

Electronic Supplementary Information

Silver-Catalyzed Three-Component Reaction via Stabilized Cation: Synthesis of Polysubstituted Tetrahydronaphthols and Tetrahydronaphthylamines

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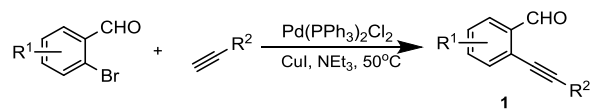
1.Experimental procedures and spectroscopic data

1. 1 General information

All reactions were carried out under an inert atmosphere of dry N₂ in Schlenk tube, solvents were purified by standard method. ¹H, ¹³C, ¹⁹F NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz for ¹H; 100 MHz for ¹³C; 376 MHz for ¹⁹F), ¹H NMR and ¹³C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 and ¹⁹F NMR chemical shifts were determined relative to CFCl₃ as external standard. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d =doublet, t = triplet, q = quartet, m = multiplet, br = broad. Infrared (IR) spectra are recorded on a Nicolet 210 spectrophotometer and were recorded in potassium bromide (KBr) pellet. Mass spectra (MS) were obtained using EI mass spectrometer. Melting points were determined using a hot stage apparatus. All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature.

1.2 General procedure for the synthesis of enynals

1.2.1 Enynals were prepared according to the literature procedures ¹⁻⁴:

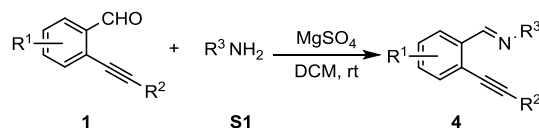


To a solution of the corresponding 2-bromobenzaldehyde (1.0 equiv.), Pd(PPh₃)₂Cl₂ (2.0 mol %), and CuI (1.0 mol %) in NEt₃ (0.25 M) was added the appropriate acetylene (1.2 equiv.). The resulting mixture was stirred under nitrogen atmosphere at 50 °C overnight. After the reaction was finished, the mixture was filtered by short silica, then the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel to afford the desired product **1**.

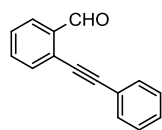
Spectral data of product **1** was consistent with data reported in the literature ¹.

1.3 Preparation of 2-alkynylarylaldimines

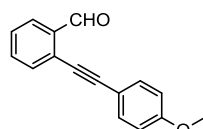
2-Alkynylarylaldimines were prepared according to the literature procedures ⁵:



A solution of aryl amines **S1** (5 mmol) and enynals **1** (5.0 mmol) in CH₂Cl₂ (20 mL) was added MgSO₄ (2.0 g), the reaction mixture was stirred at room temperature overnight. After the reaction was finished, the mixture was filtered through short pad of celite and the filtrate was concentrated under reduced pressure to afford 2-Alkynylarylaldimines **4** which were used as such without further purification.

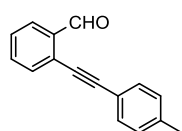
2-(Phenylethynyl)benzaldehyde (1a)¹

¹H NMR (400 MHz, CDCl₃) δ 10.63 (s, 1H), 7.92 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.63 – 7.59 (m, 1H), 7.54 (ddd, *J* = 8.9, 5.0, 1.5 Hz, 3H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.38 – 7.34 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 191.7, 135.9, 133.8, 133.3, 131.7, 129.1, 128.6, 128.6, 127.3, 126.9, 122.4, 96.4, 85.9.

2-((4-Methoxyphenyl)ethynyl)benzaldehyde (1b)¹

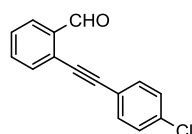
¹H NMR (400 MHz, CDCl₃) δ 10.64 (s, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.55 (s, 1H), 7.50 (d, *J* = 8.7 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 2H), 3.83 (d, *J* = 1.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 191.8, 160.3, 135.7, 133.8, 133.2, 133.1, 128.2, 127.4, 127.3, 114.4, 114.3, 96.6,

83.8, 55.4.

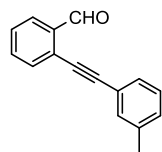
2-(p-Tolylethynyl)benzaldehyde (1c)¹

¹H NMR (400 MHz, CDCl₃) δ 10.65 (d, *J* = 0.6 Hz, 1H), 7.94 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.62 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.56 (td, *J* = 7.5, 1.4 Hz, 1H), 7.44 (dd, *J* = 14.4, 7.8 Hz, 3H), 7.18 (d, *J* = 7.9 Hz, 2H), 2.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 191.8, 139.4, 135.8, 133.7, 133.2, 131.6, 129.3, 128.4, 127.2, 127.2, 119.3, 96.7,

84.4, 21.6.

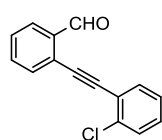
2-((4-Chlorophenyl)ethynyl)benzaldehyde (1d)¹

¹H NMR (400 MHz, CDCl₃) δ 10.61 (s, 1H), 7.95 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.64 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.60 (dd, *J* = 7.3, 1.1 Hz, 1H), 7.50 (d, *J* = 1.8 Hz, 1H), 7.49 – 7.46 (m, 2H), 7.39 – 7.34 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 191.4, 135.9, 135.2, 133.8, 133.3, 132.9, 128.9, 127.5, 126.4, 120.9, 95.1, 85.9.

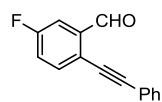
2-(m-Tolylethynyl)benzaldehyde (1e)¹

¹H NMR (400 MHz, CDCl₃) δ 10.65 (d, *J* = 0.6 Hz, 1H), 7.94 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.62 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.56 (td, *J* = 7.6, 1.3 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.26 (dd, *J* = 10.2, 4.9 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 2.36 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 191.7, 138.3, 135.9, 133.8, 133.2, 132.3,

130.0, 128.8, 128.5, 128.5, 127.3, 127.0, 122.2, 96.7, 84.6, 21.24.

2-((2-Chlorophenyl)ethynyl)benzaldehyde (1f)¹

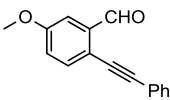
¹H NMR (400 MHz, CDCl₃) δ 10.72 (d, *J* = 0.8 Hz, 1H), 7.96 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.67 (dd, *J* = 7.7, 0.7 Hz, 1H), 7.61 – 7.56 (m, 2H), 7.49 – 7.43 (m, 2H), 7.33 – 7.24 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 191.8, 136.3, 136.1, 133.8, 133.4, 130.1, 129.5, 129.0, 127.2, 126.7, 126.4, 122.4, 93.0, 80.0.

5-Fluoro-2-(phenylethynyl)benzaldehyde (1g)¹

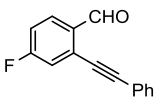
¹H NMR (400 MHz, CDCl₃) δ 10.58 (d, *J* = 3.2 Hz, 1H), 7.65 – 7.58 (m, 2H), 7.57 – 7.51 (m, 2H), 7.40 – 7.35 (m, 3H), 7.27 (td, *J* = 8.1, 2.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 190.4, 162.4 (d, *J* = 251.0 Hz), 137.8 (d, *J* = 6.6 Hz), 135.3 (d, *J* = 7.6

Hz), 131.7, 129.2, 128.6, 123.0, 123.0, 122.1, 121.5, 121.2, 113.8, 113.6, 96.1, 83.9. ^{19}F NMR (376 MHz, CDCl_3) δ -108.9.

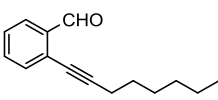
5-Methoxy-2-(phenylethynyl)benzaldehyde (1h)¹

 ^1H NMR (400 MHz, CDCl_3) δ 10.60 (s, 1H), 7.56 – 7.52 (m, 3H), 7.42 (d, J = 2.8 Hz, 1H), 7.35 (dd, J = 6.6, 3.8 Hz, 3H), 7.12 (dd, J = 8.6, 2.8 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 191.5, 159.8, 137.2, 134.6, 131.5, 128.8, 128.5, 122.7, 121.7, 119.6, 109.9, 94.9, 84.9, 55.6.

4-Fluoro-2-(phenylethynyl)benzaldehyde (1i)¹

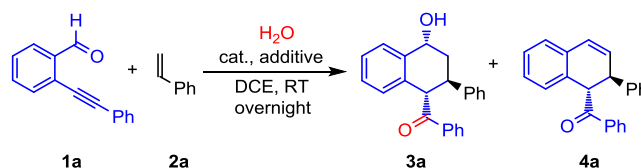
 ^1H NMR (400 MHz, CDCl_3) δ 10.55 (s, 1H), 7.96 (dd, J = 8.7, 5.9 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.44 – 7.37 (m, 3H), 7.30 (dd, J = 9.0, 2.2 Hz, 1H), 7.13 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 190.0, 165.7 (d, J = 255.0 Hz), 164.4, 132.6 (d, J = 2.9 Hz), 131.8, 130.1 (d, J = 10.3 Hz), 129.5, 129.4, 129.3, 128.6, 121.8, 119.8, 119.6, 116.6, 116.4, 97.4, 83.8 (d, J = 3.0 Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -103.27.

2-(Oct-1-yn-1-yl)benzaldehyde (1j)¹

 ^1H NMR (400 MHz, CDCl_3) δ 10.54 (d, J = 0.7 Hz, 1H), 7.90 – 7.86 (m, 1H), 7.52 – 7.47 (m, 2H), 7.40 – 7.35 (m, 1H), 2.48 (t, J = 7.1 Hz, 2H), 1.64 (dd, J = 9.5, 5.3 Hz, 2H), 1.47 (dq, J = 9.7, 7.0 Hz, 2H), 1.32 (td, J = 7.1, 3.4 Hz, 4H), 0.93 – 0.89 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 192.2, 136.0, 133.6, 133.2, 127.9, 127.8, 126.9, 98.2, 76.3, 31.3, 28.6, 28.5, 22.5, 19.6, 14.0.

1.4 Optimization of the reaction conditions for Synthesis of 3a

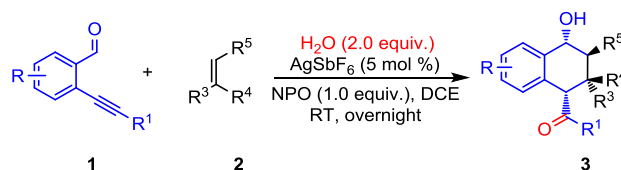
Table S1 Optimization of the Reaction Conditions for Synthesis of 3a^a



Entry	cat. (5 mol %)	additive	H ₂ O (equiv.)	Yield (%)		<i>dr</i> 3a
				3a	4a	
1	AgNTf ₂	-	-	ND	74	9:1
2	AgNTf ₂	-	0.5	24	51	9:1
3	AgNTf ₂	-	1.0	28	52	9:1
4	AgNTf ₂	-	2.0	46	25	9:1
5	AgNTf ₂	TEA	2.0	ND	ND	-
6	AgNTf ₂	Imine	2.0	ND	ND	-
7	AgNTf ₂	DMAP	2.0	ND	ND	-
8	AgNTf ₂	Pyridine	2.0	ND	ND	-
9	AgNTf ₂	NB	2.0	trace	ND	-
10	AgNTf ₂	<i>o</i> -DNB	2.0	48	trace	9:1
11	AgNTf ₂	PNO	2.0	13	trace	9:1
12	AgNTf₂	NPO	2.0	90^b	ND	9:1
13 ^c	AgNTf ₂	NPO	2.0	83	trace	9:1
14 ^d	AgNTf ₂	NPO	2.0	81	6	9:1
14 ^d	AgNTf ₂	NPO	1.0	77	14	9:1
15	AgSbF₆	NPO	2.0	89^b	trace	9:1
16	AgOTf	NPO	2.0	47	24	9:1
17	Ag ₂ CO ₃	NPO	2.0	trace	ND	-
18	-	NPO	2.0	ND	ND	-

^a Unless otherwise noted, the reaction was performed in DCE at rt for 12 h using 5 mol % catalyst, 1.0 equiv. of additive and 2.0 equiv. of H₂O under N₂. The molar ratio of **1a:2a** = 1:5. [**1a**] = 0.2M. NPO: 4-nitropyridine N-oxide; PNO: pyridine N-oxide; TEA: triethyl amine; DMAP: N,N-dimethylamino-pyridine; NB: nitrobenzene; *o*-DNB: 1,2-dinitrobenzene; Imine: (E)-N,1-diphenylmethanimine. The yields were determined by ¹H NMR. ^b Isolated yield. ^c 0.5 equivalent NPO. ^d 0.1 equiv. of NPO.

1.5 General procedure for the synthesis of 3a-3z

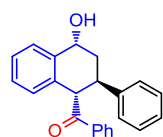


To a dichloroethane (DCE, 1.0 mL) suspension of AgSbF₆ (5 mol %) in Schlenk tube with a magnetic

bar under a nitrogen atmosphere, was added 4-Nitropyridine N-oxide (NPO, 0.20 mmol), olefin (**2**, 1.0 mmol), H₂O (0.4 mmol) and enynals (**1**, 0.2 mmol), the reaction was stirred at room temperature unless being noted. The reaction was monitored by TLC. The reaction mixture was purified by chromatography with petroleum / ethyl acetate, 4/1, **3** was obtained.

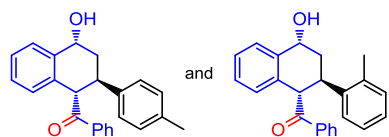
Spectral data of product **3** was consistent with data reported in the literature ⁶.

Tetrahydronaphthol (**3a**)⁶



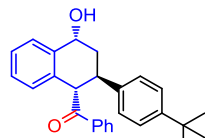
Yield: 89%; dr (*E*:*Z*) = 9:1. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 7.8 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.23 (m, 1H), 7.21 – 7.11 (m, 6H), 6.92 (d, *J* = 7.7 Hz, 1H), 4.94 (d, *J* = 9.3 Hz, 1H), 4.87 (s, 1H), 3.93 – 3.83 (m, 1H), 3.07 (br, 1H), 2.38 – 2.29 (m, 1H), 2.27 – 2.17 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 203.4, 143.5, 138.2, 137.4, 135.2, 133.2, 130.1, 129.0, 128.7, 128.6, 128.5, 128.4, 127.5, 127.5, 126.8, 67.8, 54.9, 39.4, 37.9.

Tetrahydronaphthol (**3b**)⁶



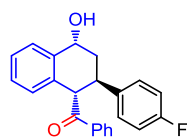
Yield: 92%; dr (*E*:*Z*) = 10:1. ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, *J* = 7.6 Hz, 2H), 7.50 – 7.42 (m, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 9.5 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.02 (q, *J* = 7.8 Hz, 3H), 6.97 – 6.88 (m, 2H), 4.91 (t, *J* = 9.7 Hz, 1H), 4.85 (s, 1H), 3.89 – 3.80 (m, 1H), 3.14 (br, 1H), 2.34 – 2.26 (m, 1H), 2.23 (d, *J* = 10.1 Hz, 3H), 2.17 (d, *J* = 15.7 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 203.4, 140.5, 138.2, 137.4, 136.3, 135.3, 133.1, 130.1, 129.3, 129.1, 129.0, 128.6, 128.4, 127.4, 127.4, 67.8, 55.1, 38.9, 38.1, 21.0.

Tetrahydronaphthol (**3c**)⁶



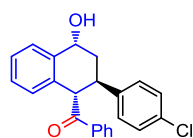
Yield: 80%; dr (*E*:*Z*) = 9:1. ¹H NMR (400 MHz, CDCl₃) δ 7.75 – 7.67 (m, 2H), 7.49 – 7.43 (m, 2H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.22 (dd, *J* = 15.7, 8.6 Hz, 3H), 7.15 (td, *J* = 7.6, 1.3 Hz, 1H), 7.09 – 7.06 (m, 2H), 6.91 (d, *J* = 7.7 Hz, 1H), 4.92 (d, *J* = 9.0 Hz, 1H), 4.84 (t, *J* = 3.5 Hz, 1H), 3.83 (m, 1H), 2.97 (br, 1H), 2.33 (m, 1H), 2.27 – 2.18 (m, 1H), 1.24 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 203.8, 149.6, 140.4, 138.4, 137.5, 135.3, 133.0, 130.0, 129.0, 129.6, 128.5, 127.4, 127.1, 125.5, 67.7, 54.9, 39.0, 37.8, 34.4, 31.34.

Tetrahydronaphthol (**3d**)⁶



Yield: 93%, dr (*E*:*Z*) = 10:1. ¹H NMR (400 MHz, CDCl₃) δ 7.78 – 7.69 (m, 2H), 7.53 – 7.43 (m, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.25 (s, 1H), 7.16 (td, *J* = 7.6, 1.3 Hz, 1H), 7.14 – 7.07 (m, 2H), 6.95 – 6.83 (m, 3H), 4.88 (t, *J* = 7.1 Hz, 2H), 3.94 – 3.84 (m, 1H), 3.03 (br, 1H), 2.36 – 2.27 (m, 1H), 2.25 – 2.15 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 203.3, 161.6 (d, *J* = 243 Hz), 139.2, 139.1, 137.9, 137.4, 135.2, 133.3, 130.2, 129.1, 129.0, 128.9, 128.7, 128.3, 127.6, 115.5, 115.3, 67.7, 55.2, 38.6, 38.0. ¹⁹F NMR (376 MHz, CDCl₃) δ -116.0.

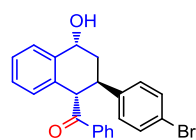
Tetrahydronaphthol (**3e**)⁶



Yield: 70%, dr (*E*:*Z*) = 4:1. ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, *J* = 7.8 Hz, 2H), 7.54 – 7.43 (m, 2H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 3H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 7.7 Hz, 1H), 4.87 (d, *J* = 9.3

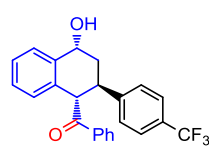
Hz, 2H), 3.94 – 3.84 (m, 1H), 3.11 (br, 1H), 2.37 – 2.25 (m, 1H), 2.26 – 2.12 (m, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ 203.0, 142.0, 137.9, 137.3, 135.0, 133.4, 132.5, 130.1, 129.0, 129.0, 128.8, 128.8, 128.7, 128.3, 127.6, 67.6, 54.9, 38.7, 37.8.

Tetrahydronaphthol (3f)⁶



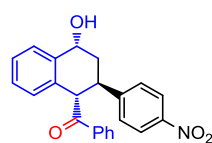
Yield: 83%, dr (*E*:*Z*) = 5:1. **¹H NMR** (400 MHz, CDCl₃) δ 7.78 – 7.70 (m, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.30 (dd, *J* = 15.2, 7.9 Hz, 3H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 7.7 Hz, 1H), 4.87 (d, *J* = 9.7 Hz, 2H), 3.92 – 3.83 (m, 1H), 3.01 (br, 1H), 2.35 – 2.26 (m, 1H), 2.23 – 2.12 (m, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ 202.9, 142.5, 137.9, 137.3, 134.9, 133.4, 131.7, 130.1, 129.3, 128.9, 128.8, 128.7, 128.4, 127.6, 120.6, 67.6, 54.8, 38.7, 37.8.

Tetrahydronaphthol (3g)⁶



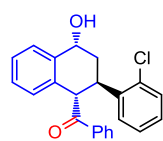
Yield: 68%, dr (*E*:*Z*) = 4:1. **¹H NMR** (400 MHz, CDCl₃) δ 7.80 – 7.74 (m, 2H), 7.56 – 7.48 (m, 4H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.33 – 7.28 (m, 3H), 7.22 (td, *J* = 7.6, 1.2 Hz, 1H), 6.98 – 6.92 (m, 1H), 4.95 (dd, *J* = 7.9, 4.9 Hz, 2H), 4.06 – 3.98 (m, 1H), 3.03 (br, 1H), 2.37 (dt, *J* = 13.5, 3.4 Hz, 1H), 2.32 – 2.22 (m, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ 202.8, 147.6, 137.8, 137.2, 134.8, 133.4, 130.2, 129.06 – 128.63, 128.3 (d, *J* = 4.3 Hz), 128.0, 127.7, 125.6 (q, *J* = 3.7 Hz), 67.5, 54.7, 39.2, 37.7. **¹⁹F NMR** (376 MHz, CDCl₃) δ -62.5.

