Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supporting Information

Photoredox Catalyzed Radical-Radical Coupling Reaction: Facile Access to Multi-Substitued Nitrogen Heterocyles

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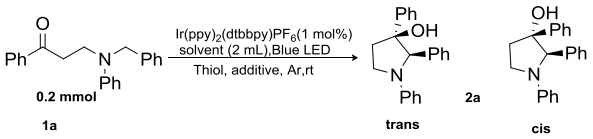
1. General information

All reactions were carried out under argon atmosphere unless otherwise noted. Dry acetonitrile and dichloromethane was distilled from CaH_2. Dry tetrahydrofuran was distilled from Na. Other dry solvents were purchased from Sigma & Aldrich. Thin layer chromatography (TLC) was performed on silica coated glass plates (GF 254) with detection by UV (λ = 254 and 366 nm). Flash chromatography was performed on silica (200-300 mesh) with the indicated eluent mixtures. ^{1}H NMR, ^{13}C NMR spectra and ^{19}F NMR spectra were recorded on Bruker AVANCE 400 spectrometer. Chemical shifts (δ) are reported in ppm downfield from tetramethyl silane. Abbreviations for signal couplings are: s, singlet; d, doublet; t, triplet; m, multiplet. The relative configuration of product 2a were determined by two-dimensional NMR spectra (COSY, HSQC, HMBC, NOESY).High resolution mass spectra were obtained using an Agilent 6210 Series TOF LC-MS equipped with electrospray ionization (ESI) probe operating in positive ion mode. Melting points (m.p.) were determined with a digital electrothermal apparatus without further correction.

2. Optimization studies

Table 1SI: Optimization studies [a]



Entry	thiol	additive	Solvent[b]	yield[%][c]	dr [d]	Time/h
1	5a (0.2eq.)	-	MeCN	36	2.5:1	12
2	5a (0.05eq.)	-	MeCN	48	3:1	12
2	5b (0.05eq.)	-	MeCN	16	3:1	12
3	5c (0. 05eq.)	-	MeCN	0	-	12
4	5d (0.05eq.)	-	MeCN	0	-	12
5	5e (0.05eq.)	-	MeCN	0	-	48
6	5d (0.1eq.)	TFA (0.1 eq.)	MeCN	30	3:1	12
7[e]	5a (0.05eq.)	-	MeCN	65	9:1	36
8	5e (0.2eq.)	K_2HPO_4 (0.2 eq.)	MeCN	41	2:1	48
9	5f (0.2eq.)	K_2HPO_4 (0.2 eq.)	MeCN	66	2:1	48
10	5g (0.2eq.)	K_2HPO_4 (0.2 eq.)	MeCN	36	3:1	48
11	5f (0.2eq.)	$CsCO_3$ (0.2 eq.)	DMF	trace	-	48
12	5f (0.2eq.)	DBU (0.2 eq.)	DMF	4	-	48
13	5f (0.2eq.)	DABCO	DMF	56	12:1	48

[a] Reaction conditions: 1a (0.2 mmol), thiol (x mol%.), additive (y mol%), room temperature, solvent (2 mL), 5 W blue LED, Argon atmosphere. [b] dry solvent. [c] isolated yield. [d] determined by H^1 NMR. [e] 0 ^oC.

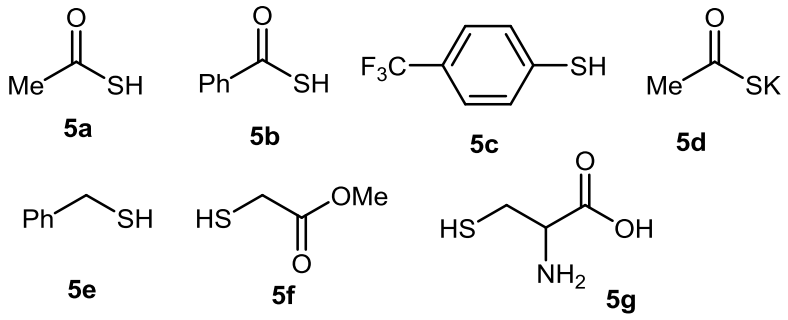
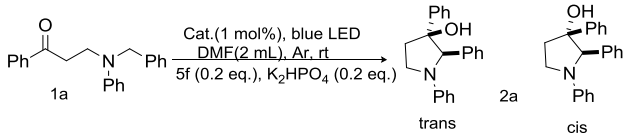
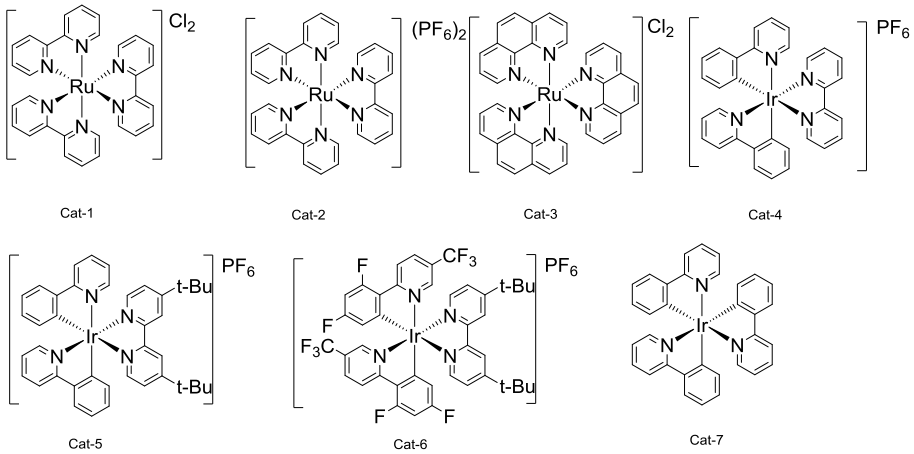


Table 2 SI. Catalyst screening for the photoredox reaction





Entry	Catalyst	yield[%]	dr	Time/h
1	Cat-1 (1 mol%)	trace	-	48
2	Cat-2 (1 mol%)	trace	-	48
3	Cat-3 (1 mol%)	trace	-	48
4	Cat-4 (1 mol%)	26	12:1	48
5	Cat-5 (2 mol%)	82	12:1	48
6	Cat-6 (1 mol%)	31	12:1	48
7	Cat-7 (1 mol%)	8	ND	48

[a] Reaction conditions: 1a (0.2 mmol), 3f (20 mol%.), K_2HPO_4 (20 mol%), room temperature, solvent (2 mL), 5 W blue LED, Argon atmosphere.

unsuccessful substrates of Table 2:

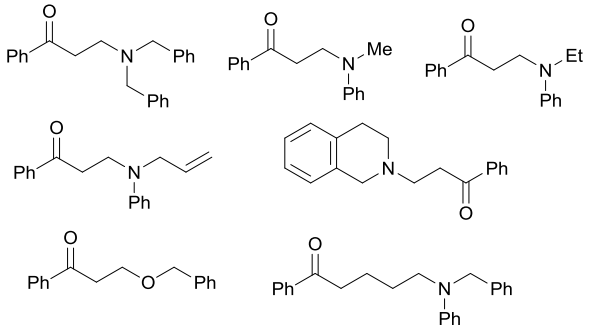
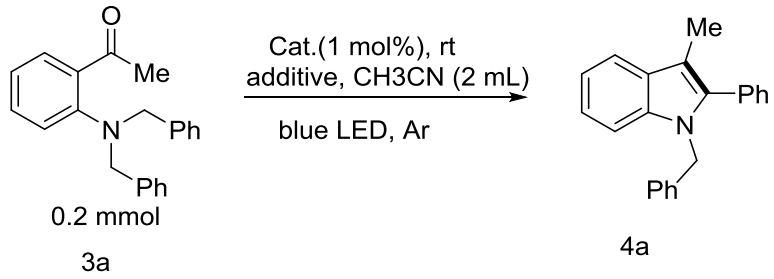


Table 3SI. Optimization studies of indole formation [a]



0.2 mmol

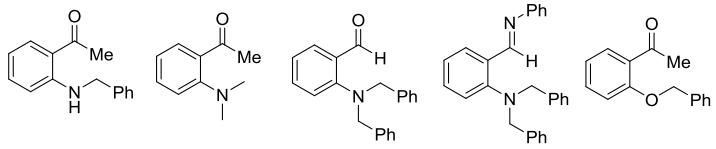
3a

4a

Entry	Catalyst	additive	Yield/%	Time/h
1	Cat-5	-	0	48
2	Cat-5	AcOH (0.1eq.)	28	48
2	Cat-5	TFA (0.1eq.)	32	48
5	Cat-5	TsOH (0.1 eq.)	13	48
6	Cat-5	$LiBF_4$ (0.1 eq.)	0	48
7	Cat-5	$Sc(OTf)_3$(0.5eq.)	0	48
9	Cat-5	TFA (0.2 eq.)	42	48
10	Cat-5	TFA (0.3 eq.)	33	48
11	Cat-5	TFA (1 eq.)	25	48
12	Cat-5	5f (0.2 eq.), K_2HPO_4 (0.2 eq.)	52	48
13	**Cat-5**	**5f (0.5 eq.), K_2HPO_4 (0.5 eq.)**	**73**	**48**
14	-	5f (0.5 eq.), K_2HPO_4 (0.5 eq.)	0	48
15[b]	Cat-5	5f (0.5 eq.), K_2HPO_4 (0.5 eq.)	0	48

[a] Reaction conditions: 3a (0.2 mmol), cat. (0.002 mmol), additive, CH_3CN (2mL) were added to 10 mL Schlenk-tube equipped under Argon atmosphere, the mixture was irradiated by a 5W blue LED for 48h. [b] no light.

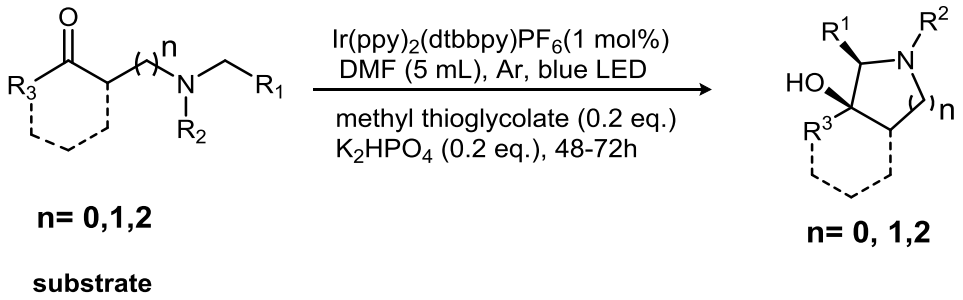
unsuccessful substrates of Table 3:



3. General procedure and characterization of products

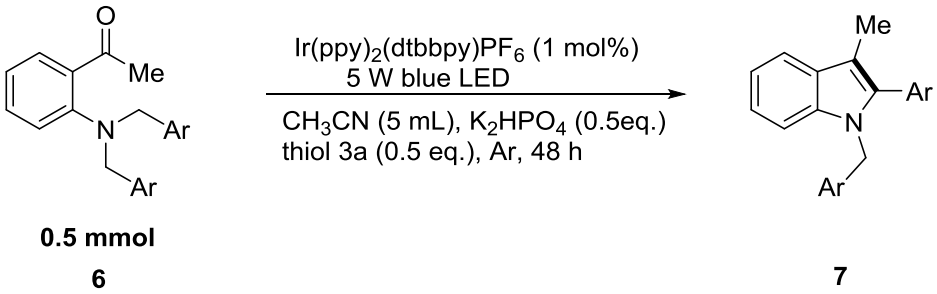
1) General procedure for radical-radical cyclization:

Procedure 3-A:



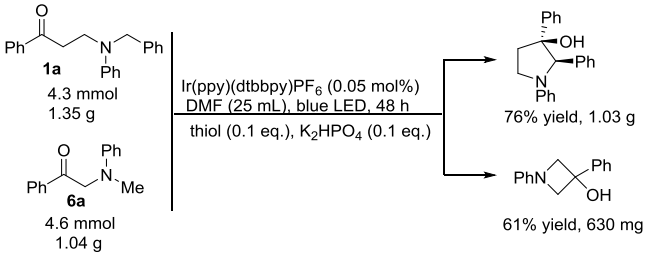
A 10 mL Schlenk-tube equipped with magnetic stirring bar was charged with substrate (0.5 mmol), $Ir(ppy)_2(dtbbpy)PF_6$(1 mol%), K_2HPO_4 (20 mol%), methyl thioglycolate (20 mol%), DMF (5 mL), the resulting mixture was evacuated and backfilled with argon by "pump-freeze-thaw" cycles (3 times). The tube was irradiated by a 5 W cyclized blue LED trip at room temperature for 48-72 hours (monitored by TLC). The reaction mixture was transferred to separating funnel, 20 mL saturated brine was added and exacted with Et_2O (3× 5 mL). The combined organic layers was dried over Na_2SO_4 and purified by flash column chromatography using petrol ether/ethyl acetate as eluent.

Procedure 3-B:



A 10 mL Schlenk-tube equipped with magnetic stirring bar was charged with **6** (0.5 mmol), $Ir(ppy)_2(dtbbpy)PF_6$(1 mol%), K_2HPO_4 (50 mol%), methyl thioglycolate (50 mol%), CH_3CN (5 mL), the resulting mixture was evacuated and backfilled with argon by "pump-freeze-thaw" cycles (3 times). The tube was irradiated by a 5 W cyclized blue LED trip at room temperature for 48 h. The solid was filter out and the solvent was evaporated in vacuum. The crude product was purified by flash chromatography to give products.

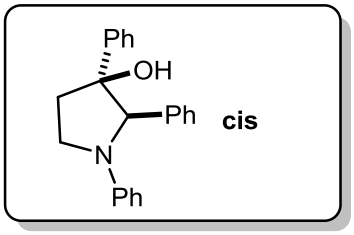
2) General procedure for gram-scale experiments:



A 50 mL Schlenk-tube equipped with magnetic stirring bar was charged with **1a** (4.3 mmol, 1.35g) or **S-5a** (4.6 mmol, 1.04g), $Ir(ppy)_2(dtbbpy)PF_6$(0.05 mol%), K_2HPO_4 (10 mol%), methyl thioglycolate (10 mol%), DMF (25 mL), the resulting mixture was evacuated and backfilled with argon by "pump-freeze-thaw" cycles (3 times). The tube was irradiated by four 3 W blue LED bulbs at room temperature for 48 hours (monitored by TLC). The reaction mixture was transferred to separating funnel, 50 mL saturated brine was added and exacted with Et_2O (3× 20 mL). The combined organic layers was dried over Na_2SO_4 and purified by flash column chromatography using petrol ether/ethyl acetate as eluent to get **2a (**1.03 g, 76% yield) or 5a (630 mg, 61% yield).

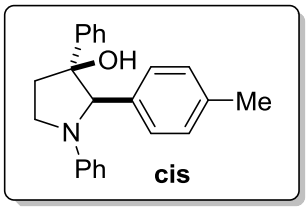
Characterization Data of Products

(trans)-1,2,3-triphenylpyrrolidin-3-ol (**2a**)



Prepared according to procedure **3-A:**Yield 85%, 48h, dr=10:1, White solid, m.p.:158.6-160.7 ^oC, ^1H NMR (400 MHz, Chloroform-*d*) δ 7.14 (s, 7H), 7.04 – 6.97 (m, 3H), 6.82 – 6.74 (m, 2H), 6.64 (t, *J* = 7.27 Hz, 1H), 6.51 (d, *J* = 8.13 Hz, 2H), 4.66 (s, 1H), 3.95 – 3.79 (m, 2H), 2.90 (ddd, *J* = 12.88, 10.60, 9.05 Hz, 1H), 2.10 (dd, *J* = 12.88, 6.00 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.71, 140.67, 139.62, 129.08, 127.82, 127.70, 127.38, 127.17, 126.93, 126.26, 116.20, 112.21, 84.84, 75.41, 46.04, 34.38. HRMS (ESI) m/z calcd for $C_{22}H_{22}NO^+$ $[M+H]^+$: 316.1696, found 316.1697

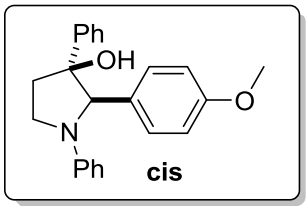
(trans)-1,3-diphenyl-2-(p-tolyl)pyrrolidin-3-ol (**2b**)



Prepared according to procedure **3-A:**Yield 85%, 48h, white solid, m.p.: 168.2-169.7 ^oC, ^1H NMR (400 MHz, Chloroform-*d*) δ 7.13 (s, 7H), 6.79 (d, *J* = 7.85 Hz, 2H), 6.67 – 6.59 (m, 3H), 6.49 (d, *J* = 7.85 Hz, 2H), 4.61 (s, 1H), 3.89 – 3.76 (m, 2H), 2.85 (ddd, *J* = 12.83, 10.50, 9.10 Hz, 1H), 2.36 (br, 1H), 2.16 (s, 3H), 2.06 (dd, *J* = 12.83, 5.97

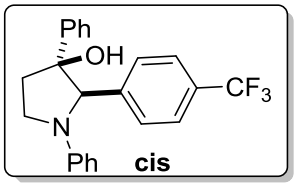
Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.78, 140.77, 136.48, 136.41, 129.09, 128.54, 127.68, 127.33, 127.10, 126.38, 116.09, 112.17, 84.77, 75.08, 45.96, 34.30, 21.04. HRMS (ESI) m/z calcd for $C_{23}H_{24}NO^+$ $[M+H]^+$: 330.1852, found 330.1854.

(trans)-2-(4-methoxyphenyl)-1,3-diphenylpyrrolidin-3-ol (**2c**)



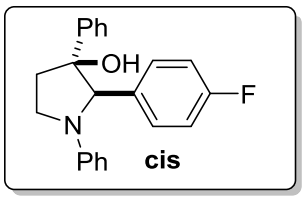
Prepared according to procedure **3-A:**Yield 51%, dr=7:1, 72h, white solid, m.p.: 155.3-157.9 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 – 7.10 (m, 7H), 6.74 – 6.60 (m, 3H), 6.58 – 6.46 (m, 4H), 4.62 (s, 1H), 3.92 – 3.79 (m, 2H), 3.67 (s, 3H), 2.88 (ddd, *J* = 12.86, 10.53, 9.07 Hz, 1H), 2.25 (br, 1H), 2.11 (dd, *J* = 12.86, 5.99 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.46, 146.73, 140.76, 131.56, 129.05, 128.19, 127.73, 127.35, 126.30, 116.11, 113.24, 112.16, 84.75, 74.77, 55.10, 45.90, 34.34. HRMS (ESI) m/z calcd for $C_{23}H_{24}NO_2^+$ $[M+H]^+$: 346.1802, found 346.1802

1,3-diphenyl-2-(4-(trifluoromethyl)phenyl)pyrrolidin-3-ol (**2d**)



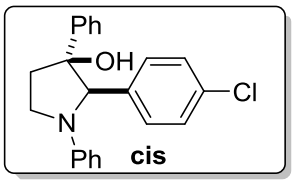
Prepared according to procedure **3-A:** Yield 93%, dr=8:1, 72h, white solid, m.p.: 169.0-171.6 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 8.51 Hz, 2H), 7.20 – 7.09 (m, 7H), 6.89 (d, *J* = 8.10 Hz, 2H), 6.68 (t, *J* = 7.06 Hz, 1H), 6.48 (d, *J* = 7.94 Hz, 2H), 4.69 (s, 1H), 3.96 – 3.80 (m, 2H), 2.86 (ddd, *J* = 12.84, 10.76, 8.94 Hz, 1H), 2.11 (dd, *J* = 13.00, 6.05 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.48, 144.06, 140.23, 129.19(q, *J* = 32Hz), 129.19, 127.93, 127.78, 127.46, 126.10, 124.77 (q, *J* = 3.74 Hz), 124.06 (q, *J* = 271 Hz), 116.67, 112.26, 84.84, 75.05, 46.10, 34.33. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.46. HRMS (ESI) m/z calcd for $C_{23}H_{21}F_3NO^+$ $[M+H]^+$: 384.1570, found 384.1564

2-(4-fluorophenyl)-1,3-diphenylpyrrolidin-3-ol (**2e**)



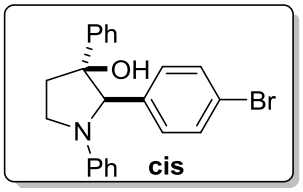
Prepared according to procedure **3-A:**Yield 75%, dr=9:1, 56h, white solid, m.p.: 182.8-183.4 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 – 7.08 (m, 7H), 6.78 – 6.61 (m, 5H), 6.49 (d, *J* = 7.92 Hz, 2H), 4.61 (s, 1H), 3.93 – 3.77 (m, 2H), 2.85 (ddd, *J* = 12.92, 10.72, 8.93 Hz, 1H), 2.34 (br, 1H), 2.08 (dd, *J* = 12.92, 5.95 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ161.78 (d, *J* = 245.26 Hz), 146.62, 140.60, 135.45, 135.42, 129.12, 128.62 (d, *J* = 7.98 Hz), 127.85, 127.54, 126.21, 116.41, 114.71 (d, *J* = 21.50 Hz), 112.25, 84.76, 74.73, 45.99, 34.24. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.71. HRMS (ESI) m/z calcd for $C_{22}H_{21}FNO^+$ $[M+H]^+$: 334.1602, found 334.1600

2-(4-chlorophenyl)-1,3-diphenylpyrrolidin-3-ol (**2f**)



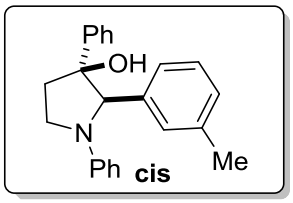
Prepared according to procedure **3-A:** Yield: 74%, dr>20:1, 60h, white solid, m.p.: 180.5-182.5 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 7.07 (m, 7H), 7.05 – 6.88 (m, 2H), 6.80 – 6.60 (m, 3H), 6.48 (d, *J* = 7.84 Hz, 2H), 4.62 (s, 1H), 3.96 – 3.78 (m, 2H), 2.85 (ddd, *J* = 12.95, 10.72, 8.90 Hz, 1H), 2.26 (br, 1H), 2.11 (dd, *J* = 12.95, 6.01 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.53, 140.43, 138.33, 132.67, 129.13, 128.49, 128.01, 127.92, 127.66, 126.19, 116.50, 112.22, 84.74, 74.77, 46.00, 34.30. HRMS (ESI) m/z calcd for $C_{22}H_{21}ClNO^+$ $[M+H]^+$: 350.1306, found 350.1306.

2-(4-bromophenyl)-1,3-diphenylpyrrolidin-3-ol (**2g**)



Prepared according to procedure **3-A:** Yield 78%,dr>20:1, 60h, white solid, m.p.: 186.7-187.8 °C,^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 – 7.03 (m, 9H), 6.71 – 6.58 (m, 3H), 6.46 (d, *J* = 7.88 Hz, 2H), 4.57 (s, 1H), 3.90 – 3.76 (m, 2H), 2.88 – 2.75 (m, 1H), 2.36(br, 1H), 2.06 (dd, *J* = 12.86, 5.53 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.53, 140.42, 138.88, 130.94, 129.15, 128.88, 127.93, 127.68, 126.23, 120.84, 116.52, 112.25, 84.69, 74.81, 46.01, 34.23. HRMS (ESI) m/z calcd for $C_{22}H_{21}BrNO^+$ $[M+H]^+$: 394.0801, found 394.0797.

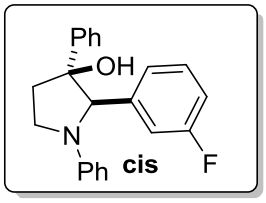
1,3-diphenyl-2-(m-tolyl)pyrrolidin-3-ol (**2h**)



Prepared according to procedure **3-A:** Yield 70%, dr=3:1, 72h, white solid, m.p.: 160.5-162.5 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18 – 7.11 (m, 7H), 6.94 –

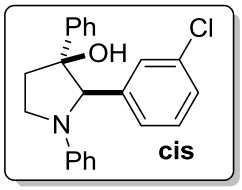
6.80 (m, 2H), 6.69 – 6.57 (m, 2H), 6.55 – 6.50 (m, 3H), 4.60 (s, 1H), 3.92 – 3.80 (m, 2H), 2.88 (ddd, *J* = 12.80, 10.61, 9.02 Hz, 1H), 2.28 (s, 1H), 2.12 – 2.05 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.83, 140.73, 139.51, 137.24, 129.06, 128.05, 127.64, 127.59, 127.32, 126.28, 124.09, 116.12, 112.19, 84.86, 75.44, 45.99, 34.35, 21.28. HRMS (ESI) m/z calcd for $C_{23}H_{24}NO^+$ $[M+H]^+$: 330.1852, found 330.1851

2-(3-fluorophenyl)-1,3-diphenylpyrrolidin-3-ol (**2i**)



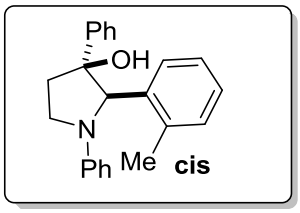
Prepared according to procedure **3-A:** Yield 77%, dr=4:1, 72h, white solid, m.p.: 180.2 -181.9 ^{o}C,^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 7.11 (m, 7H), 7.00 – 6.89 (m, 1H), 6.77 – 6.64 (m, 2H), 6.59 – 6.47 (m, 4H), 4.62 (s, 1H), 3.94 – 3.77 (m, 2H), 2.94 – 2.83 (m, 1H), 2.10 (dd, *J* = 12.93, 5.91 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ162.65 (d, *J* = 245.51 Hz), 146.59, 142.85 (d, *J* = 6.28 Hz), 140.45, 129.28 (d, *J* = 8.15 Hz), 129.13, 127.86, 127.65, 126.12, 122.96 (d, *J* = 2.64 Hz), 116.54, 114.01 (d, *J* = 7.55 Hz), 113.79 (d, *J* = 6.89 Hz), 112.25, 84.83, 75.05, 46.04, 34.37. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.65. HRMS (ESI) m/z calcd for $C_{22}H_{21}FNO^+$ $[M+H]^+$: 334.1602, found 334.1592

2-(3-chlorophenyl)-1,3-diphenylpyrrolidin-3-ol (**2j**)



Prepared according to procedure **3-A:** Yield 74%, 72h, dr=4:1, white solid, m.p.: 185.2-187.6 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 7.11 (m, 7H), 7.04 – 6.97 (m, 1H), 6.95 – 6.86 (m, 1H), 6.78 (t, *J* = 1.69 Hz, 1H), 6.72 – 6.62 (m, 2H), 6.50 (d, *J* = 7.85 Hz, 2H), 4.59 (s, 1H), 3.96 – 3.78 (m, 2H), 2.87 (ddd, *J* = 12.97, 10.87, 8.77 Hz, 1H), 2.29 (br, 1H), 2.10 (dd, *J* = 12.97, 6.09 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.61, 142.22, 140.38, 133.86, 129.14, 129.05, 127.89, 127.70, 127.17, 127.16, 126.13, 125.41, 116.58, 112.28, 84.84, 75.07, 46.06, 34.30. HRMS (ESI) m/z calcd for $C_{22}H_{21}ClNO^+$ $[M+H]^+$: 350.1306, found 350.1306

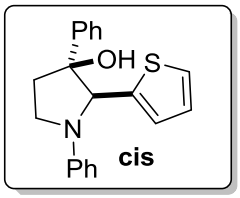
1,3-diphenyl-2-(o-tolyl)pyrrolidin-3-ol (**2k**)



Prepared according to procedure **3-A:** Yield 74%, dr=2:1, 72h, white solid, m.p.: 169.4-171.6 ^{o}C,^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.17 – 6.95 (m, 10H), 6.82 –

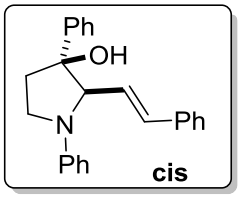
6.74 (m, 1H), 6.64 – 6.59 (m, 1H), 6.41 (d, *J* = 7.88 Hz, 2H), 4.86 (s, 1H), 3.91 – 3.74 (m, 2H), 2.84 (ddd, *J* = 13.18, 10.71, 9.00 Hz, 1H), 2.47 (s, 1H), 2.05 (dd, *J* = 13.18, 6.29 Hz, 1H), 1.71 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.65, 140.13, 137.77, 136.90, 130.21, 129.20, 127.31, 127.13, 126.33, 126.10, 126.05, 116.20, 113.19, 112.04, 84.58, 71.86, 46.02, 37.31, 19.25. HRMS (ESI) m/z calcd for $C_{23}H_{24}NO^+$ $[M+H]^+$: 330.1852, found 330.1852.

1,3-diphenyl-2-(thiophen-2-yl)pyrrolidin-3-ol (**2l**)



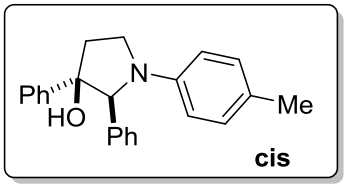
Prepared according to procedure **3-A:** Yield 76%, dr=5:1, 48h, white solid, m.p.: 153.3-156.1 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.15 (m, 7H), 6.94 (dd, *J* = 5.04, 1.08 Hz, 1H), 6.74 – 6.55 (m, 4H), 6.30 (d, *J* = 3.51 Hz, 1H), 4.86 (s, 1H), 3.84 – 3.68 (m, 2H), 3.00 (ddd, *J* = 12.84, 10.74, 8.80 Hz, 1H), 2.37 (s, 1H), 2.09 (dd, *J* = 12.87, 6.09 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.83, 145.13, 140.79, 129.13, 127.97, 127.77, 126.66, 126.28, 125.04, 124.25, 116.78, 112.31, 84.71, 71.29, 45.71, 33.98. HRMS (ESI) m/z calcd for $C_{20}H_{20}NOS^+$ $[M+H]^+$: 322.1260, found 322.1254

1,3-diphenyl-2-((E)-styryl)pyrrolidin-3-ol (**2m**)



Prepared according to procedure **3-A:** Yield 76%, dr=5:1, 60h, white solid, m.p.: 161.4-163.0 °C,^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.50 (m, 2H), 7.42 – 7.31 (m, 3H), 7.25 – 7.10 (m, 5H), 7.07 – 7.03 (m, 2H), 6.76 – 6.61 (m, 3H), 6.31 (dd, *J* = 15.80, 1.40 Hz, 1H), 5.60 (dd, *J* = 15.80, 4.43 Hz, 1H), 4.39 (d, *J* = 4.43 Hz, 1H), 3.76 – 3.71 (m, 2H), 2.90 – 2.77 (m, 1H), 2.19 – 2.13 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.28, 141.07, 136.77, 130.62, 129.12, 128.41, 128.36, 128.00, 127.35, 127.33, 126.52, 126.44, 116.25, 112.07, 83.70, 71.87, 45.45, 33.93.HRMS (ESI) m/z calcd for $C_{24}H_{24}NO^+$ $[M+H]^+$: 342.1852, found 342.1852.

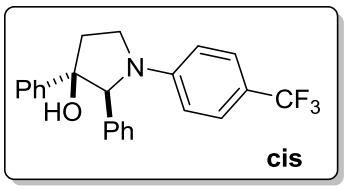
2,3-diphenyl-1-(p-tolyl)pyrrolidin-3-ol (**2n**)



Prepared according to procedure **3-A:** Yield 73%, dr=7:1, 48h, white solid, m.p.:

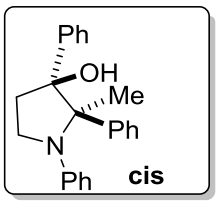
179.8-180.9 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.13 (s, 5H), 7.02 – 6.93 (m, 5H), 6.79 – 6.75 (m, 2H), 6.45 – 6.40 (m, 2H), 4.62 (s, 1H), 3.91 – 3.79 (m, 2H), 2.88 (ddd, *J* = 12.86, 10.61, 8.95 Hz, 1H), 2.32 (s, 1H), 2.20 (s, 3H), 2.15 – 2.07 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.58, 140.70, 139.81, 129.63, 127.79, 127.66, 127.32, 127.18, 126.86, 126.27, 125.17, 112.12, 84.86, 75.53, 46.08, 34.48, 20.27. HRMS (ESI) m/z calcd for $C_{23}H_{24}NO^+$ $[M+H]^+$: 330.1852,found 330.1850.

2,3-diphenyl-1-(4-(trifluoromethyl)phenyl)pyrrolidin-3-ol (**2o**)



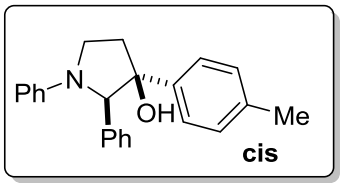
Prepared according to procedure **3-A:** Yield 52%, dr=6:1, 72h, white solid, m.p.: 159.0-161.0 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.35 (m, 2H), 7.24 – 7.13 (m, 4H), 7.07 – 7.00 (m, 3H), 6.78 – 6.64 (m, 3H), 6.52 (d, *J* = 7.88 Hz, 2H), 4.66 (s, 1H), 4.00 – 3.80 (m, 2H), 2.90 (ddd, *J* = 12.94, 10.64, 8.97 Hz, 1H), 2.42 (s, 1H), 2.14 (dd, *J* = 12.97, 6.25 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.47, 144.59, 139.07, 129.14, 128.86 (q, 97.00 Hz), 128.08, 127.35, 127.05, 126.77 (q, 270.00 Hz), 126.71, 124.49 (q, *J* = 3.75 Hz), 116.54, 112.28, 84.52, 75.57, 45.99, 34.74. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.56. HRMS (ESI) m/z calcd for $C_{23}H_{21}F_3NO^+$ $[M+H]^+$: 384.1570, found 384.1565.

2-methyl-1,2,3-triphenylpyrrolidin-3-ol (**2p**)



Prepared according to procedure **3-A:** Yield 58%, dr=7:1, 72h, white solid, m.p.: 144.0-146.0 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 – 6.96 (m, 10H), 6.71 – 6.57 (m, 3H), 6.52 (d, *J* = 7.94 Hz, 2H), 4.14 (ddd, *J* = 10.81, 9.05, 6.24 Hz, 1H), 3.80 – 3.73 (m, 1H), 2.86 (ddd, *J* = 12.73, 10.81, 8.84 Hz, 1H), 2.17 (s, 1H), 1.97 (dd, *J* = 12.73, 6.24 Hz, 1H), 1.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.74, 143.22, 140.28, 128.51, 128.04, 127.57, 127.35, 127.31, 126.51, 126.39, 116.26, 114.91, 86.47, 73.29, 47.79, 33.98, 19.88.HRMS (ESI) m/z calcd for $C_{23}H_{24}NO^+$ $[M+H]^+$: 330.1852, found 330.1852.

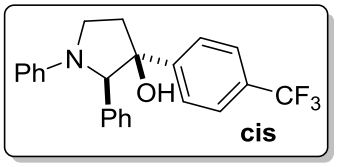
1,2-diphenyl-3-(p-tolyl)pyrrolidin-3-ol (**2q)**



Prepared according to procedure **3-A:** Yield 78%, 48h, dr=10:1, white solid, m.p.:

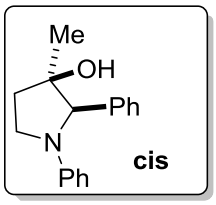
195.3-194.8 °C,^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.17 – 7.10 (m, 2H), 7.04 – 6.97 (m, 5H), 6.93 (d, *J* = 8.08 Hz, 2H), 6.80 – 6.75 (m, 2H), 6.63 (t, *J* = 7.29 Hz, 1H), 6.50 (d, *J* = 7.87 Hz, 2H), 4.63 (s, 1H), 3.92 – 3.75 (m, 2H), 2.93 – 2.78 (m, 1H), 2.32 (br, 1H), 2.25 (s, 3H), 2.05 (dd, *J* = 12.92, 6.00 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.76, 139.76, 137.73, 136.97, 129.07, 128.38, 127.81, 127.25, 126.87, 126.17, 116.12, 112.18, 84.75, 75.26, 45.99, 34.52, 21.01. HRMS (ESI) m/z calcd for $C_{23}H_{24}NO^+$ $[M+H]^+$: 330.1852, found 330.1851.

1,2-diphenyl-3-(4-(trifluoromethyl)phenyl)pyrrolidin-3-ol (**2r**)



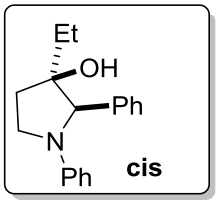
Prepared according to procedure **3-A:** Yield 52%, 48h, dr=10:1, white solid, m.p.: 188.0-190.0 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 8.27 Hz, 2H), 7.24 – 7.20 (m, 2H), 7.18 – 7.13 (m, 2H), 7.10 – 7.00 (m, 3H), 6.81 – 6.73 (m, 2H), 6.67 (t, *J* = 7.30 Hz, 1H), 6.52 (d, *J* = 7.88 Hz, 2H), 4.66 (s, 1H), 3.99 – 3.80 (m, 2H), 2.90 (ddd, *J* = 12.95, 10.64, 8.97 Hz, 1H), 2.42 (br, 1H), 2.14 (dd, *J* = 12.95, 6.25 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.47, 144.58, 139.08, 129.15, 128.86 (q, 97.00 Hz), 128.09, 127.35, 127.05, 126.77 (q, 270.00 Hz), 126.72, 124.49 (q, *J* = 3.75 Hz), 116.54, 112.28, 84.53, 75.57, 45.99, 34.74. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.56. HRMS (ESI) m/z calcd for $C_{23}H_{21}F_3NO^+$ $[M+H]^+$: 384.1570, found 384.1571.

3-methyl-1,2-diphenylpyrrolidin-3-ol (**2s**)



Prepared according to procedure **3-A:** Yield 95%, 48h, dr>20:1, white solid, m.p.: 105.0-107.0 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.08 (m, 7H), 6.63 (t, *J* = 7.29 Hz, 1H), 6.47 (d, *J* = 7.83 Hz, 2H), 4.38 (s, 1H), 3.73 – 3.57 (m, 2H), 2.12 – 2.07 (m, 1H), 1.95 (dd, *J* = 12.98, 6.52 Hz, 1H), 0.98 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.94, 141.12, 129.09, 128.57, 127.42, 126.83, 116.15, 112.31, 81.07, 74.86, 46.42, 36.67, 24.21. HRMS (ESI) m/z calcd for $C_{17}H_{20}NO^+$ $[M+H]^+$: 254.1539, found 254.1537.

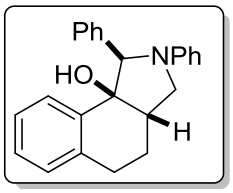
3-ethyl-1,2-diphenylpyrrolidin-3-ol (**2t**)



Prepared according to procedure **3-A:** Yield 95%, 48h, dr>20:1, white solid, m.p.: 117.1-119.4 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.06 (m, 7H), 6.66 –

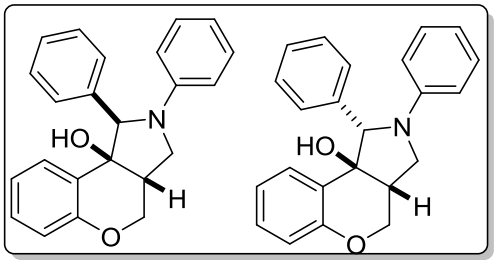
6.56 (m, 1H), 6.48 (d, *J* = 8.34 Hz, 2H), 4.41 (s, 1H), 3.78 – 3.70 (m, 1H), 3.68 – 3.58 (m, 1H), 2.08 – 1.99 (m, 2H), 1.89 (br, 1H), 1.48 – 1.36 (m, 1H), 0.98 – 0.81 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.90, 141.00, 129.05, 128.55, 127.39, 127.08, 116.06, 112.21, 83.66, 75.26, 46.36, 33.83, 29.86, 8.19. HRMS (ESI) m/z calcd for $C_{18}H_{22}NO^+$ $[M+H]^+$: 268.1696, found 268.1697.

1,2-diphenyl-hexahydrobenzoisoindol-ol (**2u**)



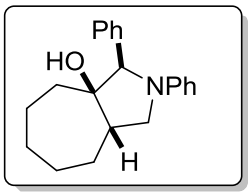
Prepared according to procedure **3-A:** Yield 61%, dr=1.5:1, 72h, white solid, m.p.: 187.8-189.6 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.26 (m, 5H), 7.22 – 7.10 (m, 3H), 7.09 – 7.02 (m, 3H), 6.58 (t, *J* = 7.28 Hz, 1H), 6.42 (d, *J* = 8.01 Hz, 2H), 4.92 (s, 1H), 4.17 (dd, *J* = 9.23, 6.68 Hz, 1H), 3.44 (dd, *J* = 9.23, 4.41 Hz, 1H), 2.97 – 2.88 (m, 2H), 2.72 – 2.62 (m, 1H), 2.06 – 2.00 (m, 1H), 1.95 (s, 1H), 1.93 – 1.87 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.02, 138.49, 137.10, 136.22, 128.89, 128.76, 128.74, 128.58, 128.05, 127.81, 127.56, 126.15, 116.13, 112.91, 79.17, 71.91, 53.07, 43.50, 27.11, 24.23. HRMS (ESI) m/z calcd for $C_{24}H_{24}NO^+$ $[M+H]^+$: 342.1852, found 342.1853.

1,2-diphenyl-tetrahydrochromeno[3,4-c]pyrrol-9b(1H)-ol (**2v**)



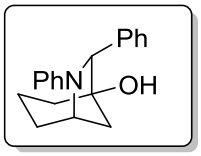
Prepared according to procedure **3-A:** We tried several times but failed to get pure single diastereoisomer of **2w**, the analytical data showed next was detected with the mixture of two diastereoisomers. Yield 59%, 72h, dr=1.5:1, white solid, m.p.: 178.0-180.0 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.23 (m, 5H), 7.15 – 6.87 (m, 5H), 6.81 – 6.76 (m, 1H), 6.65 – 6.50 (m, 1H), 6.46 – 6.31 (m, 2H), 5.02 – 4.94 (m, 1H), 4.24 – 4.02 (m, 2H), 3.98 – 3.83 (m, 1H), 3.62 – 3.43 (m, 1H), 2.73 – 2.57 (m, 1H), 1.75 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.33, 153.19, 146.07, 145.24, 137.49, 137.03, 128.47, 128.35, 128.00, 127.92, 127.34, 127.29, 127.13, 127.03, 126.90, 126.02, 124.11, 122.38, 120.59, 119.41, 116.16, 115.91, 115.51, 115.40, 112.33, 111.30, 79.03, 73.91, 73.84, 70.65, 65.01, 61.79, 48.64, 46.57, 42.97, 41.09. HRMS (ESI) m/z calcd for $C_{23}H_{22}NO_2^+$ $[M+H]^+$: 344.1645, found 344.1645.

2,3-diphenyloctahydrocyclohepta[c]pyrrol-3a(1H)-ol(**2w**)



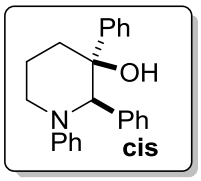
Prepared according to procedure **3-A:** Yield 71%, 48h, dr=3:1, white solid, m.p.: 158.4-159.7 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.27 (m, 2H), 7.26 – 7.22 (m, 1H), 7.22 – 7.17 (m, 2H), 7.14 – 7.08 (m, 2H), 6.61 (t, *J* = 7.28 Hz, 1H), 6.44 (d, *J* = 7.88 Hz, 2H), 4.50 (s, 1H), 3.80 – 3.73 (m, 1H), 3.31 – 3.21 (m, 1H), 2.48 – 2.36 (m, 1H), 1.89 – 1.43 (m, 10H), 1.33 – 1.23 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.61, 140.76, 129.01, 128.49, 127.33, 127.31, 115.92, 111.96, 83.19, 77.51, 53.10, 42.81, 37.51, 26.99, 25.30, 23.23, 22.12. HRMS (ESI) m/z calcd for $C_{21}H_{26}NO^{+}$ $[M+H]^{+}$: 308.2009, found 308.2009.

6,7-diphenyl-6-azabicyclo[3.2.1]octan-1-ol (**2x**)



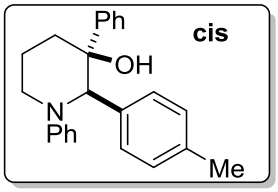
Prepared according to procedure **3-A:** Yield 90%, dr=13:1, 48h, white solid, m.p.: 160.1-161.5 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.25 (m, 5H), 7.14 – 7.06 (m, 2H), 6.61 (t, *J* = 7.28 Hz, 1H), 6.48 (d, *J* = 8.02 Hz, 2H), 4.40 – 4.33 (m, 1H), 4.28 (s, 1H), 2.34 – 2.11 (m, 2H), 1.97 – 1.81 (m, 2H), 1.73 – 1.57 (m, 2H), 1.38 – 1.28 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.07, 138.90, 129.02, 128.74, 127.87, 127.73, 116.11, 112.82, 77.03, 69.35, 54.21, 42.47, 38.08, 25.65, 18.72.HRMS (ESI) m/z calcd for $C_{19}H_{22}NO^{+}$ $[M+H]^{+}$: 280.1696, found 280.1697.

1,2,3-triphenylpiperidin-3-ol (**4a**)



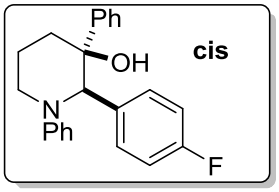
Prepared according to procedure **3-A:**Yield 78%, 48h, dr=9:1, yellow oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.31 (m, 2H), 7.20 – 7.11 (m, 5H), 7.02 – 6.91 (m, 5H), 6.89 – 6.84 (m, 2H), 6.79 – 6.73 (m, 1H), 4.86 (s, 1H), 3.83 (s, 1H), 3.63 – 3.53 (m, 2H), 2.69 – 2.54 (m, 1H), 2.40 – 2.22 (m, 1H), 2.11 – 2.03 (m, 1H), 1.99 – 1.92 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.86, 144.01, 137.84, 129.56, 129.03, 127.81, 127.54, 127.24, 126.83, 126.40, 119.78, 117.31, 74.35, 72.91, 43.25, 29.05, 20.53. HRMS (ESI) m/z calcd for $C_{23}H_{24}NO^{+}$ $[M+H]^{+}$: 330.1852, found 330.1852.

1,3-diphenyl-2-(p-tolyl)piperidin-3-ol (**4b**)



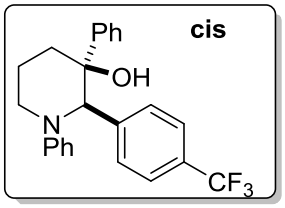
Prepared according to procedure **3-A:**Yield 69%, 48h, dr=6:1, clear oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.36 (m, 2H), 7.22 – 7.12 (m, 5H), 6.96 – 6.91 (m, 2H), 6.79 – 6.72 (m, 5H), 4.84 (s, 1H), 3.87 (s, 1H), 3.61 – 3.53 (m, 2H), 2.63 (td, *J* = 13.14, 4.99 Hz, 1H), 2.36 – 2.25 (m, 1H), 2.13 (s, 3H), 2.10 – 2.03 (m, 1H), 2.00 – 1.93 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.95, 144.08, 136.30, 134.48, 129.44, 129.00, 128.26, 127.78, 127.16, 126.43, 119.73, 117.35, 74.29, 72.66, 43.12, 29.09, 20.91, 20.59. HRMS (ESI) m/z calcd for $C_{24}H_{26}NO^{+}$ $[M+H]^{+}$: 344.2009, found 344.2009.

2-(4-fluorophenyl)-1,3-diphenylpiperidin-3-ol (**4c**)



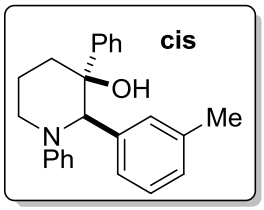
Prepared according to procedure **3-A:**Yield 76%, 48h, dr=7:1, clear oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.31 (m, 2H), 7.23 – 7.13 (m, 5H), 6.91 (d, *J* = 7.99 Hz, 2H), 6.85 – 6.74 (m, 3H), 6.67 – 6.60 (m, 2H), 4.84 (s, 1H), 3.79 (s, 1H), 3.60 – 3.50 (m, 2H), 2.58 (td, *J* = 13.11, 4.94 Hz, 1H), 2.39 – 2.24 (m, 1H), 2.12 – 2.04 (m, 1H), 2.00 – 1.93 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ161.56 (d, *J* = 246.05 Hz), 150.67, 143.84, 133.66, 131.00 (d, *J* = 7.80 Hz), 129.07, 127.92, 127.36, 126.33, 120.02, 117.40, 114.42 (d, *J* = 20.98 Hz), 74.26, 72.35, 43.23, 28.96, 20.45. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.51.HRMS (ESI) m/z calcd for $C_{23}H_{23}FNO^{+}$ $[M+H]^{+}$: 348.1758, found 348.1759.

1,3-diphenyl-2-(4-(trifluoromethyl)phenyl)piperidin-3-ol(**4d**)



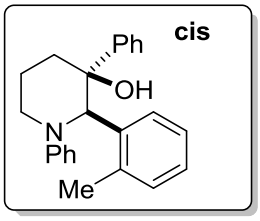
Prepared according to procedure **3-A:** Yield 65%, 48h, dr=8:1, yellow oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.02 (m, 9H), 6.96 (d, *J* = 7.48 Hz, 2H), 6.92 – 6.81 (m, 3H), 4.31 (s, 1H), 3.67 (s, 1H), 3.55 – 3.44 (m, 1H), 3.02 – 2.90 (m, 1H), 2.39 – 2.20 (m, 2H), 2.09 – 1.99 (m, 1H), 1.92 – 1.80 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.90, 144.05, 141.60, 129.84, 128.76, 128.33 (q, *J* = 33.18 Hz), 127.76, 126.79, 125.12, 125.01, 124.18, 124.11 (q, *J* = 271.95 Hz), 123.50 (q, *J* = 3.75 Hz), 74.29, 73.83, 59.01, 37.46, 22.16. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.61.HRMS (ESI) m/z calcd for $C_{24}H_{23}F_3NO^{+}$ $[M+H]^{+}$: 398.1726, found 398.1726.

1,3-diphenyl-2-(m-tolyl)piperidin-3-ol (**4e**)



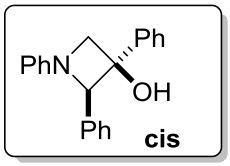
Prepared according to procedure **3-A:** Yield 74%, 48h, dr=3:1, white solid, m.p.: 116.1-118.4 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (dd, *J* = 8.07, 1.48 Hz, 2H), 7.22 – 7.12 (m, 5H), 6.97 – 6.69 (m, 6H), 6.53 (s, 1H), 4.82 (s, 1H), 3.79 (s, 1H), 3.62 (dd, *J* = 9.31, 3.43 Hz, 2H), 2.60 (td, *J* = 13.12, 4.96 Hz, 1H), 2.39 – 2.25 (m, 1H), 2.04 (s, 4H), 1.99 – 1.90 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.89, 144.12, 137.76, 136.83, 130.63, 129.02, 127.72, 127.50, 127.31, 127.20, 126.46, 126.39, 119.58, 117.09, 74.45, 72.60, 43.30, 28.99, 21.42, 20.50. HRMS (ESI) m/z calcd for $C_{24}H_{26}NO^{+}$ $[M+H]^{+}$: 344.2009, found 344.2008.

1,3-diphenyl-2-(o-tolyl)piperidin-3-ol(**4f**)



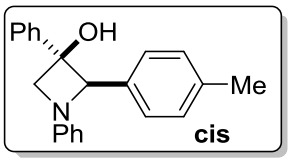
Prepared according to procedure **3-A:** Yield 68%, 48h, dr=3:1, white solid, m.p.: 89.0-91.0 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 7.79 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.15 – 7.03 (m, 7H), 6.98 – 6.89 (m, 3H), 6.76 (t, *J* = 7.28 Hz, 1H), 6.70 (d, *J* = 7.46 Hz, 1H), 5.06 (s, 1H), 3.94 – 3.81 (m, 2H), 3.50 (ddd, *J* = 12.40, 6.59, 1.95 Hz, 1H), 2.76 (td, *J* = 13.39, 5.12 Hz, 1H), 2.44 – 2.31 (m, 1H), 2.17 – 2.10 (m, 1H), 1.84 – 1.74 (m, 1H), 1.58 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.05, 143.33, 138.30, 137.59, 130.47, 128.85, 127.83, 127.29, 127.01, 126.93, 126.33, 125.21, 120.14, 117.90, 74.75, 66.83, 43.45, 29.38, 20.16, 20.10. HRMS (ESI) m/z calcd for $C_{24}H_{26}NO^{+}$ $[M+H]^{+}$: 344.2009, found 344.2008.

1,2,3-triphenylazetidin-3-ol (**5a**)



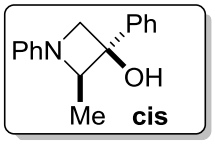
Prepared according to procedure **3-A:** Yield 65%, 72h, dr=2:1, yellow oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.35 (m, 2H), 7.23 – 7.01 (m, 10H), 6.82 (t, *J* = 7.36 Hz, 1H), 6.61 – 6.56 (m, 2H), 5.18 (s, 1H), 4.68 (d, *J* = 7.72 Hz, 1H), 3.99 (d, *J* = 7.72 Hz, 1H), 2.50 (br, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.93, 140.01, 137.87, 130.92, 128.95, 127.76, 127.35, 127.09, 126.52, 125.99, 118.95, 113.53, 80.43, 65.59, 64.45. HRMS (ESI) m/z calcd for $C_{21}H_{20}NO^{+}$ $[M+H]^{+}$: 302.1539, found 302.1537.

1,3-diphenyl-2-(p-tolyl)azetidin-3-ol (**5b**)



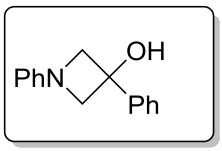
Prepared according to procedure **3-A:** Yield 58%, 72h, dr=2:1, yellow oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.34 (m, 2H), 7.21 – 7.14 (m, 4H), 7.13 – 7.08 (m, 1H), 6.99 (d, *J* = 8.00 Hz, 2H), 6.88 (d, *J* = 7.92 Hz, 2H), 6.81 (t, *J* = 7.36 Hz, 1H), 6.58 (d, *J* = 7.63 Hz, 2H), 5.13 (s, 1H), 4.66 (d, *J* = 7.68 Hz, 1H), 3.96 (d, *J* = 7.74 Hz, 1H), 2.50 (s, 1H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.04, 140.14, 136.66, 134.84, 128.92, 128.50, 127.77, 127.32, 126.50, 126.03, 118.87, 113.55, 80.42, 77.44, 64.43, 21.10. HRMS (ESI) m/z calcd for $C_{22}H_{22}NO^+$ $[M+H]^+$: 316.1696, found 316.1698.

2-methyl-1,3-diphenylazetidin-3-ol (**5c**)



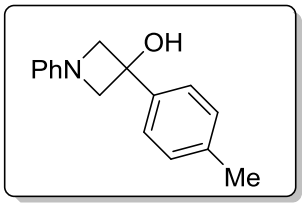
Prepared according to procedure **3-A:** Yield 71%, 72h, dr=2:1, clear oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.54 (m, 2H), 7.40 – 7.33 (m, 2H), 7.31 – 7.25 (m, 1H), 7.21 – 7.15 (m, 4H), 6.75 (t, *J* = 7.35 Hz, 1H), 6.59 (d, *J* = 8.55 Hz, 2H), 4.45 (d, *J* = 8.51 Hz, 1H), 4.14 (q, *J* = 6.39 Hz, 1H), 3.76 (d, *J* = 7.93 Hz, 1H), 2.20 (s, 1H), 0.95 (d, *J* = 6.40 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.13, 139.67, 128.04, 127.25, 126.67, 124.95, 117.66, 111.95, 74.29, 71.50, 64.45, 17.00. HRMS (ESI) m/z calcd for $C_{16}H_{18}NO^+$ $[M+H]^+$: 240.1383, found 240.1384.

1,3-diphenylazetidin-3-ol (**5d**)



Prepared according to procedure **3-A:** Yield 66%, 48h, white solid, m.p.: 78.8-80.4 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.54 (m, 2H), 7.42 – 7.35 (m, 2H), 7.34 – 7.20 (m, 3H), 6.85 – 6.72 (m, 1H), 6.57 – 6.42 (m, 2H), 4.21 (d, *J* = 8.06 Hz, 2H), 4.05 (d, *J* = 8.06 Hz, 2H), 2.83 (br, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.24, 143.49, 129.02, 128.60, 127.74, 124.72, 118.14, 112.11, 72.31, 67.04. HRMS (ESI) m/z calcd for $C_{15}H_{16}NO^+$ $[M+H]^+$: 226.1226, found 226.1227.

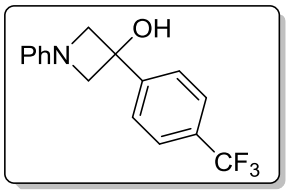
1-phenyl-3-(p-tolyl)azetidin-3-ol (**5e**)



Prepared according to procedure **3-A:** Yield 65%, 48h, white solid, m.p.: 116.0-118.0

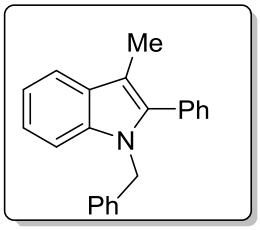
^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.41 (m, 2H), 7.28 – 7.16 (m, 4H), 6.83 – 6.74 (m, 1H), 6.55 – 6.48 (m, 2H), 4.20 (d, *J* = 8.34 Hz, 2H), 4.05 (d, *J* = 8.34 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.30, 140.59, 137.47, 129.25, 129.00, 124.66, 118.03, 112.07, 72.28, 67.00, 21.10. HRMS (ESI) m/z calcd for $C_{16}H_{18}NO^+$ $[M+H]^+$: 240.1383, found 240.1383.

1-phenyl-3-(4-(trifluoromethyl)phenyl)azetidin-3-ol (**5f**)



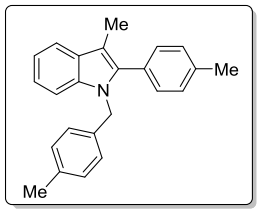
Prepared according to procedure **3-A:** Yield 71%, 48h, white solid, m.p.: 97.6-98.4 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.17 Hz, 2H), 7.63 (d, *J* = 8.28 Hz, 2H), 7.28 – 7.21 (m, 2H), 6.83 – 6.77 (m, 1H), 6.55 – 6.50 (m, 2H), 4.19 (d, *J* = 8.15 Hz, 2H), 4.09 (d, *J* = 8.15 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.93, 140.01, 137.87, 130.92, 128.95, 127.76, 127.35, 127.09, 126.52, 125.99, 118.95, 113.53, 80.43, 65.59, 64.45. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.43. HRMS (ESI) m/z calcd for $C_{16}H_{15}F_3NO^+$ $[M+H]^+$: 294.1100, found 294.1099.

1-benzyl-3-methyl-2-phenyl-1H-indole (**7a**)



Prepared according to procedure **3-B**:Yield 68%, white solid, m.p.: 126.0-128.0 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.60 (m, 1H), 7.42 – 7.30 (m, 5H), 7.24 – 7.13 (m, 6H), 6.95 (d, *J* = 6.52 Hz, 3H), 5.23 (s, 2H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.49, 137.76, 136.80, 132.01, 130.53, 128.83, 128.54, 128.32, 127.87, 126.97, 126.05, 121.90, 119.37, 118.84, 110.16, 109.14, 47.58, 9.43. HRMS (ESI) m/z calcd for $C_{22}H_{20}N^+$ $[M+H]^+$: 298.1590, found 298.1590.

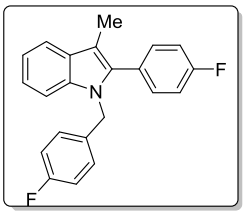
3-methyl-1-(4-methylbenzyl)-2-(p-tolyl)-1H-indole (**7b**)



Prepared according to procedure **3-B:**Yield 70%, white solid, m.p.: 121.7-123.9 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.58 (m, 1H), 7.25 – 7.09 (m, 7H), 7.01 (d, *J* = 7.85 Hz, 2H), 6.84 (d, *J* = 7.85 Hz, 2H), 5.17 (s, 2H), 2.37 (s, 3H), 2.30 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.84, 137.62, 136.72, 136.46, 135.52, 130.38, 129.19, 129.04, 129.02, 128.84, 125.94, 121.70, 119.24, 118.71, 110.18,

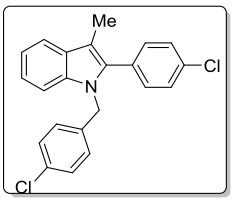
108.72, 47.29, 21.29, 21.02, 9.46. HRMS (ESI) m/z calcd for $C_{24}H_{24}N^+$ $[M+H]^+$: 326.1903, found 326.1904.

1-(4-fluorobenzyl)-2-(4-fluorophenyl)-3-methyl-1H-indole (**7c**)



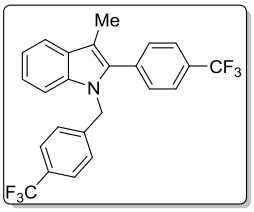
Prepared according to procedure **3-B:** Yield 65%, white solid, m.p.: 111.1-113.0 ^oC, ^1H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.57 (m, 1H), 7.27 – 7.21 (m, 2H), 7.20 – 7.13 (m, 3H), 7.12 – 7.05 (m, 2H), 6.92 – 6.82 (m, 4H), 5.15 (s, 2H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.41 (d, *J* = 66.17 Hz), 160.96 (d, *J* = 63.54 Hz), 136.68, 136.46, 133.99 (d, *J* = 3.17 Hz), 132.20 (d, *J* = 8.16 Hz), 128.70, 127.90 (d, *J* = 3.54 Hz), 127.58 (d, *J* = 8.09 Hz), 122.18, 119.58, 118.98, 115.58, 115.36, 109.91, 109.64, 46.79, 9.33. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.40, -115.56.HRMS (ESI) m/z calcd for $C_{22}H_{18}F_2N^+$ $[M+H]^+$: 326.1903, found 326.1903.

1-(4-chlorobenzyl)-2-(4-chlorophenyl)-3-methyl-1H-indole (**7d**)



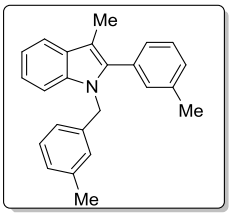
Prepared according to procedure **3-B:** Yield 67%, white solid, m.p.: 132.7.0-134.5 ^oC, ^1H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.60 (m, 1H), 7.40 – 7.10 (m, 11H), 6.85 – 6.80 (m, 2H), 5.15 (s, 2H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.89, 136.79, 136.28, 134.17, 132.96, 131.73, 130.33, 128.84, 128.81, 128.75, 127.37, 122.43, 119.77, 119.13, 110.01, 109.98, 46.97, 9.40. HRMS (ESI) m/z calcd for $C_{22}H_{18}Cl_2N^+$ $[M+H]^+$: 366.0811, found 366.0815.

3-methyl-1-(4-(trifluoromethyl)benzyl)-2-(4-(trifluoromethyl)phenyl)-1H-indole (**7e**)



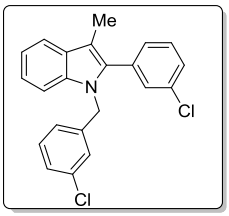
Prepared according to procedure **3-B**: Yield 52%, white solid, m.p.: 103.4-105.1 ^oC, ^1H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.62 (m, 3H), 7.49 (d, *J* = 8.09 Hz, 2H), 7.41 (d, *J* = 7.99 Hz, 2H), 7.23 – 7.13 (m, 3H), 7.02 (d, *J* = 7.97 Hz, 2H), 5.27 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.16, 137.09, 135.93, 135.52, 130.66, 130.22, 129.90, 129.81, 129.49, 128.84, 126.21, 125.72 (q, *J* = 3.82 Hz), 125.47 (q, *J* = 3.91 Hz), 122.87, 120.05, 119.36, 110.88, 109.98, 47.31, 9.41. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.54 , -62.63. HRMS (ESI) m/z calcd for $C_{24}H_{18}F_6N^+$ $[M+H]^+$: 434.1338, found 434.1336.

3-methyl-1-(3-methylbenzyl)-2-(m-tolyl)-1H-indole (**7f**)



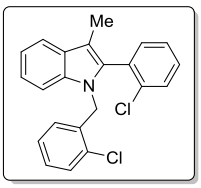
Prepared according to procedure **3-B**: Yield 63%, white solid, m.p.: 105.3.0-107.4 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.58 (m, 1H), 7.31 – 7.24 (m, 1H), 7.21 – 7.06 (m, 7H), 6.99 (d, *J* = 7.54 Hz, 1H), 6.81 (s, 1H), 6.74 (d, *J* = 7.60 Hz, 1H), 5.17 (s, 2H), 2.33 (s, 3H), 2.31 (s, 2H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.65, 138.15, 138.04, 137.91, 136.91, 132.00, 131.36, 128.88, 128.66, 128.48, 128.23, 127.78, 127.66, 126.90, 123.30, 121.83, 119.30, 118.82, 110.22, 108.89, 47.70, 21.47, 9.53. HRMS (ESI) m/z calcd for $C_{24}H_{24}N^{+}$ $[M+H]^{+}$: 326.1903, found 326.1903.

1-(3-chlorobenzyl)-2-(3-chlorophenyl)-3-methyl-1H-indole (**7g**)



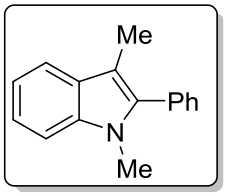
Prepared according to procedure **3-B**: Yield 60%, white solid, m.p.: 119.0-121.0 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65-7.62 (m, 1H), 7.38 – 7.27 (m, 3H), 7.23 – 7.11 (m, 6H), 6.95 (s, 1H), 6.76 (d, *J* = 7.31 Hz, 1H), 5.17 (s, 2H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.36, 136.94, 136.02, 134.63, 134.36, 133.70, 130.51, 130.01, 129.74, 128.78, 128.63, 128.23, 127.51, 126.28, 124.25, 122.60, 119.82, 119.24, 110.32, 110.00, 47.18, 9.44. HRMS (ESI) m/z calcd for $C_{22}H_{18}Cl_2N^{+}$ $[M+H]^{+}$: 366.0811, found 366.0809.

1-(2-chlorobenzyl)-2-(2-chlorophenyl)-3-methyl-1H-indole (**7h**)



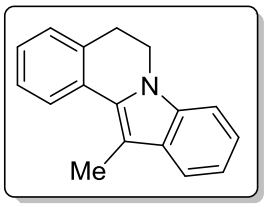
Prepared according to procedure **3-B**: Yield 56%, white solid, m.p.: 127.5-129.1 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.63 (m, 1H), 7.51 – 7.46 (m, 1H), 7.37 – 7.31 (m, 1H), 7.29 – 7.20 (m, 3H), 7.19 – 7.06 (m, 4H), 7.02 – 6.95 (m, 1H), 6.46 (d, *J* = 7.81 Hz, 1H), 5.31 (d, *J* = 17.65 Hz, 1H), 5.12 (d, *J* = 17.73 Hz, 1H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.48, 135.55, 135.45, 134.47, 132.91, 131.73, 130.76, 130.04, 129.83, 129.06, 128.46, 128.16, 127.61, 126.92, 126.59, 122.21, 119.46, 119.10, 110.79, 109.94, 45.01, 9.29. HRMS (ESI) m/z calcd for $C_{22}H_{18}Cl_2N^{+}$ $[M+H]^{+}$: 366.0811, found 366.0811.

1,3-dimethyl-2-phenyl-1H-indole (**7i**)



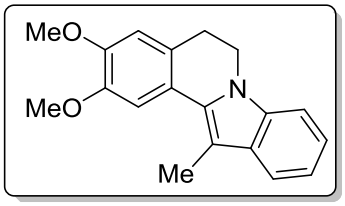
Prepared according to procedure **3-B**: Yield 62%, white solid, m.p.: 64.0-65.9 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 7.86 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.43 – 7.37 (m, 3H), 7.35 – 7.31 (m, 1H), 7.28 – 7.22 (m, 1H), 7.18 – 7.12 (m, 1H), 3.60 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.61, 137.17, 132.12, 128.39, 128.30, 127.70, 121.69, 119.07, 118.77, 109.20, 108.50, 30.90, 9.34. HRMS (ESI) m/z calcd for $C_{16}H_{16}N^+$ $[M+H]^+$: 222.1277, found 222.1277.

12-methyl-5,6-dihydroindolo[2,1-a]isoquinoline (**7j**)



Prepared according to procedure **3-B**: Yield 91%, white solid (slowly turn into yellow solid while exposure to air), m.p.: 150.1-151.7 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 7.81 Hz, 1H), 7.61 (d, *J* = 7.90 Hz, 1H), 7.39 – 7.16 (m, 5H), 7.10 (t, *J* = 7.41 Hz, 1H), 4.19 (t, *J* = 6.33 Hz, 2H), 3.10 (t, *J* = 6.33 Hz, 2H), 2.62 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.23, 133.41, 130.62, 130.25, 129.32, 128.30, 127.03, 126.52, 125.49, 121.85, 118.93, 118.79, 108.52, 107.11, 40.04, 30.18, 10.72. HRMS (ESI) m/z calcd for $C_{17}H_{16}N^+$ $[M+H]^+$: 234.1277, found 234.1277

2,3-dimethoxy-12-methyl-5,6-dihydroindolo[2,1-a]isoquinoline (**7k**)

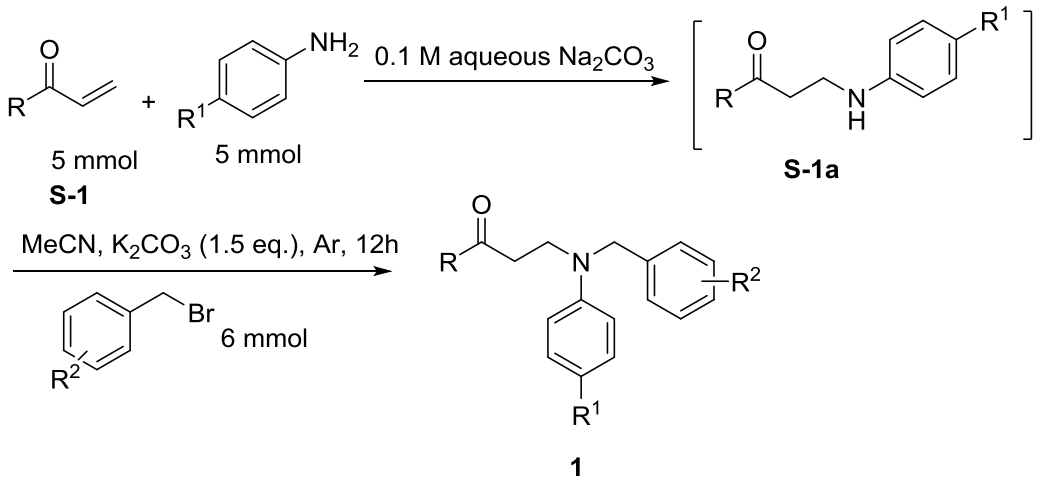


Prepared according to procedure **3-B**: Yield 87%, white solid (slowly turn into green solid while exposure to air), m.p.: 130.0-132.3 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 7.87 Hz, 1H), 7.40 (s, 1H), 7.30 – 7.25 (m, 1H), 7.22 – 7.16 (m, 1H), 7.13 – 7.07 (m, 1H), 6.81 (s, 1H), 4.19 (t, *J* = 6.37 Hz, 2H), 3.97 (s, 3H), 3.93 (s,3H), 3.07 (t, *J* = 6.34 Hz, 2H), 2.63 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.93, 147.81, 135.18, 130.81, 129.46, 126.25, 122.89, 121.50, 118.88, 118.47, 111.56, 109.05, 108.35, 105.34, 56.09, 55.99, 40.19, 29.70, 10.61. HRMS (ESI) m/z calcd for $C_{19}H_{20}NO_2^+$ $[M+H]^+$: 294.1489, found 294.1489.

4. Substrates synthetic procedures and Analytical Data

(1) Procedure for the preparation of substrates of **1a-1x**

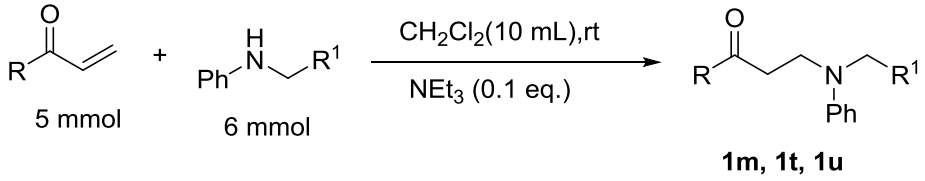
Procedure **4-A:**



Procedure **4-A**: The corresponding aniline (5 mmol) were added to aqueous sodium carbonate solution (0.1 M, 5 ml) at room temperature, then enone[1] **(**5 mmol) was added via a syringe. The mixture was stirred at room temperature for 12 hours and extracted with 10 mL ethyl acetate for three times. The combined organic layers washed with brine (20 ml), dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting solid **S-1a** was used in the next step without any further purification.

To a solution of **S-1a**, K_2CO_3 (7.5 mmol) in MeCN (10 mL) was added benzyl bromide (6 mmol), the reaction mixture was heated to reflux for 12 h under Ar atmosphere. After the completion of the reaction as shown by TLC, water (10 mL) was used to dilute the reaction. The organic layer was extracted with ethyl acetate (10 mL × 3). The combined organic layer was washed with saturated brine, dried with Na_2SO_4. The crude product was purified by flash chromatography with PE/EA as elute.

Procedure **4-B:**



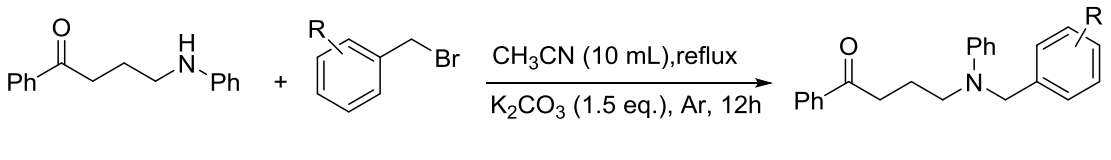
Procedure **4-B:** The corresponding *N*-substituted aniline (6 mmol), enone (5 mmol), NEt_3 (0.5 mmol) were added to 10 mL CH_2Cl_2. The resulting mixture was stirred at room temperature for 12h. Then the reaction was concentrated in vacuo. The crude product was purified via flash chromatography with PE/EA as elute.

(2) Procedure for the preparation of substrates of **Table 3**

The aminoacetophenone derivatives were prepared according to reported procedures,[2] the spectral data was identical to that reported in the literature.

(3) Procedure for the preparation of substrates of **S5a-5f**

Procedure **4-C**:



5 mmol

6 mmol

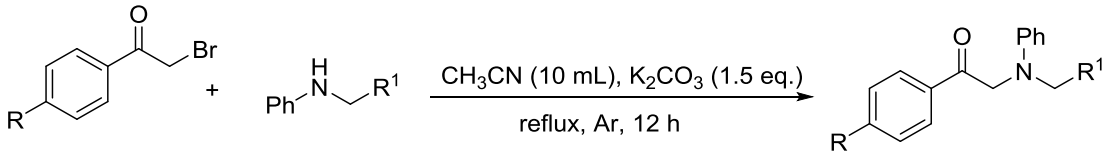
S-3

S(4a-4f)

To a solution of **S-3**[3], K_2CO_3 (7.5 mmol) in MeCN (10 mL) was added benzyl bromide (6 mmol), The reaction mixture was heated to reflux for 24 h under Ar atmosphere. After the completion of the reaction as shown by TLC, water (10 mL) was used to dilute the reaction. The organic layer was extracted with ethyl acetate (10 mL × 3). The combined organic layer was washed with saturated brine, dried with Na_2SO_4. The crude product was purified by flash chromatography with PE/EA as elute.

(4)Procedure for the preparation of substrates of **S5a-5f**

Procedure **4-D**:



5 mmol

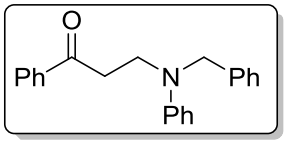
5 mmol

S(5a-5f)

The corresponding 2-Br-phenylethanone (5 mmol), *N*-substituted aniline (5 mmol), K_2CO_3 (7.5 mmol) were dissolved in CH_3CN(10 mL) and heated to reflux for 24 h under Ar atmosphere. The reaction was then filtered and concentrated in vacuo. The crude product was purified via flash chromatography with PE/EA as elute.

