colerless oil. Yield: 78%.

Table S1. Optimization for Pd-catalyzed allylic etherification of (E)-1,3-di-phenylallyl acetate (3) with benzyl alcohol



S-3a

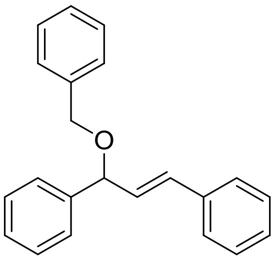
1

Entry	Catalyst	Ligand	Base	Solvent	Yield^{iso} (%)
1	$Pd(OAc)_2$	PPh_3	K_2CO_3	DCM	51
2	$[(C_3H_5)PdCl]_2$	PPh_3	K_2CO_3	DCM	62
3	$Pd(PPh_3)_2Cl_2$	PPh_3	K_2CO_3	DCM	51
4	$[(C_3H_5)PdCl]_2$	$(PPh_2)_2O$	K_2CO_3	DCM	53
5	$[(C_3H_5)PdCl]_2$	$(PPh3)_2O$	Cs_2CO_3	DCM	78
6	$[(C_3H_5)PdCl]_2$	$(PPh_2)_2O$	Et_3N	DCM	55
7	$[(C_3H_5)PdCl]_2$	DPPE	Cs_2CO_3	DCM	68
8	$[(C_3H_5)PdCl]_2$	BINAP	Cs_2CO_3	DCM	61
9	$[(C_3H_5)PdCl]_2$	P^tBu_3	Cs_2CO_3	DCM	33
10	$[(C_3H_5)PdCl]_2$	$(PPh_2)_2O$	Cs_2CO_3	THF	70
11	$[(C_3H_5)PdCl]_2$	$(PPh_2)_2O$	Cs_2CO_3	MeCN	62
12	$[(C_3H_5)PdCl]_2$	$(PPh_2)_2O$	Cs_2CO_3	Toluene	55

6. Typical Procedure for synthesis of 1,3,4-triphenylbutan-1-one (2a)

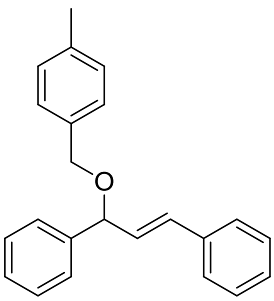
To a solution of allylic ether **1a** (0.5 mmol,) in 4 mL of THF, 0.24 mL (0.6 mmol) of a solution of *n*-BuLi in hexane was dropwise added at -78 ℃. The resulting solution was further stirred at -40 ℃. After completion of the reaction, the resulting solution was quenched with a piece of ice and saturated aqueous NH_4Cl solution (10mL). The mixture was then extracted with DCM (3 x 8 mL), dried over anhydrous Na_2SO_4, evaporated at reduced pressure and the desired compound 1,3,4-triphenylbutan-1-one **2a** was obtained in 80% yield (0.135g) after column purification using PE/EA (20:1) as solvent.

7. Charcter of the representative substrates 1 and product 2



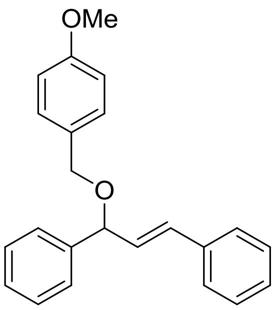
1a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 7.7 Hz, 2H), 7.31 (s, 2H), 7.26 (d, J = 8.1 Hz, 2H), 7.23 (s, 2H), 7.19 (s, 2H), 7.14 (d, J = 7.2 Hz, 1H), 6.54 (d, J = 15.9 Hz, 1H), 6.26 (dd, J = 15.9, 7.0 Hz, 1H), 4.93 (d, J = 7.0 Hz, 1H), 4.49 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.19, 138.47, 136.63, 131.61, 130.32, 128.60, 128.45, 127.78, 127.60, 127.04, 126.67, 81.65, 70.16.



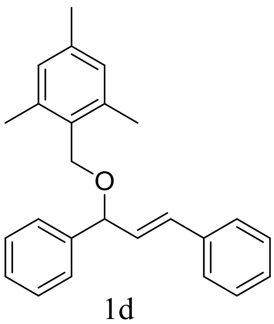
1b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.7 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.32-7.26 (m, 1H), 7.25-7.18 (m, 1H), 7.15 (d, J = 7.6 Hz, 1H), 6.61 (d, J = 15.9 Hz, 1H), 6.32 (dd, J = 15.9, 6.9 Hz, 1H), 4.99 (d, J = 7.0 Hz, 1H), 4.53 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 141.31, 137.28, 136.71, 135.43, 131.53, 130.47, 129.15, 128.59, 127.93, 127.74, 127.08, 126.68, 81.42, 70.04, 21.26.



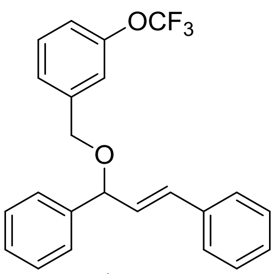
1c

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.7 Hz, 2H), 7.33 (t, J = 7.0 Hz, 4H), 7.25 (dd, J = 14.2, 7.5 Hz, 5H), 7.17 (t, J = 7.2 Hz, 1H), 6.86 (d, J = 7.9 Hz, 2H), 6.59 (d, J = 15.9 Hz, 1H), 6.31 (dd, J = 15.9, 6.9 Hz, 1H), 4.97 (d, J = 6.9 Hz, 1H), 4.48 (s, 2H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.34, 141.43, 136.79, 131.58, 130.64, 130.60, 129.49, 128.68, 127.86, 127.83, 127.17, 126.76, 113.97, 81.43, 69.94, 55.34.



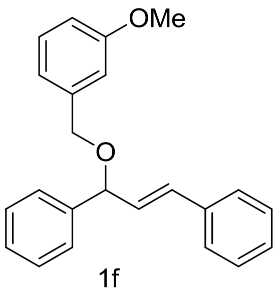
1d

1H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.5 Hz, 2H), 7.58 (t, J = 7.1 Hz, 4H), 7.49 (t, J = 7.6 Hz, 3H), 7.42 (d, J = 7.0 Hz, 1H), 7.08 (s, 2H), 6.86 (d, J = 15.9 Hz, 1H), 6.59 (dd, J = 15.9, 6.6 Hz, 1H), 5.22 (d, J = 6.7 Hz, 1H), 4.75 (dd, J = 25.3, 10.3 Hz, 2H), 2.55 (s, 6H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, CDCl3) δ 141.65, 138.16, 137.74, 136.93, 131.62, 131.39, 130.88, 129.18, 128.75, 128.69, 127.86, 127.27, 126.79, 82.40, 65.19, 21.24, 19.82.



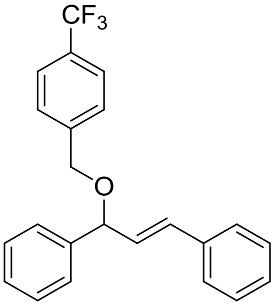
1e

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.5 Hz, 2H), 7.37 (d, J = 7.2 Hz, 4H), 7.33 (s, 1H), 7.28 (t, J = 8.0 Hz, 5H), 7.20 (dd, J = 15.7, 8.2 Hz, 1H), 7.11 (d, J = 7.8 Hz, 1H), 6.63 (d, J = 15.9 Hz, 1H), 6.33 (dd, J = 15.9, 7.0 Hz, 1H), 4.99 (d, J = 7.0 Hz, 1H), 4.60-4.49 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.49, 141.07, 140.89, 136.52, 131.92, 129.98, 129.82, 128.72, 128.66, 127.98, 127.95, 127.03, 126.72, 125.80, 82.18, 69.36.



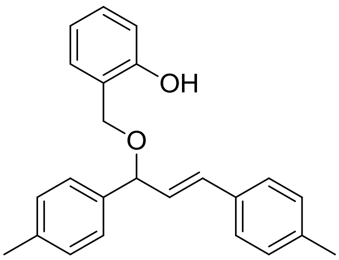
1f

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 7.4 Hz, 2H), 7.44 (d, J = 7.6 Hz, 2H), 7.33 (t, J = 7.6 Hz, 1H), 7.24 (t, J = 7.9 Hz, 1H), 7.17 (d, J = 7.4 Hz, 2H), 6.95 (t, J = 7.4 Hz, 1H), 6.79 (d, J = 8.2 Hz, 1H), 6.63 (d, J = 15.9 Hz, 2H), 6.34 (dd, J = 15.9, 6.9 Hz, 2H), 5.03 (d, J = 6.9 Hz, 1H), 4.62 (q, J = 12.8 Hz, 1H), 3.71(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.16, 141.64, 136.90, 131.48, 130.80, 128.81, 128.68, 128.63, 128.60, 127.82, 127.76, 127.15, 126.79, 120.62, 110.28, 82.25, 65.50, 55.36.



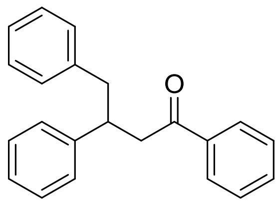
1g

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.8 Hz, 2H), 7.47 (d, J = 7.9 Hz, 2H), 7.43 (d, J = 7.5 Hz, 2H), 7.37 (d, J = 3.2 Hz, 4H), 7.29 (t, J = 6.7 Hz, 3H), 7.23 (d, J = 7.5 Hz, 1H), 6.64 (d, J = 15.9 Hz, 1H), 6.33 (dd, J = 15.9, 7.0 Hz, 1H), 5.00 (d, J = 7.0 Hz, 1H), 4.65-4.53 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.69, 140.85, 136.47, 131.91, 129.94, 128.71, 128.65, 127.98, 127.66, 126.98, 126.70, 125.41, 82.25, 69.41.



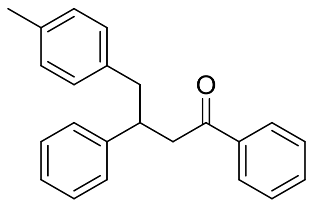
1h

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 7.9 Hz, 2H), 7.70 (d, J = 7.9 Hz, 2H), 7.61 (d, J = 7.6 Hz, 2H), 7.54 (d, J = 7.5 Hz, 2H), 7.45 (d, J = 7.6 Hz, 2H), 7.35 (d, J = 7.6 Hz, 2H), 6.88 (d, J = 15.9 Hz, 1H), 6.58 (dd, J = 15.8, 7.0 Hz, 1H), 5.22 (d, J = 7.0 Hz, 1H), 4.92-4.74 (m, 2H), 2.82-2.41 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.14, 138.26, 137.89, 137.77, 134.01, 131.82, 129.56, 129.53, 129.33, 127.79, 127.17, 126.82, 125.46, 82.43, 69.42, 21.33.



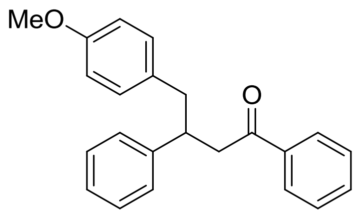
2a

1,3,4-triphenylbutan-1-one (2a): white solid, 135.1mg, 80% yield. [1]H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.6 Hz, 1H), 7.43 (t, J = 7.3 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H), 7.18-7.05 (m, 4H), 6.99 (d, J = 7.2 Hz, 1H), 3.59 (p, J = 7.0 Hz, 1H), 3.23 (qd, J = 16.8, 6.9 Hz, 2H), 2.97- 2.83 (m, 2H). [13]C NMR (100 MHz, $CDCl_3$) δ 198.90, 144.14, 139.84, 137.22, 132.94, 129.30, 128.53, 128.38, 128.20, 128.02, 127.69, 126.42, 126.12, 44.17, 43.05, 43.01.



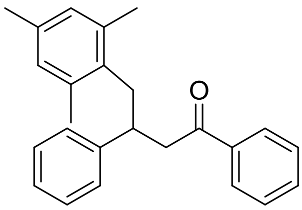
2b

1,3-diphenyl-4-(p-tolyl)butan-1-one (2b): white solid. 119.2mg, 76% yield. [1]H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 7.9 Hz, 2H), 7.57 (t, J = 7.3 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 7.29 (d, J = 7.2 Hz, 2H), 7.25 (d, J = 7.7 Hz, 3H), 7.08 (d, J = 7.8 Hz, 2H), 7.03 (d, J = 7.6 Hz, 2H), 3.75-3.68 (m, 1H), 3.43-3.28 (m, 2H), 3.00 (d, J = 7.4 Hz, 2H), 2.34 (s, 3H). [13]C NMR (100 MHz, $CDCl_3$) δ 198.98, 144.31, 137.25, 136.71, 135.55, 132.90, 129.18, 128.92, 128.51, 128.37, 128.02, 127.70, 126.38, 44.14, 43.08, 42.58, 21.04. HR-MS calcd for $C_{23}H_{23}ONa$ $[M+Na]^+$, 337.1568, Found 337.1563.