Tetrahydronaphthol (3h)⁶



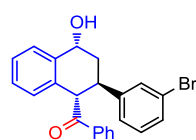
Yield: 46%, dr (*E*:*Z*) = 2:1. **¹H NMR** (400 MHz, CDCl₃) δ 8.07 (d, *J* = 8.7 Hz, 2H), 7.76 (dd, *J* = 13.4, 6.0 Hz, 2H), 7.56 (dd, *J* = 13.1, 6.2 Hz, 1H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.40 – 7.32 (m, 5H), 7.18 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 4.94 (dd, *J* = 10.9, 6.8 Hz, 2H), 4.13 – 4.03 (m, 1H), 2.38 – 2.31 (m, 1H), 2.30 – 2.21 (m, 1H). **¹³C NMR** (100MHz, CDCl₃) δ 202.3, 151.1, 146.9, 137.5, 137.1, 134.6, 133.6, 130.2, 129.0, 128.9, 128.7, 128.5, 127.8, 123.9, 67.4, 54.5, 39.2, 37.5.

Tetrahydronaphthol (3i)⁶



Yield: 85%, dr (*E*:*Z*) = 6:1. **¹H NMR** (400 MHz, CDCl₃) δ 7.87 – 7.82 (m, 2H), 7.57 – 7.49 (m, 2H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.28 (m, 3H), 7.20 (dtd, *J* = 9.0, 7.6, 1.4 Hz, 2H), 7.12 (td, *J* = 7.6, 1.7 Hz, 1H), 7.02 – 6.97 (m, 1H), 5.13 (d, *J* = 8.5 Hz, 1H), 4.89 (t, *J* = 3.6 Hz, 1H), 4.51 – 4.40 (m, 1H), 3.33 (br, 1H), 2.35 (dt, *J* = 13.6, 4.3 Hz, 1H), 2.32 – 2.24 (m, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ 202.7, 140.8, 138.5, 136.8, 134.7, 133.8, 133.3, 132.9, 130.1, 129.8, 129.0, 128.7, 128.6, 128.0, 127.6, 127.2, 67.7, 53.0, 36.8, 36.2.

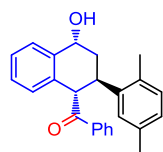
Tetrahydronaphthol (3j)⁶



Yield: 79%, dr (*E*:*Z*) = 5:1. **¹H NMR** (400 MHz, CDCl₃) δ 7.81 – 7.70 (m, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.44 (d, *J* = 6.9 Hz, 1H), 7.39 – 7.29 (m, 3H), 7.29 – 7.22 (m, 2H), 7.15 (td, *J* = 7.6, 1.3 Hz, 1H), 7.10 – 7.00 (m, 2H), 6.90 (t, *J* = 9.3 Hz, 1H), 4.87 (dd, *J* = 9.9, 6.5 Hz, 2H), 3.96 – 3.77 (m, 1H), 3.31 (br, 1H), 2.29 (dt, *J*

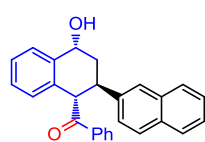
= 13.6, 3.4 Hz, 1H), 2.23 – 2.10 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 203.1, 145.9, 137.8, 137.3, 134.9, 133.4, 130.7, 130.2, 130.0, 129.0, 128.8, 128.7, 128.4, 128.4, 127.6, 126.3, 122.7, 67.5, 54.8, 39.1, 37.7.

Tetrahydronaphthol (3k)⁶



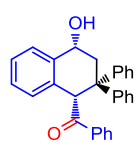
Yield: 81%, dr (*E*:*Z*) = 13:1. ^1H NMR (400 MHz, CDCl_3) δ 7.77 – 7.71 (m, 2H), 7.46 (m, 2H), 7.32 (dd, *J* = 10.7, 4.8 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.17 (td, *J* = 7.6, 1.3 Hz, 1H), 7.08 (s, 1H), 6.95 (d, *J* = 7.7 Hz, 1H), 6.89 (d, *J* = 7.7 Hz, 1H), 6.84 (t, *J* = 6.4 Hz, 1H), 5.04 (d, *J* = 9.3 Hz, 1H), 4.85 (t, *J* = 3.1 Hz, 1H), 4.13 (m, 1H), 3.30 (br, 1H), 2.22 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 203.9, 141.6, 138.3, 137.4, 135.6, 135.5, 133.2, 132.7, 130.5, 130.1, 128.9, 128.7, 128.6, 128.5, 127.5, 127.2, 127.1, 68.0, 54.2, 38.4, 34.3, 21.2, 19.0.

Tetrahydronaphthol (3l)⁶



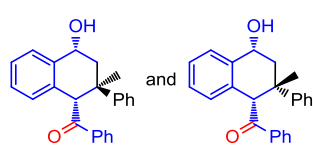
Yield: 84%, dr (*E*:*Z*) = 10:1. ^1H NMR (400 MHz, CDCl_3) δ 7.76 (dd, *J* = 10.9, 7.8 Hz, 4H), 7.71 – 7.66 (m, 1H), 7.61 (s, 1H), 7.51 (d, *J* = 6.9 Hz, 1H), 7.49 – 7.39 (m, 3H), 7.38 – 7.28 (m, 4H), 7.21 (td, *J* = 7.6, 1.4 Hz, 1H), 6.99 (d, *J* = 7.7 Hz, 1H), 5.10 (d, *J* = 9.2 Hz, 1H), 4.94 (t, *J* = 3.2 Hz, 1H), 4.16 – 4.06 (m, 1H), 3.18 (br, 1H), 2.43 (dt, *J* = 13.7, 3.8 Hz, 1H), 2.33 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 203.3, 141.0, 138.2, 137.3, 135.1, 133.5, 133.2, 132.5, 130.1, 129.0, 128.7, 128.6, 128.5, 127.7, 127.6, 126.3, 126.1, 125.6, 67.8, 54.7, 39.4, 38.1.

Tetrahydronaphthol (3m)⁶



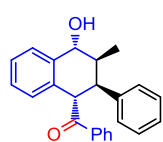
Yield: 81%, dr (*E*:*Z*) > 20:1. ^1H NMR (400 MHz, CDCl_3) δ 7.68 – 7.58 (m, 3H), 7.39 – 7.30 (m, 1H), 7.25 – 7.19 (m, 3H), 7.17 – 7.09 (m, 6H), 7.07 (d, *J* = 7.3 Hz, 3H), 6.94 (dd, *J* = 10.4, 4.8 Hz, 2H), 6.84 (dd, *J* = 8.2, 6.4 Hz, 1H), 5.79 (s, 1H), 4.13 (dd, *J* = 10.6, 5.8 Hz, 1H), 3.49 (dd, *J* = 12.1, 10.9 Hz, 1H), 2.75 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 201.7, 146.7, 145.9, 140.5, 138.6, 134.8, 132.4, 128.4, 128.2, 128.1, 127.8, 127.8, 127.8, 127.5, 127.4, 126.4, 126.2, 67.6, 53.1, 49.8, 38.9.

Tetrahydronaphthol (3n)⁶



Yield: 89%, dr (*E*:*Z*) = 2:1. ^1H NMR (400 MHz, CDCl_3) δ 8.16 – 8.13 (m, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.65 – 7.58 (m, 3H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.42 – 7.32 (m, 5H), 7.26 (dt, *J* = 7.5, 1.5 Hz, 4H), 7.22 – 7.11 (m, 3H), 7.11 – 7.04 (m, 3H), 7.00 – 6.94 (m, 3H), 5.54 (s, 1H), 5.08 (s, 1H), 4.99 (dd, *J* = 9.3, 7.0 Hz, 1H), 4.35 (t, *J* = 8.2 Hz, 1H), 3.12 – 3.02 (m, 1H), 2.84 (br, 1H), 2.62 (d, *J* = 8.3 Hz, 1H), 2.41 (m, 1H), 1.43 (s, 3H), 1.29 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 202.1, 201.9, 146.5, 145.5, 140.2, 139.3, 138.8, 138.5, 134.7, 134.1, 133.5, 132.4, 129.0, 128.9, 128.8, 128.5, 128.3, 128.2, 128.1, 128.0, 127.6, 127.5, 127.5, 126.5, 126.3, 126.0, 125.74, 67.7, 67.1, 56.3, 52.3, 42.6, 41.8, 41.2, 38.1, 30.5, 27.2.

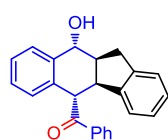
Tetrahydronaphthol (3o)⁶



Yield: 77%, dr (*E*:*Z*) > 20:1. ^1H NMR (400 MHz, CDCl_3) δ 7.73 – 7.65 (m, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.43 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.26 (dd, *J*

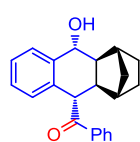
= 10.0, 4.4 Hz, 1H), 7.23 (t, J = 6.4 Hz, 2H), 7.19 – 7.15 (m, 2H), 7.14 – 7.10 (m, 2H), 6.91 (d, J = 7.6 Hz, 1H), 5.01 (d, J = 8.1 Hz, 1H), 4.67 (d, J = 2.2 Hz, 1H), 3.41 (dd, J = 11.8, 8.2 Hz, 1H), 2.19 (m, 1H), 0.99 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 204.0, 143.6, 139.7, 137.0, 134.6, 133.4, 130.0, 129.2, 128.8, 128.7, 128.6, 128.4, 128.2, 127.5, 126.8, 73.0, 56.0, 45.7, 39.8, 16.2.

Tetrahydronaphthol (3p)⁶



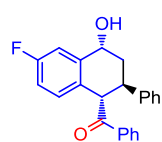
Yield: 86%, dr ($E:Z$) = 20:1. ^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, J = 7.4 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.55 – 7.47 (m, 3H), 7.23 (dd, J = 9.2, 5.2 Hz, 1H), 7.14 (d, J = 5.2 Hz, 4H), 7.11 – 7.06 (m, 1H), 6.88 (d, J = 7.5 Hz, 1H), 4.86 (d, J = 5.2 Hz, 1H), 4.68 (d, J = 5.7 Hz, 1H), 4.17 (br, 1H), 4.13 (dd, J = 8.6, 5.2 Hz, 1H), 3.21 – 3.05 (m, 2H), 2.79 (dd, J = 15.0, 5.4 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 203.6, 146.1, 142.5, 139.8, 136.9, 134.2, 134.0, 129.2, 129.1, 128.2, 127.7, 127.6, 127.5, 127.3, 127.1, 124.9, 124.3, 72.1, 52.1, 45.5, 44.8, 36.5.

Tetrahydronaphthol (3q)⁶



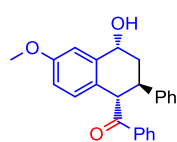
Yield: 31%, dr ($E:Z$) = 6:1. ^1H NMR (400 MHz, CDCl_3) δ 8.03 – 7.97 (m, 2H), 7.58 (td, J = 7.3, 5.4 Hz, 2H), 7.49 (dd, J = 11.9, 7.9 Hz, 2H), 7.31 – 7.25 (m, 1H), 7.08 (t, J = 7.5 Hz, 1H), 6.76 (d, J = 7.6 Hz, 1H), 4.50 (d, J = 9.6 Hz, 1H), 4.28 (d, J = 10.8 Hz, 1H), 2.57 (d, J = 3.5 Hz, 1H), 2.40 (t, J = 10.1 Hz, 1H), 1.96 (d, J = 3.5 Hz, 1H), 1.69 (d, J = 10.4 Hz, 1H), 1.66 – 1.58 (m, 2H), 1.57 – 1.50 (m, 1H), 1.33 (d, J = 8.0 Hz, 1H), 1.27 (d, J = 9.7 Hz, 2H), 1.17 (d, J = 10.4 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 202.8, 140.7, 138.3, 135.8, 133.5, 128.9, 128.5, 126.9, 126.8, 125.5, 122.7, 70.7, 52.2, 48.2, 45.6, 41.8, 40.1, 33.7, 29.6, 29.4.

Tetrahydronaphthol (3r)⁶



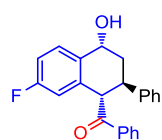
Yield: 88%, dr ($E:Z$) > 20:1. ^1H NMR (400 MHz, CDCl_3) δ 7.74 (d, J = 7.8 Hz, 2H), 7.50 (t, J = 7.3 Hz, 1H), 7.35 (t, J = 7.7 Hz, 2H), 7.25 – 7.17 (m, 3H), 7.17 – 7.11 (m, 3H), 6.88 (d, J = 6.5 Hz, 2H), 4.92 (d, J = 8.5 Hz, 1H), 4.80 (s, 1H), 3.86 – 3.78 (m, 1H), 3.05 (br, 1H), 2.37 – 2.17 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 203.1, 161.8 ((d, J = 245 Hz), 143.2, 140.7, 140.6, 137.1, 133.3, 130.7, 130.2, 130.1, 128.9, 128.7, 128.7, 127.4, 126.9, 116.2, 116.0, 115.9, 115.7, 67.4, 53.7, 39.5, 37.6. ^{19}F NMR (376 MHz, CDCl_3) δ -114.6.

Tetrahydronaphthol (3s)⁶



Yield: 83%, dr ($E:Z$) = 4:1. ^1H NMR (400 MHz, DMSO) δ 7.84 (d, J = 7.5 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.7 Hz, 2H), 7.20 (t, J = 7.1 Hz, 4H), 7.09 (d, J = 7.8 Hz, 1H), 7.01 (d, J = 2.7 Hz, 1H), 6.75 (dd, J = 8.5, 2.7 Hz, 1H), 6.66 (d, J = 8.5 Hz, 1H), 5.40 (d, J = 4.2 Hz, 1H), 4.99 (d, J = 10.3 Hz, 1H), 4.76 – 4.66 (m, 1H), 3.82 – 3.76 (m, 1H), 3.74 (s, 3H), 2.27 (td, J = 13.1, 3.7 Hz, 1H), 2.01 (dt, J = 13.3, 3.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO) δ 202.7, 158.2, 144.3, 140.6, 137.8, 133.5, 129.1, 129.0, 128.7, 128.7, 128.6, 127.9, 126.8, 115.0, 114.4, 66.1, 55.5, 53.5, 39.38, 38.5.

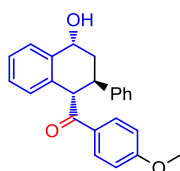
Tetrahydronaphthol (3t)⁶



Yield: 83%, dr ($E:Z$) > 20:1. ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, J = 7.9 Hz, 2H), 7.49 (t, J = 7.4 Hz, 1H), 7.44 (dd, J = 8.4, 6.0 Hz, 1H), 7.34 (t, J = 7.7 Hz, 2H), 7.23 – 7.17 (m, 2H), 7.17 – 7.11 (m, 3H), 6.96 (m, 1H), 6.61 (dd, J = 9.6, 2.0 Hz, 1H), 4.91

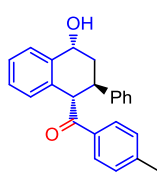
(d, $J = 9.2$ Hz, 1H), 4.85 (s, 1H), 3.90 – 3.80 (m, 1H), 3.11 (br, 1H), 2.37 – 2.18 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 202.8, 161.4 (d, $J = 246$ Hz) 143.1, 137.4, 137.3, 137.2, 134.3, 131.8, 131.7, 128.9, 128.7, 127.5, 127.0, 114.9, 114.8, 114.7, 114.6, 67.1, 54.6, 39.2, 37.9. ^{19}F NMR (376 MHz, CDCl_3) δ -112.81.

Tetrahydronaphthol (3u)⁶



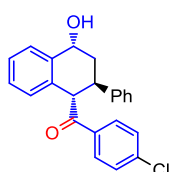
Yield: 77%, dr ($E:Z$) = 20:1. ^1H NMR (400 MHz, CDCl_3) δ 7.79 – 7.73 (m, 2H), 7.44 (d, $J = 6.9$ Hz, 1H), 7.28 – 7.23 (m, 1H), 7.21 (d, $J = 9.0$ Hz, 1H), 7.19 – 7.14 (m, 4H), 7.14 – 7.10 (m, 1H), 6.91 (d, $J = 7.7$ Hz, 1H), 6.83 – 6.78 (m, 2H), 4.89 (d, $J = 9.2$ Hz, 1H), 4.85 (s, 1H), 3.87 (m, 1H), 3.78 (s, 3H), 2.34 (m, 1H), 2.20 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 201.8, 163.7 143.8, 138.3, 135.5, 131.5, 130.3, 130.0, 128.6, , 128.4, 127.5, 127.4, 126.8, 113.8, 67.8, 55.5, 54.4, 39.4, 38.0.

Tetrahydronaphthol (3v)⁶



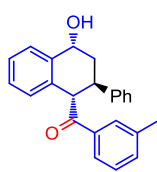
Yield: 83%, dr ($E:Z$) = 10:1. ^1H NMR (400 MHz, CDCl_3) δ 7.66 (d, $J = 8.3$ Hz, 2H), 7.44 (m, 1H), 7.28 – 7.23 (m, 1H), 7.21 – 7.17 (m, 3H), 7.17 – 7.10 (m, 5H), 6.91 (d, $J = 7.7$ Hz, 1H), 4.92 (d, $J = 9.2$ Hz, 1H), 4.86 (t, $J = 3.3$ Hz, 1H), 3.88 (m, 1H), 3.23 (br, 1H), 2.36 – 2.30 (m, 4H), 2.20 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 203.0, 144.1, 143.7, 138.2, 135.4, 134.9, 130.0, 129.4, 129.2, 128.6, 128.4, 127.6, 127.4, 126.8, 67.8, 54.6, 39.3, 37.9, 21.6.

Tetrahydronaphthol (3w)⁶



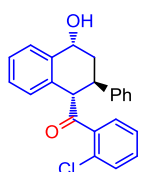
Yield: 85%, dr ($E:Z$) = 10:1. ^1H NMR (400 MHz, CDCl_3) δ 7.65 (d, $J = 8.6$ Hz, 2H), 7.45 (d, $J = 7.5$ Hz, 1H), 7.31 – 7.24 (m, 3H), 7.23 – 7.17 (m, 2H), 7.15 (dd, $J = 10.0$, 5.1 Hz, 4H), 6.88 (d, $J = 7.7$ Hz, 1H), 4.88 (t, $J = 3.2$ Hz, 1H), 4.84 (d, $J = 9.8$ Hz, 1H), 3.90 – 3.82 (m, 1H), 3.11 (br, 1H), 2.32 (m, 1H), 2.27 – 2.18 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 202.2, 143.2, 139.7, 137.9, 135.6, 135.0, 130.4, 130.3, 128.9, 128.7, 128.3, 127.6, 127.5, 127.0, 67.7, 55.5, 39.4, 37.8.

Tetrahydronaphthol (3x)⁶



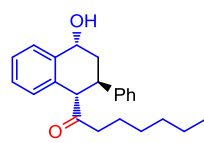
Yield: 76%, dr ($E:Z$) > 20:1. ^1H NMR (400 MHz, CDCl_3) δ 7.56 – 7.50 (m, 2H), 7.46 – 7.42 (m, 1H), 7.30 – 7.20 (m, 3H), 7.20 – 7.09 (m, 6H), 6.90 (d, $J = 7.7$ Hz, 1H), 4.94 (d, $J = 9.3$ Hz, 1H), 4.84 (t, $J = 3.0$ Hz, 1H), 3.88 (m, 1H), 3.27 (br, 1H), 2.33 (m, 1H), 2.28 (s, 3H), 2.25 – 2.16 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 203.7, 143.7, 138.4, 138.3, 137.5, 135.4, 134.0, 130.1, 129.5, 128.6, 128.6, 128.5, 128.4, 127.6, 127.4, 126.8, 126.2, 67.8, 54.8, 39.4, 37.9, 21.3.