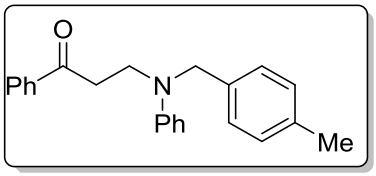
Analytical Data of new substrates

3-(benzyl(phenyl)amino)-1-phenylpropan-1-one (**1a**)



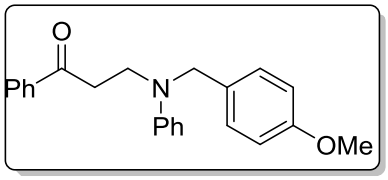
Prepared according to procedure **4-A**:75% in total yield, white solid, m.p.: 89.8-90.6 ^oC, ^1H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.84 (m, 2H), 7.57 – 7.35 (m, 3H), 7.31 – 7.13 (m, 7H), 6.78 – 6.64 (m, 3H), 4.58 (s, 2H), 3.90 (t, *J* = 7.16 Hz, 2H), 3.30 (t, *J* = 7.16 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.28, 147.99, 138.88, 136.86, 133.30, 129.47, 128.69, 128.66, 128.08, 126.94, 126.67, 116.69, 112.42, 54.88, 46.39, 36.06.HRMS (ESI) m/z calcd for $C_{22}H_{22}NO^+$ $[M+H]^+$: 316.1696, found 316.1692.

3-((4-methylbenzyl)(phenyl)amino)-1-phenylpropan-1-one (**1b**)



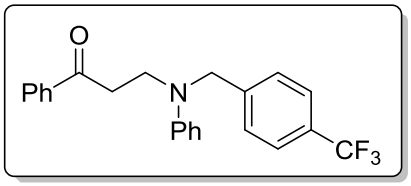
Prepared according to procedure **4-A**:77% in total yield, white solid, m.p.: 72.0-73.0 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.87 (m, 2H), 7.56 – 7.51 (m, 1H), 7.46 – 7.39 (m, 2H), 7.22 – 7.17 (m, 2H), 7.14 – 7.07 (m, 4H), 6.77 – 6.66 (m, 3H), 4.54 (s, 2H), 3.88 (t,*J*=7.20Hz, 2H), 3.30 (t, *J*=7.20Hz ,2H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.34, 148.03, 136.84, 136.49, 135.72, 133.28, 129.44, 129.33, 128.67, 128.08, 126.64, 116.59, 112.39, 54.59, 46.30, 36.02, 21.11. HRMS (ESI) m/z calcd for $C_{23}H_{24}NO^{+}$ $[M+H]^{+}$: 330.1852, found 330.1855.

3-((4-methoxybenzyl)(phenyl)amino)-1-phenylpropan-1-one (**1c**)



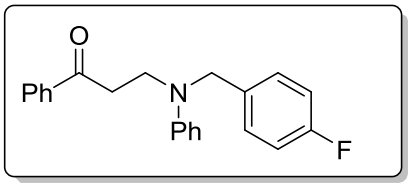
Prepared according to procedure **4-A**:65% in total yield, white solid, m.p.: 71.0-72.3 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 7.93 Hz, 2H), 7.53 (t, *J* = 7.38 Hz, 1H), 7.42 (t, *J* = 7.76 Hz, 2H), 7.24 – 7.11 (m, 4H), 6.82 (d, *J* = 8.53 Hz, 2H), 6.77 – 6.67 (m, 3H), 4.51 (s, 2H), 3.87 (t, *J* = 7.15 Hz, 2H), 3.75 (s, 3H), 3.28 (t, *J* = 7.15 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.33, 158.64, 148.06, 136.86, 133.27, 130.72, 129.44, 128.67, 128.07, 127.88, 116.65, 114.07, 112.52, 55.30, 54.24, 46.18, 36.02. HRMS (ESI) m/z calcd for $C_{23}H_{24}NO_2^{+}$ $[M+H]^{+}$: 346.1802, found 346.1207.

1-phenyl-3-(phenyl(4-(trifluoromethyl)benzyl)amino)propan-1-one (**1d**)



Prepared according to procedure **4-A**:70% in total yield, white solid, m.p.: 73.2-74,7 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 7.58 Hz, 2H), 7.55 (dd, *J* = 13.03, 7.56 Hz, 3H), 7.43 (t, *J* = 7.74 Hz, 2H), 7.33 (d, *J* = 8.06 Hz, 2H), 7.25 – 7.16 (m, 2H), 6.72 (dd, *J* = 16.18, 7.99 Hz, 3H), 4.65 (s, 2H), 3.93 (t, *J* = 6.91 Hz, 2H), 3.33 (t, *J* = 6.91 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.34.^{13}C NMR (101 MHz, $CDCl_3$) δ 199.05, 147.55, 143.26, 136.76, 133.38, 129.54, 129.23 (q, *J* = 32.03 Hz), 128.69, 128.02, 126.84, 125.58 (q, *J* = 3.77 Hz), 123.23 (q, *J* = 69.89 Hz), 117.13, 112.46, 54.76, 46.53, 36.11.HRMS (ESI) m/z calcd for $C_{23}H_{21}F_3NO^{+}$ $[M+H]^{+}$: 384.1570, found 384.1568.

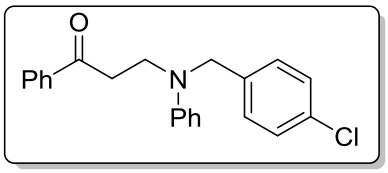
3-((4-fluorobenzyl)(phenyl)amino)-1-phenylpropan-1-one (**1e**)



Prepared according to procedure **4-A**:72% in total yield, white solid, m.p.: 69.5-71.5

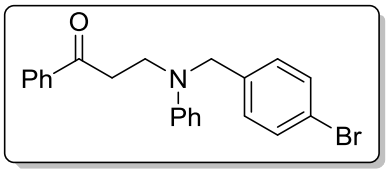
^{o}C,^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 7.42 Hz, 2H), 7.55 (t, *J* = 7.39 Hz, 1H), 7.47 – 7.39 (m, 2H), 7.24 – 7.14 (m, 4H), 7.00 – 6.92 (m, 2H), 6.76 – 6.68 (m, 3H), 4.54 (s, 2H), 3.89 (t, *J* = 7.07 Hz, 2H), 3.30 (t, *J* = 7.07 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.21, 161.88 (d, *J* = 244.65 Hz), 147.77, 136.78, 134.43, 134.40, 133.35, 129.49, 128.69, 128.18, 128.14 (d, *J* = 7.89 Hz), 116.90, 115.45 (d, *J* = 21.36 Hz), 112.50, 54.27, 46.29, 36.00. HRMS (ESI) m/z calcd for $C_{22}H_{21}FNO^{+}$ $[M+H]^{+}$: 334.1602, found 334.1600.

3-((4-chlorobenzyl)(phenyl)amino)-1-phenylpropan-1-one (**1f**)



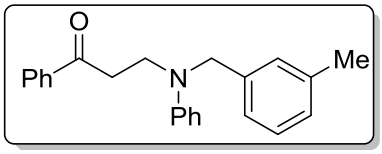
Prepared according to procedure **4-A**:77% in total yield, white solid, m.p.: 86.0-88.2 ^{o}C,^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.83 (m, 2H), 7.59 – 7.53 (m, 1H), 7.48 – 7.41 (m, 2H), 7.28 – 7.12 (m, 2H), 6.79 – 6.66 (m, 3H), 4.55 (s, 2H), 3.90 (t, *J* = 6.98 Hz, 2H), 3.31 (t, *J* = 6.98 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.13, 147.66, 137.38, 136.76, 133.33, 132.54, 129.47, 128.74, 128.67, 128.02, 127.97, 116.96, 112.47, 54.41, 46.39, 36.04. HRMS (ESI) m/z calcd for $C_{22}H_{21}ClNO^{+}$ $[M+H]^{+}$: 350.1306, found350.1306.

3-((4-bromobenzyl)(phenyl)amino)-1-phenylpropan-1-one (**1g**)



Prepared according to procedure **4-A**:81% in total yield, white solid, m.p.: 104.0-105.5 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.85 (m, 2H), 7.60 – 7.51 (m, 1H), 7.51 – 7.35 (m, 4H), 7.24 – 7.18 (m, 2H), 7.15 – 7.05 (m, 2H), 6.78 – 6.65 (m, 3H), 4.54 (s, 2H), 3.90 (t, *J* = 7.02 Hz, 2H), 3.32 (t, *J* = 7.02 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.10, 147.60, 136.71, 133.33, 131.66, 129.46, 129.28, 129.02, 128.66, 128.33, 128.00, 116.94, 112.42, 54.45, 46.38, 36.01. HRMS (ESI) m/z calcd for $C_{22}H_{21}BrNO^{+}$ $[M+H]^{+}$: 394.0801, found 394.0801.

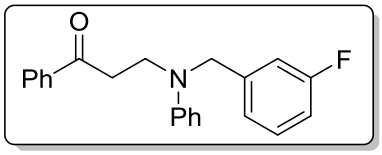
3-((3-methylbenzyl)(phenyl)amino)-1-phenylpropan-1-one (**1h**)



Prepared according to procedure **4-A**:71% in total yield, white solid, m.p.: 62.3-63.9 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.85 (m, 2H), 7.54 – 7.48 (m, 1H), 7.44 – 7.37 (m, 2H), 7.24 – 7.13 (m, 3H), 7.06 – 6.98 (m, 3H), 6.76 – 6.66 (m, 3H), 4.53 (s, 2H), 3.89 (t, *J* = 7.55 Hz, 2H), 3.29 (t, *J* = 7.55 Hz, 2H), 2.28 (s, 3H). ^{13}C

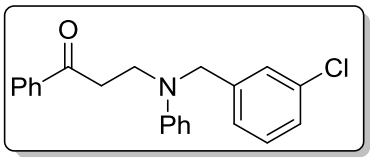
NMR (101 MHz, $CDCl_3$) δ 199.34, 148.11, 138.92, 138.33, 136.89, 133.33, 129.50, 128.72, 128.60, 128.12, 127.76, 127.35, 123.77, 116.65, 112.42, 54.86, 46.36, 36.01, 21.60. HRMS (ESI) m/z calcd for $C_{23}H_{24}NO^+$ $[M+H]^+$: 330.1852, found 330.1850.

3-((3-fluorobenzyl)(phenyl)amino)-1-phenylpropan-1-one (**1i**)



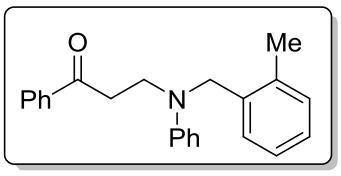
Prepared according to procedure **4-A**:65% in total yield, white solid, m.p.: 68.4-70.0 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.88 (m, 2H), 7.59 – 7.52 (m, 1H), 7.48 – 7.41 (m, 2H), 7.28 – 7.17 (m, 3H), 7.01 (d, *J* = 7.73 Hz, 1H), 6.96 – 6.87 (m, 2H), 6.76 – 6.68 (m, 3H), 4.58 (s, 2H), 3.91 (t, *J* = 7.05 Hz, 2H), 3.33 (t, *J* = 7.05 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.13, 163.23 (d, *J* = 246.08 Hz), 147.66, 141.87 (d, *J* = 6.62 Hz), 136.79, 133.31, 130.13 (d, *J* = 8.33 Hz), 129.46, 128.67, 128.03, 122.09 (d, *J* = 2.70 Hz), 116.98, 113.79 (d, *J* = 21.16 Hz), 113.45 (d, *J* = 21.81 Hz), 112.46, 54.63 (d, *J* = 2.13 Hz), 46.45, 36.04. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.88. HRMS (ESI) m/z calcd for $C_{22}H_{21}FNO^+$ $[M+H]^+$: 334.1602, found 334.1602.

3-((3-chlorobenzyl)(phenyl)amino)-1-phenylpropan-1-one (**1j**)



Prepared according to procedure **4-A**: 69% in total yield, white solid, m.p.: 77.4-78.9 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 7.32 Hz, 2H), 7.59 – 7.51 (m, 1H), 7.48 – 7.39 (m, 2H), 7.24 – 7.18 (m, 5H), 7.12 – 7.06 (m, 1H), 6.76 – 6.66 (m, 3H), 4.55 (s, 2H), 3.90 (t, *J* = 7.02 Hz, 2H), 3.31 (t, *J* = 7.02 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.12, 147.65, 141.28, 136.78, 134.60, 133.35, 129.94, 129.51, 128.70, 128.05, 127.15, 126.67, 124.74, 117.04, 112.49, 54.60, 46.42, 36.02. HRMS (ESI) m/z calcd for $C_{22}H_{21}ClNO^+$ $[M+H]^+$: 350.1306, found 350.1307.

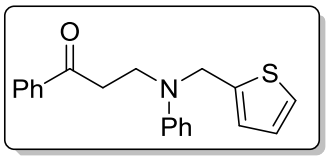
3-((2-methylbenzyl)(phenyl)amino)-1-phenylpropan-1-one (**1k**)



Prepared according to procedure **4-A**:76% in total yield, white solid, m.p.: 96.0-97.0 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.86 (m, 1H), 7.58 – 7.50 (m,1H), 7.46 – 7.37 (m, 1H), 7.24 – 7.04 (m, 3H), 6.74 – 6.65 (m, 2H), 4.49 (s, 1H), 3.89 (t, *J* = 7.15 Hz, 1H), 3.33 (t, *J* = 7.15 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.31, 148.02, 136.87, 135.98, 135.49, 133.33, 130.39, 129.49, 128.71, 128.10, 126.83, 126.28, 126.16, 116.58, 112.18, 52.90, 46.30, 36.10, 19.08. HRMS (ESI) m/z calcd

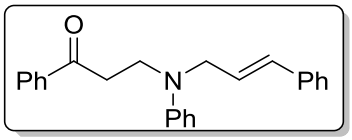
for $C_{23}H_{24}NO^+$ $[M+H]^+$: 330.1852, found 330.1854.

1-phenyl-3-(phenyl(thiophen-2-ylmethyl)amino)propan-1-one (**1l**)



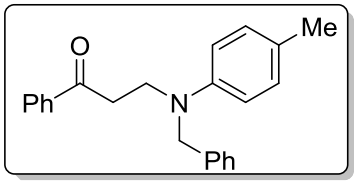
Prepared according to procedure **4-A**:59% in total yield, white solid, m.p.: 42.0-44.0 ^oC, ^1H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.20 Hz, 2H), 7.43 – 7.38 (m, 1H), 7.32 – 7.26 (m, 2H), 7.19 – 7.12 (m, 2H), 7.02 (dd, *J* = 4.86, 1.35 Hz, 1H), 6.85 – 6.79 (m, 2H), 6.74 (d, *J* = 8.60 Hz, 2H), 6.68 (t, *J* = 7.19 Hz, 1H), 4.61 (s, 2H), 3.79 (t, *J* = 6.99 Hz, 2H), 3.16 (t, *J* = 6.99 Hz ,2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.15, 147.66, 142.93, 136.97, 133.42, 129.67, 128.85, 128.23, 127.08, 125.07, 124.55, 117.48, 113.23, 50.67, 46.15, 36.40. HRMS (ESI) m/z calcd for $C_{20}H_{20}NOS^+$ $[M+H]^+$: 322.1260, found 322.1261.

3-(cinnamyl(phenyl)amino)-1-phenylpropan-1-one (**1m**)



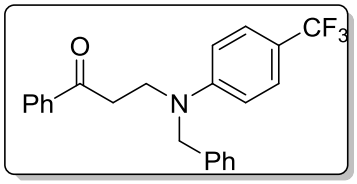
Prepared according to procedure **4-B**: 90% yield, white solid, m.p.: 91.5-92.7 ^oC, ^1H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.87 (m, 2H), 7.56 – 7.49 (m, 1H), 7.44 – 7.37 (m, 2H), 7.33 – 7.16 (m, 8H), 6.81 – 6.68 (m, 3H), 6.51 (d, *J* = 15.94 Hz, 1H), 6.23 (dt, *J* = 15.91, 5.36 Hz, 1H), 4.12 (dd, *J* = 5.32, 1.39 Hz, 2H), 3.86 (d, 2H), 3.30 (d, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.32, 147.67, 136.79, 136.78, 133.20, 131.24, 129.42, 128.60, 128.48, 128.02, 127.39, 126.29, 125.86, 116.53, 112.32, 53.12, 45.88, 36.17. HRMS (ESI) m/z calcd for $C_{24}H_{24}NO^+$ $[M+H]^+$: 342.1852, found 342.1854.

3-(benzyl(p-tolyl)amino)-1-phenylpropan-1-one (**1n**)



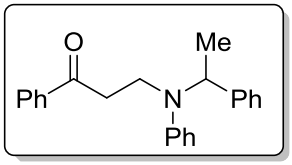
Prepared according to procedure **4-B**: 85% yield, white solid, m.p.: 81.9-83.7 ^oC, ^1H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.84 (m, 2H), 7.56 – 7.51 (m, 1H), 7.45 – 7.39 (m, 2H), 7.31 – 7.18 (m, 5H), 7.01 (d, *J* = 8.40 Hz, 2H), 6.66 (d, *J* = 8.51 Hz, 2H), 4.54 (s, 2H), 3.86 (t, *J* = 7.20 Hz, 2H), 3.28 (t, *J* = 7.20 Hz, 2H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.33, 145.83, 139.06, 136.84, 133.17, 129.90, 128.59, 128.54, 128.01, 126.80, 126.69, 125.91, 112.76, 55.12, 46.52, 36.01, 20.18. HRMS (ESI) m/z calcd for $C_{23}H_{24}NO^+$ $[M+H]^+$: 330.1852, found 330.1852.

3-(benzyl(4-(trifluoromethyl)phenyl)amino)-1-phenylpropan-1-one (**1o**)



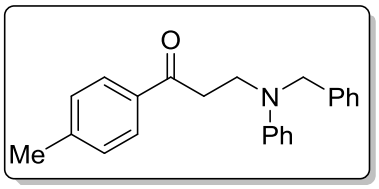
Prepared according to procedure **4-B**: 92% yield, white solid, m.p.: 75.5-77.5 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.86 (m, 2H), 7.59 – 7.54 (m, 1H), 7.48 – 7.38 (m, 4H), 7.38 – 7.16 (m, 6H), 6.73 (d, *J* = 8.77 Hz, 2H), 4.65 (s, 2H), 3.96 (t, *J* = 7.06 Hz, 2H), 3.33 (t, *J* = 7.06 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.71, 150.09, 137.70, 136.60, 133.45, 128.78, 128.71, 128.00, 127.18, 126.69 (q, *J* = 3.80 Hz), 126.35, 118.00 (q, *J* = 32.78 Hz), 111.95, 111.31, 54.58, 46.34, 35.82. HRMS (ESI) m/z calcd for $C_{23}H_{21}F_3NO^+$ $[M+H]^+$: 384.1570, found 384.1572.

1-phenyl-3-(phenyl(1-phenylethyl)amino)propan-1-one (**1p**)



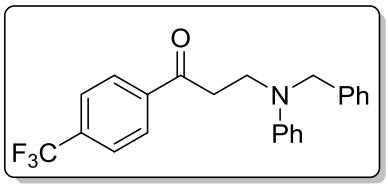
Prepared according to procedure **4-A:** 52% in total yield, white solid, m.p.: 39.8-42.3 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 7.75 Hz, 2H), 7.55 – 7.49 (m, 1H), 7.43 – 7.20 (m, 10H), 6.91 – 6.84 (m, 2H), 6.80 – 6.73 (m, 1H), 5.13 (q, *J* = 6.82 Hz, 1H), 3.67 – 3.48 (m, 2H), 3.13 (ddd, *J* = 15.87, 9.47, 5.59 Hz, 1H), 2.99 (ddd, *J* = 15.87, 9.67, 5.52 Hz, 1H), 1.57 (d, *J* = 6.82 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.45, 148.28, 142.54, 136.75, 133.13, 129.44, 128.56, 128.47, 127.99, 127.30, 127.09, 117.46, 114.39, 57.34, 41.06, 37.33, 16.87. HRMS (ESI) m/z calcd for $C_{23}H_{24}NO^+$ $[M+H]^+$: 330.1852, found 330.1852.

3-(benzyl(phenyl)amino)-1-(p-tolyl)propan-1-one (**1q**)



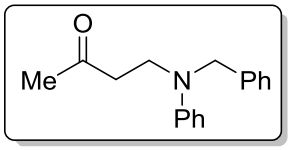
Prepared according to procedure **4-A:** 57% in total yield, white solid, m.p.: 59.3-60.6 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.11 Hz, 2H), 7.30 – 7.14 (m, 9H), 6.75 – 6.65 (m, 3H), 4.56 (s, 2H), 3.88 (t, *J* =7.2 Hz, 2H), 3.26 (t, *J* =7.2 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.95, 148.04, 144.15, 138.95, 134.47, 129.50, 129.41, 128.69, 128.25, 126.95, 126.70, 116.66, 112.41, 54.86, 46.52, 35.95, 21.75. HRMS (ESI) m/z calcd for $C_{23}H2_4NO^+$ $[M+H]^+$: 330.1852, found 330.1852.

3-(benzyl(phenyl)amino)-1-(4-(trifluoromethyl)phenyl)propan-1-one (**1r**)



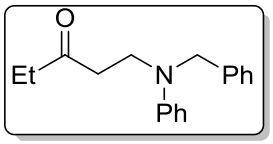
Prepared according to procedure **4-A:** 63% in total yield, white solid, m.p.: 63.0-64.6 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.14 Hz, 2H), 7.65 (d, *J* = 8.25 Hz, 2H), 7.30 – 7.18 (m, 7H), 6.77 – 6.67 (m, 3H), 4.57 (s, 2H), 3.90 (t, *J* = 7.05 Hz, 2H), 3.30 (t, *J* = 7.05 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.31, 147.96, 139.46, 138.83, 134.50 (q, *J* = 32.66 Hz), 129.55, 128.71, 128.43, 127.04, 126.74, 125.75 (q, *J* = 3.69 Hz), 123.66(q, *J* = 123.66 Hz), 116.99, 112.58, 55.01, 46.20, 36.47. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.97. HRMS (ESI) m/z calcd for $C_{23}H_{21}F_3NO^+$ $[M+H]^+$: 384.1570, found 384.1572.

4-(benzyl(phenyl)amino)butan-2-one (**1s**)



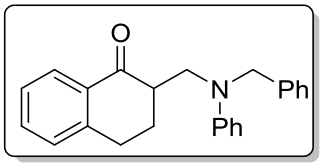
Prepared according to procedure **4-B:** 92% yield, white solid, m.p.: 59.0-60.0 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.23 (m, 2H), 7.22 – 7.12 (m, 5H), 6.71 – 6.63 (m, 3H), 4.51 (s, 2H), 3.68 (t, *J* = 7.05 Hz, 2H), 2.74 (t, *J* = 7.05 Hz, 2H), 2.07 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.61, 147.46, 138.33, 129.37, 128.57, 126.97, 126.77, 117.23, 112.84, 55.12, 45.81, 40.96, 30.50. HRMS (ESI) m/z calcd for $C_{17}H_{20}NO^+$ $[M+H]^+$: 254.1539, found 254.1539.

1-(benzyl(phenyl)amino)pentan-3-one (**1t**)



Prepared according to procedure **4-B:** 92% yield, white solid, m.p.: 45.0-46.0 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.24 (m, 2H), 7.23 – 7.13 (m, 5H), 6.72 – 6.64 (m, 3H), 4.52 (s, 2H), 3.71 (t, *J* = 7.02 Hz, 2H), 2.73 (t, *J* = 7.02 Hz, 2H), 2.37 (q, *J* = 7.30 Hz, 2H), 1.01 (t, *J* = 7.30 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.44, 148.00, 138.91, 129.41, 128.64, 126.90, 126.63, 116.68, 112.43, 54.78, 45.86, 39.84, 36.65, 7.74. HRMS (ESI) m/z calcd for $C_{18}H_{22}NO^+$ $[M+H]^+$: 268.1696, found 268.1696.

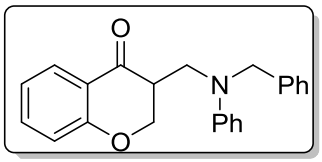
2-((benzyl(phenyl)amino)methyl)-3,4-dihydronaphthalen-1(2H)-one (**1u**)



Prepared according to procedure **4-A:** 48% in total yield, white solid, m.p.: 93.1-94.3

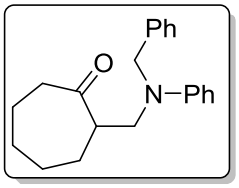
^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 7.81 Hz, 1H), 7.45 (t, *J* = 7.45 Hz, 1H), 7.32 – 7.26 (m, 3H), 7.24 – 7.15 (m, 6H), 6.81 – 6.64 (m, 3H), 4.76 (d, *J* = 17.12 Hz, 1H), 4.57 (d, *J* = 17.12 Hz, 1H), 4.34 (dd, *J* = 15.23, 3.87 Hz, 1H), 3.45 (dd, *J* = 15.09, 8.65 Hz, 1H), 3.09 – 2.98 (m, 1H), 2.98 – 2.91 (m, 2H), 2.42 – 2.31 (m, 1H), 1.99 – 1.85 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.41, 148.15, 143.99, 138.72, 133.45, 132.50, 129.34, 128.76, 128.61, 127.30, 126.85, 126.72, 126.67, 116.63, 112.69, 55.76, 51.74, 46.56, 28.73, 27.69. HRMS (ESI) m/z calcd for $C_{24}H_{24}NO^{+}$ $[M+H]^{+}$: 342.1852, found 342.1852.

3-((benzyl(phenyl)amino)methyl)chroman-4-one (**1v**)



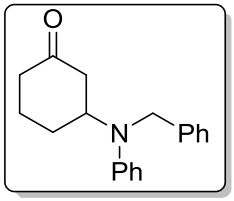
Prepared according to procedure **4-A:** 56% in total yield, white solid, m.p.: 95.4-96.6 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.85 (m, 1H), 7.50 – 7.42 (m, 1H), 7.32 – 7.16 (m, 7H), 7.06 – 6.93 (m, 2H), 6.88 – 6.70 (m, 3H), 4.72 (d, *J* = 17.02 Hz, 1H), 4.60 (d, *J* = 17.02 Hz, 1H), 4.49 (dd, *J* = 11.60, 3.81 Hz, 1H), 4.38 (dd, *J* = 11.60, 6.49 Hz, 1H), 4.08 – 3.97 (m, 1H), 3.61 – 3.49 (m, 1H), 3.25 – 3.14 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.17, 161.53, 147.71, 138.24, 136.14, 129.48, 128.70, 127.36, 127.04, 126.70, 121.68, 120.73, 117.93, 117.46, 113.11, 68.93, 55.57, 48.72, 45.25. HRMS (ESI) m/z calcd for $C_{23}H_{22}NO_2^{+}$ $[M+H]^{+}$: 344.1645, found 344.1645.

2-((benzyl(phenyl)amino)methyl)cycloheptan-1-one (**1w**)



Prepared according to procedure **4-A:** 65% in total yield, yellow oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.24 (m, 3H), 7.23 – 7.12 (m, 5H), 6.72 – 6.64 (m, 3H), 4.68 – 4.51 (m, 2H), 3.86 (dd, *J* = 14.93, 6.85 Hz, 1H), 3.39 (dd, *J* = 14.94, 6.64 Hz, 1H), 3.14 – 3.01 (m, 1H), 2.46 – 2.43 (m, 1H), 1.96 – 1.77 (m, 4H), 1.66 – 1.57 (m, 1H), 1.48 – 1.23 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.98, 148.29, 138.83, 129.24, 128.51, 126.69, 126.55, 116.51, 112.56, 55.41, 53.13, 50.62, 43.55, 29.39, 29.00, 28.77, 23.88.HRMS (ESI) m/z calcd for $C_{21}H_{26}NO^{+}$ $[M+H]^{+}$: 308.2009, found 308.2009.

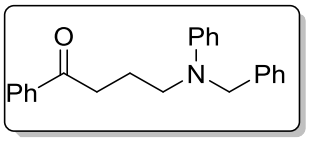
3-(benzyl(phenyl)amino)cyclohexan-1-one (**1x**)



Prepared according to procedure **4-A:** 72% in total yield, white solid, m.p.: 73.5-75.7

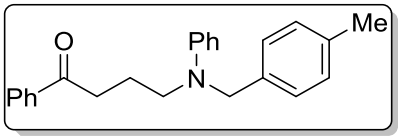
^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 6.51 Hz, 4H), 7.25 – 7.13 (m, 3H), 6.77 – 6.67 (m, 3H), 4.50 (dd, *J* = 17.68 Hz, 2H), 4.20 – 4.05 (m, 1H), 2.74 – 2.64 (m, 1H), 2.51 – 2.35 (m, 2H), 2.28 – 2.18 (m, 1H), 2.15 – 2.00 (m, 2H), 1.80 – 1.54 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.42, 148.49, 139.84, 129.27, 128.52, 126.73, 126.23, 117.78, 113.81, 57.13, 49.46, 45.90, 40.90, 29.48, 22.41. HRMS (ESI) m/z calcd for $C_{19}H_{22}NO^+$ $[M+H]^+$: 280.1696, found 280.1696.

4-(benzyl(phenyl)amino)-1-phenylbutan-1-one (**S-4a**)



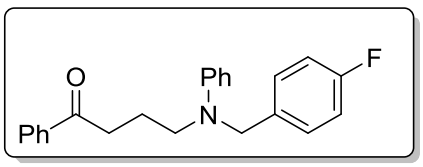
Prepared according to procedure **4-C:** 89% yield, white solid, m.p.: 77.0-78.0 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.84 (m, 2H), 7.55 – 7.47 (m, 1H), 7.45 – 7.37 (m, 2H), 7.31 – 7.22 (m, 3H), 7.22 – 7.13 (m, 5H), 6.74 (d, *J* = 8.13 Hz, 2H), 6.66 (t, *J* = 7.24 Hz, 1H), 4.53 (s, 2H), 3.46 (t, 2H), 2.95 (t, *J* = 6.88 Hz, 2H), 2.13 – 2.03 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.44, 148.44, 138.88, 136.77, 132.99, 129.20, 128.53, 128.49, 127.91, 126.71, 126.55, 116.27, 112.31, 54.48, 50.47, 35.55, 21.48. HRMS (ESI) m/z calcd for $C_{23}H_{24}NO^+$ $[M+H]^+$: 330.1852, found 330.1853.

4-((4-methylbenzyl)(phenyl)amino)-1-phenylbutan-1-one (**S-4b**)



Prepared according to procedure **4-C:** 95% yield, white solid, m.p.: 101.3-102.8 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 7.45 Hz, 2H), 7.50 – 7.44 (m, 1H), 7.40 – 7.33 (m, 2H), 7.15 – 7.07 (m, 2H), 7.06 – 7.00 (m, 4H), 6.68 (d, *J* = 8.53 Hz, 2H), 6.59 (t, *J* = 7.25 Hz, 1H), 4.45 (s, 2H), 3.39 (t, *J* = 7.50 Hz, 2H), 2.91 (t, *J* = 6.91 Hz, 2H), 2.23 (s, 3H), 2.06 – 1.97 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.54, 147.58, 135.84, 135.28, 134.77, 131.97, 128.18, 127.53, 126.93, 125.59, 115.24, 111.40, 53.32, 49.37, 34.64, 20.57, 20.00. HRMS (ESI) m/z calcd for $C_{24}H_{26}NO^+$ $[M+H]^+$: 344.2009, found 344.2009.

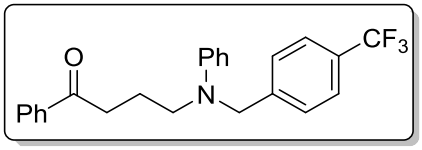
4-((4-fluorobenzyl)(phenyl)amino)-1-phenylbutan-1-one (**S-4c**)



Prepared according to procedure **4-C:** 86% yield, white solid, m.p.: 102.5-103.5 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 7.46 Hz, 2H), 7.53 – 7.34 (m, 3H), 7.16 – 7.06 (m, 4H), 6.94 – 6.85 (m, 2H), 6.71 – 6.57 (m, 3H), 4.45 (s, 2H), 3.39 (t, *J* = 7.59 Hz, 2H), 2.93 (t, *J* = 6.83 Hz, 2H), 2.08 – 1.95 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.46, 160.77 (d, *J* = 244.43 Hz), 147.32, 135.80, 133.45 (d, *J* = 2.96 Hz), 132.05, 128.25, 127.57, 127.11 (d, *J* = 7.87 Hz), 126.92, 115.58, 114.32 (d, *J* = 21.38

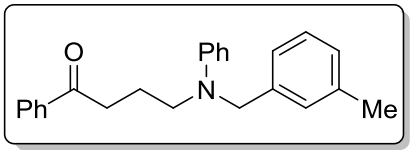
Hz), 111.53, 53.00, 49.46, 34.54, 20.50. HRMS (ESI) m/z calcd for $C_{23}H_{23}FNO^+$ $[M+H]^+$: 348.1758, found 348.1758.

1-phenyl-4-(phenyl(4-(trifluoromethyl)benzyl)amino)butan-1-one (**S-4d**)



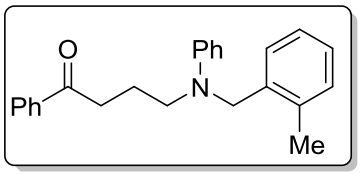
Prepared according to procedure **4-C:** 83% yield, white solid, m.p.: 94.2-96.1 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 7.70 Hz, 2H), 7.56 – 7.49 (m, 3H), 7.43 (t, *J* = 7.56 Hz, 2H), 7.32 (d, *J* = 7.89 Hz, 2H), 7.19 (t, *J* = 7.75 Hz, 2H), 6.76 – 6.66 (m, 3H), 4.59 (s, 2H), 3.48 (t, *J* = 7.58 Hz 2H), 3.00 (t, *J* = 6.70 Hz, 2H), 2.16 – 2.04 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.22. ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.45, 148.20, 143.44, 136.87, 133.18, 129.42, 129.18(q, *J* = 32 Hz), 128.67, 127.99, 126.95, 125.56 (q, *J* = 3.73 Hz), 124.30 (q, *J* = 270 Hz), 116.91, 112.57, 54.46, 50.84, 35.52, 21.59. HRMS (ESI) m/z calcd for $C_{24}H_{23}F_3NO^+$ $[M+H]^+$: 398.1726, found 398.1726.

4-((3-methylbenzyl)(phenyl)amino)-1-phenylbutan-1-one (**S-4e**)



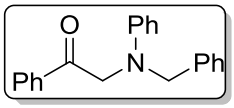
Prepared according to procedure **4-C:** 90% yield, white solid, m.p.: 52.3-53.3 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 6.96 Hz, 2H), 7.48 – 7.30 (m, 3H), 7.11 – 7.05 (m, 3H), 6.94 (s, 3H), 6.71 – 6.54 (m, 3H), 4.43 (s, 2H), 3.38 (t, *J* = 7.46 Hz,2H), 2.89 (t, *J* = 6.72 Hz, 2H), 2.20 (s, 3H), 2.06 – 1.95 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.59, 148.71, 139.03, 138.23, 136.94, 133.07, 129.29, 128.63, 128.51, 128.03, 127.62, 127.34, 123.77, 116.35, 112.48, 54.66, 50.50, 35.73, 21.57, 21.55.HRMS (ESI) m/z calcd for $C_{24}H_{26}NO^+$ $[M+H]^+$: 344.2009, found 344.2009.

4-((2-methylbenzyl)(phenyl)amino)-1-phenylbutan-1-one (**S-4f**)



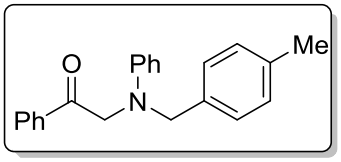
Prepared according to procedure **4-C:** 83% yield, white solid, m.p.: 84.0-86.0 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.90 (m, 2H), 7.58 – 7.52 (m, 1H), 7.48 – 7.42 (m, 2H), 7.23 – 7.06 (m, 7H), 6.73 – 6.64 (m, 3H), 4.47 (s, 2H), 3.48 (t, 2H), 3.01 (t, *J* = 6.88 Hz, 2H), 2.31 (s, 3H), 2.17 – 2.09 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.57, 148.56, 136.91, 136.02, 135.45, 133.08, 130.30, 129.28, 128.62, 128.01, 126.66, 126.21, 126.05, 116.24, 112.17, 52.54, 50.43, 35.67, 21.67, 18.97. HRMS (ESI) m/z calcd for $C_{24}H_{26}NO^+$ $[M+H]^+$: 344.2009, found 344.2011.

2-(benzyl(phenyl)amino)-1-phenylethan-1-one (**S-5a**)



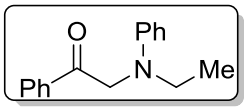
Prepared according to procedure **4-D:** 95% yield, white solid, m.p.: 106.4-107.9 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.95 (m, 2H), 7.63 – 7.56 (m, 1H), 7.47 (t, *J* = 7.67 Hz, 2H), 7.36 – 7.24 (m, 5H), 7.20 – 7.12 (m, 2H), 6.72 (t, *J* = 7.29 Hz, 1H), 6.64 (d, *J* = 8.00 Hz, 2H), 4.81 (s, 2H), 4.69 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.21, 148.87, 138.67, 135.32, 133.59, 129.19, 128.80, 128.65, 127.78, 127.04, 126.81, 117.38, 112.50, 56.58, 55.72. HRMS (ESI) m/z calcd for $C_{21}H_{20}NO^+$ $[M+H]^+$: 302.1539, found 302.1539.

2-((4-methylbenzyl)(phenyl)amino)-1-phenylethan-1-one (**S-5b**)



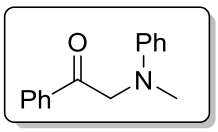
Prepared according to procedure **4-D:** 93% yield, white solid, m.p.: 96.0-97.7 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 7.81 Hz, 2H), 7.59 (t, *J* = 7.30 Hz, 1H), 7.47 (t, *J* = 7.65 Hz, 2H), 7.23 – 7.11 (m, 6H), 6.77 – 6.60 (m, 3H), 4.79 (s, 2H), 4.65 (s, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.34, 149.02, 136.69, 135.58, 135.45, 133.57, 129.37, 129.22, 128.82, 127.82, 126.90, 117.35, 112.58, 56.50, 55.44, 21.10.HRMS (ESI) m/z calcd for $C_{22}H_{22}NO^+$ $[M+H]^+$: 316.1696, found 316.1694.

2-(ethyl(phenyl)amino)-1-phenylethan-1-one (S-**5c**)



Prepared according to procedure **4-D:** 89% yield, white solid, m.p.: 89.0-90.6 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 7.96 (m, 2H), 7.64 – 7.57 (m, 1H), 7.53 – 7.45 (m, 2H), 7.22 – 7.14 (m, 2H), 6.68 (t, *J* = 7.27 Hz, 1H), 6.61 (d, *J* = 8.15 Hz, 2H), 4.73 (s, 2H), 3.49 (q, *J* = 7.10 Hz, 2H), 1.22 (t, *J* = 7.10 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.54, 148.04, 135.51, 133.49, 129.25, 128.81, 127.86, 116.74, 112.21, 56.76, 46.16, 12.49. HRMS (ESI) m/z calcd for $C_{16}H_{18}NO^+$ $[M+H]^+$: 240.1383, found 240.1382.

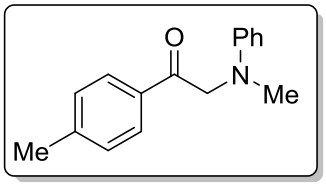
2-(methyl(phenyl)amino)-1-phenylethan-1-one (**S-5d**)



Prepared according to procedure **4-D:** 95% yield, white solid, m.p.: 111.9-113.0 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.95 (m, 2H), 7.54 – 7.44 (m, 2H), 7.25 – 7.14 (m, 2H), 6.76 – 6.64 (m, 3H), 4.77 (s, 2H), 3.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.47, 149.21, 135.49, 133.52, 129.20, 128.81, 127.81, 117.14, 112.31, 59.00, 39.57. HRMS (ESI) m/z calcd for $C_{15}H_{16}NO^+$ $[M+H]^+$: 226.1226, found

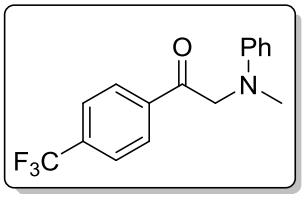
226.1225.

2-(methyl(phenyl)amino)-1-(p-tolyl)ethan-1-one (S-**5e**)



Prepared according to procedure **4-D:** 92% yield, white solid, m.p.: 89.8.0-91.6.0 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.02 Hz, 2H), 7.27 (d, *J* = 8.03 Hz, 2H), 7.22 – 7.15 (m, 2H), 6.74 – 6.62 (m, 3H), 4.72 (s, 2H), 3.08 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.10, 149.29, 144.41, 133.01, 129.49, 129.20, 127.94, 117.02, 112.27, 58.86, 39.59, 21.76. HRMS (ESI) m/z calcd for $C_{16}H_{18}NO^+$ $[M+H]^+$: 240.1383, found 240.1384.

2-(methyl(phenyl)amino)-1-(4-(trifluoromethyl)phenyl)ethan-1-one (**S-5f**)



Prepared according to procedure **4-D:** 92% yield, white solid, m.p.: 86.0-88.0 ^{o}C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 8.13 Hz, 2H), 7.76 (d, *J* = 8.24 Hz, 2H), 7.28 – 7.17 (m, 2H), 6.82 – 6.62 (m, 3H), 4.76 (s, 2H), 3.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.95, 148.97, 138.08, 134.80 (d, *J* = 32.69 Hz), 129.29, 128.21, 125.89 (q, *J* = 3.75 Hz), 123.51 (d, *J* = 272.91 Hz), 117.51, 112.42, 59.37, 39.58. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.19.HRMS (ESI) m/z calcd for $C_{16}H_{15}F_3NO^+$ $[M+H]^+$: 294.1100, found 294.1100.

Reference:

[1] a)T. Slagbrand, H. Lundberg, H. Adolfsson, *Chem. Eur. J.* **2014**, 20, 16102 – 16106; b) A. Bugarin, K. D. Jones, B. T. Connell, *Chem. Commun.* **2010**, 46, 1715-1717.

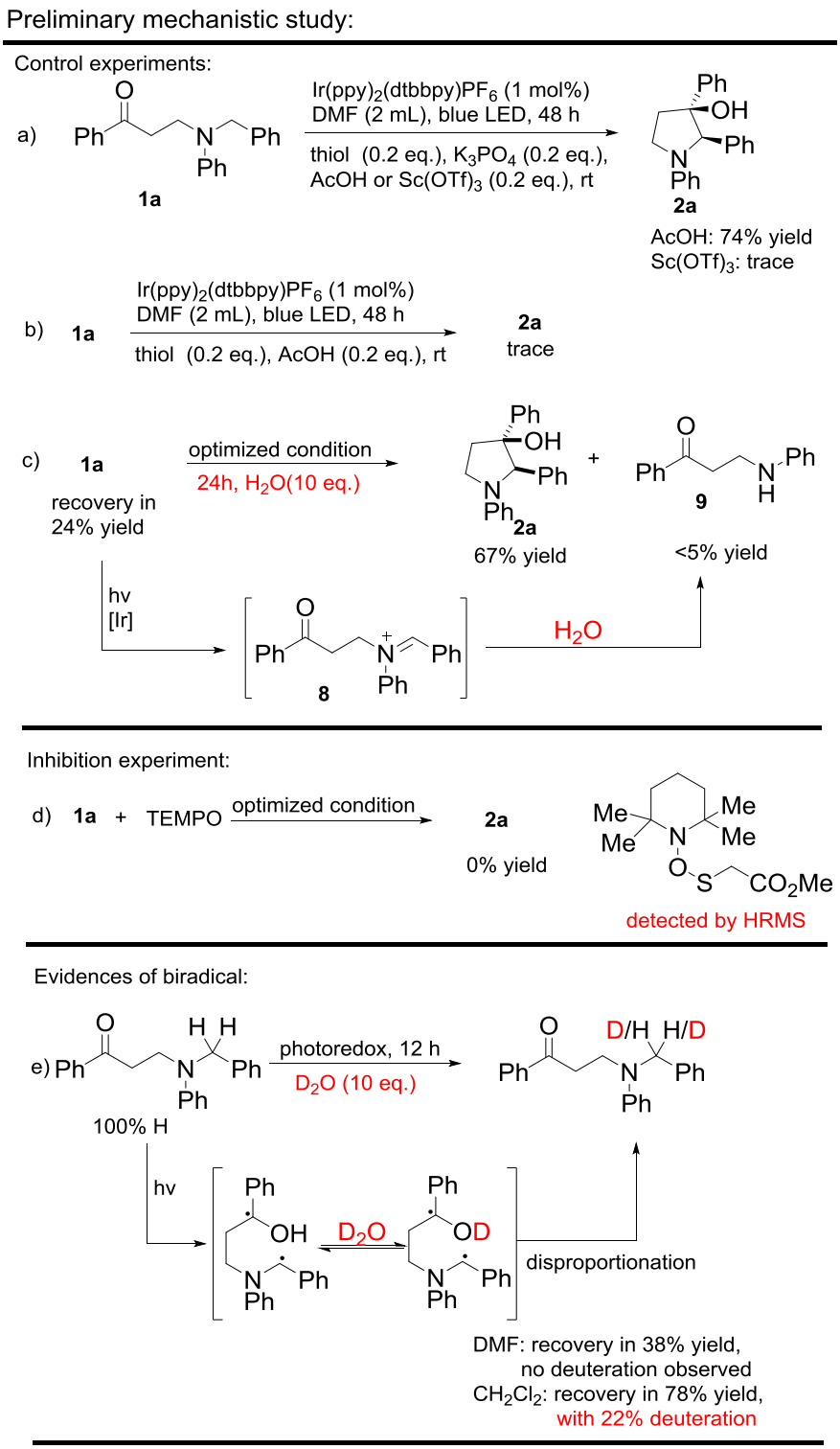
[2] W. Wei, X. Dong, S. Nie, Y. Chen, X. Zhang, M. Yan, *Org. Lett.* **2013**,15, 6018-6021.

[3] A. Bunrit, C. Dahlstrand, S. K. Olsson, P. Srifa, G. Huang, A. Orthaber, P. J. R. Sjöberg, S. Biswas, F. Himo, J. S. M. Samec, *J. Am. Chem. Soc.*, **2015**, 137,4646–4649.

5. Preliminary mechanistic study:

To better understand the reaction process, we conducted a series of tested experiments (Scheme 1). Treatment of **1a** with 0.2 eq. K_3PO_4 and 0.2 eq. AcOH afforded product **2a** in 74% yield (*vs* 7% yield with only K_3PO_4). However, replacement of AcOH by Lewis acid $Sc(OTf)_3$ lead to no conversion (Scheme 1-a). These experiments indicated that proton may play an important role in the reaction. This finding implied that a proton-coupled

electron transfers (PCET) process may be involved in the reaction pathway.[4] Further experiments also indicated the necessity of base to generate more reductive thiol anion (Scheme 1-b).[5] With 10 eq. H_2O added in reaction system, 67% yield of **2a** could be obtained in 24h, and only trace mount of hydrolysis product 9 was detected (Scheme 1-c). This result indicated that iminium **8** was not the main reaction intermediate, which ruled out the nucleophilic cyclization pathway via the addition of ketyl to iminium.[4b] Radical inhibitor TEMPO significantly inhibited the cyclization reaction. The generation of thiyl radical was experimentally demonstrated by trapping the thiyl radical with TEMPO (Scheme 1-d). The biradical intermediate prefers to go through a disproportionation process in nonpolar solvent. But in strong polar solvent, the hydroxyl (OH) of biradical intermediate forms hydrogen bond with solvent molecule which selectively prevents the disproportionation reaction.[6] Then we subjected **1a** to optimized condition with an addition of 10 eq. D_2O and recovered **1a** after 12 hours. With DCM as solvent, 22% deuteration was detected at benzyl position while no deuteration was observed in DMF. This result implied the existence of biradical intermediate in catalytic process (Scheme 1-e).



Scheme 1. Mechanistic investigation of the radical-radical coupling reaction.

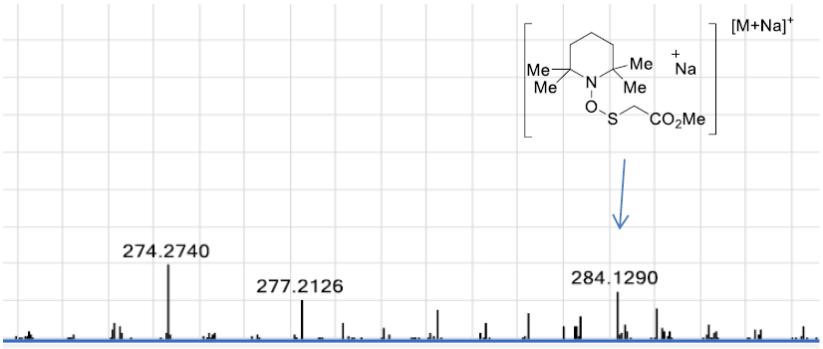
Generally procedure of control experiments:

The control experiments were performed according *procedure* ***3-A*** mentioned above in 0.2 mmol scale.

Generally procedure for inhibition experiments:

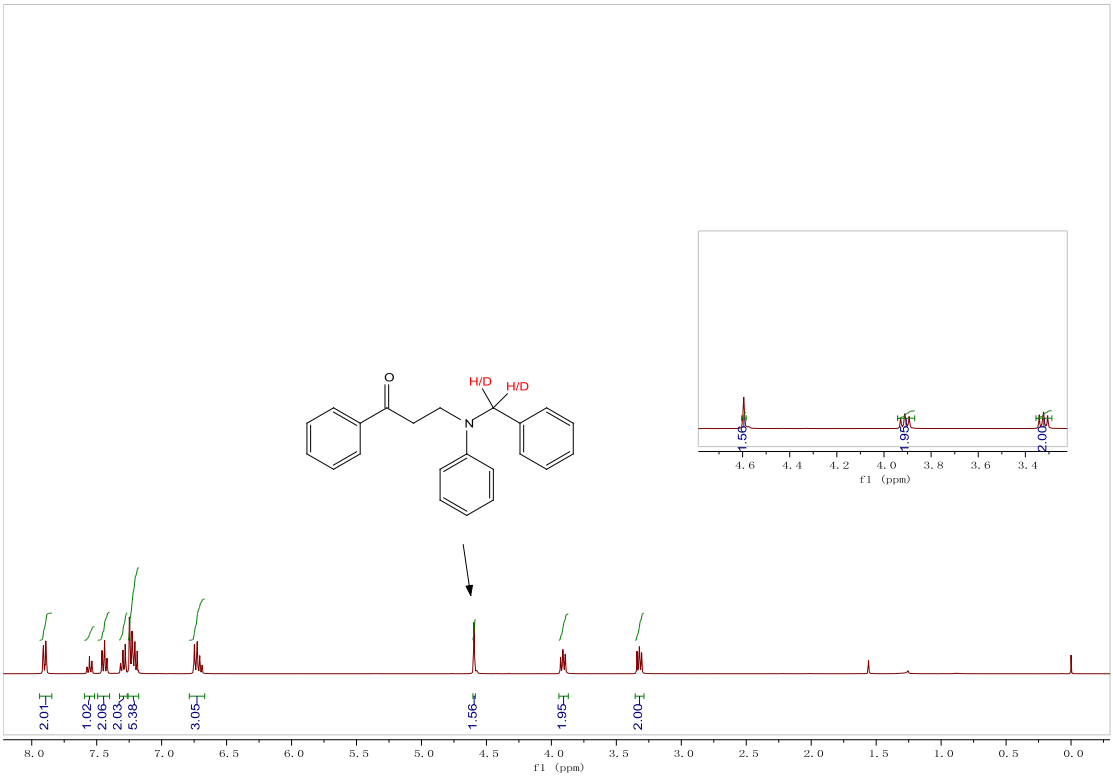
A 10 mL Schlenk-tube equipped with magnetic stirring bar was charged with substrate **1a**(0.2 mmol), TEMPO (0.2 mmol), $Ir(ppy)_2(dtbbpy)PF_6$(1 mol%), K_2HPO_4

(20 mol%), methyl thioglycolate (20 mol%), DMF (2 mL), the resulting mixture was evacuated and backfilled with argon by "pump-freeze-thaw" cycles (3 times). The tube was irradiated by a 5 W cyclized blue LED trip. The reaction was monitored by TLC after 24h, and no reaction occurred. Then the reaction was stopped and detected the mixture by HRMS.



Generally procedure of deuteration experiments:

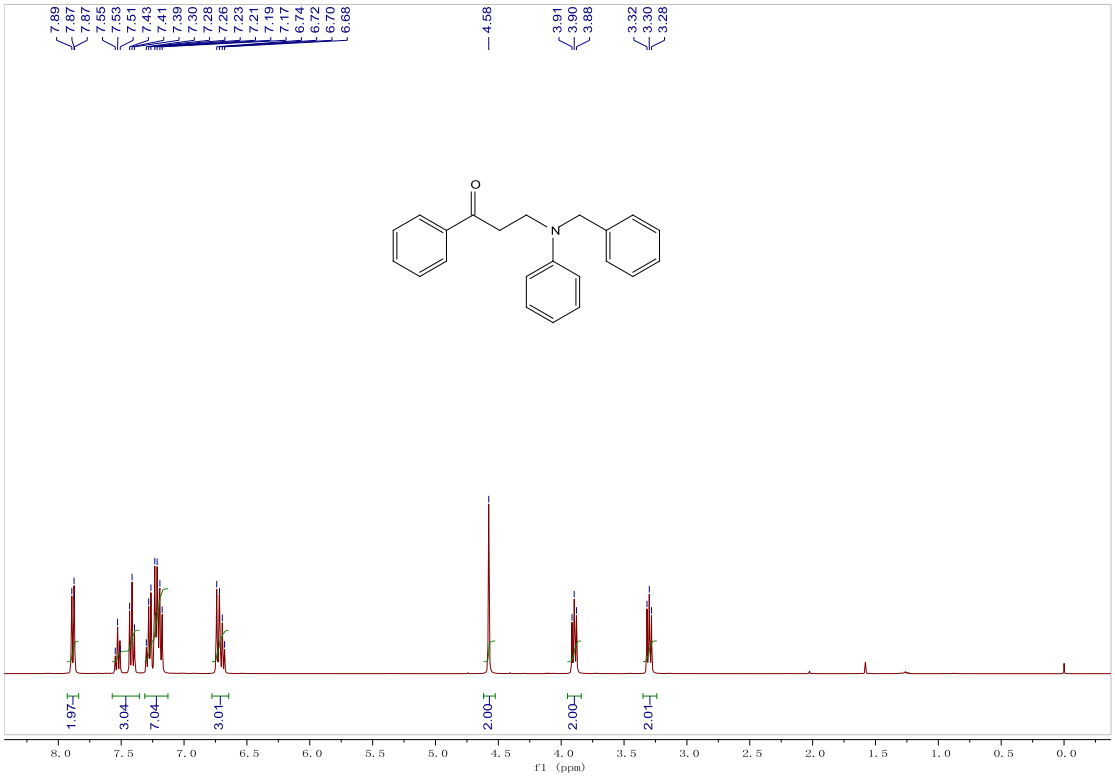
A 10 mL Schlenk-tube equipped with magnetic stirring bar was charged with substrate **1a**(0.1 mmol), $Ir(ppy)_2(dtbbpy)PF_6$(1 mol%), K_2HPO_4 (20 mol%), methyl thioglycolate (20 mol%), D_2O (1 mmol), solvent (DCM or DMF, 1 mL), the resulting mixture was evacuated and backfilled with argon by "pump-freeze-thaw" cycles (3 times). The tube was irradiated by a 5 W cyclized blue LED trip and stopped after 12 h. The reaction mixture was transferred to separating funnel, 10 mL saturated brine was added and exacted with Et_2O (2× 5 mL). The combined organic layers was dried over Na_2SO_4 and purified by flash column chromatography to recover substrate **1a**.

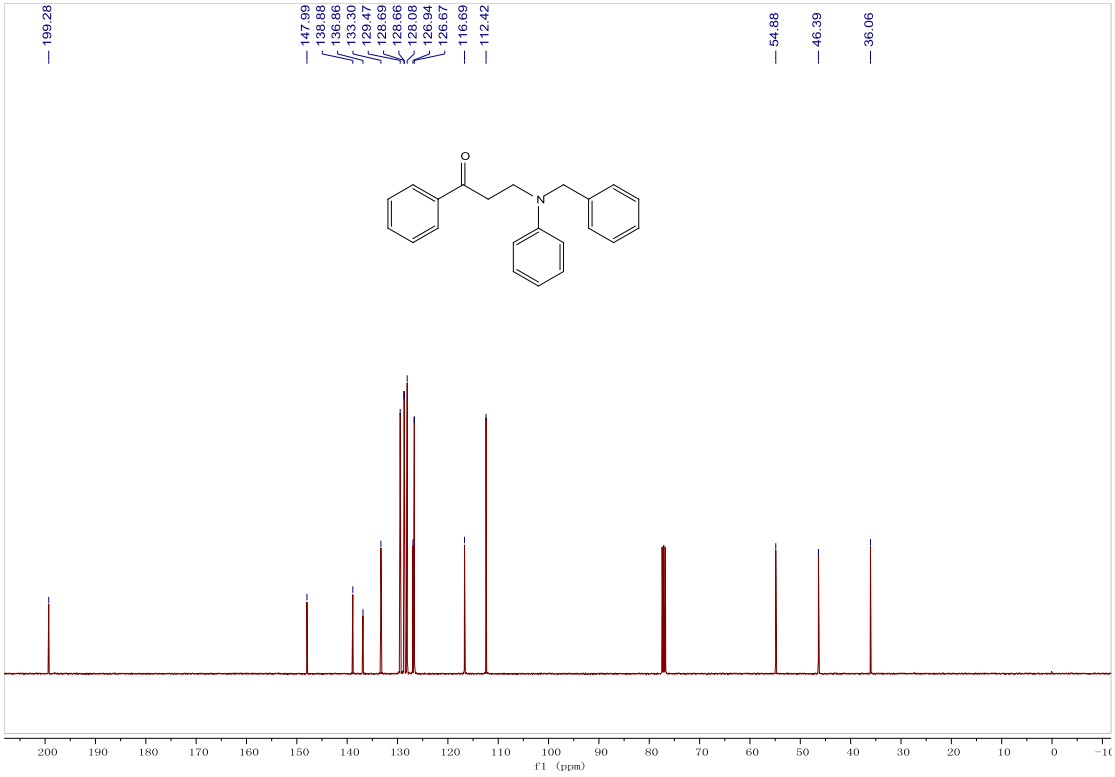


[4] a) K. T. Tarantino, P. Liu and R. R. Knowles, *J. Am. Chem. Soc.*, 2013, **135**, 10022; b) L. J. Rono, H. G. Yayla, D. Y. Wang, M. F. Armstrong and R. R. Knowles, *J. Am. Chem. Soc.*, **2013**, ***135***, 17735.
[5] a) K. Qvortrup, D. A. Rankic and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2014, **136**, 626; b) D. Hager and D. W. C. MacMillan, *J. Am. Chem. Soc.*, **2014**, ***136***, 16986.
[6] a) P. J. Wagner, P. A. Kelso, R. G. Zepp, *J. Am. Chem. Soc.* **1972**, 94, 7480-7488; b) N. J. Turro, V.Ramamurthy, J. C. Scaiano, *Modern molecular photochemistry of organic molecules,* Photochemistry & Photobiology, **2012**.

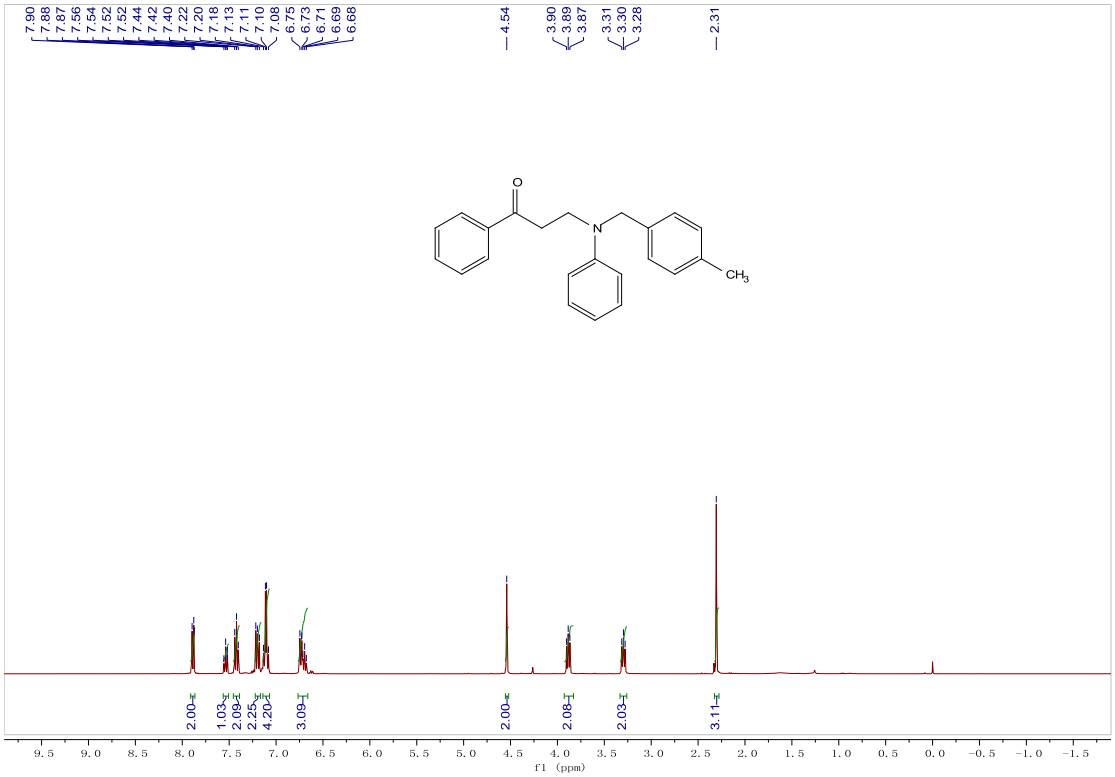
6. NMR-Spectra of substrates

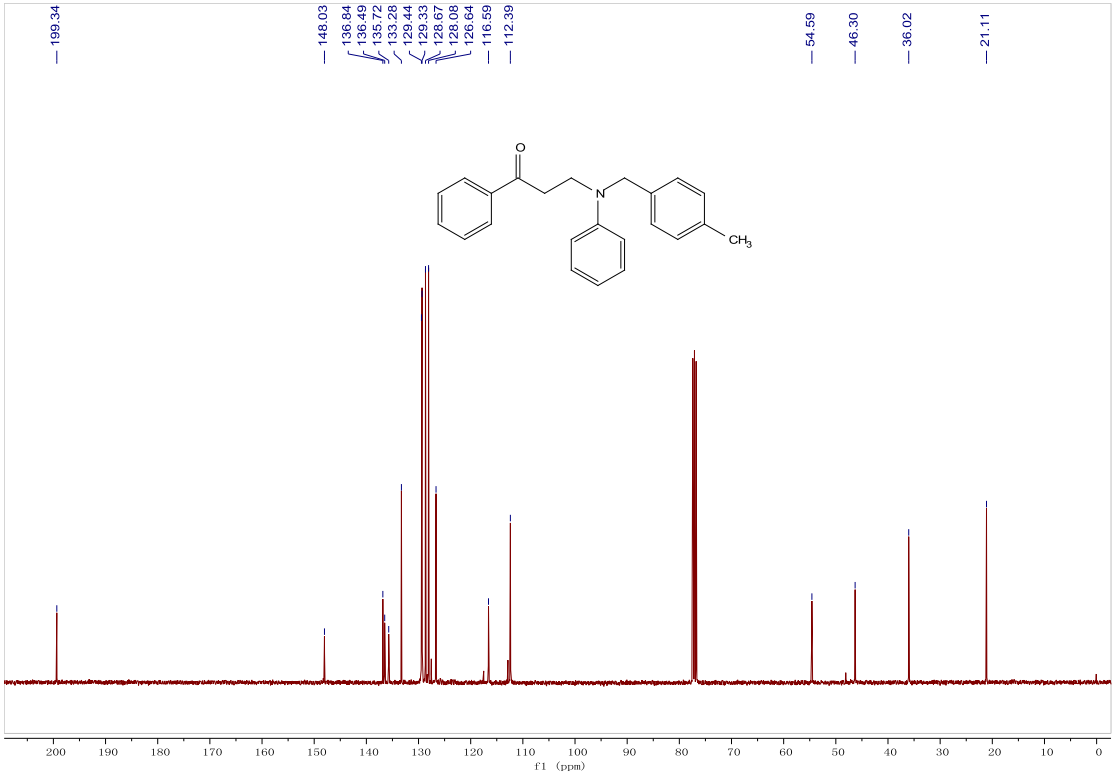
3-(benzyl(phenyl)amino)-1-phenylpropan-1-one (**1a**)



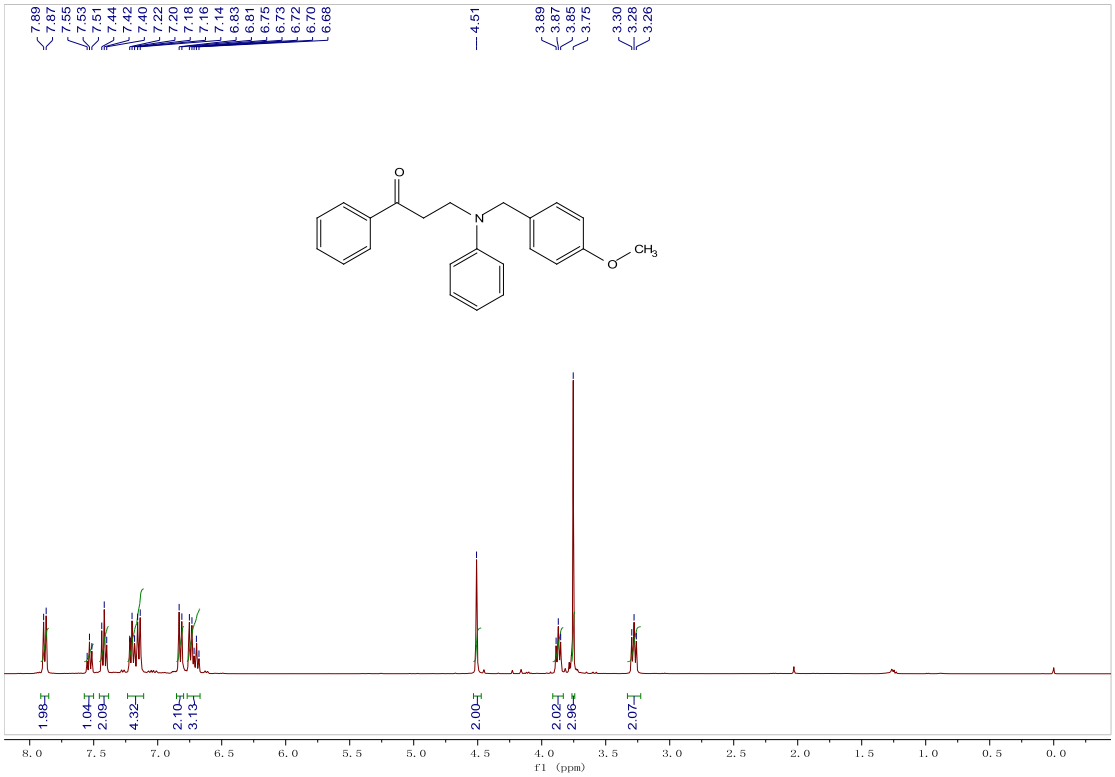


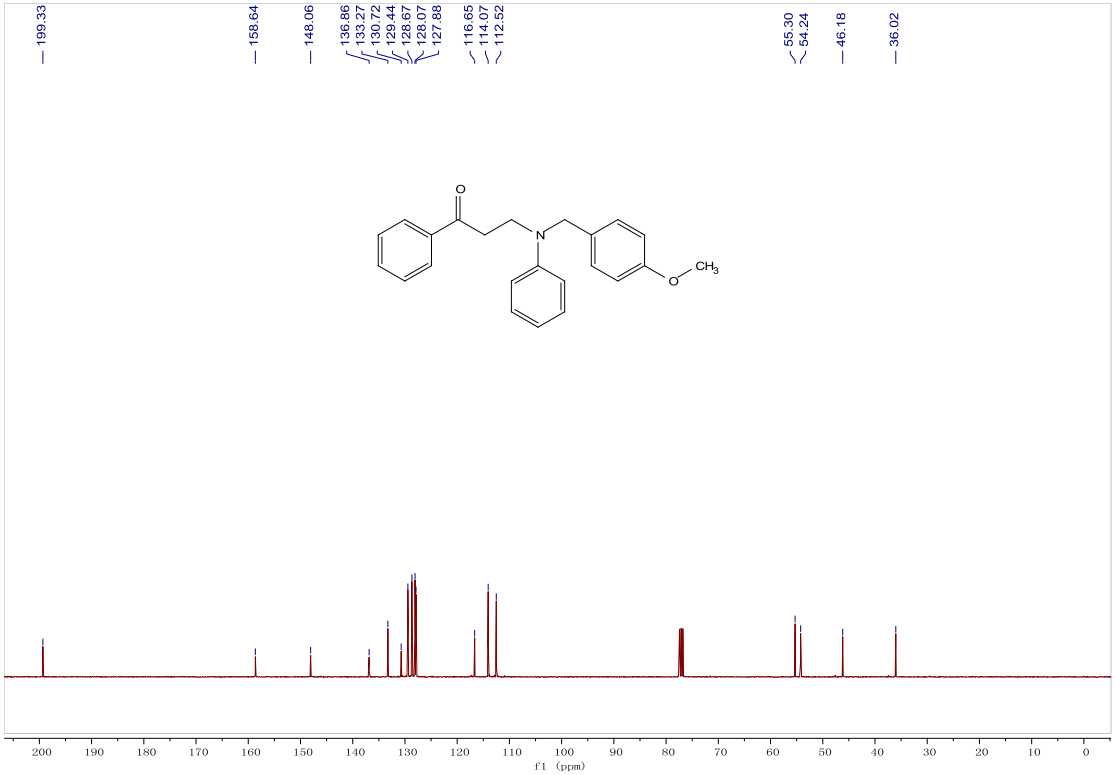
3-((4-methylbenzyl)(phenyl)amino)-1-phenylpropan-1-one (**1b**)



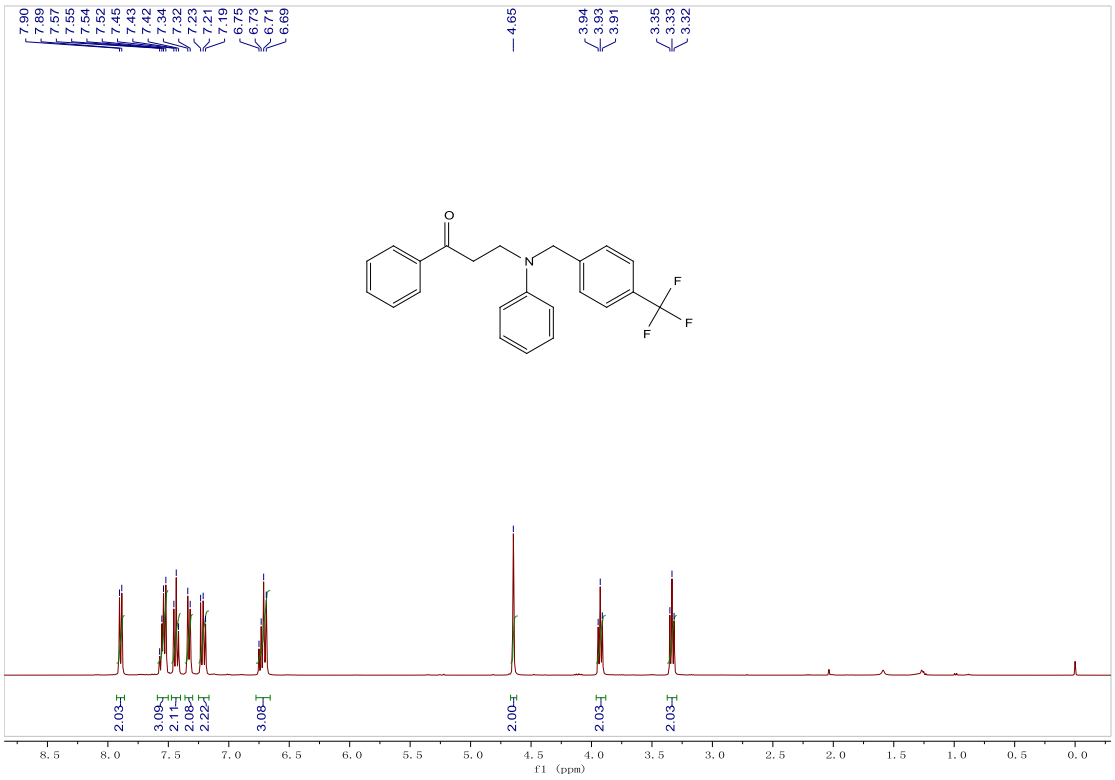


3-((4-methoxybenzyl)(phenyl)amino)-1-phenylpropan-1-one (**1c**)