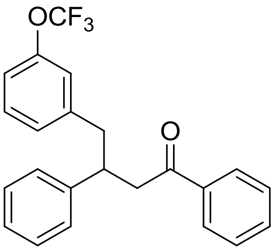
2c

4-(4-methoxyphenyl)-1,3-diphenylbutan-1-one (2c): white solid. 63% yield. 104.1mg. [1]H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 7.9 Hz, 1H), 7.51 (t, J = 7.3 Hz, 0H), 7.40 (t, J = 7.4 Hz, 1H), 7.24 (t, J = 7.4 Hz, 1H), 7.15 (dd, J = 11.5, 7.5 Hz, 1H), 6.97 (d, J = 7.7 Hz, 1H), 6.74 (d, J = 7.5 Hz, 1H), 3.74 (s, 3H), 3.62 (p, J = 7.2 Hz, 1H), 3.35-3.21 (m, 2H), 2.99-2.84 (m, 2H). [13]C NMR (100MHz, $CDCl_3$) δ 198.99, 157.97, 144.24, 137.24, 132.91, 131.88, 130.22, 128.52, 128.36, 128.01, 127.71, 126.37, 113.60, 55.19, 44.09, 43.95, 42.11. HR-MS calcd for $C_{23}H_{22}O_2Na$ $[M+Na]^+$, 353.1517, Found 353.1500.



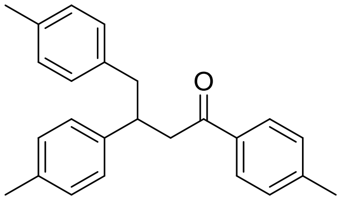
2d

4-mesityl-1,3-diphenylbutan-1-one (2d) : white solid, 111.2mg, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.7 Hz, 2H), 7.61 (t, J = 7.1 Hz, 4H), 7.50 (t, J = 7.4 Hz, 3H), 7.40-7.34 (m, 1H), 7.31 (d, J = 7.4 Hz, 1H), 6.92 (s, 1H), 3.82-3.71 (m, 1H), 3.61 (dd, J = 16.1, 8.3 Hz, 1H), 3.41 (dd, J = 16.1, 5.5 Hz, 1H), 3.17 (dd, J = 13.6, 7.9 Hz, 1H), 2.99 (dd, J = 13.7, 7.3 Hz, 1H), 2.36 (s, 6H), 2.32 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 196.70, 142.33, 134.93, 134.62, 133.13, 131.35, 130.65, 126.88, 126.28, 126.13, 125.79, 125.32, 124.22, 41.20, 39.22, 34.75, 18.62, 18.02.



2e

1,3-diphenyl-4-(3-(trifluoromethoxy)phenyl)butan-1-one (2e) : yellow oil. 117.2mg. 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 7.7 Hz, 2H), 7.45 (t, J = 7.3 Hz, 1H), 7.34 (t, J = 7.4 Hz, 2H), 7.19 (t, J = 7.3 Hz, 1H), 7.12 (dd, J = 13.3, 7.2 Hz, 2H), 6.95 (d, J = 7.7 Hz, 1H), 6.85 (s, 0H), 3.70-3.59 (m, 1H), 3.38-3.21 (m, 1H), 3.05 (dd, J = 13.4, 6.0 Hz, 1H), 2.87 (dd, J = 13.2, 8.8 Hz, 1H). ^{13}C NMR (100MHz, $CDCl_3$) δ 198.57, 149.14, 143.49, 142.35, 137.18, 133.13, 129.48, 128.65, 128.54, 128.05, 127.82, 127.73, 126.71, 44.24, 42.96, 42.61.



2f

1,3,4-tri-p-tolylbutan-1-one: white solid. 116.4mg, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.5 Hz, 1H), 7.10 (d, J = 7.8 Hz, 1H), 7.03- 6.95 (m, 1H), 6.94-6.86 (m, 1H), 3.52 (p, J = 7.1 Hz, 0H), 3.15 (t, J = 6.1 Hz, 1H), 2.83 (d, J = 7.4 Hz, 1H), 2.28 (s, 3H), 2.19 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.73, 143.60, 141.23, 136.92, 135.72, 135.45, 134.82, 129.18, 129.06, 128.89, 128.19, 127.53, 44.16, 42.72, 42.62, 21.62, 21.05.

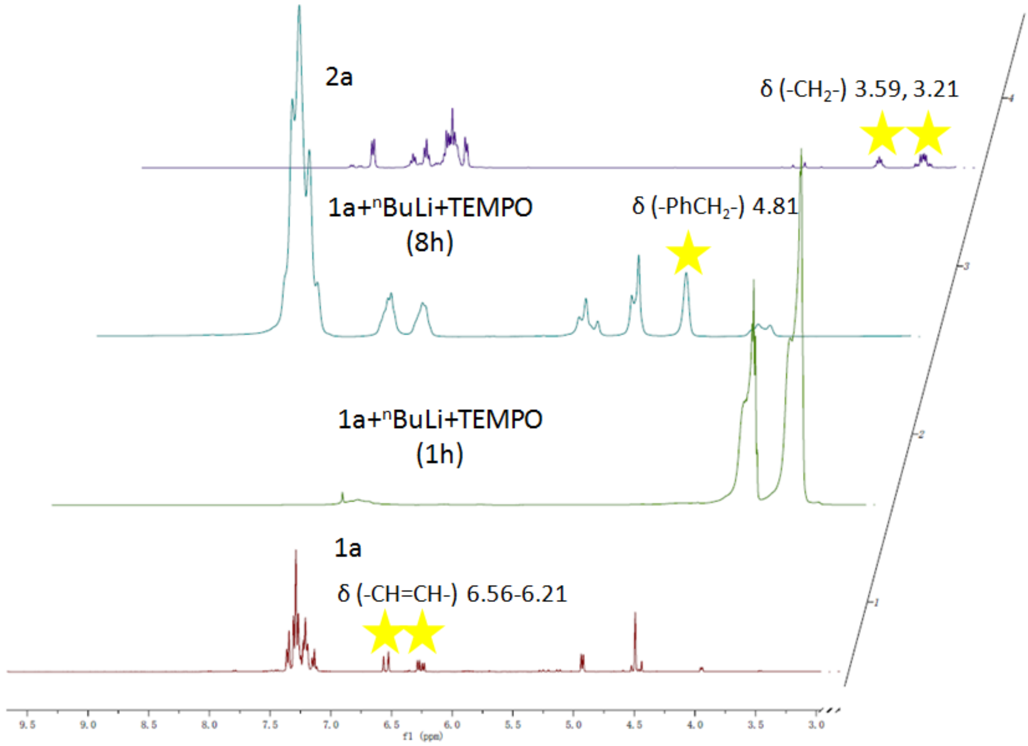
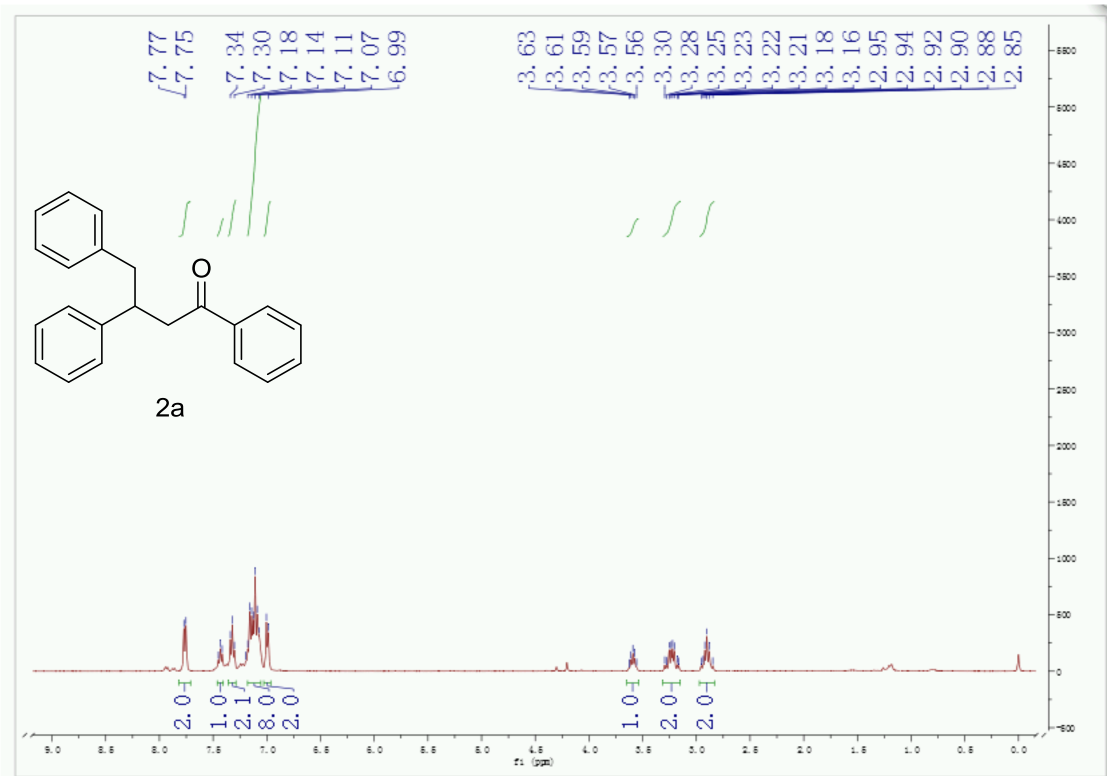
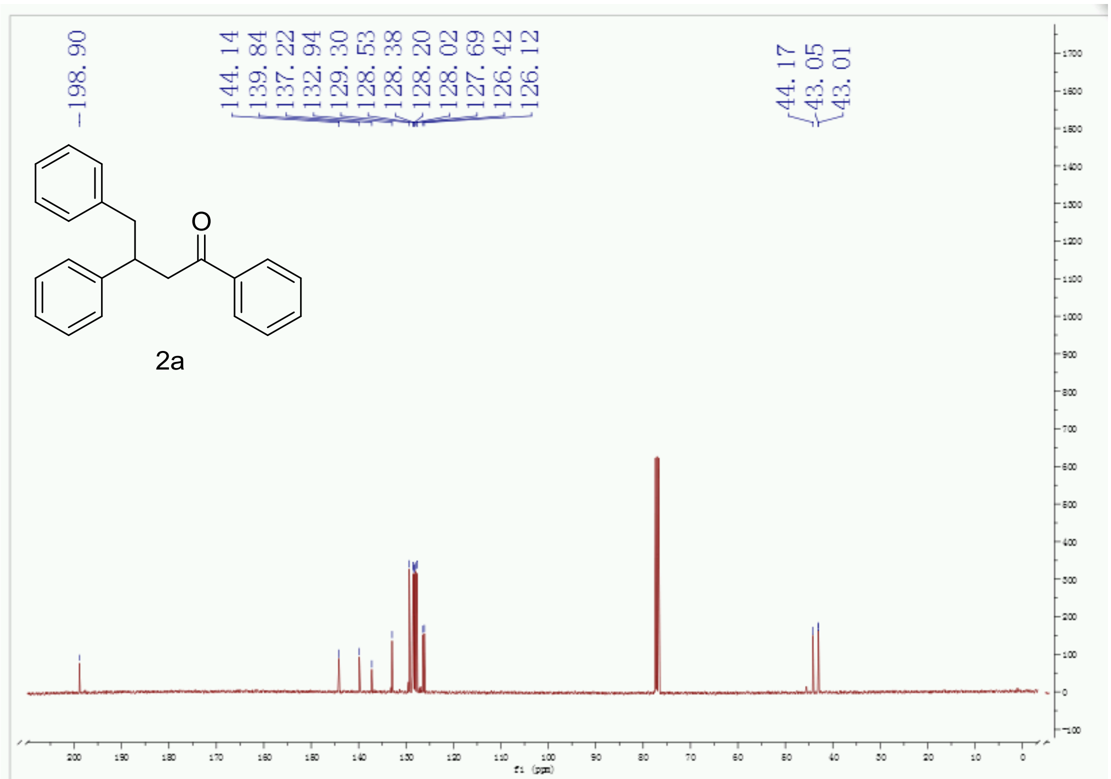
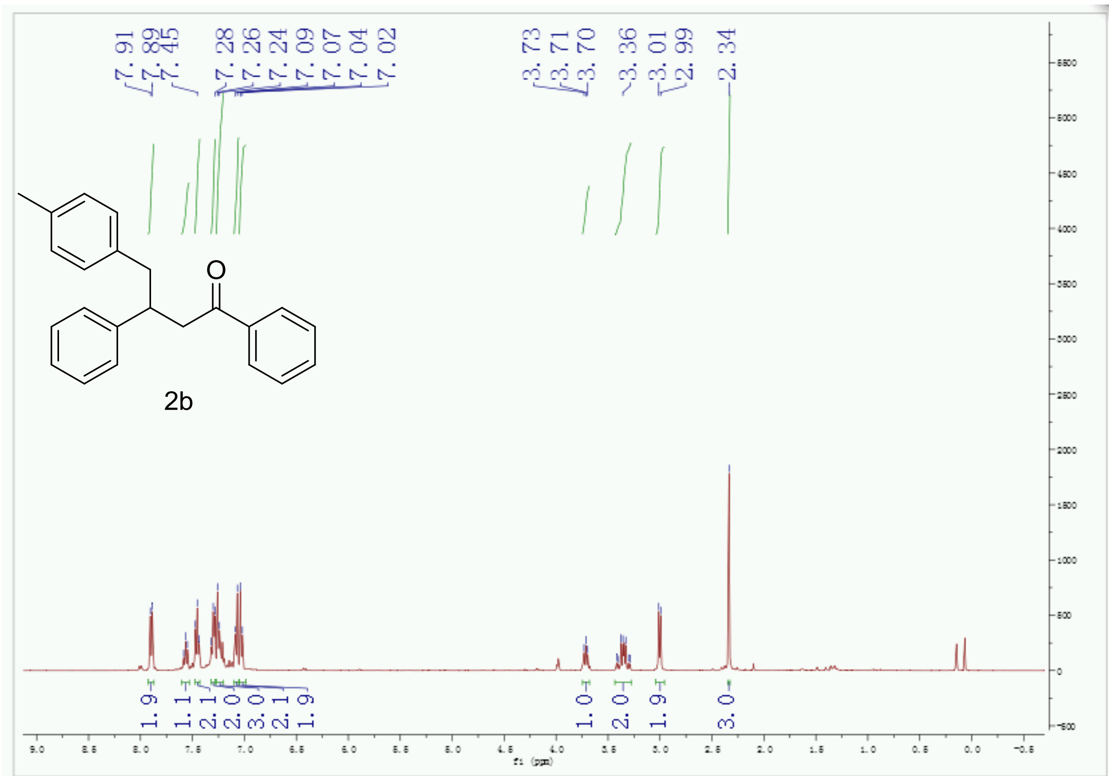