Tetrahydronaphthol (3y)⁶



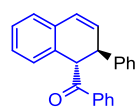
Yield: 71%, dr ($E:Z$) > 20:1. ^1H NMR (400 MHz, CDCl_3) δ 7.44 (dd, $J = 7.5$, 1.1 Hz, 1H), 7.30 – 7.23 (m, 3H), 7.22 – 7.15 (m, 2H), 7.15 – 7.03 (m, 6H), 6.99 (d, $J = 1.5$ Hz, 1H), 4.97 (d, $J = 8.8$ Hz, 1H), 4.76 (t, $J = 3.5$ Hz, 1H), 3.83 – 3.72 (m, 1H), 3.08 (br, 1H), 2.29 (m, 1H), 2.15 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 205.3, 143.4, 139.1, 138.6, 134.2, 131.9, 131.5, 130.6, 130.0, 129.8, 129.0, 128.7, 128.5, 127.7, 127.6, 126.8, 126.6, 67.5, 57.8, 39.5.

Tetrahydronaphthol (3z)⁶



Yield: 79%, dr (*E:Z*) > 20:1. ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, *J* = 7.5 Hz, 1H), 7.34 – 7.28 (m, 3H), 7.24 (dd, *J* = 11.3, 5.8 Hz, 4H), 6.97 (d, *J* = 7.2 Hz, 1H), 4.84 (s, 1H), 4.12 (d, *J* = 10.0 Hz, 1H), 3.67 – 3.58 (m, 1H), 2.73 (s, 1H), 2.43 – 2.34 (m, 1H), 2.30 – 2.17 (m, 2H), 2.08 (td, *J* = 13.3, 3.1 Hz, 1H), 1.47 – 1.35 (m, 2H), 1.25 – 1.18 (m, 2H), 1.12 (dd, *J* = 11.0, 7.7 Hz, 4H), 0.83 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 213.0, 143.5, 137.9, 134.1, 130.2, 128.8, 128.6, 128.1, 127.5, 127.5, 126.9, 67.7, 59.9, 42.5, 38.3, 31.4, 28.6, 23.2, 22.4, 14.0.

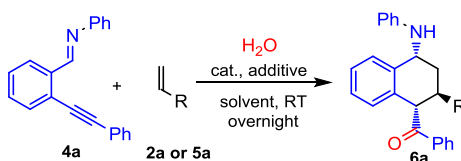
phenyl-2-phenyl-1,2-dihydronaphthalen-1-yl)methanone (4a)



¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 7.8 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 4.1 Hz, 5H), 7.16 (d, *J* = 6.0 Hz, 2H), 7.05 (t, *J* = 7.3 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 6.62 (d, *J* = 9.6 Hz, 1H), 5.97 (dd, *J* = 9.6, 4.1 Hz, 1H), 5.01 (d, *J* = 7.9 Hz, 1H), 4.21 – 4.16 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 201.1, 142.9, 137.2, 133.7, 133.0, 131.9, 130.3, 128.7, 128.7, 128.6, 128.0, 127.9, 127.8, 127.7, 127.4, 127.0, 126.6, 53.5, 44.0.

1.6 Optimization of the reaction conditions for Synthesis of 6a

Table S2. Optimization of the Reaction Conditions for Synthesis of 6a^a

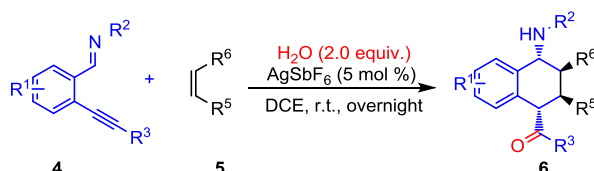


Entry	R	cat. (5 mol %)	temp (°C)	solvent	additive	H ₂ O (equiv)	yield (%)	dr
1	Ph	AgSbF ₆	rt	DCE	NPO (1.0 eq)	2.0	ND	-
2	OEt	AgSbF ₆	rt	DCE	NPO (1.0 eq)	2.0	77	13:1
3	OEt	AgSbF ₆	rt	DCE	-	2.0	86	13:1
4	OEt	AgSbF ₆	rt	CH ₂ Cl ₂	-	1.0	82	13:1
5	OEt	AgSbF ₆	rt	CH ₂ Cl ₂	-	1.0	85	13:1
6	OEt	-	rt	CH ₂ Cl ₂	-	-	ND	-
7	Ph	AgSbF ₆	40	DCE	-	2.0	ND	-
8	Ph	AgSbF ₆	60	DCE	-	2.0	trace	> 20:1
9	Ph	AgSbF ₆	80	DCE	-	2.0	30	> 20:1
10	Ph	AgSbF ₆	100	DCE	-	2.0	50	> 20:1
12	Ph	AgSbF ₆	110	DCE	-	2.0	44	> 20:1
13	Ph	AgSbF ₆	100	toluene	-	2.0	35	> 20:1
14	Ph	AgSbF ₆	100	THF	-	2.0	27	> 20:1
15	Ph	AgSbF ₆	100	1,4-dioxane	-	2.0	16	> 20:1
16	Ph	AgSbF ₆	100	CH ₃ CN	-	2.0	45	> 20:1
17	Ph	AgSbF ₆	100	DCE	NPO (1.0 eq)	2.0	22	> 20:1

^a Unless otherwise noted, the reaction was performed in DCE for 12 h using 5 mol % catalyst, 1.0 equiv.

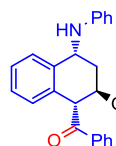
of additive and 2.0 equiv. of H₂O under N₂. The molar ratio of 4a:2a or 5a = 1:5. [1a] = 0.2M. NPO: 4-nitropyridine N-oxide; The yields and dr value were determined by ¹H NMR. ^b Isolated yield.

1.7 General procedure for the synthesis of 6a-6u



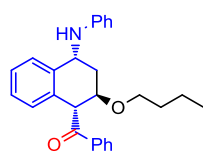
To a dichloromethane (DCE, 1.0 mL) suspension of AgSbF₆ (5 mol %) in Schlenk tube with a magnetic bar under a nitrogen atmosphere, was added olefin (**5**, 1.0 mmol), enynimines (**4**, 0.2 mmol) and H₂O (0.4 mmol), the reaction was stirred at room temperature unless being noted. The reaction was monitored by TLC. The reaction mixture was purified by chromatography with petroleum / ethyl acetate, 20/1, **6** was obtained.

Tetrahydronaphthylamines (6a)



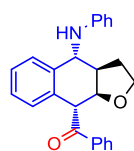
Yellow oil, purified by chromatography (PE/EA = 20/1), yield = 86%, 63.8 mg, *dr* = 13:1; ¹H NMR (400 MHz, CDCl₃) δ 8.14 – 8.09 (m, 2H), 7.62 (dd, *J* = 8.3, 6.4 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.24 – 7.19 (m, 3H), 7.16 – 7.12 (m, 1H), 6.88 (d, *J* = 7.7 Hz, 1H), 6.75 – 6.69 (m, 3H), 4.98 (d, *J* = 6.9 Hz, 1H), 4.84 (t, *J* = 4.9 Hz, 1H), 4.26 – 4.20 (m, 1H), 3.58 – 3.51 (m, 1H), 3.35 (m, 1H), 2.42 (m, 1H), 2.09 – 2.02 (m, 1H), 1.03 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 202.7, 147.3, 138.2, 138.1, 134.7, 133.5, 129.5, 129.0, 128.9, 128.7, 127.9, 127.3, 117.5, 113.0, 75.1, 64.7, 53.2, 50.6, 32.4, 15.4. IR (KBr, cm⁻¹) 3398, 3057, 2973, 2927, 2865, 1680, 1598, 1500, 1442, 1322, 1212, 1171, 1093, 989, 748, 695, 508. HRMS (ESI) Calcd for C₂₅H₂₆NO₂ (M+H)⁺ 372.1958, found 372.1962.

Tetrahydronaphthylamines (6b)



Yellow oil, purified by chromatography (PE/EA = 20/1), yield = 78%, 62.2 mg, *dr* = 13:1; ¹H NMR (400 MHz, CDCl₃) δ 8.14 – 8.07 (m, 2H), 7.62 (ddd, *J* = 6.6, 3.9, 1.2 Hz, 1H), 7.53 (dd, *J* = 10.5, 4.7 Hz, 2H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.26 – 7.18 (m, 4H), 7.14 (td, *J* = 7.5, 1.4 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.73 (dd, *J* = 7.8, 6.6 Hz, 3H), 4.98 (d, *J* = 6.9 Hz, 1H), 4.85 (t, *J* = 4.8 Hz, 1H), 4.24 – 4.18 (m, 1H), 3.50 (dt, *J* = 9.2, 6.4 Hz, 1H), 3.27 (dt, *J* = 9.2, 6.6 Hz, 1H), 2.42 (m, 1H), 2.04 (m, 1H), 1.38 (m, 2H), 1.18 (dd, *J* = 15.1, 7.4 Hz, 2H), 0.77 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 202.8, 147.3, 138.2, 138.1, 134.7, 133.4, 129.5, 128.9, 128.8, 128.7, 127.9, 127.3, 117.4, 113.0, 75.4, 69.1, 53.1, 50.6, 32.2, 31.9, 19.2, 13.8. IR (KBr, cm⁻¹) 3397, 3057, 3019, 2969, 2924, 2863, 1680, 1597, 1502, 1439, 1365, 1321, 1212, 1171, 1125, 1090, 989, 943, 869, 747, 694, 628, 507, 472. HRMS (ESI) Calcd for C₂₇H₃₀NO₂ (M+H)⁺ 400.2271, found 400.2273.

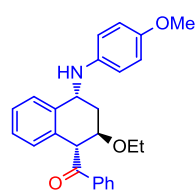
Tetrahydronaphthylamines (6c)



Yellow oil, purified by chromatography (PE/EA = 20/1), yield = 52%, 38.4mg, *dr* = 20:1; ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, *J* = 7.3 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H),

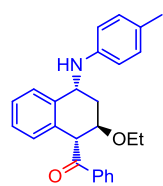
7.49 (t, $J = 7.6$ Hz, 2H), 7.35 (s, 1H), 7.20 (t, $J = 7.8$ Hz, 3H), 7.13 (t, $J = 7.0$ Hz, 1H), 6.93 (s, 1H), 6.74 (t, $J = 7.3$ Hz, 1H), 6.68 (d, $J = 7.8$ Hz, 2H), 4.81 (d, $J = 7.5$ Hz, 1H), 4.75 – 4.68 (m, 1H), 4.37 (d, $J = 9.2$ Hz, 1H), 4.21 (s, 1H), 4.05 – 3.95 (m, 1H), 3.70 (td, $J = 8.8, 6.3$ Hz, 1H), 2.57 – 2.43 (m, 1H), 2.31 – 2.20 (m, 1H), 1.93 – 1.84 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 200.9, 147.7, 139.7, 137.8, 134.3, 133.6, 129.5, 128.8, 127.4, 127.3, 127.2, 125.6, 117.7, 113.0, 79.1, 67.8, 56.7, 51.56, 4.91, 31.5. IR (KBr, cm^{-1}) 3377, 3057, 2975, 2913, 2866, 1921, 1673, 1594, 1509, 1440, 1363, 1319, 1273, 1210, 1171, 1066, 991, 946, 865, 807, 742, 692, 644, 578, 507, 459. HRMS (ESI) Calcd for $\text{C}_{25}\text{H}_{24}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$ 370.1802, found 370.1800.

Tetrahydronaphthylamines (6d)



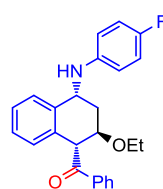
Yellow oil, purified by chromatography (PE/EA = 20/1), yield = 56%, 45.0 mg, $dr > 20:1$; ^1H NMR (400 MHz, CDCl_3) δ 8.14 – 8.09 (m, 2H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.53 (t, $J = 7.6$ Hz, 2H), 7.43 (d, $J = 7.5$ Hz, 1H), 7.20 (t, $J = 7.4$ Hz, 1H), 7.13 (td, $J = 7.5, 1.2$ Hz, 1H), 6.88 (d, $J = 7.7$ Hz, 1H), 6.86 – 6.78 (m, 2H), 6.72 – 6.67 (m, 2H), 4.96 (d, $J = 7.0$ Hz, 1H), 4.75 (t, $J = 4.8$ Hz, 1H), 4.27 – 4.20 (m, 1H), 3.76 (s, 3H), 3.58 – 3.50 (m, 1H), 3.40 – 3.30 (m, 1H), 2.41 (m, 1H), 2.02 (m, 1H), 1.03 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (100MHz, CDCl_3) δ 202.8, 152.2, 141.5, 138.3, 138.3, 134.6, 133.4, 128.9, 128.9, 128.9, 128.7, 127.8, 127.3, 115.1, 114.6, 75.0, 64.7, 55.8, 53.3, 51.7, 32.4, 15.4. IR (KBr, cm^{-1}) 3399, 3062, 2973, 2929, 2866, 2832, 1680, 1587, 1511, 1447, 1336, 1285, 1238, 1173, 1126, 1089, 1035, 988, 822, 749, 696, 623. HRMS (ESI) Calcd for $\text{C}_{26}\text{H}_{28}\text{NO}_3$ ($\text{M}+\text{H}$) $^+$ 402.2064, found 402.2067.

Tetrahydronaphthylamines (6e)



Yellow solid, m.p = 107-108 $^{\circ}\text{C}$, purified by chromatography (PE/EA = 20/1), yield = 86%, 66.2 mg, $dr > 20:1$; ^1H NMR (400 MHz, CDCl_3) δ 8.11 (d, $J = 7.5$ Hz, 2H), 7.62 (t, $J = 7.3$ Hz, 1H), 7.52 (t, $J = 7.6$ Hz, 2H), 7.42 (d, $J = 7.6$ Hz, 1H), 7.20 (dd, $J = 12.8, 5.3$ Hz, 1H), 7.13 (t, $J = 7.4$ Hz, 1H), 7.03 (d, $J = 7.8$ Hz, 2H), 6.87 (d, $J = 7.6$ Hz, 1H), 6.65 (d, $J = 8.0$ Hz, 2H), 4.96 (d, $J = 6.8$ Hz, 1H), 4.80 (s, 1H), 4.23 (t, $J = 7.6$ Hz, 1H), 3.96 (br, 1H), 3.59 – 3.50 (m, 1H), 3.39 – 3.29 (m, 1H), 2.46 – 2.37 (m, 1H), 2.26 (s, 3H), 2.04 (dd, $J = 15.7, 6.5$ Hz, 1H), 1.03 (td, $J = 7.0, 1.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 202.7, 145.1, 138.3, 138.3, 134.7, 133.4, 130.0, 129.0, 128.9, 128.9, 128.7, 127.9, 127.3, 126.7, 113.2, 75.1, 64.7, 53.2, 51.0, 32.4, 20.5, 15.4. IR (KBr, cm^{-1}) 3398, 3061, 3022, 2974, 2923, 2865, 1860, 1612, 1518, 1445, 1366, 1331, 1289, 1212, 1173, 1127, 1090, 989, 946, 905, 809, 750, 696, 625, 580, 508, 465. HRMS (ESI) Calcd for $\text{C}_{26}\text{H}_{28}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$ 386.2115, found 386.2118.

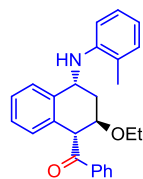
Tetrahydronaphthylamines (6f)



Yellow oil, purified by chromatography (PE/EA = 20/1), yield = 60%, 46.7 mg, $dr > 20:1$; ^1H NMR (400 MHz, CDCl_3) δ 8.15 – 8.09 (m, 2H), 7.62 (t, $J = 7.3$ Hz, 1H), 7.53 (t, $J = 7.7$ Hz, 2H), 7.41 (d, $J = 7.6$ Hz, 1H), 7.20 (t, $J = 7.4$ Hz, 1H), 7.13 (t, $J = 7.5$ Hz, 1H), 6.90 (dd, $J = 16.6, 7.7$ Hz, 3H), 6.69 – 6.59 (m, 2H), 5.02 – 4.95 (m, 1H), 4.76 (s, 1H), 4.26 – 4.18 (m, 1H), 3.54 (m, 1H), 3.42 – 3.29 (m, 1H), 2.39 (m, 1H), 2.07 – 1.99 (m, 1H), 1.04 (td, $J = 7.0, 1.6$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 202.7, 155.8 (d, $J = 233\text{Hz}$), 143.6, 138.1, 138.0, 134.6, 133.5, 128.9, 128.8, 128.8, 127.9, 127.3, 115.9, 115.7, 114.0, 75.0, 64.7, 53.1, 51.3, 32.1, 15.3. ^{19}F NMR (376 MHz, CDCl_3) δ -127.8. IR (KBr, cm^{-1}) 3401, 3063, 2975,

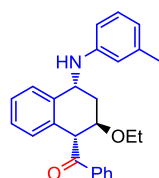
2929, 2867, 1680, 1606, 1589, 1510, 1445, 1326, 1281, 1216, 1125, 1092, 989, 907, 822, 753, 696, 623, 508. **HRMS** (ESI) Calcd for $C_{25}H_{25}FNO_2$ (M+H)⁺ 390.1864, found 390.1861.

Tetrahydronaphthylamines (6g)



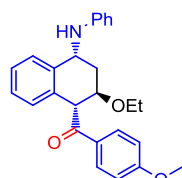
Yellow oil, purified by chromatography (PE/EA = 20/1), yield = 65%, 50.2 mg, *dr* > 20:1; **¹H NMR** (400 MHz, CDCl₃) δ 8.14 – 8.09 (m, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 5.6 Hz, 1H), 7.14 (dd, *J* = 11.8, 4.4 Hz, 2H), 7.09 (d, *J* = 7.2 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.68 (t, *J* = 7.3 Hz, 1H), 4.98 (d, *J* = 6.6 Hz, 1H), 4.91 (t, *J* = 4.8 Hz, 1H), 4.28 – 4.20 (m, 1H), 3.54 (dq, *J* = 9.2, 7.0 Hz, 1H), 3.35 (dq, *J* = 9.2, 7.0 Hz, 1H), 2.44 (m, 1H), 2.15 (s, 3H), 2.07 (m, 1H), 1.04 (t, *J* = 7.0 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 202.5, 145.3, 138.4, 138.1, 134.7, 133.4, 130.5, 128.9, 128.9, 128.8, 128.7, 127.9, 127.4, 127.2, 122.2, 117.0, 109.8, 75.1, 64.7, 53.3, 50.4, 32.3, 17.8, 15.4. **IR** (KBr, cm⁻¹) 3429, 3060, 2975, 2924, 2856, 1683, 1667, 1593, 1509, 1444, 1313, 1250, 1210, 1171, 1085, 1040, 987, 914, 802, 746, 697, 628, 574, 477. **HRMS** (ESI) Calcd for $C_{26}H_{28}NO_2$ (M+H)⁺ 386.2115, found 386.2113.

Tetrahydronaphthylamines (6h)



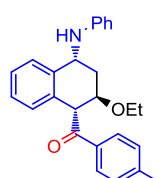
Yellow oil, purified by chromatography (PE/EA = 20/1), yield = 73%, 56.4 mg, *dr* > 20:1; **¹H NMR** (400 MHz, CDCl₃) δ 8.15 – 8.08 (m, 2H), 7.62 (m, 1H), 7.53 (dd, *J* = 10.5, 4.7 Hz, 2H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.16 – 7.08 (m, 2H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.59 – 6.52 (m, 3H), 4.97 (d, *J* = 7.0 Hz, 1H), 4.84 (t, *J* = 4.8 Hz, 1H), 4.27 – 4.20 (m, 1H), 3.55 (dq, *J* = 9.2, 7.0 Hz, 1H), 3.35 (dq, *J* = 9.3, 7.0 Hz, 1H), 2.47 – 2.37 (m, 1H), 2.30 (s, 3H), 2.04 (m, 1H), 1.04 (t, *J* = 7.0 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 202.7, 147.3, 139.2, 138.2, 138.2, 134.6, 133.4, 129.3, 128.9, 128.90, 128.8, 128.7, 127.8, 127.3, 118.3, 113.7, 110.0, 75.1, 64.7, 53.2, 50.6, 32.4, 21.7, 15.3. **IR** (KBr, cm⁻¹) 3396, 3057, 3025, 2973, 2924, 2863, 1680, 1597, 1486, 1444, 1327, 1289, 1213, 1172, 1091, 990, 909, 849, 762, 695, 590, 476. **HRMS** (ESI) Calcd for $C_{26}H_{28}NO_2$ (M+H)⁺ 386.2115, found 386.2113.