1-phenyl-3-(phenyl(4-(trifluoromethyl)benzyl)amino)propan-1-one (**1d**)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7.43
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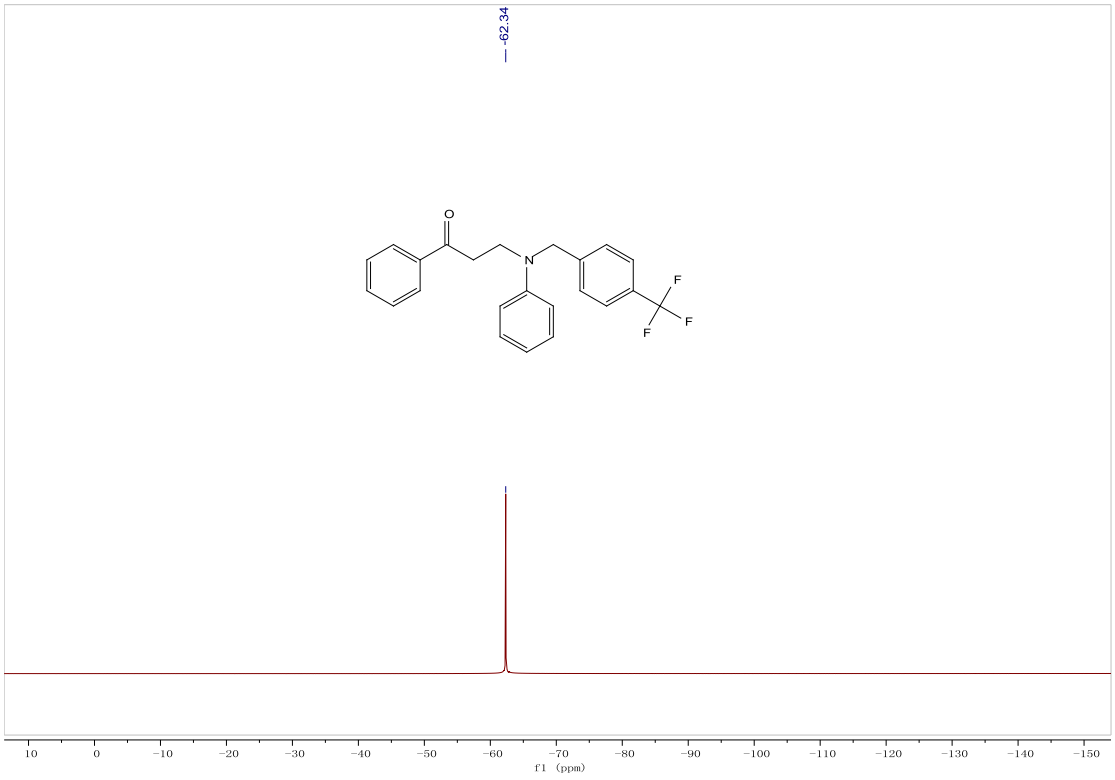
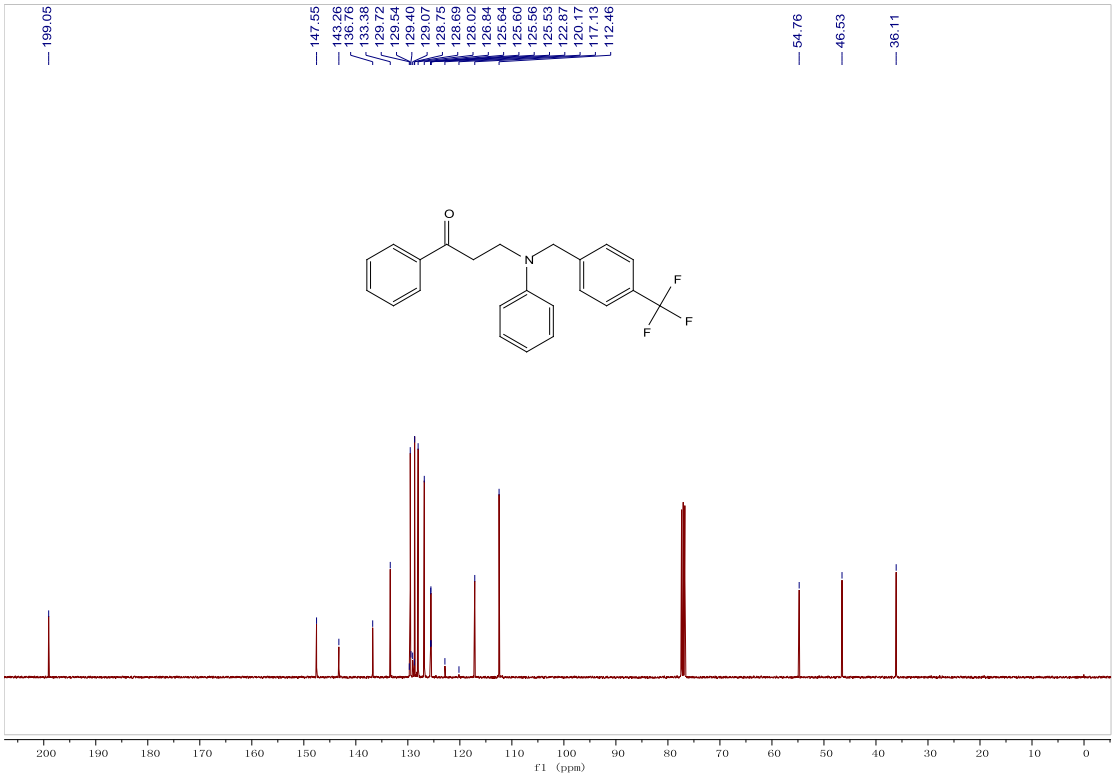
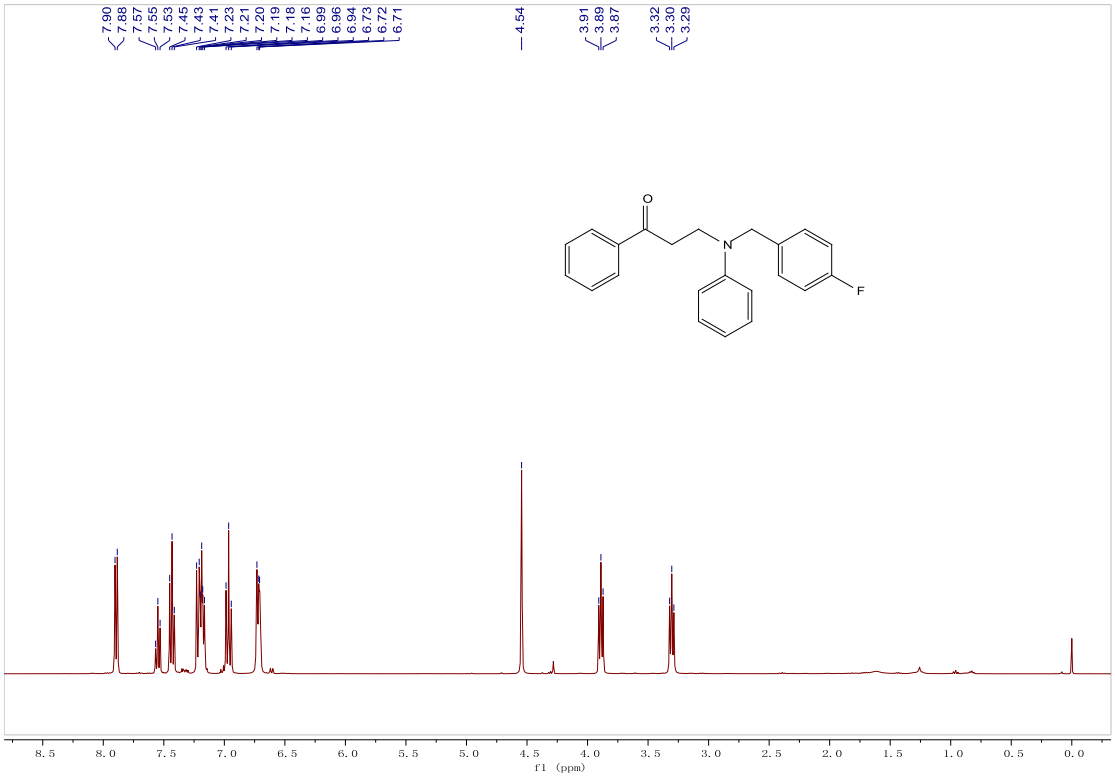
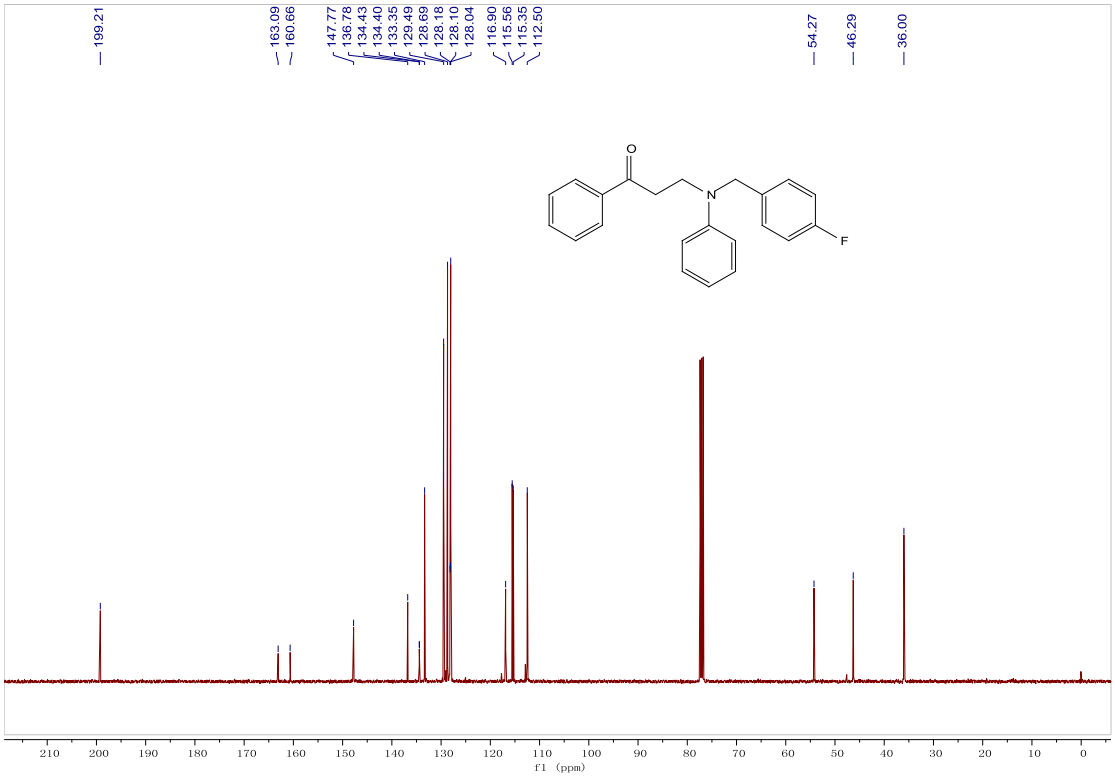
7.34
7.32
7.23
7.21
7.19
6.75
6.73
6.71
6.69
4.65
3.94
3.93
3.91
3.35
3.33
3.32
O
N
F
F
F
2.03
3.09
2.11
2.08
2.22
3.08
2.00
2.03
2.03
f1 (ppm)


-62.34
O
N
F
F
F
f1 (ppm)



3-((4-fluorobenzyl)(phenyl)amino)-1-phenylpropan-1-one (**1e**)

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128.18
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128.04
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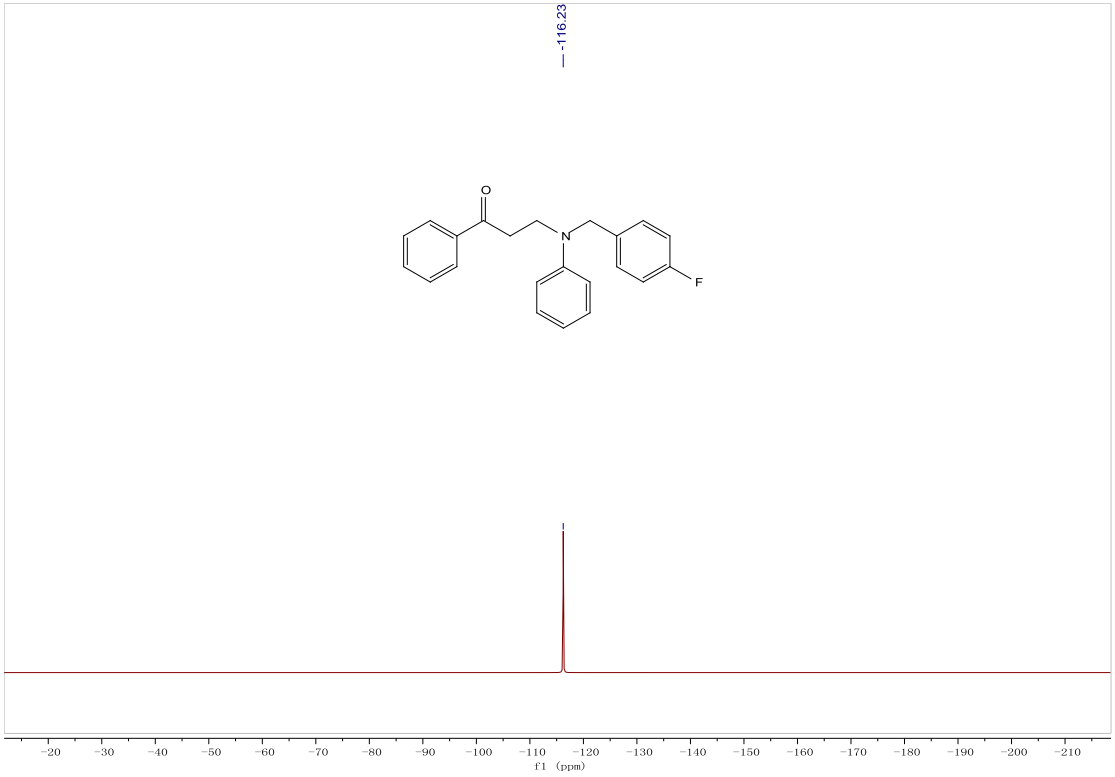
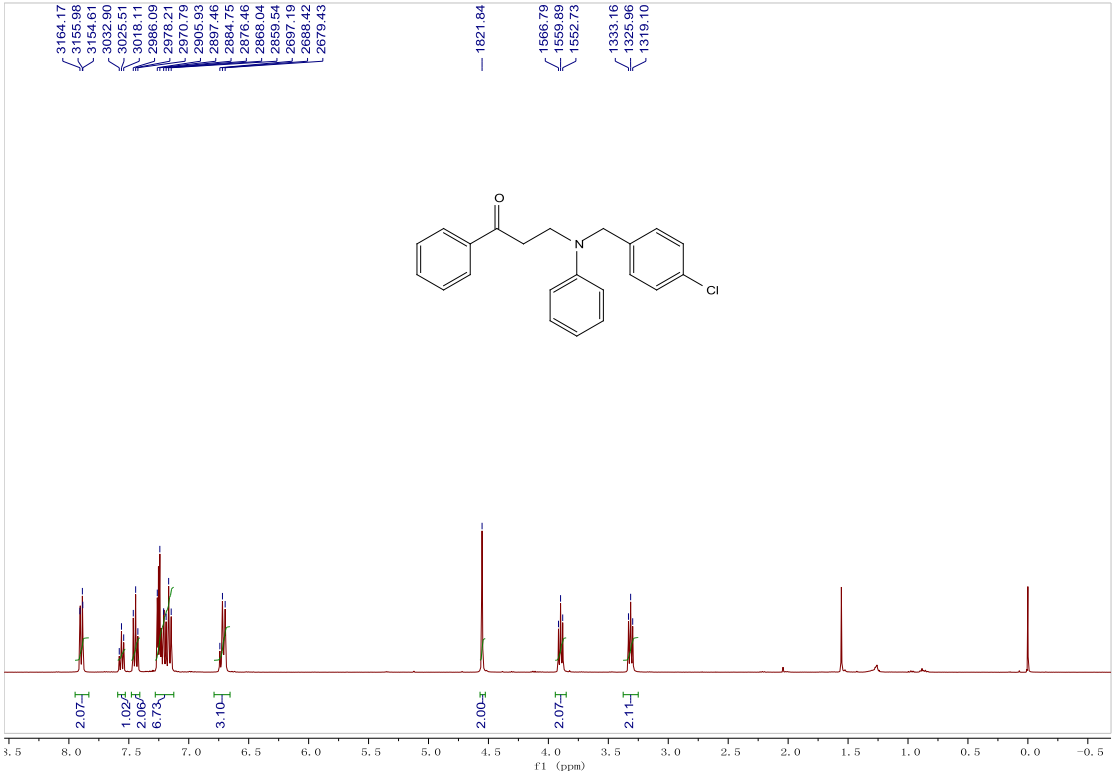
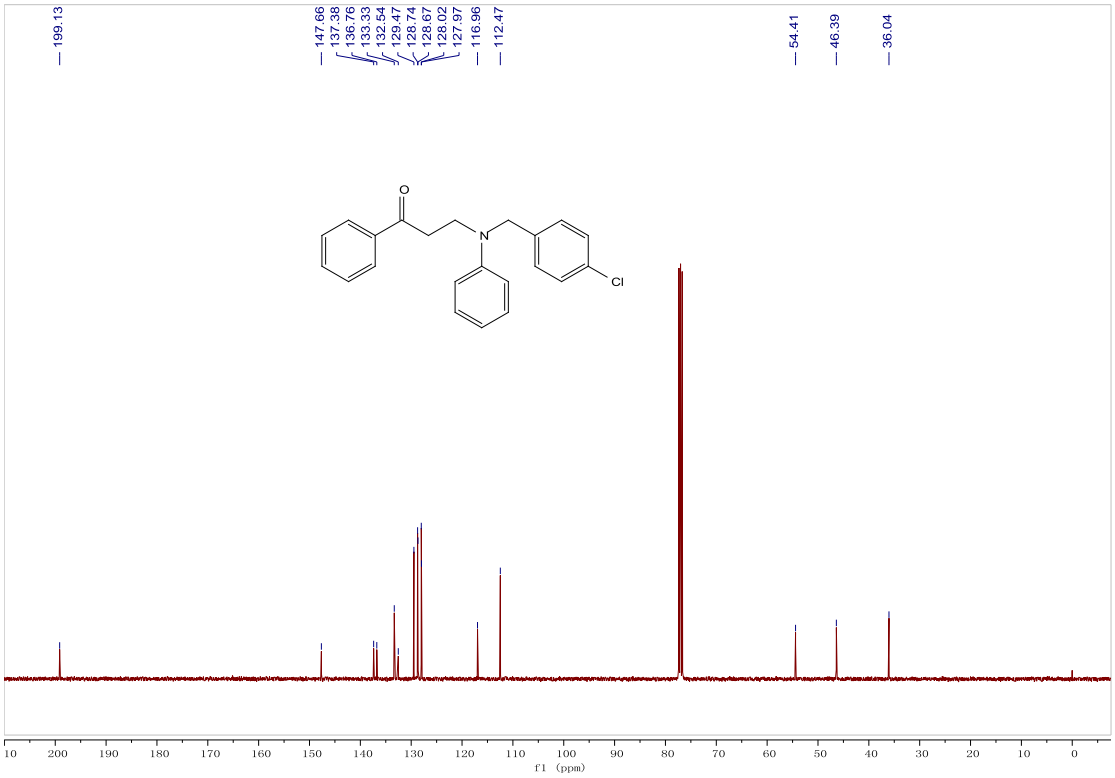
115.56
115.35
112.50
54.27
46.29
36.00
O
N
F
f1 (ppm)

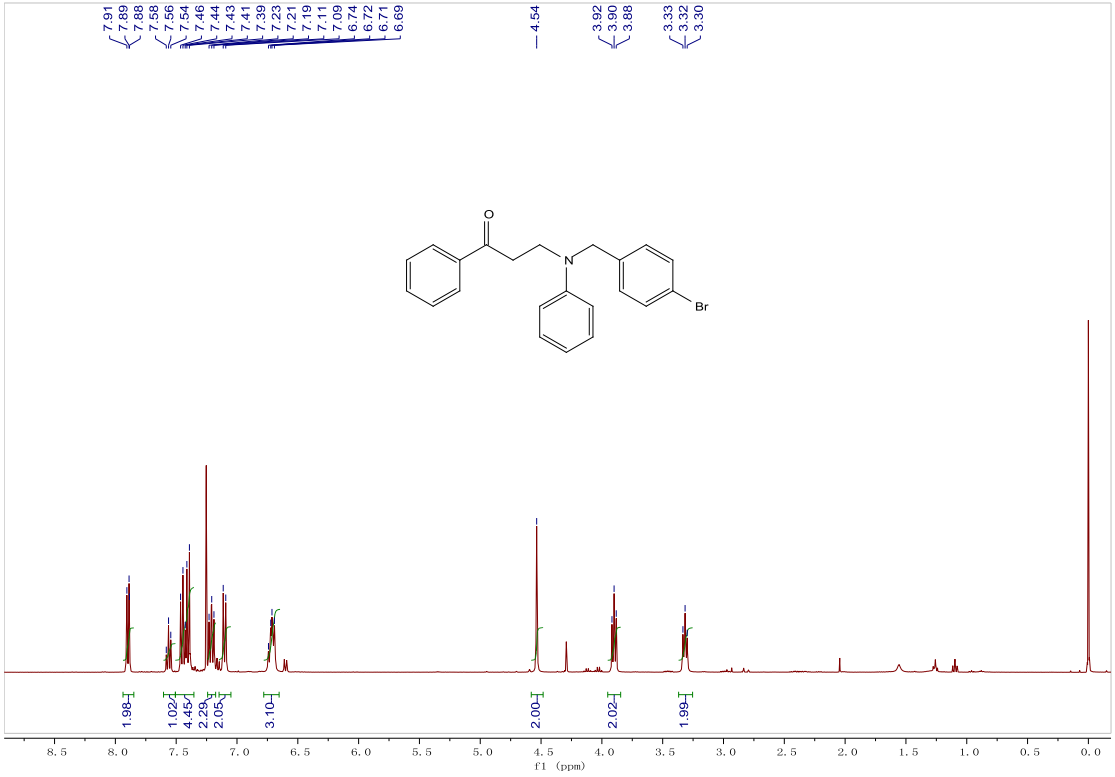

-116.23
O
N
F
f1 (ppm)

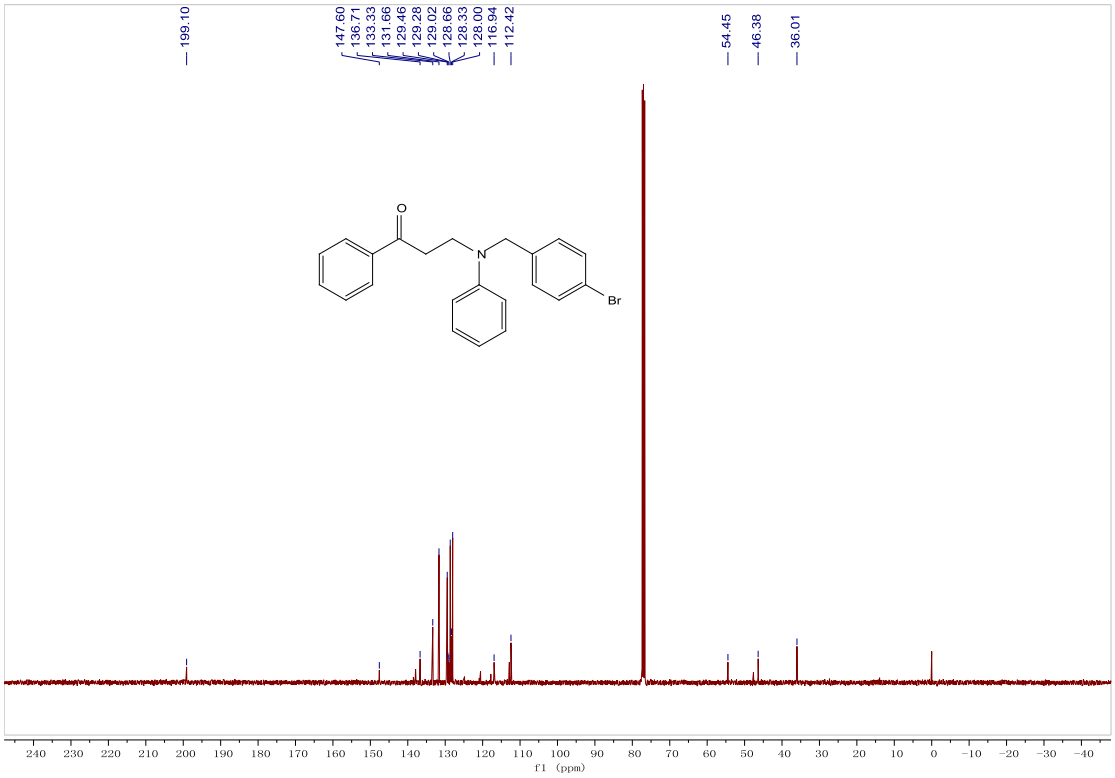
3-((4-chlorobenzyl)(phenyl)amino)-1-phenylpropan-1-one (**1f**)



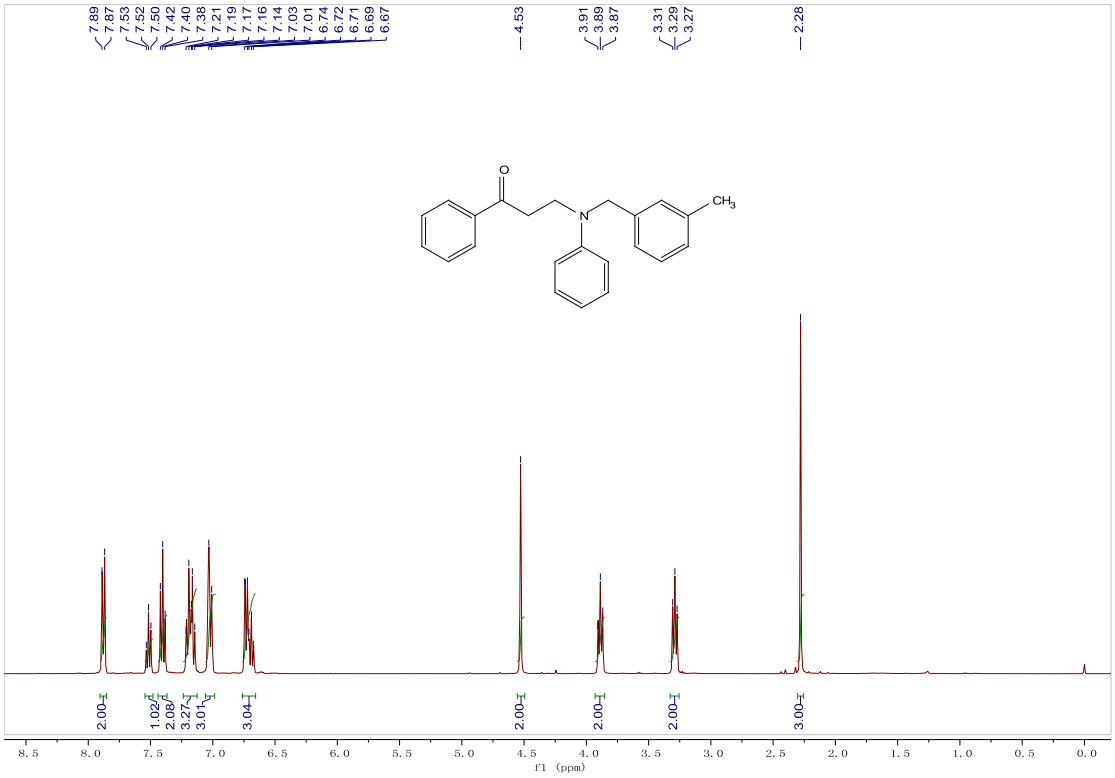


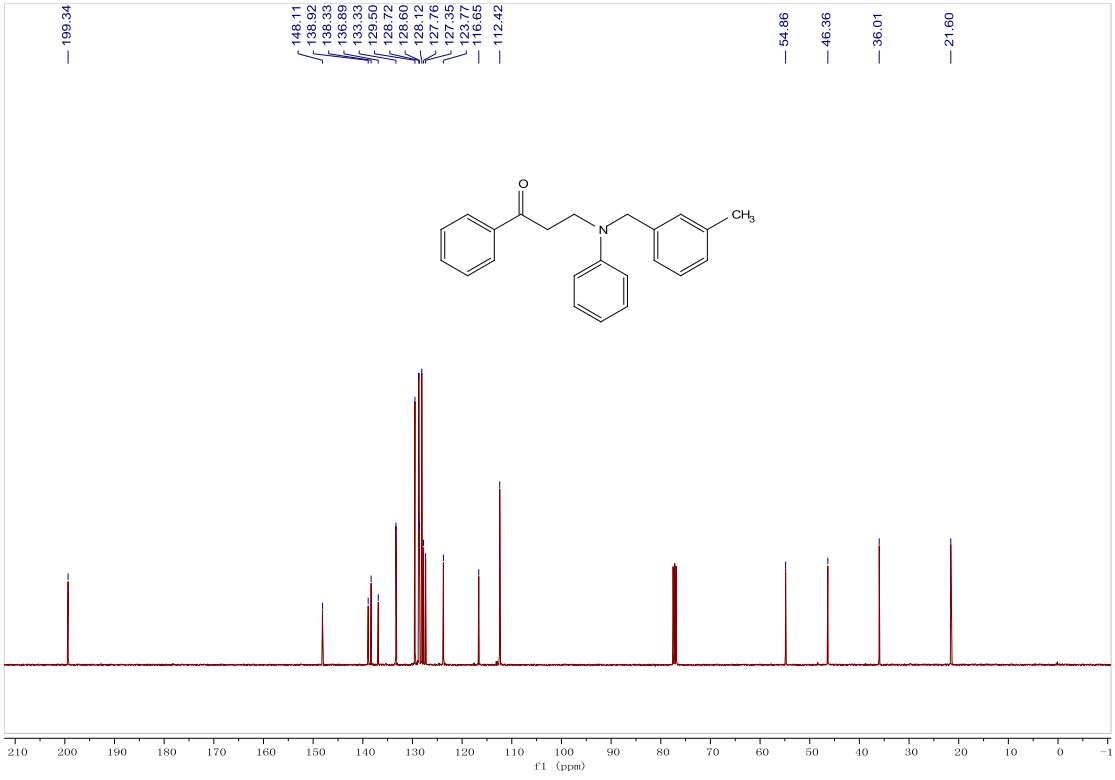
3-((4-bromobenzyl)(phenyl)amino)-1-phenylpropan-1-one (**1g**)



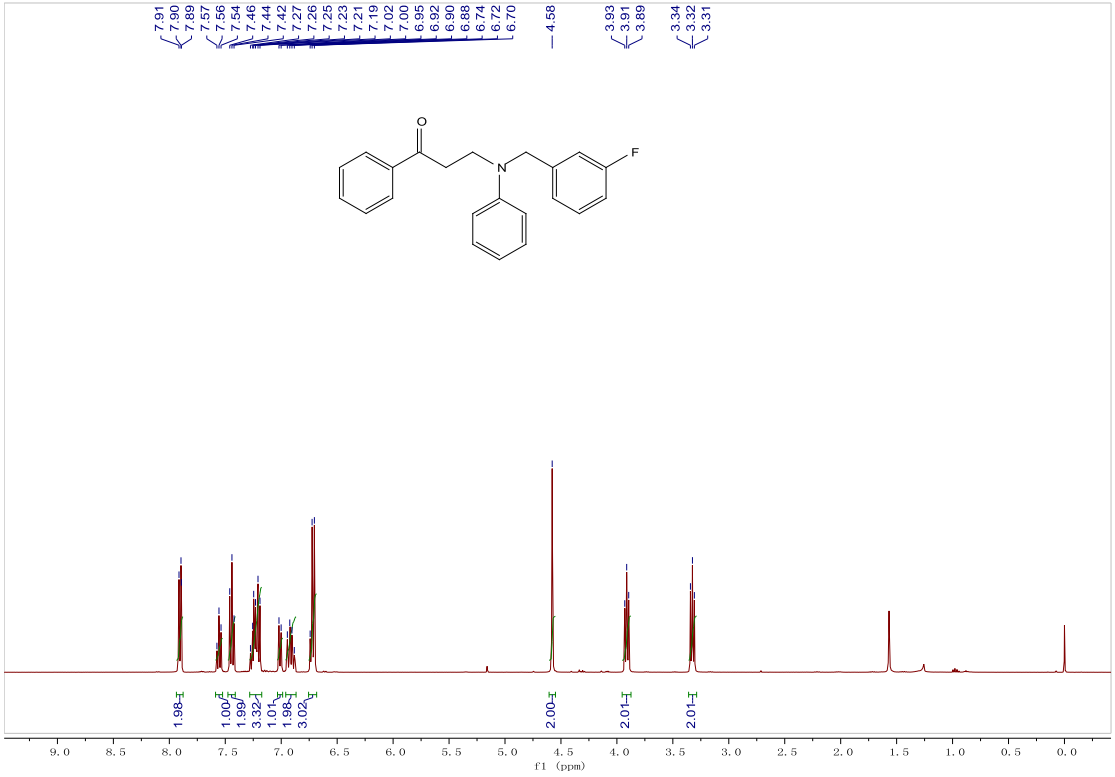


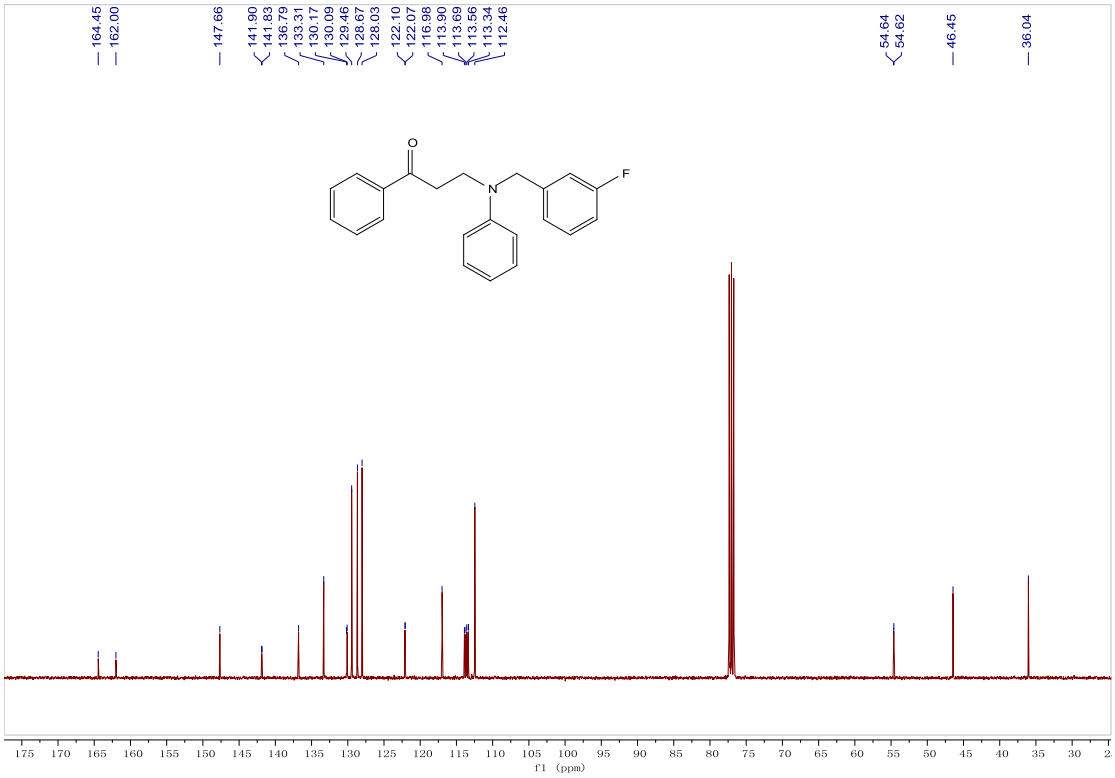
3-((3-methylbenzyl)(phenyl)amino)-1-phenylpropan-1-one (**1h**)

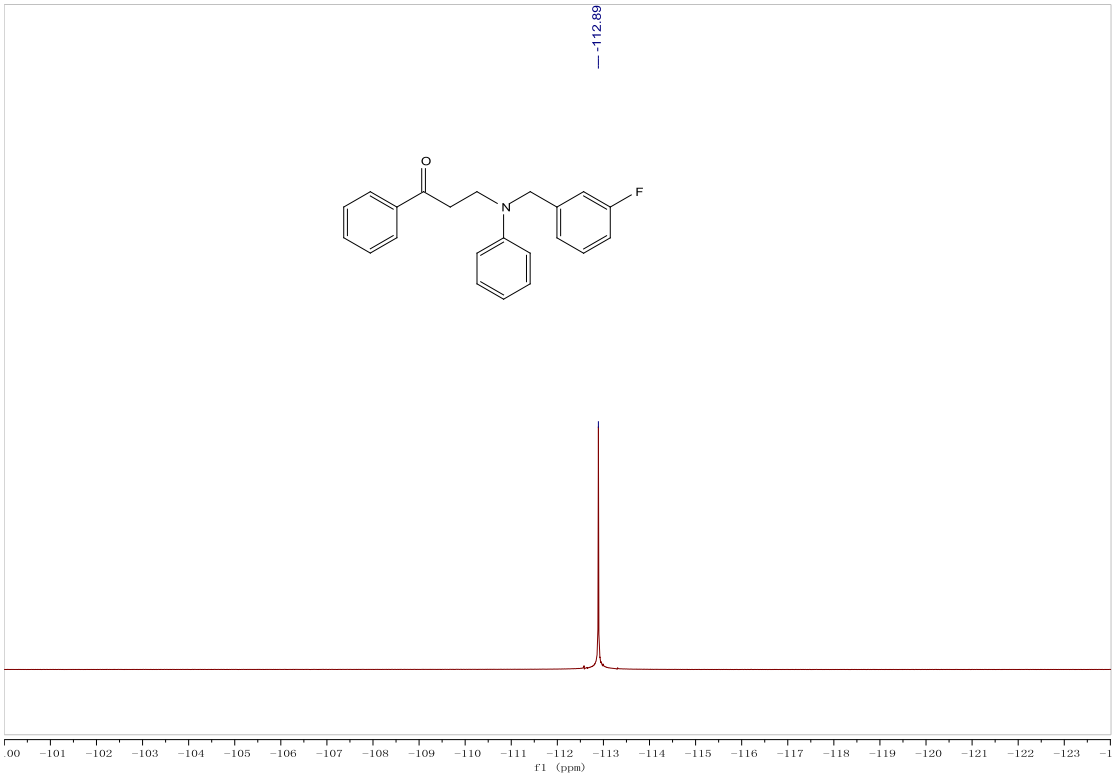




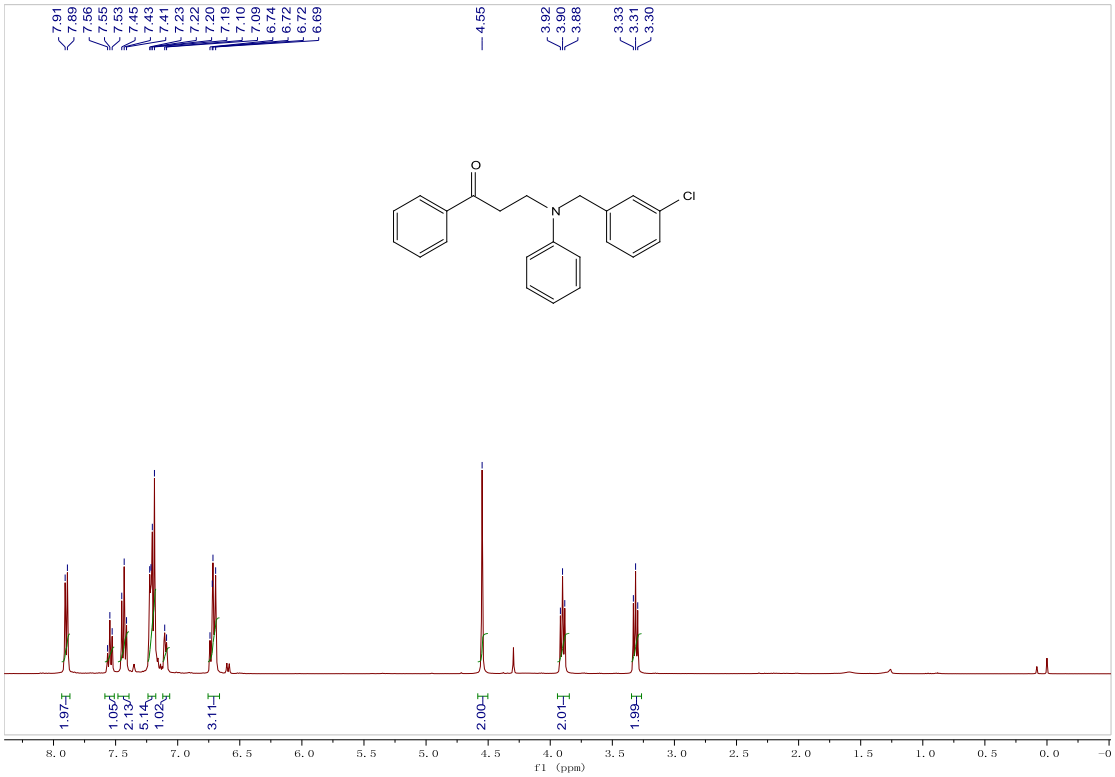
3-((3-fluorobenzyl)(phenyl)amino)-1-phenylpropan-1-one (**1i**)

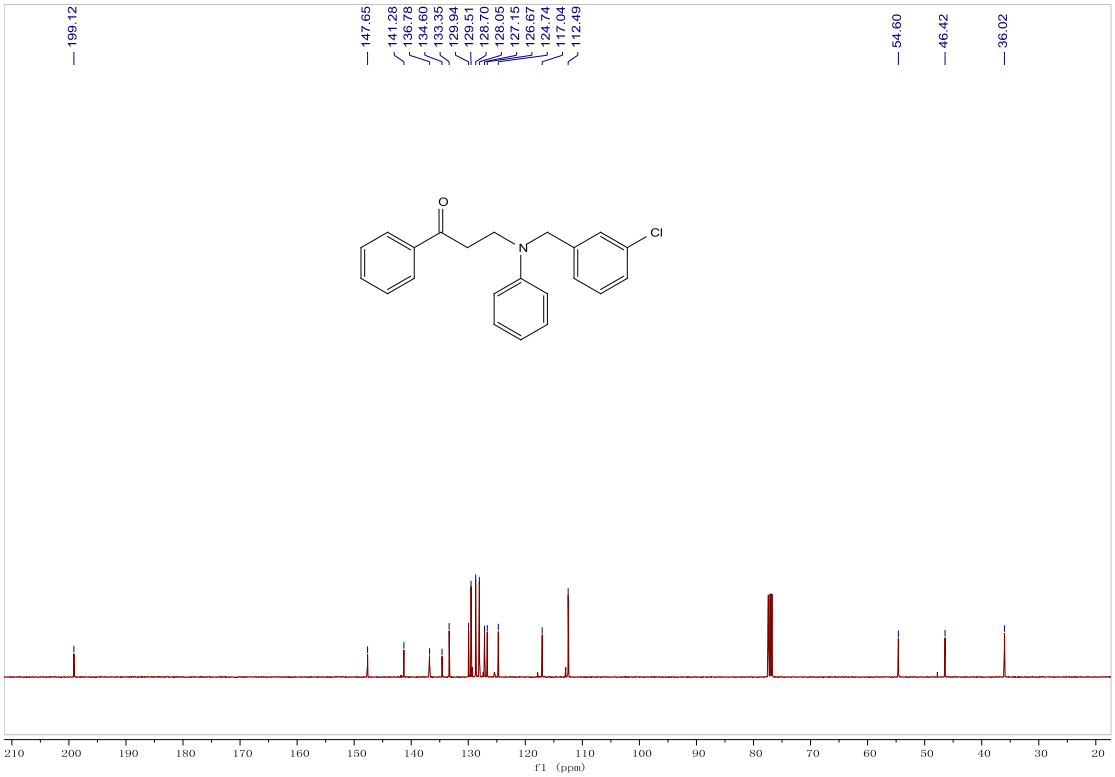




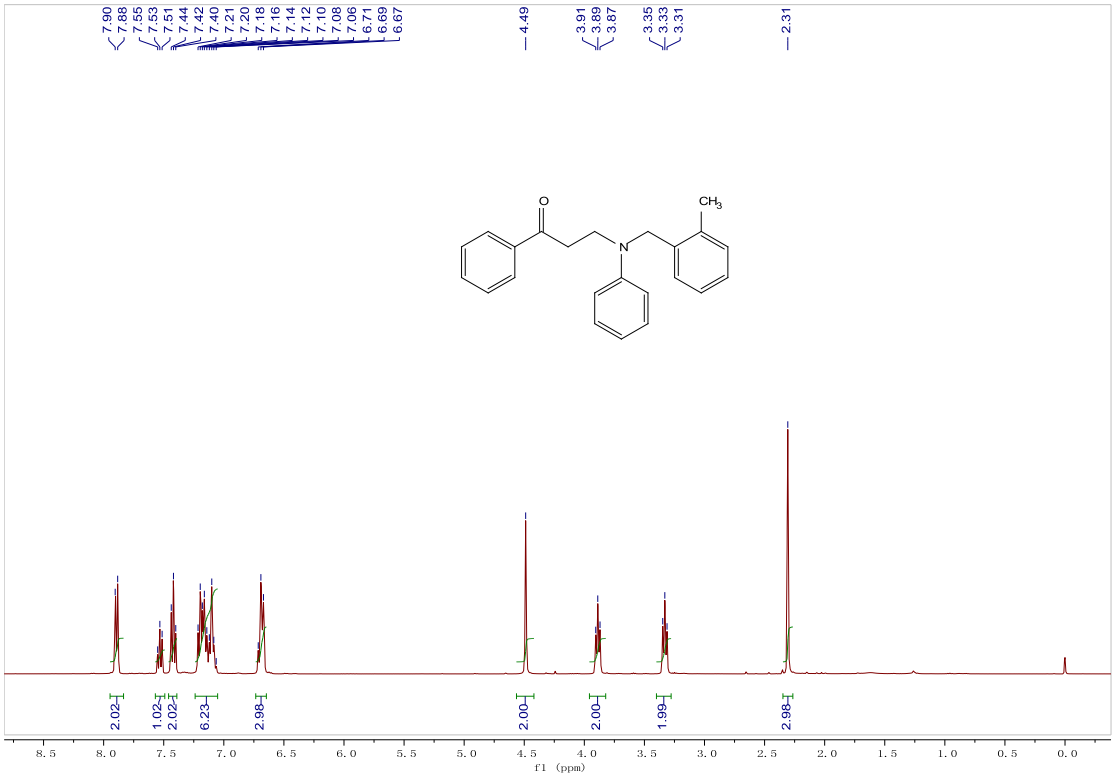


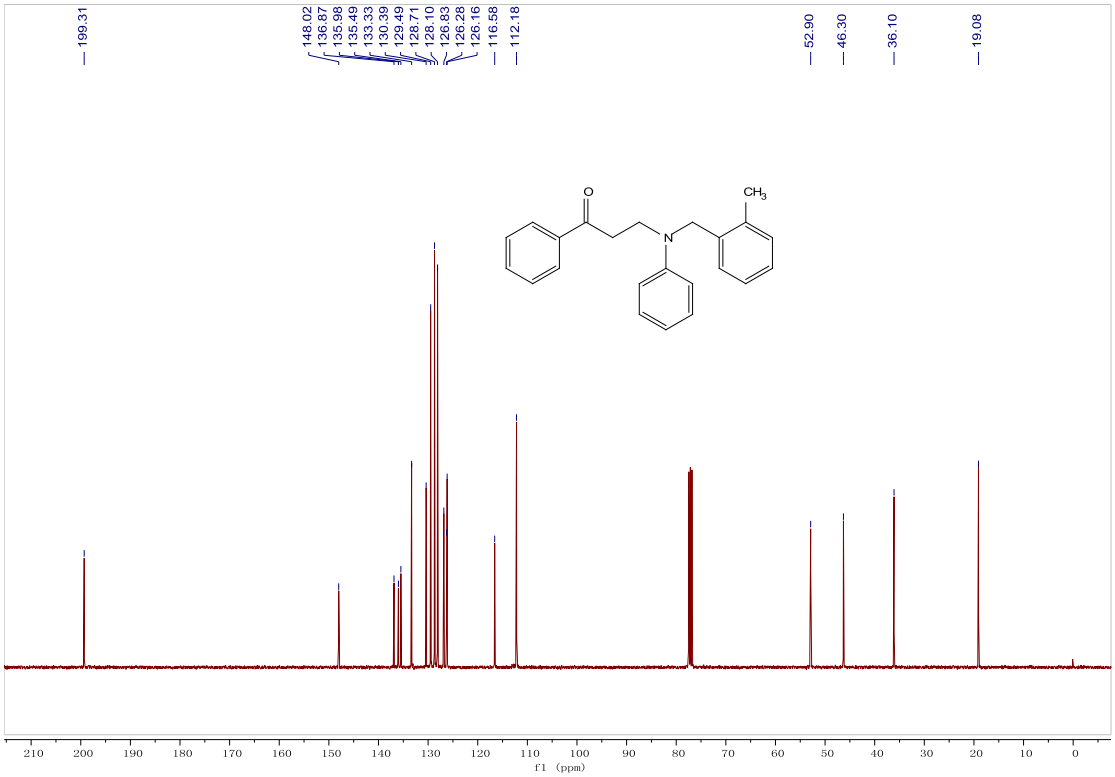
3-((3-chlorobenzyl)(phenyl)amino)-1-phenylpropan-1-one (**1j**)



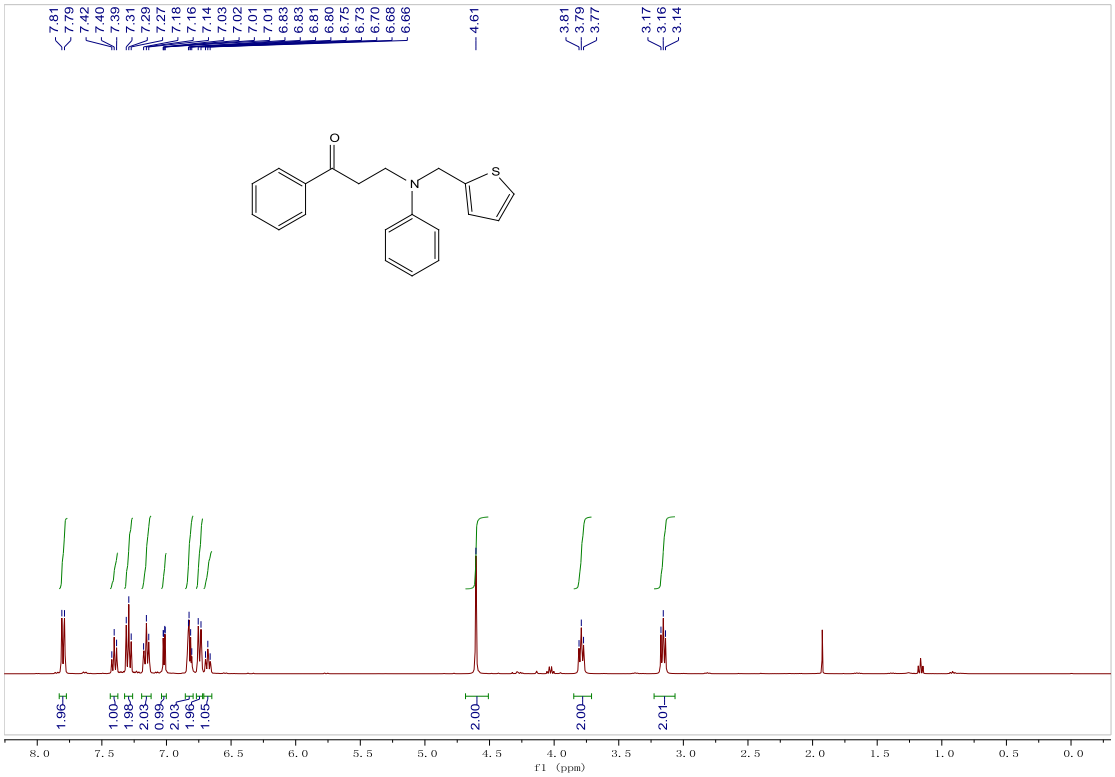


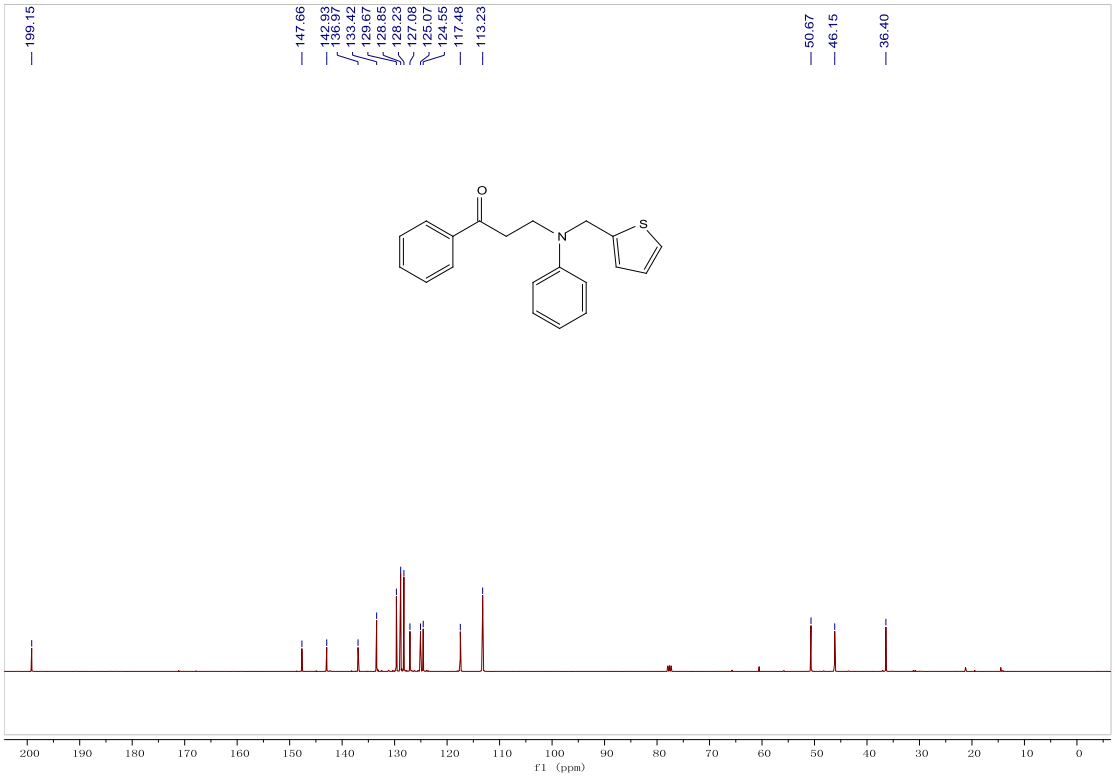
3-((2-methylbenzyl)(phenyl)amino)-1-phenylpropan-1-one (**1k**)



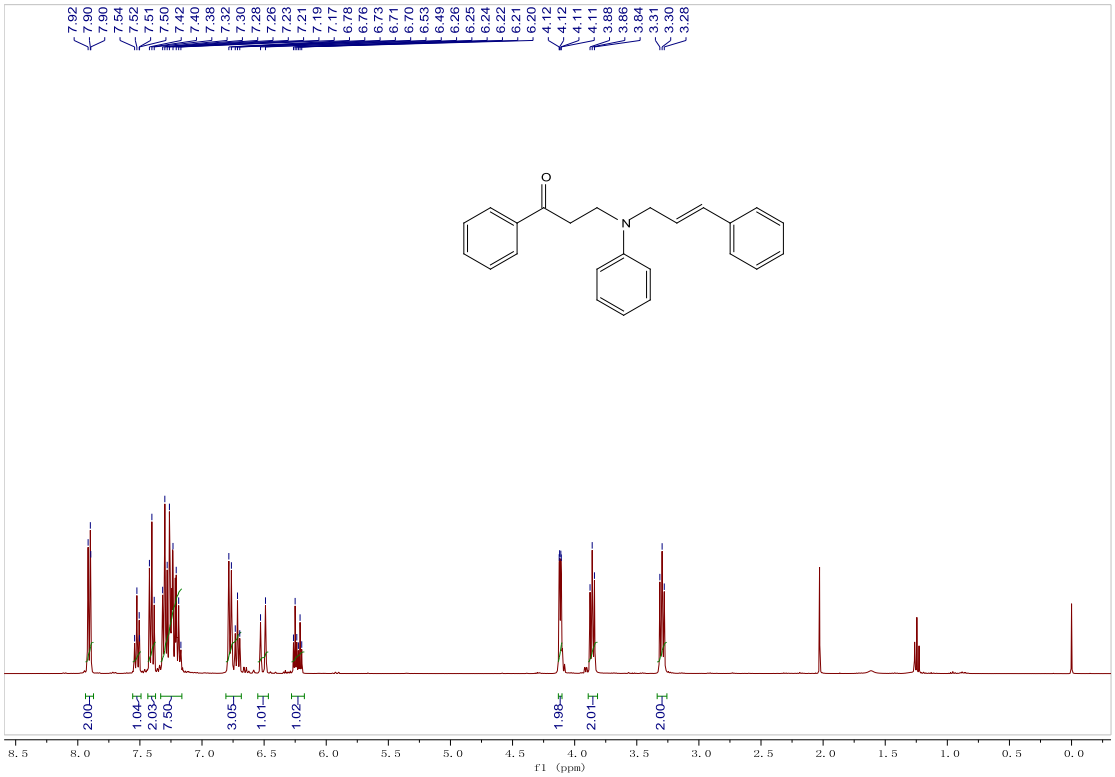


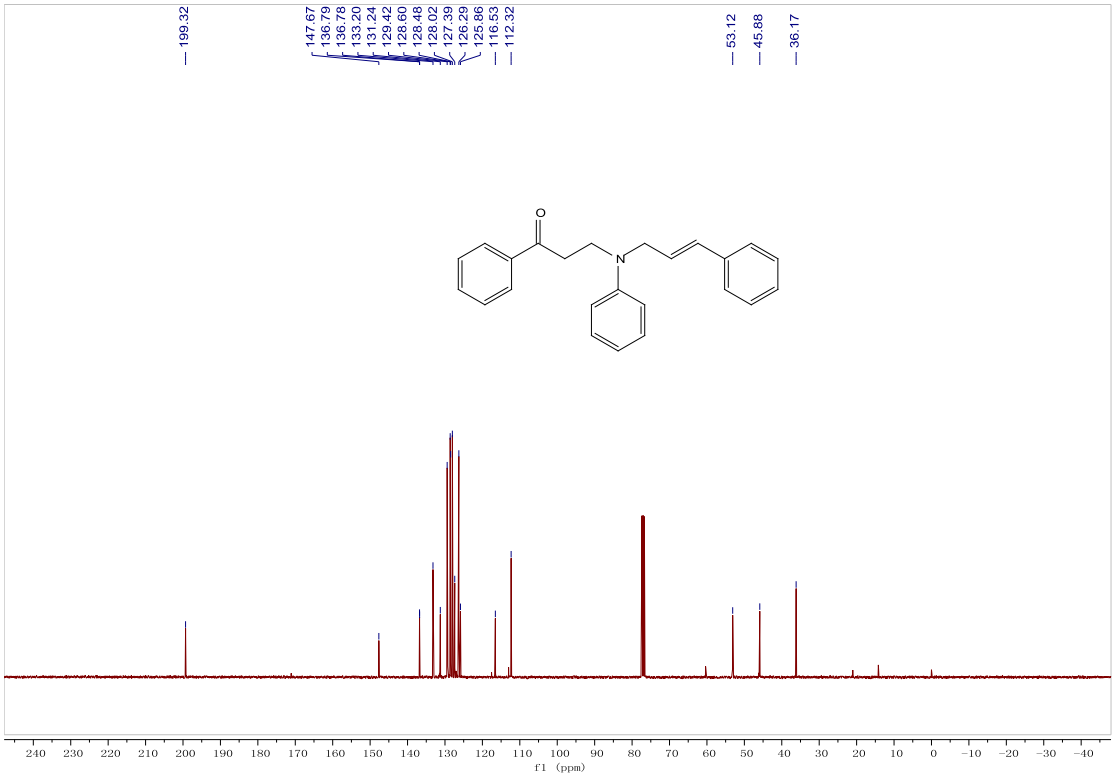
1-phenyl-3-(phenyl(thiophen-2-ylmethyl)amino)propan-1-one (**1l**)



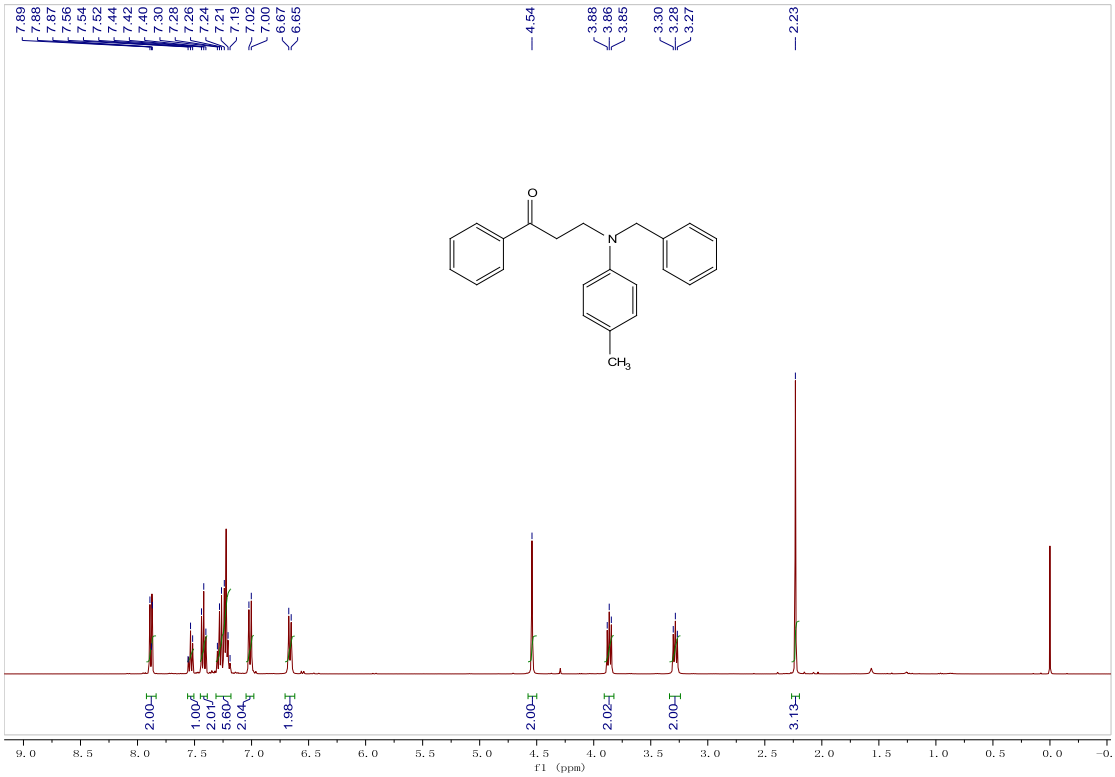


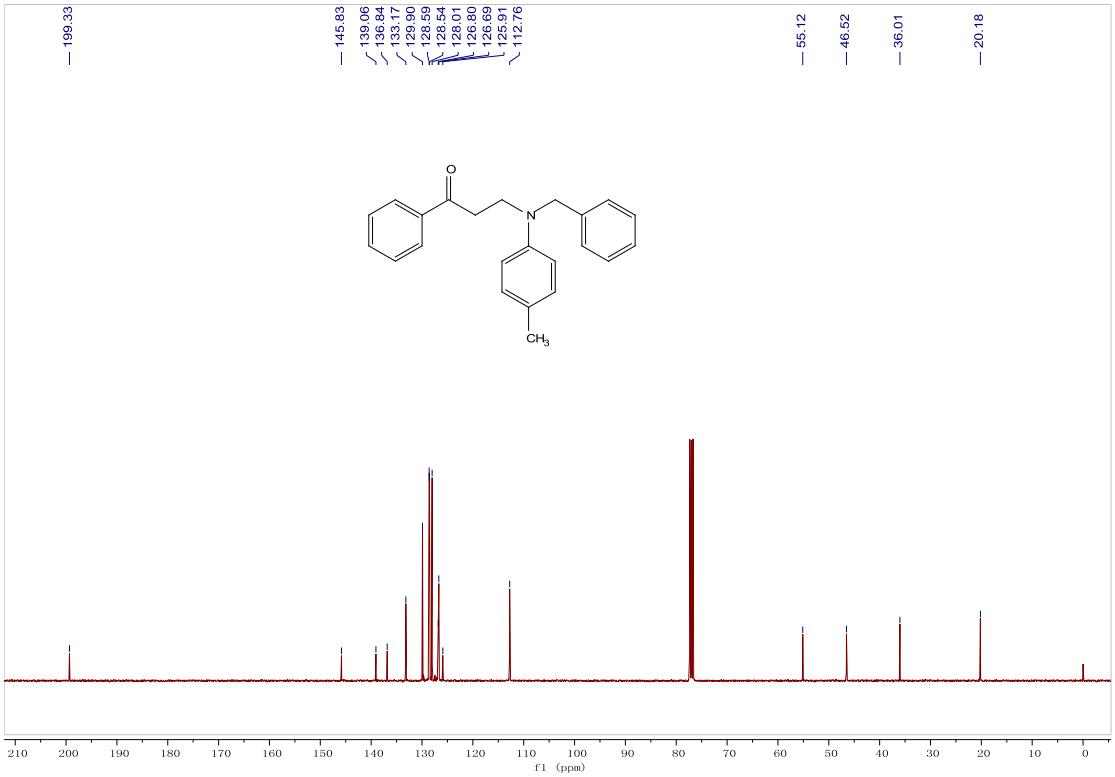
3-(cinnamyl(phenyl)amino)-1-phenylpropan-1-one (**1m**)



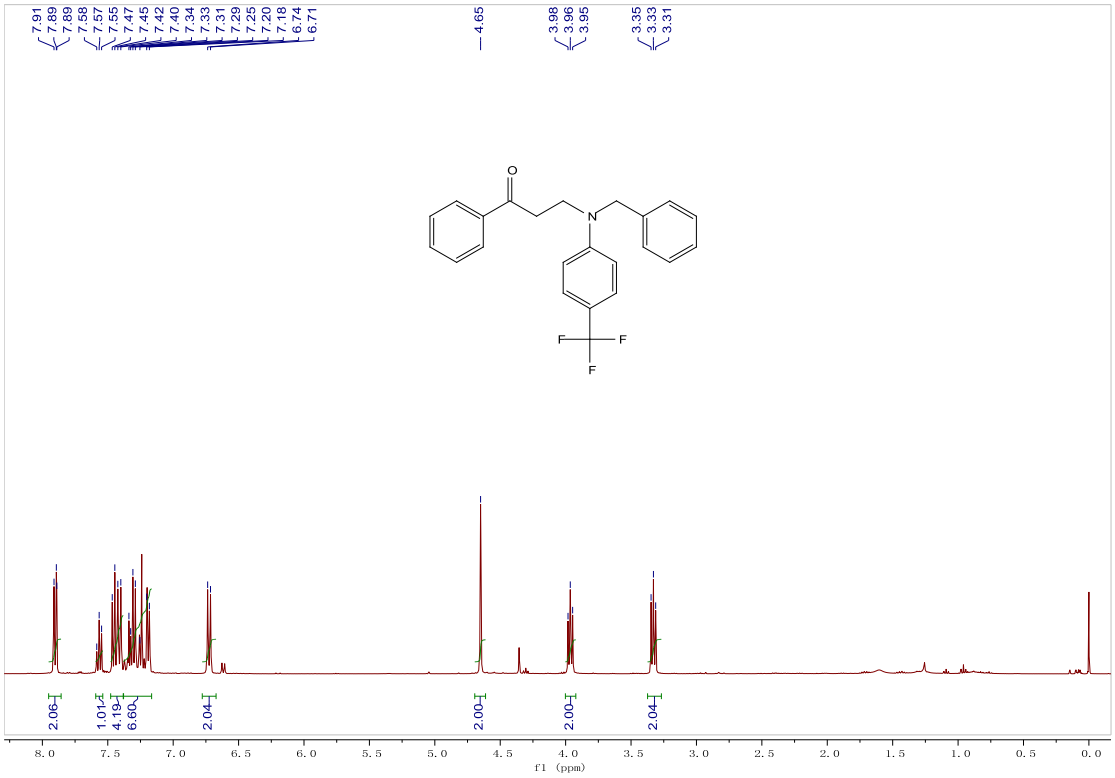


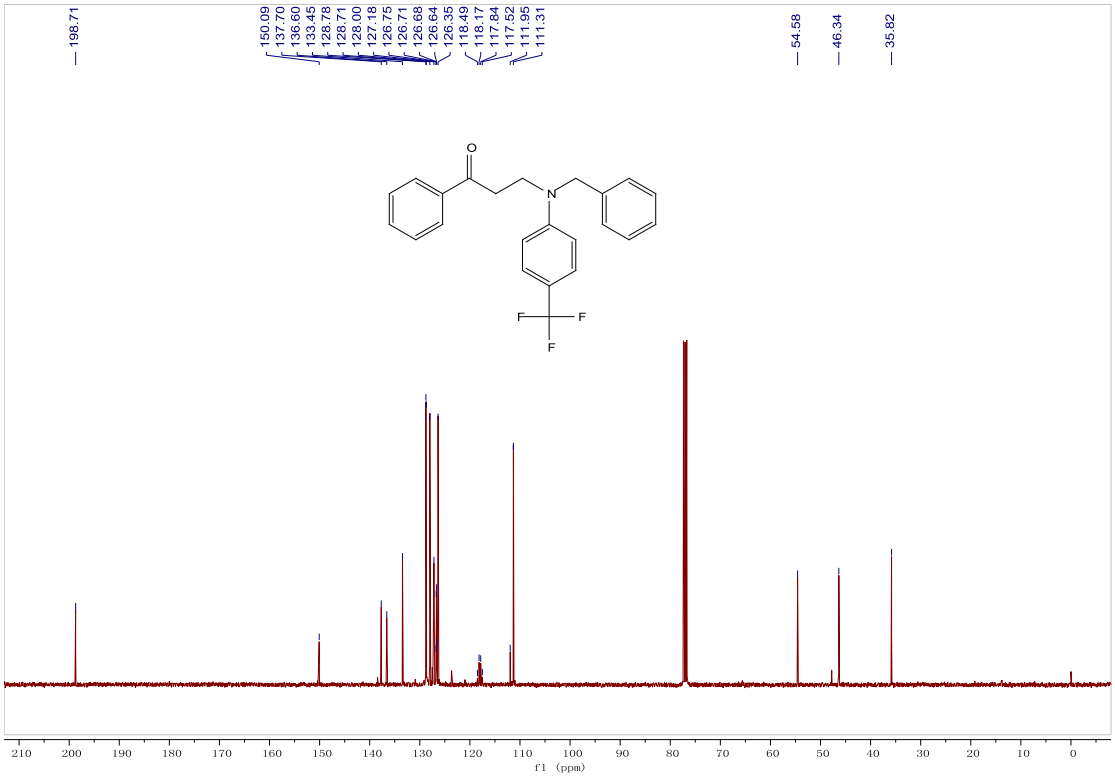
3-(benzyl(p-tolyl)amino)-1-phenylpropan-1-one (**1n**)



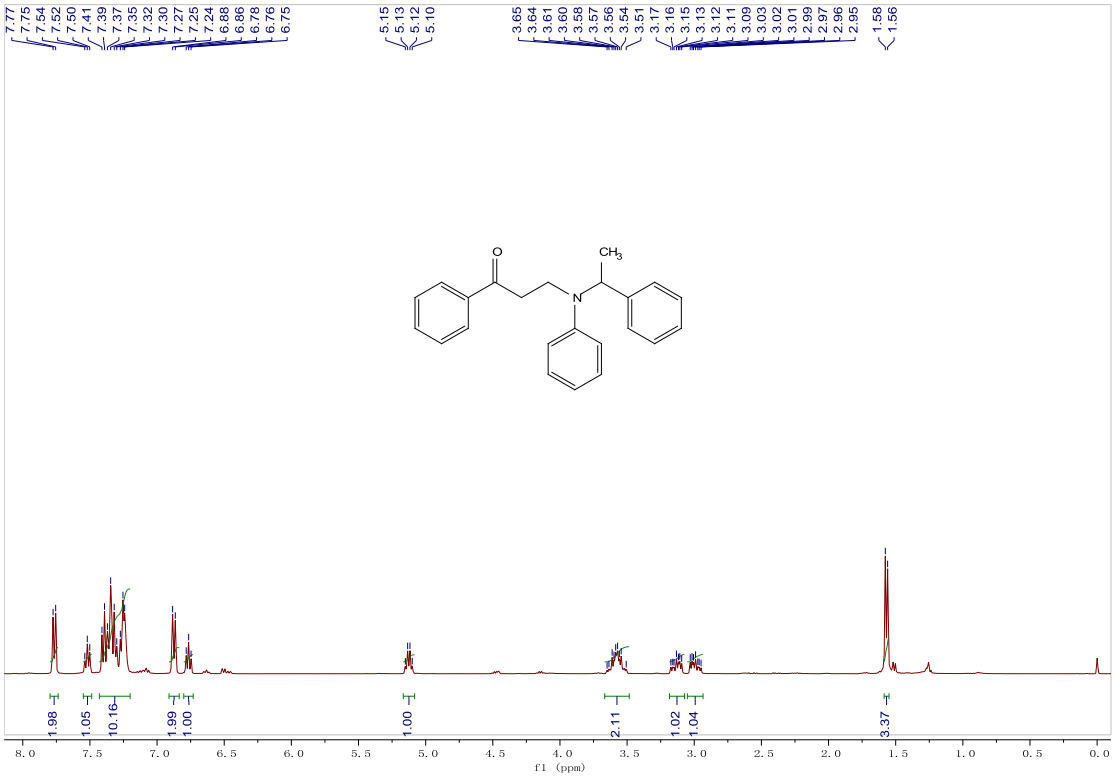


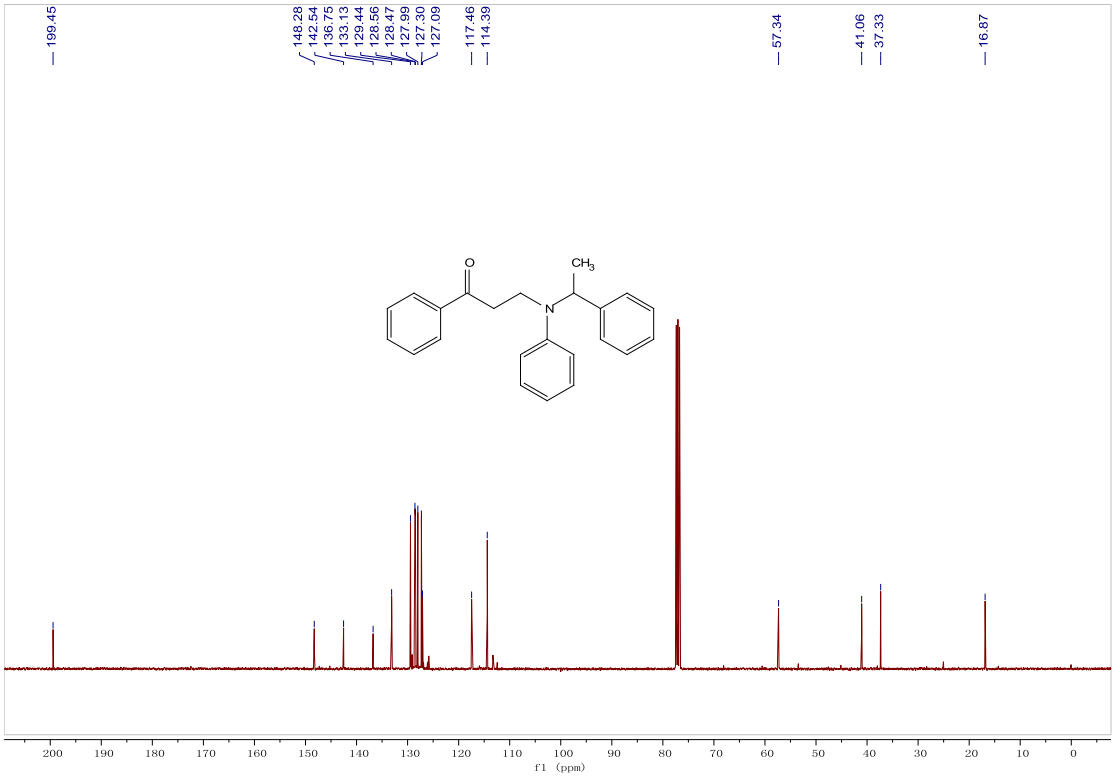
3-(benzyl(4-(trifluoromethyl)phenyl)amino)-1-phenylpropan-1-one (**1o**)