Figure S1. No reaction when the addition of TEMPO to lithium-promoted [1,4]-Wittig rearrangement

8. $^{1}H/^{13}C$-NMR of the products 2 and representative substrates



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7.89
7.45
7.28
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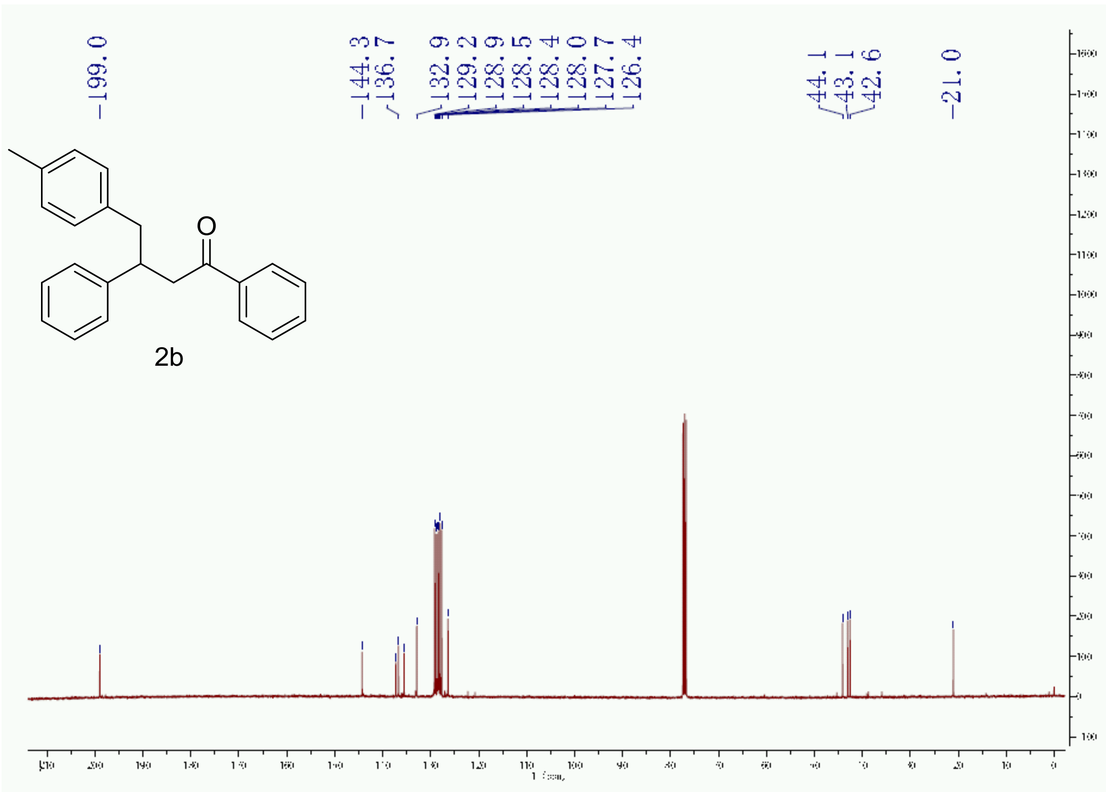
7.24
7.09
7.07
7.04
7.02
3.73
3.71
3.70
3.36
3.01
2.99
2.34
O
2b
1.9
1.1
2.1
2.0
3.0
2.1
1.9
1.0
2.0
1.9
3.0
f1 (ppm)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132.9
129.2
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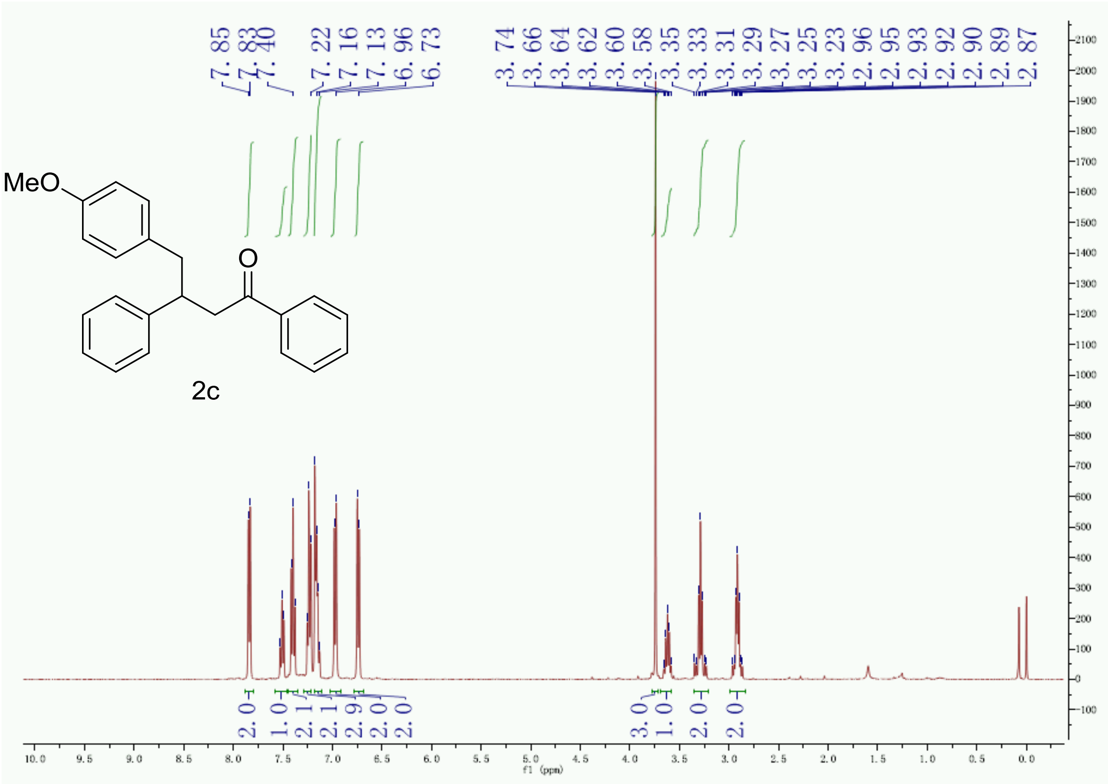
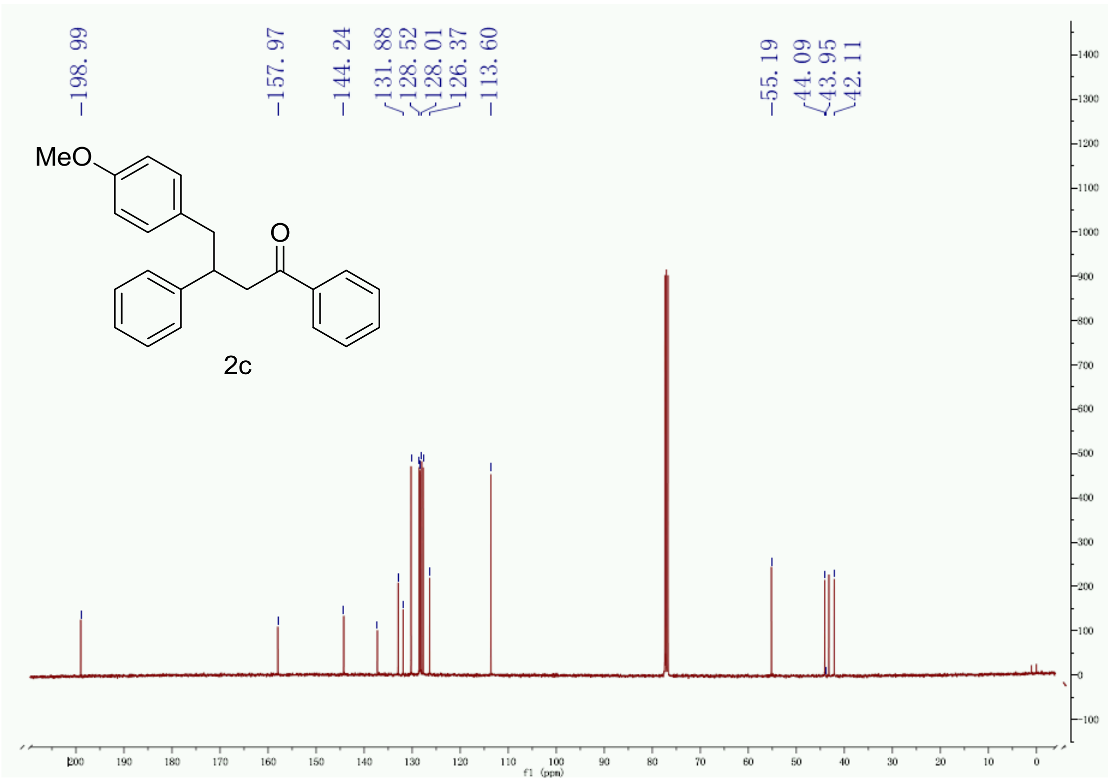
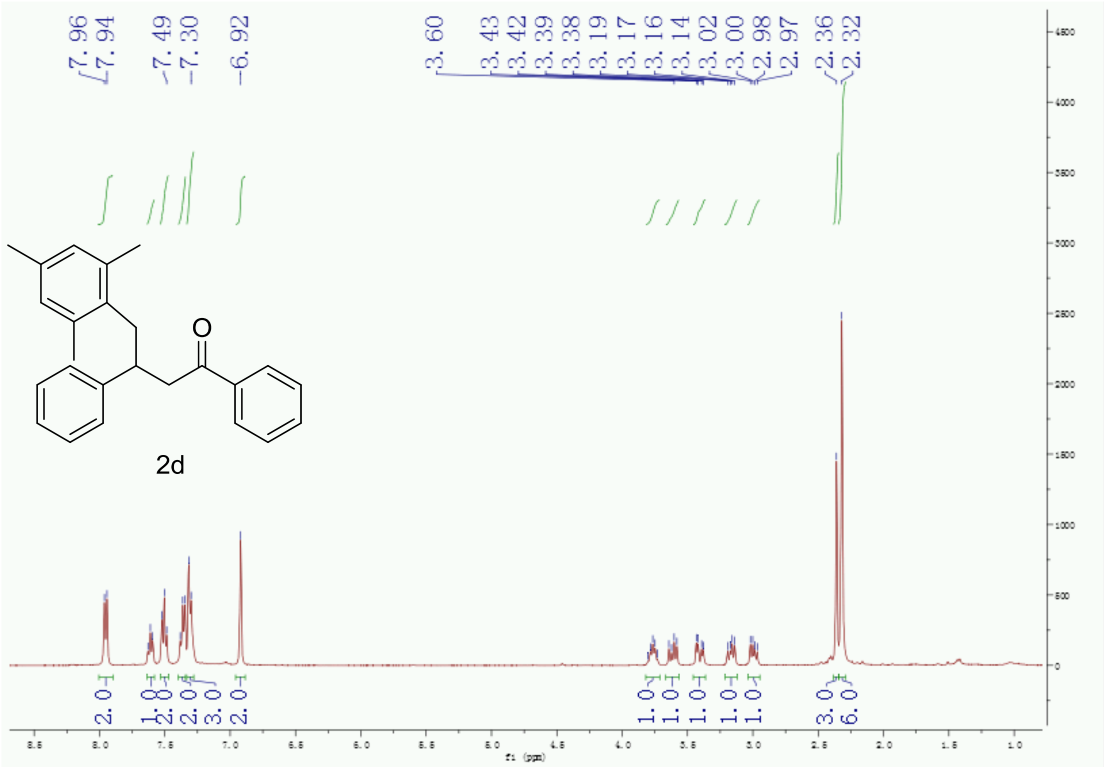
128.5
128.4
128.0
127.7
126.4
44.1
43.1
42.6
21.0
O
2b