Tetrahydronaphthylamines (6j)



Yellow solid, m. p. = 83–84 °C, purified by chromatography (PE/EA = 15/1), yield = 75%, 60.3 mg, *dr* = 15:1; **¹H NMR** (400 MHz, CDCl₃) δ 8.14 – 8.08 (m, 2H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.24 – 7.17 (m, 3H), 7.12 (td, *J* = 7.5, 1.4 Hz, 1H), 7.02 – 6.98 (m, 2H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.75 – 6.69 (m, 3H), 4.93 (d, *J* = 6.8 Hz, 1H), 4.83 (t, *J* = 4.8 Hz, 1H), 4.25 – 4.20 (m, 1H), 3.88 (s, 3H), 3.57 – 3.50 (m, 1H), 3.35 (dq, *J* = 9.3, 7.0 Hz, 1H), 2.43 (m, 1H), 2.07 – 2.00 (m, 1H), 1.04 (t, *J* = 7.0 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 200.9, 163.9, 147.3, 138.1, 134.9, 131.3, 131.2, 129.4, 128.9, 128.7, 127.8, 127.2, 117.3, 114.0, 113.0, 75.1, 64.7, 55.5, 52.7, 50.6, 32.4, 15.4. **IR** (KBr, cm⁻¹) 3396, 3057, 2973, 2928, 2872, 2843, 1732, 1670, 1600, 1504, 1451, 1424, 1366, 1320, 1259, 1216, 1170, 1089, 1079, 1026, 984, 950, 907, 837, 745, 691, 622, 586, 510, 468. **HRMS** (ESI) Calcd for $C_{26}H_{28}NO_3$ (M+H)⁺ 402.2064, found 402.2060.

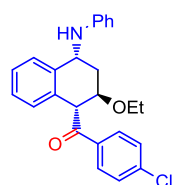
Tetrahydronaphthylamines (6k)



Brown solid, m. p. = 131–132 °C, purified by chromatography (PE/EA = 20/1), yield = 80%, 61.8 mg, *dr* = 19:1; **¹H NMR** (400 MHz, CDCl₃) δ 8.02 (d, *J* = 8.1 Hz, 2H), 7.42

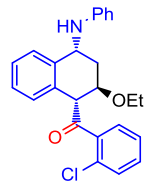
(d, $J = 7.7$ Hz, 1H), 7.33 (d, $J = 8.2$ Hz, 2H), 7.23 (s, 1H), 7.23 – 7.16 (m, 3H), 7.13 (dd, $J = 10.6$, 4.2 Hz, 1H), 6.88 (d, $J = 7.7$ Hz, 1H), 6.75 – 6.70 (m, 3H), 4.95 (d, $J = 6.8$ Hz, 1H), 4.84 (s, 1H), 4.27 – 4.20 (m, 1H), 3.58 – 3.50 (m, 1H), 3.36 (dq, $J = 9.1$, 7.0 Hz, 1H), 2.45 (s, 3H), 2.34 – 2.16 (m, 1H), 2.09 – 2.01 (m, 1H), 1.04 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 202.1, 147.3, 144.4, 138.1, 135.7, 134.8, 129.5, 129.4, 129.0, 128.9, 128.7, 127.8, 127.2, 117.4, 112.9, 75.0, 64.7, 52.9, 50.6, 32.3, 21.7, 15.4. **IR** (KBr, cm^{-1}) 3396, 3056, 3021, 2974, 2926, 2862, 1677, 1602, 1502, 1440, 1371, 1324, 1284, 1177, 1124, 1092, 988, 949, 908, 822, 745, 691, 625, 589, 510, 472. **HRMS** (ESI) Calcd for $\text{C}_{26}\text{H}_{28}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$ 386.2115, found 386.2118.

Tetrahydronaphthylamines (6l)



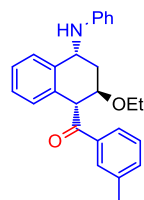
Yellow oil, purified by chromatography (PE/EA = 20/1), yield = 78%, 63.2mg, $dr = 17:1$; ^1H NMR (400 MHz, CDCl_3) δ 8.07 – 8.04 (m, 2H), 7.52 – 7.48 (m, 2H), 7.41 (d, $J = 7.5$ Hz, 1H), 7.24 – 7.19 (m, 3H), 7.16 – 7.12 (m, 1H), 6.84 (d, $J = 7.6$ Hz, 1H), 6.76 – 6.69 (m, 3H), 4.90 (d, $J = 7.2$ Hz, 1H), 4.83 (t, $J = 4.6$ Hz, 1H), 4.24 – 4.17 (m, 1H), 3.58 – 3.52 (m, 1H), 3.31 (dq, $J = 9.3$, 7.0 Hz, 1H), 2.44 (m, 1H), 2.05 – 1.98 (m, 1H), 1.02 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 201.7, 147.1, 140.0, 138.0, 136.6, 134.5, 130.3, 129.4, 129.1, 129.1, 128.5, 128.0, 127.4, 117.5, 112.9, 75.1, 64.7, 53.2, 50.7, 32.3, 15.3. **IR** (KBr, cm^{-1}) 3396, 3057, 2972, 2926, 2865, 1682, 1596, 1497, 1439, 1321, 1280, 1211, 1170, 1092, 998, 907, 828, 748, 691, 630, 543, 470. **HRMS** (ESI) Calcd for $\text{C}_{25}\text{H}_{25}\text{ClNO}_2$ ($\text{M}+\text{H}$) $^+$ 406.1568, found 406.1569.

Tetrahydronaphthylamines (6m)



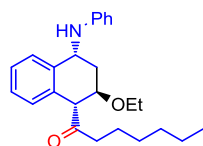
Yellow oil, purified by chromatography (PE/EA = 20/1), yield = 68%, 55.1mg, $dr > 20:1$; ^1H NMR (400 MHz, CDCl_3) δ 7.59 (dd, $J = 7.6$, 1.7 Hz, 1H), 7.46 (dt, $J = 9.4$, 4.8 Hz, 2H), 7.41 (td, $J = 7.6$, 1.8 Hz, 1H), 7.34 (td, $J = 7.4$, 1.3 Hz, 1H), 7.25 – 7.17 (m, 4H), 7.07 (dd, $J = 7.0$, 1.7 Hz, 1H), 6.75 – 6.67 (m, 3H), 4.83 (t, $J = 5.2$ Hz, 2H), 4.22 – 4.15 (m, 1H), 3.96 (br, 1H), 3.53 (dq, $J = 9.1$, 7.0 Hz, 1H), 3.34 (dq, $J = 9.2$, 7.0 Hz, 1H), 2.36 (m, 1H), 2.08 (m, 1H), 1.05 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 204.2, 147.3, 139.8, 138.2, 133.3, 132.0, 131.3, 130.8, 129.7, 129.5, 129.3, 128.8, 127.8, 127.6, 126.9, 117.4, 112.9, 74.8, 64.4, 57.0, 50.1, 32.1, 15.3. **IR** (KBr, cm^{-1}) 3399, 3058, 2973, 2927, 2869, 1696, 1597, 1502, 1424, 1371, 1318, 1253, 1208, 1094, 1073, 988, 950, 871, 748, 695, 640, 509, 466. **HRMS** (ESI) Calcd for $\text{C}_{25}\text{H}_{25}\text{ClNO}_2$ ($\text{M}+\text{H}$) $^+$ 406.1568, found 406.1571.

Tetrahydronaphthylamines (6n)



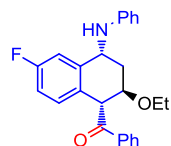
Yellow oil, purified by chromatography (PE/EA = 20/1), yield = 72%, 55.4mg, $dr > 20:1$; ^1H NMR (400 MHz, CDCl_3) δ 7.96 – 7.87 (m, 2H), 7.47 – 7.40 (m, 3H), 7.24 – 7.18 (m, 3H), 7.14 (td, $J = 7.5$, 1.3 Hz, 1H), 6.88 (d, $J = 7.6$ Hz, 1H), 6.73 (dd, $J = 7.5$, 5.2 Hz, 3H), 4.97 (d, $J = 6.9$ Hz, 1H), 4.85 (t, $J = 4.5$ Hz, 1H), 4.27 – 4.20 (m, 1H), 4.07 (br, 1H), 3.55 (dq, $J = 9.2$, 7.0 Hz, 1H), 3.36 (dq, $J = 9.3$, 7.0 Hz, 1H), 2.48 – 2.38 (m, 4H), 2.05 (m, 1H), 1.05 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 202.8, 147.2, 138.7, 138.2, 138.0, 134.7, 134.2, 129.4, 129.3, 128.9, 128.7, 128.7, 127.8, 127.2, 126.1, 117.4, 112.9, 75.0, 64.7, 53.1, 50.6, 32.3, 21.4, 15.3. **IR** (KBr, cm^{-1}) 3396, 3054, 2970, 2922, 2868, 1678, 1597, 1500, 1426, 1366, 1318, 1243, 1165, 1091, 990, 954, 750, 693, 631, 587, 466. **HRMS** (ESI) Calcd for $\text{C}_{26}\text{H}_{28}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$ 386.2115, found 386.2115.

Tetrahydronaphthylamines (6o)



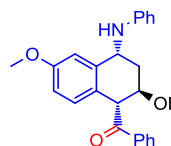
Yellow oil, purified by chromatography (PE/EA = 20/1), yield = 81%, 61.4mg, *dr* > 20:1; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.42 – 7.36 (m, 1H), 7.21 (dt, J = 10.2, 5.9 Hz, 4H), 6.97 – 6.90 (m, 1H), 6.76 – 6.65 (m, 3H), 4.78 (t, J = 4.9 Hz, 1H), 4.05 – 3.99 (m, 2H), 3.58 (m, 1H), 3.37 (dq, J = 9.2, 7.0 Hz, 1H), 2.76 – 2.58 (m, 2H), 2.39 – 2.31 (m, 1H), 1.94 (m, 1H), 1.69 – 1.59 (m, 2H), 1.32 (dt, J = 11.6, 6.0 Hz, 6H), 1.14 (t, J = 7.0 Hz, 3H), 0.89 (t, J = 6.7 Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 212.3, 147.2, 137.7, 133.7, 129.4, 129.1, 128.4, 127.9, 127.45, 117.5, 112.9, 74.6, 64.2, 58.4, 50.6, 44.5, 32.1, 31.6, 28.9, 23.4, 22.5, 15.4, 14.0. **IR** (KBr, cm^{-1}) 3396, 3056, 2966, 2925, 2859, 1711, 1600, 1502, 1440, 1368, 1314, 1248, 1171, 1126, 1096, 956, 869, 749, 693, 628, 507, 465. **HRMS** (ESI) Calcd for $\text{C}_{25}\text{H}_{34}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$ 380.2584, found 380.2586.

Tetrahydronaphthylamines (6p)



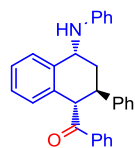
Yellow oil, purified by chromatography (PE/EA = 20/1), yield = 46%, 35.5mg, *dr* = 20:1; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.10 (d, J = 7.9 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.7 Hz, 2H), 7.24 – 7.18 (m, 3H), 6.85 (d, J = 6.8 Hz, 2H), 6.73 (dd, J = 12.4, 7.8 Hz, 3H), 4.96 (d, J = 5.4 Hz, 1H), 4.82 (s, 1H), 4.21 – 4.12 (m, 1H), 4.04 (br, 1H), 3.57 (dt, J = 7.1, 6.5 Hz, 1H), 3.46 – 3.37 (m, 1H), 2.24 (m, 1H), 2.19 – 2.10 (m, 1H), 1.09 (td, J = 7.0, 1.5 Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 201.7, 161.9 (d, J = 244.0 Hz), 147.1, 141.0, 140.9, 137.6, 133.6, 130.6, 130.5, 129.8, 129.8, 129.5, 128.9, 128.8, 117.7, 115.1, 114.9, 114.9, 114.7, 113.1, 74.8, 64.7, 52.2, 49.8, 31.7, 15.4. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -114.7, -114.7. **IR** (KBr, cm^{-1}) 3396, 3351, 3056, 2974, 2927, 2863, 1681, 1603, 1500, 1445, 1369, 1322, 1248, 1212, 1176, 1091, 993, 963, 914, 878, 809, 748, 695, 566, 512, 467. **HRMS** (ESI) Calcd for $\text{C}_{25}\text{H}_{25}\text{FNO}_2$ ($\text{M}+\text{H}$) $^+$ 390.1864, found 390.1869.

Tetrahydronaphthylamines (6q)



White solid, m. p. = 108-109 °C, purified by chromatography (PE/EA = 15/1), yield = 52%, 41.8mg, *dr* = 18:1; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.10 (d, J = 7.4 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.22 (dd, J = 10.7, 4.9 Hz, 2H), 6.97 (d, J = 2.6 Hz, 1H), 6.79 (d, J = 8.6 Hz, 1H), 6.75 – 6.69 (m, 4H), 4.91 (d, J = 6.6 Hz, 1H), 4.81 (t, J = 5.0 Hz, 1H), 4.24 – 4.17 (m, 1H), 3.70 (s, 3H), 3.58 – 3.50 (m, 1H), 3.40 – 3.30 (m, 1H), 2.37 (m, 1H), 2.05 (m, 1H), 1.04 (t, J = 7.0 Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 202.7, 158.7, 147.2, 139.4, 138.1, 133.4, 129.7, 129.4, 128.8, 126.6, 117.5, 114.7, 113.0, 75.1, 64.7, 55.3, 52.5, 50.71, 32.1, 15.4. **IR** (KBr, cm^{-1}) 3395, 3055, 2970, 2927, 2867, 2839, 1680, 1603, 1501, 1438, 1368, 1323, 1250, 1181, 1035, 992, 874, 809, 750, 695, 572, 512, 473. **HRMS** (ESI) Calcd for $\text{C}_{26}\text{H}_{28}\text{NO}_3$ ($\text{M}+\text{H}$) $^+$ 402.2064, found 402.2069.

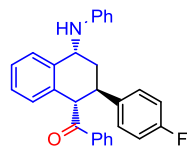
Tetrahydronaphthylamines (6r)



Brown solid, m. p. = 82-83 °C, purified by chromatography (PE/EA = 20/1), yield = 50%, 40.3mg, *dr* > 20:1; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.77 – 7.71 (m, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.44 (d, J = 7.1 Hz, 1H), 7.36 (t, J = 7.7 Hz, 2H), 7.25 (s, 1H), 7.21 – 7.14 (m, 7H), 7.13 – 7.08 (m, 1H), 6.91 (d, J = 7.7 Hz, 1H), 6.75 – 6.66 (m, 3H), 5.07 (d, J = 9.2 Hz, 1H), 4.76 (t, J = 3.4 Hz, 1H), 4.36 (br, 1H), 3.72 (m, 1H), 2.47 (dt, J = 13.3, 3.4 Hz, 1H),

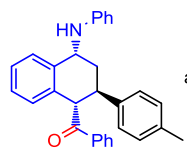
2.28 – 2.19 (m, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ 203.6, 147.1, 143.5, 138.2, 137.8, 136.1, 133.2, 130.3, 129.5, 128.7, 128.6, 128.5, 128.2, 127.6, 127.4, 126.8, 117.4, 113.0, 53.6, 50.9, 40.2, 34.0. **IR** (KBr, cm⁻¹) 3407, 3337, 3058, 3021, 2944, 2919, 2857, 1678, 1595, 1499, 1441, 1326, 1256, 1211, 1169, 1111, 1068, 994, 909, 865, 758, 696, 589, 541, 505, 473. **HRMS** (ESI) Calcd for C₂₉H₂₆NO (M+H)⁺ 404.2009, found 404.2014.

Tetrahydronaphthylamines (6s)

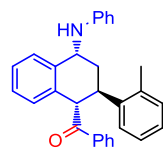


Yellow oil, purified by chromatography (PE/EA = 20/1), yield = 33%, 27.8mg, *dr* > 20:1; **¹H NMR** (400 MHz, CDCl₃) δ 7.77 – 7.72 (m, 2H), 7.50 (dd, *J* = 10.6, 4.2 Hz, 1H), 7.42 (d, *J* = 6.9 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.22 (t, *J* = 7.1 Hz, 2H), 7.18 – 7.15 (m, 2H), 7.11 (ddd, *J* = 8.7, 4.6, 1.6 Hz, 2H), 6.91 – 6.80 (m, 3H), 6.73 – 6.67 (m, 3H), 5.00 (d, *J* = 9.5 Hz, 1H), 4.76 (s, 1H), 4.31 (br, 1H), 3.72 (m, 1H), 2.44 (dt, *J* = 13.3, 3.3 Hz, 1H), 2.18 (d, *J* = 3.1 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 203.4, 161.6 (d, *J* = 244.0 Hz), 146.9, 139.2, 139.1, 138.1, 137.5, 136.0, 133.3, 130.4, 129.4, 129.1, 129.0, 128.7, 128.6, 128.4, 128.2, 127.4, 117.4, 115.5, 115.2, 112.9, 53.8, 51.0, 39.4, 34.1. **¹⁹F NMR** (376 MHz, CDCl₃) δ -115.92. **IR** (KBr, cm⁻¹) 3402, 3055, 3016, 2951, 2920, 2856, 1677, 1597, 1503, 1437, 1322, 1303, 1221, 1166, 1108, 1068, 996, 905, 828, 748, 696, 543, 504. **HRMS** (ESI) Calcd for C₂₉H₂₅FNO (M+H)⁺ 422.1915, found 422.1919.

Tetrahydronaphthylamines (6t)

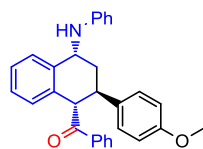


and



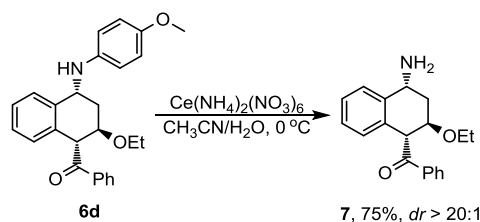
Yellow oil, purified by chromatography (PE/EA = 20/1), yield = 70%, 50.0mg, *dr* > 20:1; **¹H NMR** (400 MHz, CDCl₃) δ 7.74 (dd, *J* = 10.0, 4.2 Hz, 2H), 7.46 (m, 2H), 7.37 – 7.31 (m, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.15 (dd, *J* = 15.9, 7.7 Hz, 3H), 6.95 (m, 5H), 6.71 – 6.65 (m, 3H), 5.05 (dd, *J* = 9.1, 4.4 Hz, 1H), 4.73 (d, *J* = 3.3 Hz, 1H), 4.32 (br, 1H), 3.73 – 3.64 (m, 1H), 2.44 (m, 1H), 2.24 – 2.14 (m, 4H). **¹³C NMR** (100 MHz, CDCl₃) δ 203.7, 203.5, 147.1, 143.4, 140.4, 138.2, 138.1, 138.1, 137.91, 137.8, 136.3, 136.2, 136.1, 133.1, 130.3, 130.2, 129.4, 129.3, 128.7, 128.7, 128.6, 128.5, 128.5, 128.18, 128.1, 127.5, 127.4, 127.3, 124.4, 117.3, 113.0, 53.6, 50.9, 40.0, 39.6, 34.2, 34.1, 21.4, 21.0. **IR** (KBr, cm⁻¹) 3041, 3055, 3017, 2951, 2919, 2858, 1727, 1678, 1598, 1502, 1438, 1321, 1253, 1212, 1173, 1111, 1070, 993, 905, 864, 818, 746, 696, 544, 506. **HRMS** (ESI) Calcd for C₃₀H₂₈NO (M+H)⁺ 418.2165, found 418.2171.