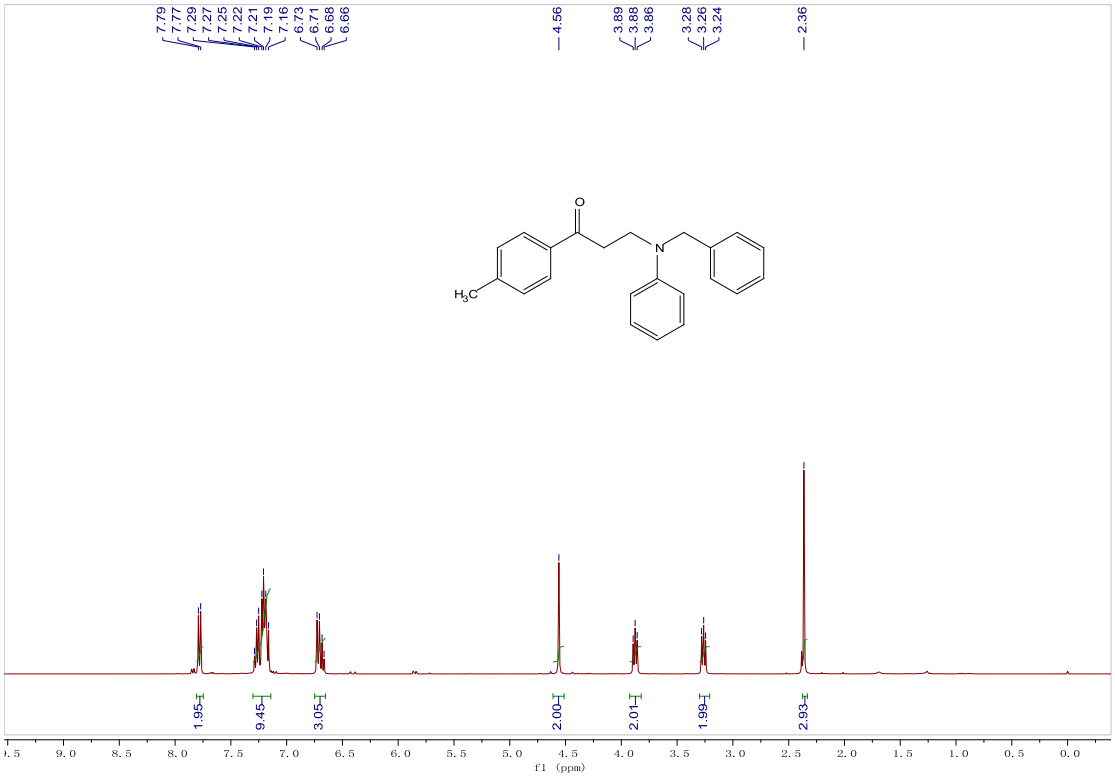


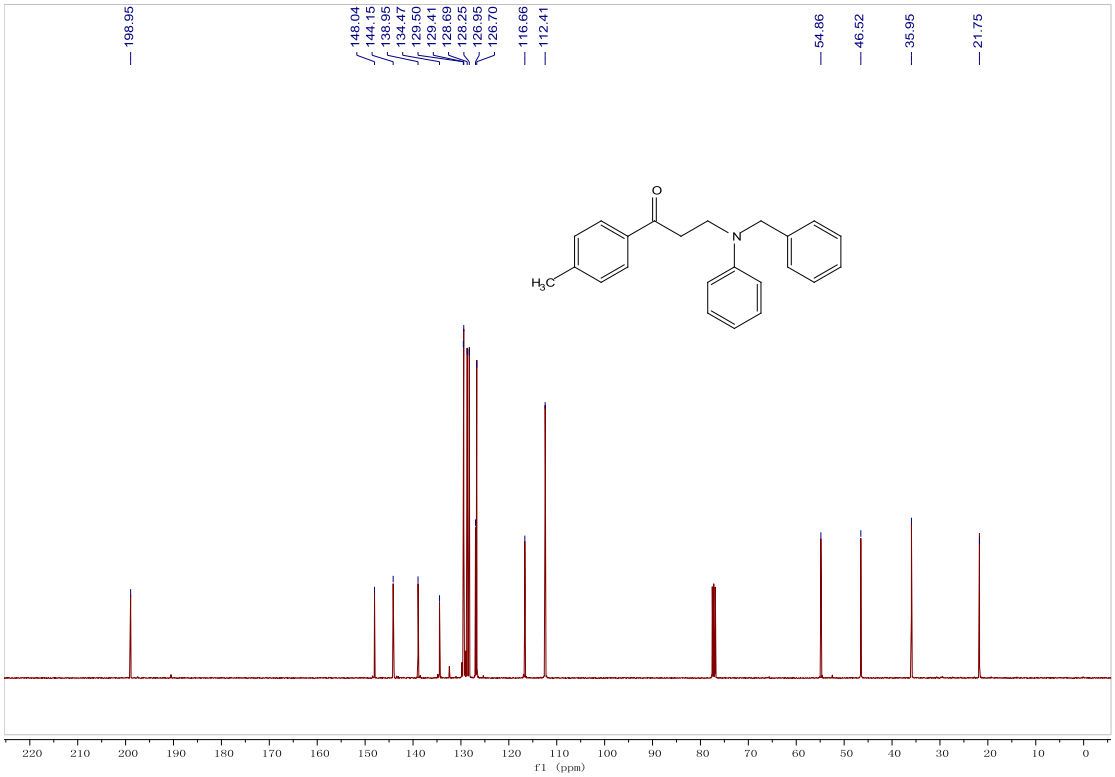
1-phenyl-3-(phenyl(1-phenylethyl)amino)propan-1-one (**1p**)



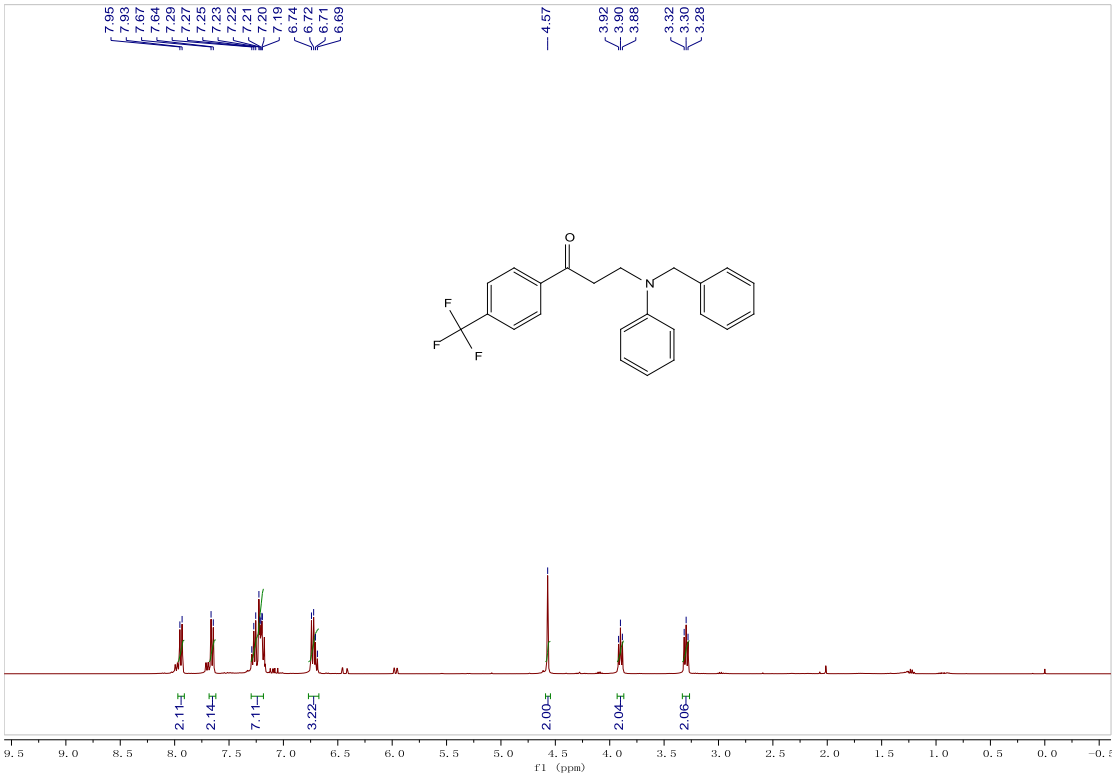


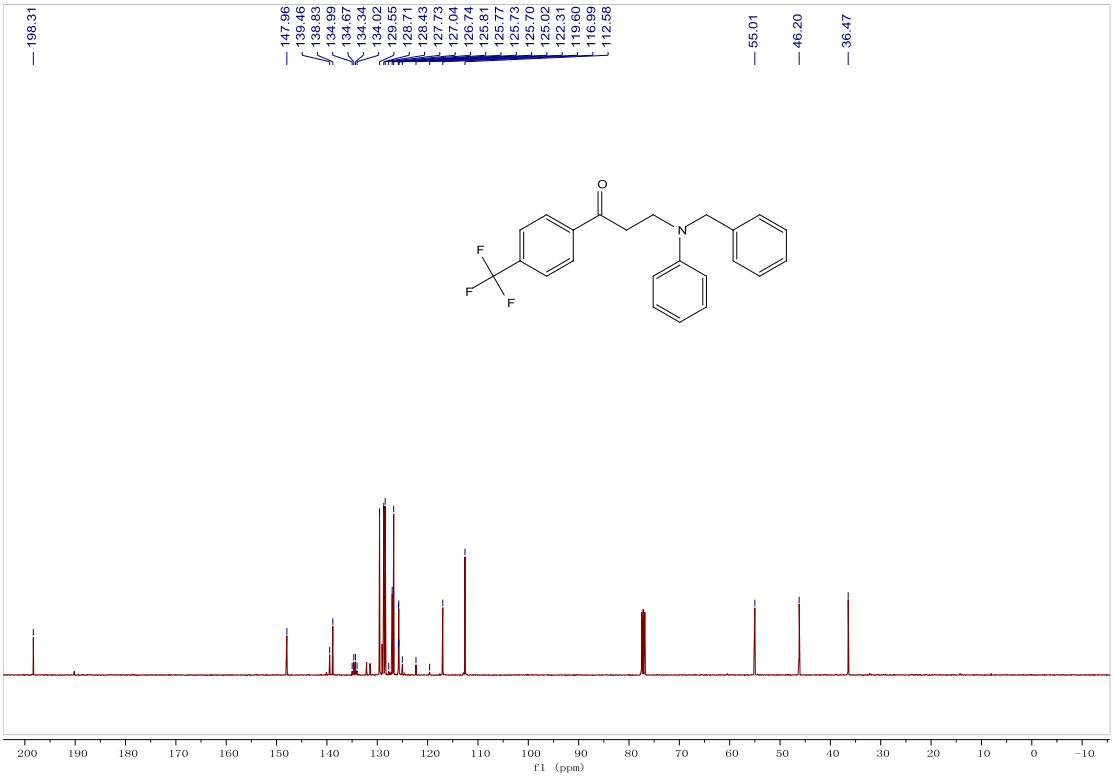
3-(benzyl(phenyl)amino)-1-(p-tolyl)propan-1-one (**1q**)





3-(benzyl(phenyl)amino)-1-(4-(trifluoromethyl)phenyl)propan-1-one (**1r**)

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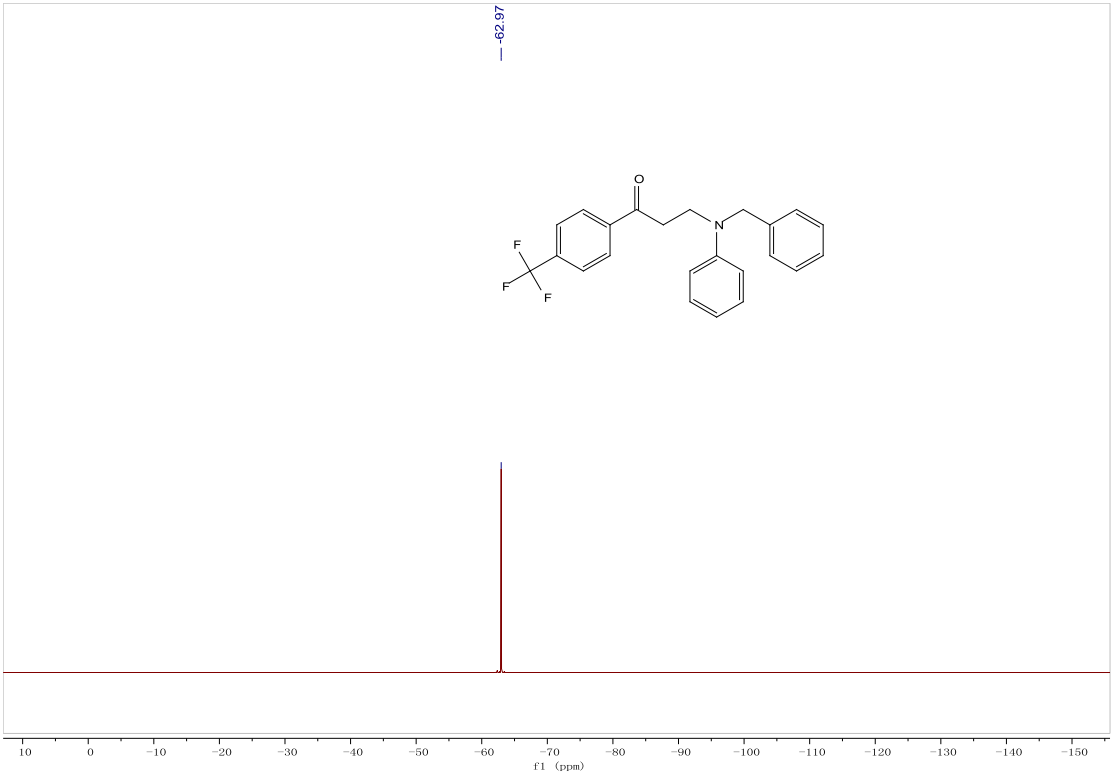
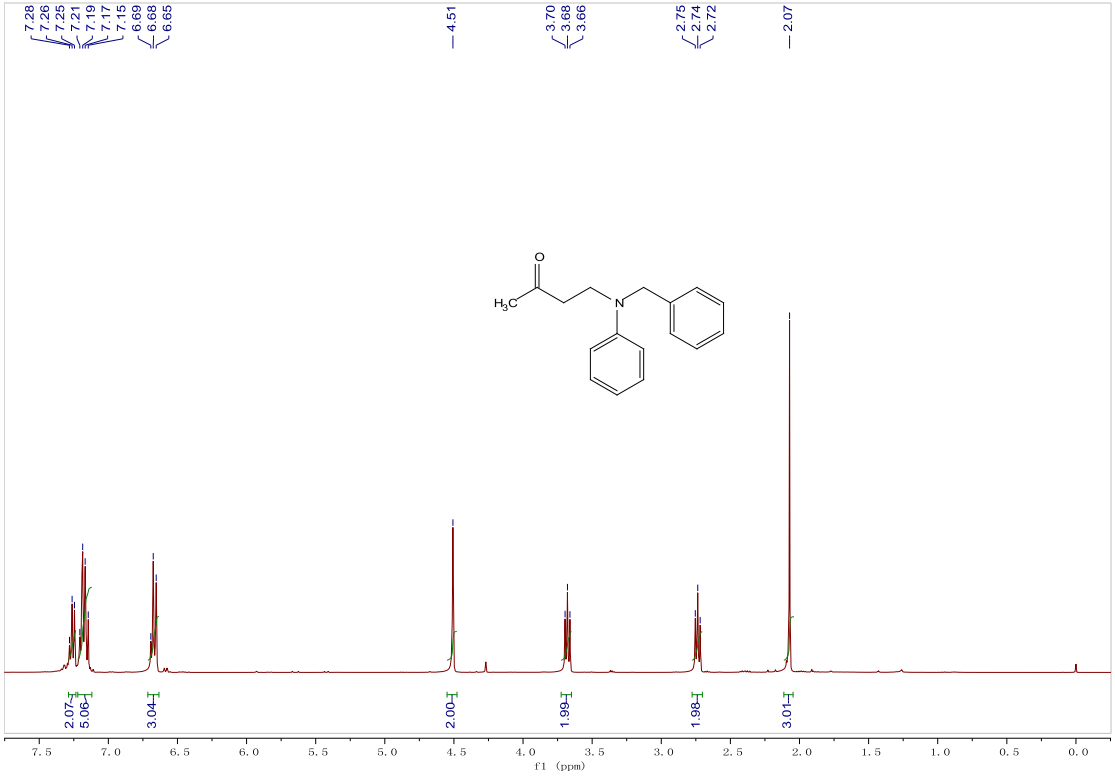
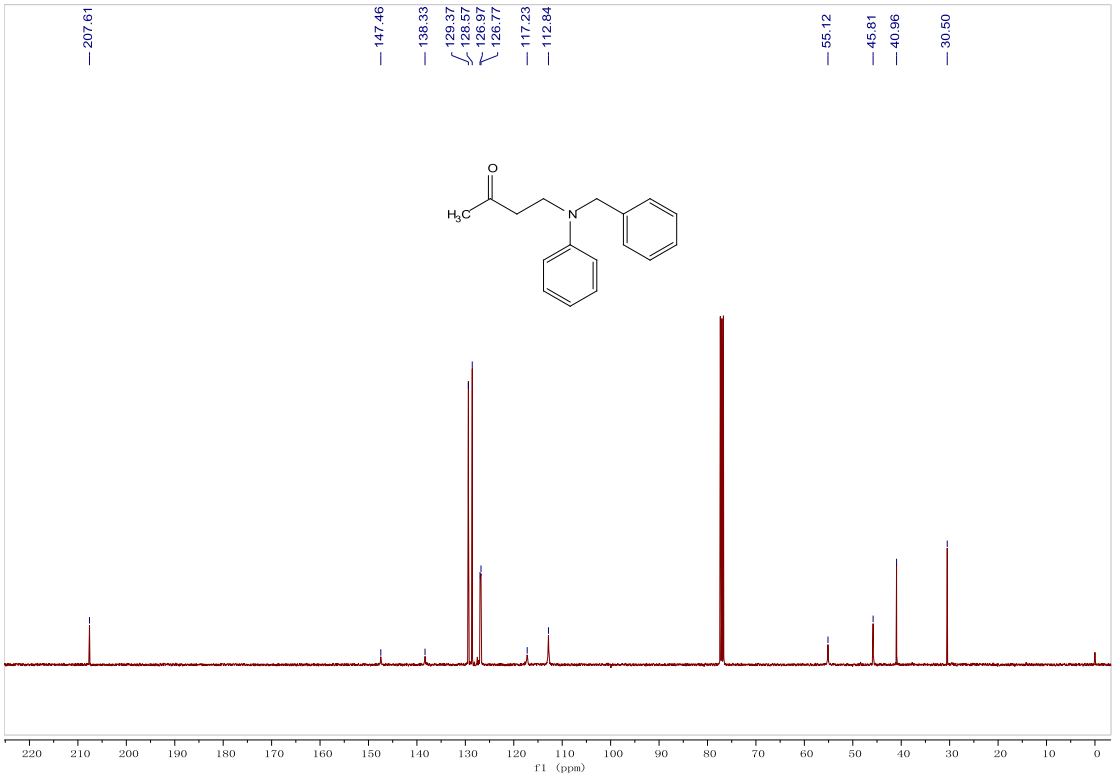
125.81
125.77
125.73
125.70
125.02
122.31
119.60
116.99
112.58
55.01
46.20
36.47
O
N
F
F
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

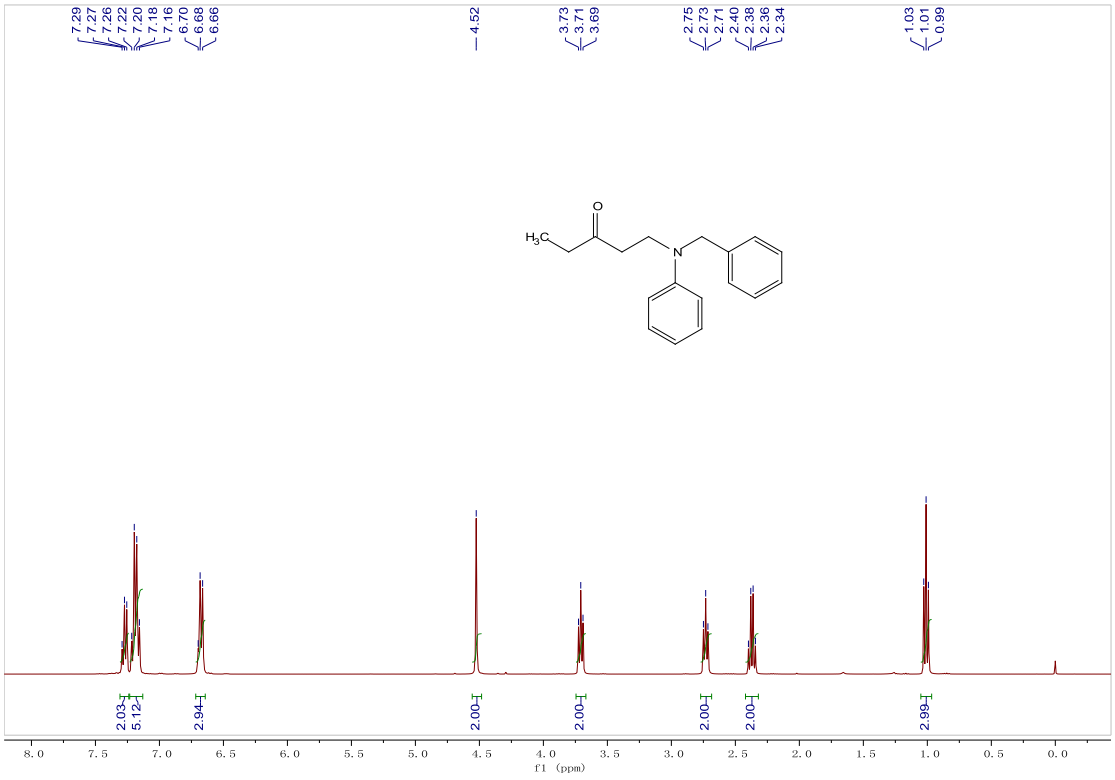

-62.97
O
N
F
F
F
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150
f1 (ppm)

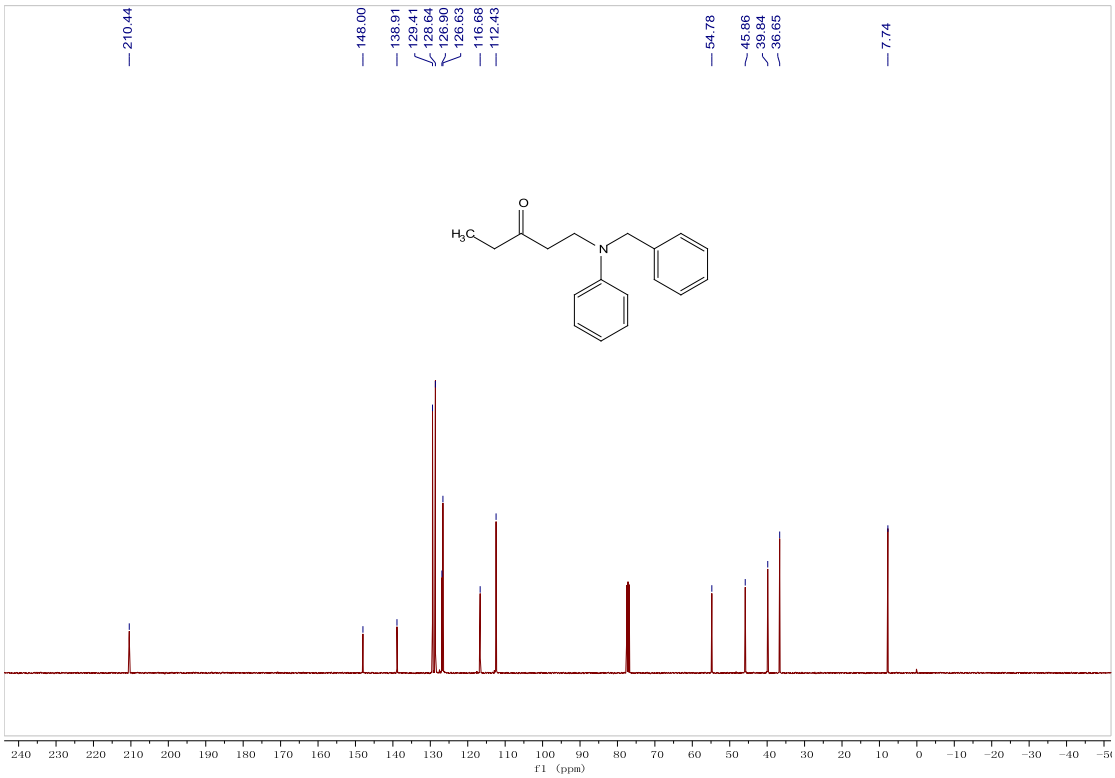
4-(benzyl(phenyl)amino)butan-2-one (**1s**)



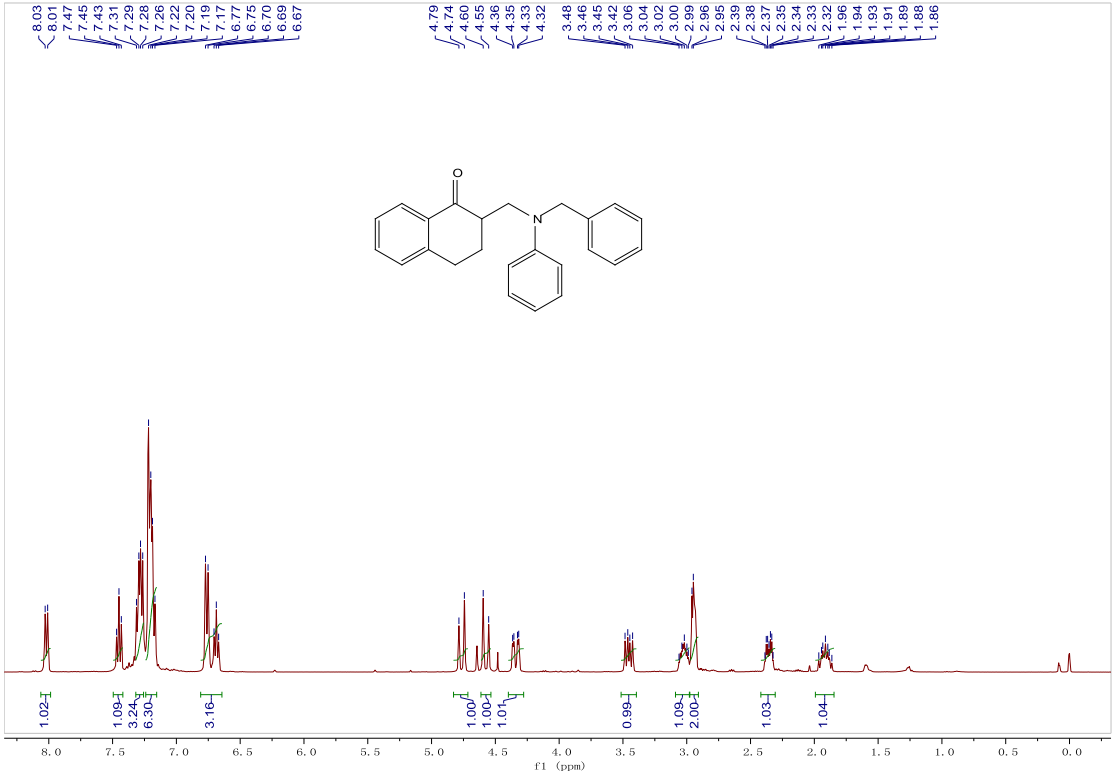


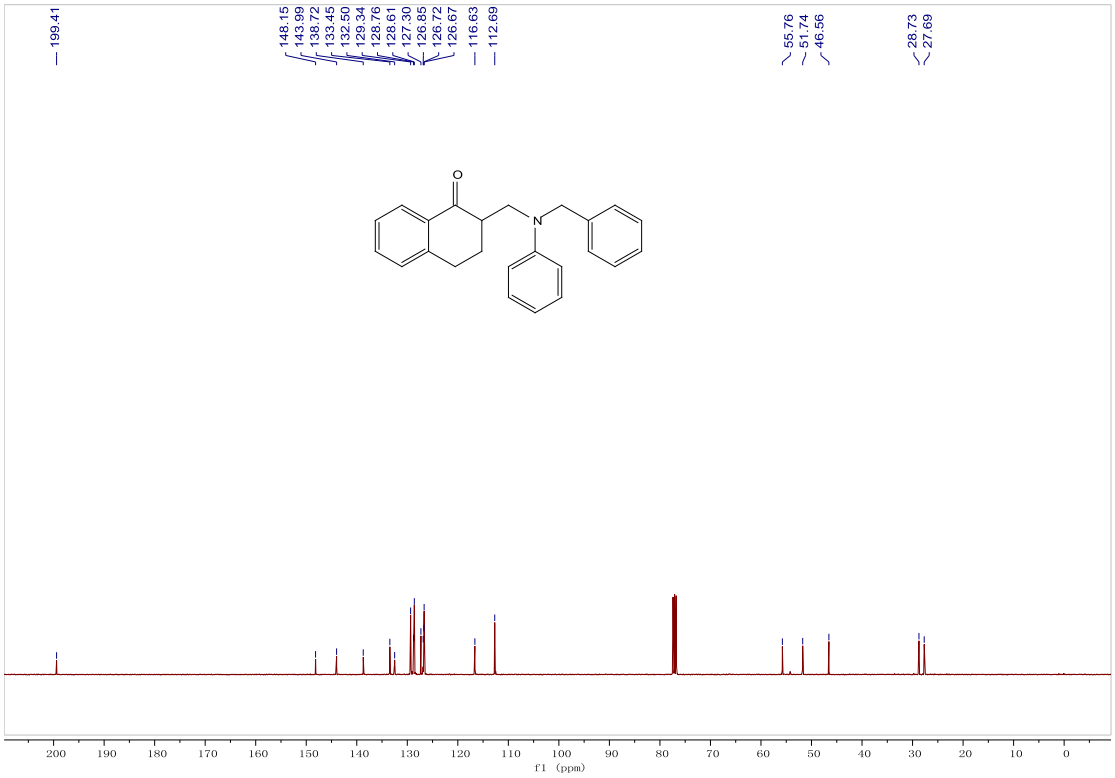
1-(benzyl(phenyl)amino)pentan-3-one (**1t**)



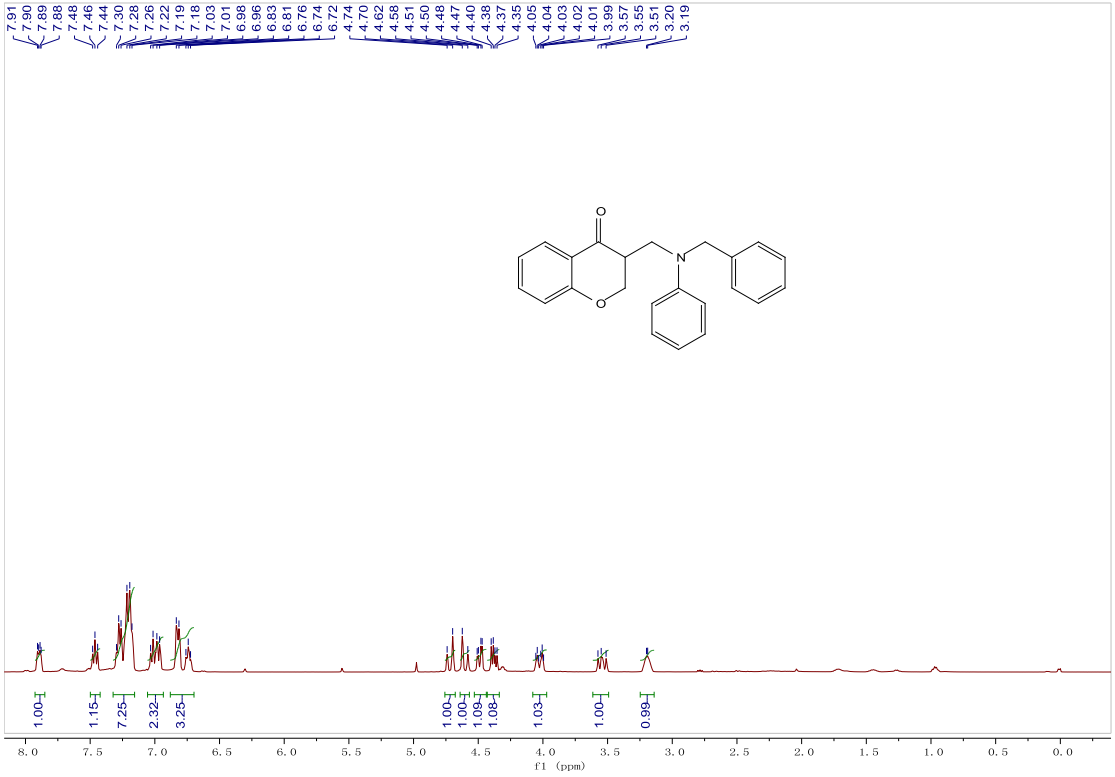


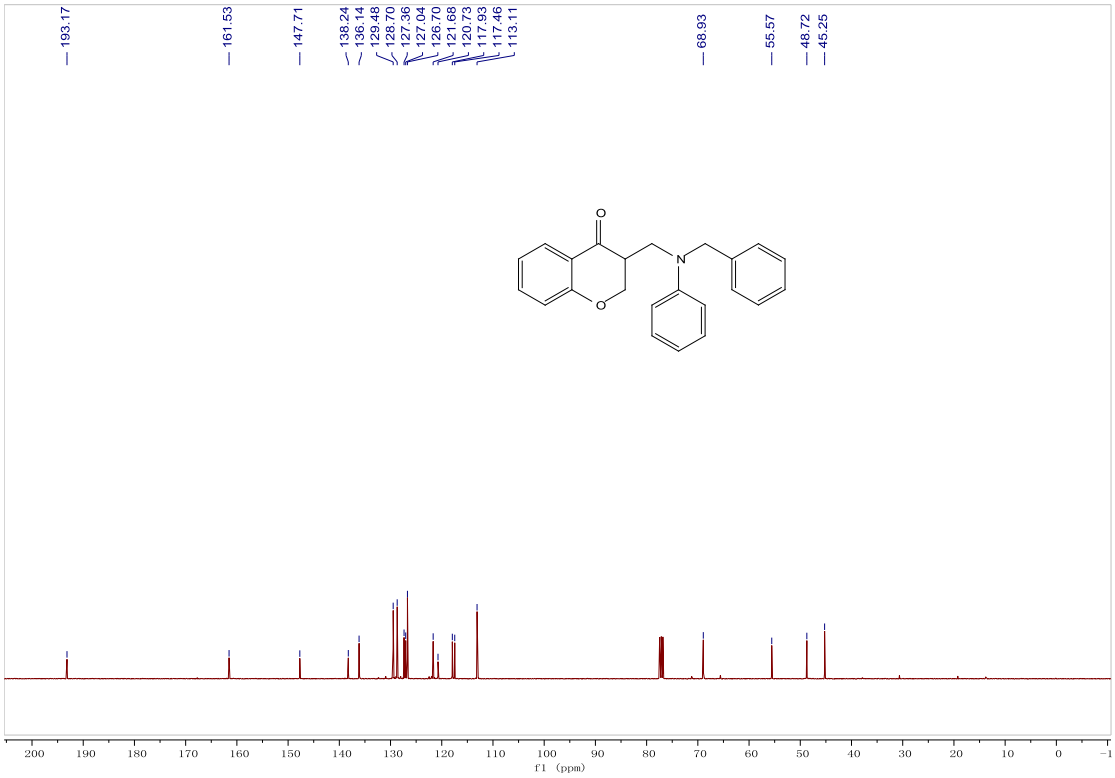
2-((benzyl(phenyl)amino)methyl)-3,4-dihydronaphthalen-1(2H)-one (**1u**)



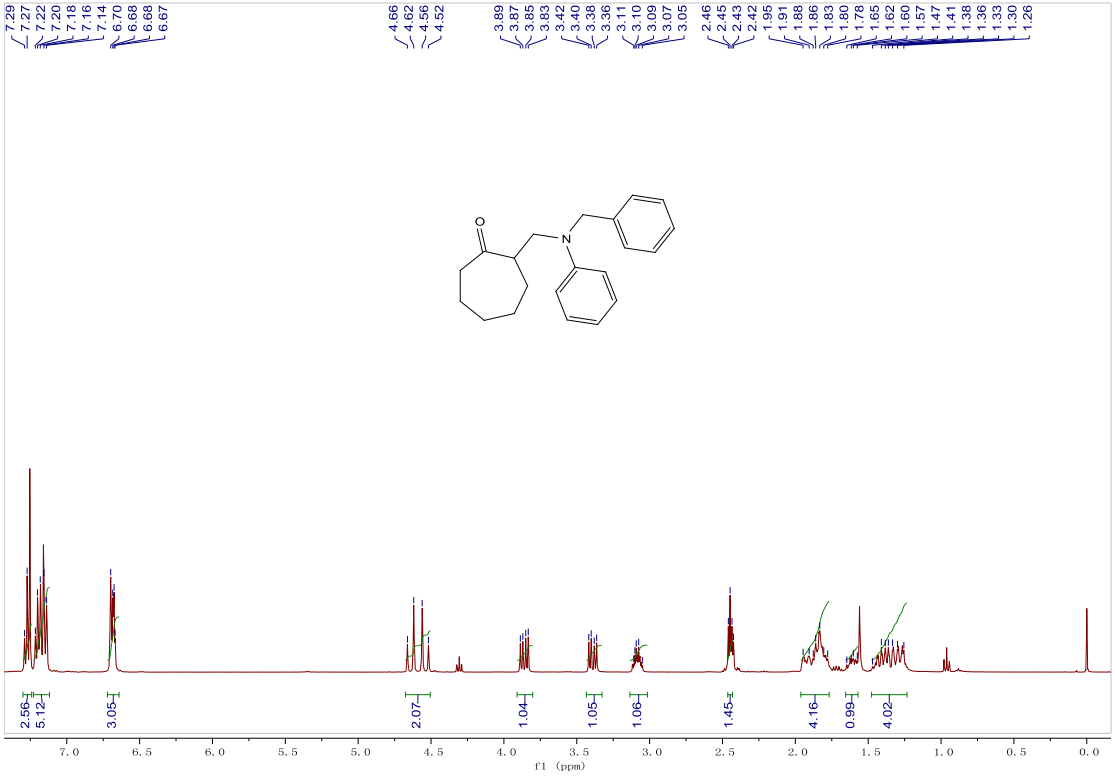


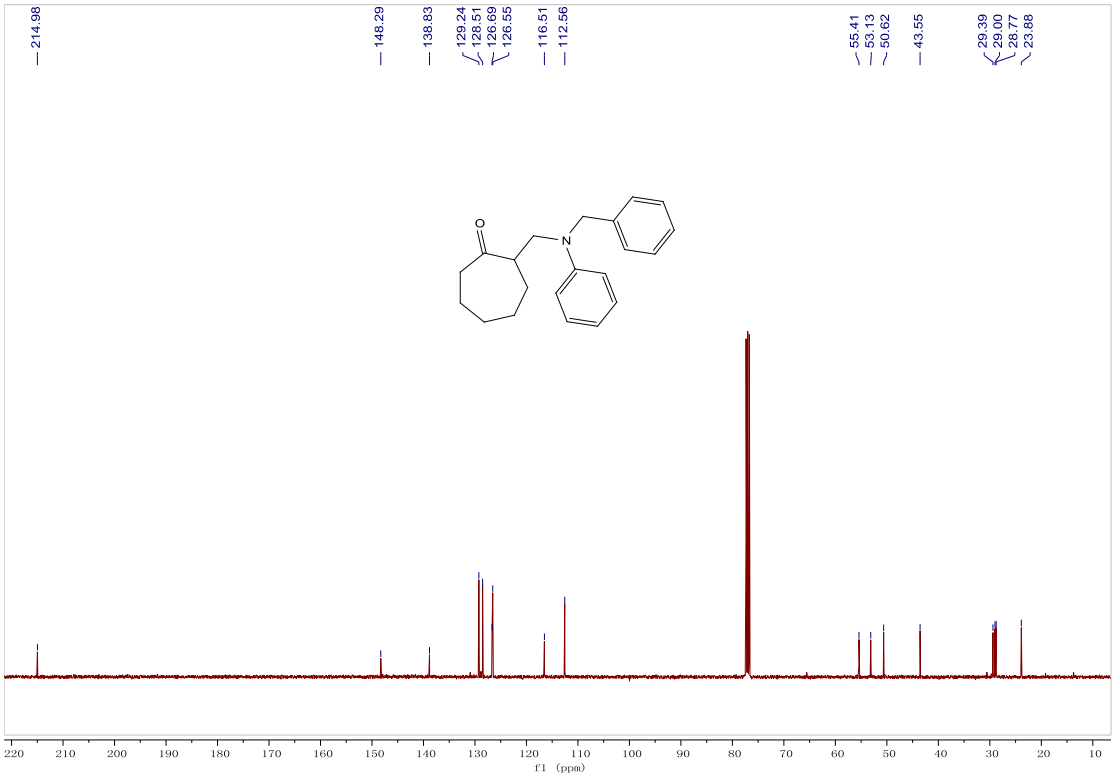
3-((benzyl(phenyl)amino)methyl)chroman-4-one (**1v**)



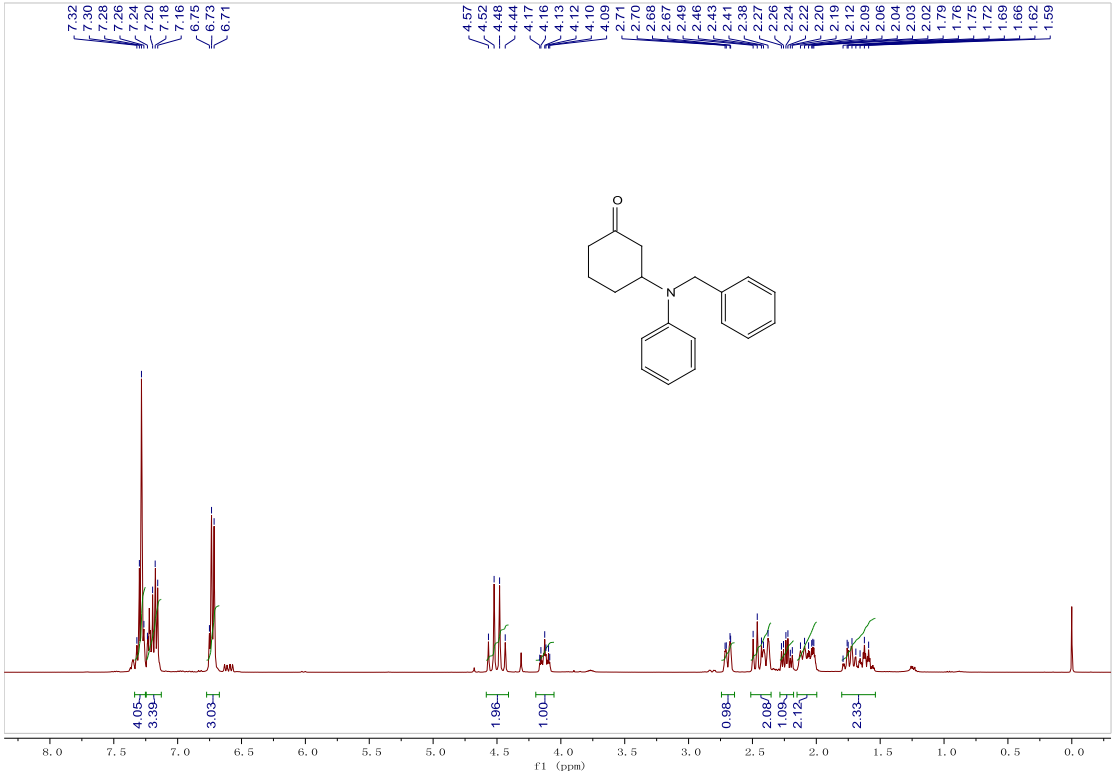


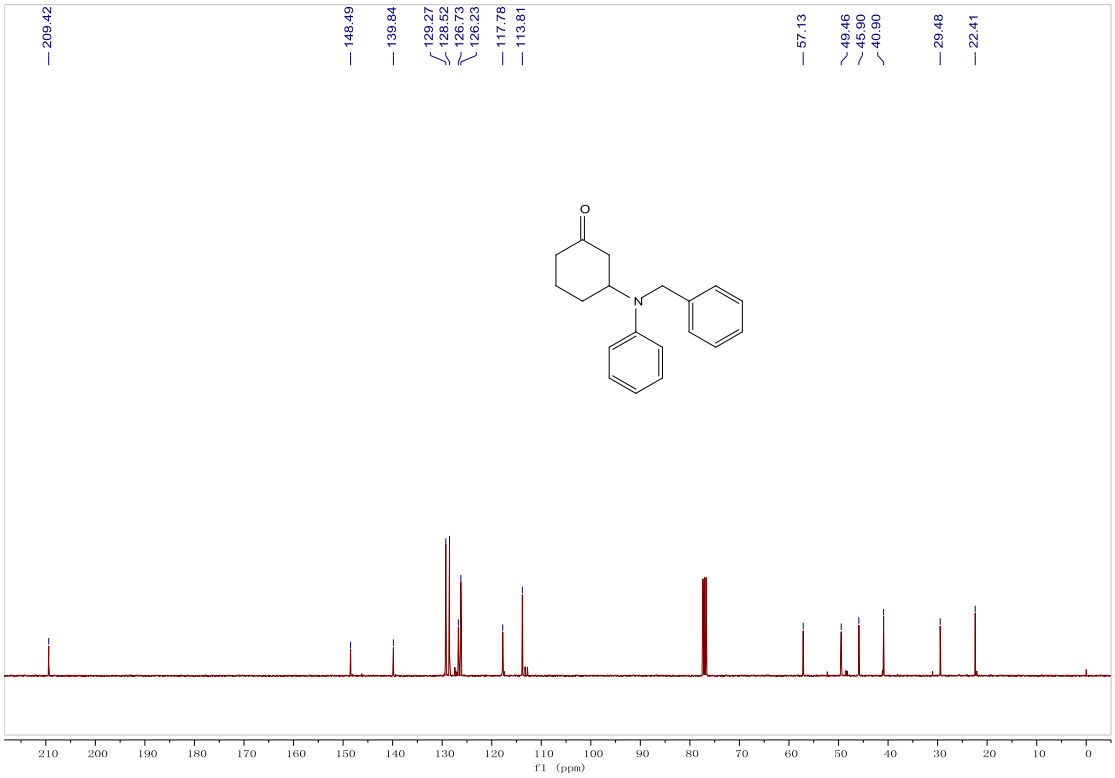
2-((benzyl(phenyl)amino)methyl)cycloheptan-1-one (**1w**)



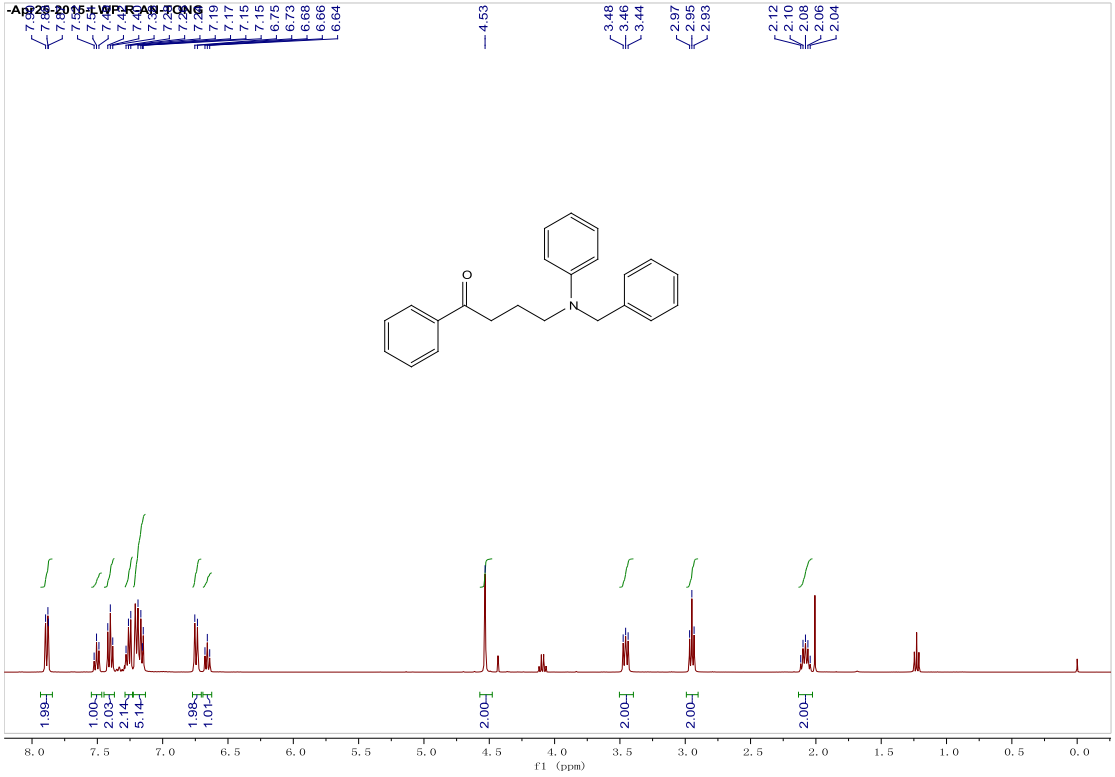


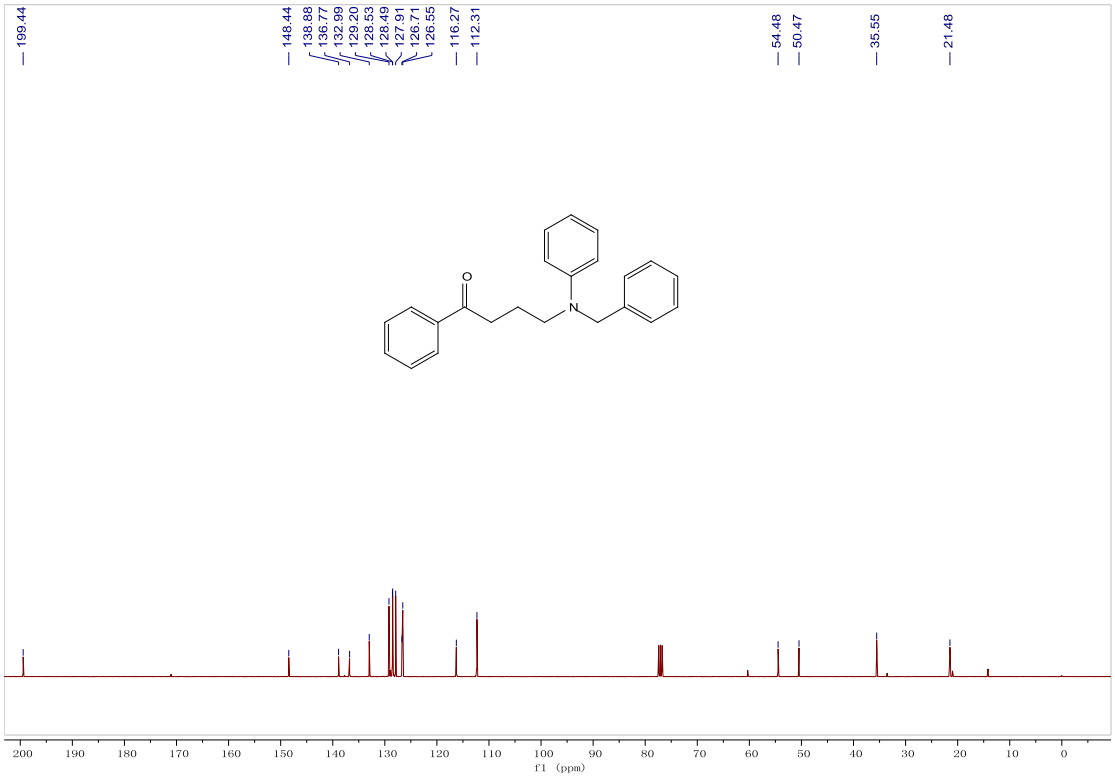
3-(benzyl(phenyl)amino)cyclohexan-1-one (**1x**)



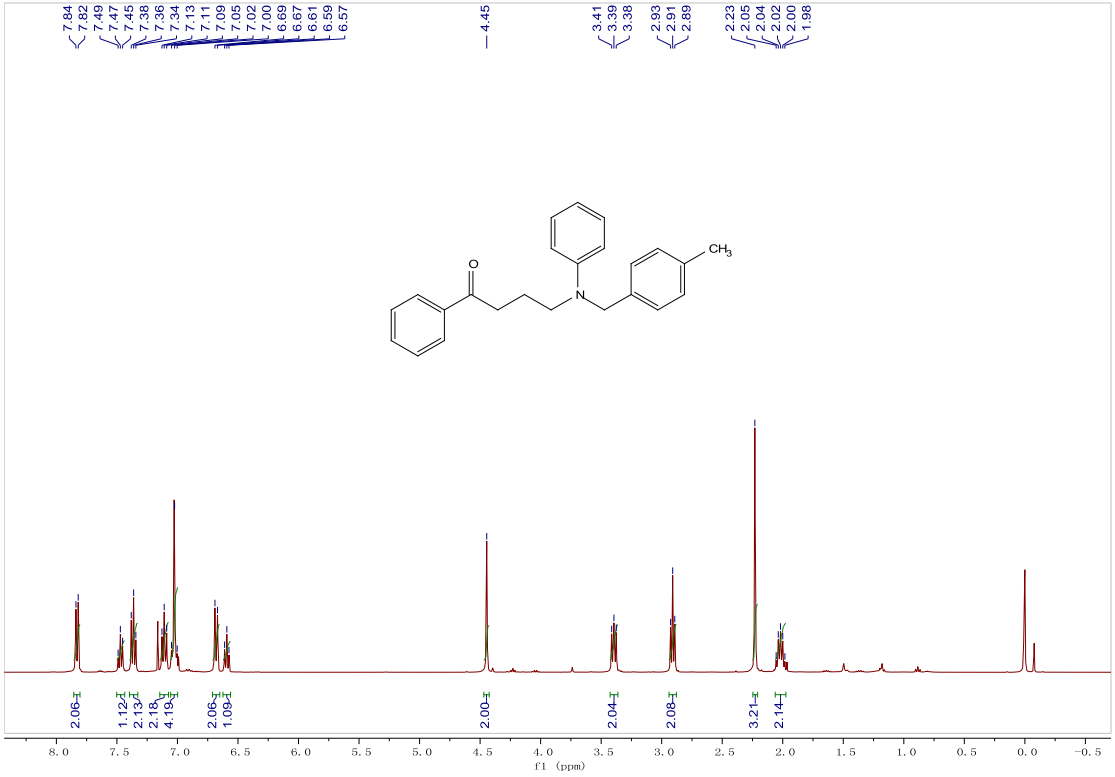


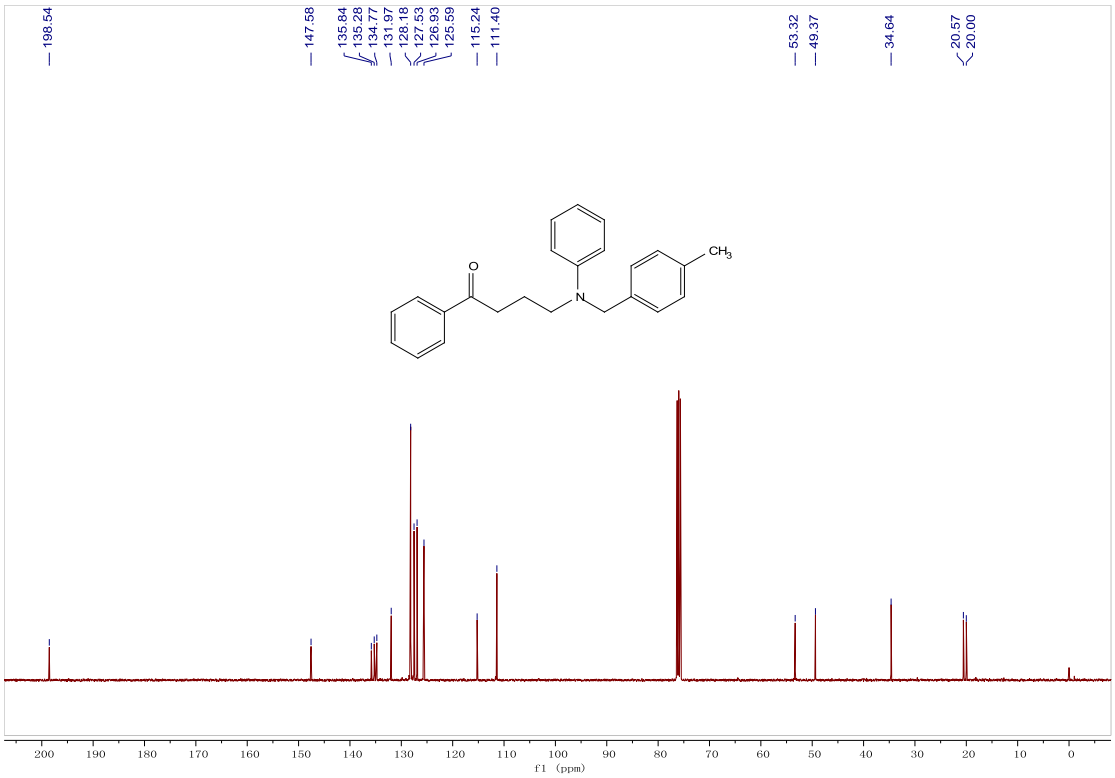
4-(benzyl(phenyl)amino)-1-phenylbutan-1-one (**S-6a**)



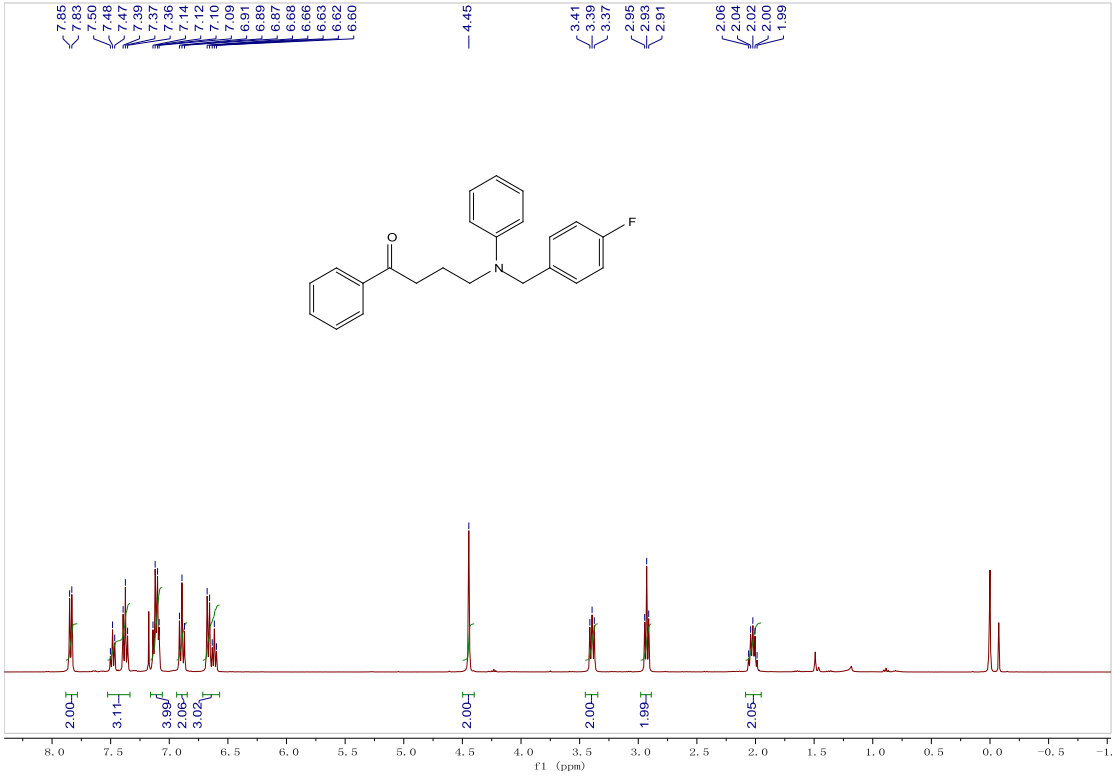


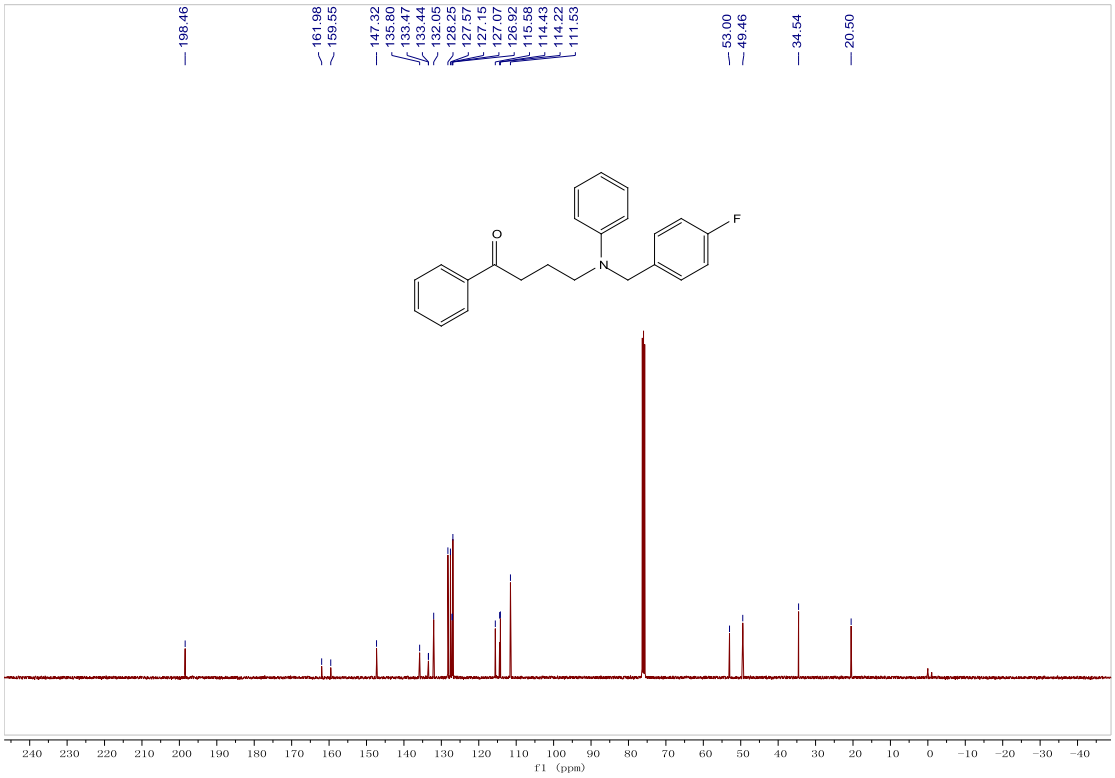
4-((4-methylbenzyl)(phenyl)amino)-1-phenylbutan-1-one (**S-6b**)



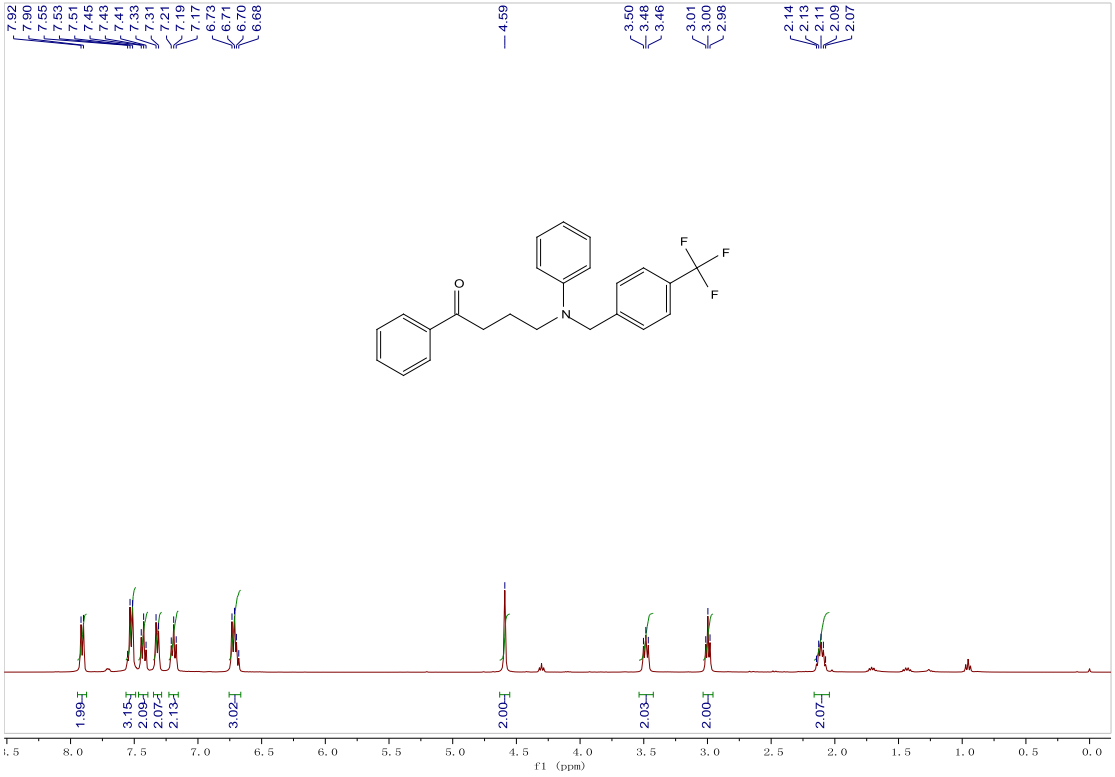


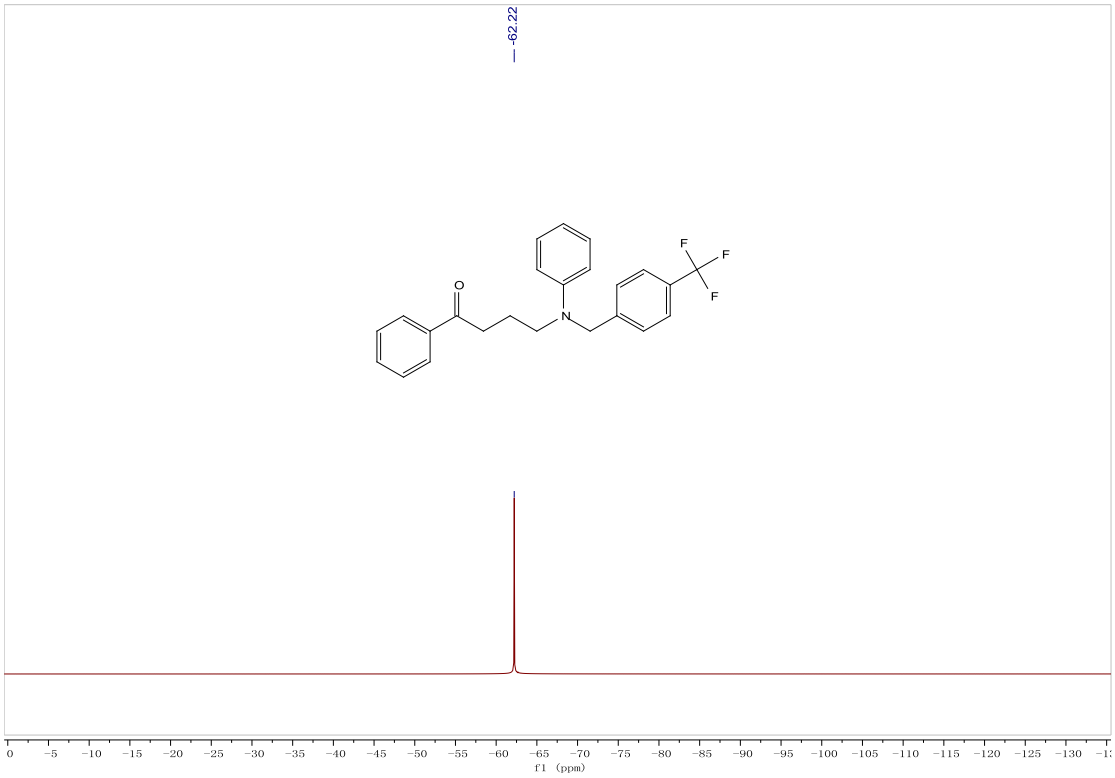
4-((4-fluorobenzyl)(phenyl)amino)-1-phenylbutan-1-one (**S-6c**)

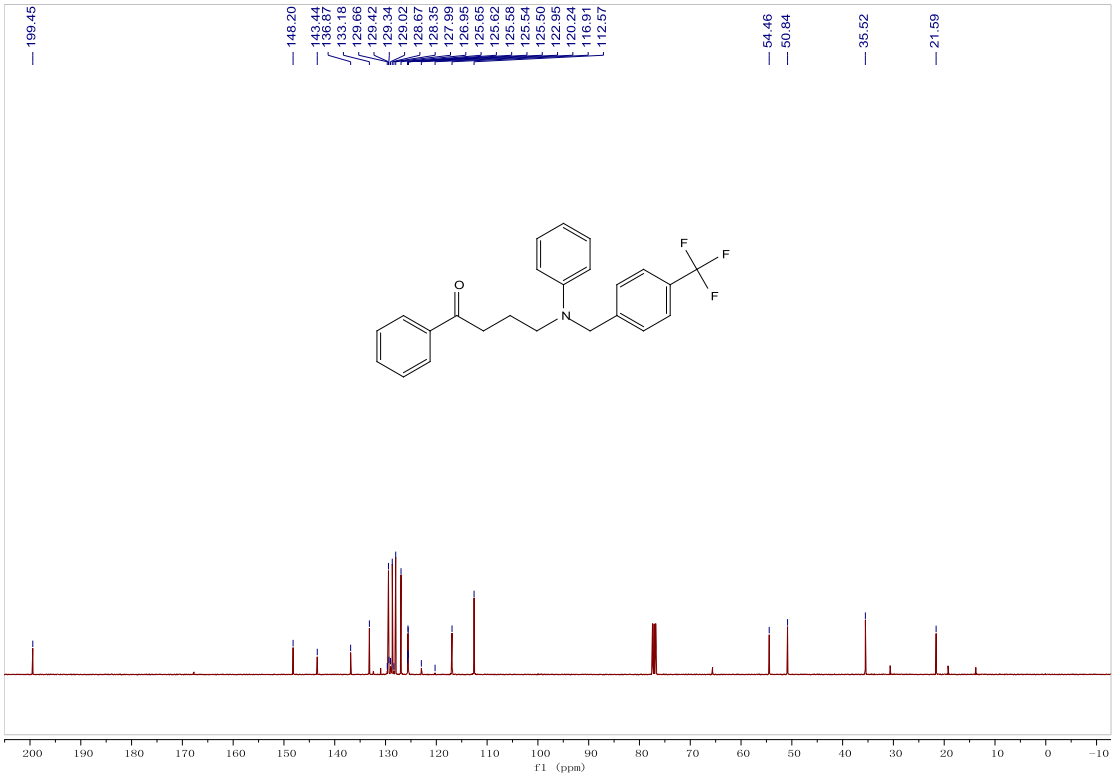




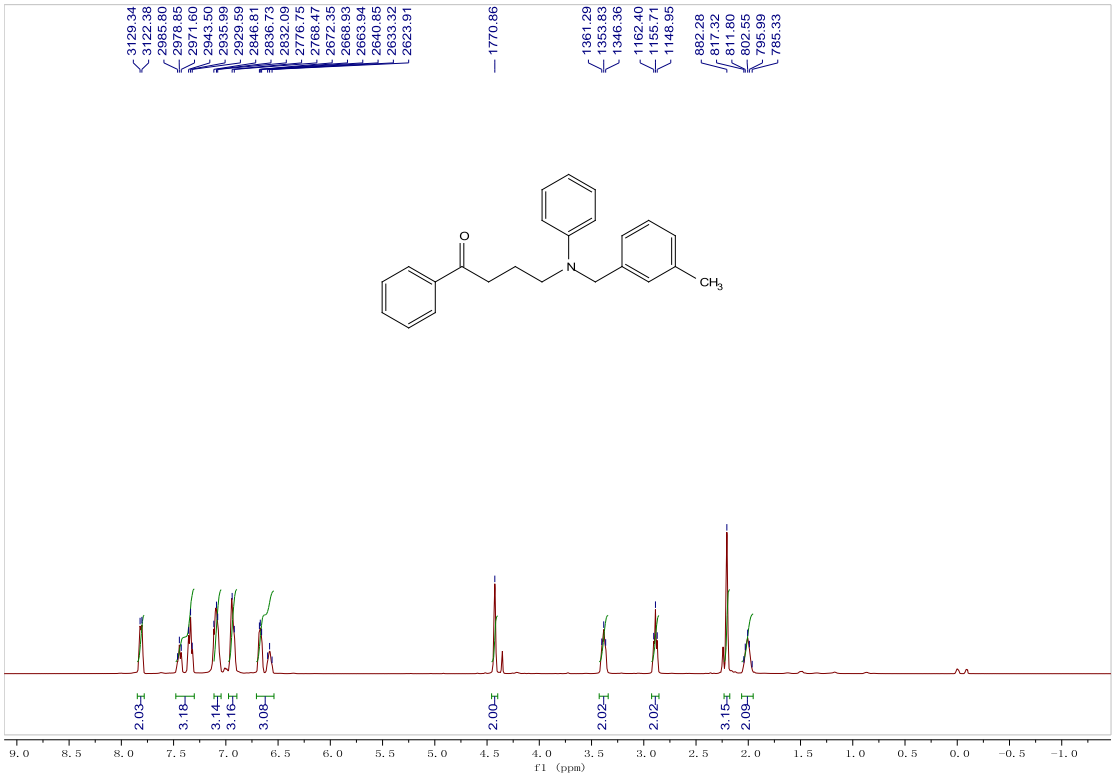
1-phenyl-4-(phenyl(4-(trifluoromethyl)benzyl)amino)butan-1-one (**S-6d**)