MeO
O
2c


MeO
O
2c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6.92
3.60
3.43
3.42
3.39
3.38
3.19
3.17
3.16
3.14
3.02
3.00
2.98
2.97
2.36
2.32
O
2d
2.0
1.0
2.0
2.0
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1.0
1.0
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1.0
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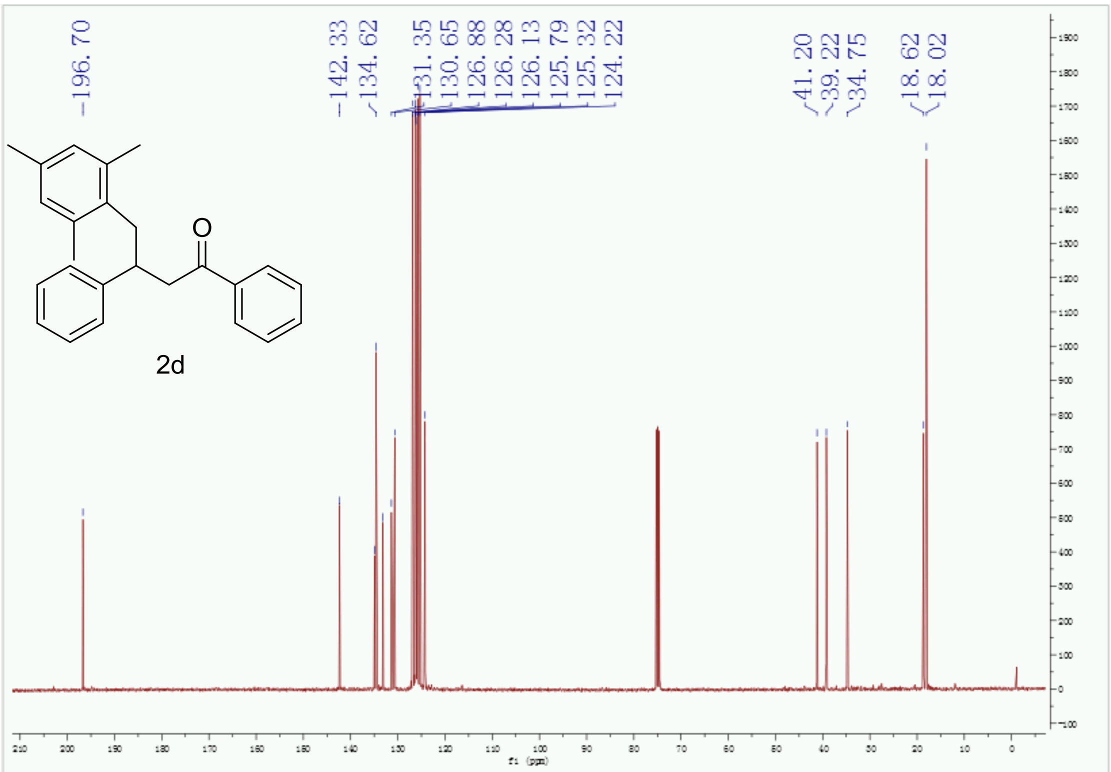
6.0
f1 (ppm)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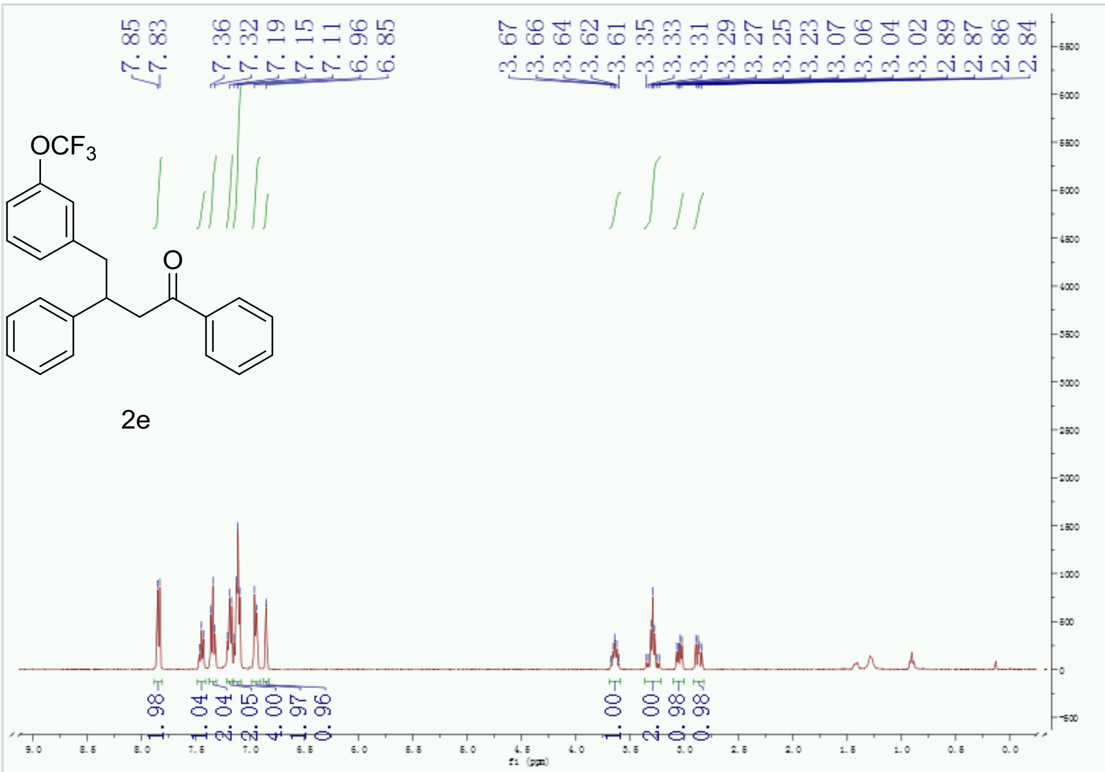
131.35
130.65
126.88
126.28
126.13
125.79
125.32
124.22
41.20
39.22
34.75
18.62
18.02
O
2d
f1 (ppm)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3.62
3.61
3.35
3.33
3.31
3.29
3.27
3.25
3.23
3.07
3.06
3.04
3.02
2.89
2.87
2.86
2.84
OCF3
O
2e
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2.05
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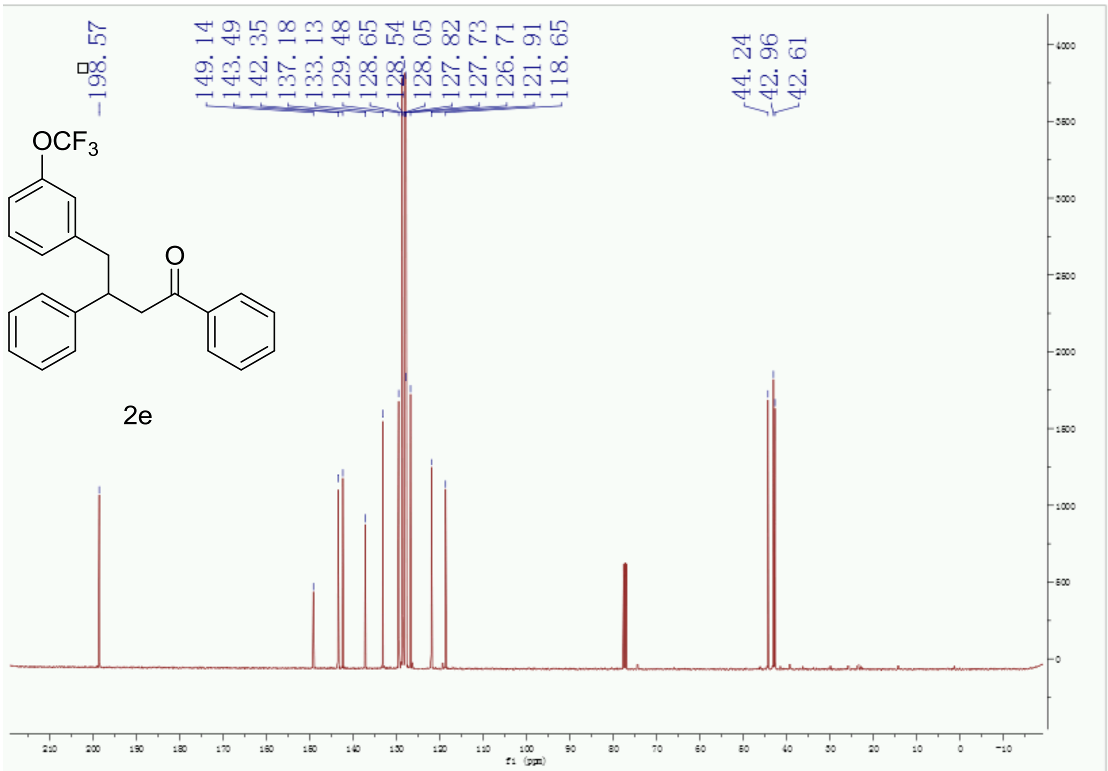
0.98
0.98
f1 (ppm)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142.35
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128.65
128.54
128.05
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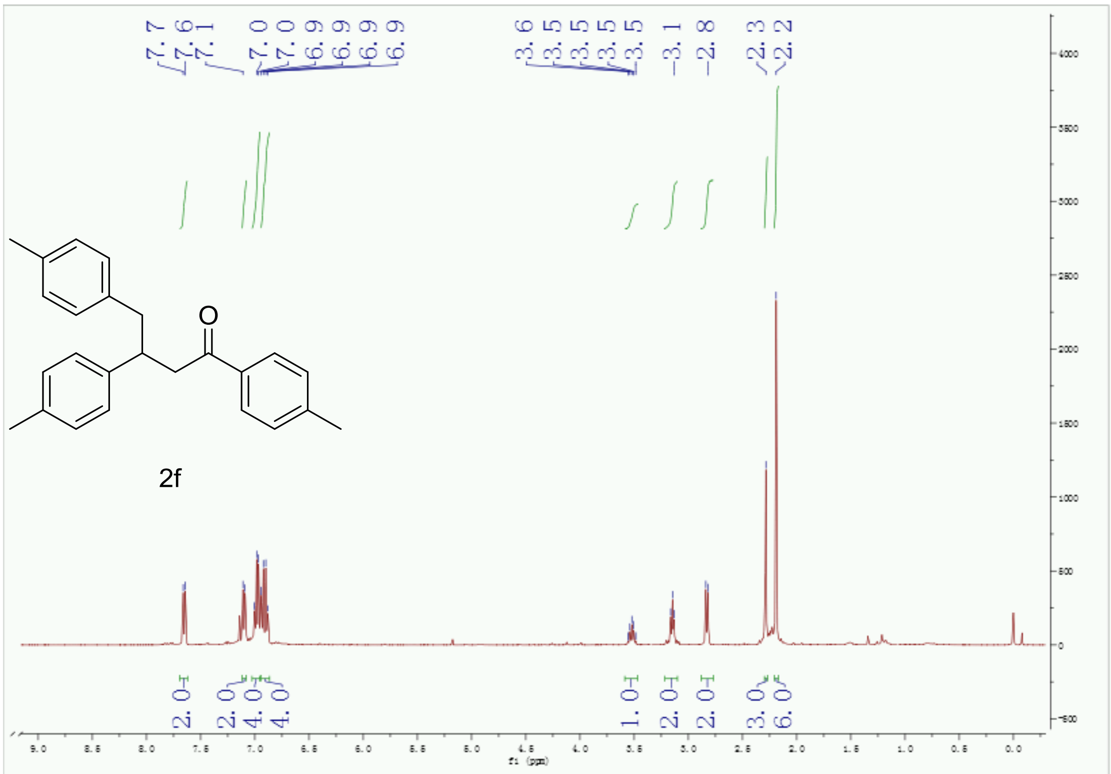
127.73
126.71
121.91
118.65
44.24
42.96
42.61
OCF3
O
2e
f1 (ppm)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6.9
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3.1
2.8
2.3
2.2
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2.0
4.0
4.0
1.0
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3.0
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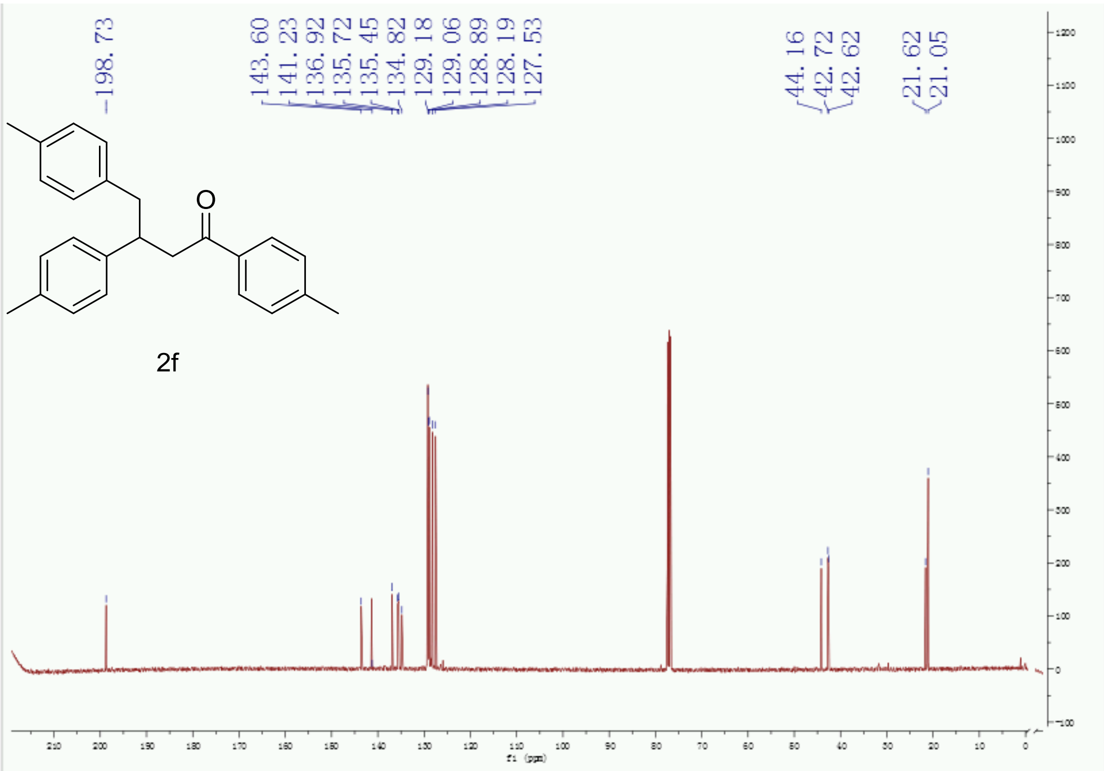
O
2f
f1 (ppm)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129.18
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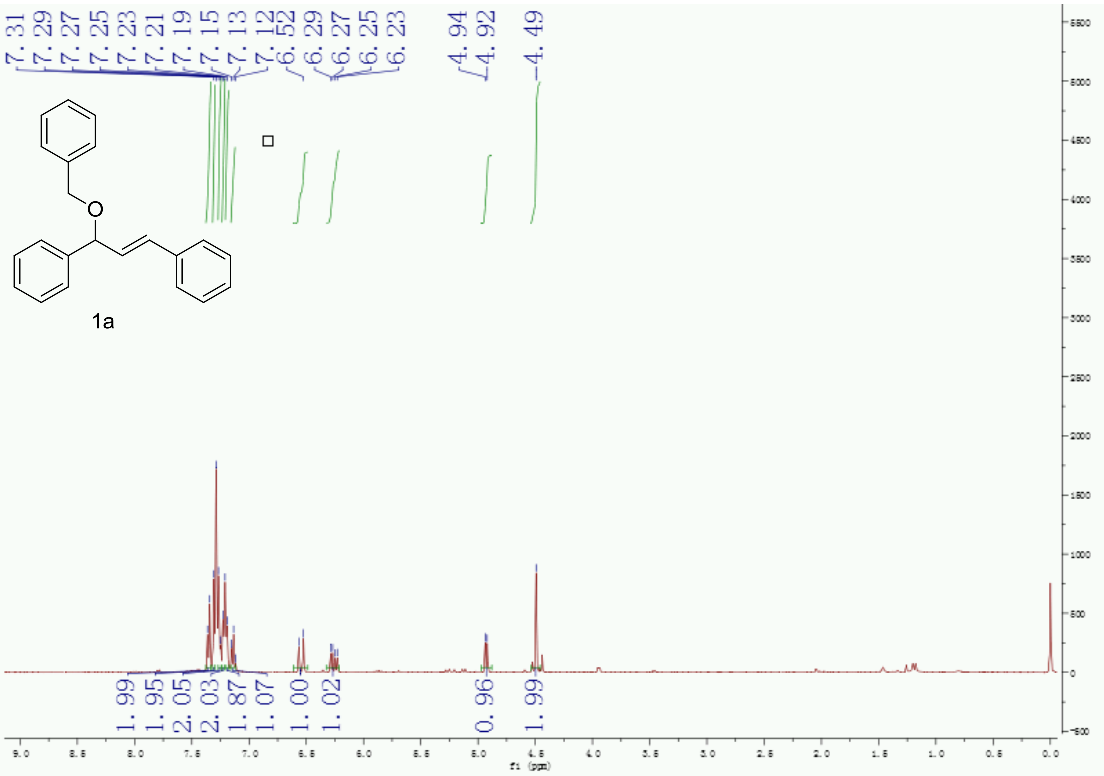
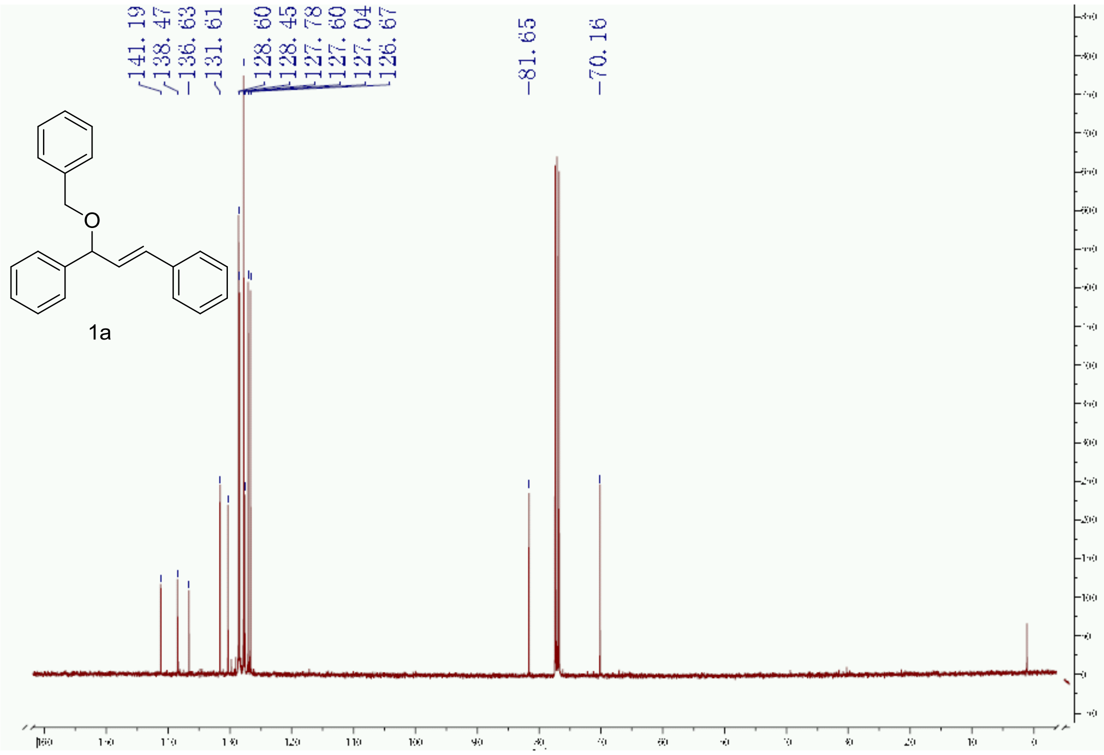
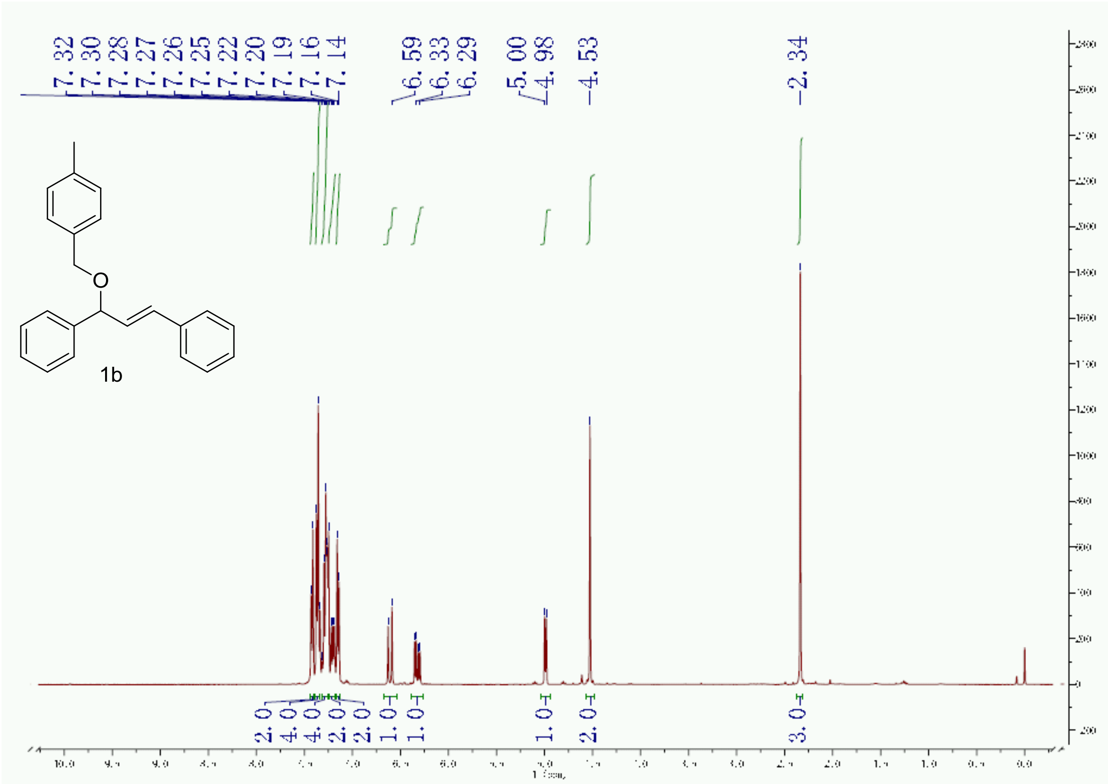
128.89
128.19
127.53
44.16
42.72
42.62
21.62
21.05
O
2f
f1 (ppm)