Tetrahydronaphthylamines (6u)



Yellow oil, purified by chromatography (PE/EA = 15/1), yield = 77%, 66.7mg, *dr* > 20:1; **¹H NMR** (400 MHz, CDCl₃) δ 7.75 (d, *J* = 7.6 Hz, 2H), 7.49 – 7.38 (m, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.22 – 7.11 (m, 4H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 7.5 Hz, 1H), 6.67 (t, *J* = 8.2 Hz, 5H), 5.02 (d, *J* = 9.1 Hz, 1H), 4.73 (s, 1H), 4.32 (br, 1H), 3.73 – 3.57 (m, 4H), 2.41 (d, *J* = 13.3 Hz, 1H), 2.16 (td, *J* = 13.1, 3.4 Hz, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ 203.6, 158.3, 147.1, 138.2, 137.8, 136.2, 135.6, 133.2, 130.3, 129.5, 128.78, 128.7, 128.5, 128.1, 127.3, 117.4, 114.0, 113.0, 55.2, 53.8, 51.0, 39.3, 34.3. **IR** (KBr, cm⁻¹) 3403, 3056, 3014, 2948, 2919, 2838, 1677, 1602, 1505, 1435, 1307, 1250, 1212, 1179, 1110, 1033, 993, 904, 824, 743, 696, 547. **HRMS** (ESI) Calcd for C₂₀H₂₈NO₂ (M+H)⁺ 434.2115, found 434.2115.

1.8 Chemical transformation of 6d

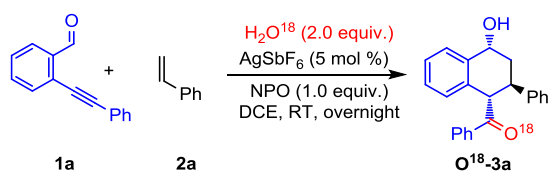


To a solution of compound **6d** (41.2mg, 0.2mmol) in MeCN/H₂O (4:1, 1mL) was added ceric ammonium nitrate (548.2 mg, 0.8 mmol) at 0 °C, and the reaction mixture was stirred for 1 hour. The reaction was quenched with 10% aqueous NaOH and adjusted to pH = 9 to give a mass. The mass was filtered through a pad of celite, washed with DCM. The solution was extracted with DCM. The organic phase was washed with brine and dried over anhydrous Na₂SO₄. The solvent was removed and the residue was purified on PE:EA=10:1 to give a brown oil.

(4-Amino-2-ethoxy-1,2,3,4-tetrahydronaphthalen-1-yl)(phenyl)methanone (**7**)

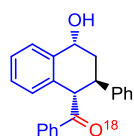
Brown solid, m. p. = 104-105 °C, purified by chromatography (PE/EA = 10/1), yield = 75%, 44.3 mg, *dr* > 20:1; **¹H NMR** (400 MHz, CDCl₃) δ 7.90 – 7.83 (m, 2H), 7.46 – 7.39 (m, 3H), 7.35 (m, 2H), 7.24 (qd, *J* = 4.7, 1.7 Hz, 2H), 5.64 (dd, *J* = 3.2, 1.9 Hz, 1H), 5.13 (d, *J* = 3.3 Hz, 1H), 3.81 (dt, *J* = 8.6, 3.0 Hz, 1H), 3.66 (dq, *J* = 9.2, 7.0 Hz, 1H), 3.43 (dq, *J* = 9.2, 7.0 Hz, 1H), 2.30 – 2.20 (m, 1H), 1.37 – 1.32 (m, 1H), 1.09 (t, *J* = 7.0 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 173.8, 140.7, 136.2, 134.4, 130.6, 128.6, 126.6, 126.3, 126.3, 125.5, 122.8, 73.6, 63.9, 62.1, 47.2, 34.4, 15.2. **IR** (KBr, cm⁻¹) 3650, 3072, 2968, 2925, 2857, 1731, 1679, 1603, 1568, 1448, 1347, 1164, 1096, 1049, 968, 874, 759, 692, 580, 523. **HRMS** (ESI) Calcd for C₁₉H₂₉NO₂ (M+H)⁺ 296.1642, found 296.1639.

1.9 Procedure for the preparation of the O¹⁸-3a



To a dichloroethane (DCE, 1.0 mL) suspension of AgSbF₆ (5 mol %) in Schlenk tube with a magnetic bar under a nitrogen atmosphere, was added 4-Nitropyridine N-oxide (NPO, 0.20 mmol), olefin (**2a**, 1.0 mmol), H₂O¹⁸ (0.4 mmol) and enynals (**1a**, 0.2mmol), the reaction was stirred at room temperature. The reaction was monitored by TLC. The reaction mixture was purified by chromatography with petroleum / ethyl acetate, 4/1, **O¹⁸-3a** was obtained. The labelled ¹⁸O was on the carbonyl group as the ¹³C NMR illustrated (Figure S1).

¹⁸O-3a



¹³C NMR (100 MHz, CDCl₃) δ 203.4, 143.5, 138.1, 137.3, 135.2, 133.2, 130.0, 128.9, 128.6, 128.6, 128.6, 128.4, 127.5, 127.5, 126.8, 67.8, 54.8, 39.3, 37.8. HRMS (ESI) Calcd for (M+Na)⁺ 353.13930, found 353.13980.

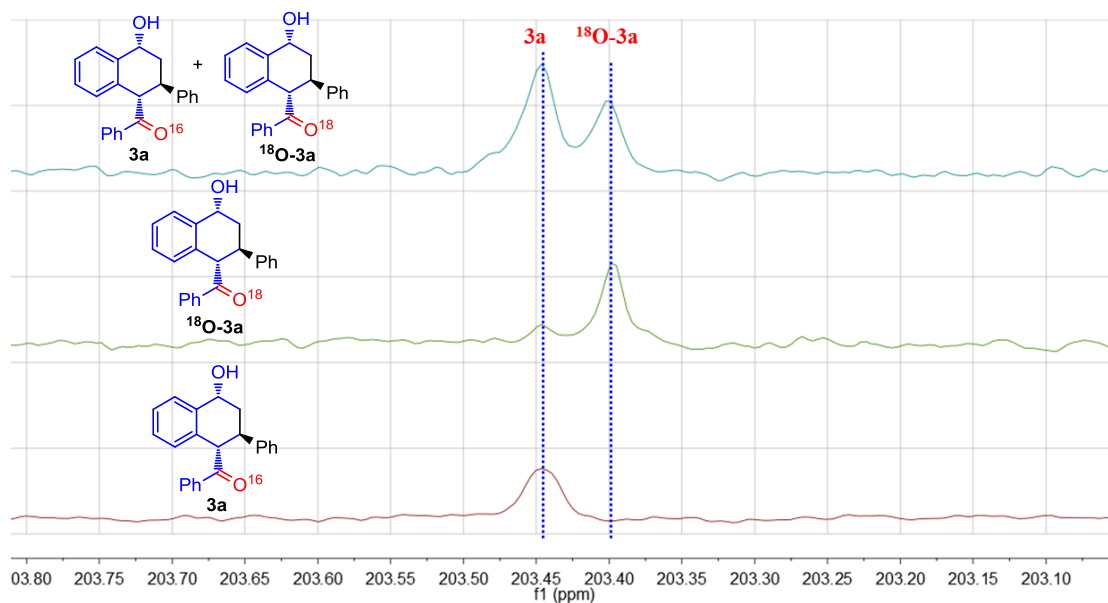


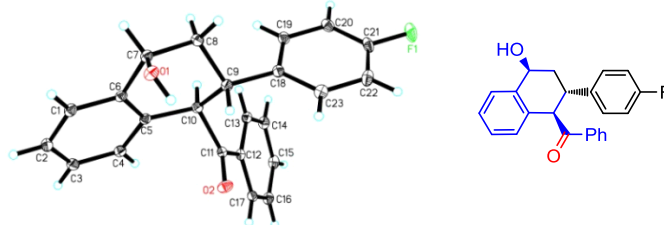
Figure S1. Comparison and assignment of the carbonyl carbon signal in ¹³C NMR spectra of ¹⁸O-3a and 3a

2. References

- [1] Zhu, S.; Zhang, Z.; Huang, X.; Jiang, H.; Guo, Z. *Chem. Eur. J.* **2013**, *19*, 4695.
- [2] Zhu, S.; Huang, H.; Zhang, Z.; Ma, T.; Jiang, H. *J. Org. Chem.* **2014**, *79*, 6113.
- [3] Zhu, S.; Hu, L.; Jiang, H. *Org. Biomol. Chem.* **2014**, *12*, 4104.
- [4] Zhu, S.; Guo, Z.; Huang, Z.; Jiang, H. *Chem. Eur. J.* **2014**, *20*, 2425.
- [5] Obika, S.; Kono, S.; Yasui, Y.; Yanada, R.; Takemoto, Y. *J. Org. Chem.* **2007**, *72*, 4462.
- [6] Zhu, S.; Liang, R.; Jiang, H.; Wu, W. *Angew. Chem., Int. Ed.* **2012**, *51*, 10861.

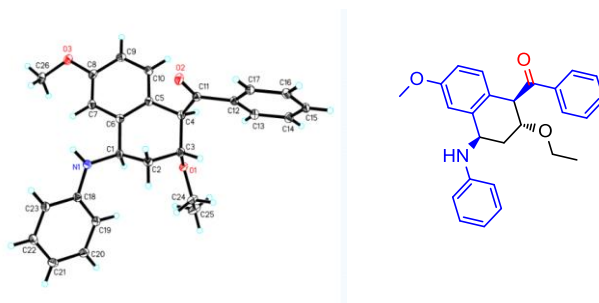
3. X-Ray diffraction analysis

3.1 Crystal data and structure refinement for 3d



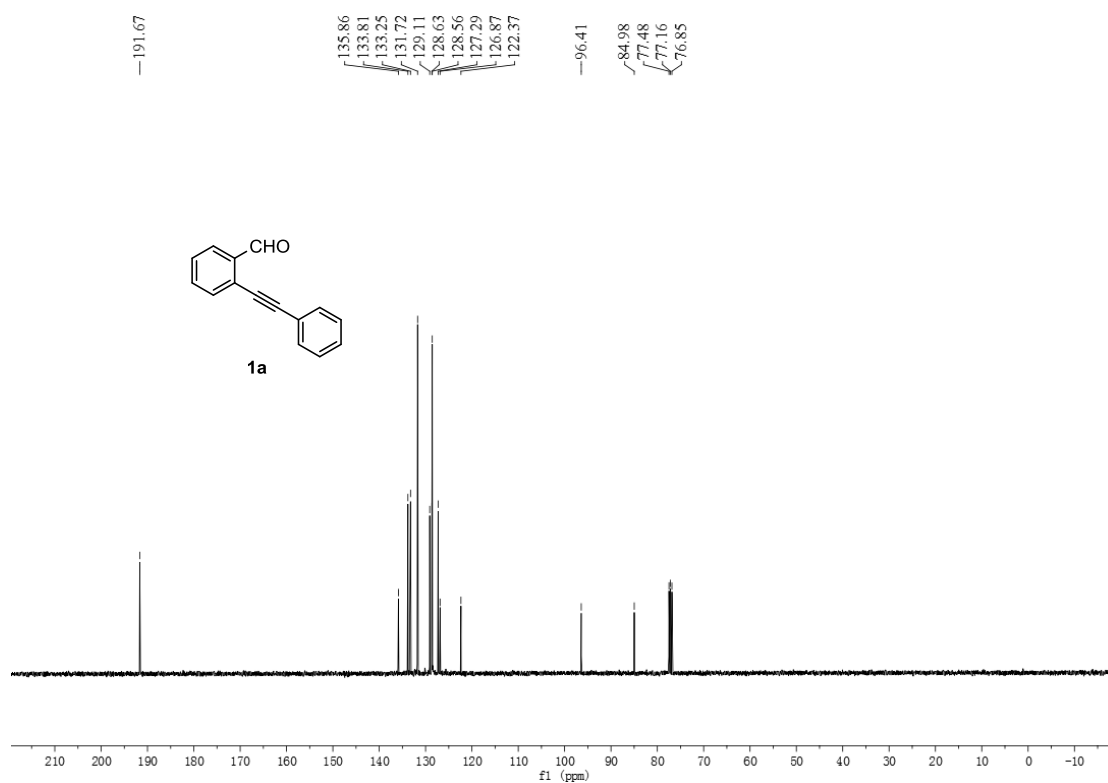
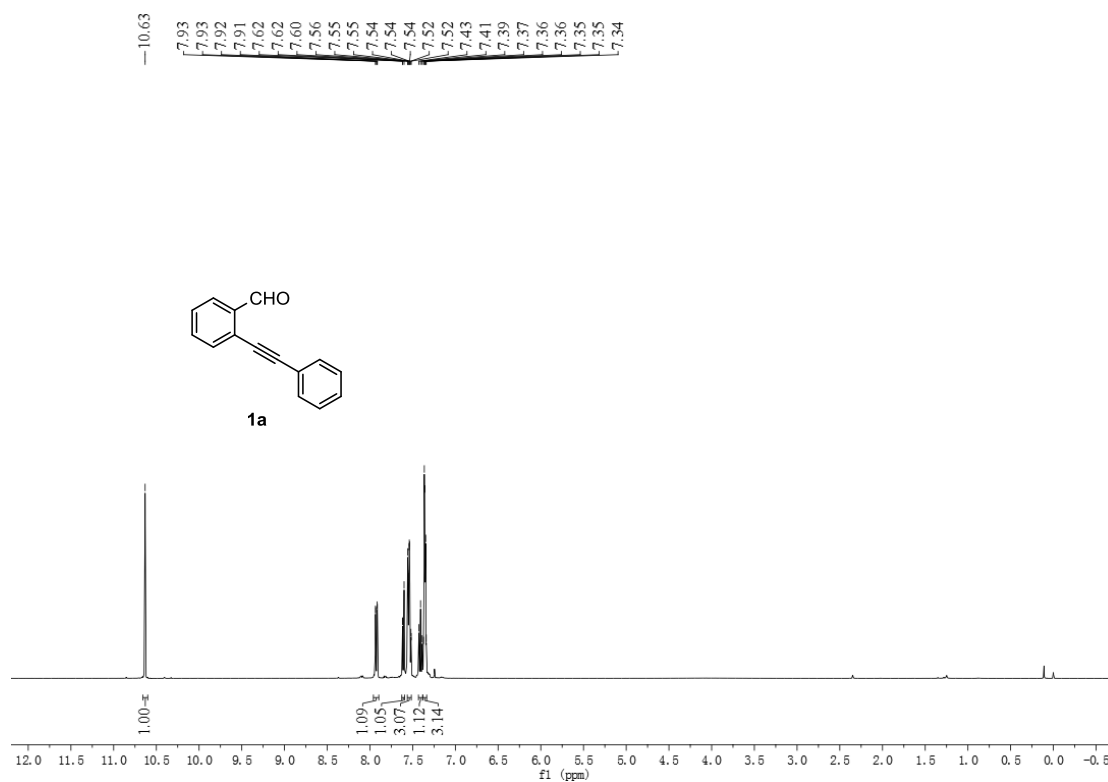
CCDC number	1589273
Identification code	3d
Empirical formula	C ₂₃ H ₁₉ FO ₂
Formula weight	346.38
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	8.9683(5)
b/Å	9.8217(5)
c/Å	11.3530(7)
α /°	75.074(5)
β /°	77.458(5)
γ /°	63.345(5)
Volume/Å ³	857.58(9)
Z	2
ρ_{calc} /cm ³	1.341
μ /mm ⁻¹	0.092
F(000)	364.0
Crystal size/mm ³	0.14 × 0.12 × 0.11
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/°	4.72 to 59.058
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -15 ≤ l ≤ 15
Reflections collected	14359
Independent reflections	4222 [R_{int} = 0.0439, R_{sigma} = 0.0516]
Data/restraints/parameters	4222/0/236
Goodness-of-fit on F ²	1.034
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0489, wR_2 = 0.1073
Final R indexes [all data]	R_1 = 0.0681, wR_2 = 0.1198
Largest diff. peak/hole / e Å ⁻³	0.28/-0.30

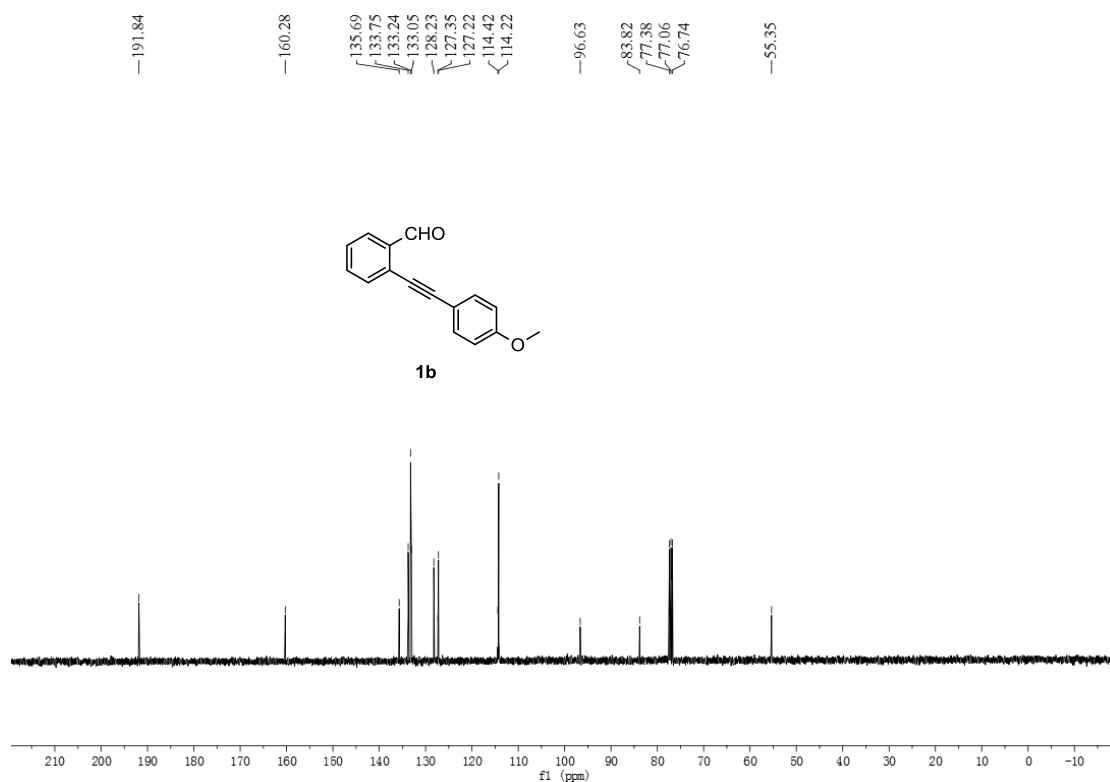
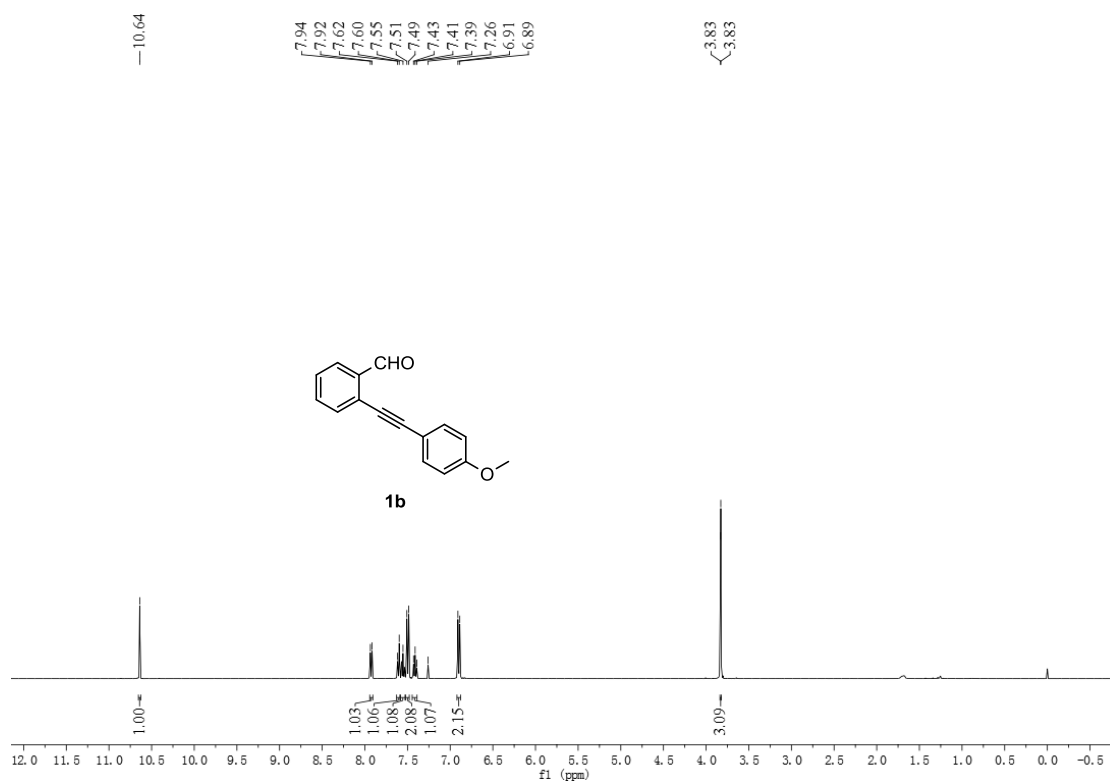
3.2 Crystal data and structure refinement for 6q