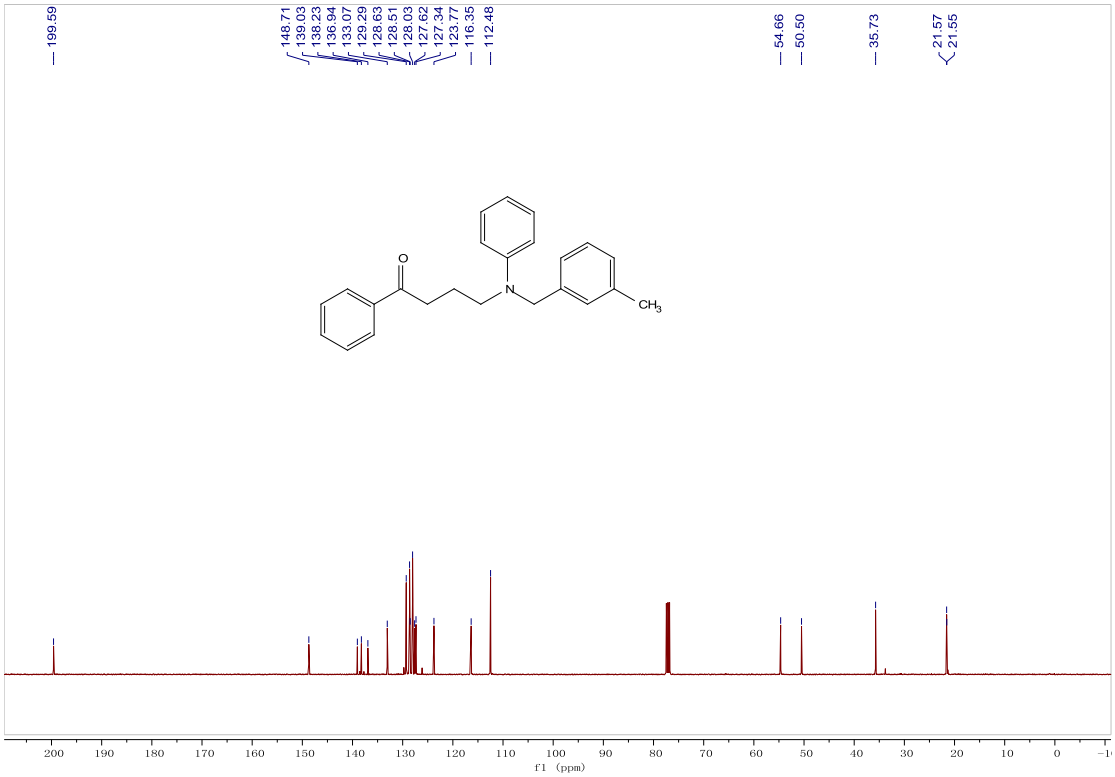




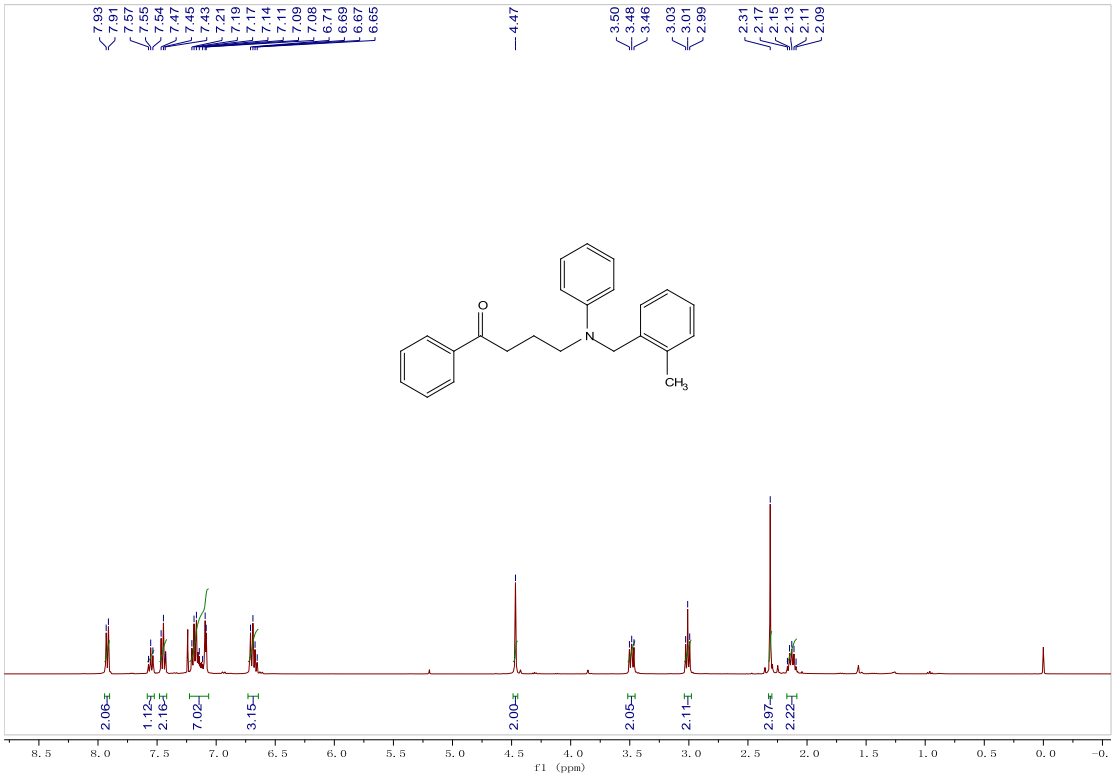


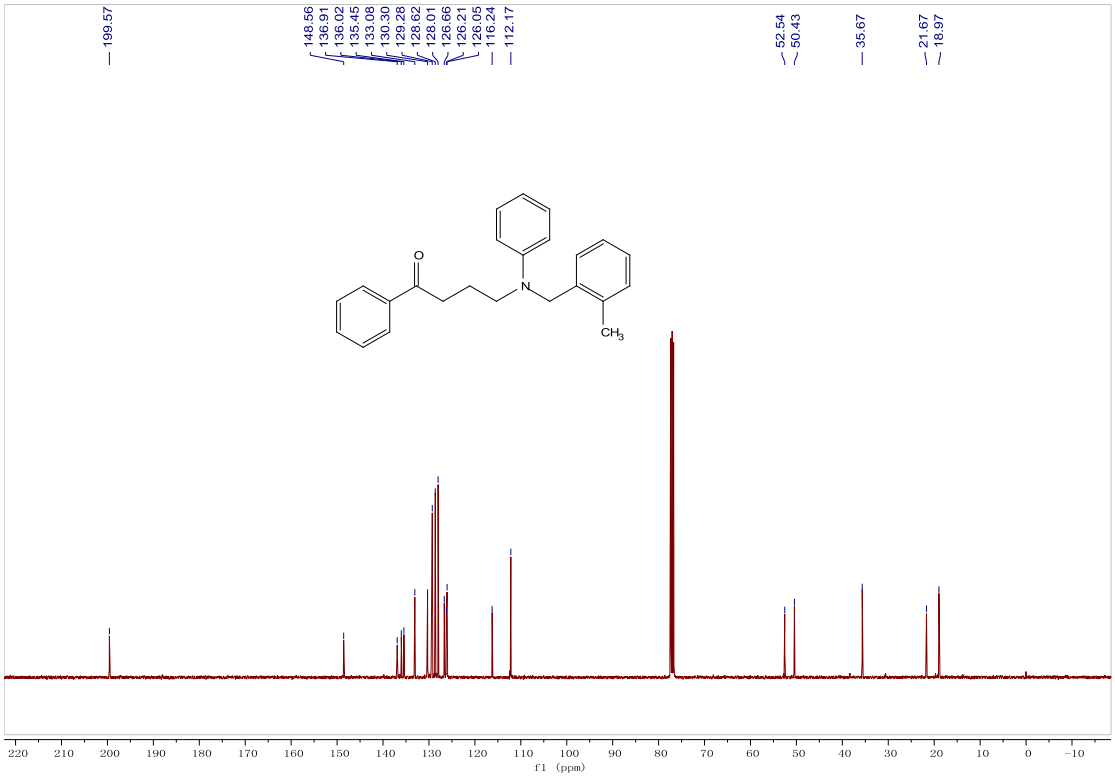
4-((3-methylbenzyl)(phenyl)amino)-1-phenylbutan-1-one (**S-6e**)



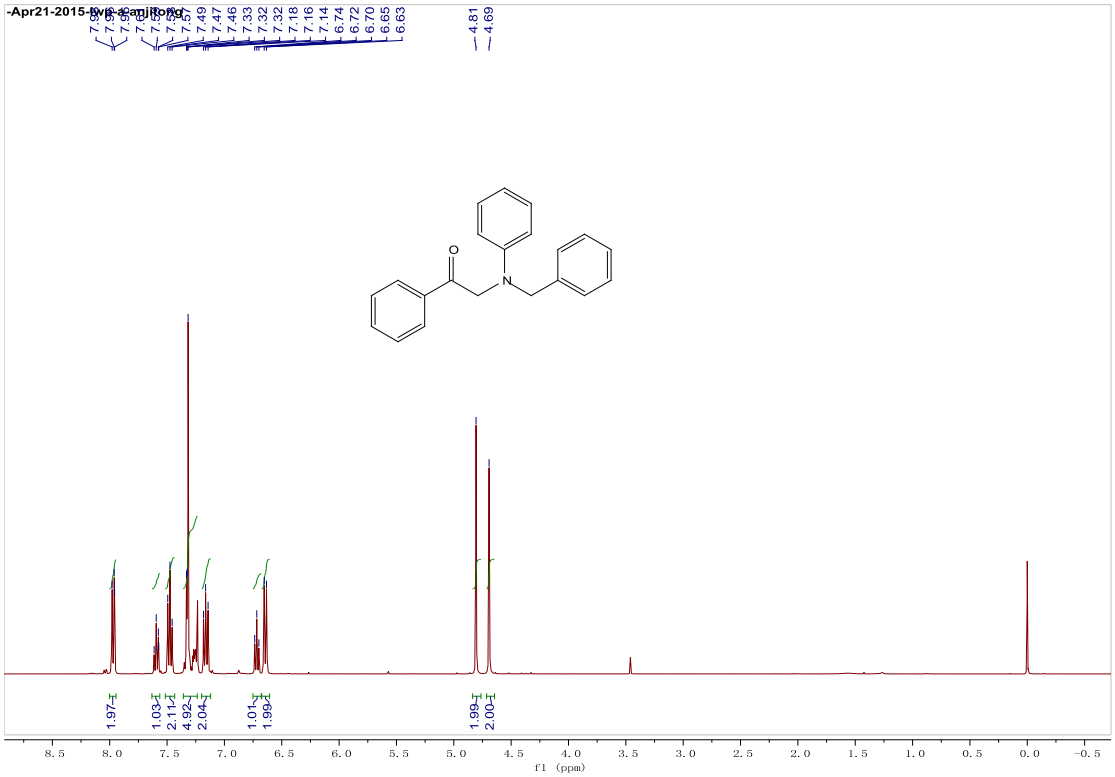


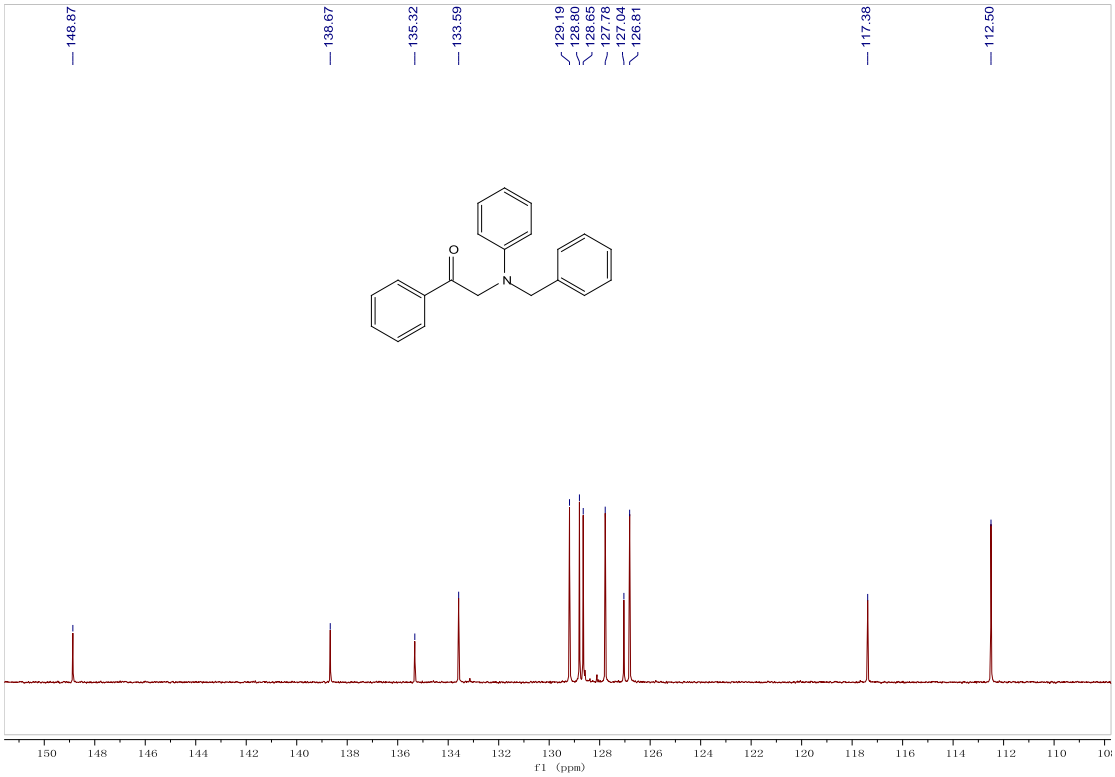
4-((2-methylbenzyl)(phenyl)amino)-1-phenylbutan-1-one (**S-6f**)



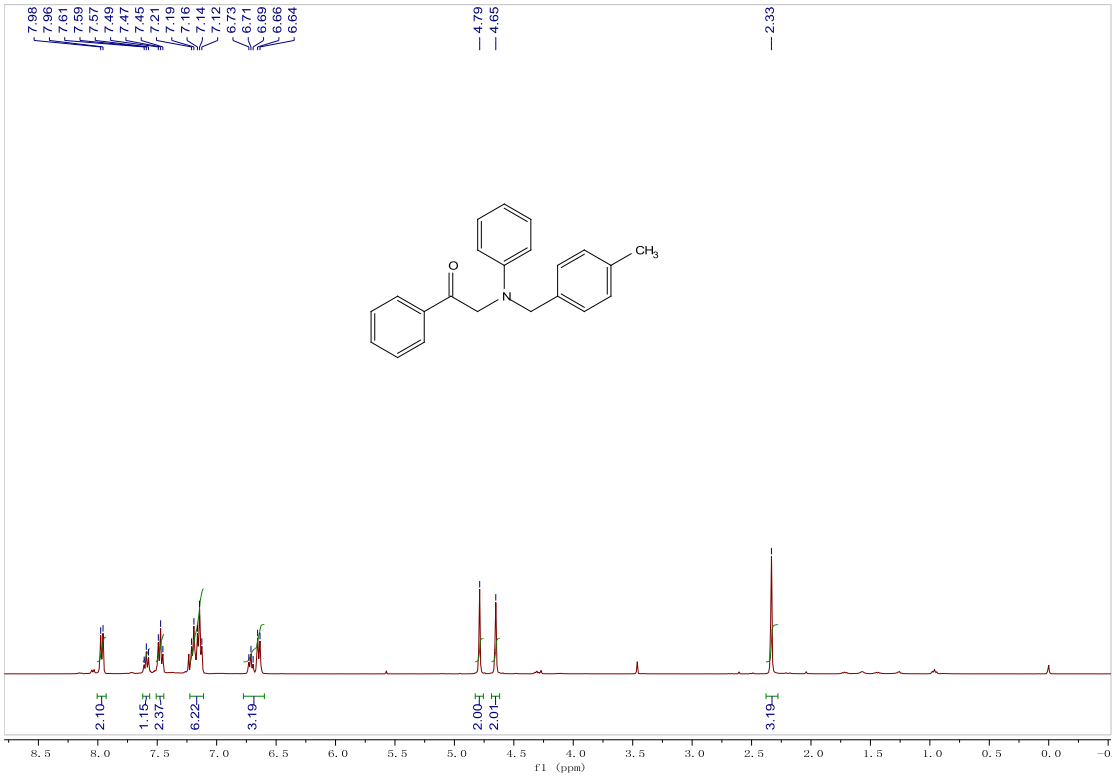


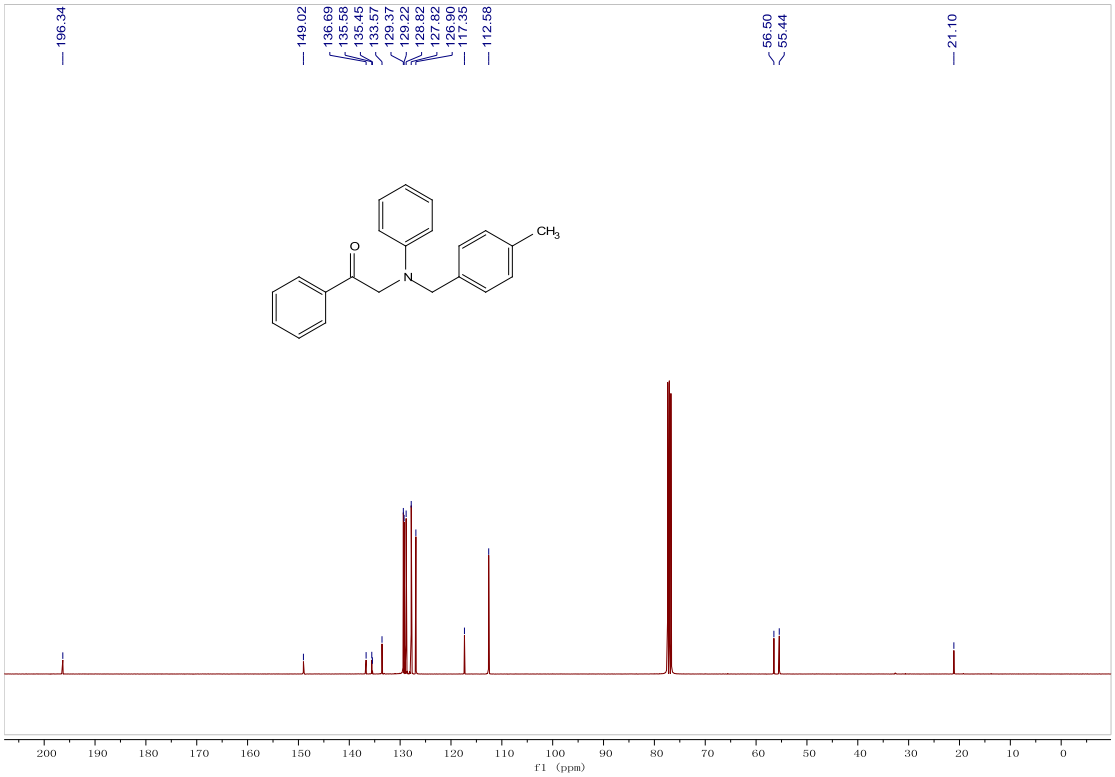
2-(benzyl(phenyl)amino)-1-phenylethan-1-one (**S-6g**)



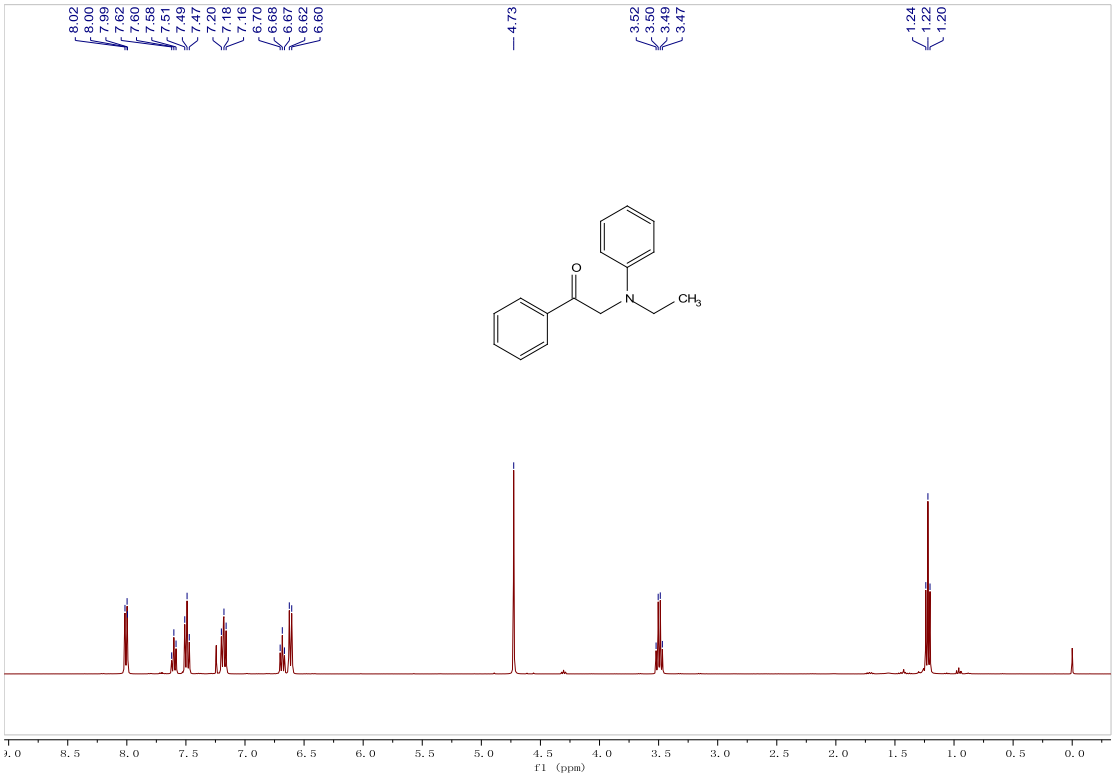


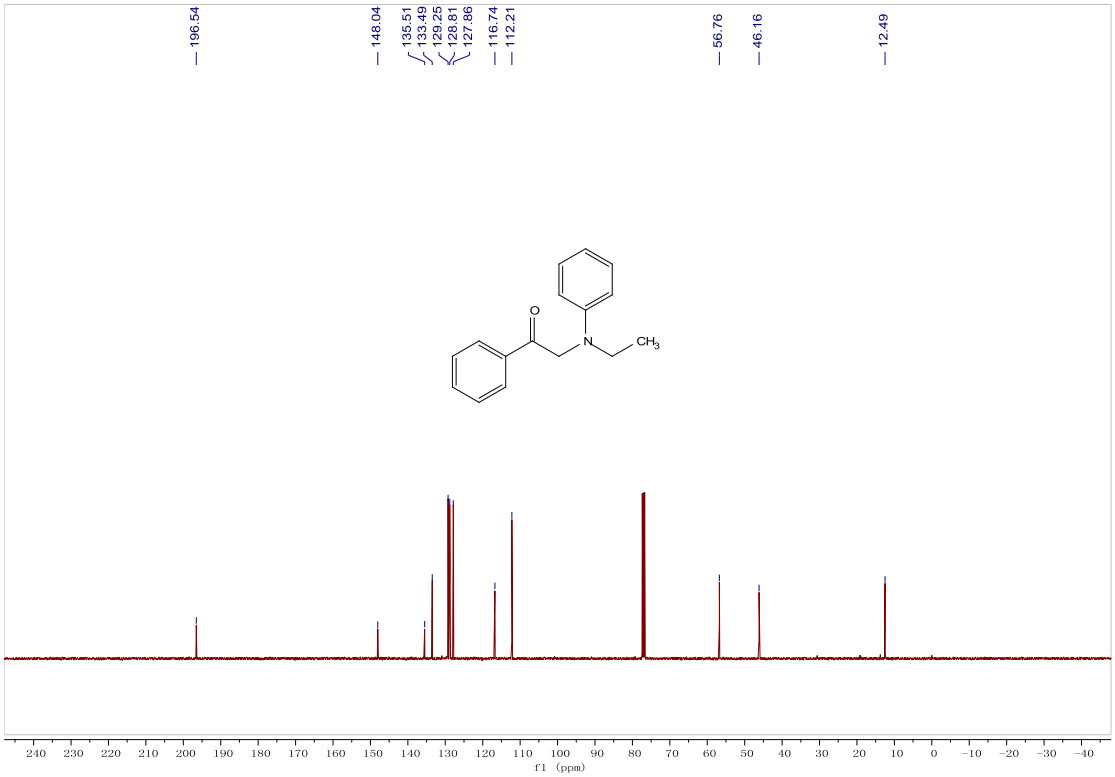
2-((4-methylbenzyl)(phenyl)amino)-1-phenylethan-1-one (**S-6h**)



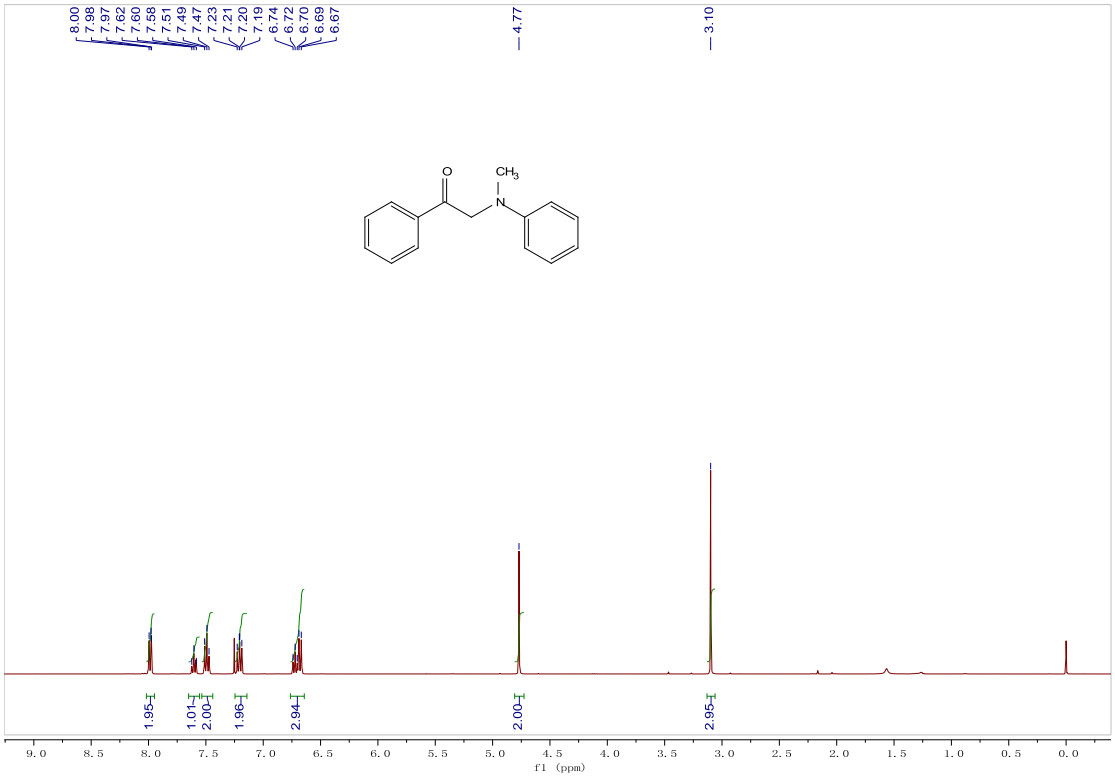


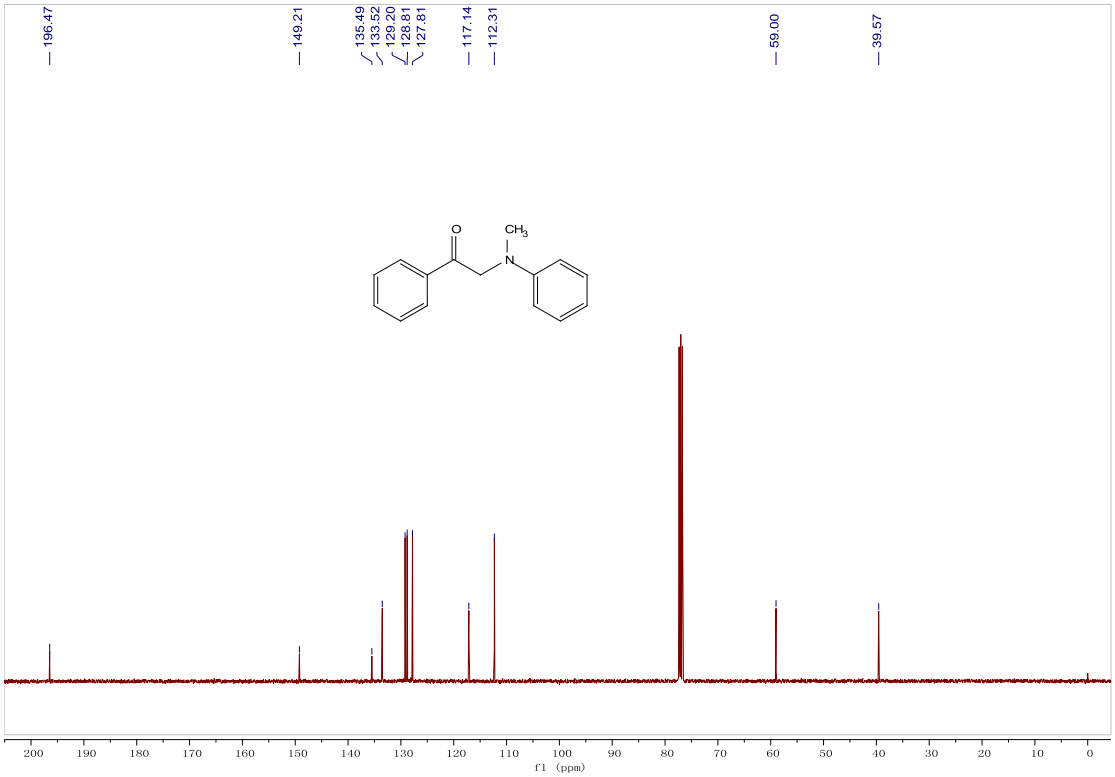
2-(ethyl(phenyl)amino)-1-phenylethan-1-one (S-**6i**)



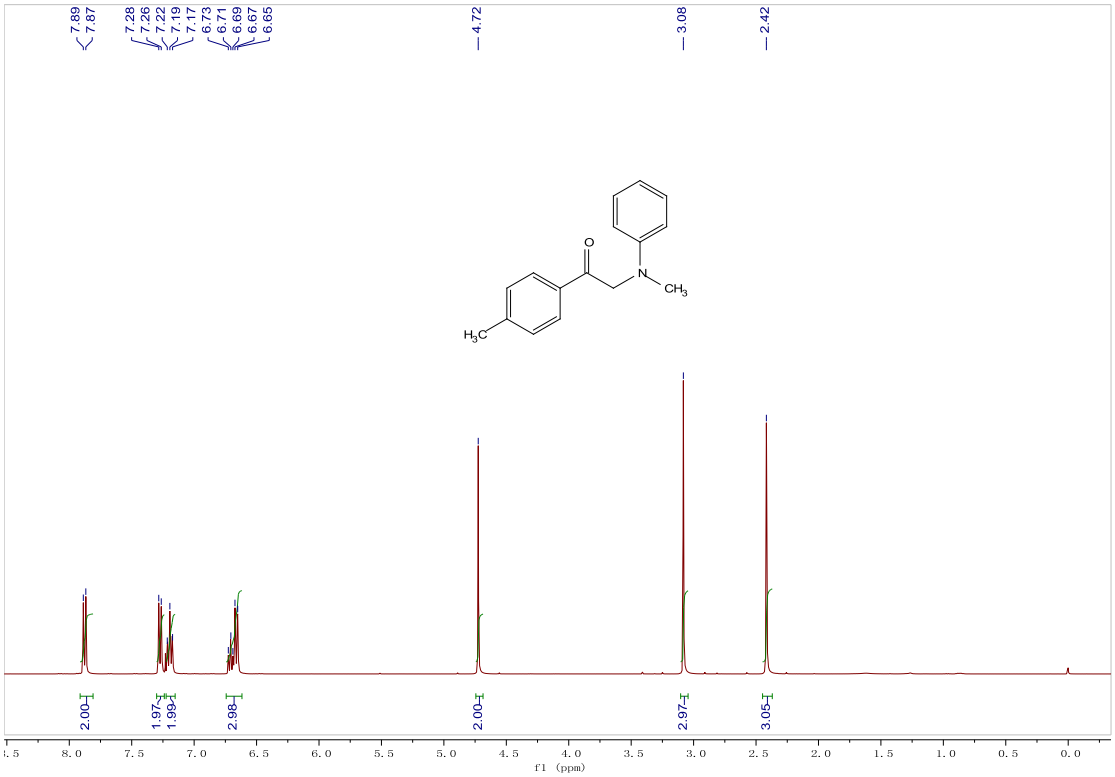


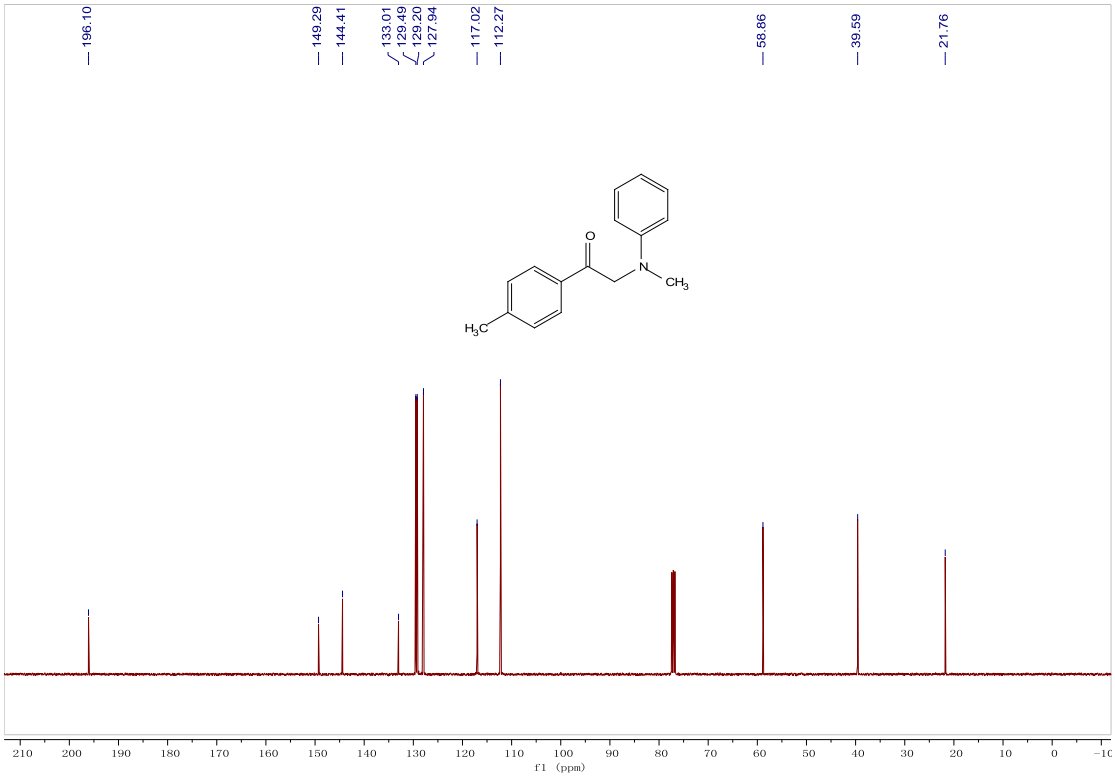
2-(methyl(phenyl)amino)-1-phenylethan-1-one (**S-6j**)



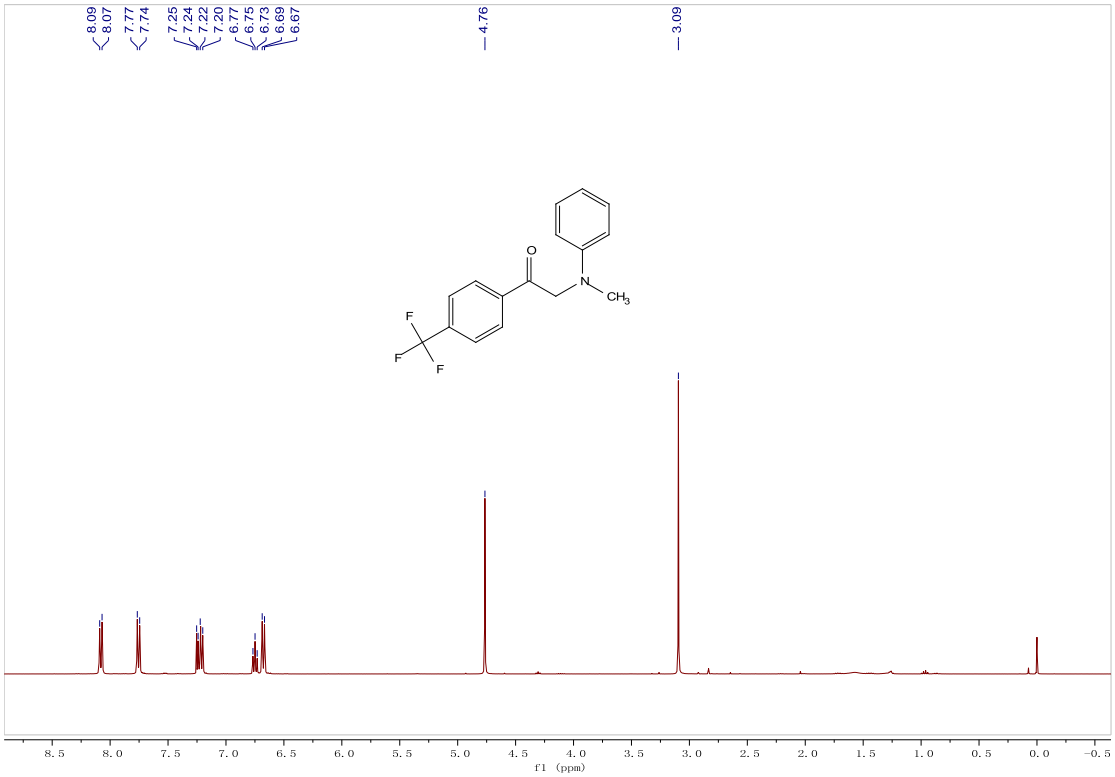


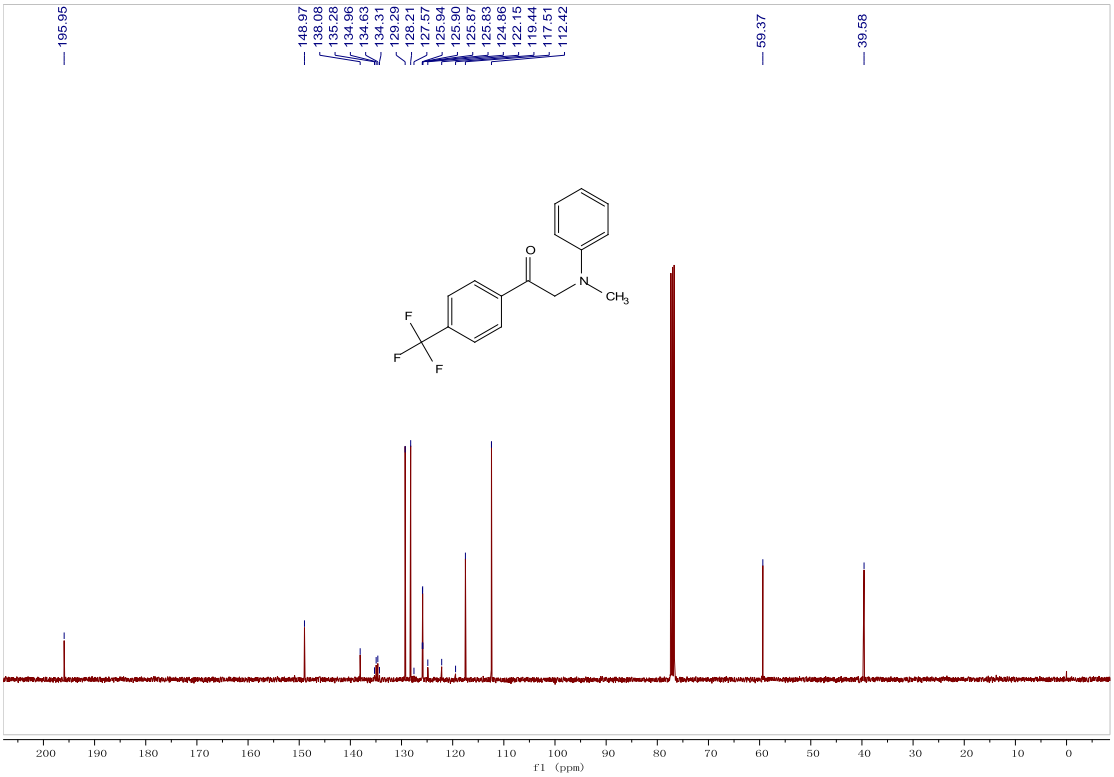
2-(methyl(phenyl)amino)-1-(p-tolyl)ethan-1-one (**S-6k**)





2-(methyl(phenyl)amino)-1-(4-(trifluoromethyl)phenyl)ethan-1-one (**S-6l**)




195.95
148.97
138.08
135.28
134.96
134.63
134.31
129.29
128.21
127.57
125.94
125.90
125.87
125.83
124.86
122.15
119.44
117.51
112.42
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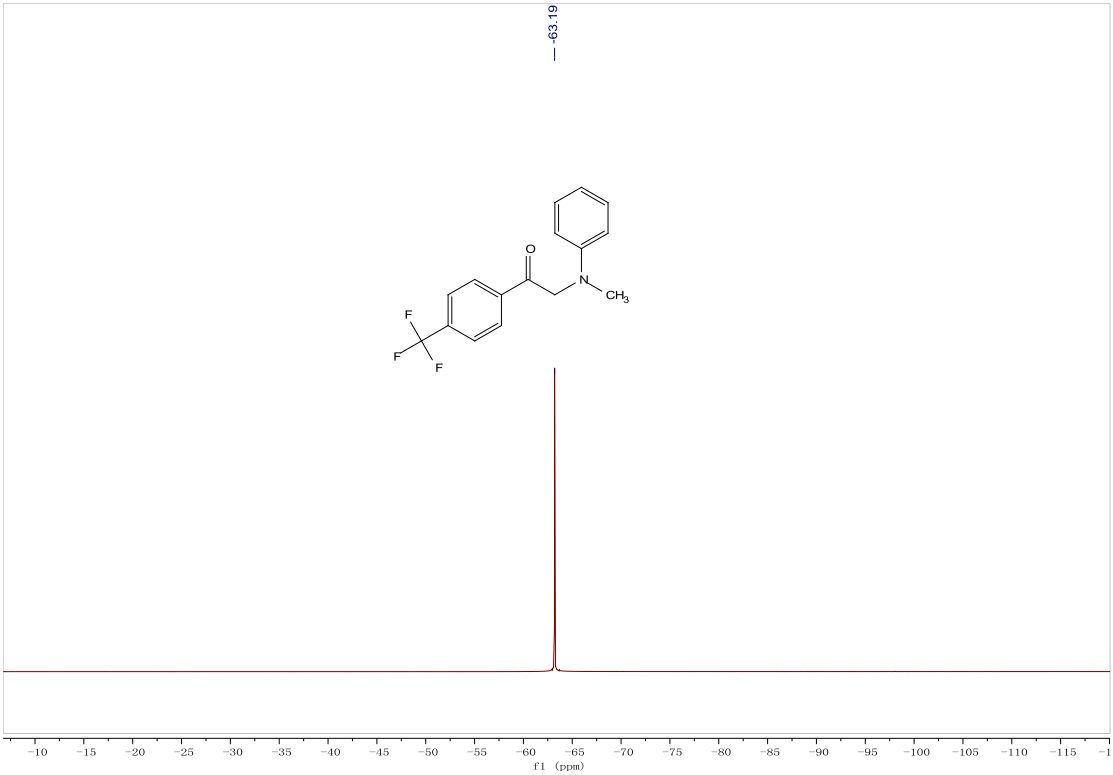
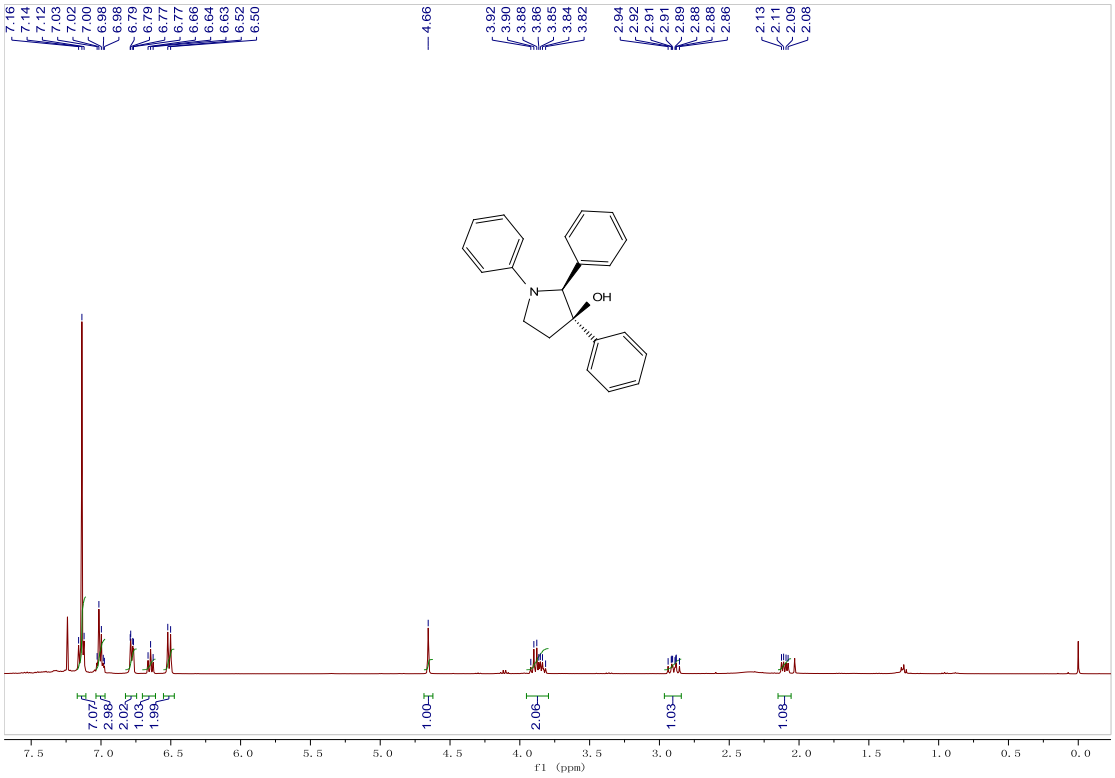
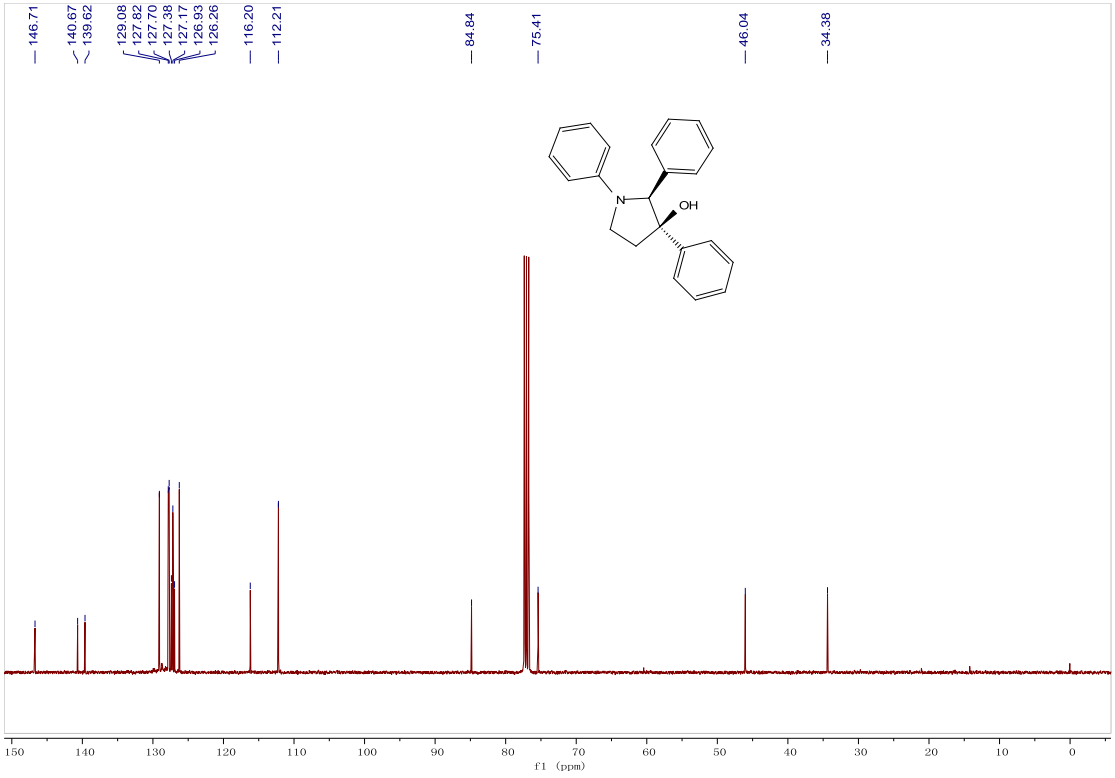
CH3
F
F
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-63.19
O
N
CH3
F
F
F
-10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115
f1 (ppm)

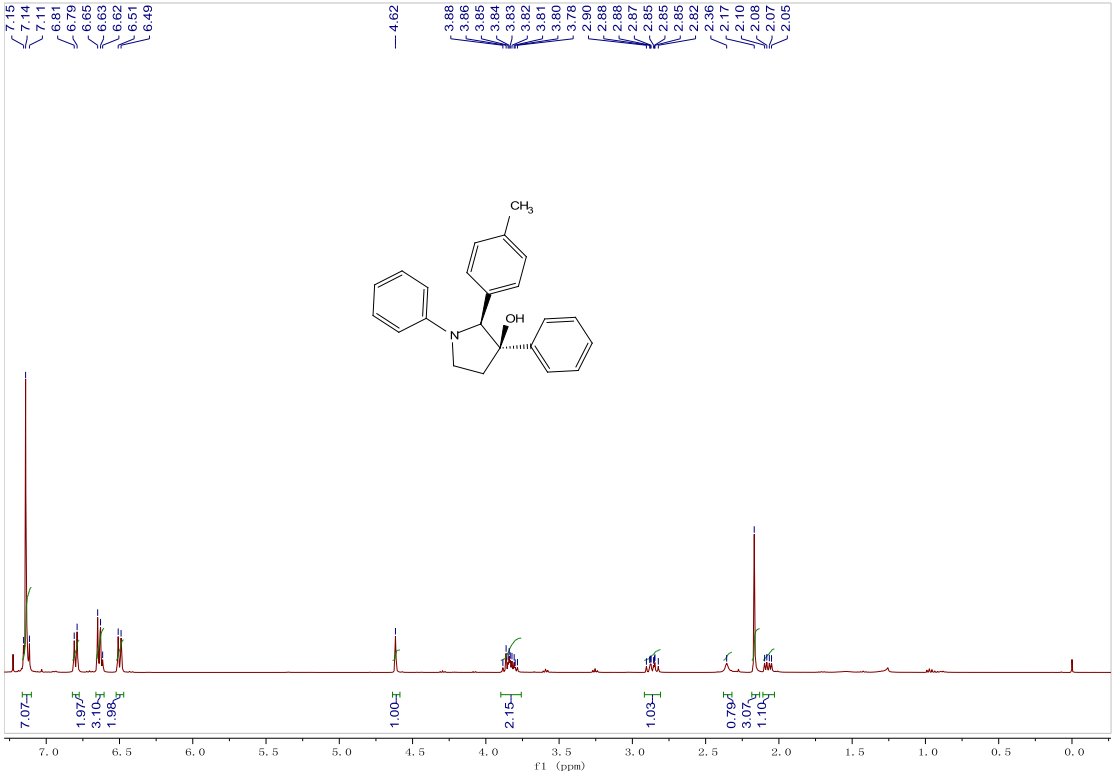
7. NMR spectra of products

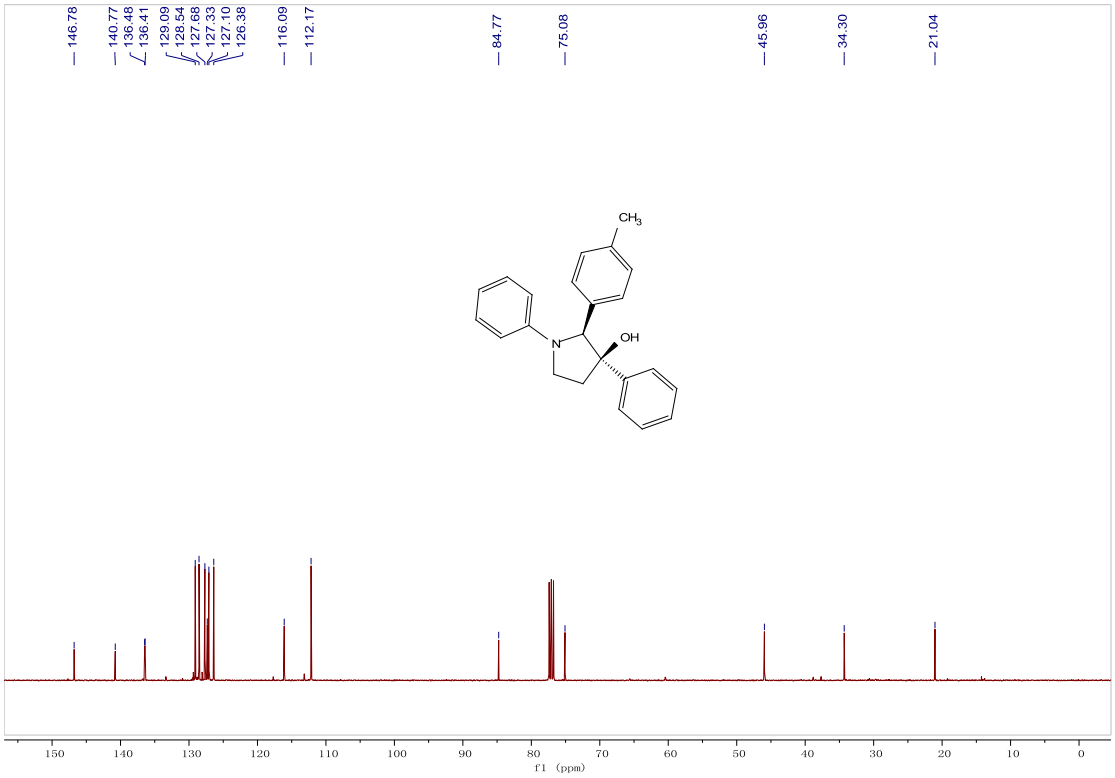
(trans)-1,2,3-triphenylpyrrolidin-3-ol (**2a**)



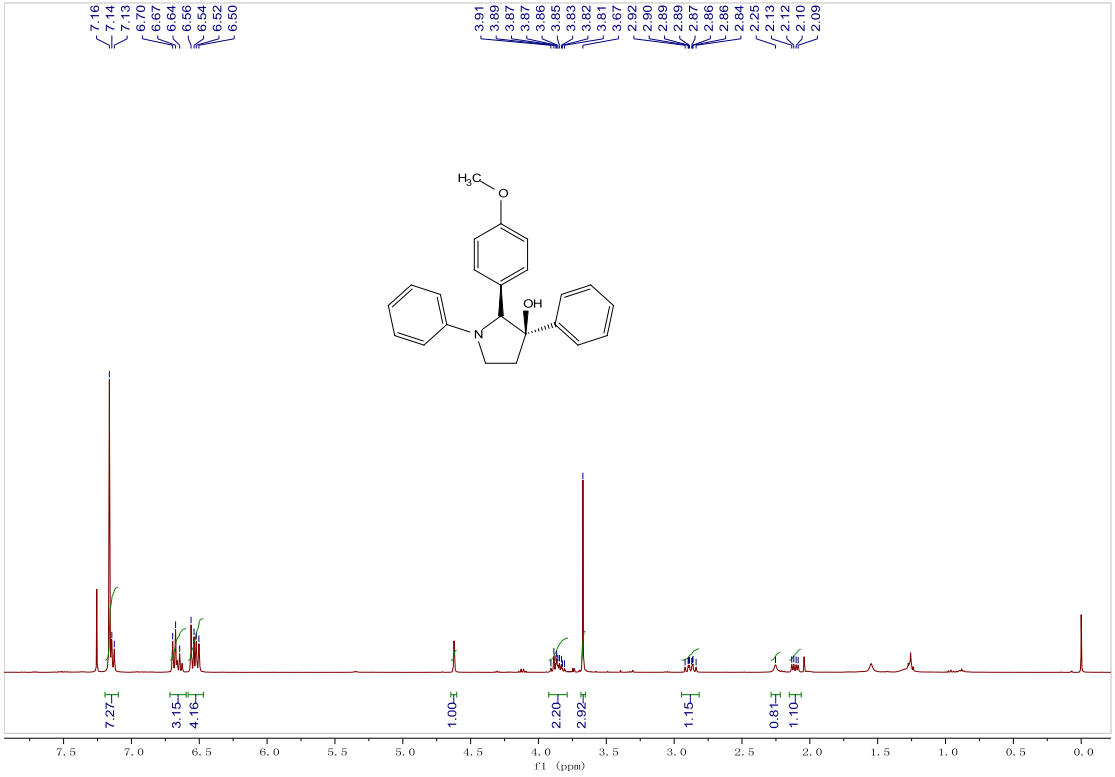


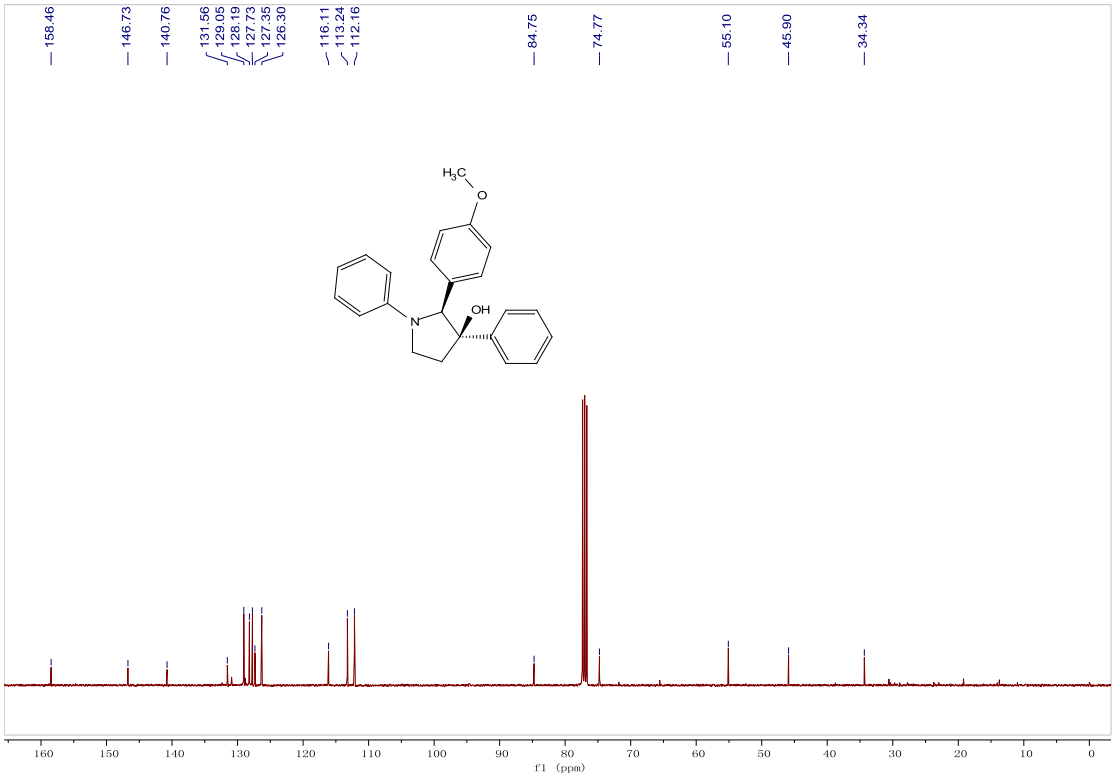
(trans)-1,3-diphenyl-2-(p-tolyl)pyrrolidin-3-ol (**2b**)



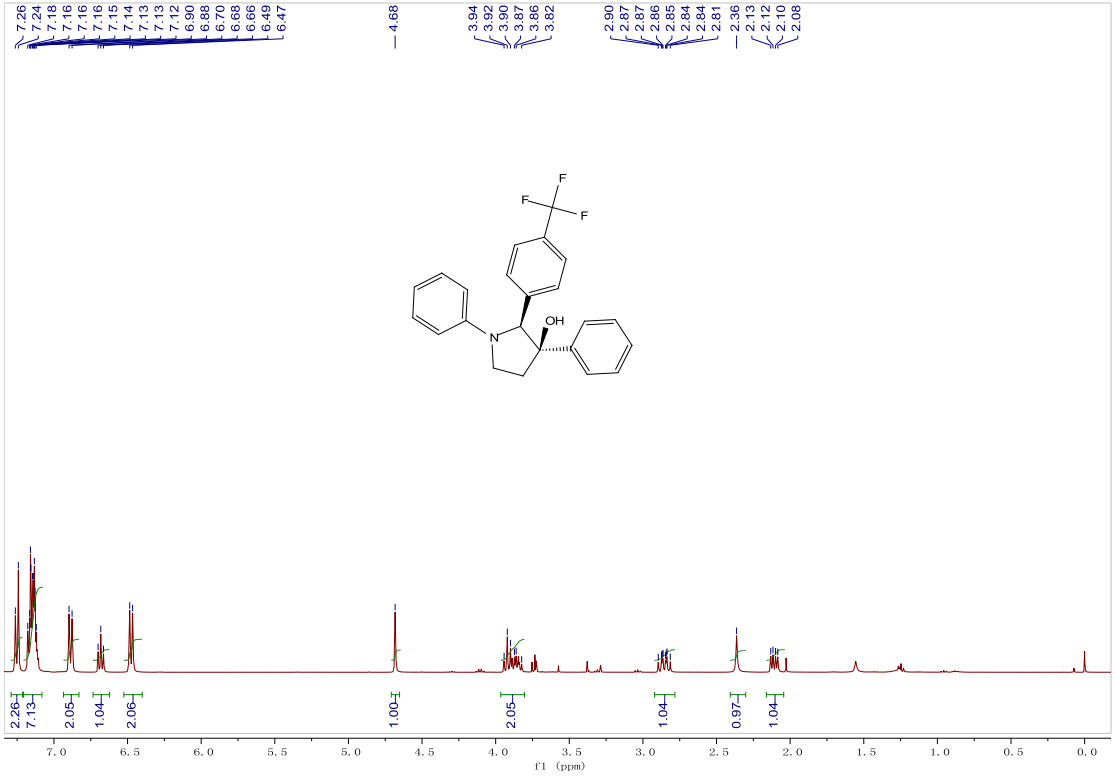


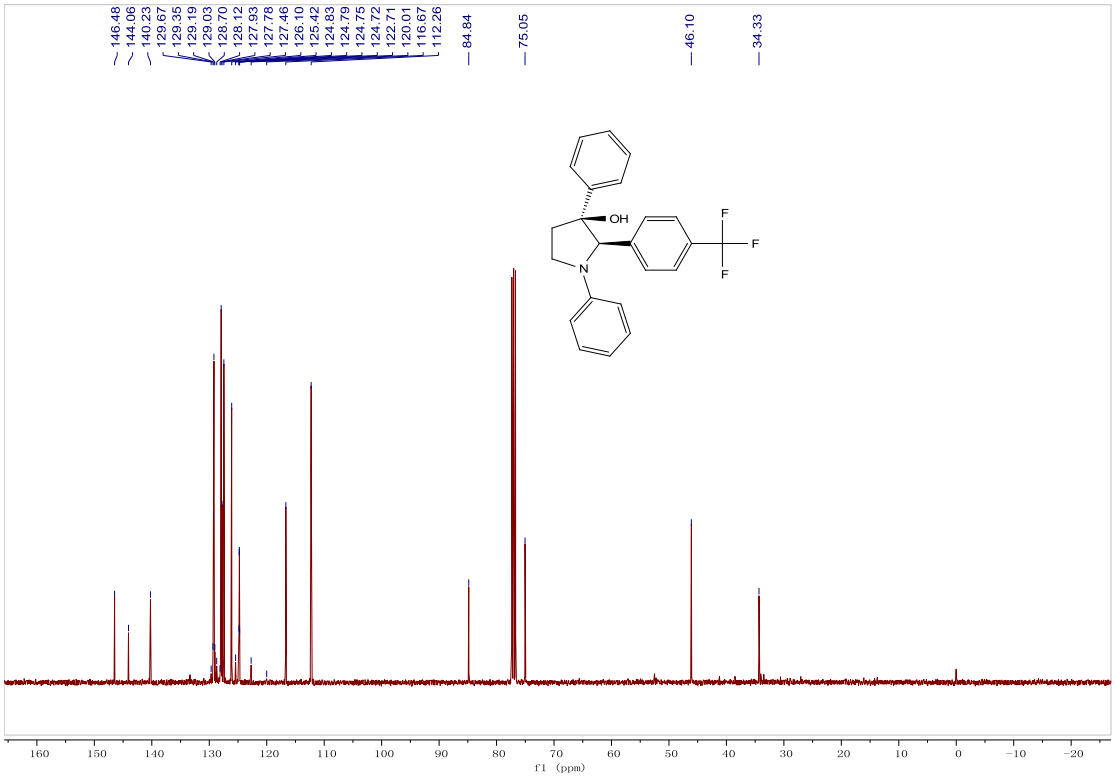
(trans)-2-(4-methoxyphenyl)-1,3-diphenylpyrrolidin-3-ol (**2c**)

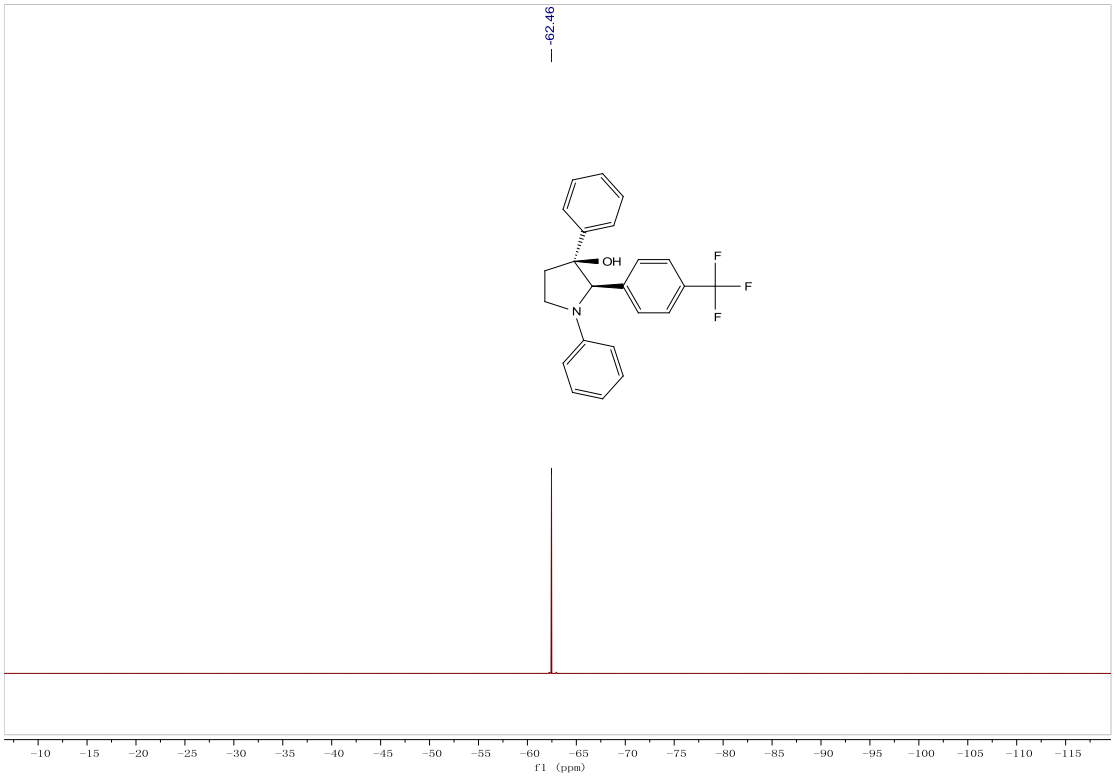




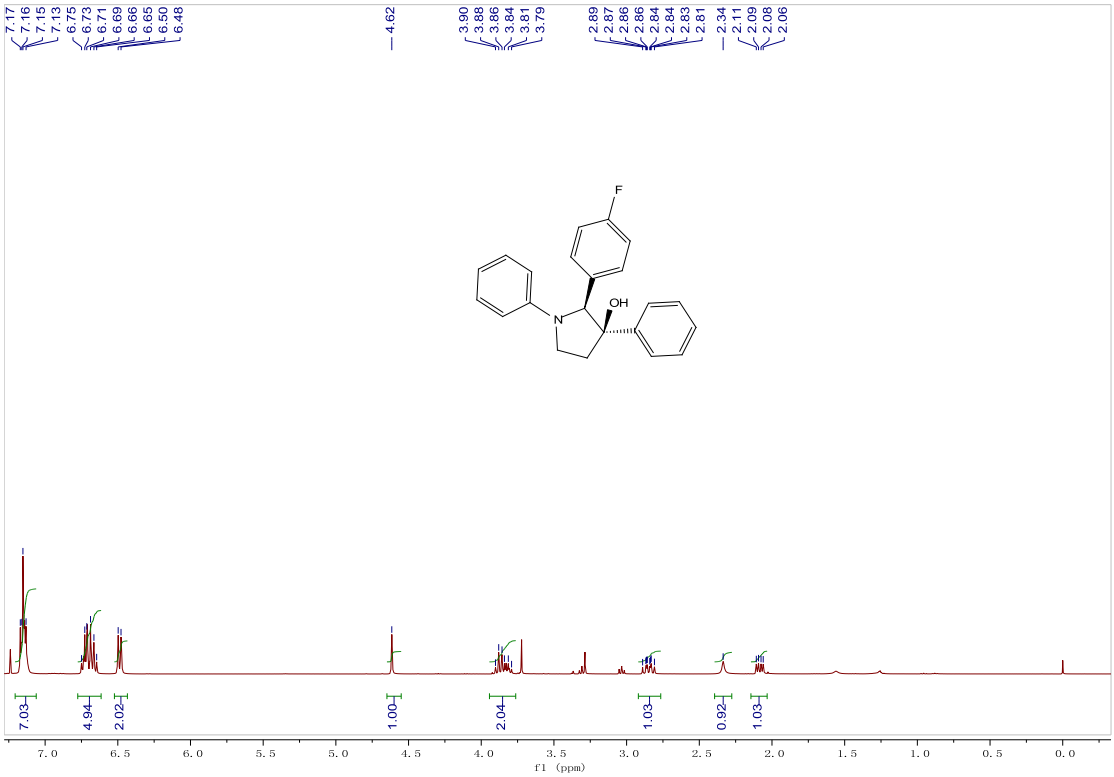
1,3-diphenyl-2-(4-(trifluoromethyl)phenyl)pyrrolidin-3-ol (**2d**)

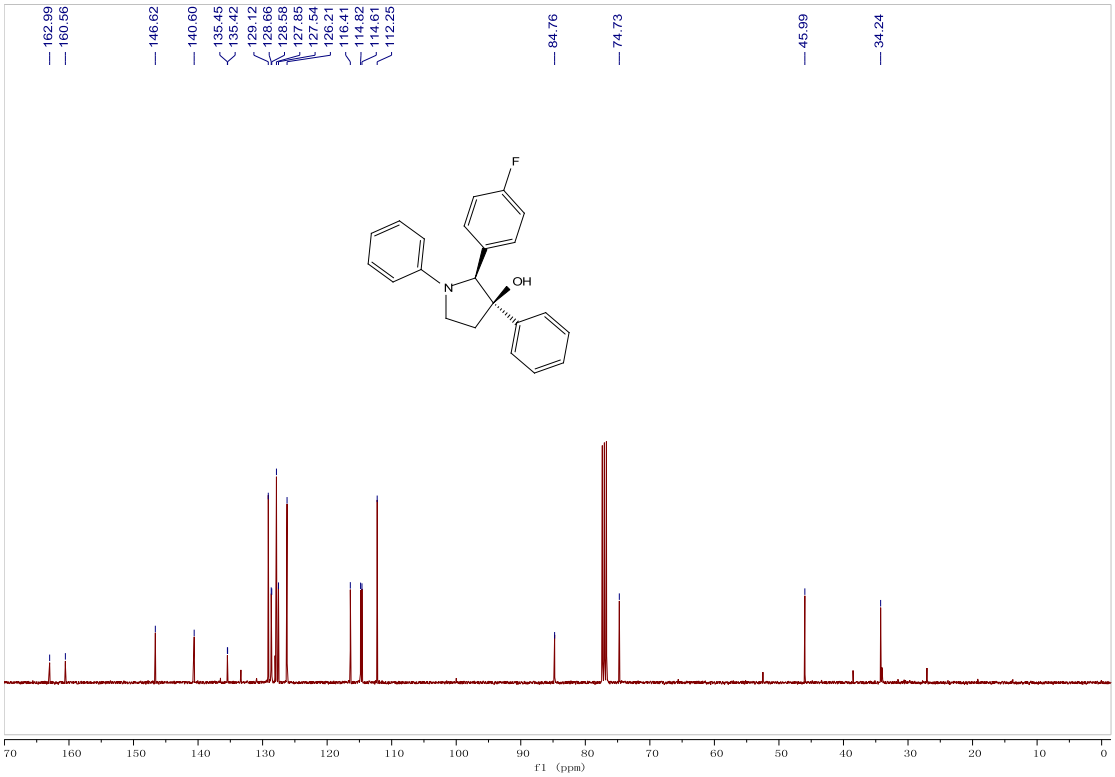






2-(4-fluorophenyl)-1,3-diphenylpyrrolidin-3-ol (**2e**)

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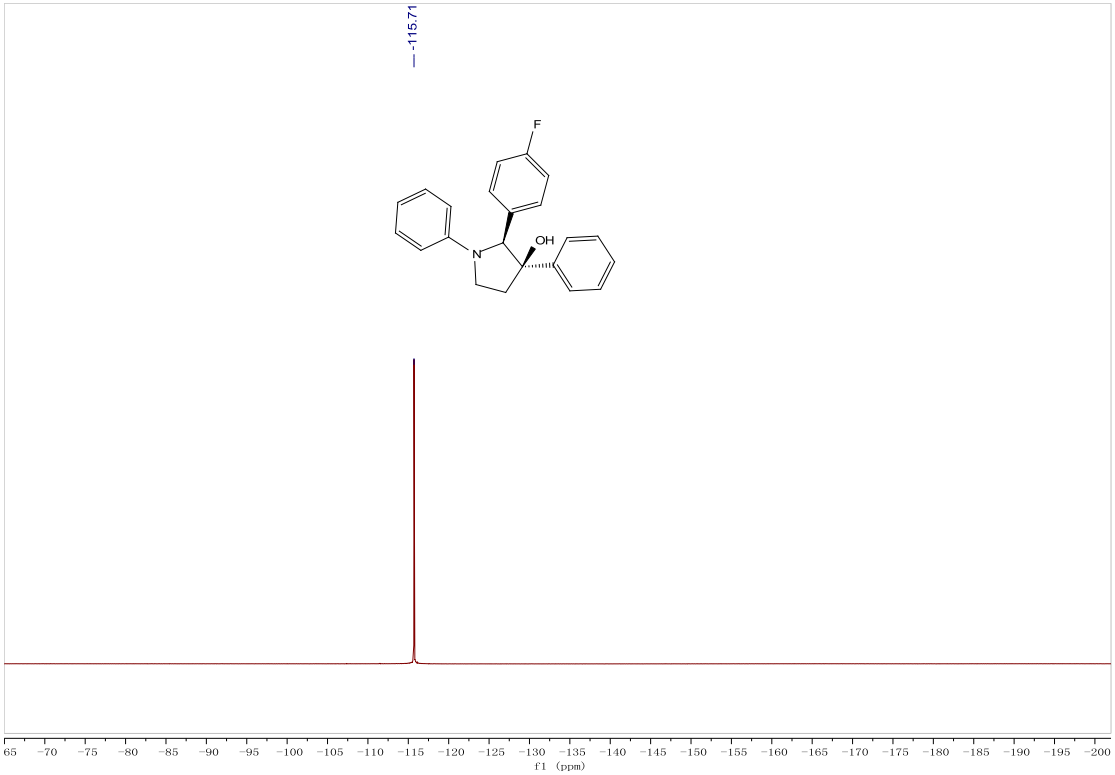
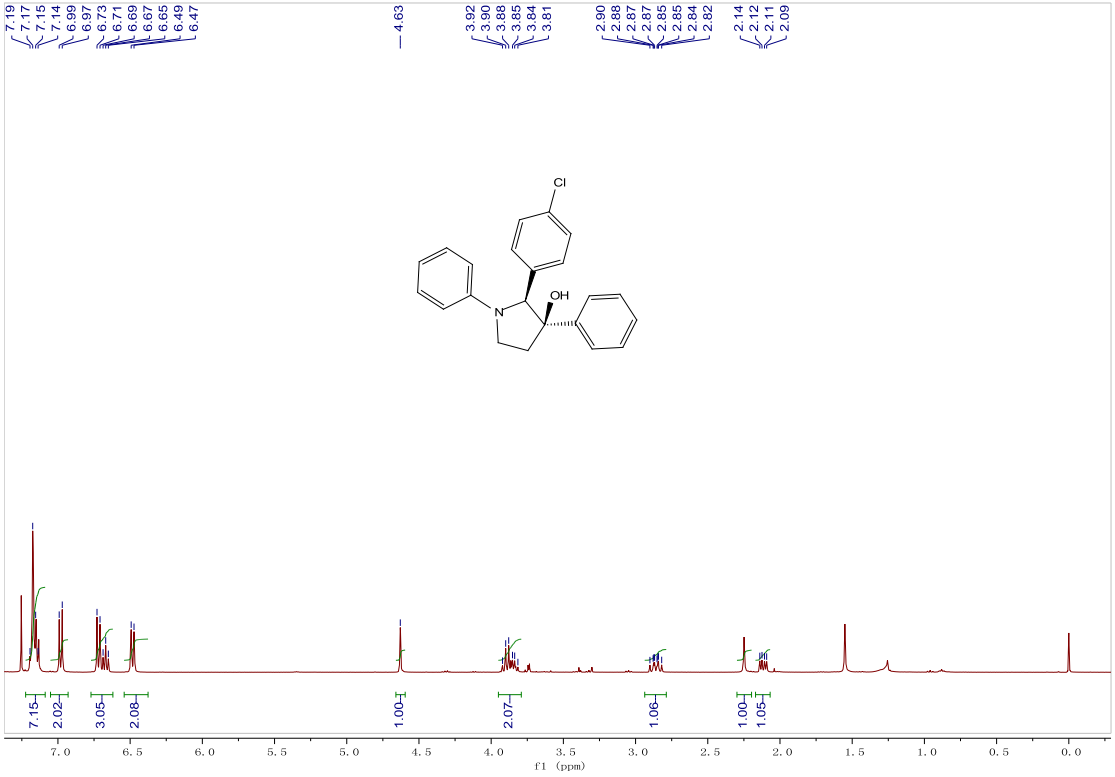
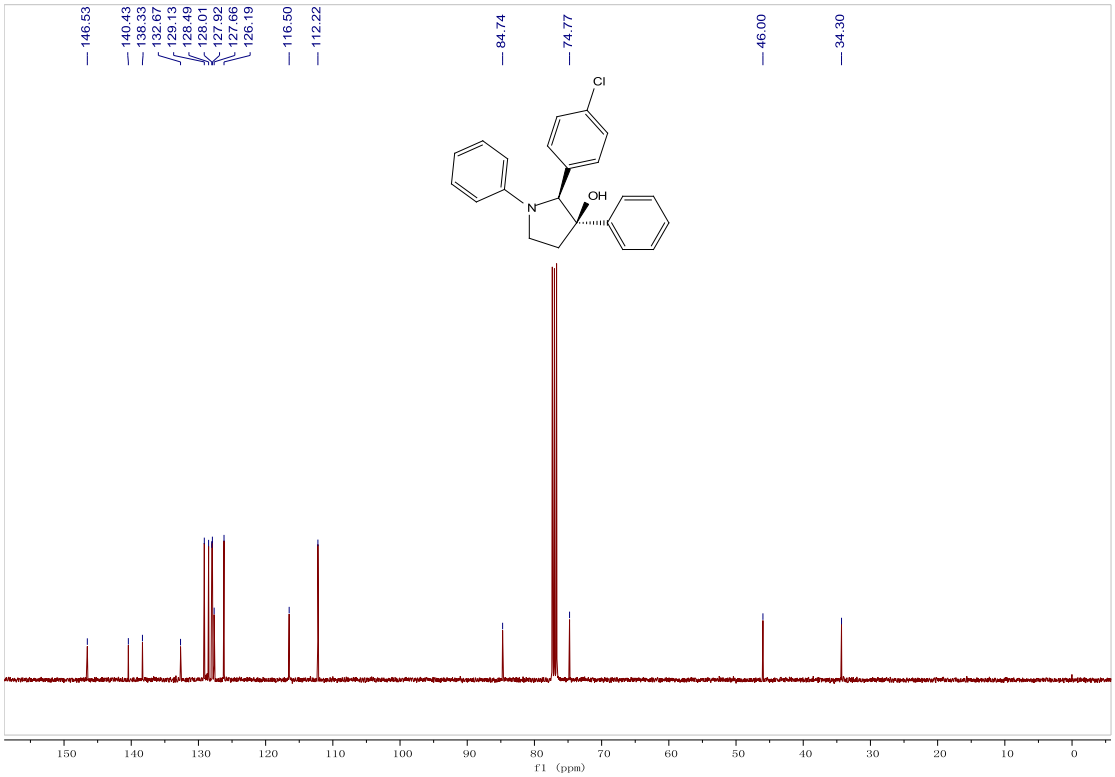
160.56
146.62
140.60
135.45
135.42
129.12
128.66
128.58
127.85
127.54
126.21
116.41
114.82
114.61
112.25
84.76
74.73
45.99
34.24
F
OH
N
f1 (ppm)