2. $^{1}H/^{13}C$-NMR of the products 1 and representative substrates



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6.29
5.00
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4.0
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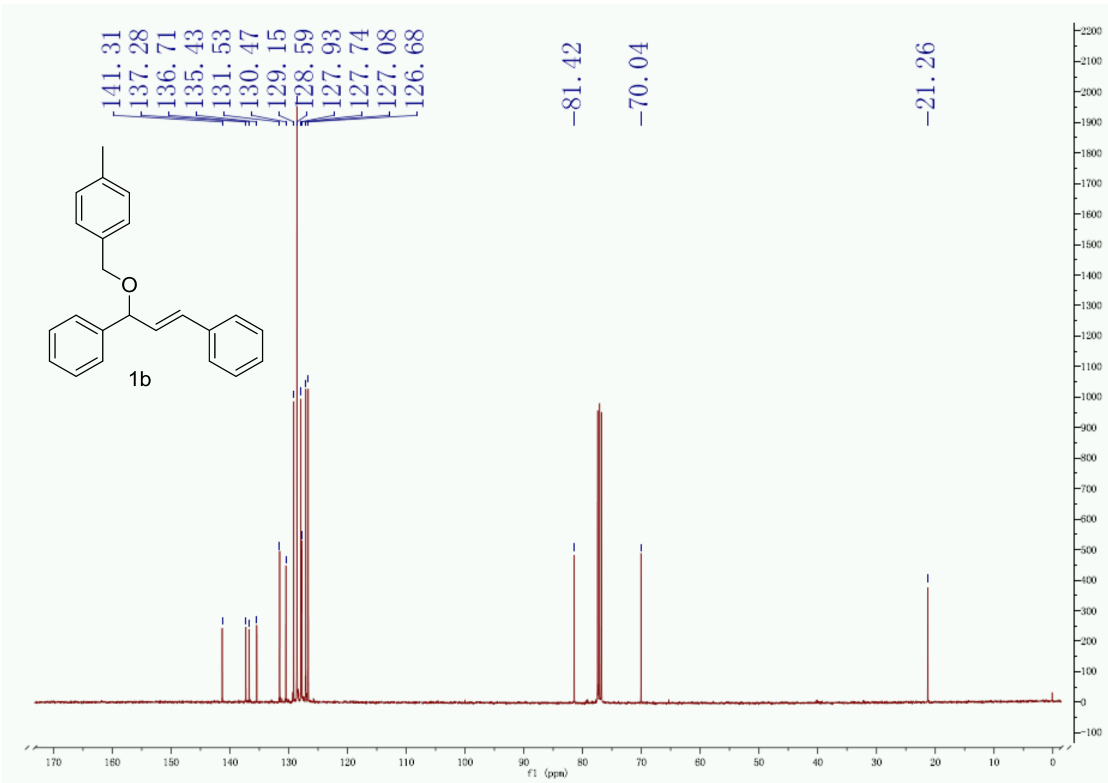
2.0
3.0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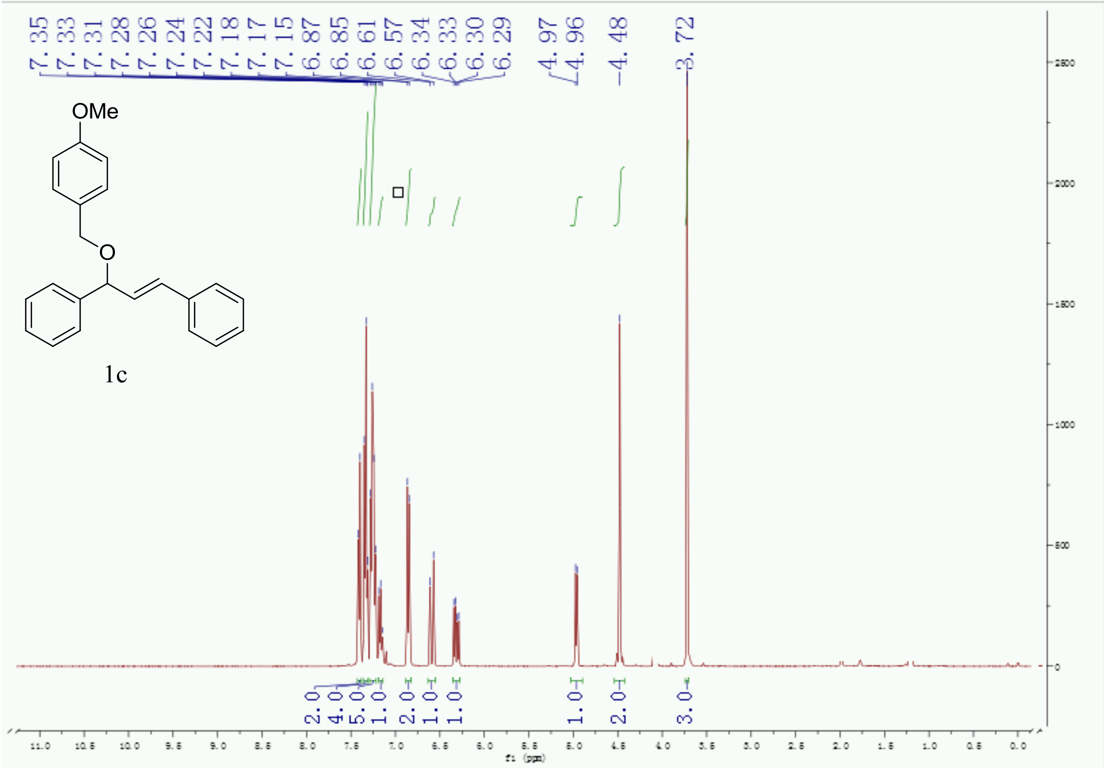
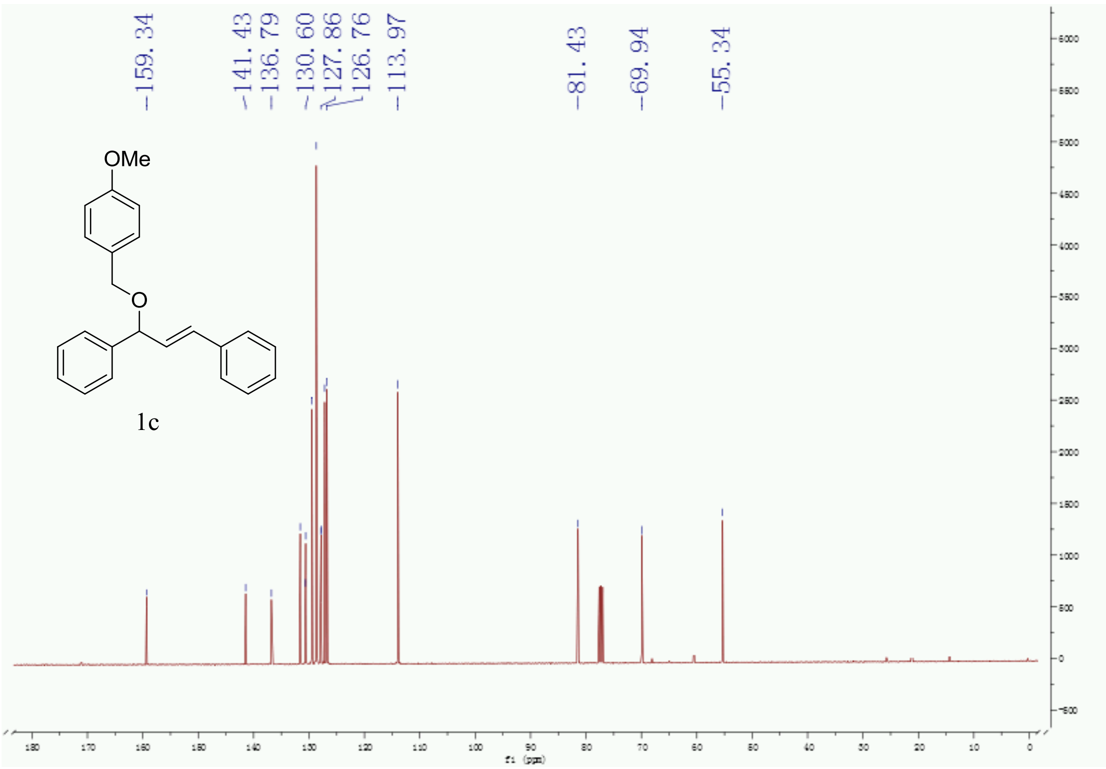
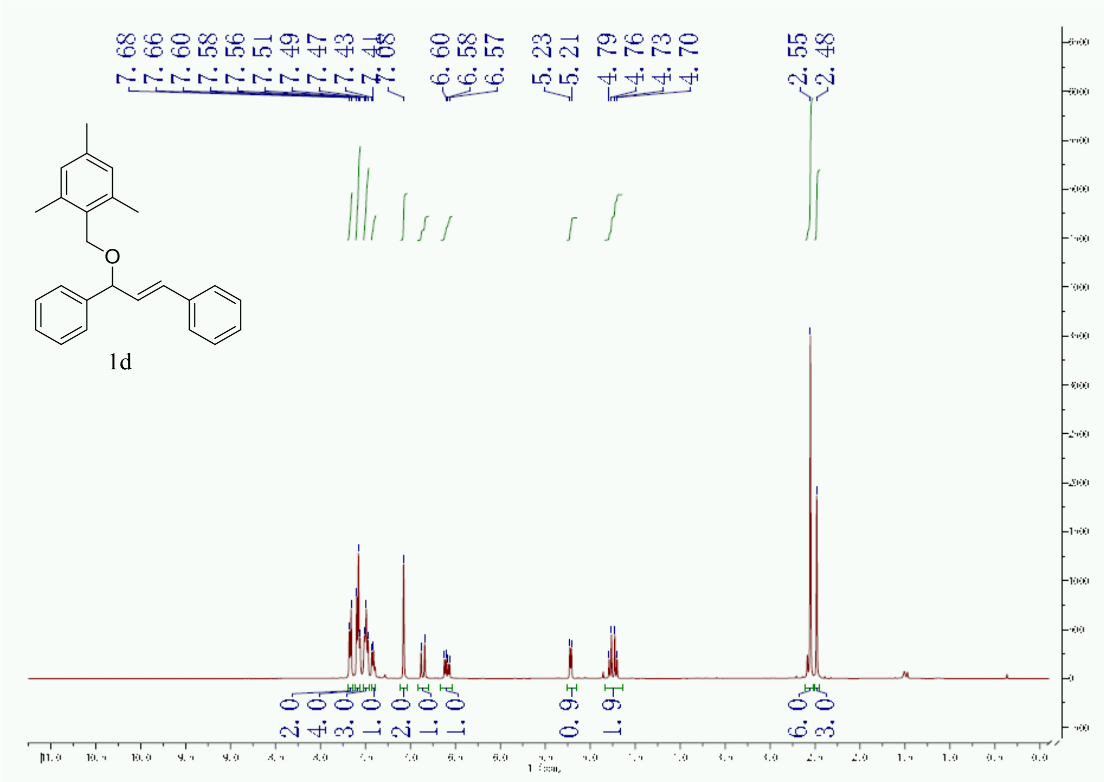
1b
f1 (ppm)