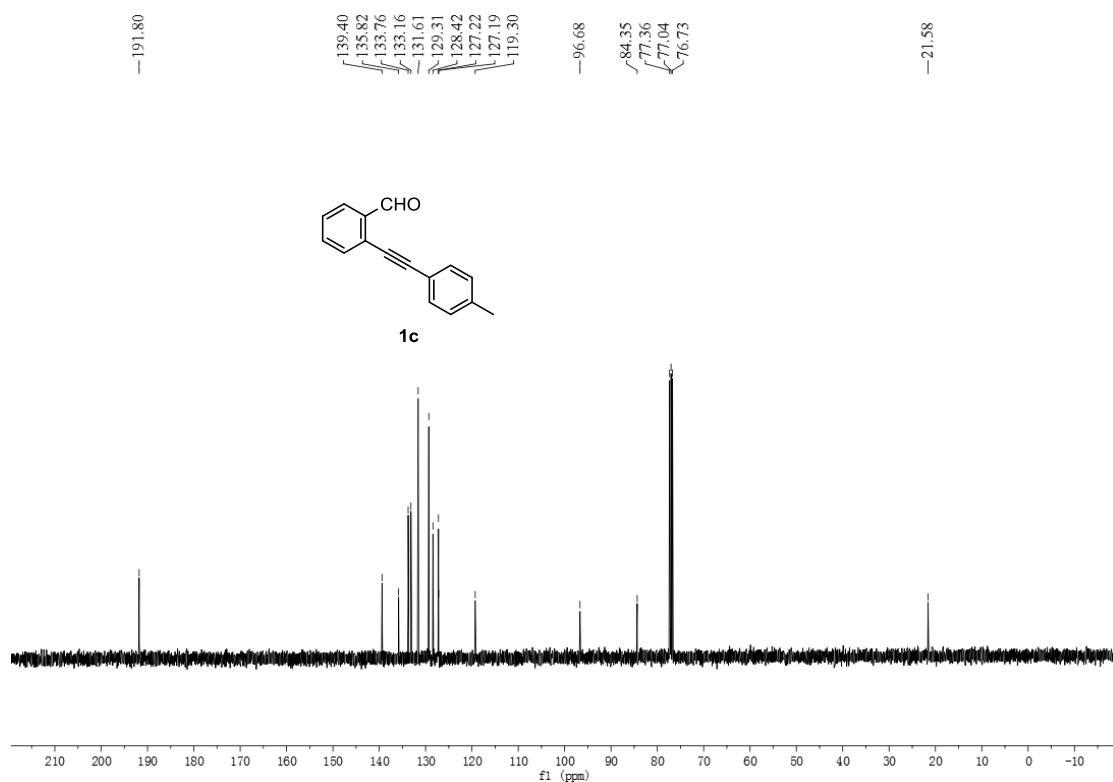
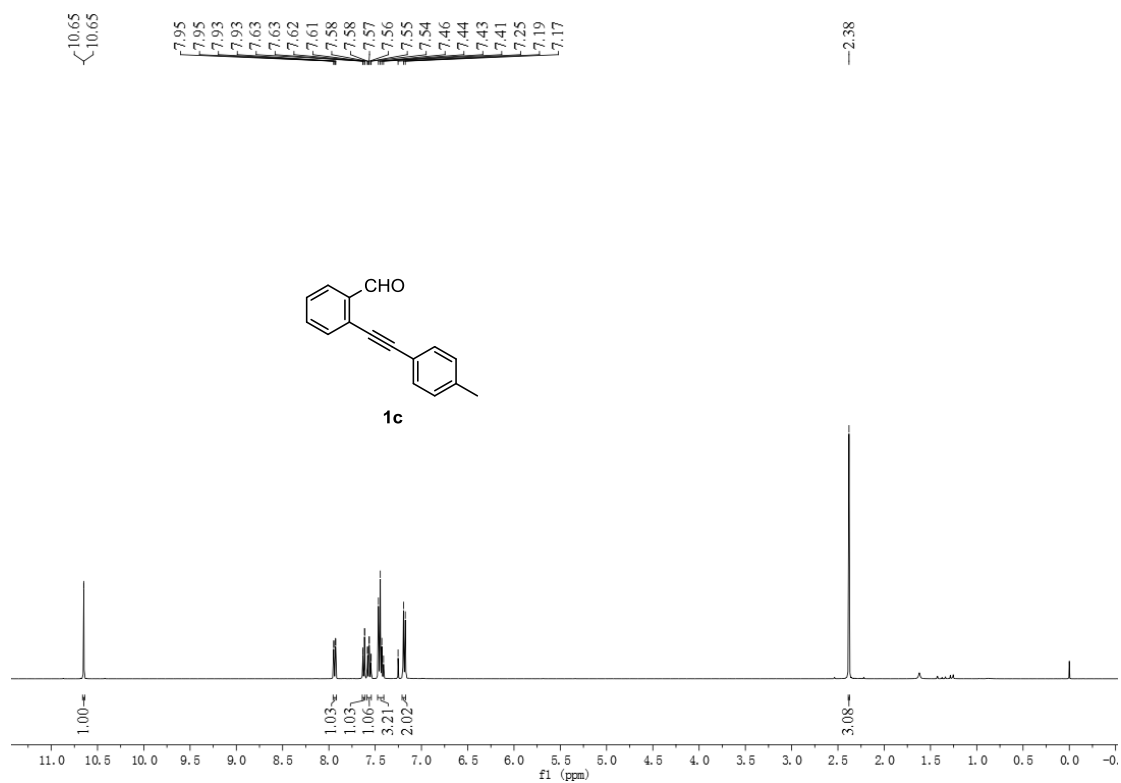


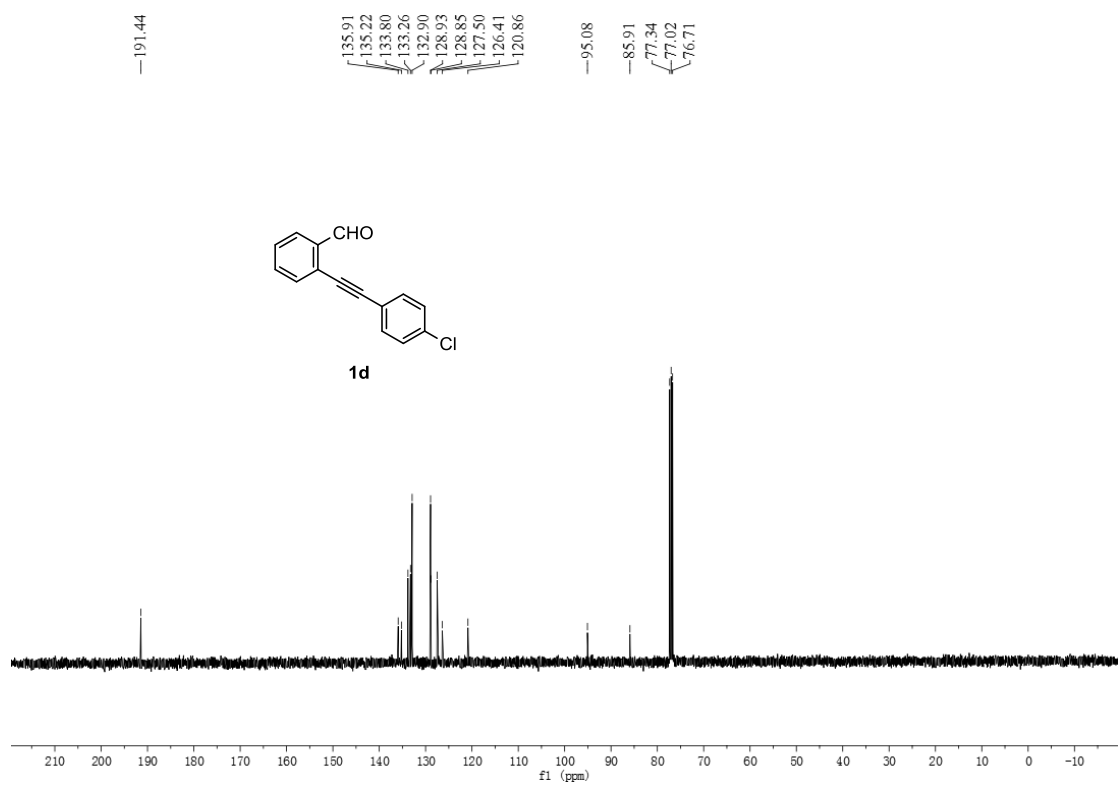
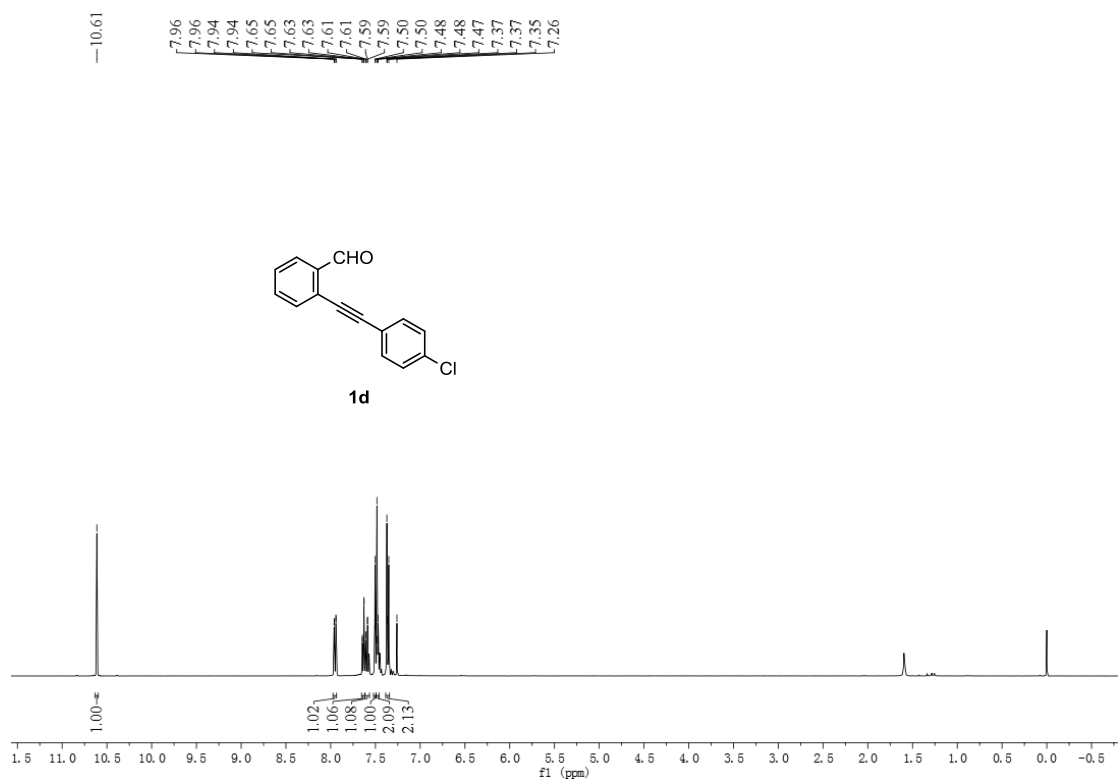
CCDC number	1524750
Identification code	6q
Empirical formula	C ₂₆ H ₂₇ NO ₃
Formula weight	401.48
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.2089(3)
b/Å	10.5763(4)
c/Å	10.9769(4)
α /°	100.503(3)
β /°	95.221(3)
γ /°	91.160(3)
Volume/Å ³	1046.09(7)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.275
μ/mm^{-1}	0.658
F(000)	428.0
Crystal size/mm ³	0.25 × 0.21 × 0.18
Radiation	Cu K α (λ = 1.54184)
2 θ range for data collection/°	8.23 to 147.28
Index ranges	-9 ≤ h ≤ 11, -10 ≤ k ≤ 13, -13 ≤ l ≤ 13
Reflections collected	6974
Independent reflections	4070 [R_{int} = 0.0153, R_{sigma} = 0.0185]
Data/restraints/parameters	4070/0/273
Goodness-of-fit on F ²	1.044
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0398, wR_2 = 0.1020
Final R indexes [all data]	R_1 = 0.0418, wR_2 = 0.1039
Largest diff. peak/hole / e Å ⁻³	0.34/-0.35

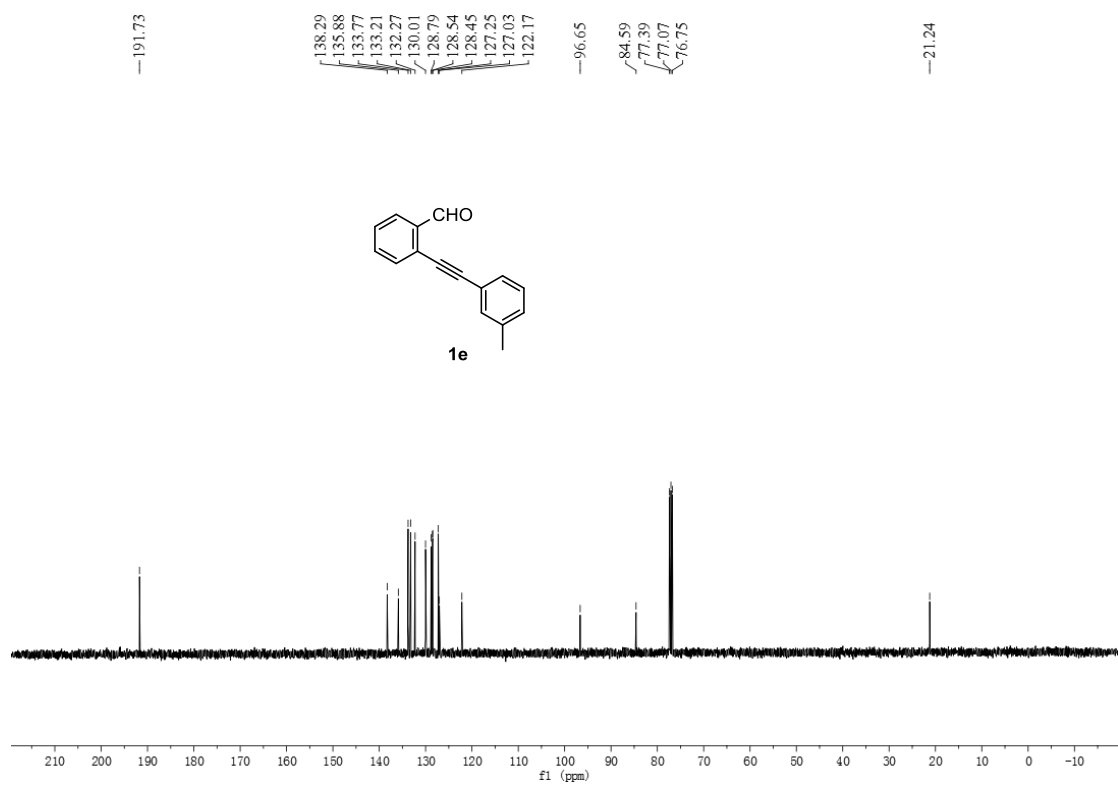
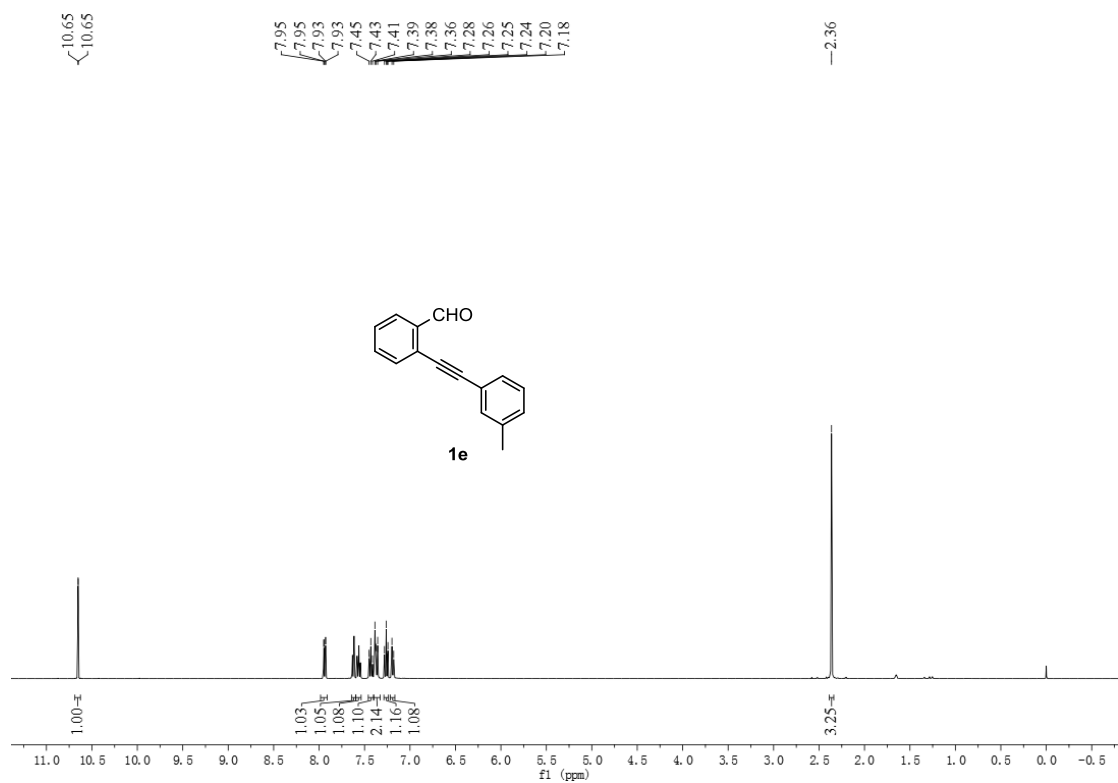
4. Copies of NMR spectra