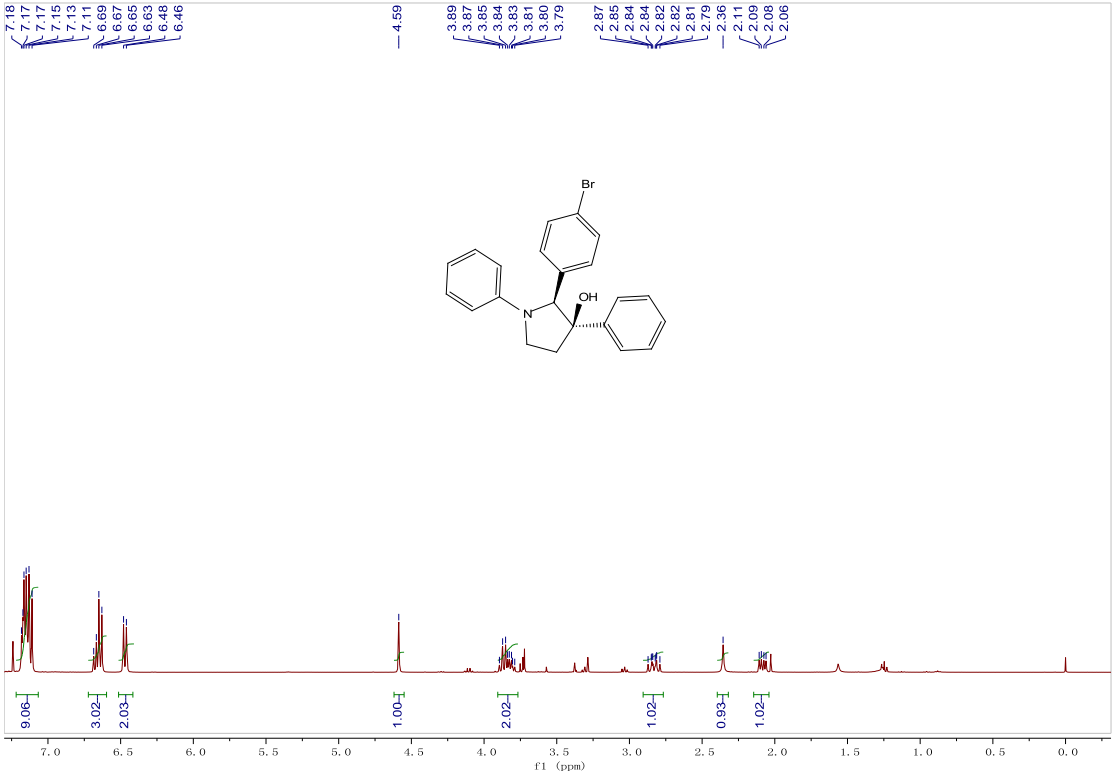

-115.71
F
OH
N
f1 (ppm)

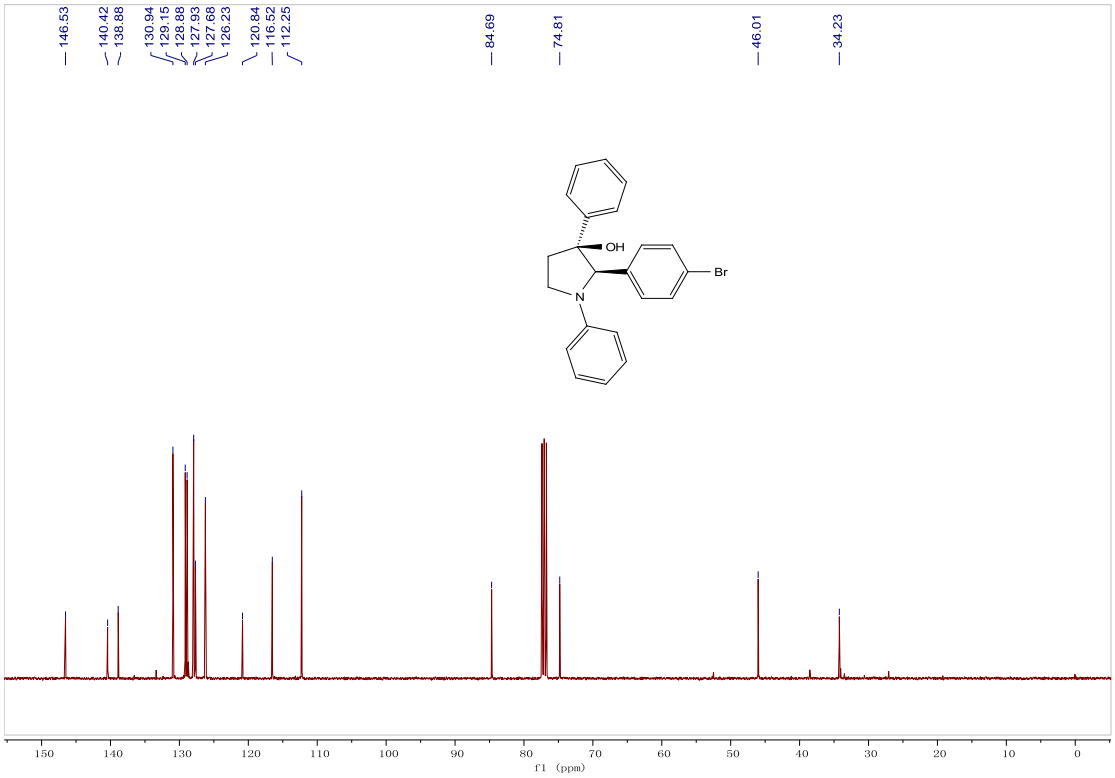
2-(4-chlorophenyl)-1,3-diphenylpyrrolidin-3-ol (**2f**)



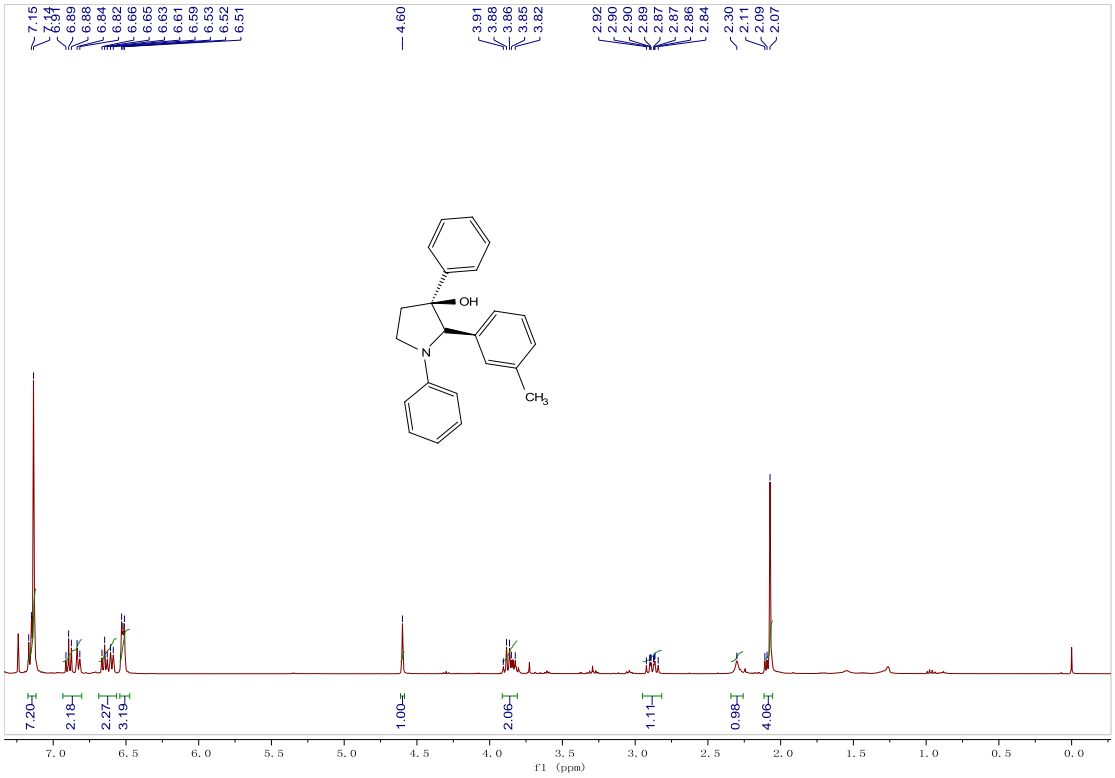


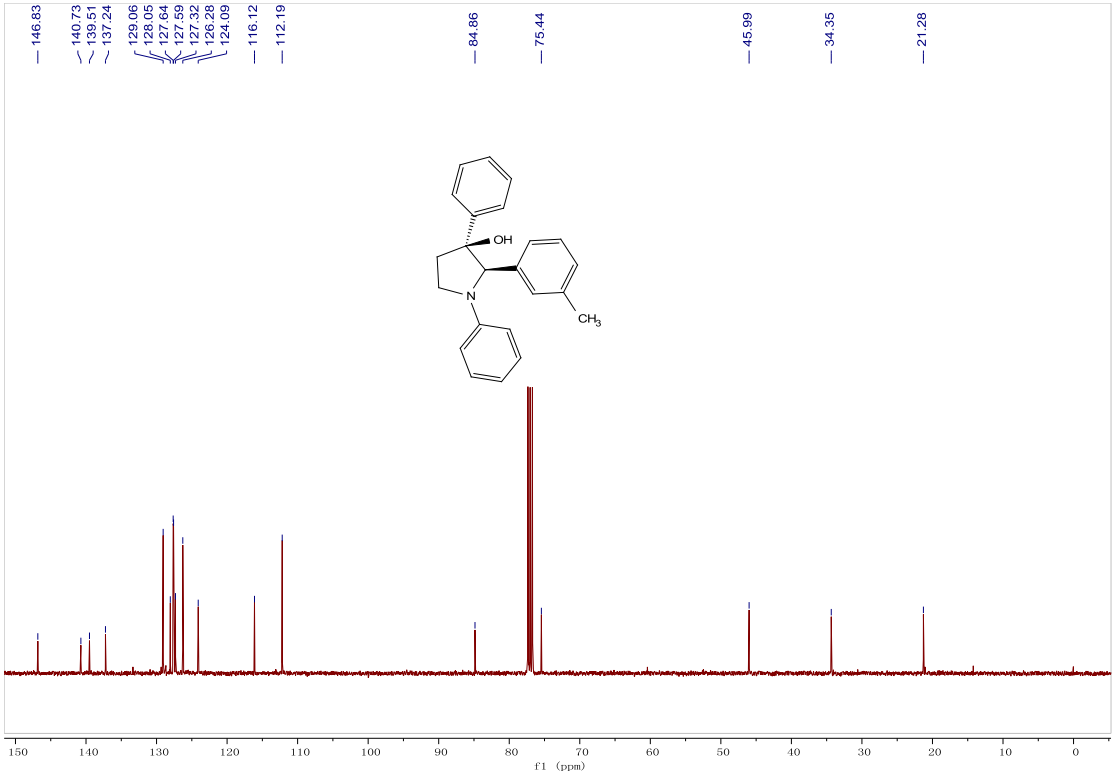
2-(4-bromophenyl)-1,3-diphenylpyrrolidin-3-ol (**2g**)



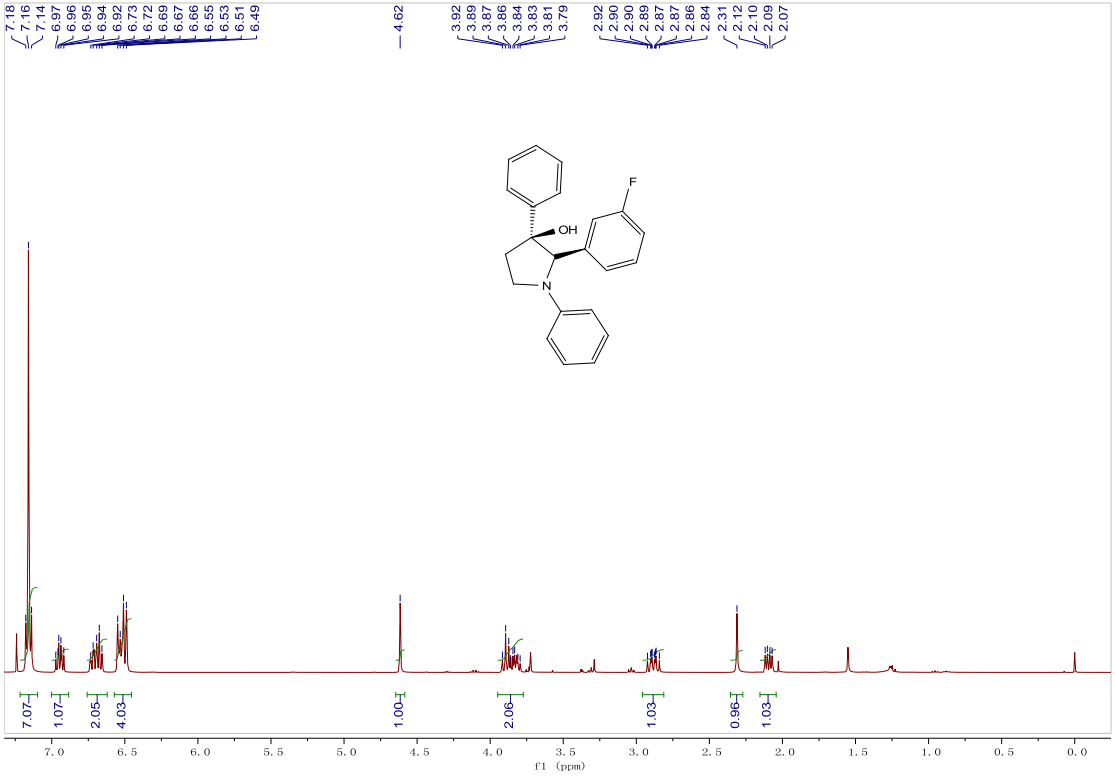


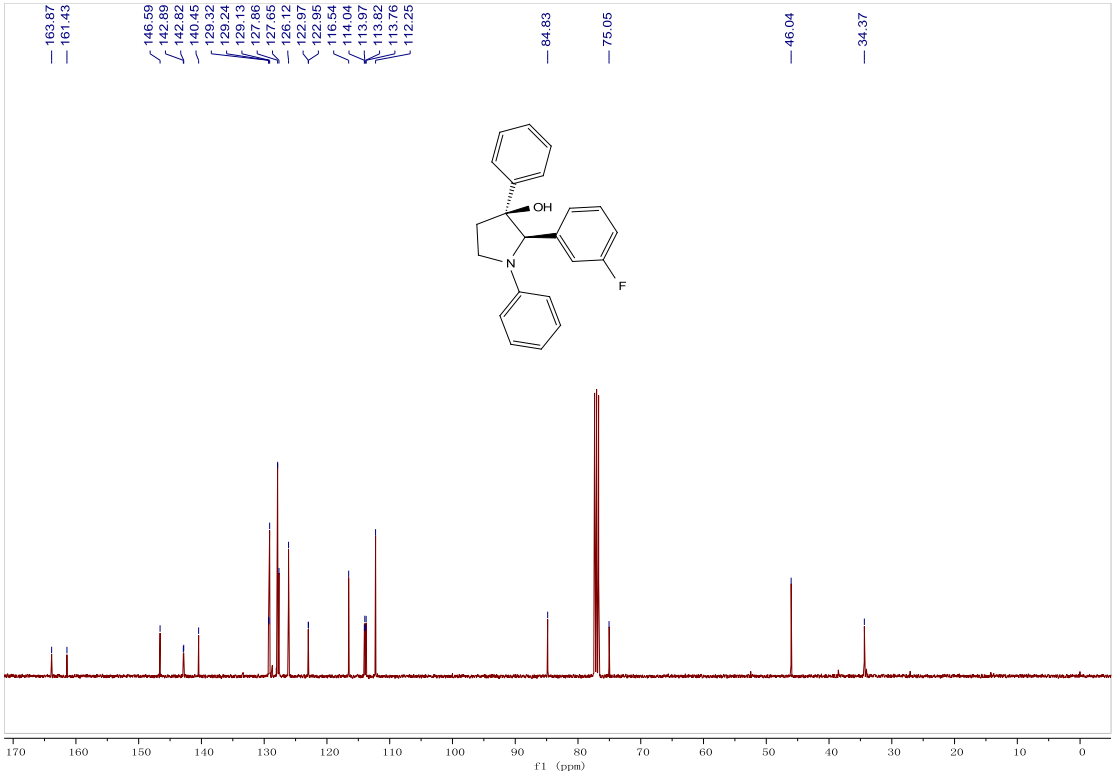
1,3-diphenyl-2-(m-tolyl)pyrrolidin-3-ol (**2h**)

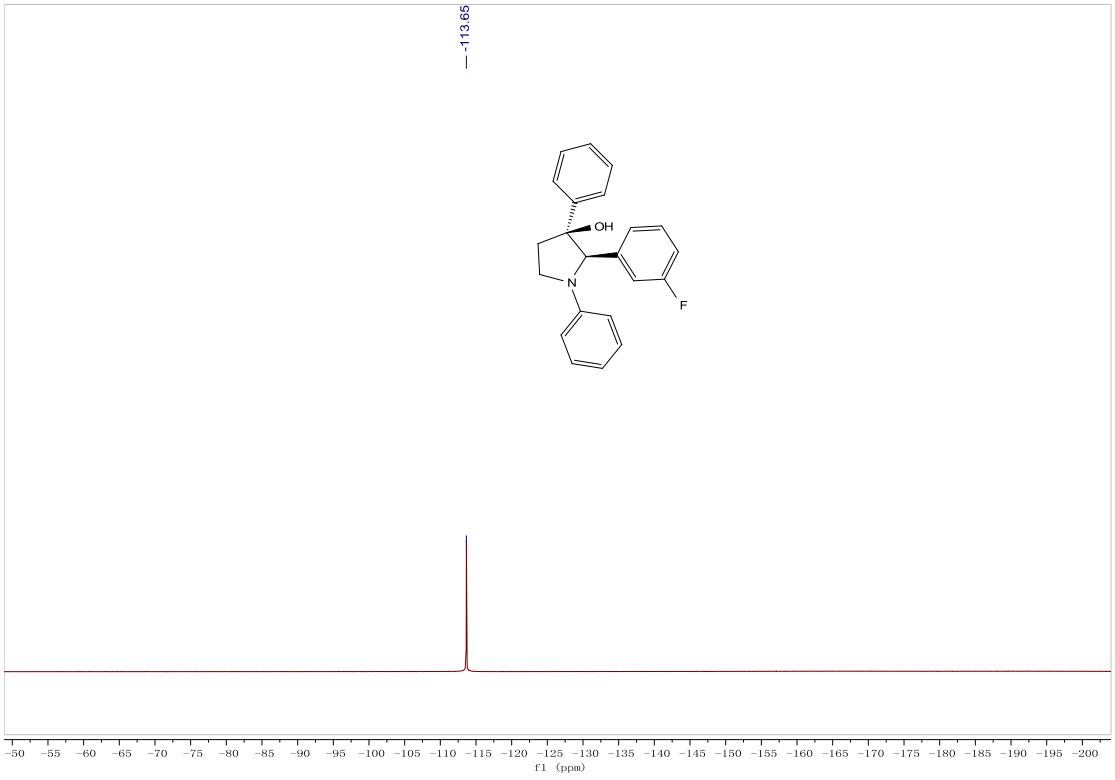




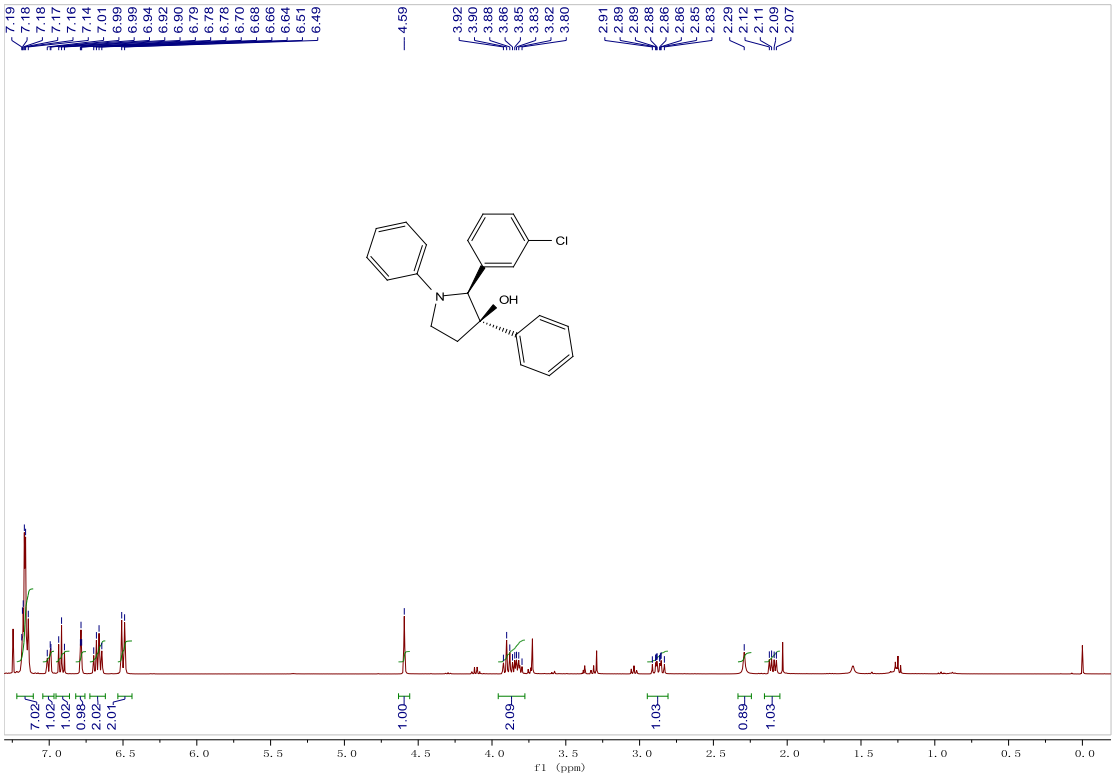
2-(3-fluorophenyl)-1,3-diphenylpyrrolidin-3-ol (**2i**)

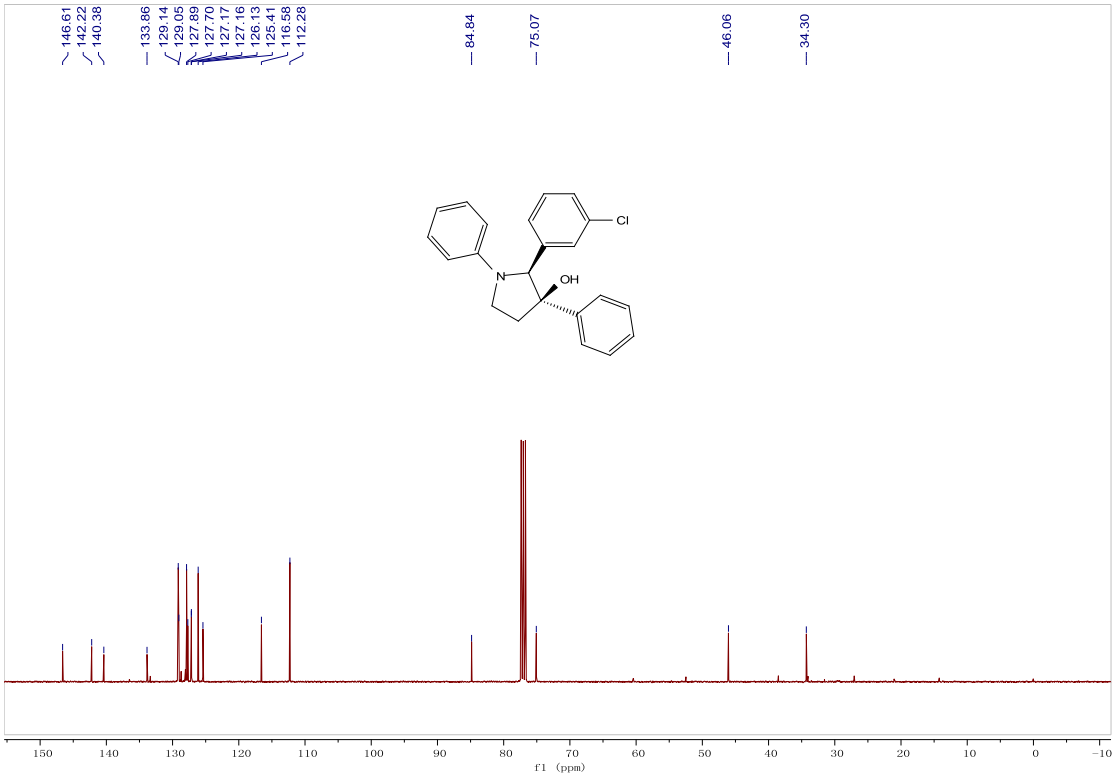




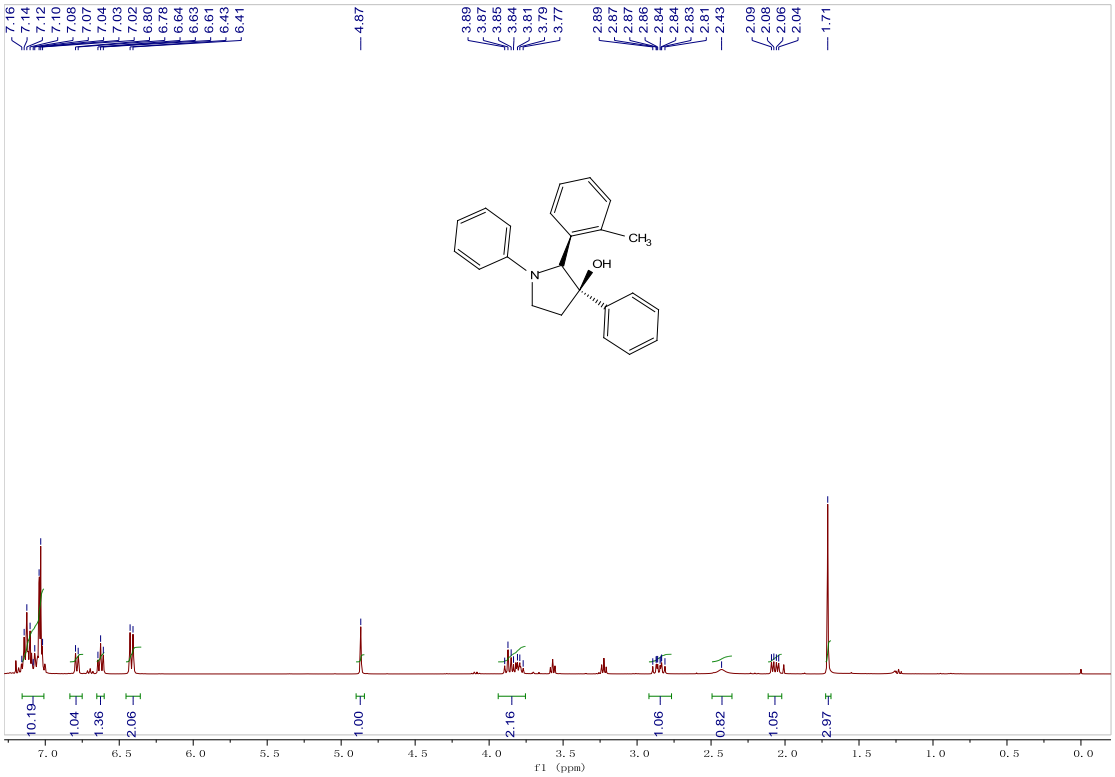


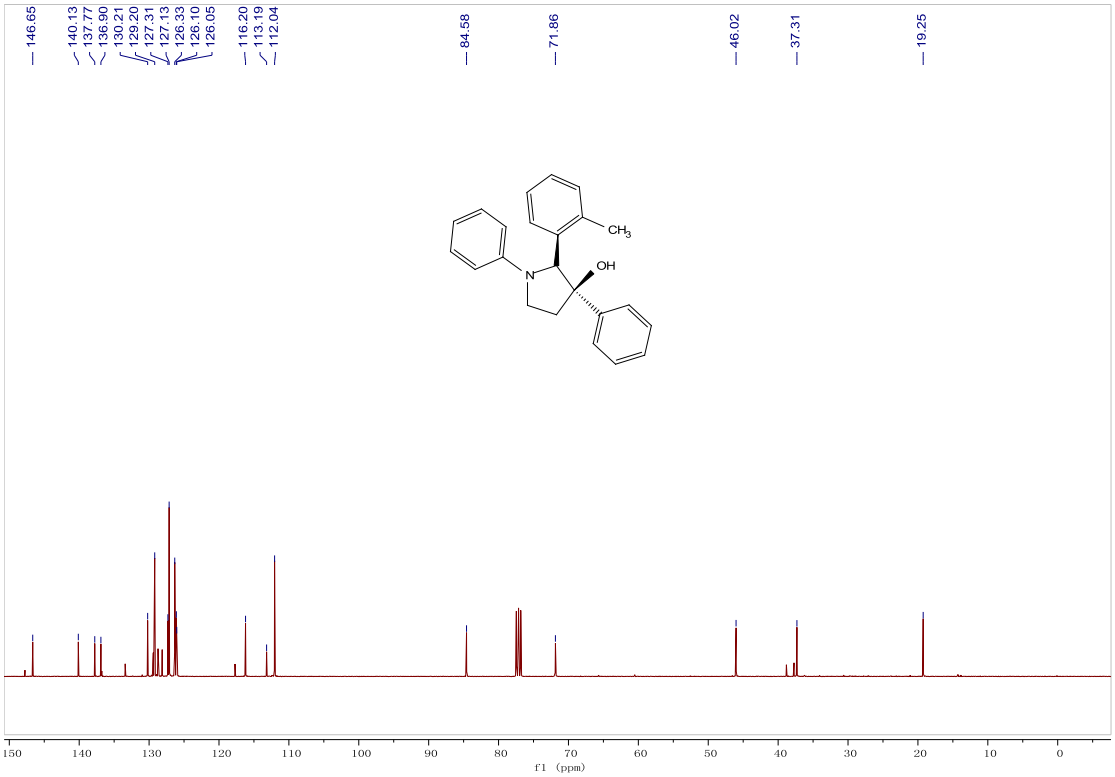
2-(3-chlorophenyl)-1,3-diphenylpyrrolidin-3-ol (**2j**)



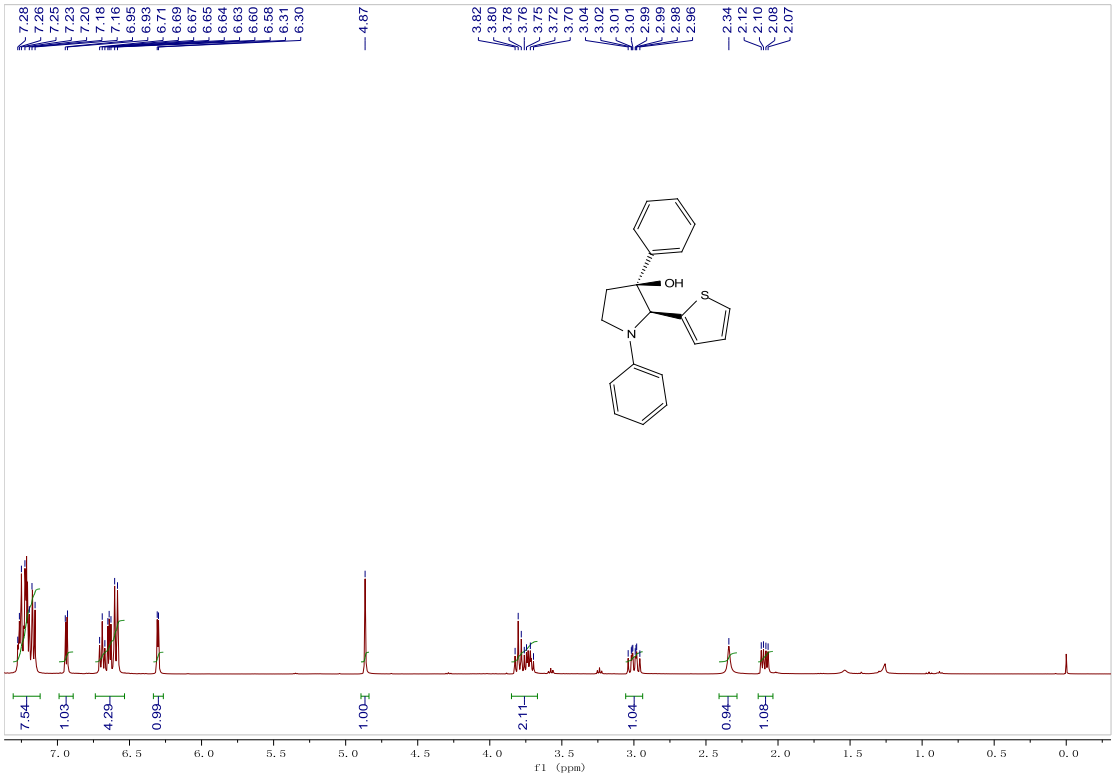


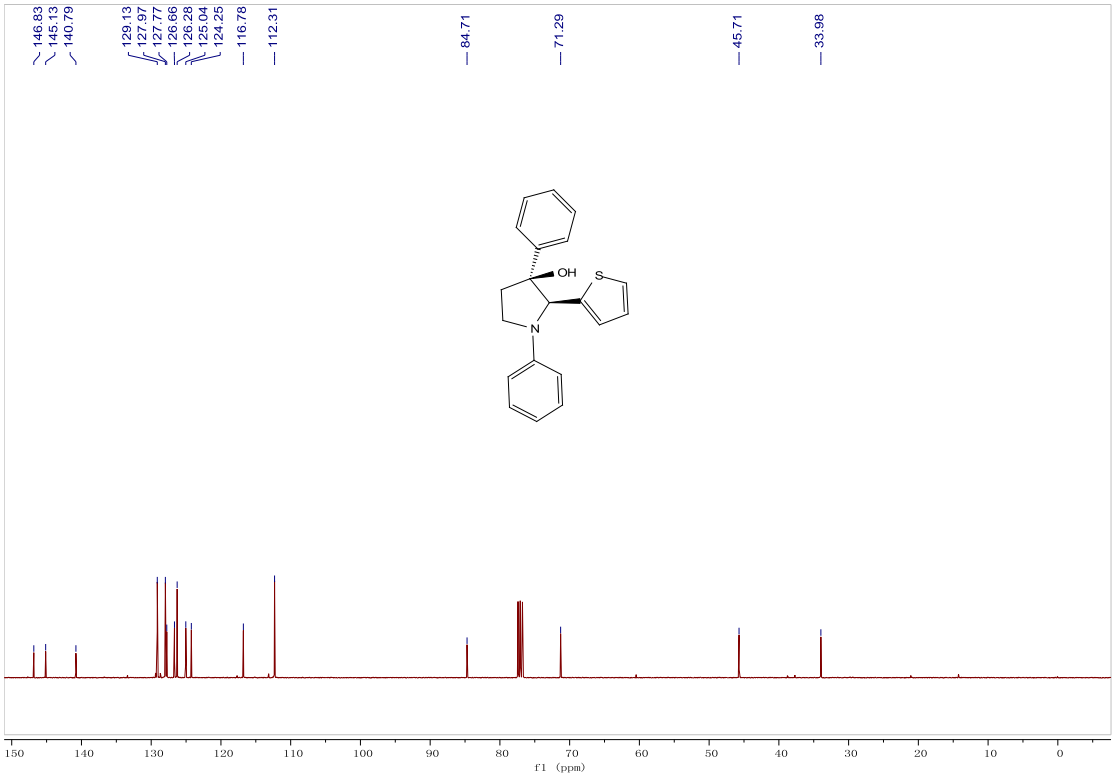
1,3-diphenyl-2-(o-tolyl)pyrrolidin-3-ol (**2k**)



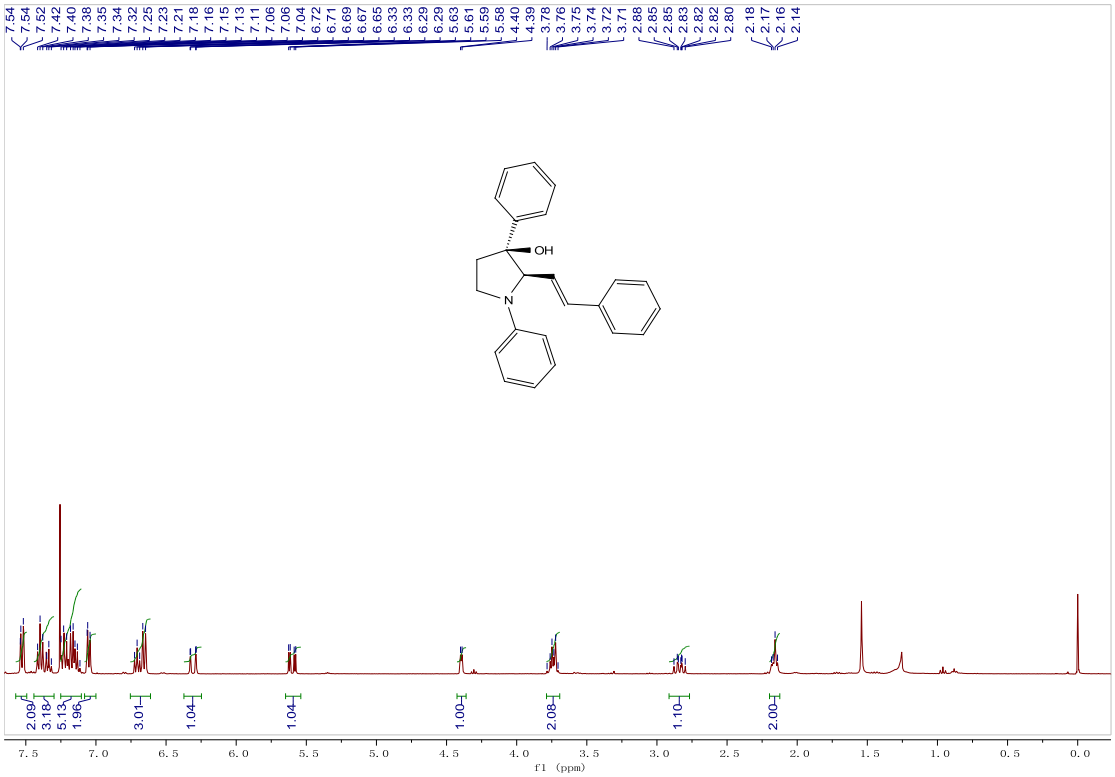


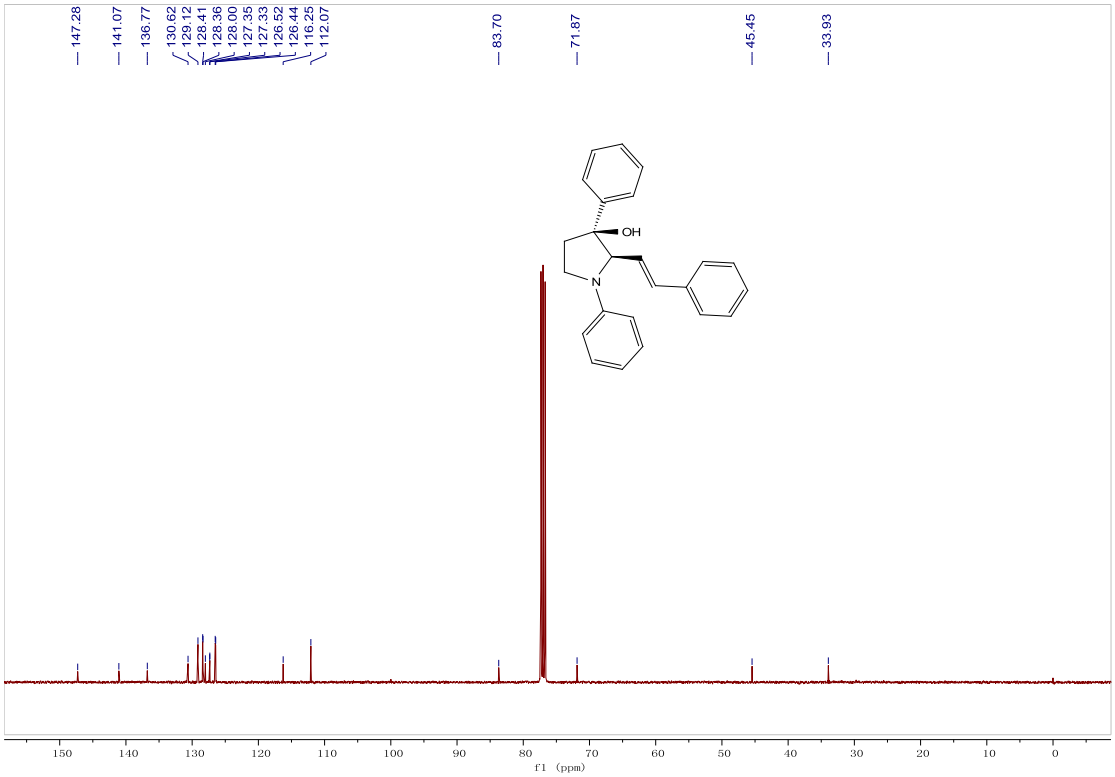
1,3-diphenyl-2-(thiophen-2-yl)pyrrolidin-3-ol (**2l**)



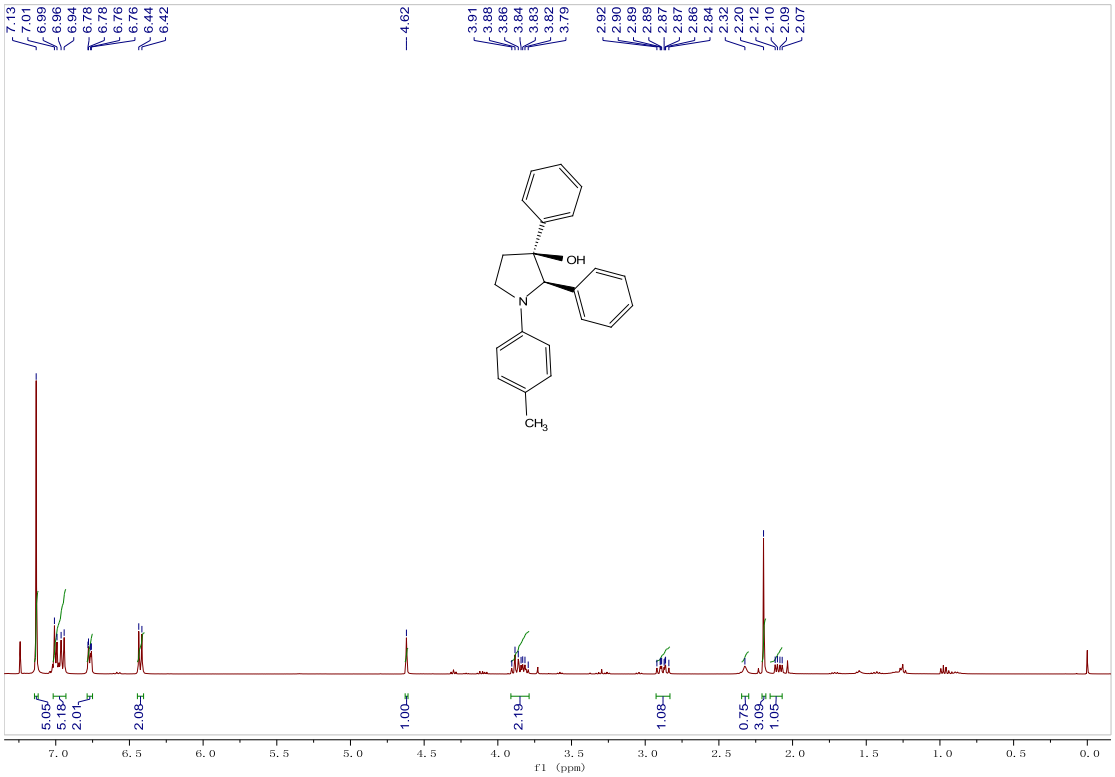


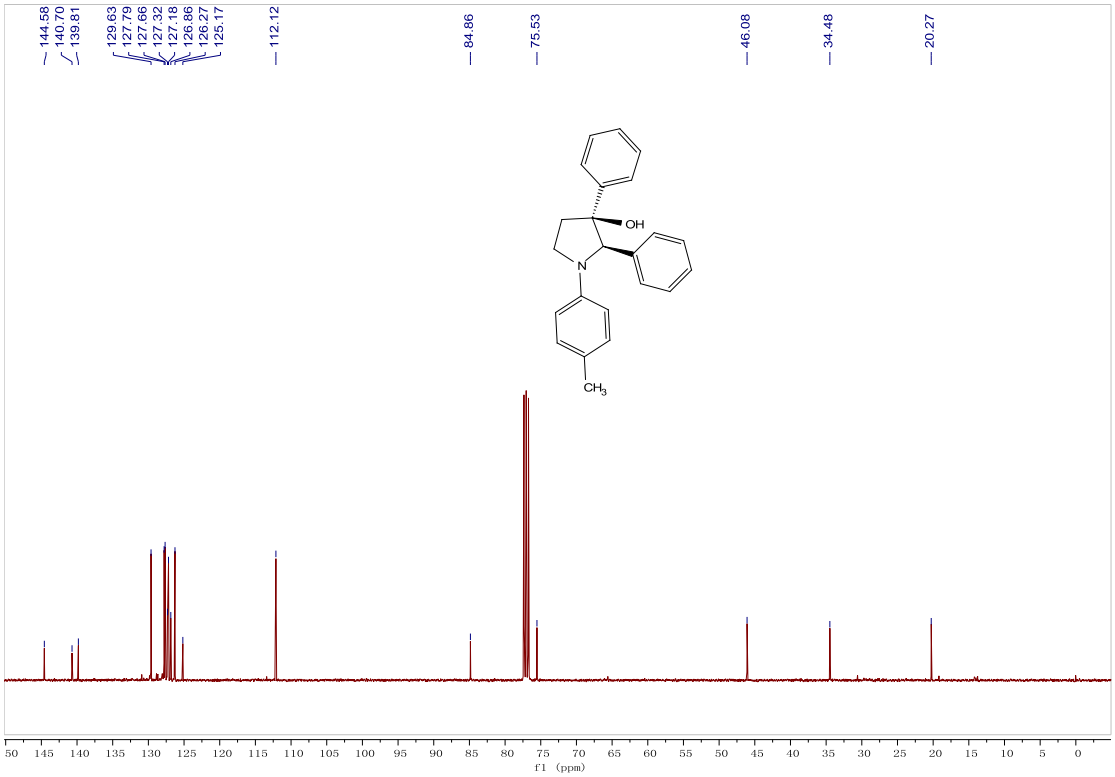
1,3-diphenyl-2-((E)-styryl)pyrrolidin-3-ol (**2m**)



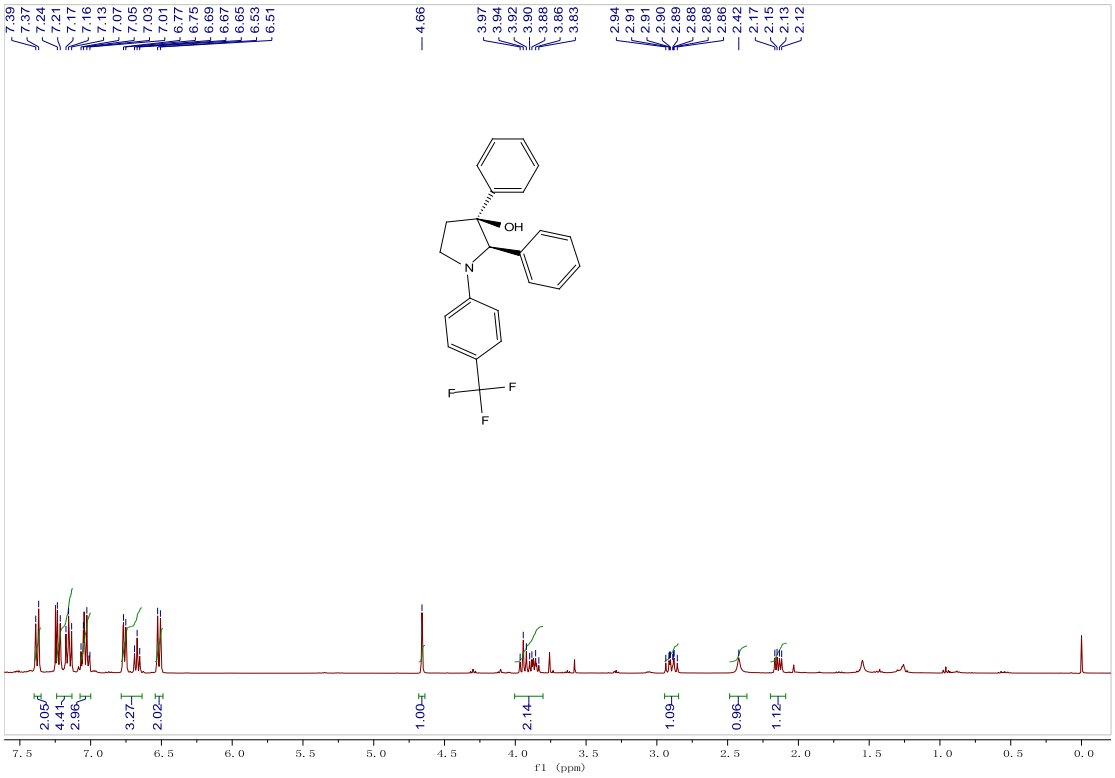


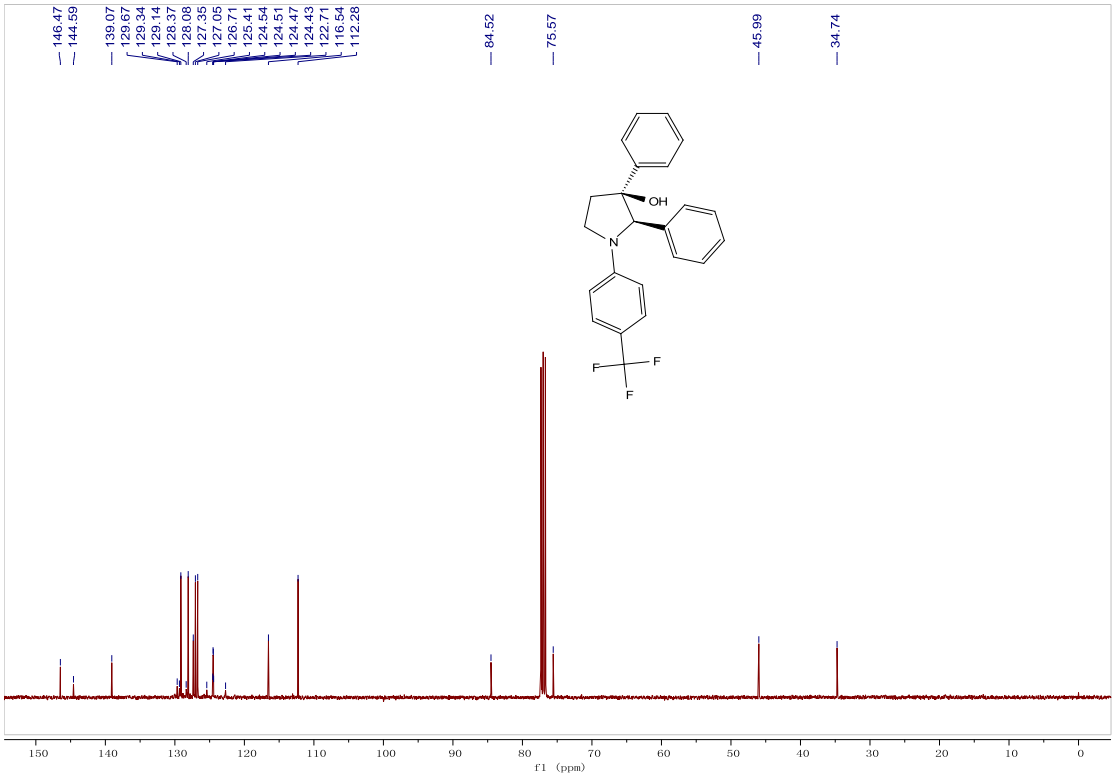
2,3-diphenyl-1-(p-tolyl)pyrrolidin-3-ol (**2n**)





2,3-diphenyl-1-(4-(trifluoromethyl)phenyl)pyrrolidin-3-ol (**2o**)

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129.14
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125.41
124.54
124.51
124.47
124.43
122.71
116.54
112.28
84.52
75.57
45.99
34.74
OH
N
F
F
F
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130
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110
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90
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70
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50
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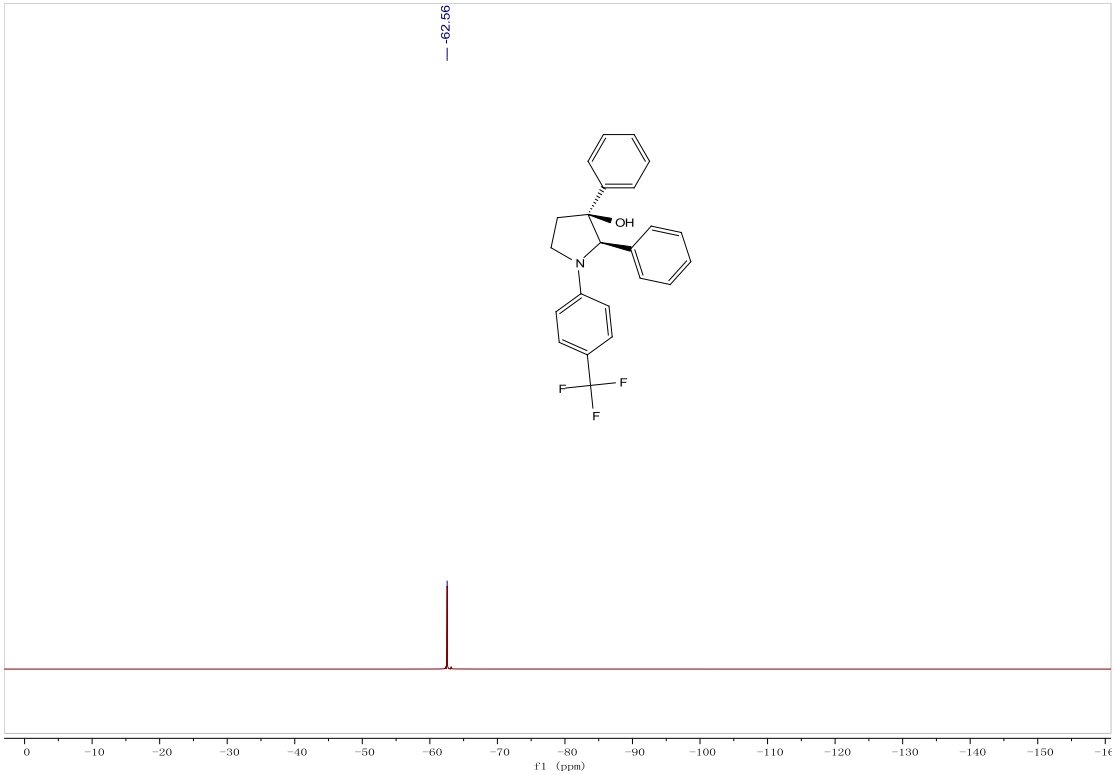
0
f1 (ppm)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F
F
F
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-10
-20
-30
-40
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-60
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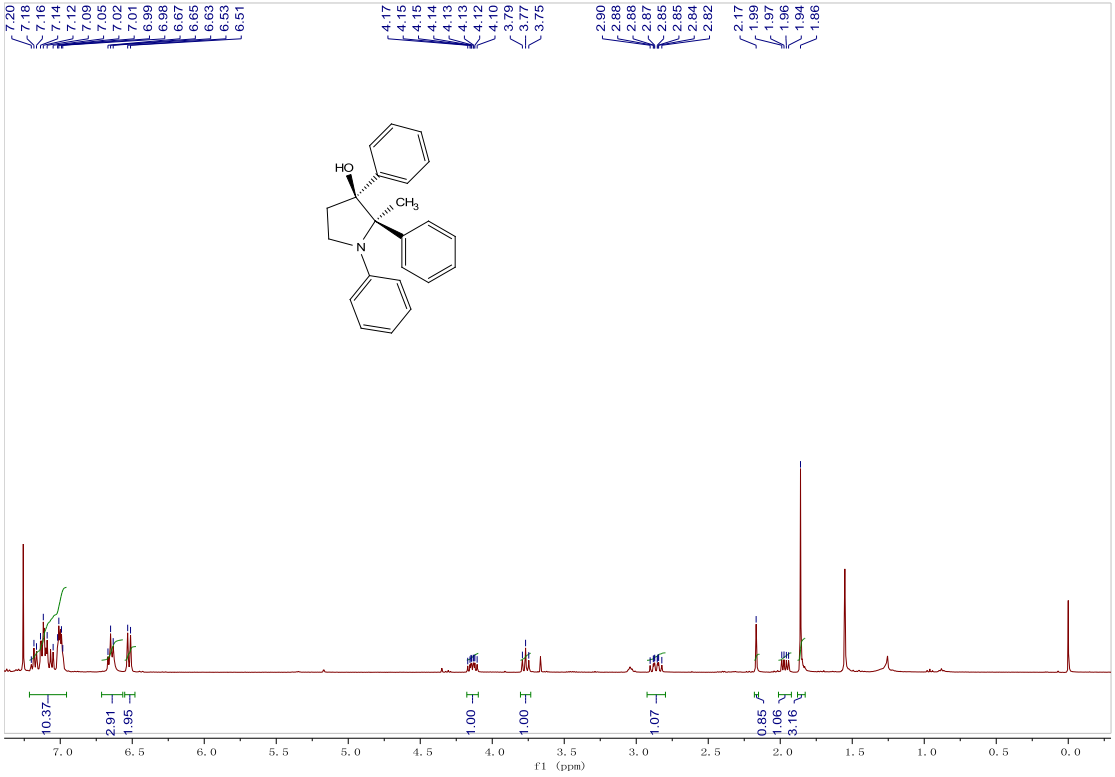
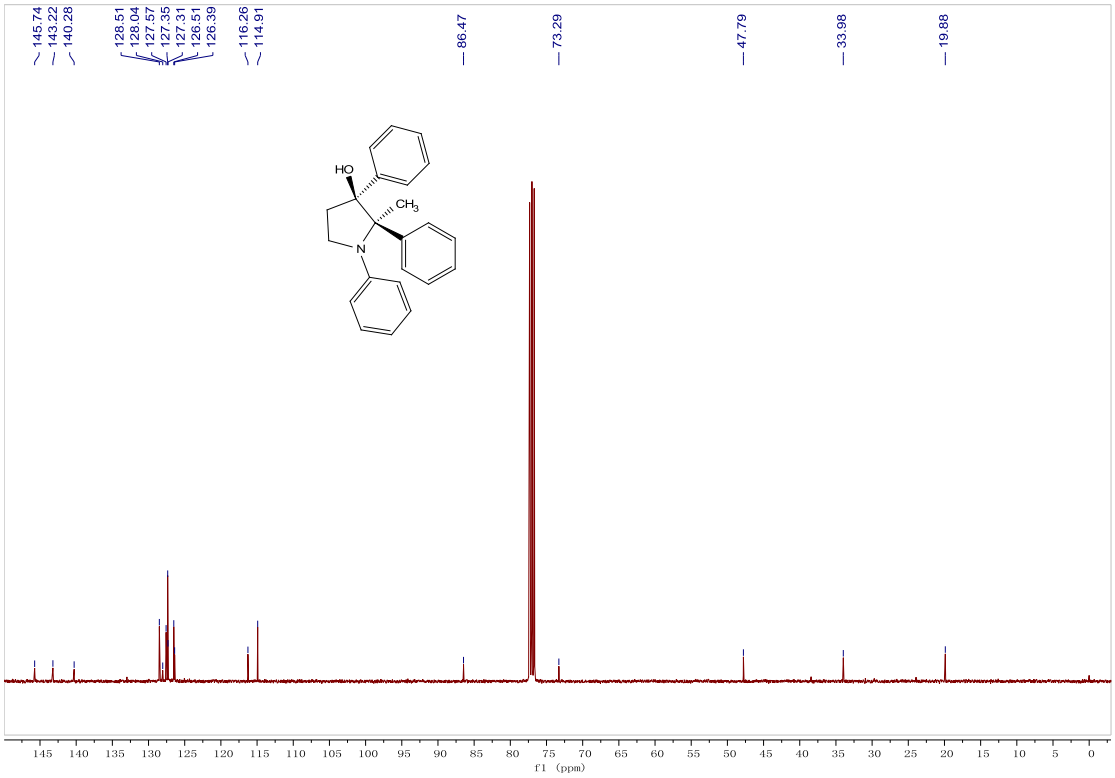
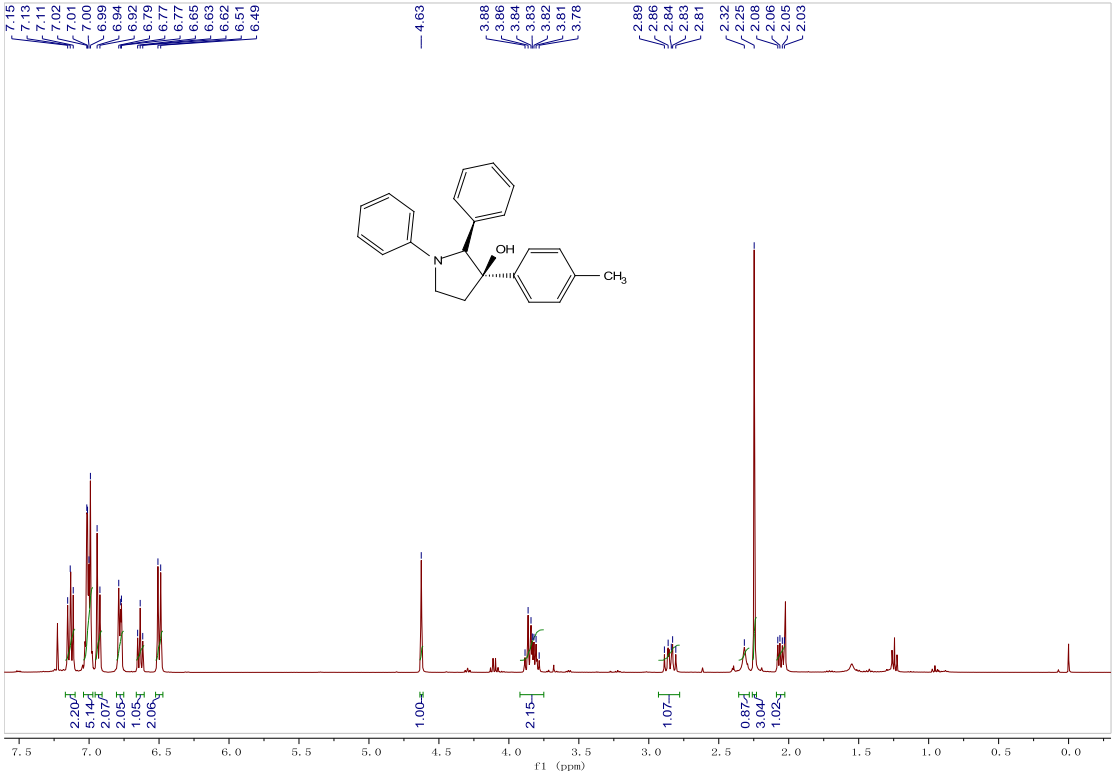
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)

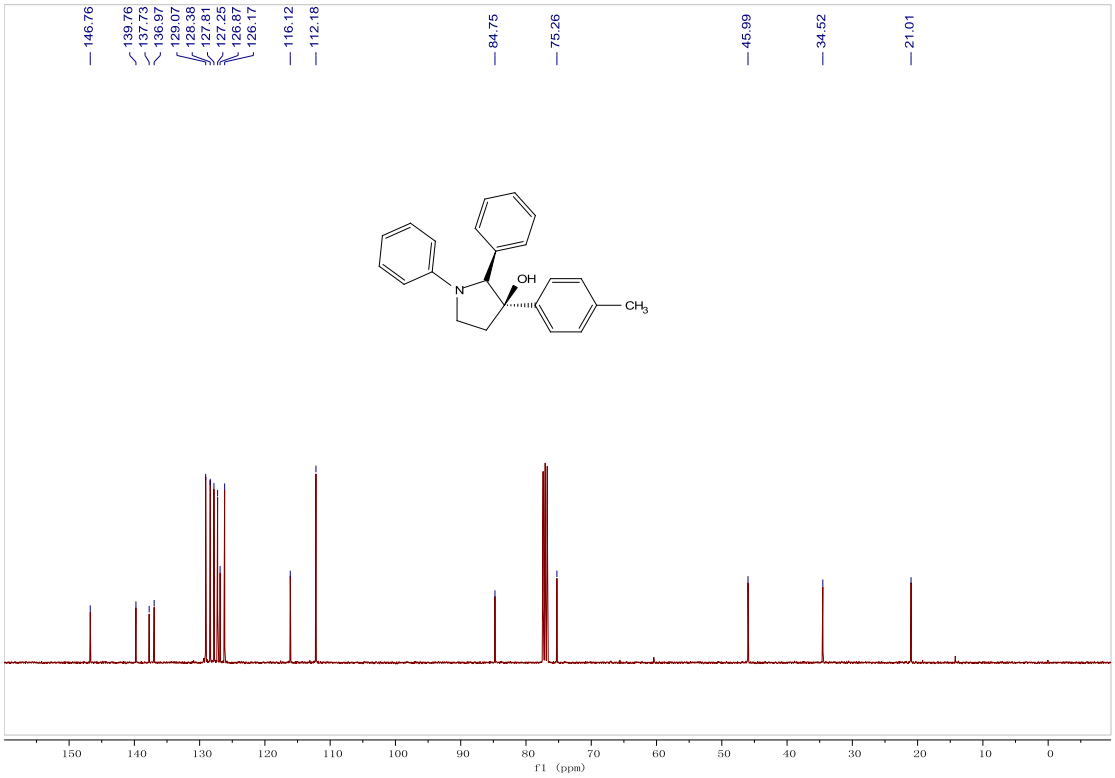
2-methyl-1,2,3-triphenylpyrrolidin-3-ol (**2p**)



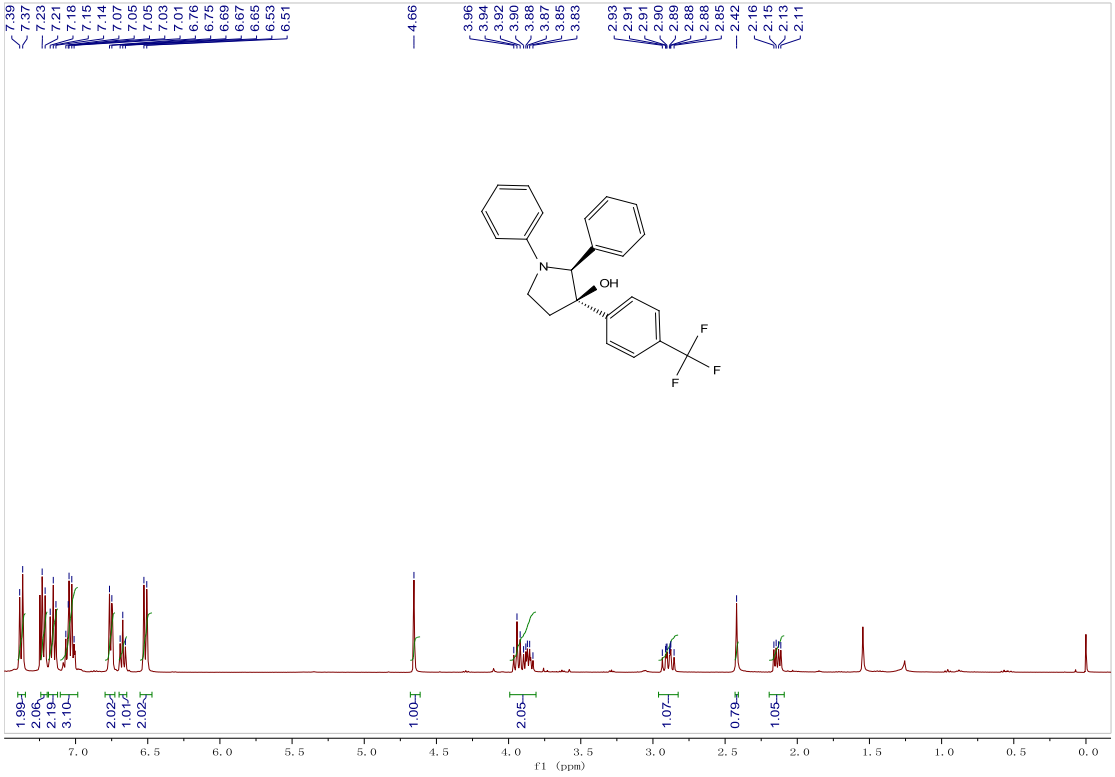


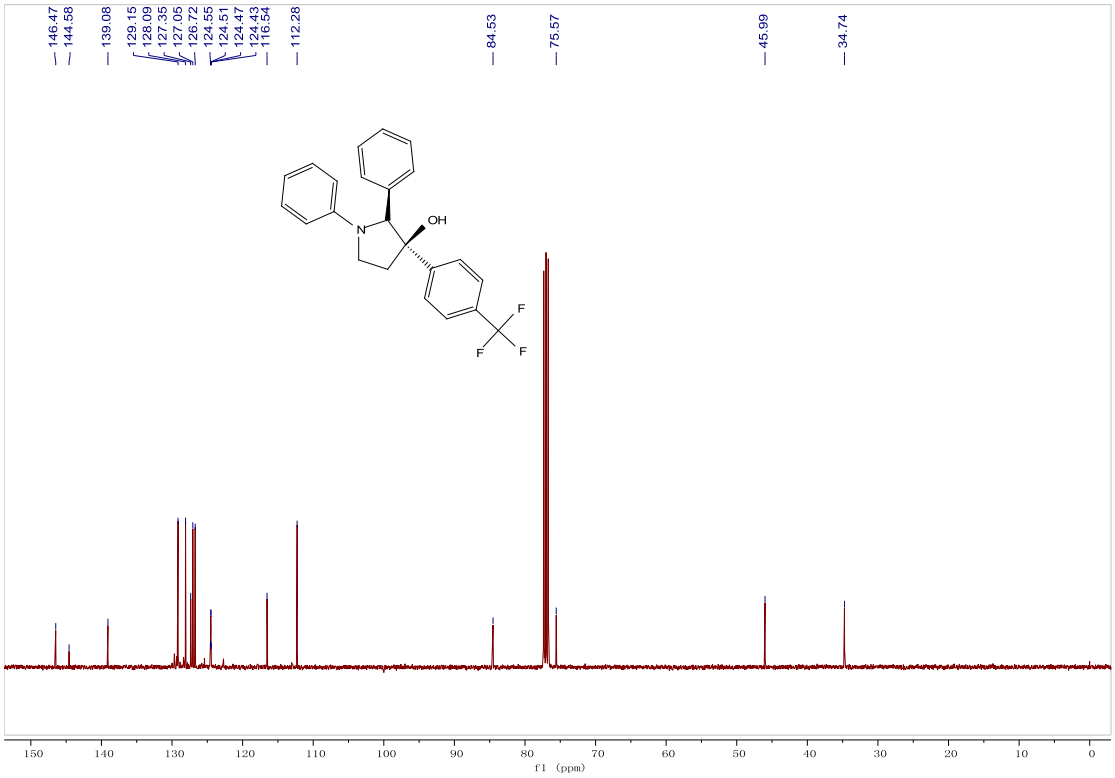
1,2-diphenyl-3-(p-tolyl)pyrrolidin-3-ol (**2q)**