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6.58
6.57
5.23
5.21
4.79
4.76
4.73
4.70
2.55
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3.0
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1.0
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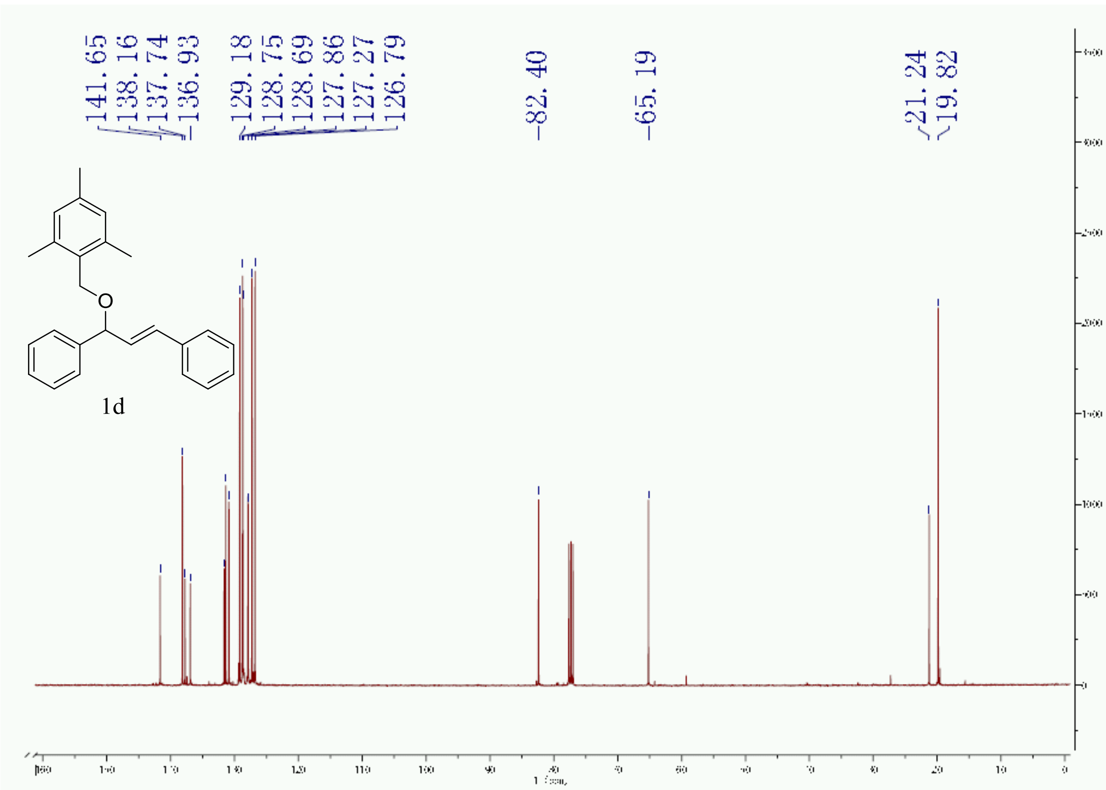
1.9
6.0
3.0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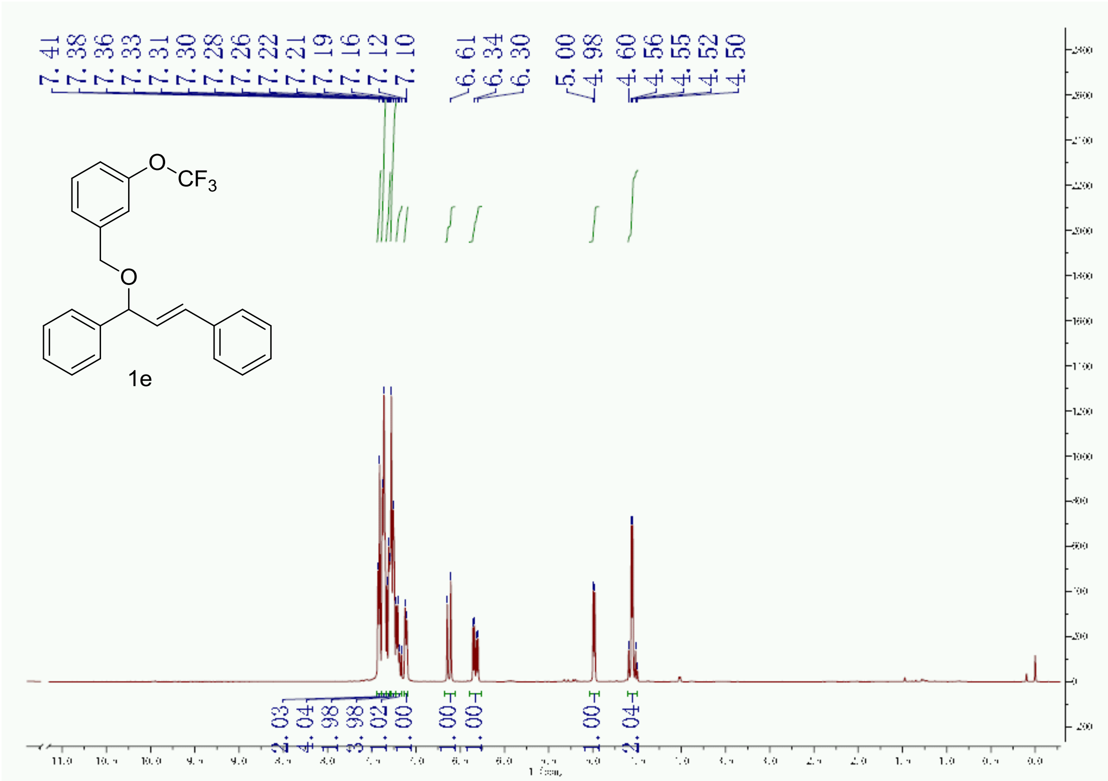
19.82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4.60
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4.55
4.52
4.50
O
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1.00
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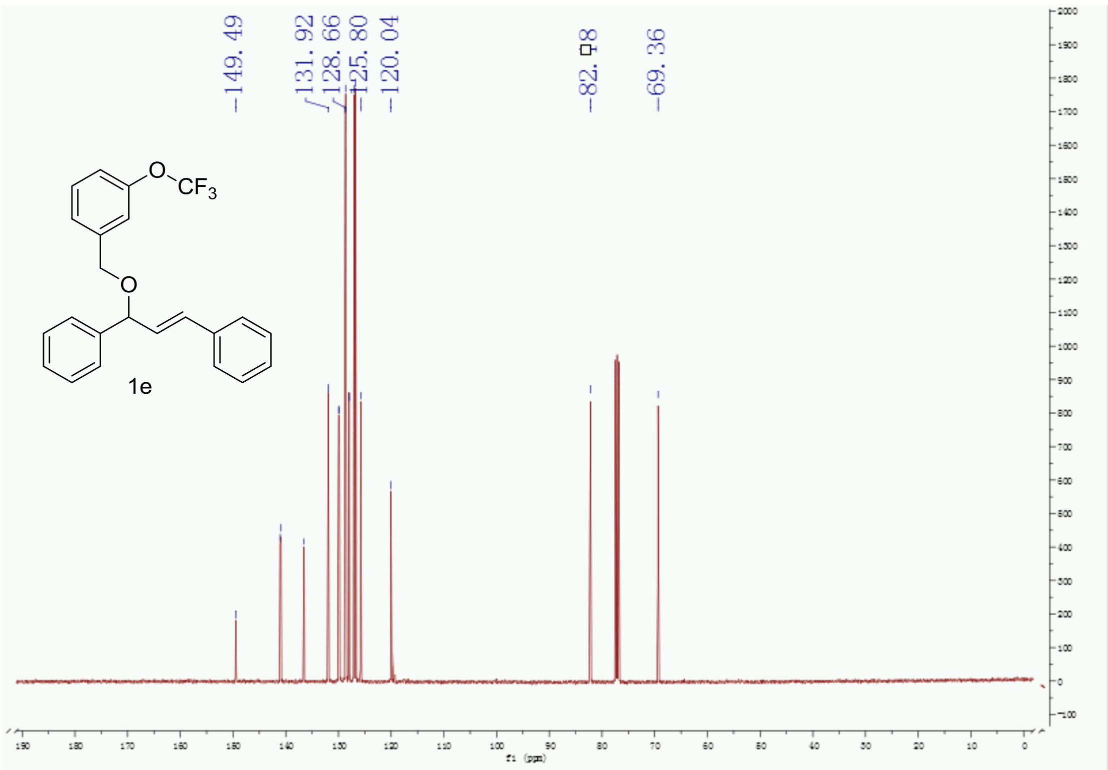
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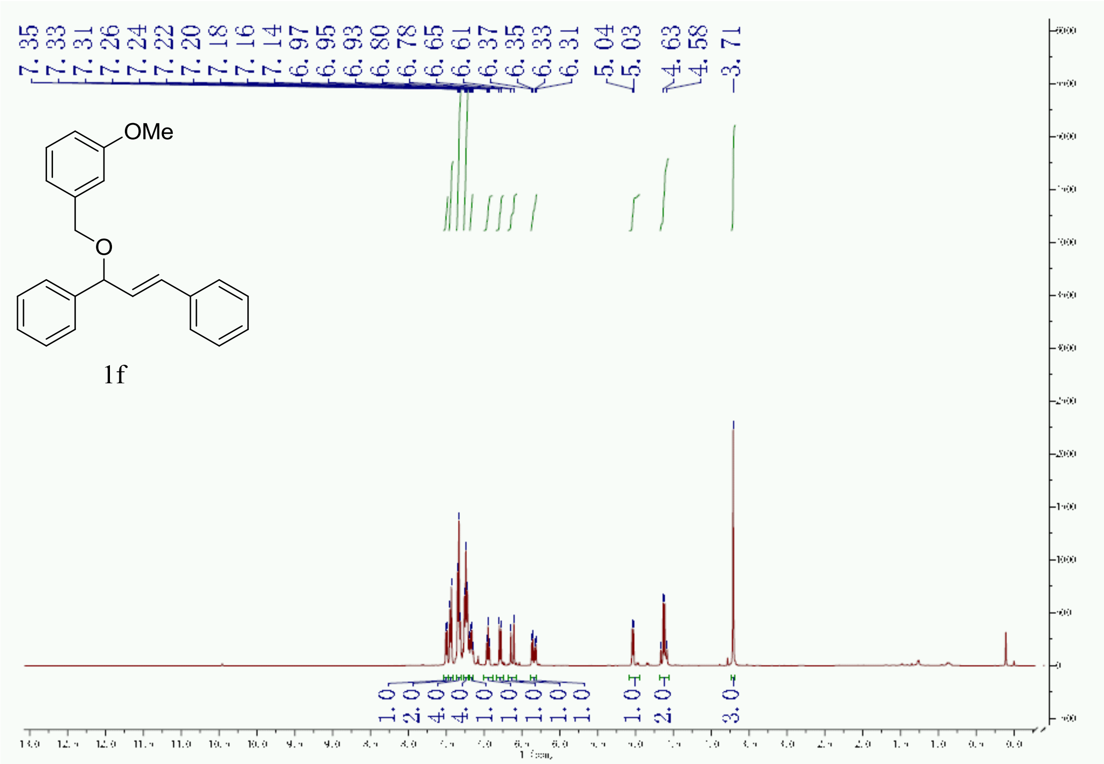