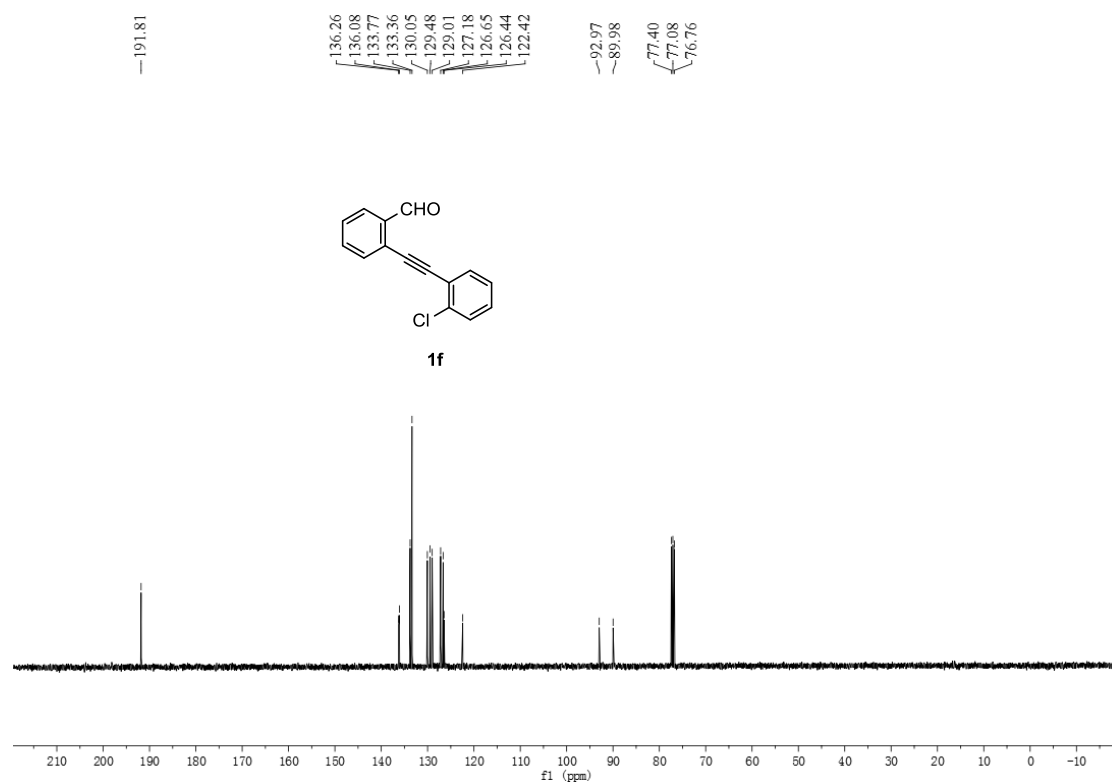
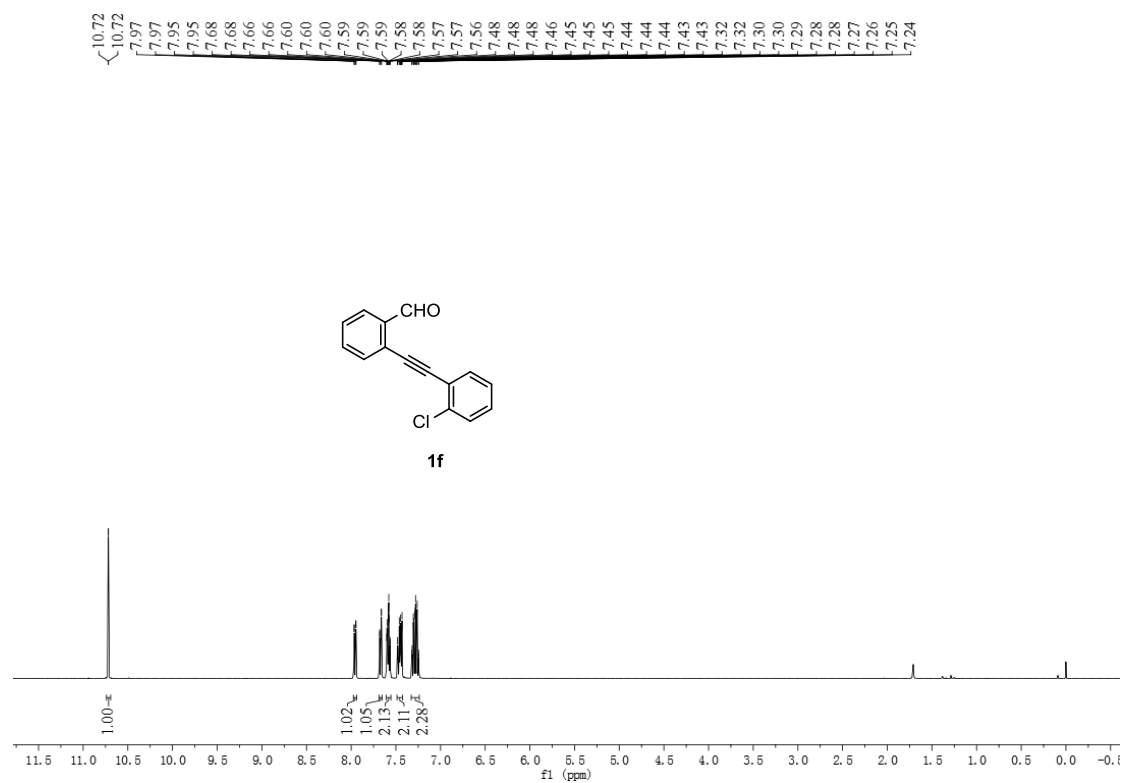


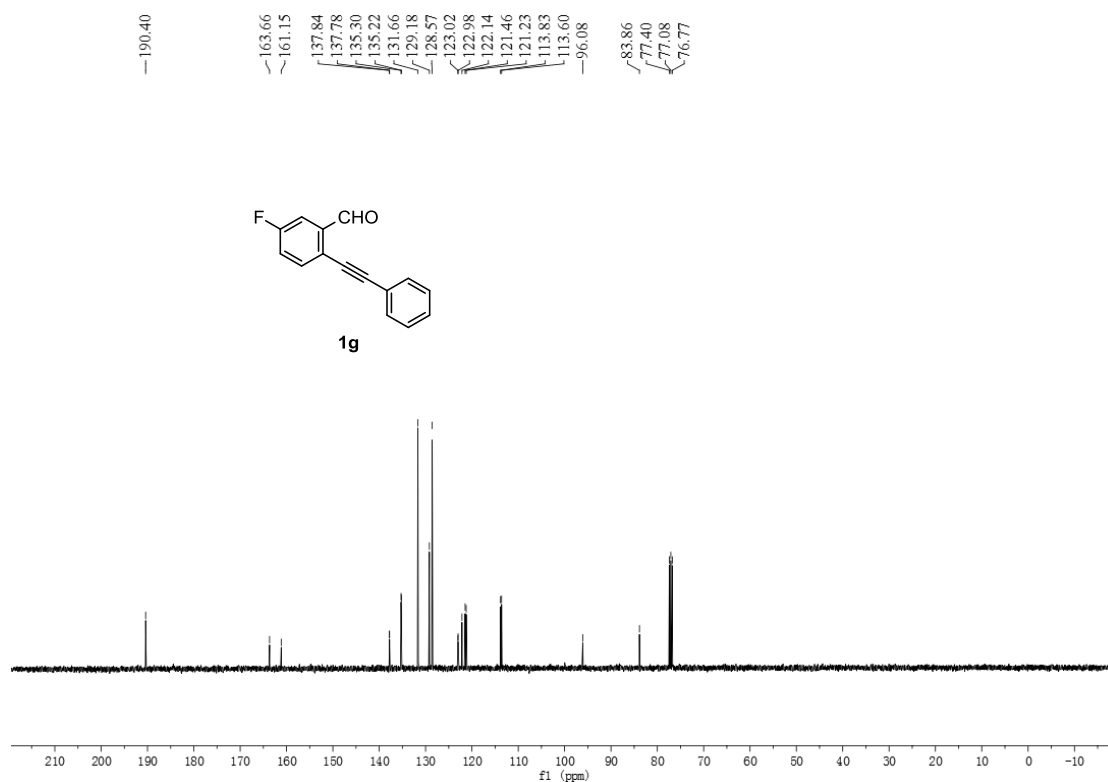
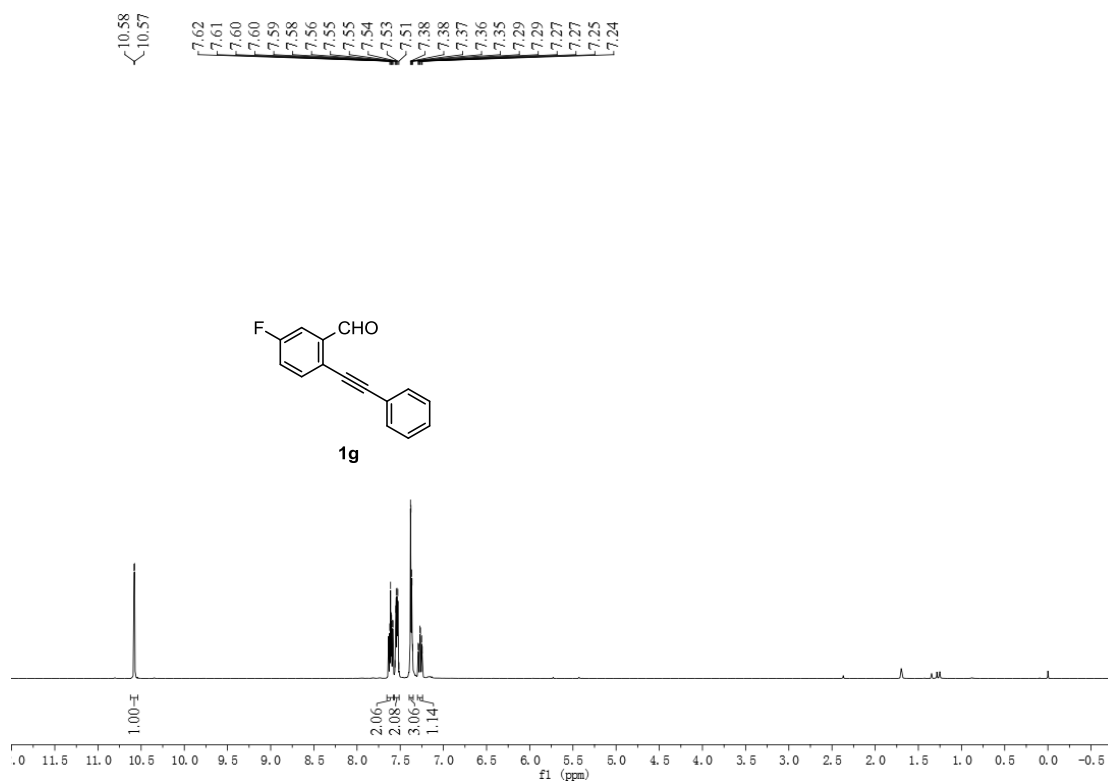


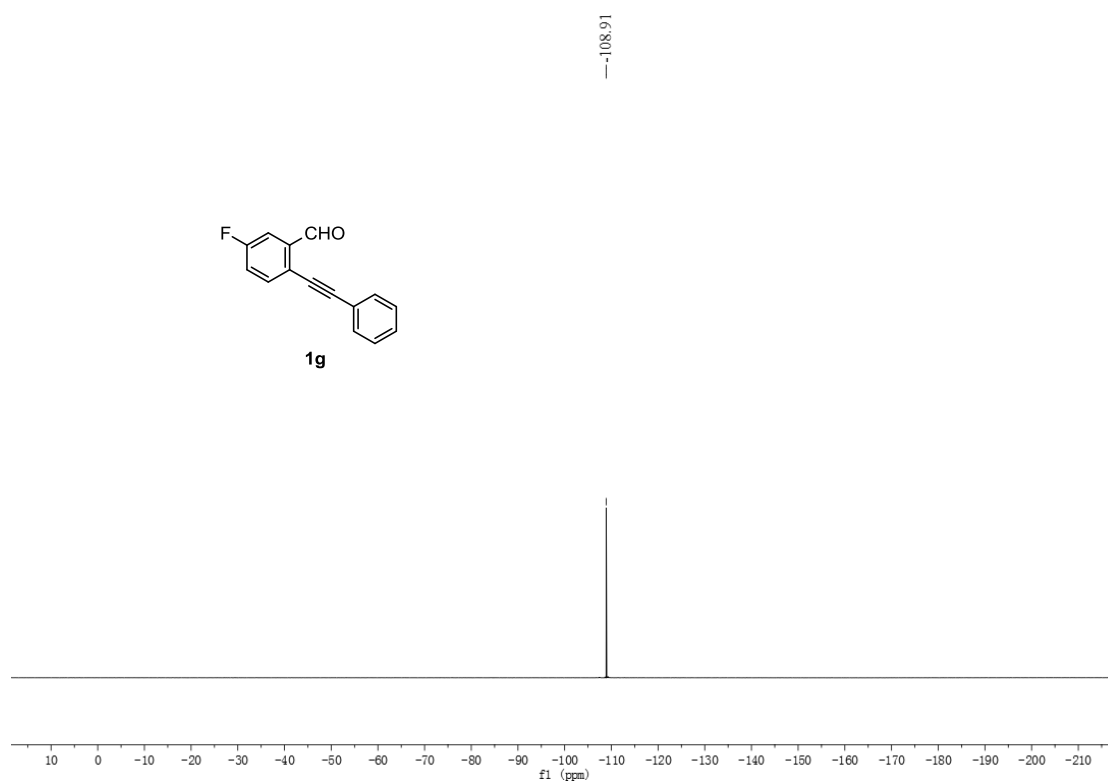


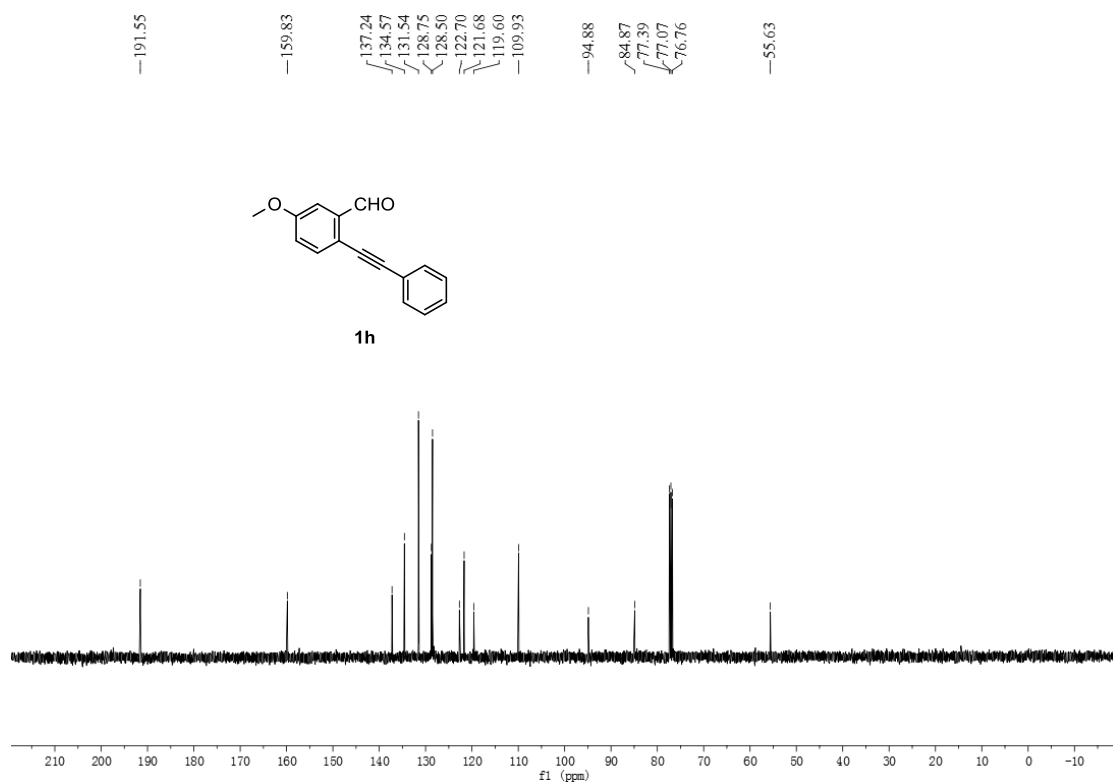
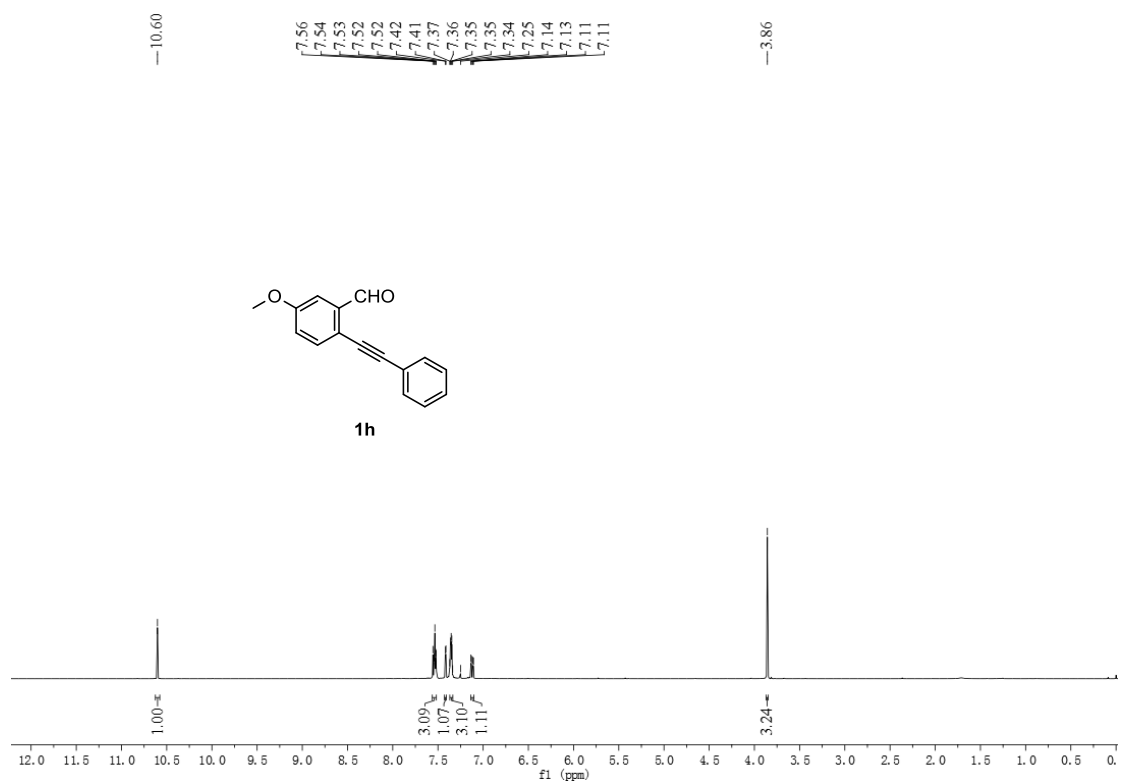