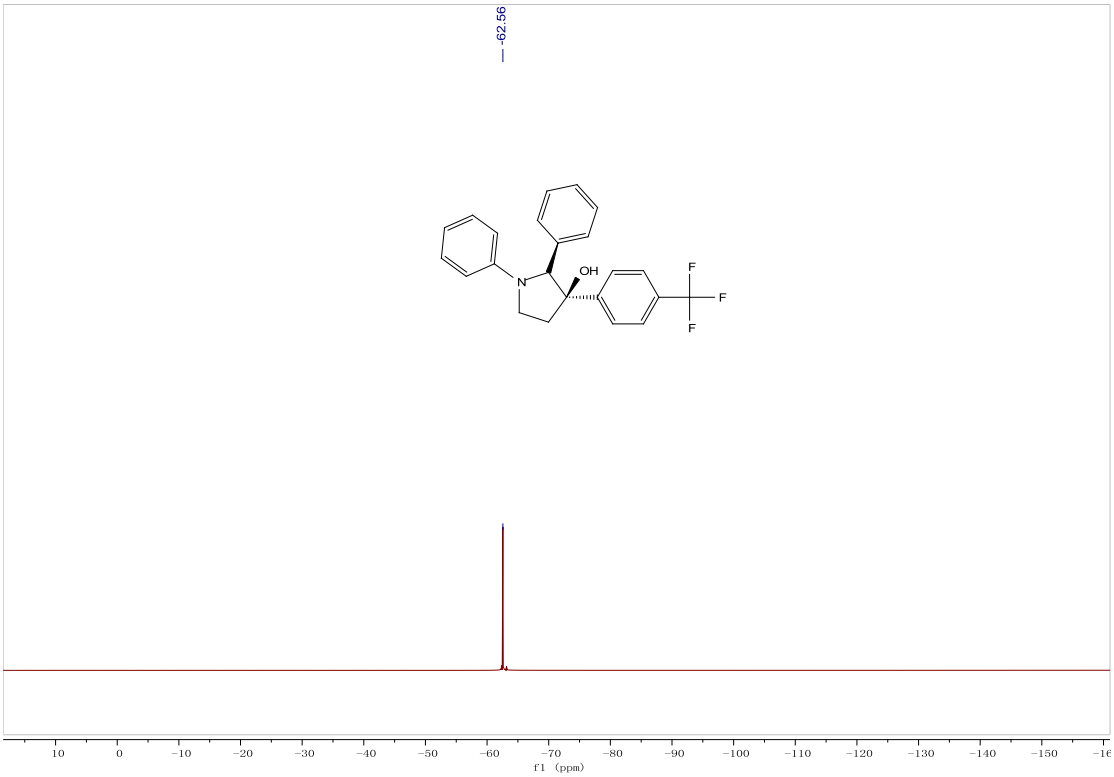




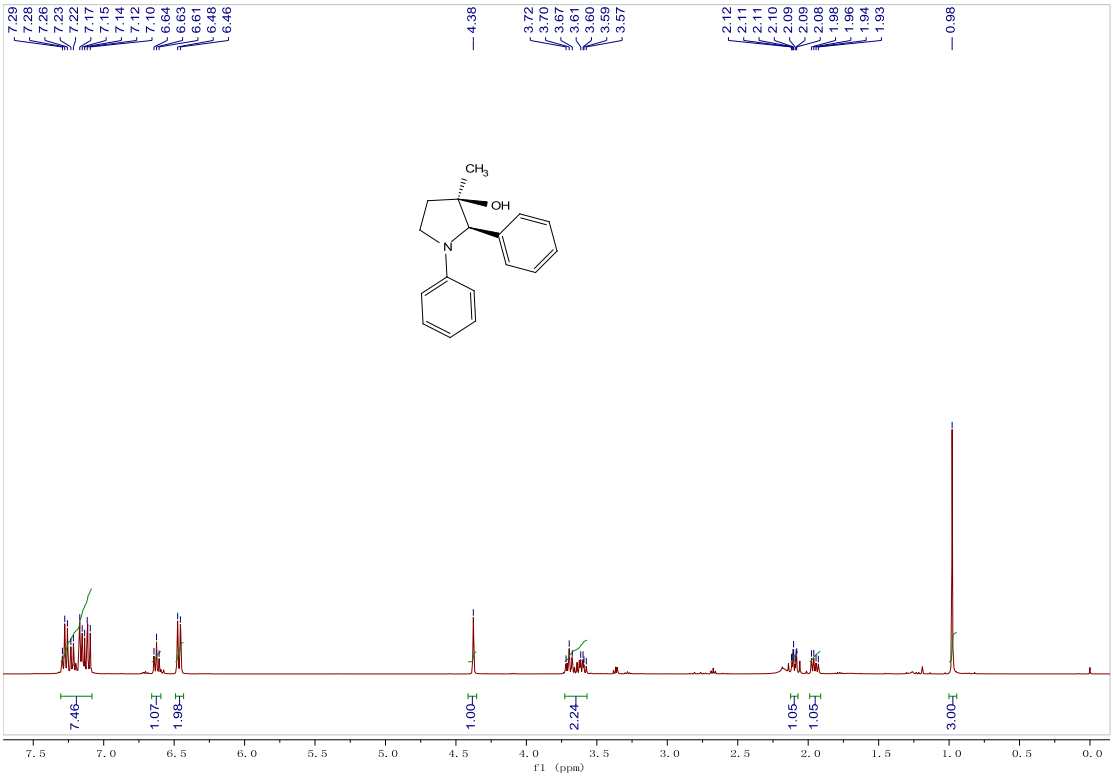
1,2-diphenyl-3-(4-(trifluoromethyl)phenyl)pyrrolidin-3-ol (**2r**)

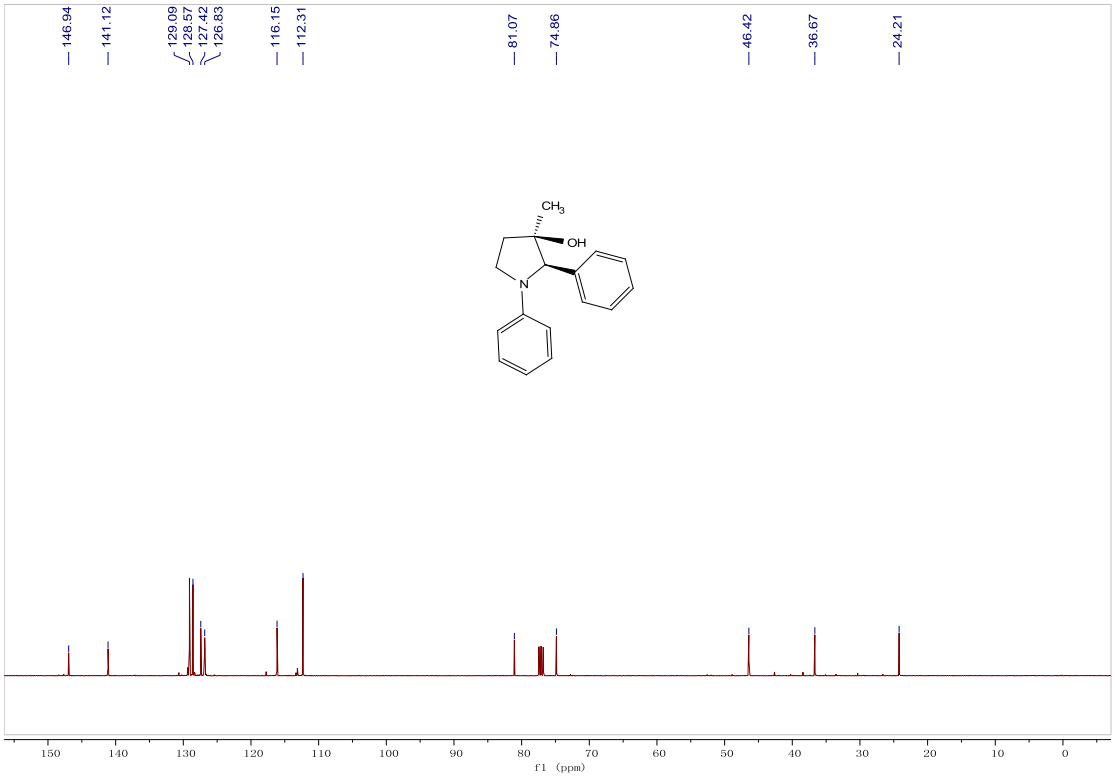




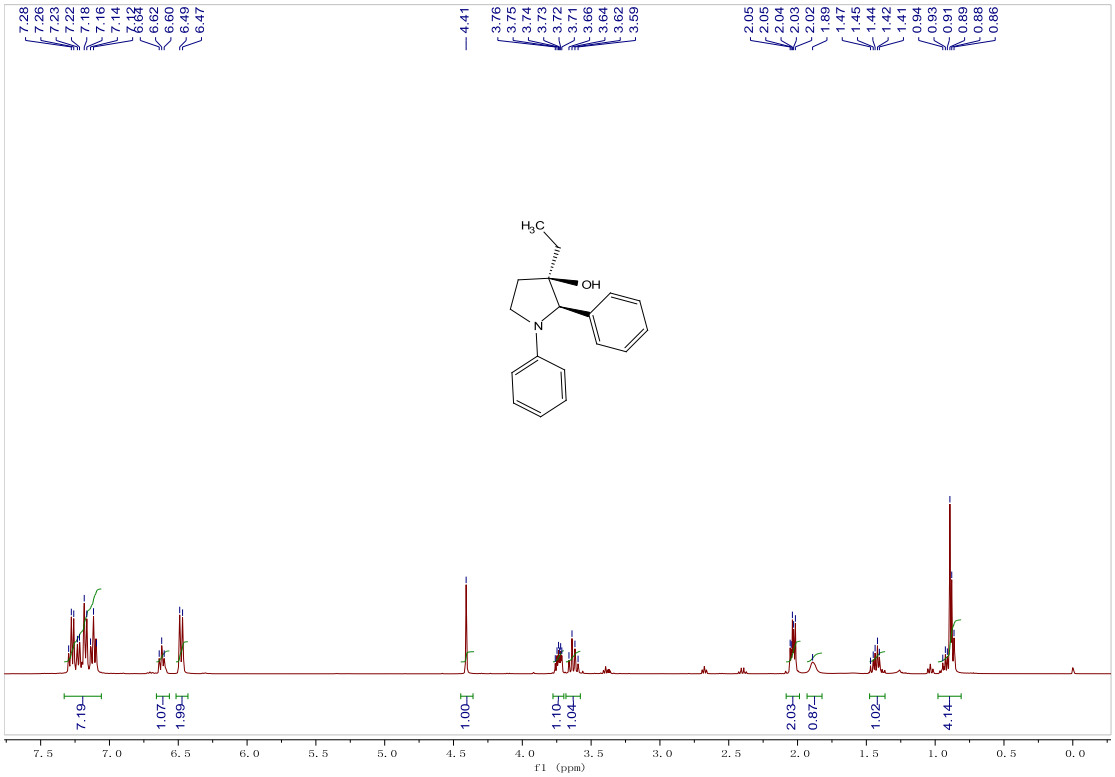


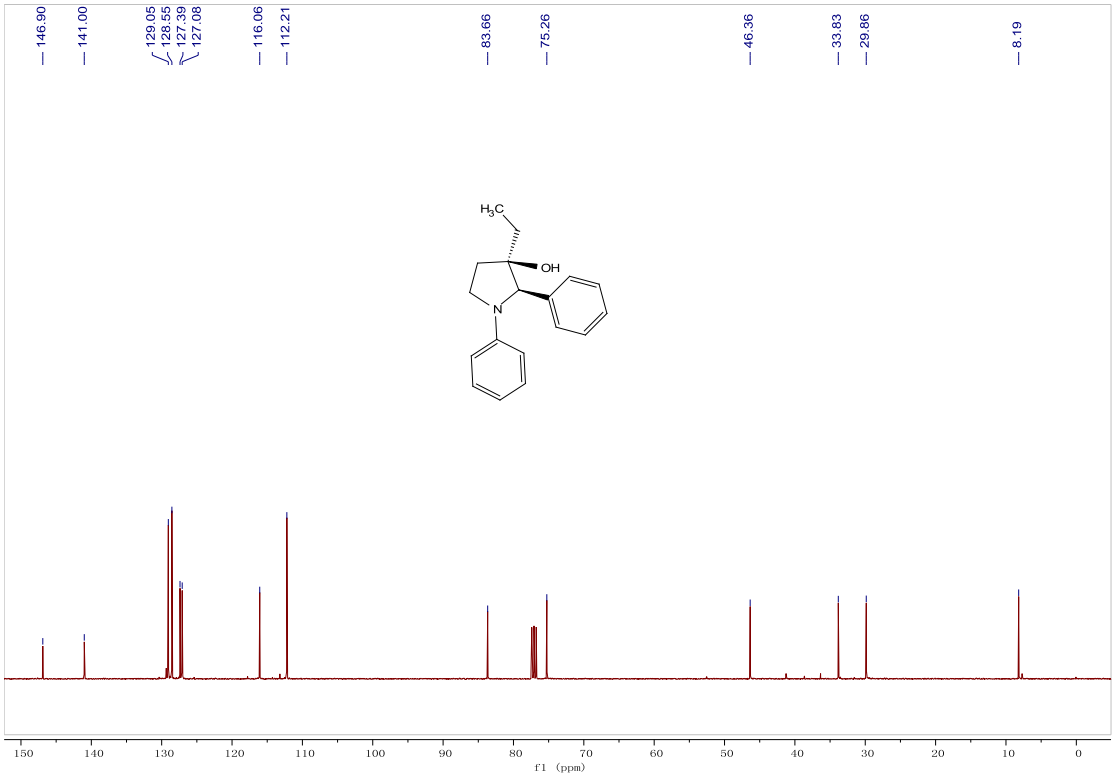
3-methyl-1,2-diphenylpyrrolidin-3-ol (**2s**)



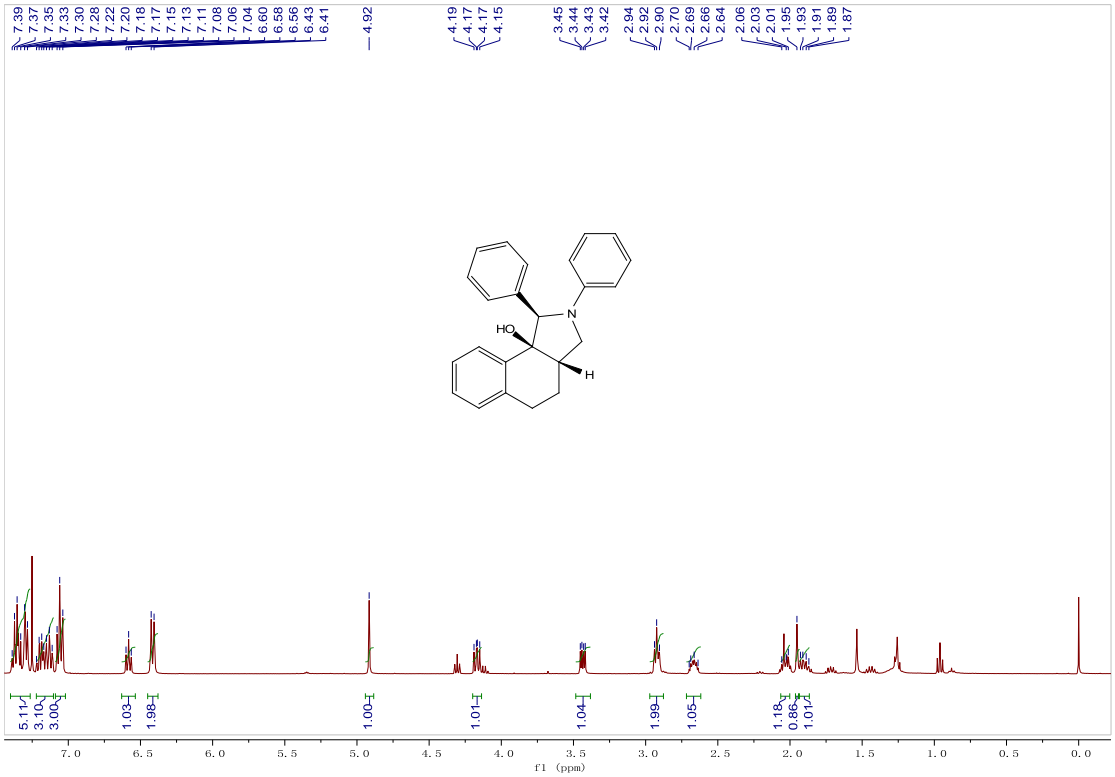


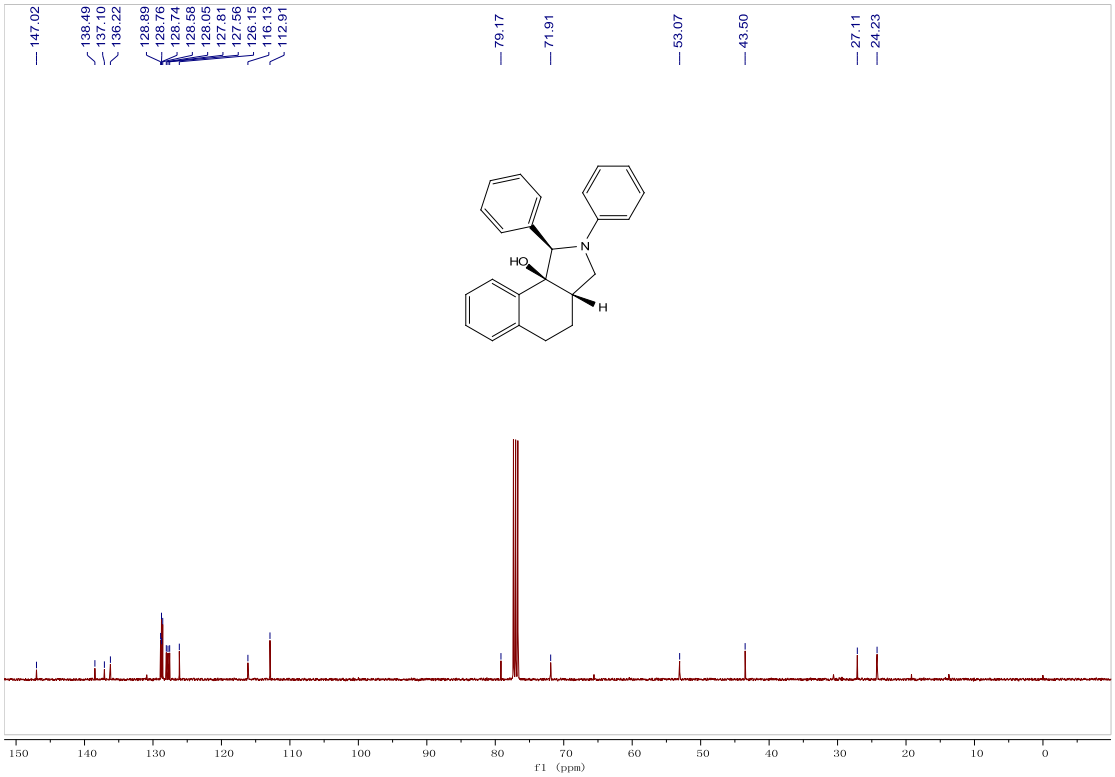
3-ethyl-1,2-diphenylpyrrolidin-3-ol (**2t**)



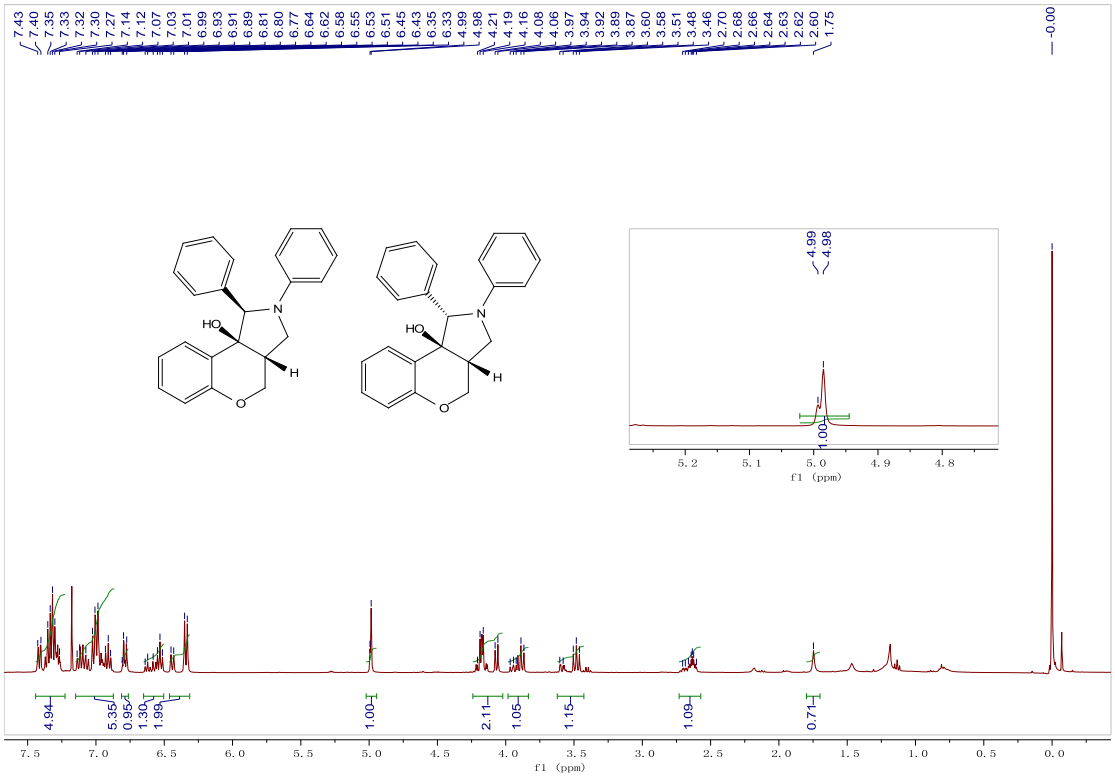


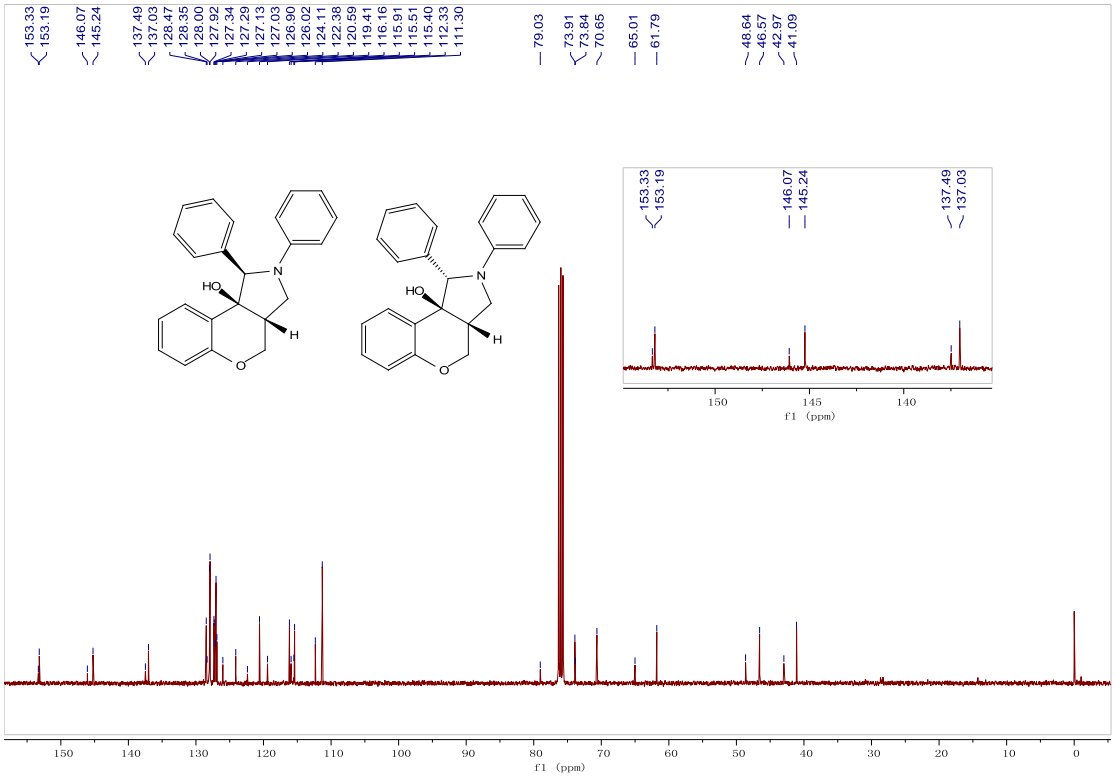
1,2-diphenyl-hexahydrobenzoisoindol-ol (**2u**)



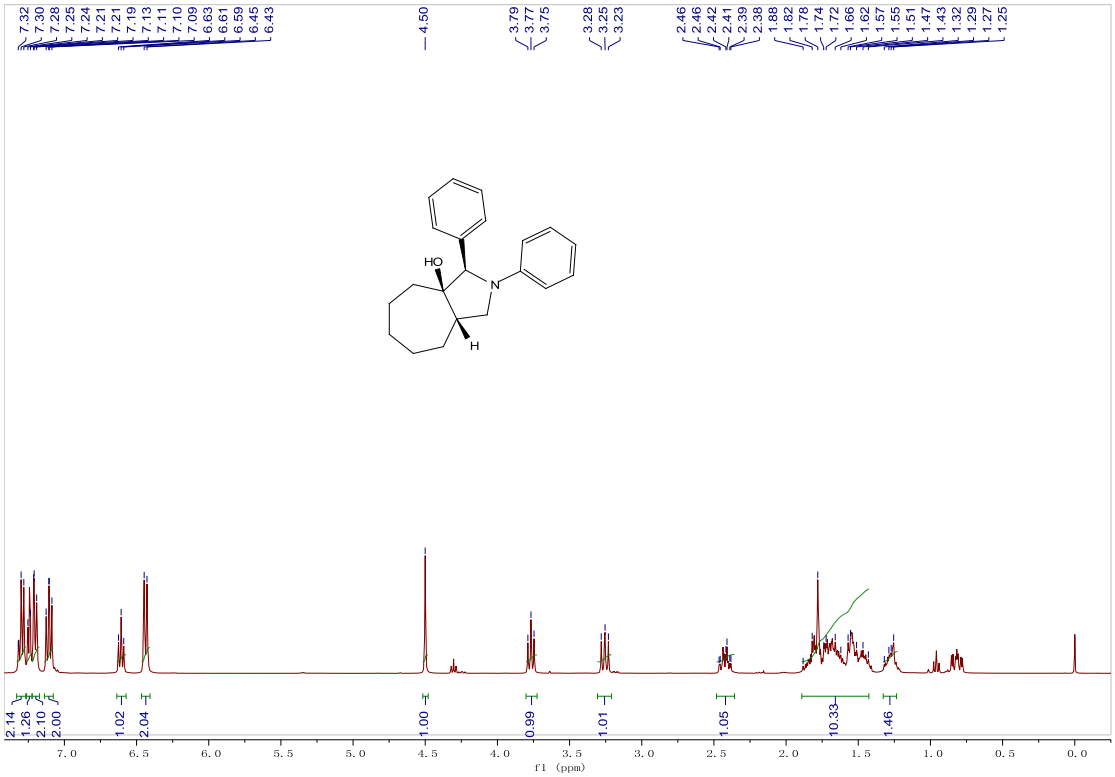


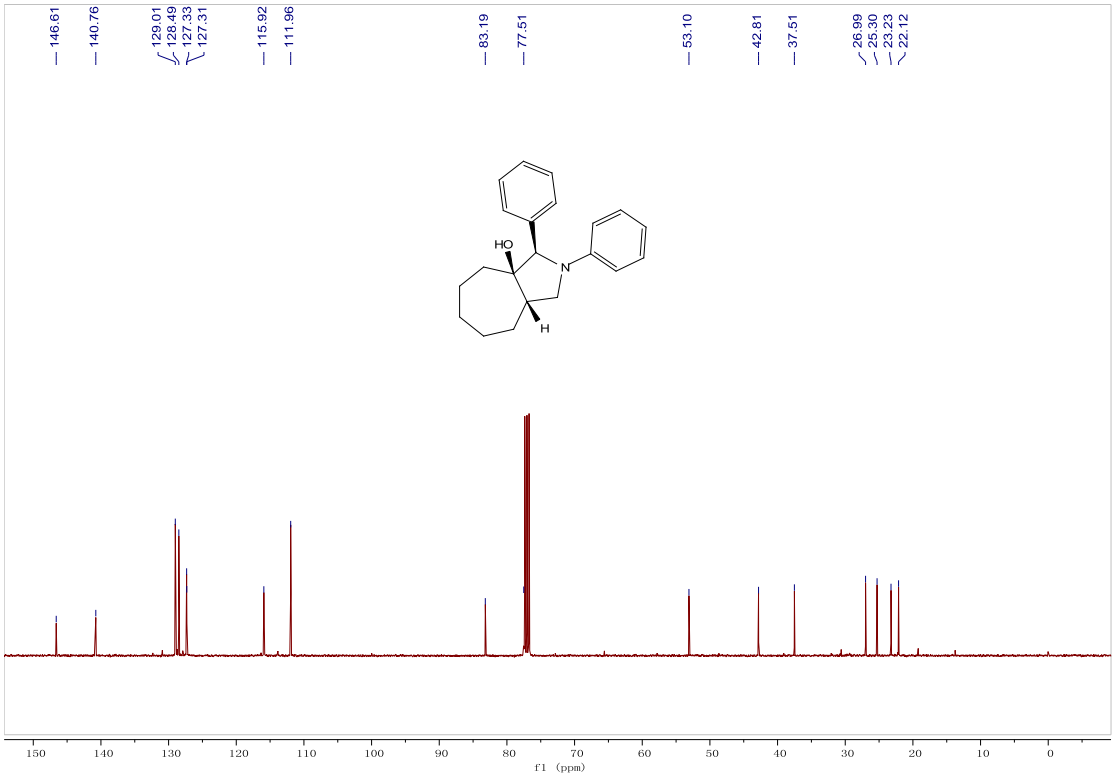
1,2-diphenyl-tetrahydrochromeno[3,4-c]pyrrol-9b(1H)-ol (**2v**)



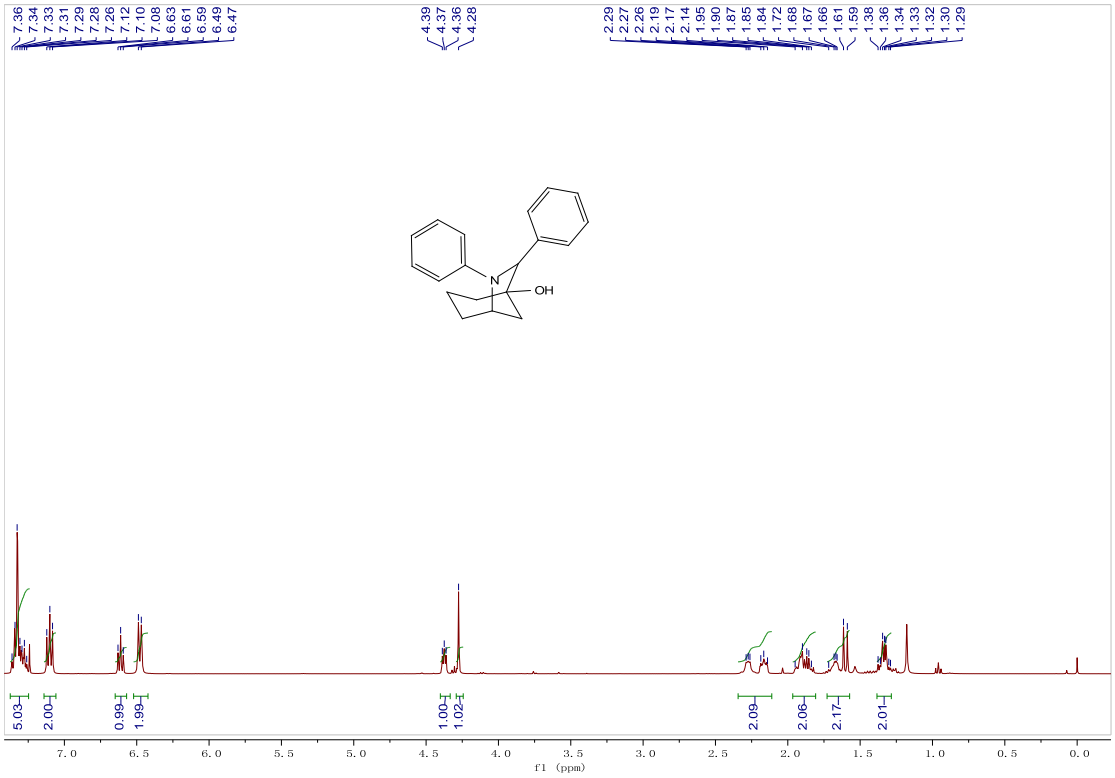


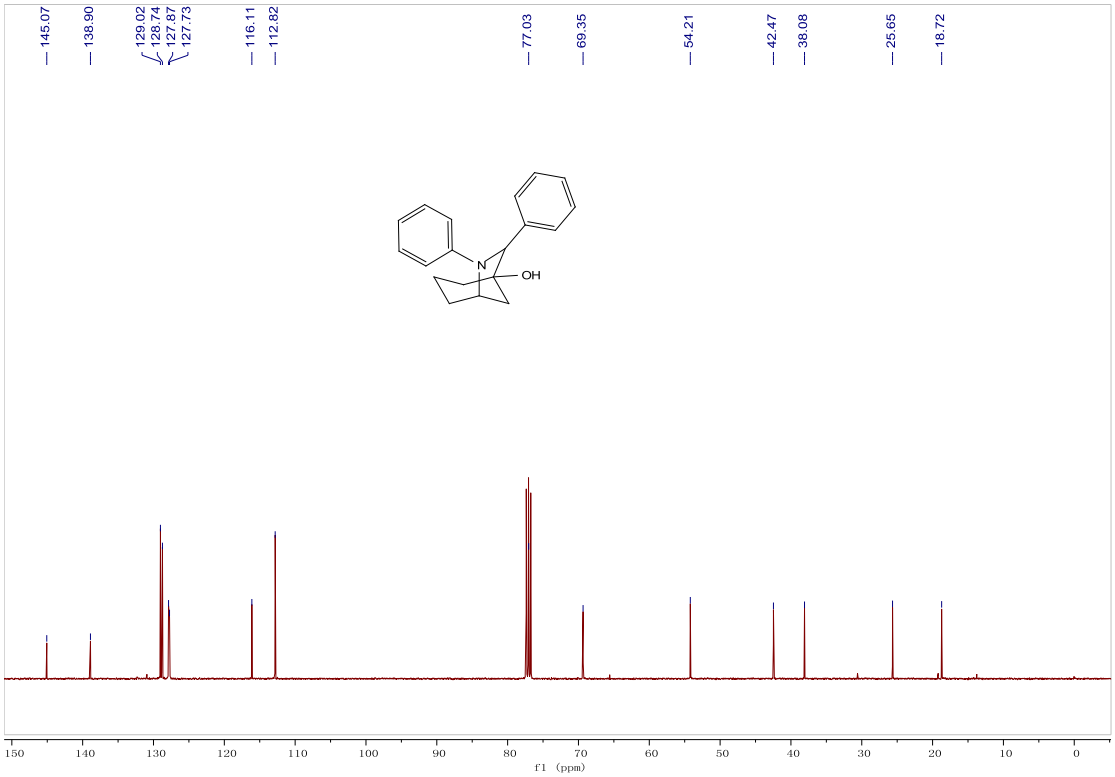
2,3-diphenyloctahydrocyclohepta[c]pyrrol-3a(1H)-ol(**2w**)



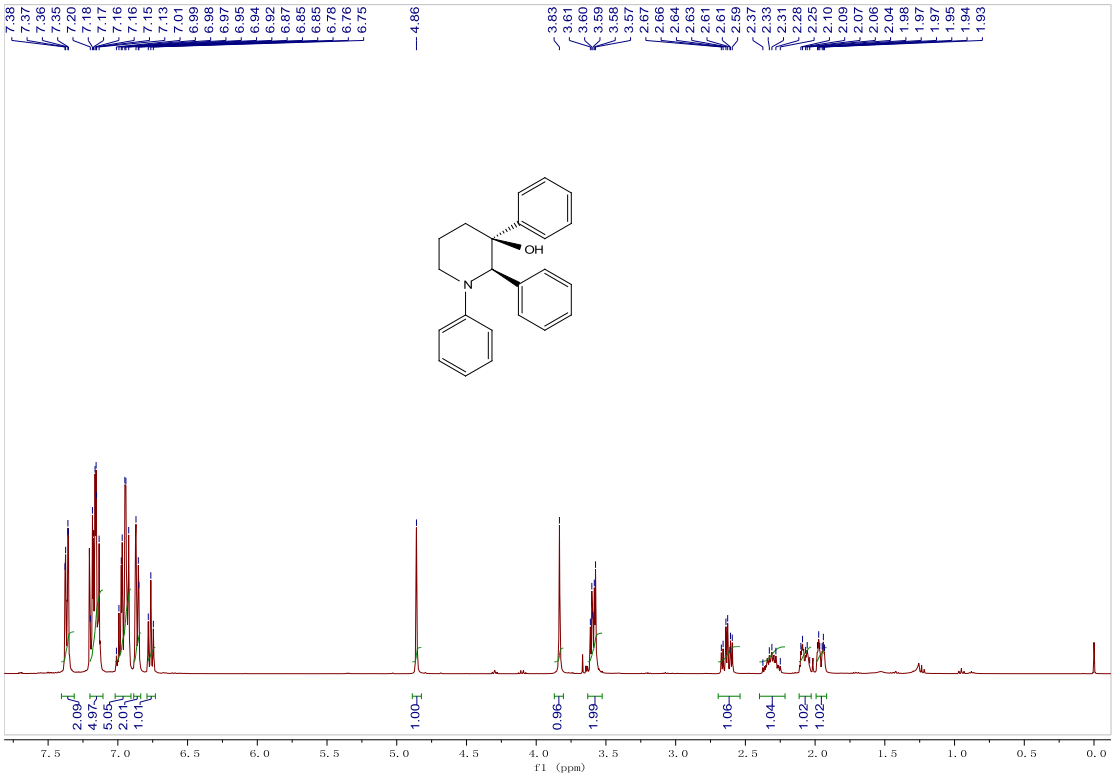


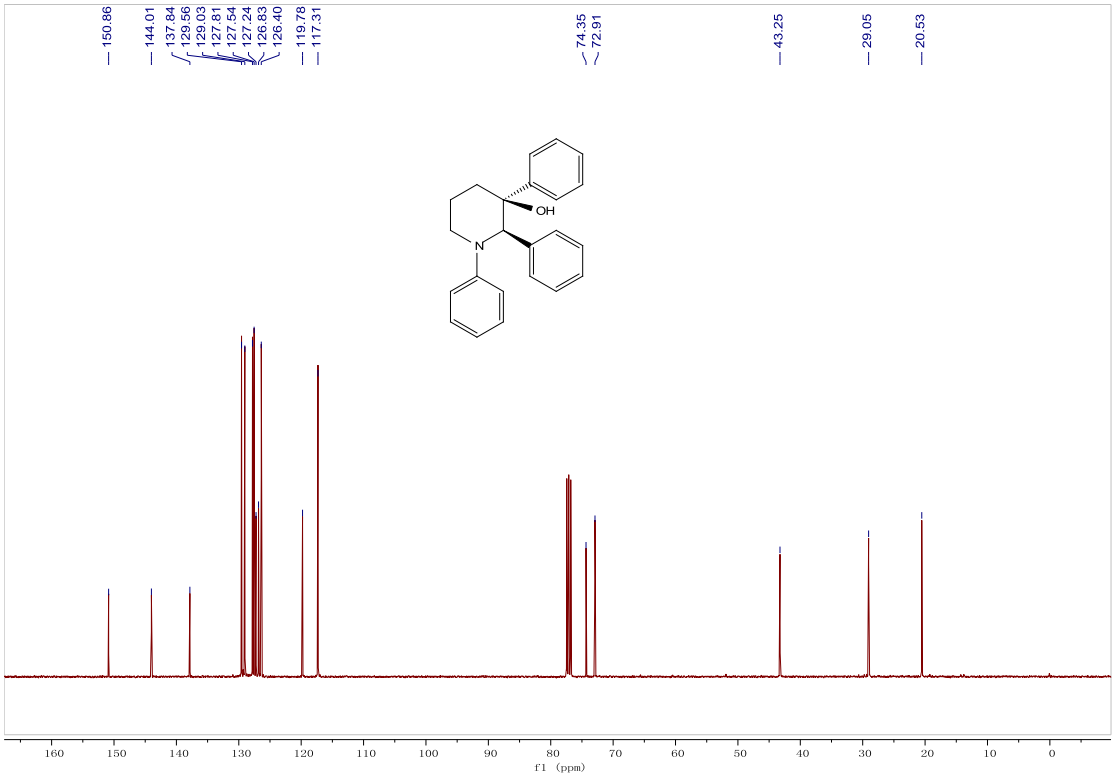
6,7-diphenyl-6-azabicyclo[3.2.1]octan-1-ol (**2x**)



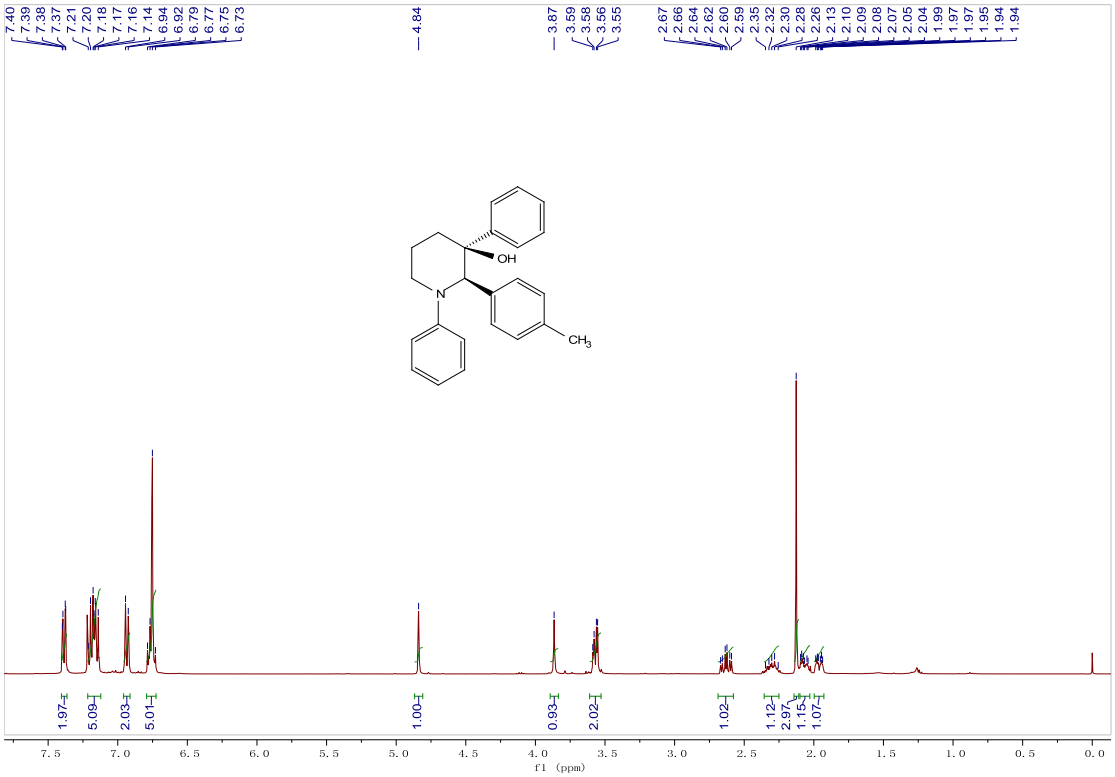


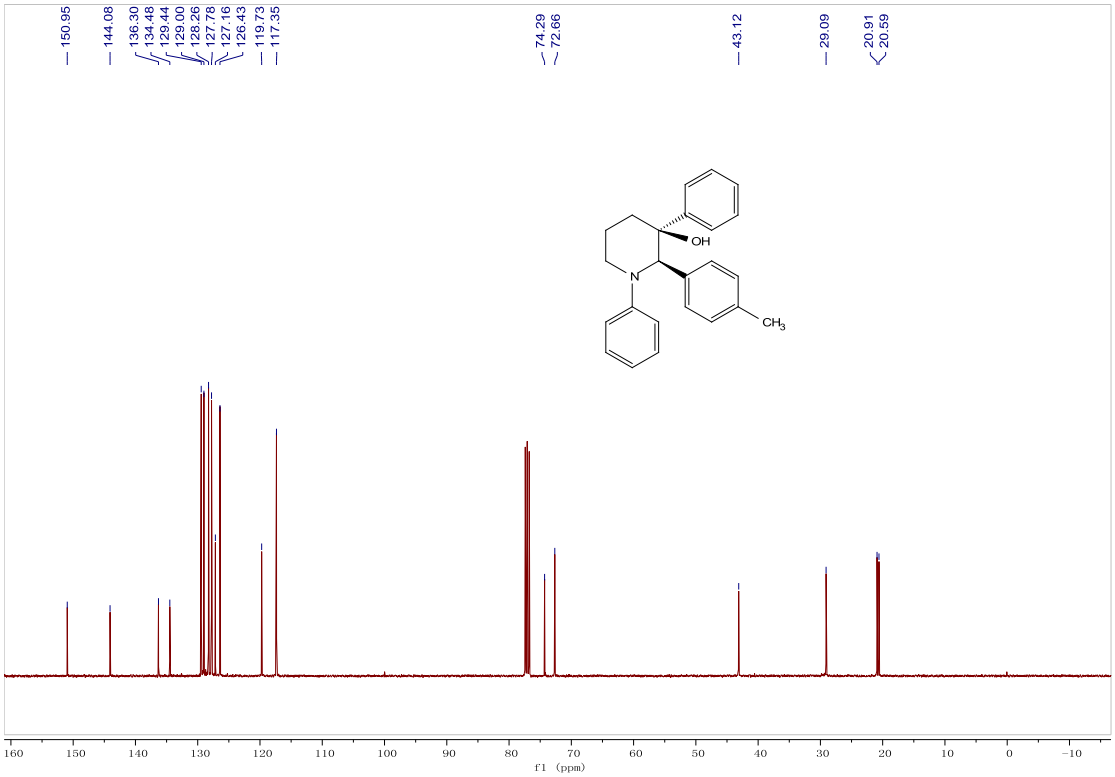
1,2,3-triphenylpiperidin-3-ol (**4a**)



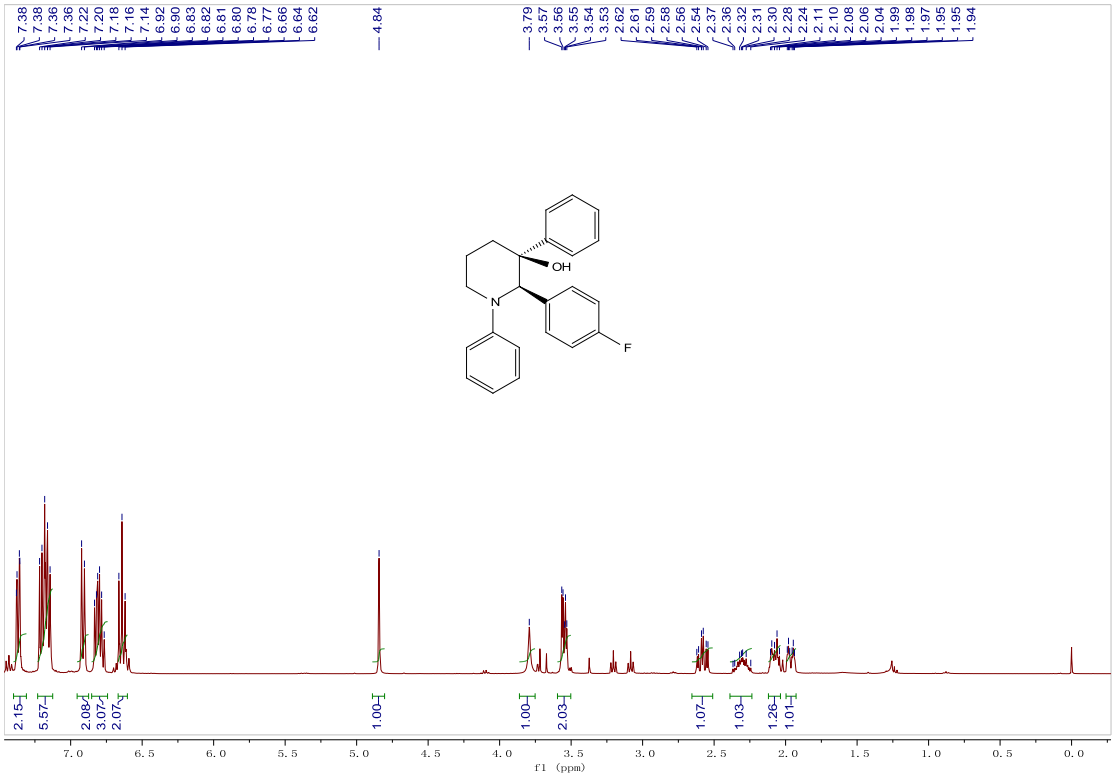


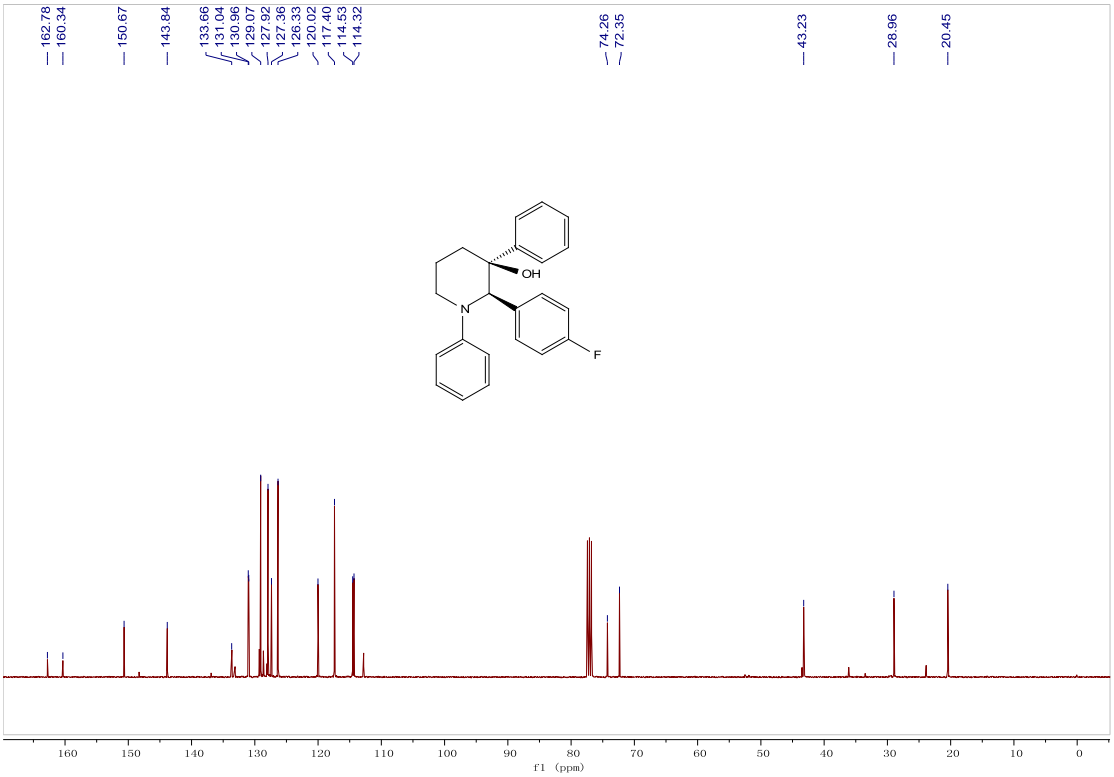
1,3-diphenyl-2-(p-tolyl)piperidin-3-ol (**4b**)





2-(4-fluorophenyl)-1,3-diphenylpiperidin-3-ol (**4c**)

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127.36
126.33
120.02
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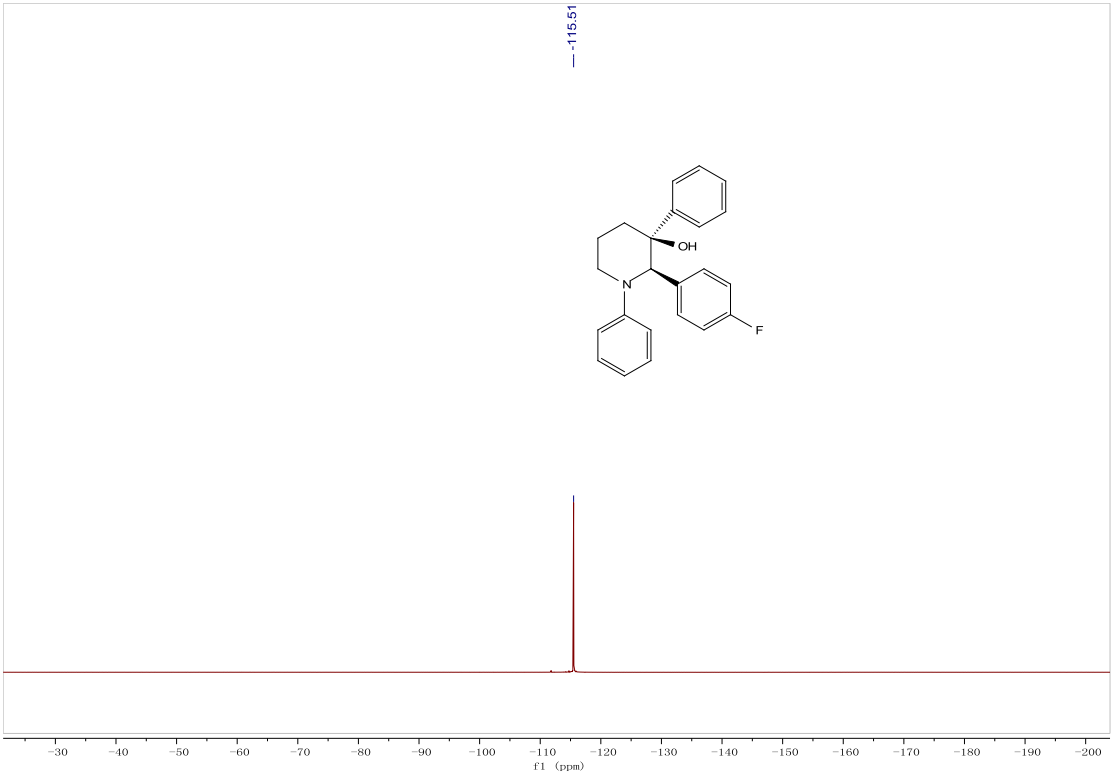
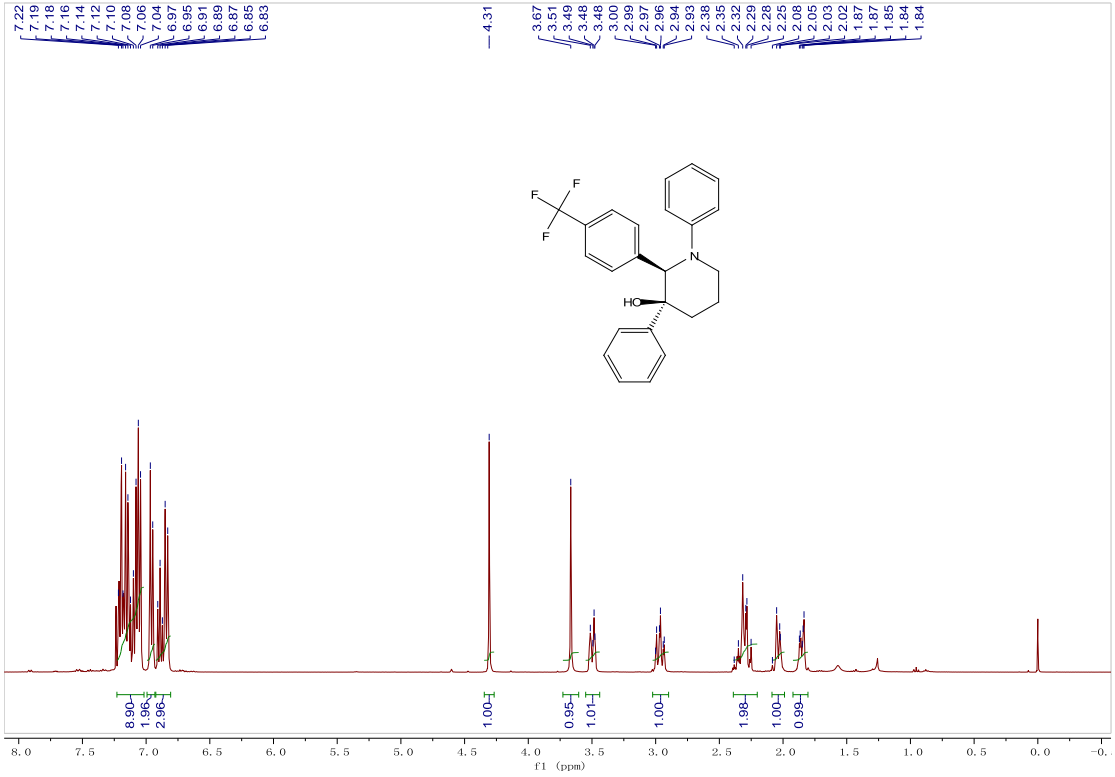
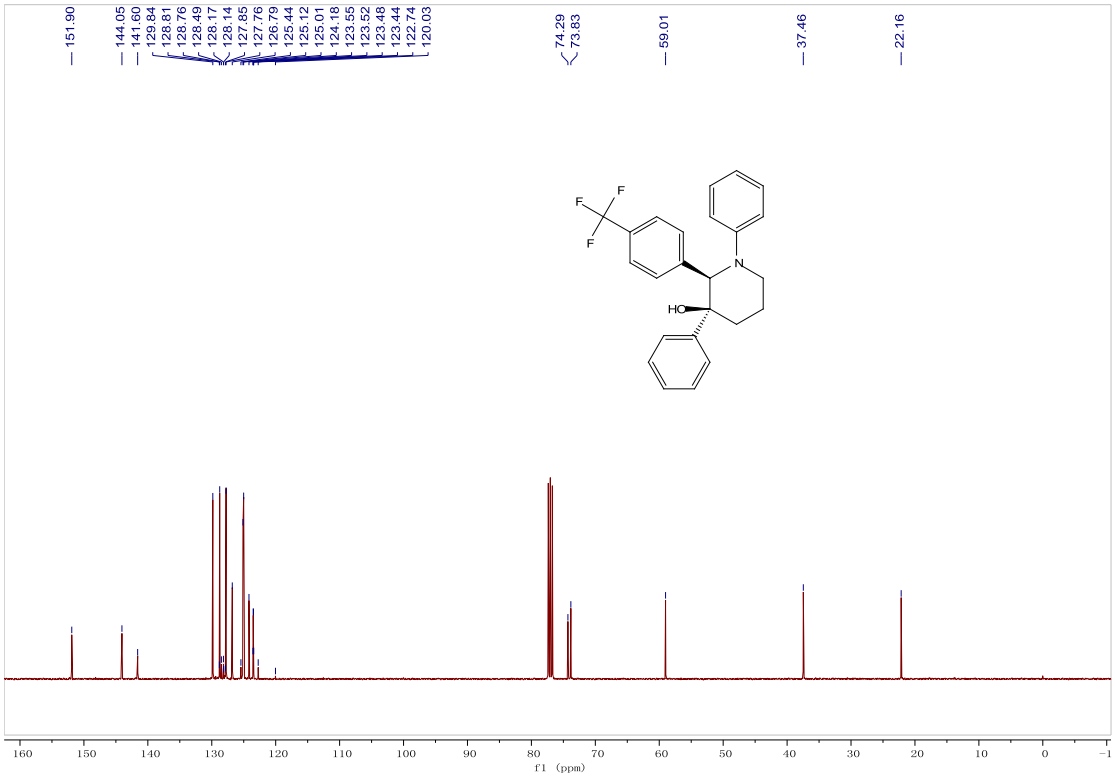
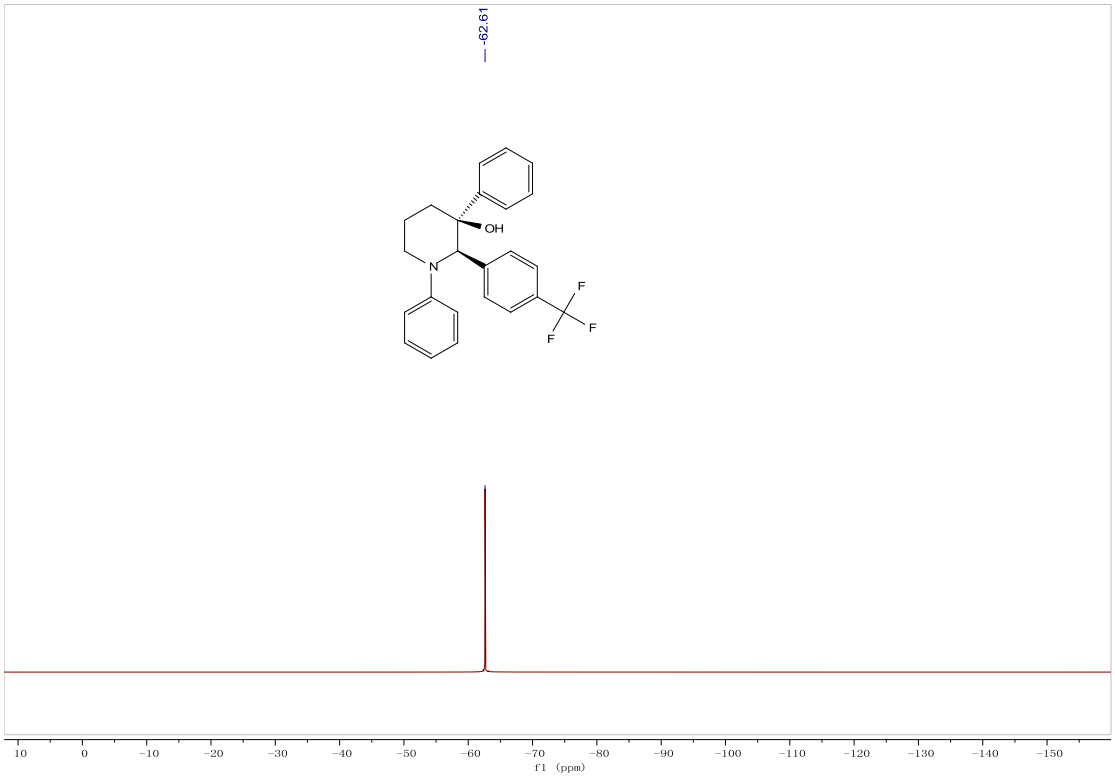
114.53
114.32
74.26
72.35
43.23
28.96
20.45
OH
N
F
f1 (ppm)


-115.51
OH
N
F
f1 (ppm)

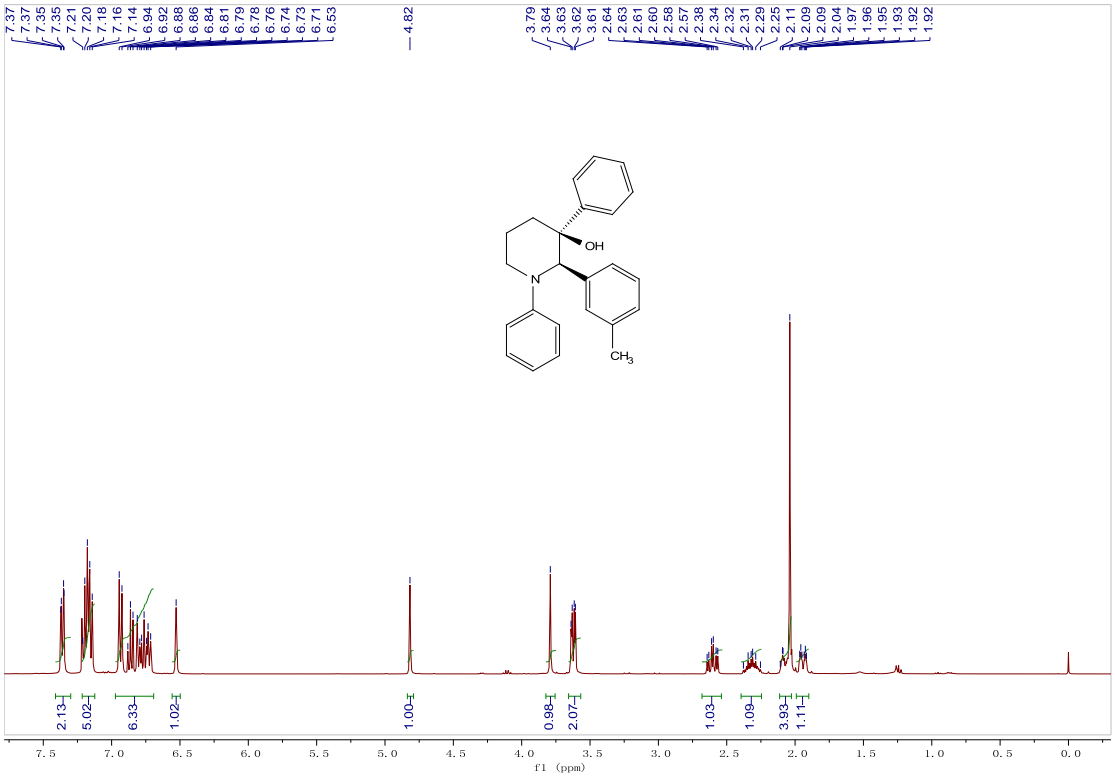
1,3-diphenyl-2-(4-(trifluoromethyl)phenyl)piperidin-3-ol(**4d**)

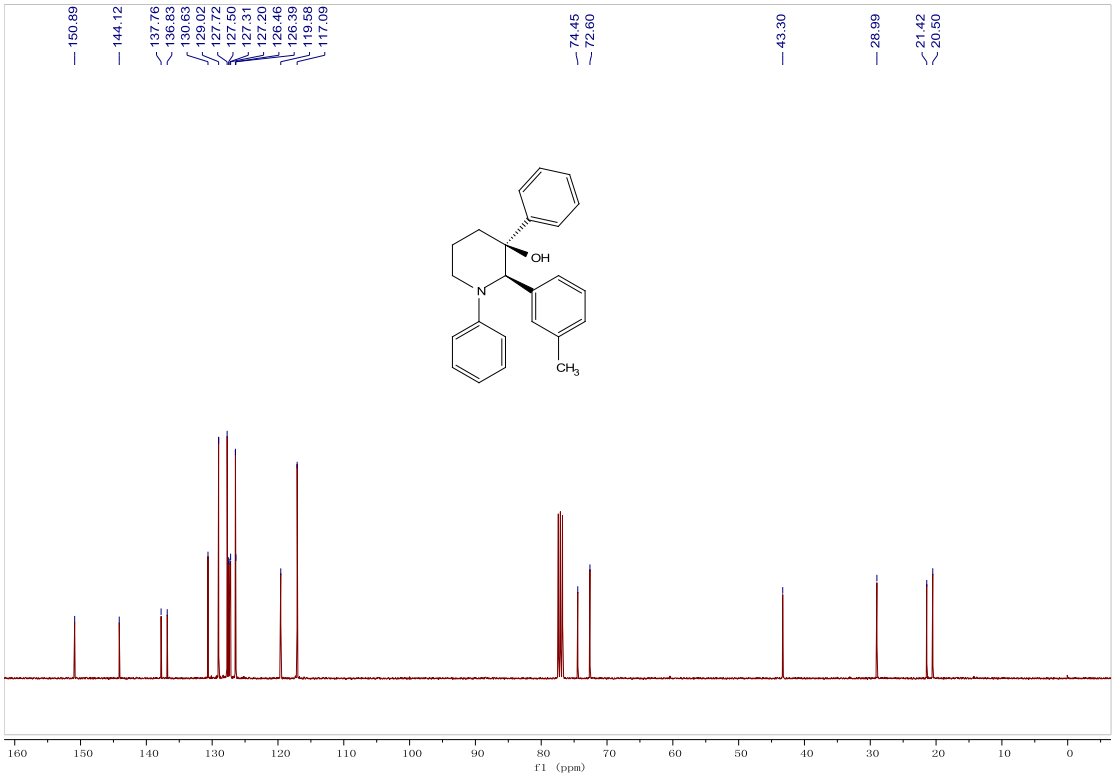




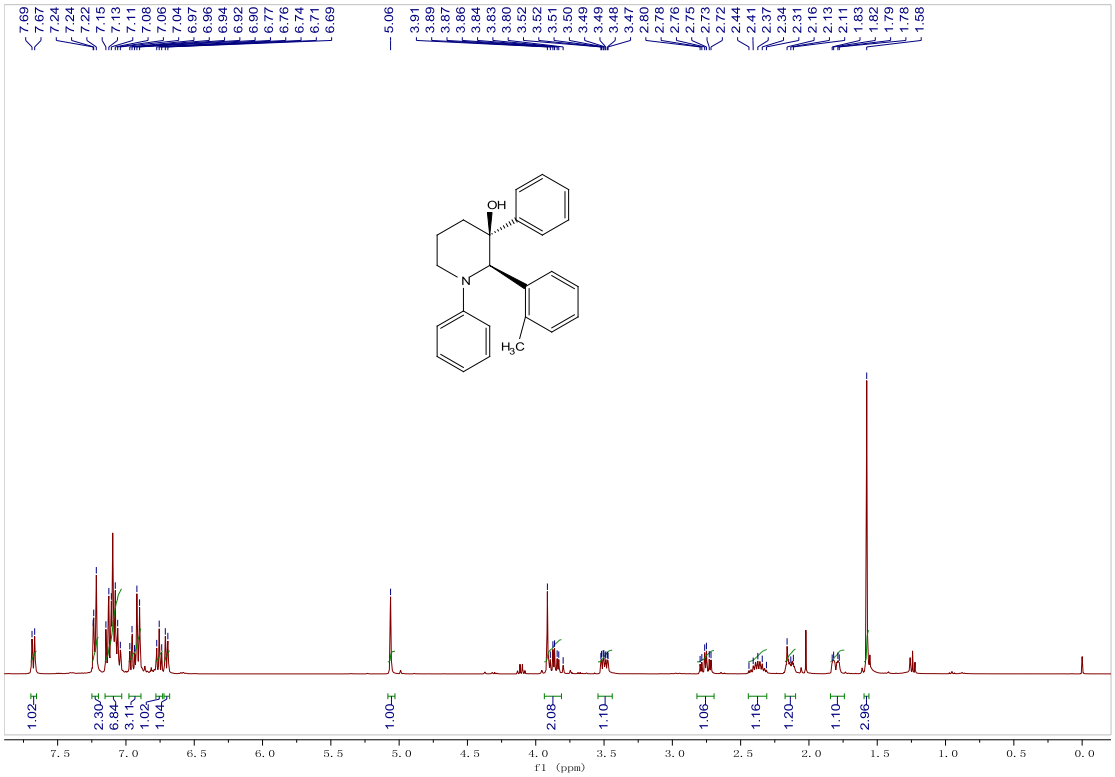


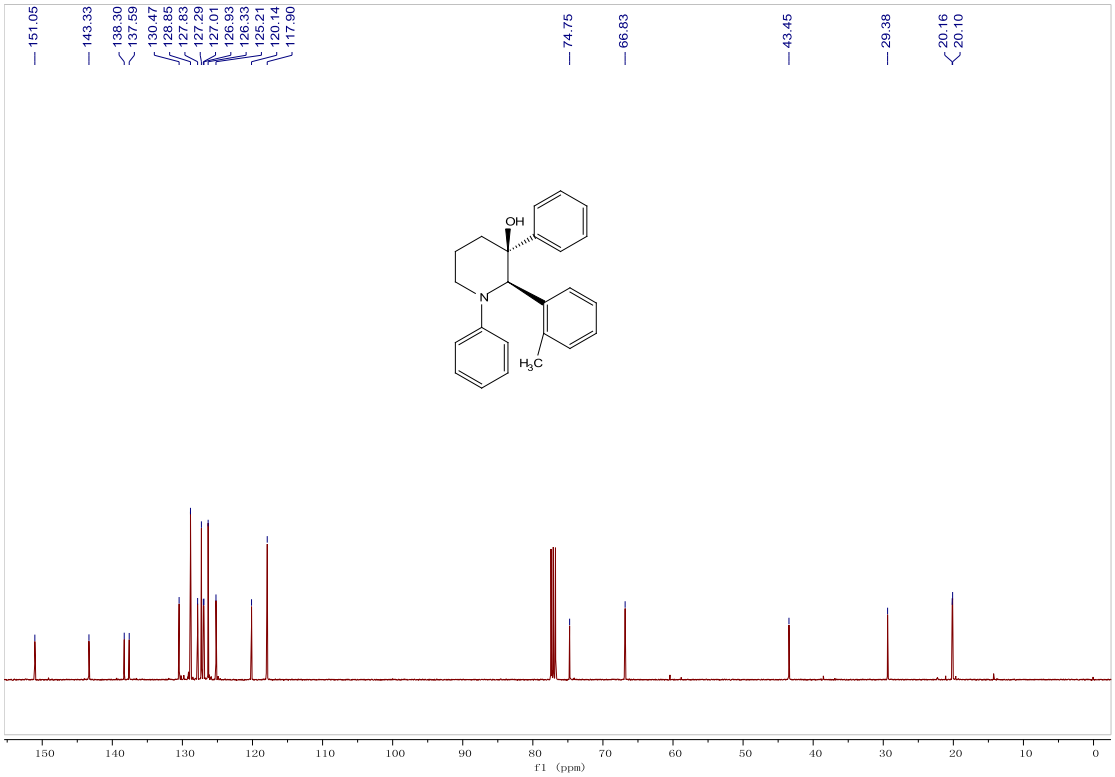
1,3-diphenyl-2-(m-tolyl)piperidin-3-ol (**4e**)