CF3
O
1e
f1 (ppm)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6.80
6.78
6.65
6.61
6.37
6.35
6.33
6.31
5.04
5.03
4.63
4.58
3.71
OMe
O
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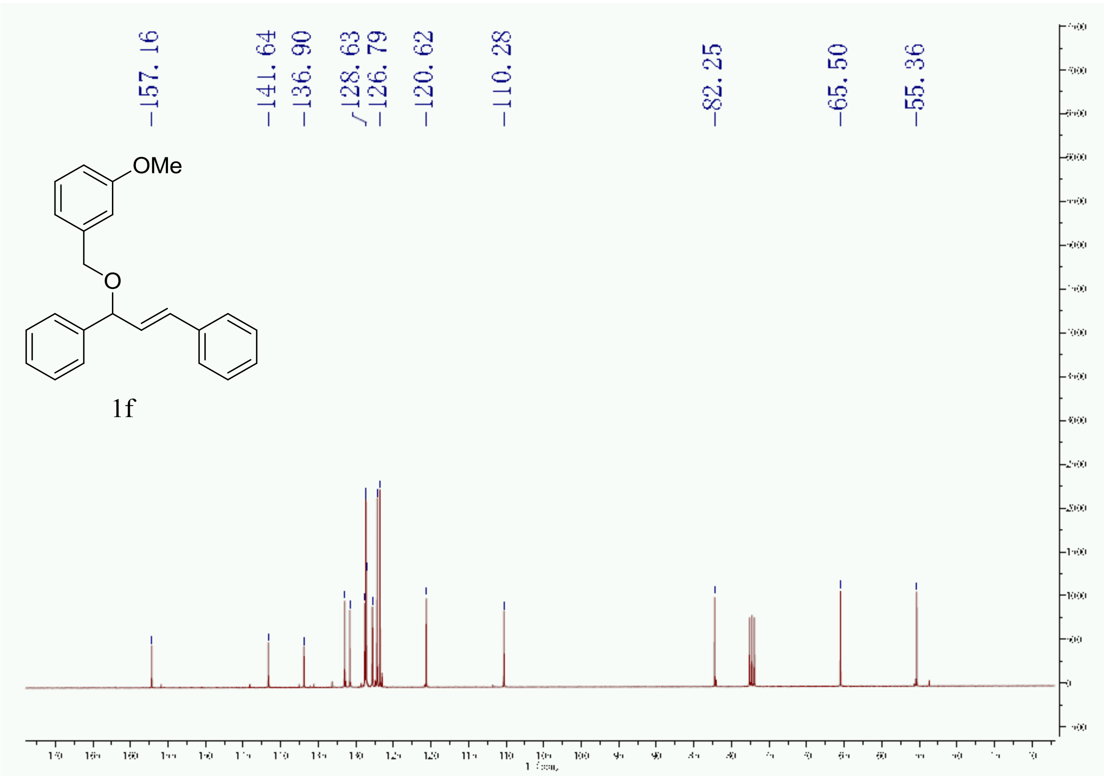
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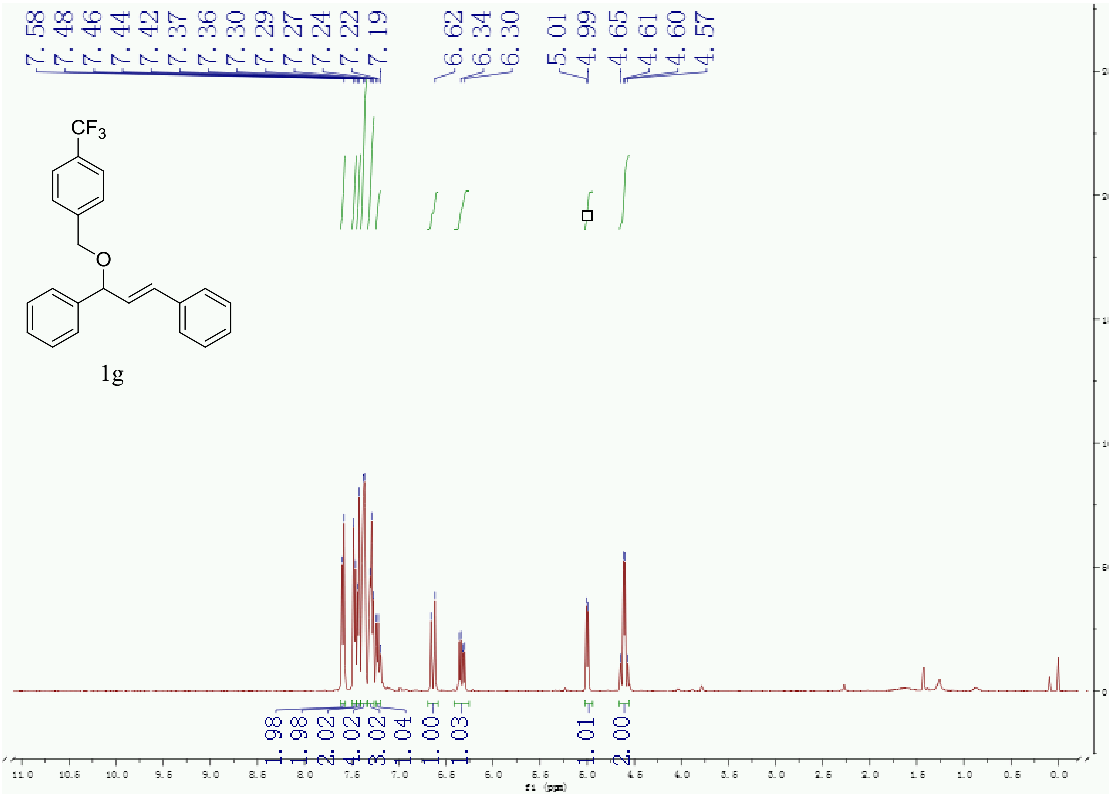
OMe
O
1f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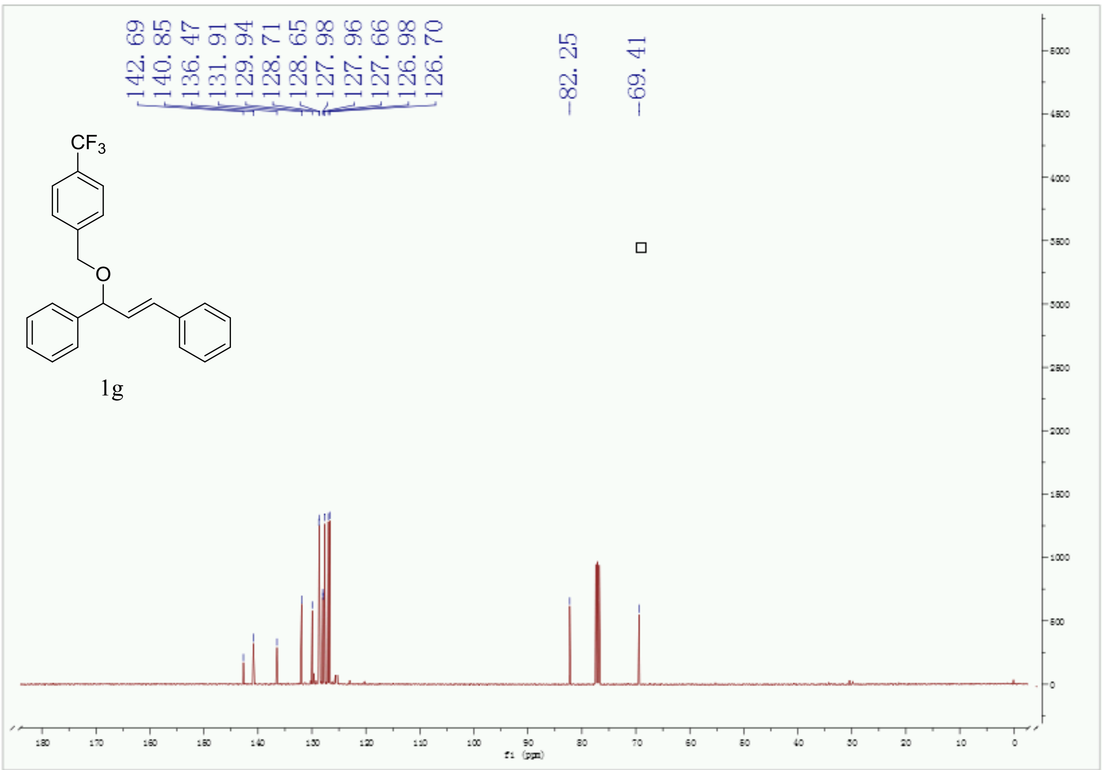
2.00
f1 (ppm)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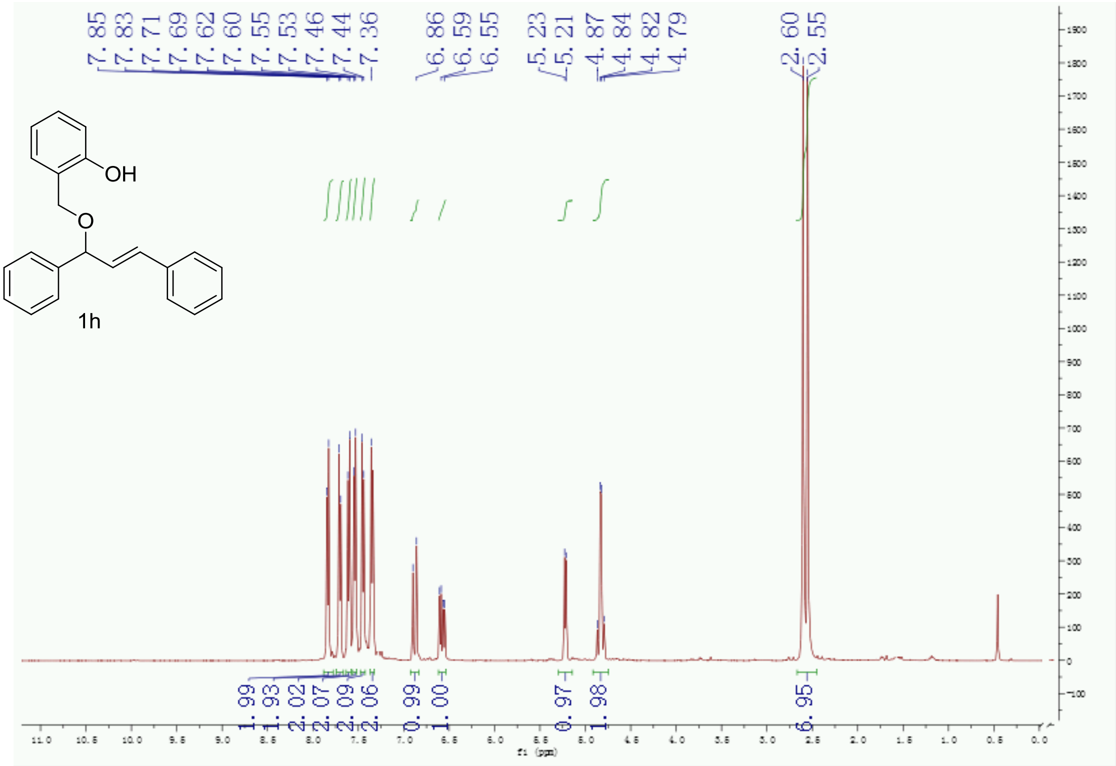
1g
f1 (ppm)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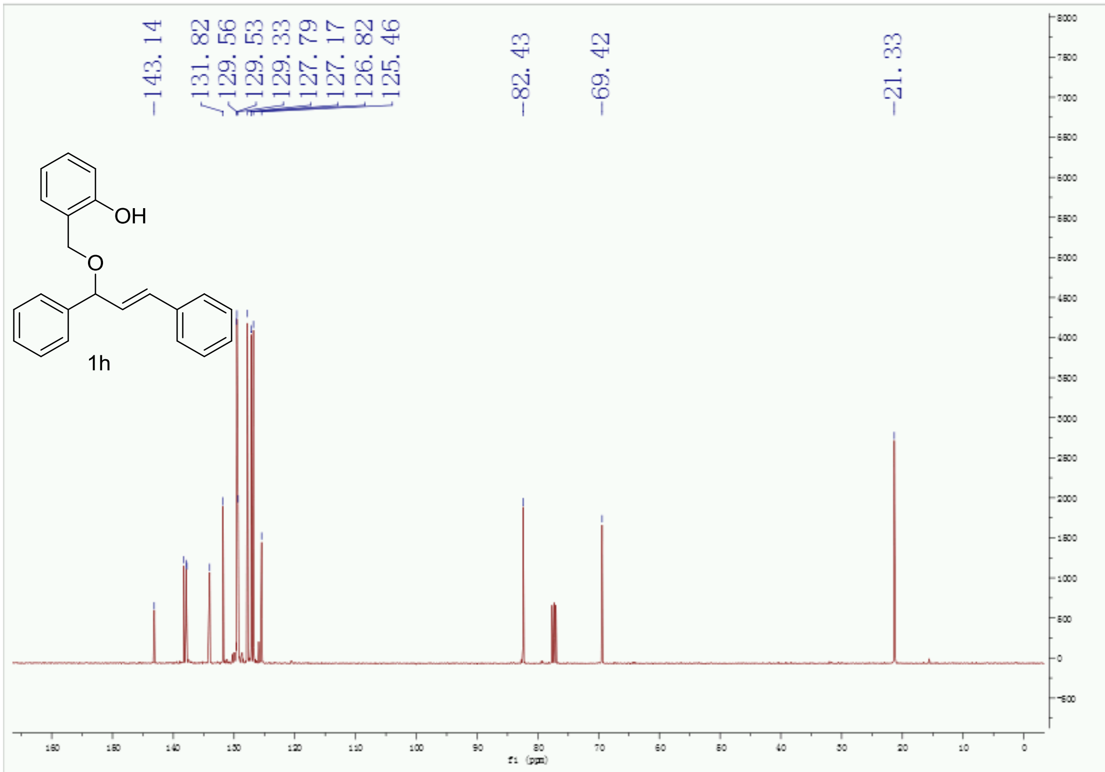
f1 (ppm)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82.43
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OH
O
1h
f1 (ppm)