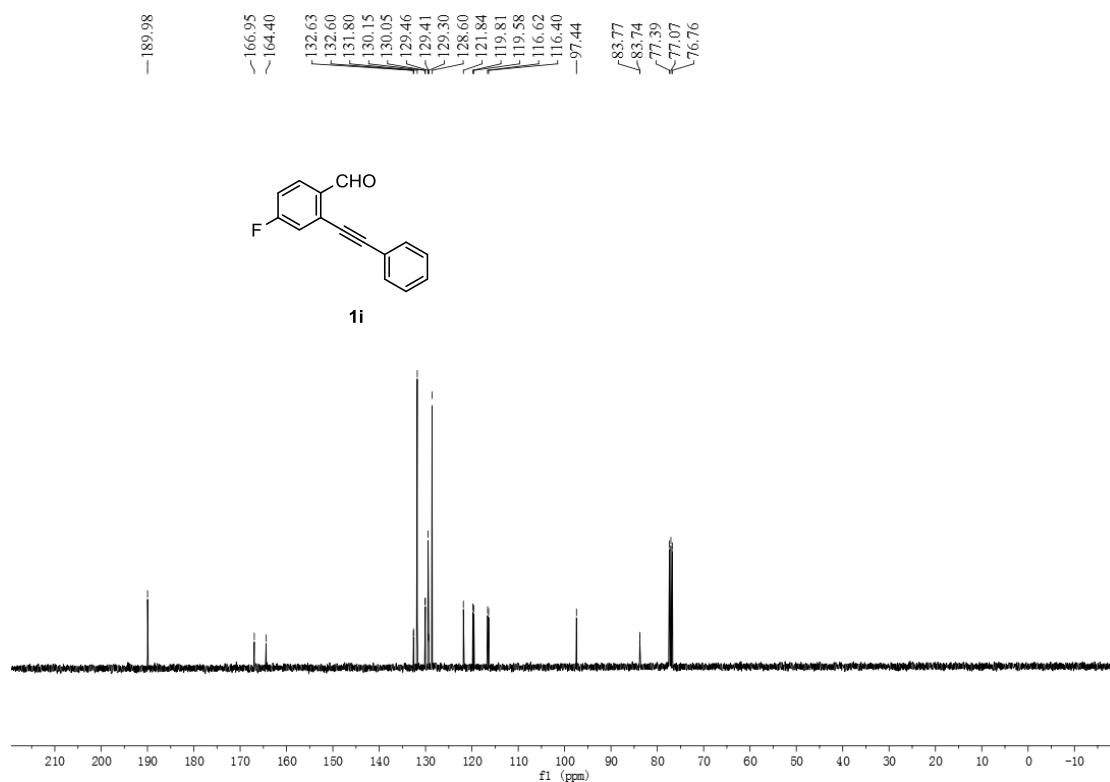
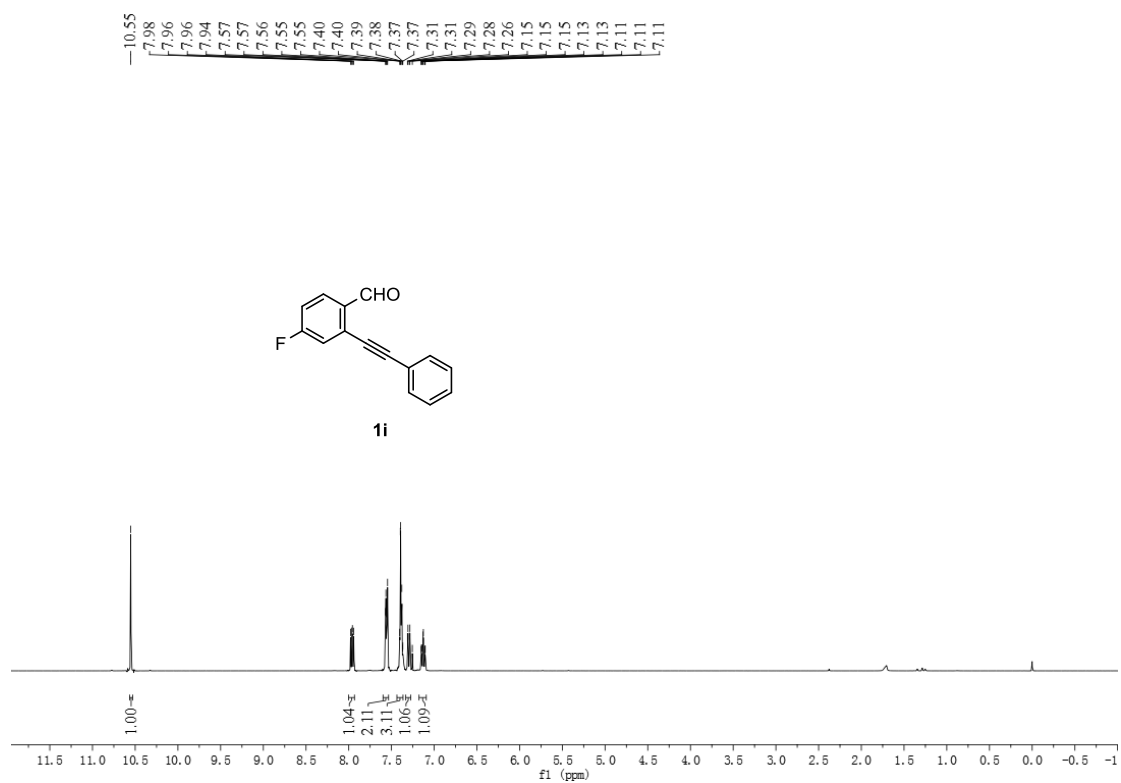


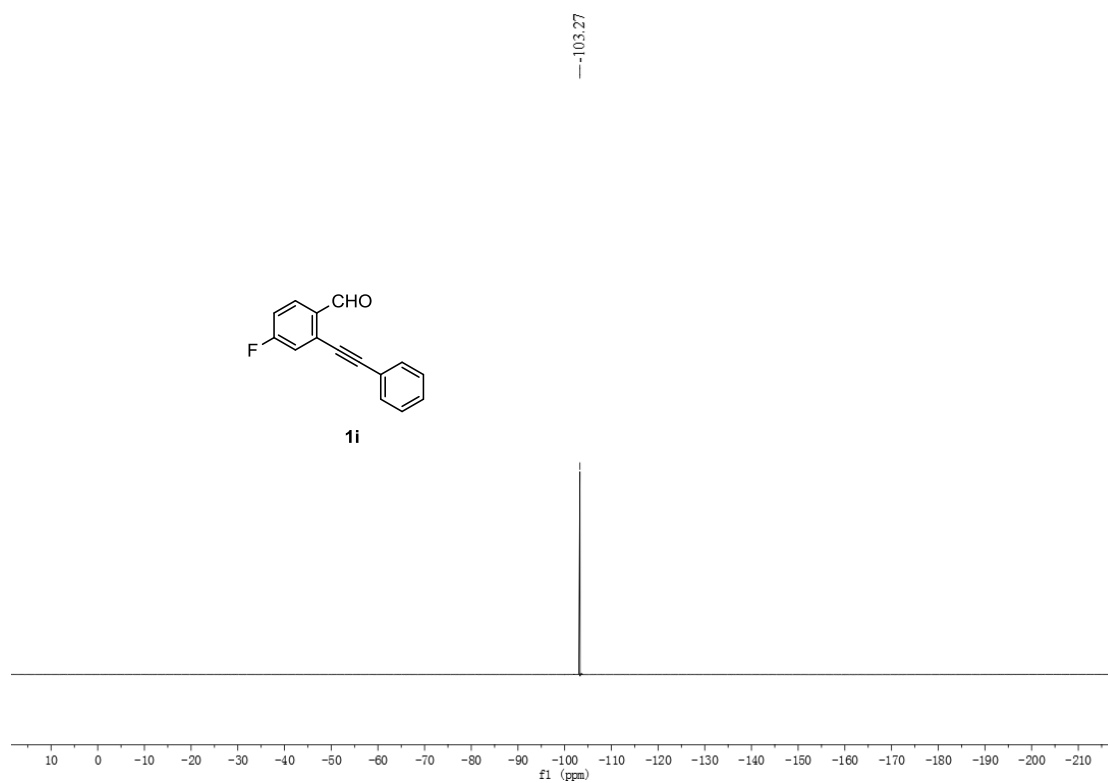


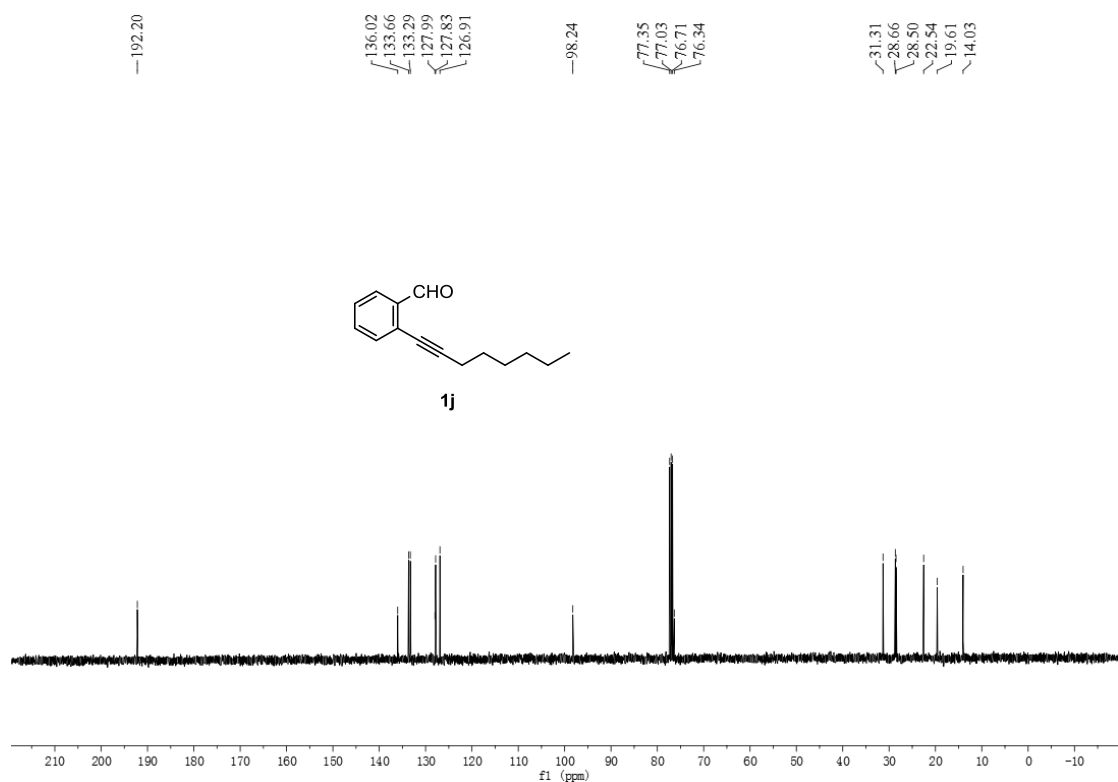
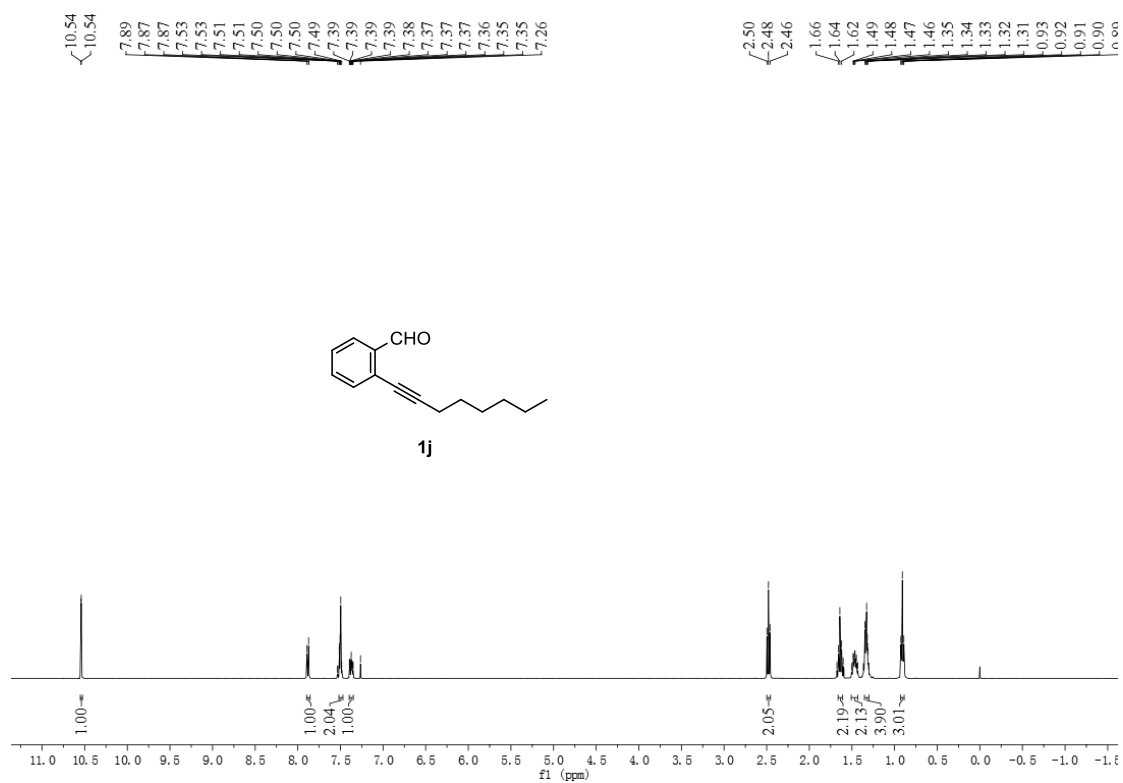


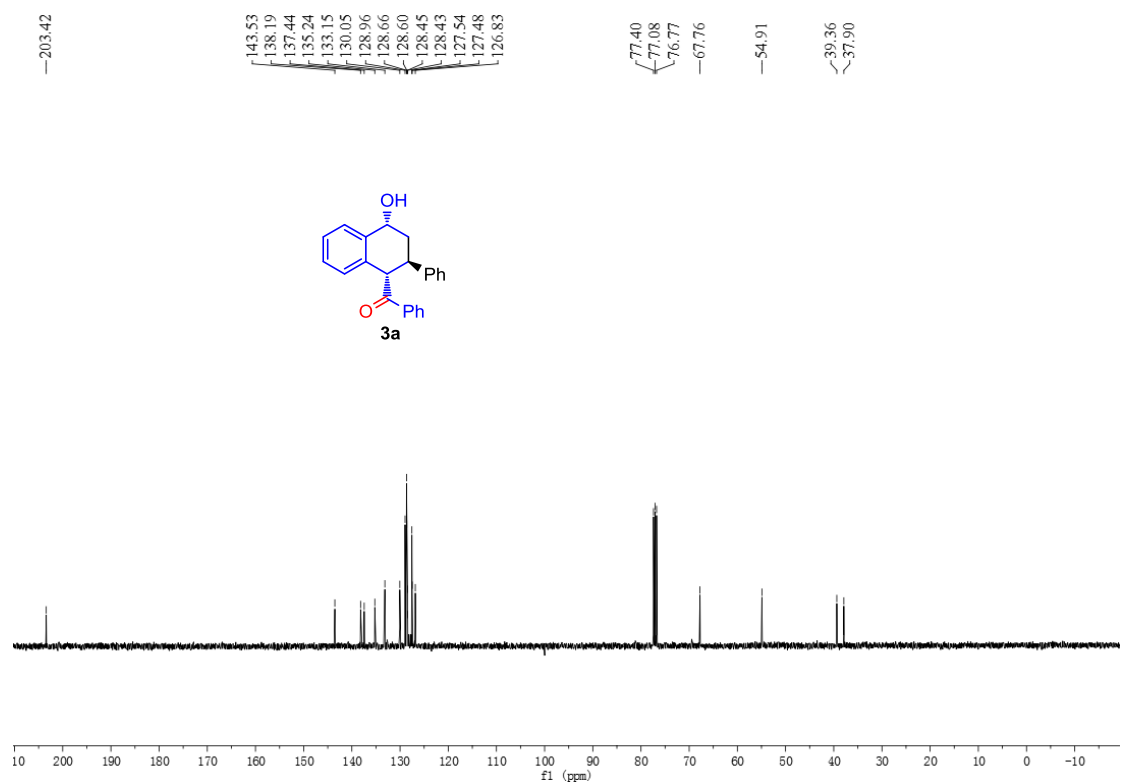
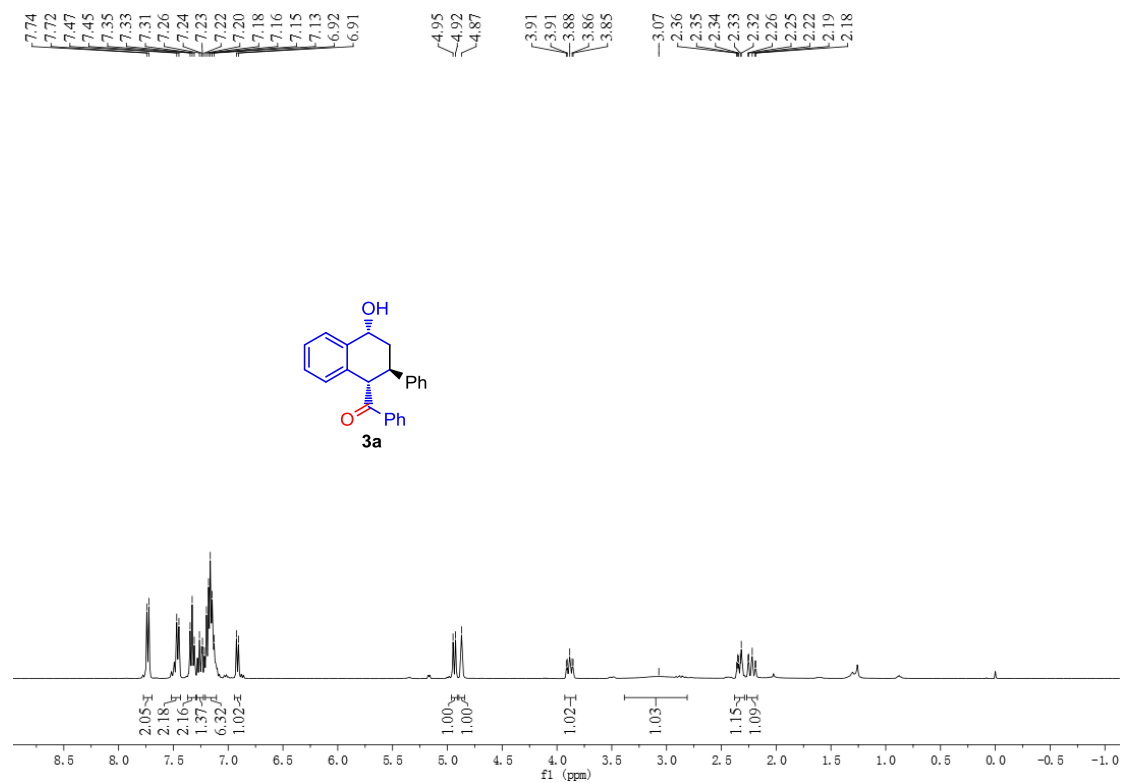




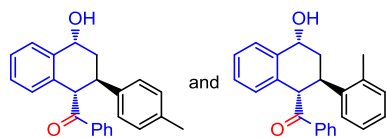




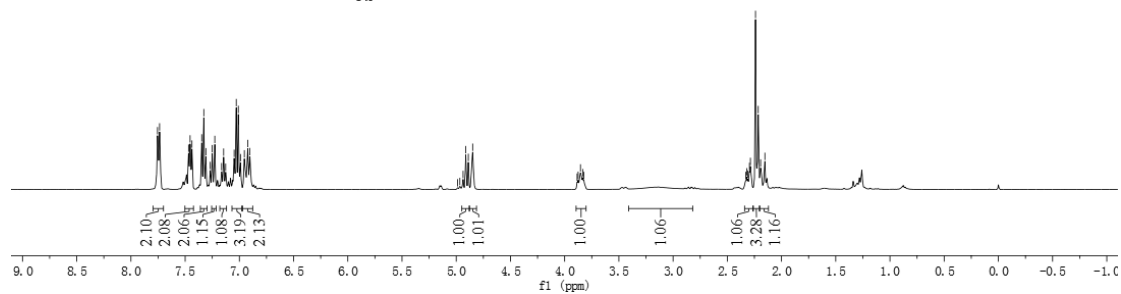




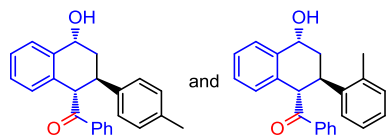
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3b



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38.01
21.41
21.02



3b