9. HR-MS of Representative products: 2b and 2c

Mass Spectrum SmartFormula Report

Analysis Info

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Method	tune_100-500_pos150113.m	Operator	Jiang
Sample Name	trz-7	Instrument / Ser#	micrOTOF-Q II 10324
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
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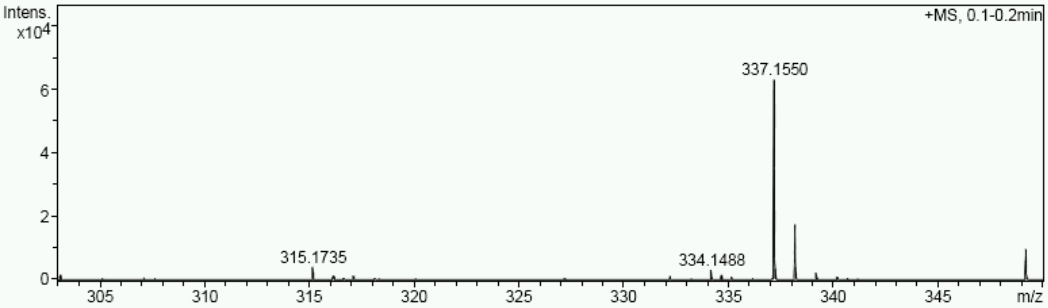
Scan End	800 m/z	Set Collision Cell RF	120.0 Vpp	Set Divert Valve	Source



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337.1550	1	C 23 H 22 Na O	100.00	337.1563	1.3	3.8	16.9	12.5	even	ok

Mass Spectrum SmartFormula Report

Analysis Info

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Method	tune_100-500_pos150113.m	Operator	Jiang
Sample Name	trz-7	Instrument / Ser#	micrOTOF-Q II 10324
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
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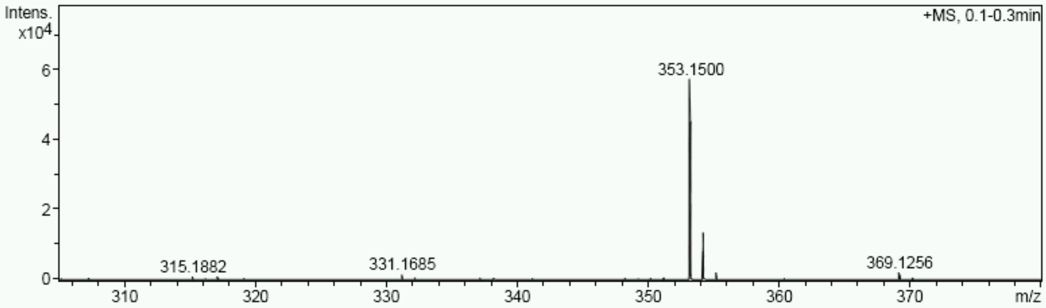
Scan End	800 m/z	Set Collision Cell RF	120.0 Vpp	Set Divert Valve	Source



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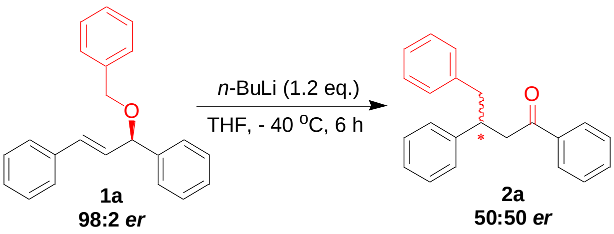
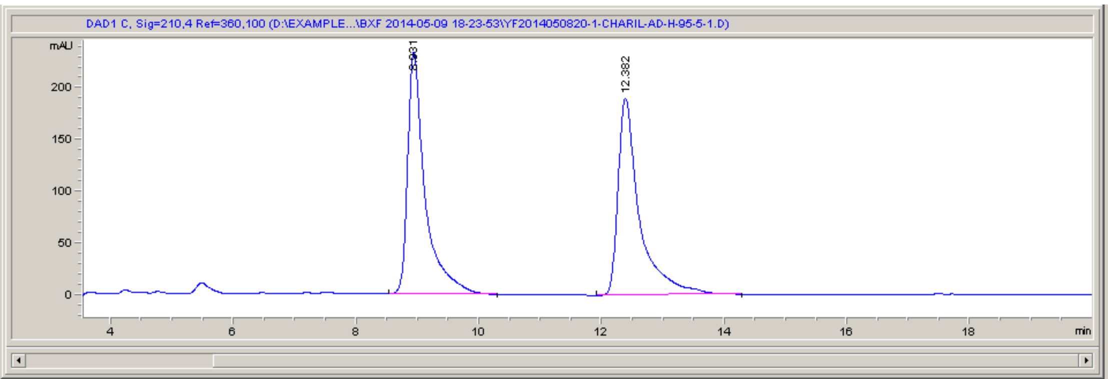
353.1500	1	C 23 H 22 Na O 2	100.00	353.1512	1.2	3.4	5.8	12.5	even	ok

10 HPLC Charts of enantioselective [1,4]-Wittig rearrangement





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样品	YF2014050820-1-Charil-AD-H-95-5-1
样品信息	
条形码	
操作者	HWS
方法	BXF-SXYH.M
分析时间	19.993 min

#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	8.931	4637.4	233.8	0.2854	0.483	49.886
2	12.382	4658.5	190.3	0.3535	0.464	50.114

HPLC conditions: chiralcel AD-H, *n*-hexane/2-propanol = 95/5, 1.0 mL/min