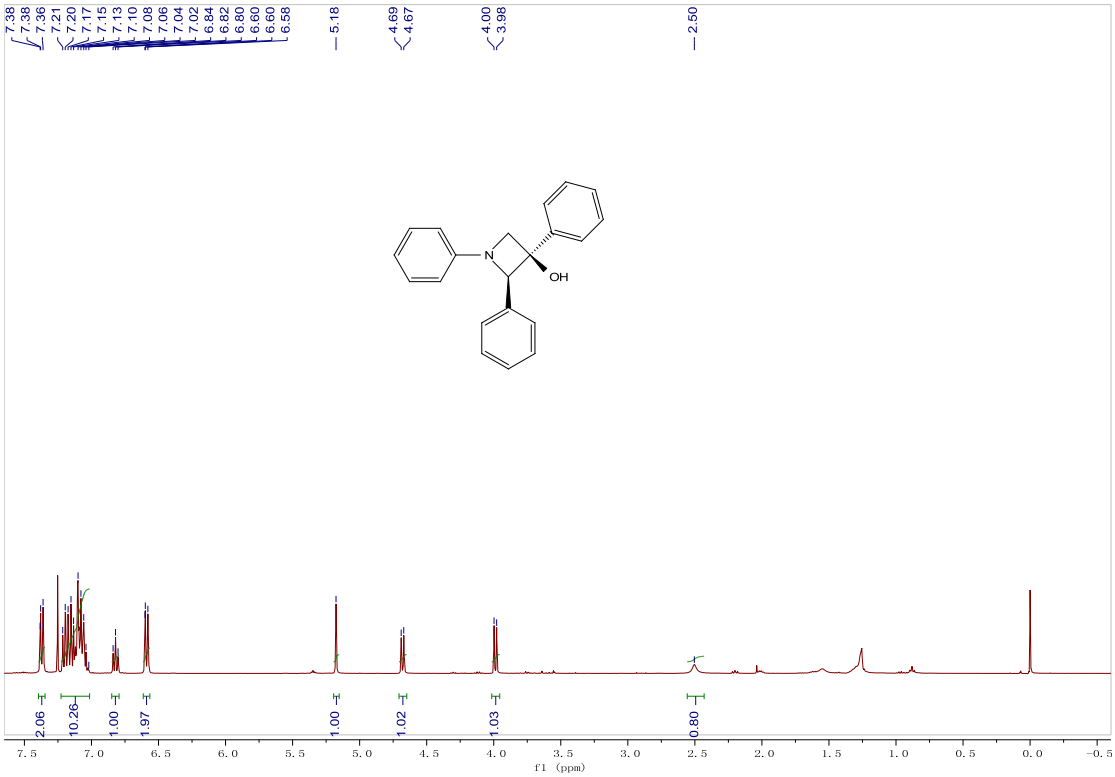


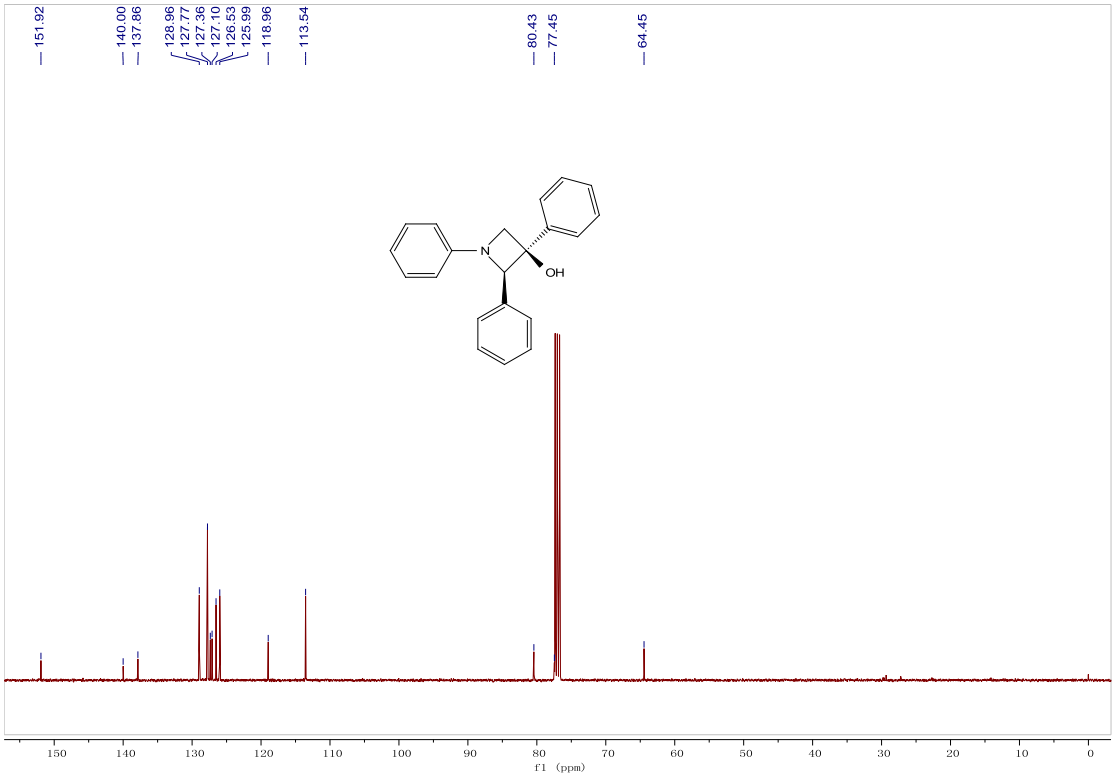
1,3-diphenyl-2-(o-tolyl)piperidin-3-ol(**4f**)



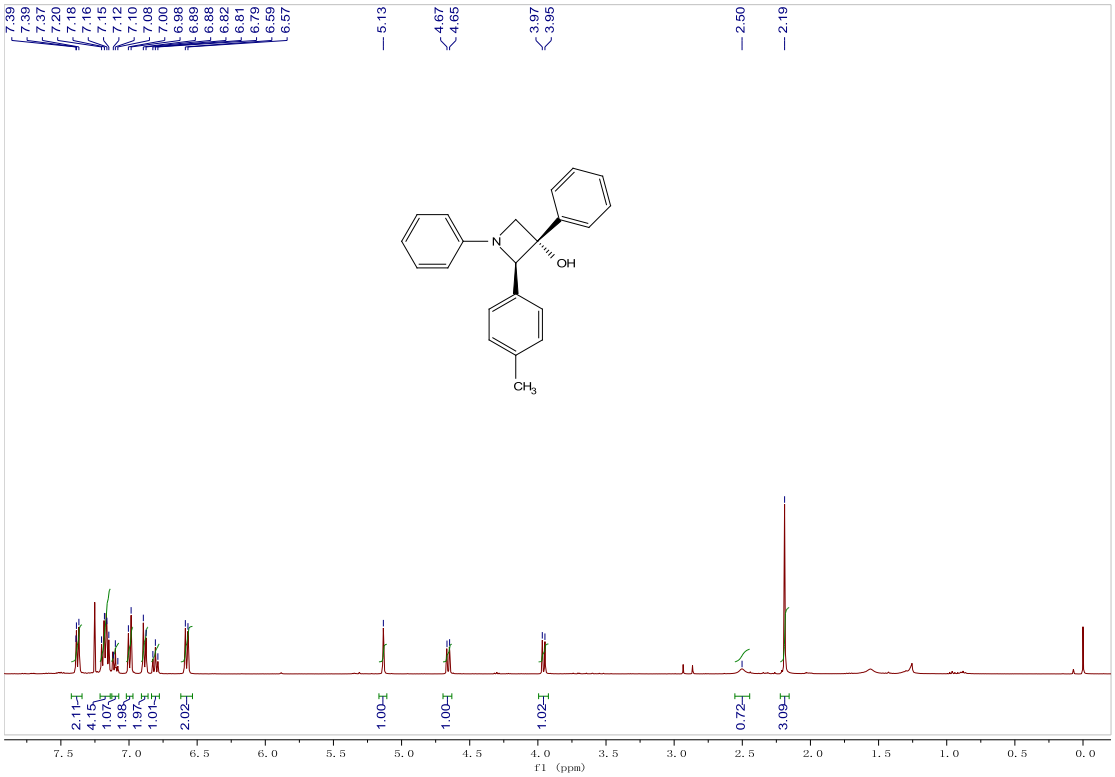


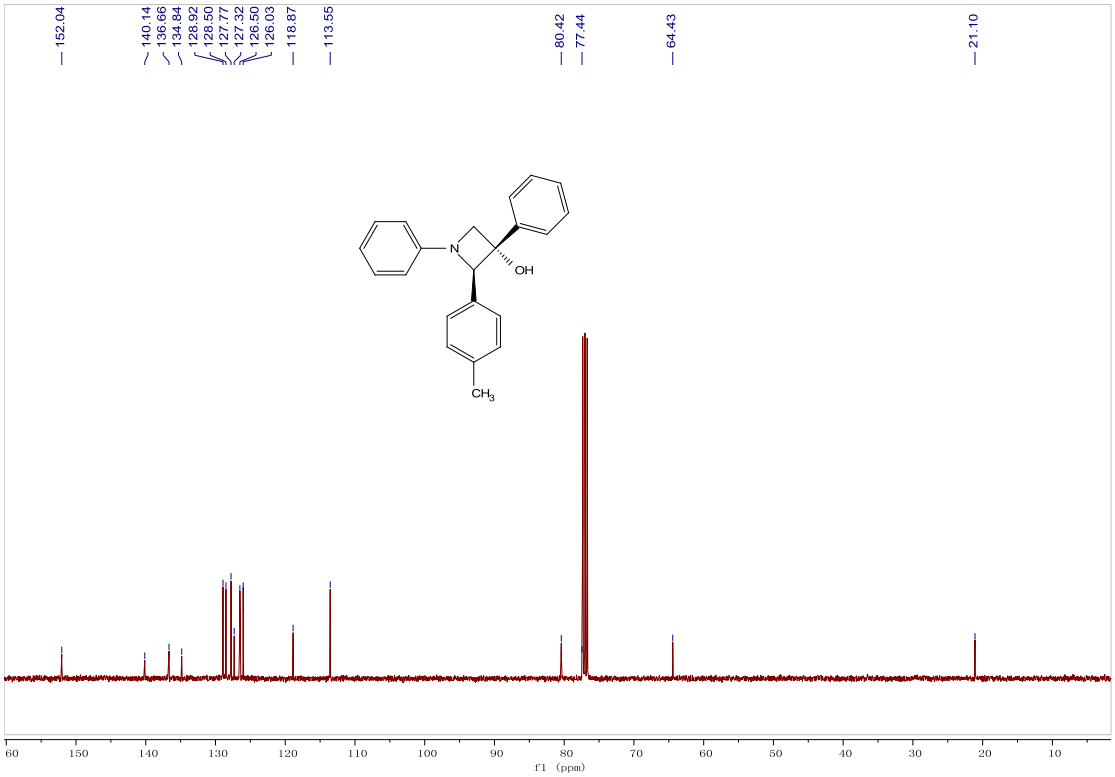
1,2,3-triphenylazetidin-3-ol (**5a**)



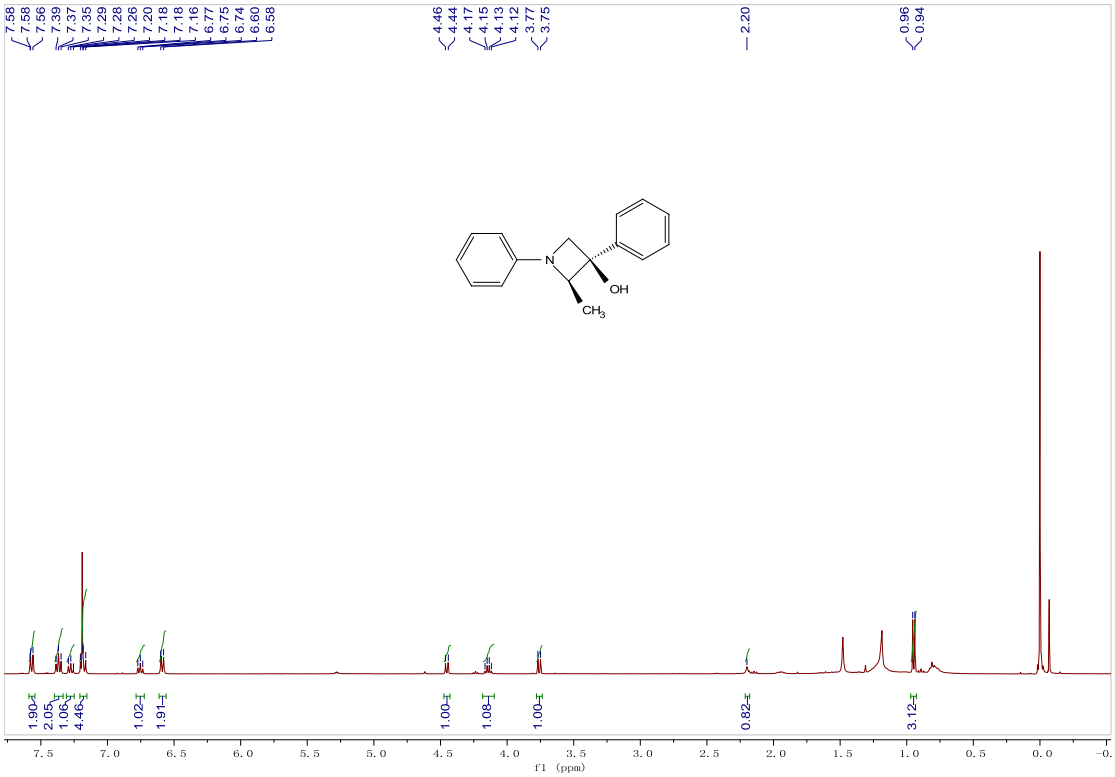


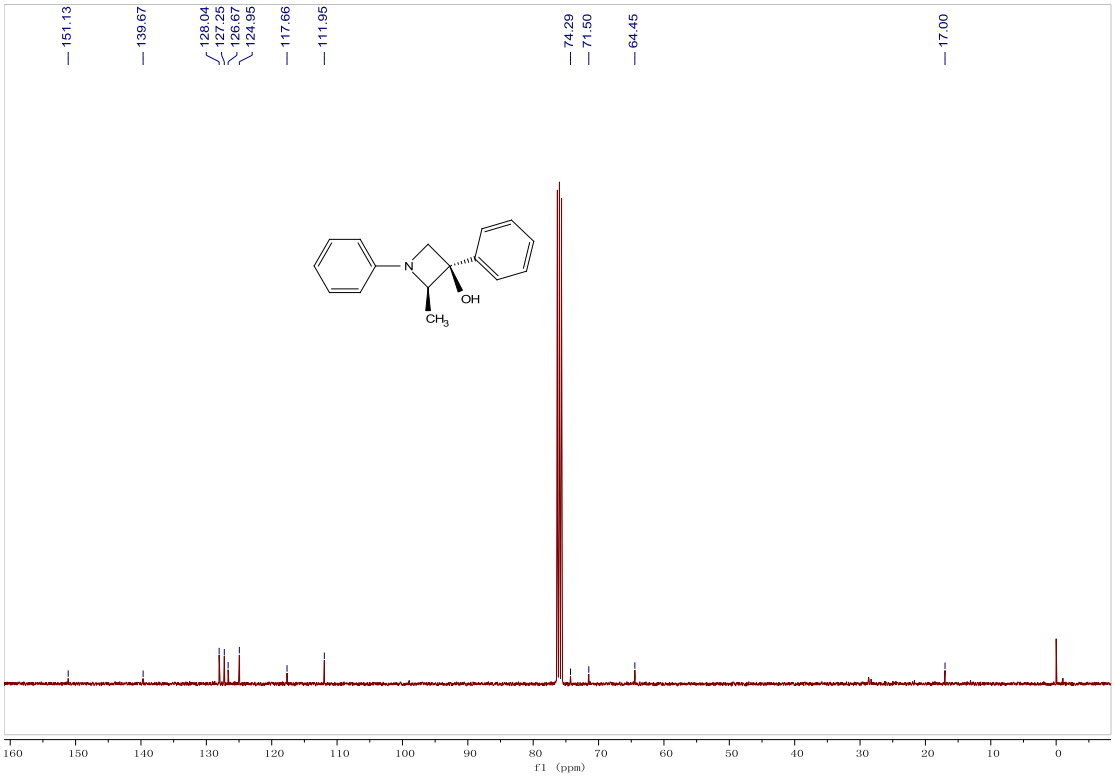
1,3-diphenyl-2-(p-tolyl)azetidin-3-ol (**5b**)



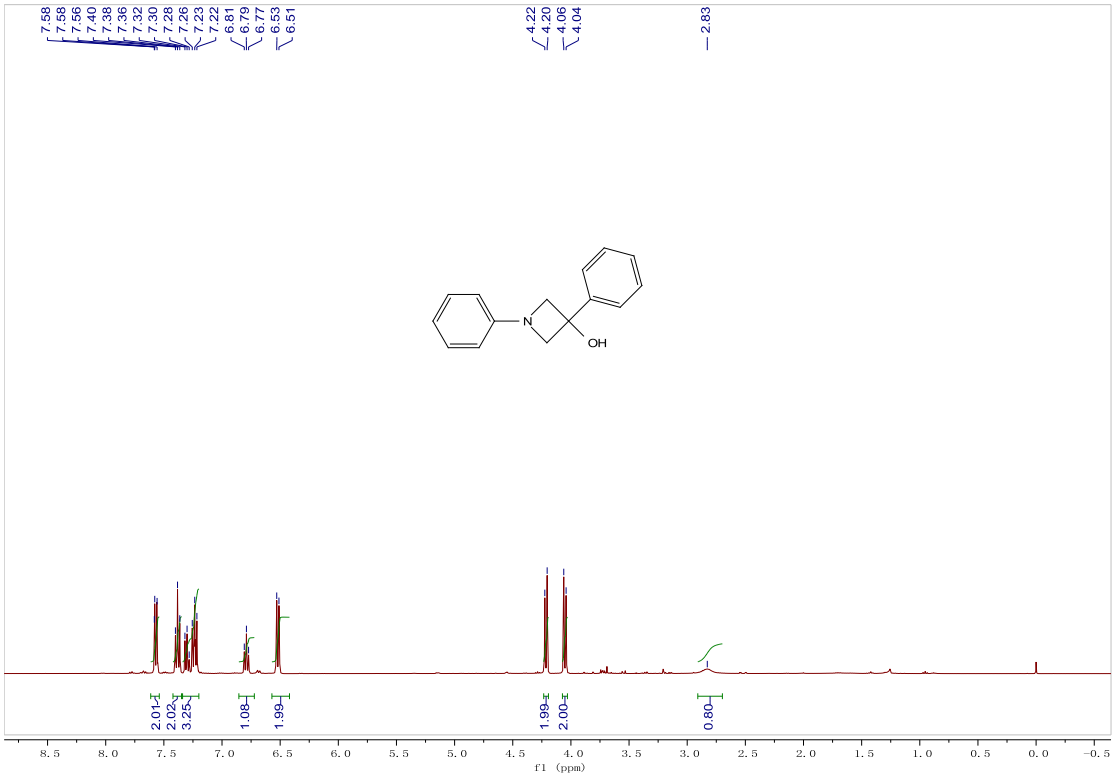


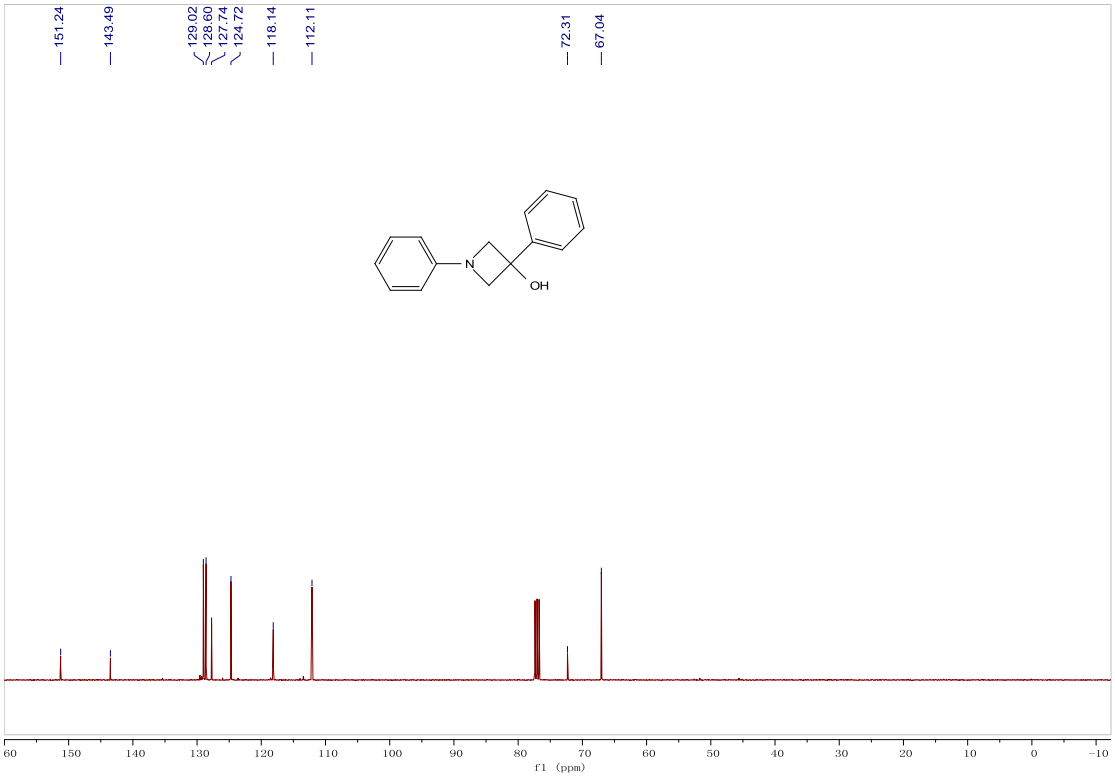
2-methyl-1,3-diphenylazetidin-3-ol (**5c**)



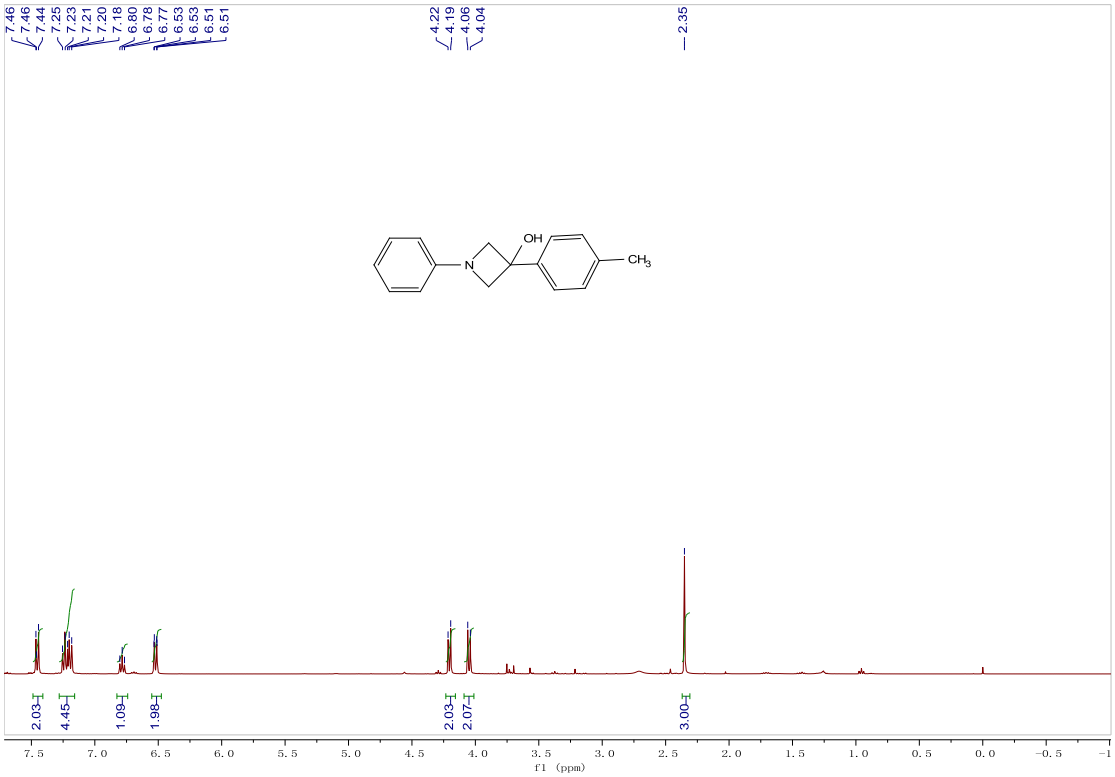


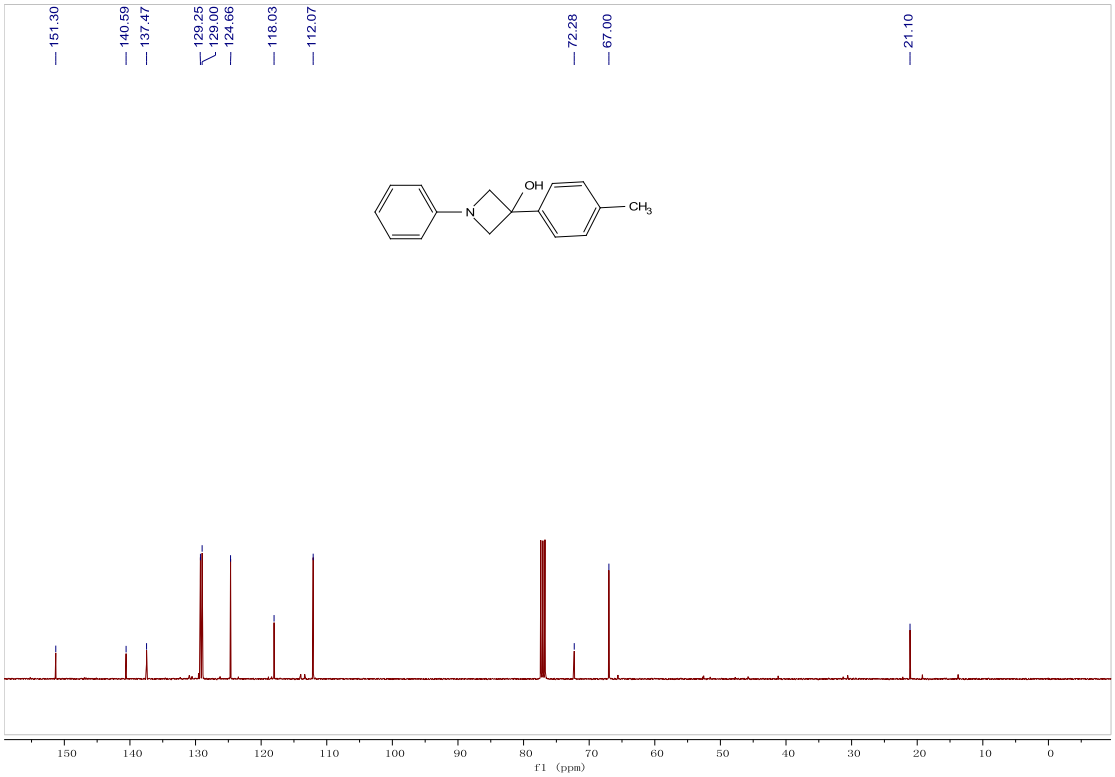
1,3-diphenylazetidin-3-ol (**5d**)



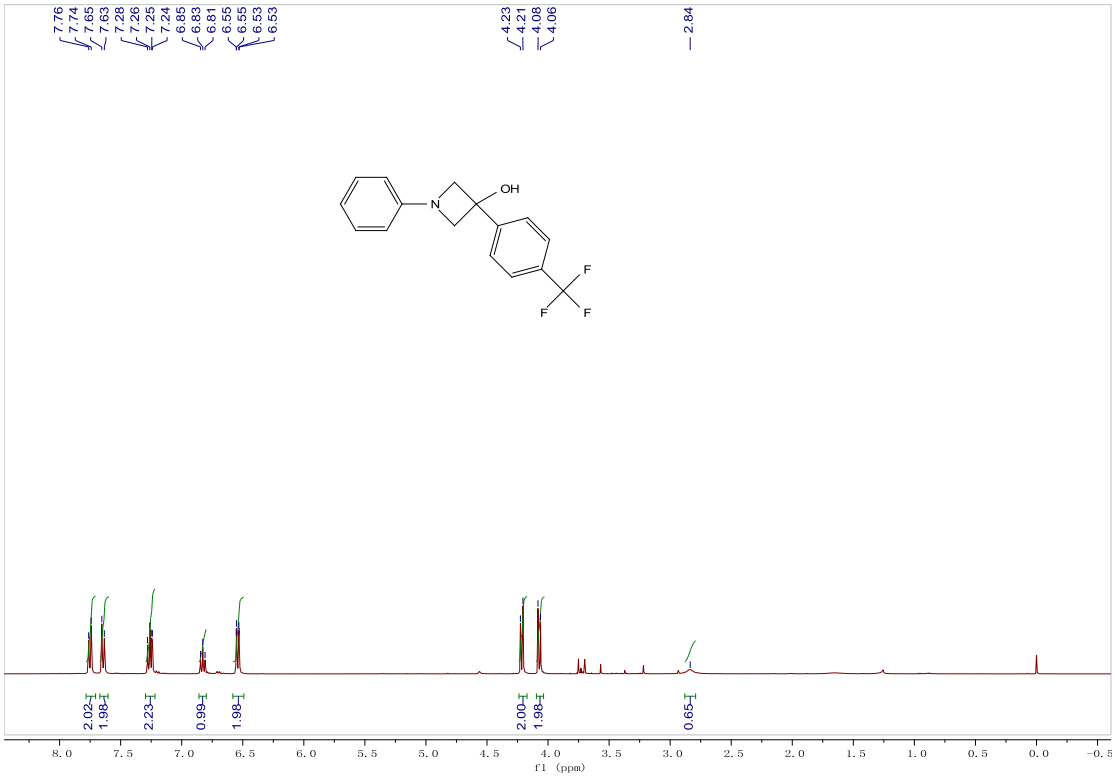


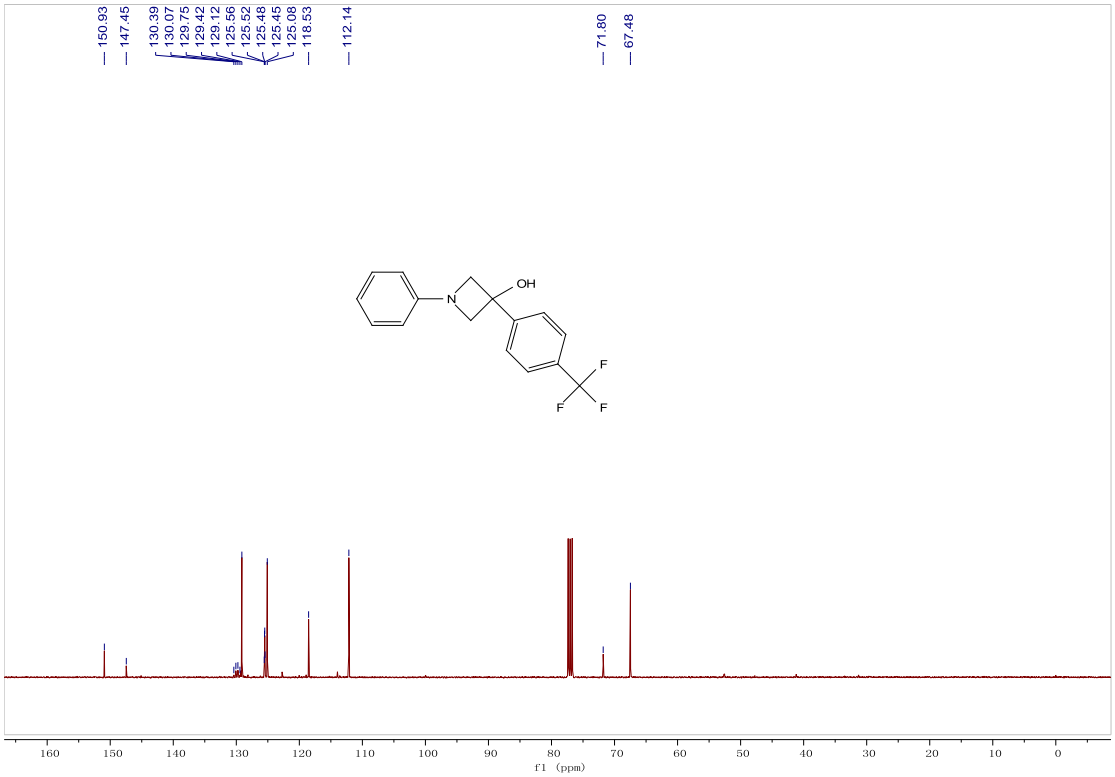
1-phenyl-3-(p-tolyl)azetidin-3-ol (**5e**)





1-phenyl-3-(4-(trifluoromethyl)phenyl)azetidin-3-ol (**5f**)

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112.14
71.80
67.48
OH
N
F
F
F
160
150
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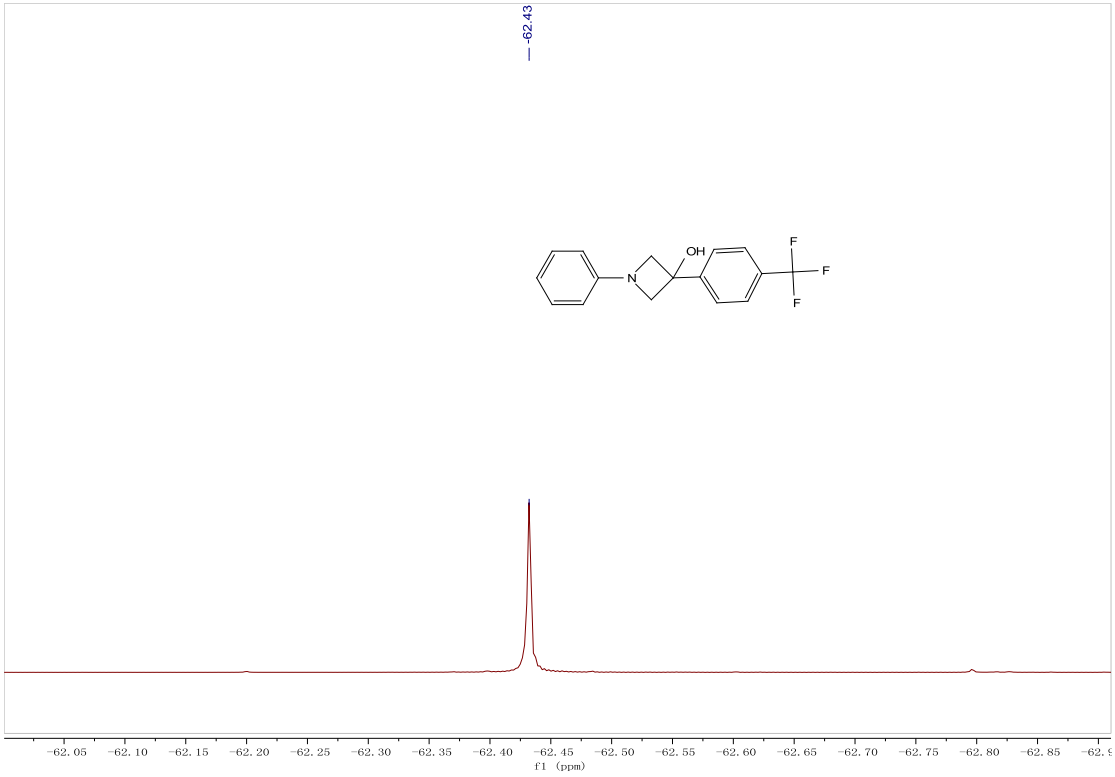
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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OH
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F
F
F
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-62.40
-62.45
-62.50
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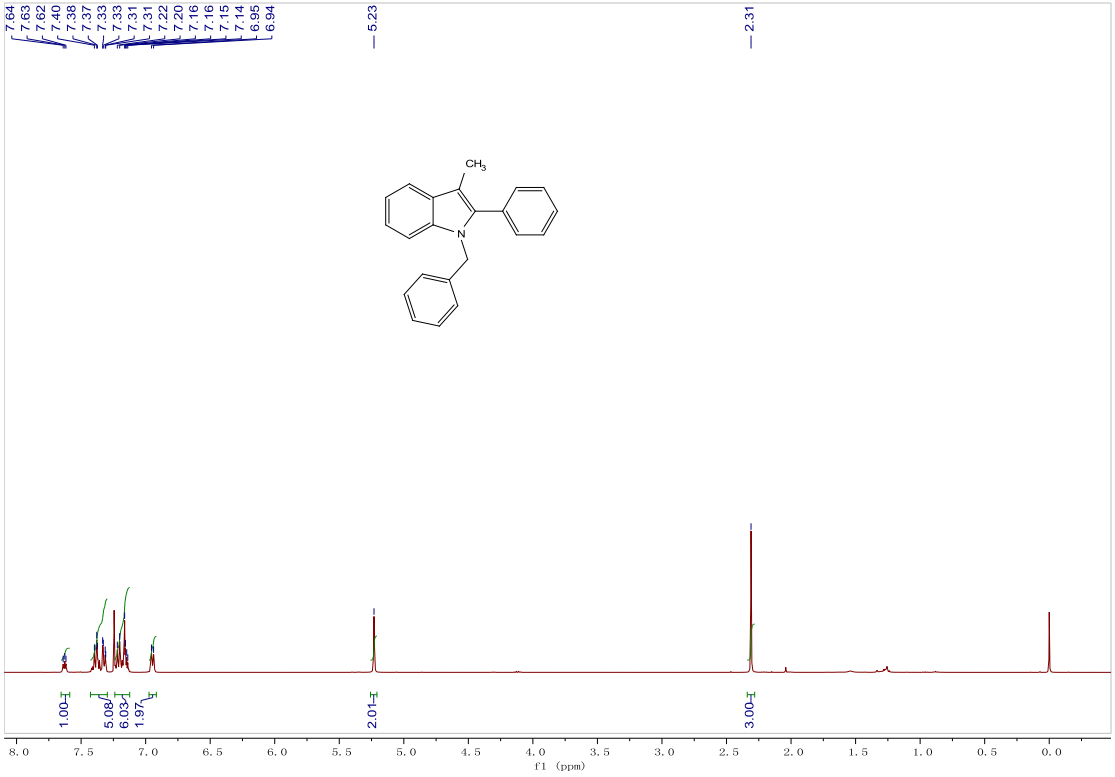
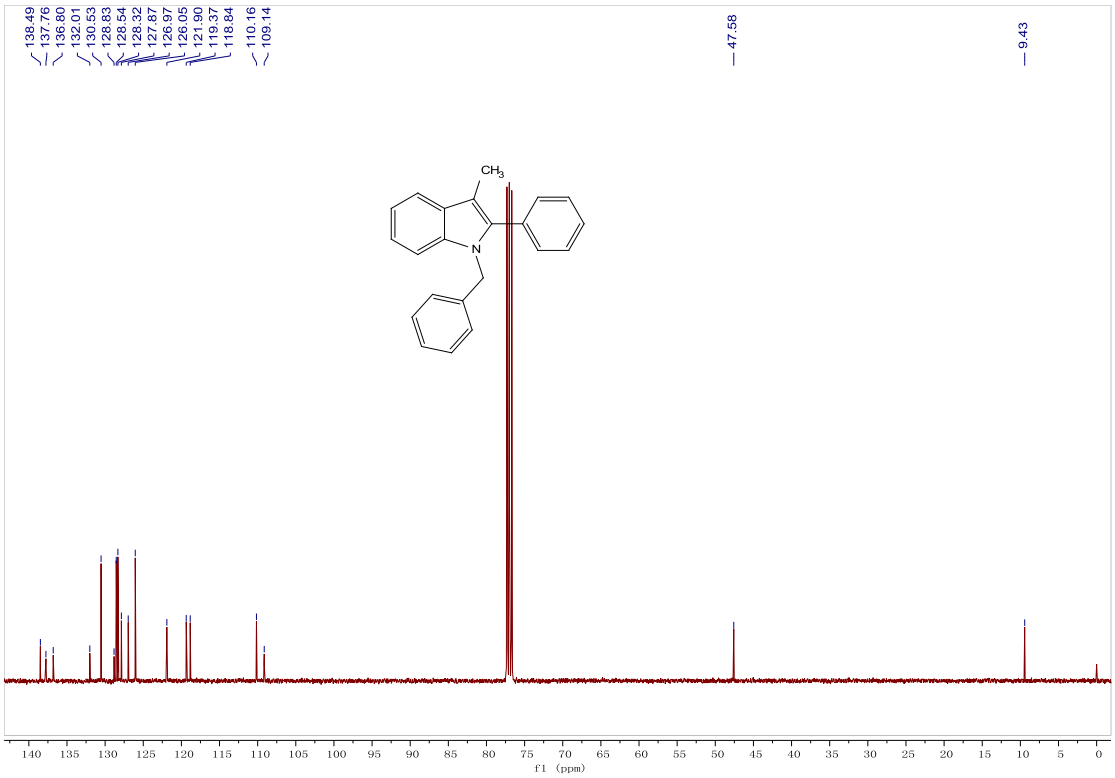
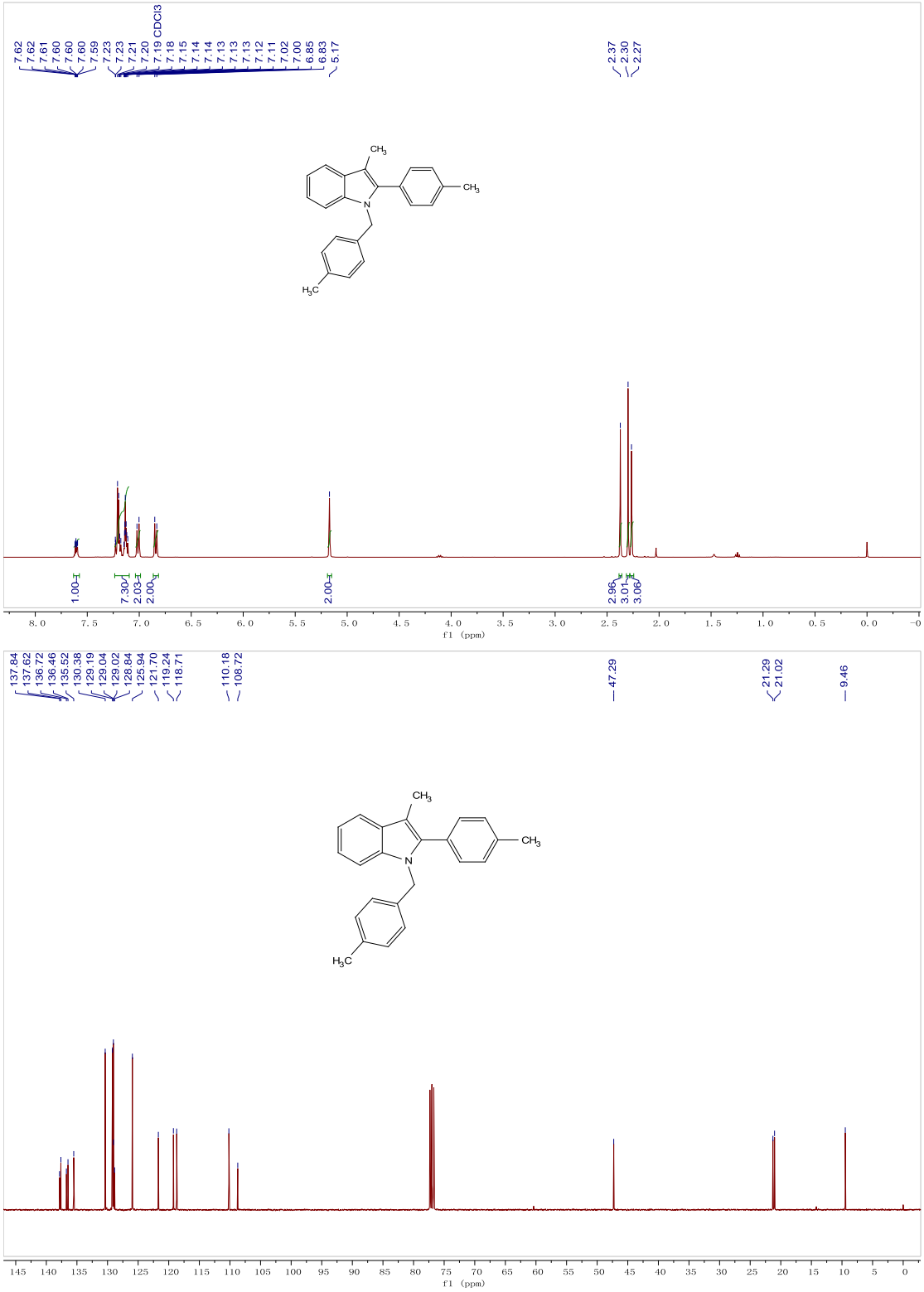
-62.60
-62.65
-62.70
-62.75
-62.80
-62.85
f1 (ppm)

1-benzyl-3-methyl-2-phenyl-1H-indole (**4a**)

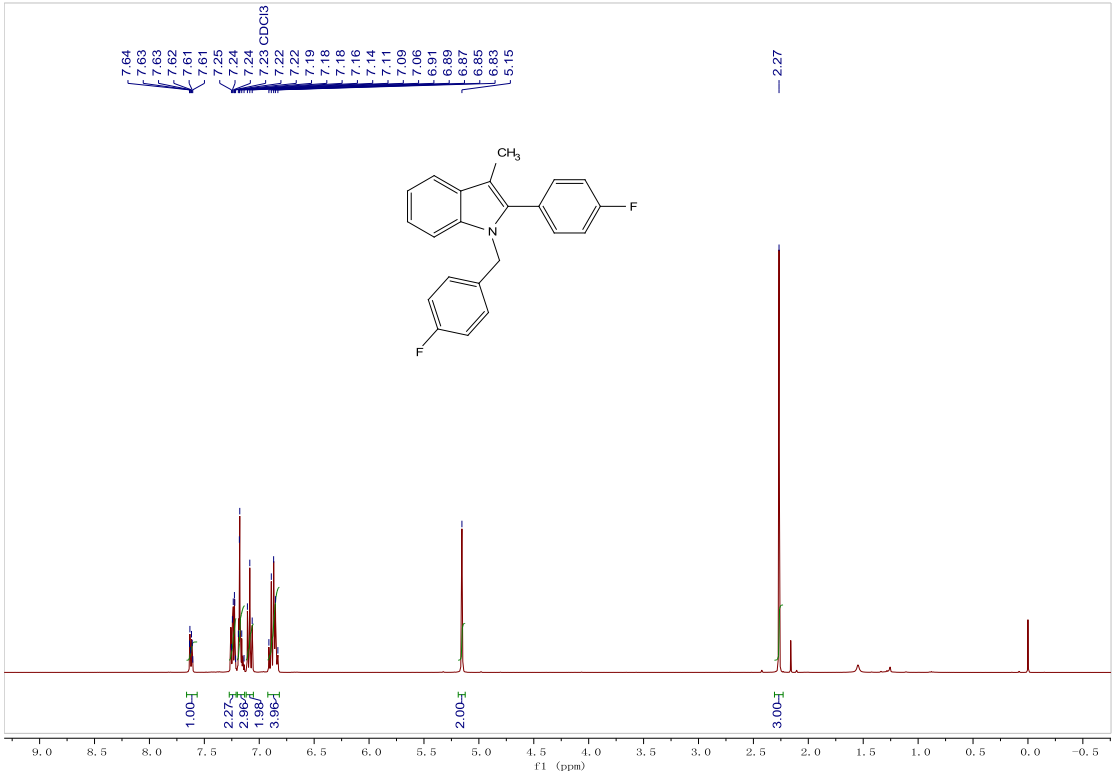


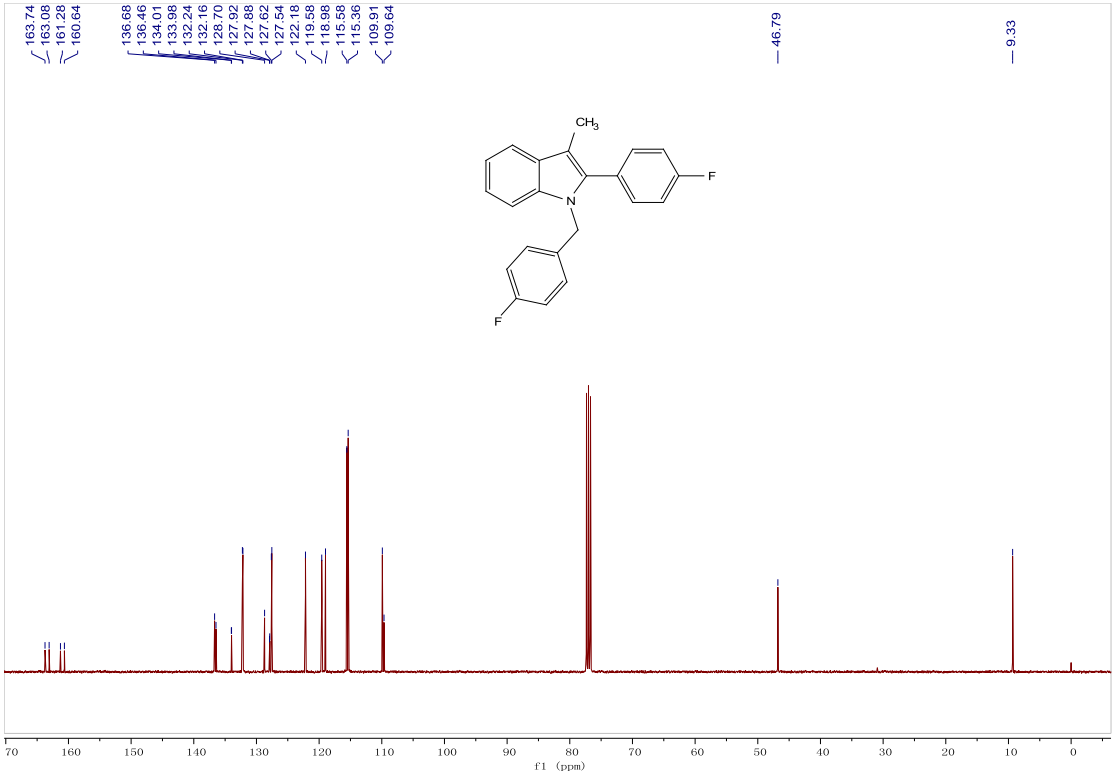


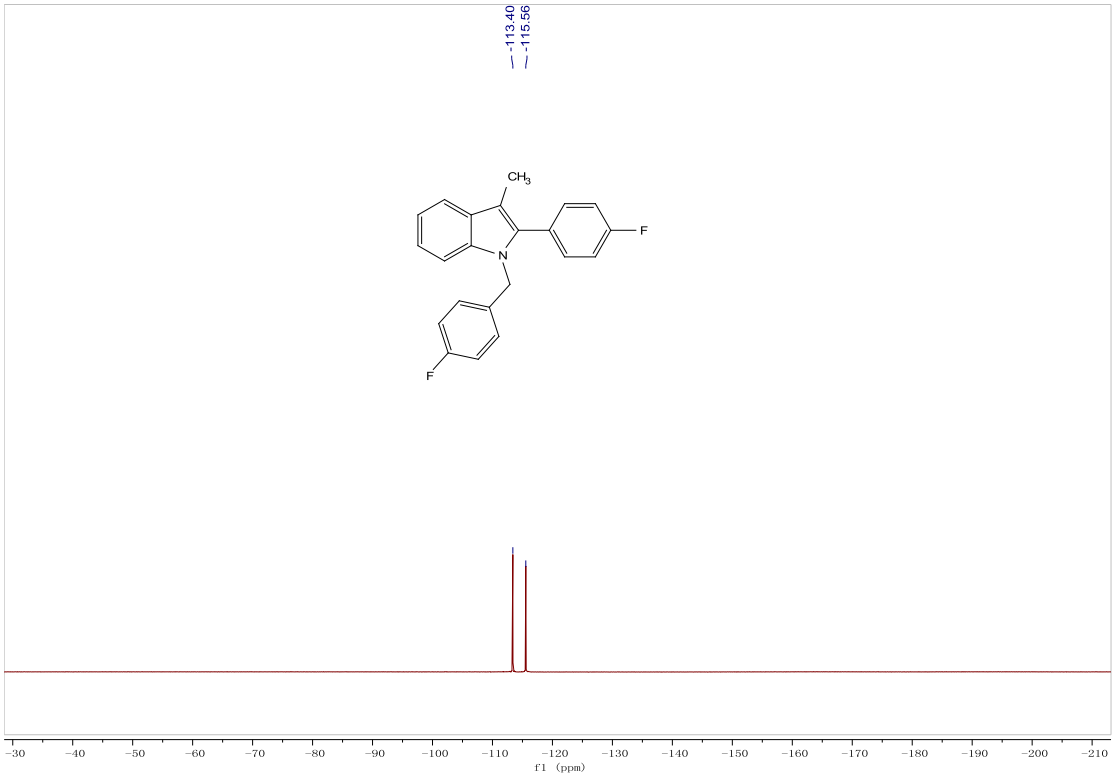
3-methyl-1-(4-methylbenzyl)-2-(p-tolyl)-1H-indole (**4b**)



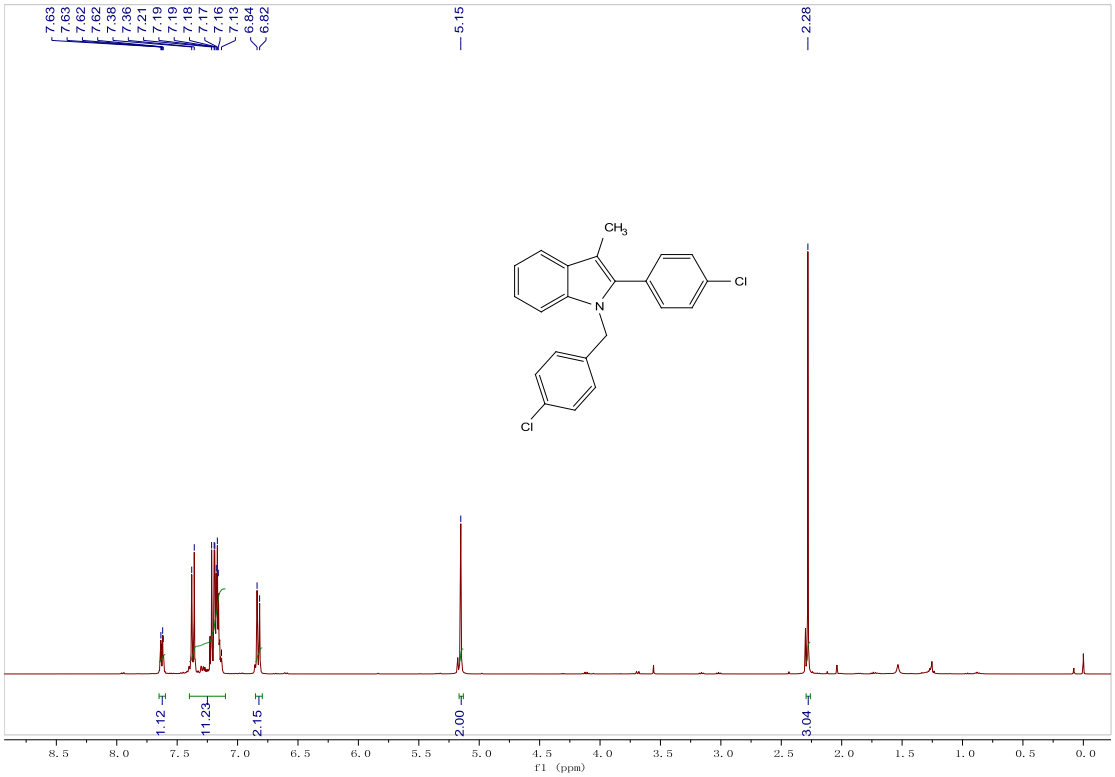
1-(4-fluorobenzyl)-2-(4-fluorophenyl)-3-methyl-1H-indole (**4c**)

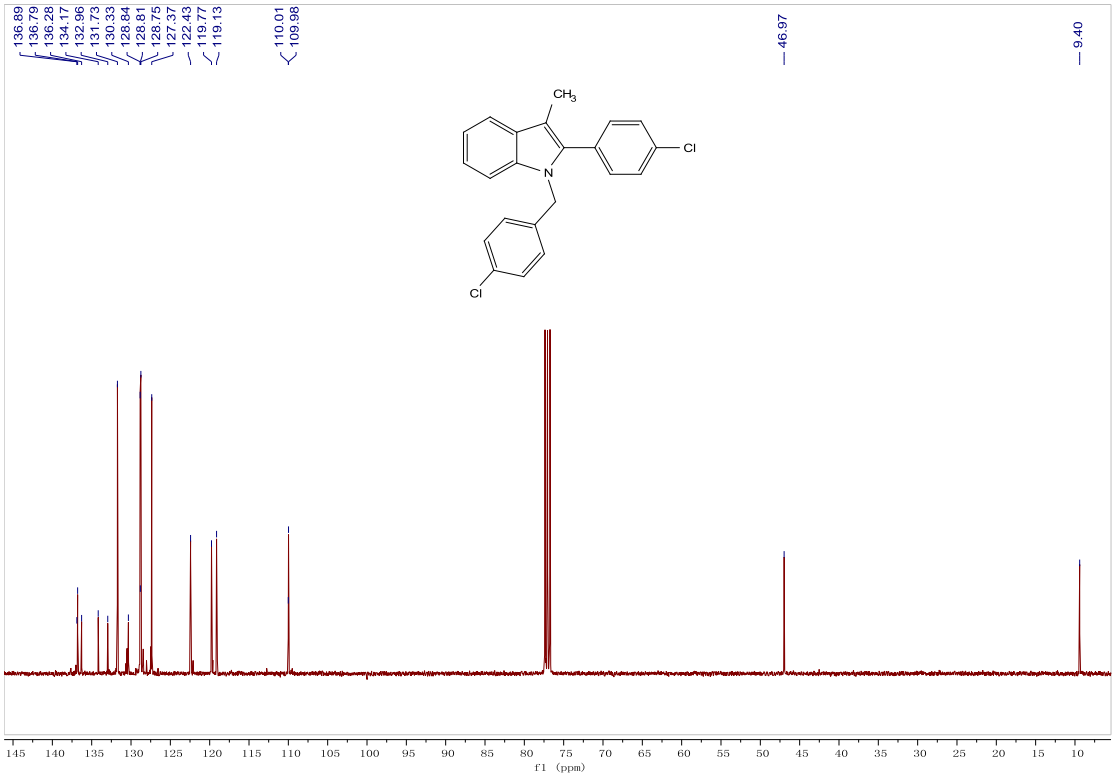




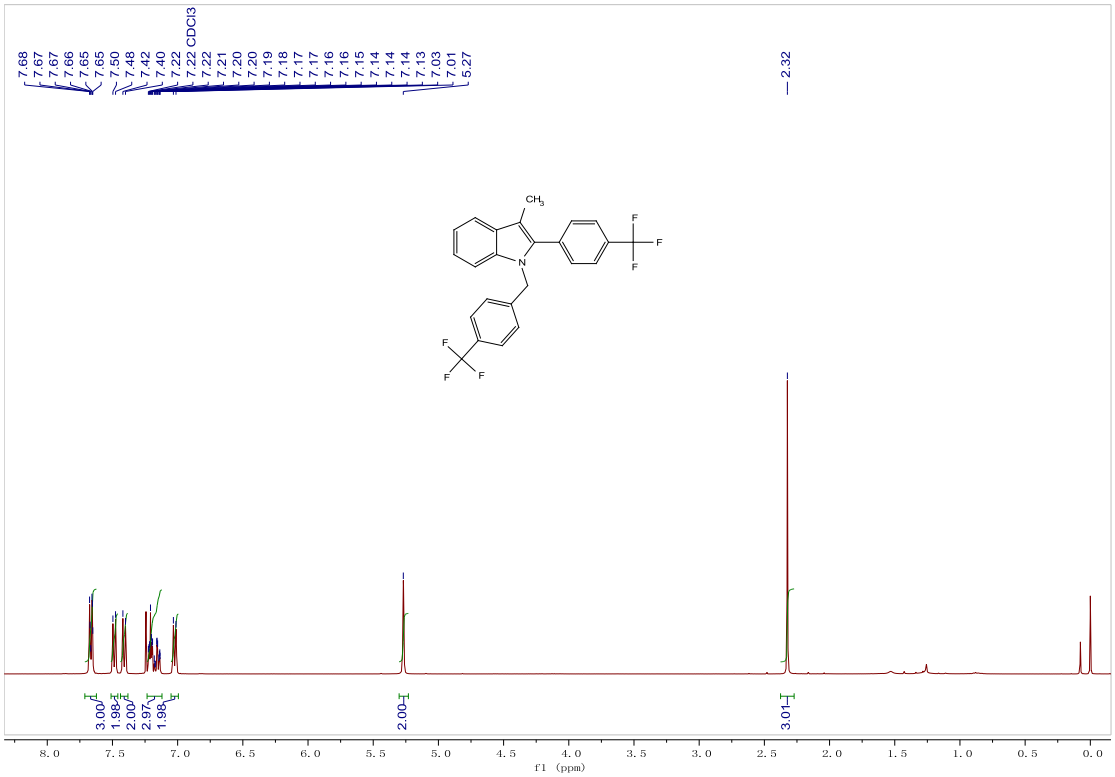


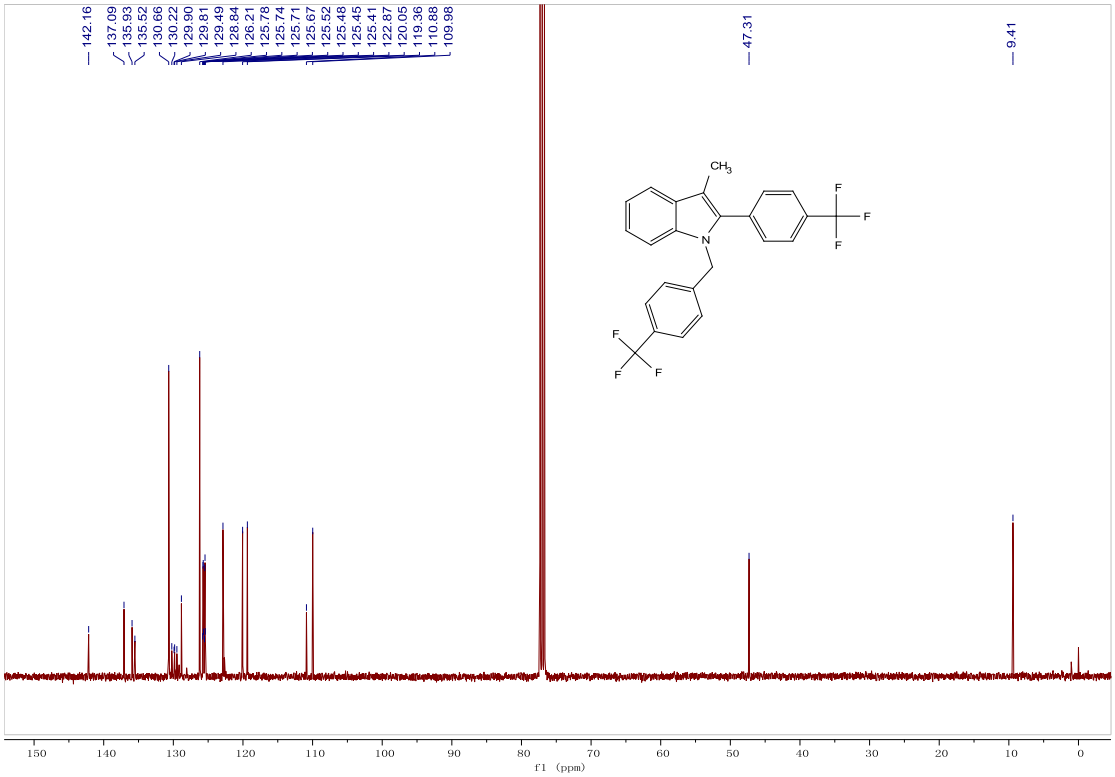
1-(4-chlorobenzyl)-2-(4-chlorophenyl)-3-methyl-1H-indole (**4d**)

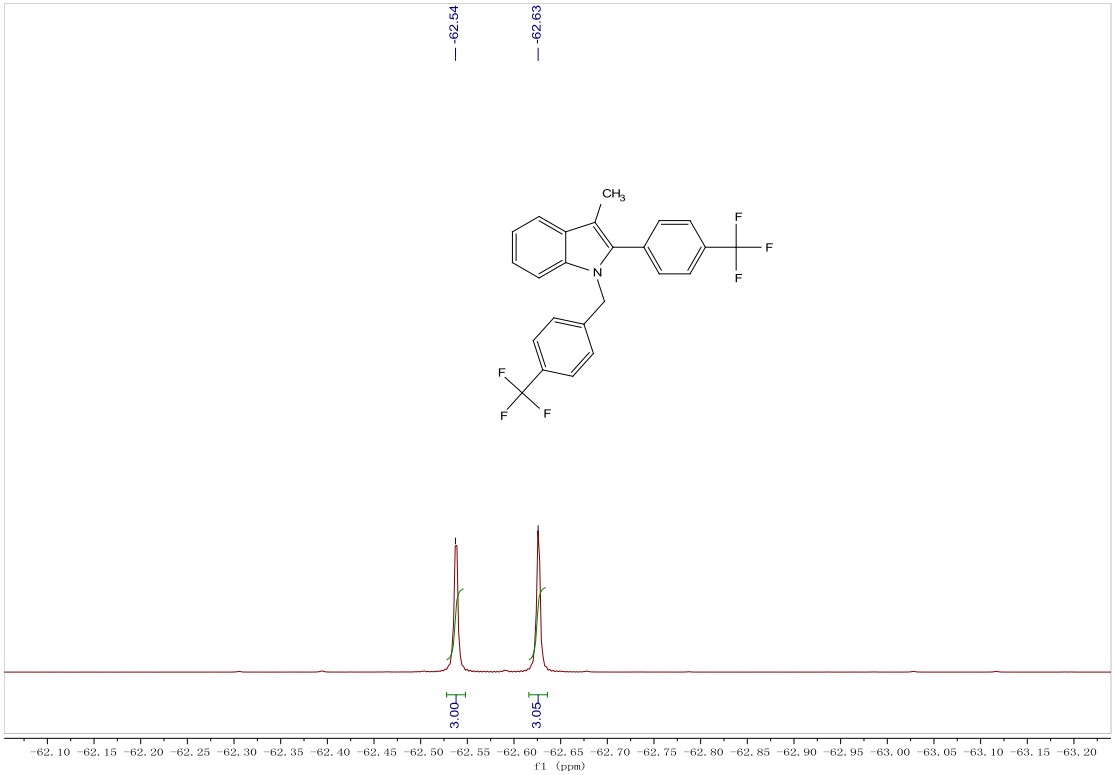




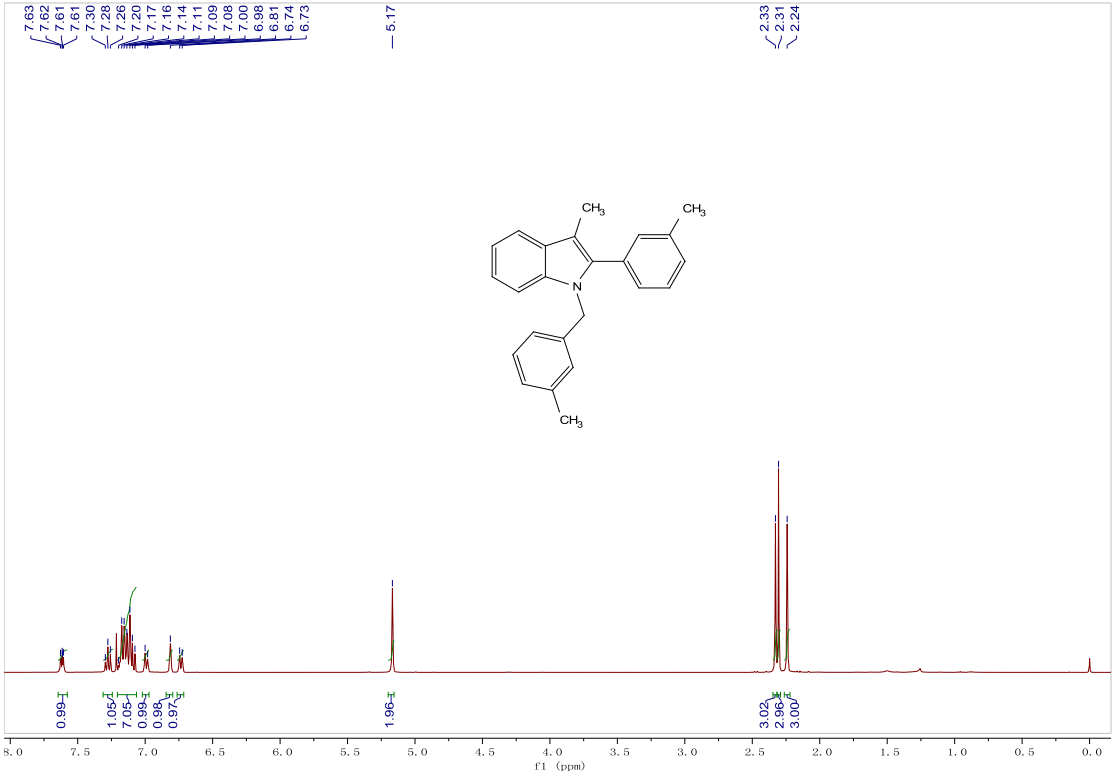
3-methyl-1-(4-(trifluoromethyl)benzyl)-2-(4-(trifluoromethyl)phenyl)-1H-indole (**4e**)

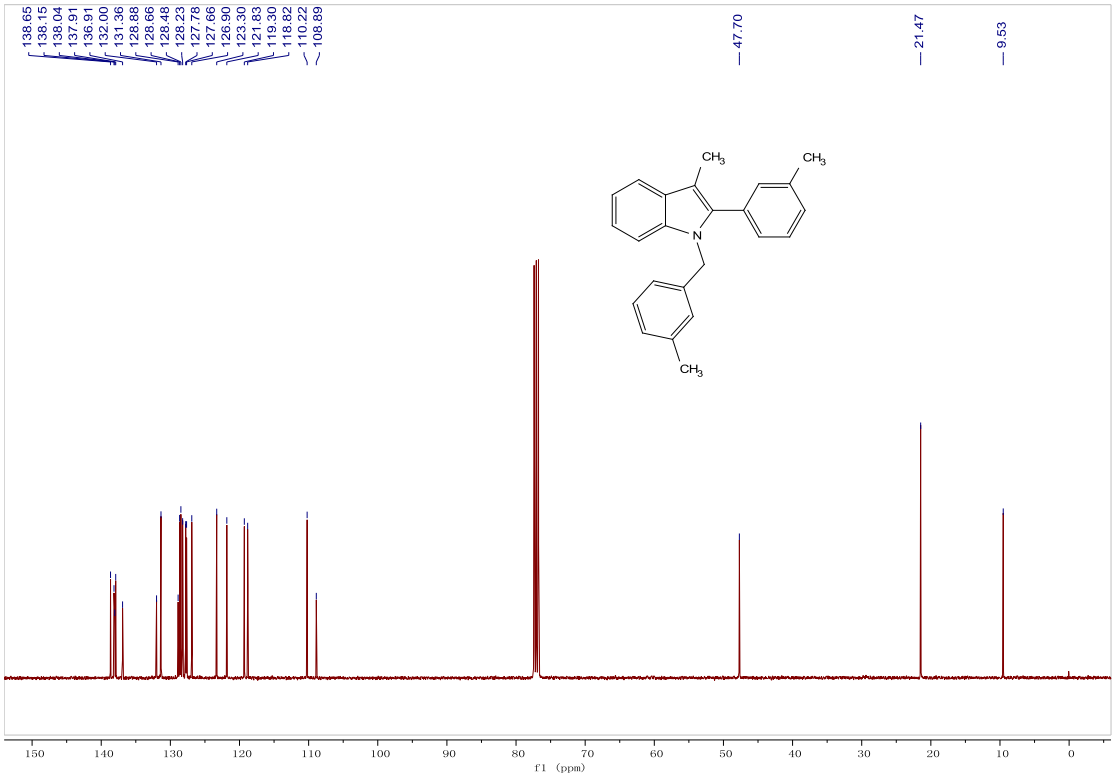



142.16
137.09
135.93
135.52
130.66
130.22
129.90
129.81
129.49
128.84
126.21
125.78
125.74
125.71
125.67
125.52
125.48
125.45
125.41
122.87
120.05
119.36
110.88
109.98
47.31
9.41
CH3
F
F
F
N
F
F
F
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

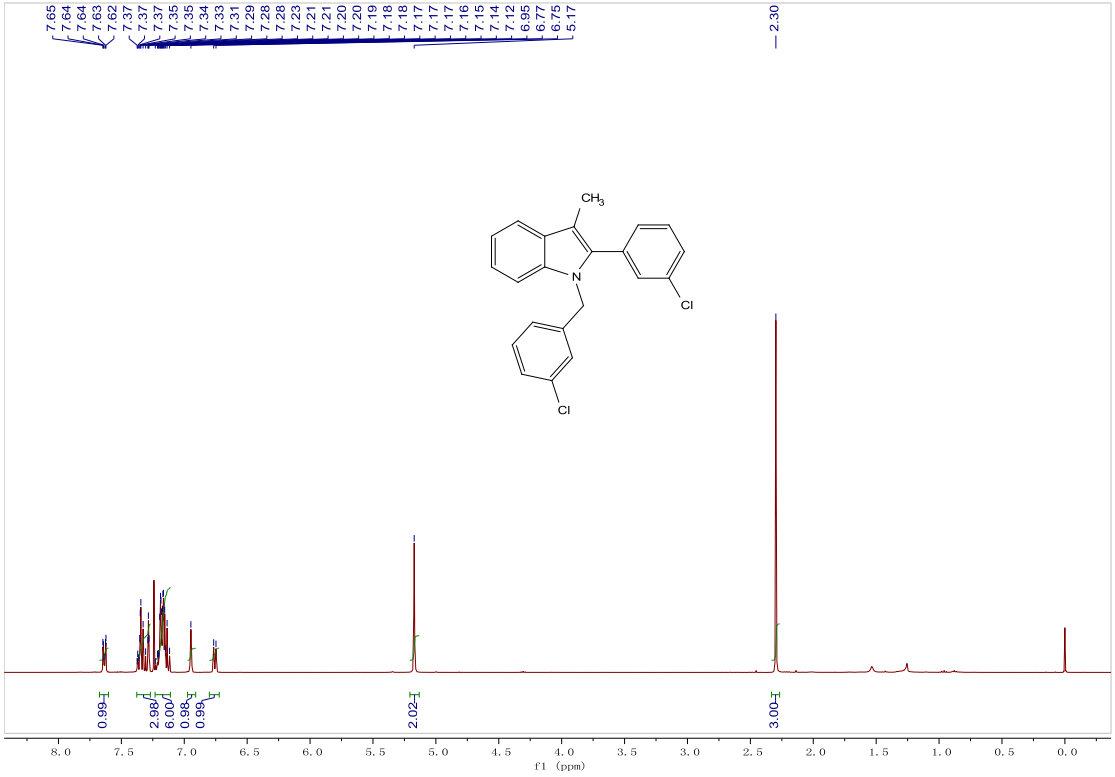

-62.54
-62.63
CH3
F
F
F
N
F
F
F
3.00
3.05
−62.10 −62.15 −62.20 −62.25 −62.30 −62.35 −62.40 −62.45 −62.50 −62.55 −62.60 −62.65 −62.70 −62.75 −62.80 −62.85 −62.90 −62.95 −63.00 −63.05 −63.10 −63.15 −63.20
f1 (ppm)

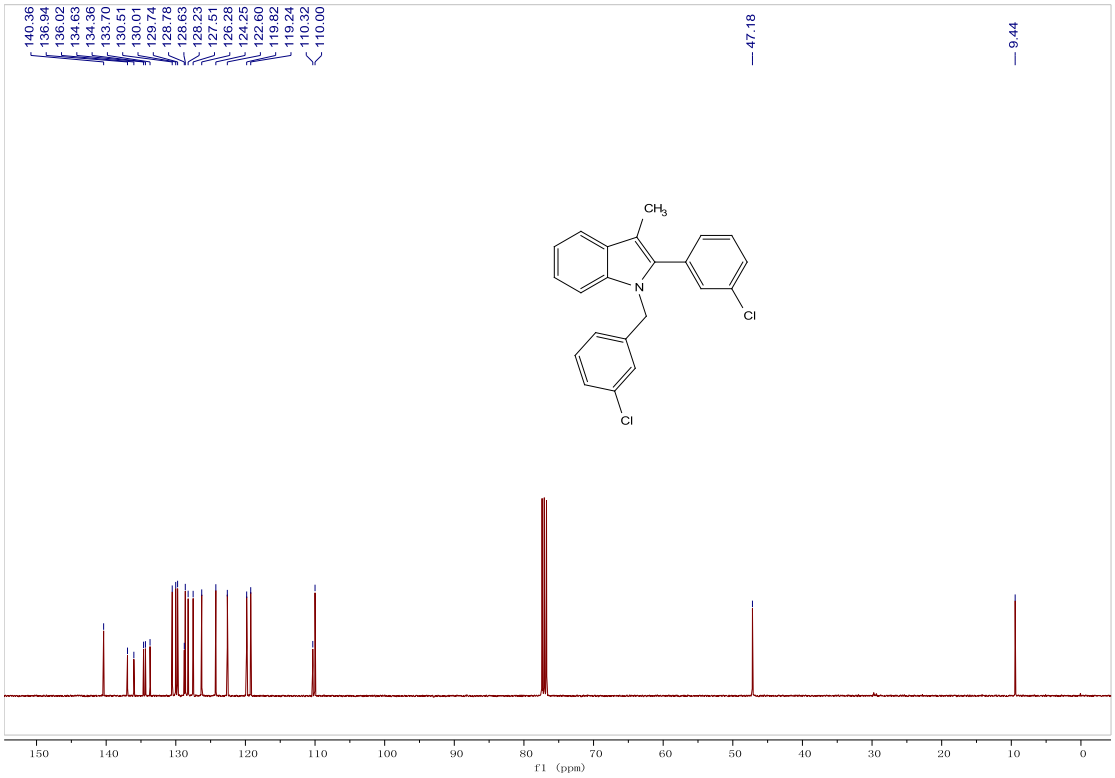
3-methyl-1-(3-methylbenzyl)-2-(m-tolyl)-1H-indole (**4f**)



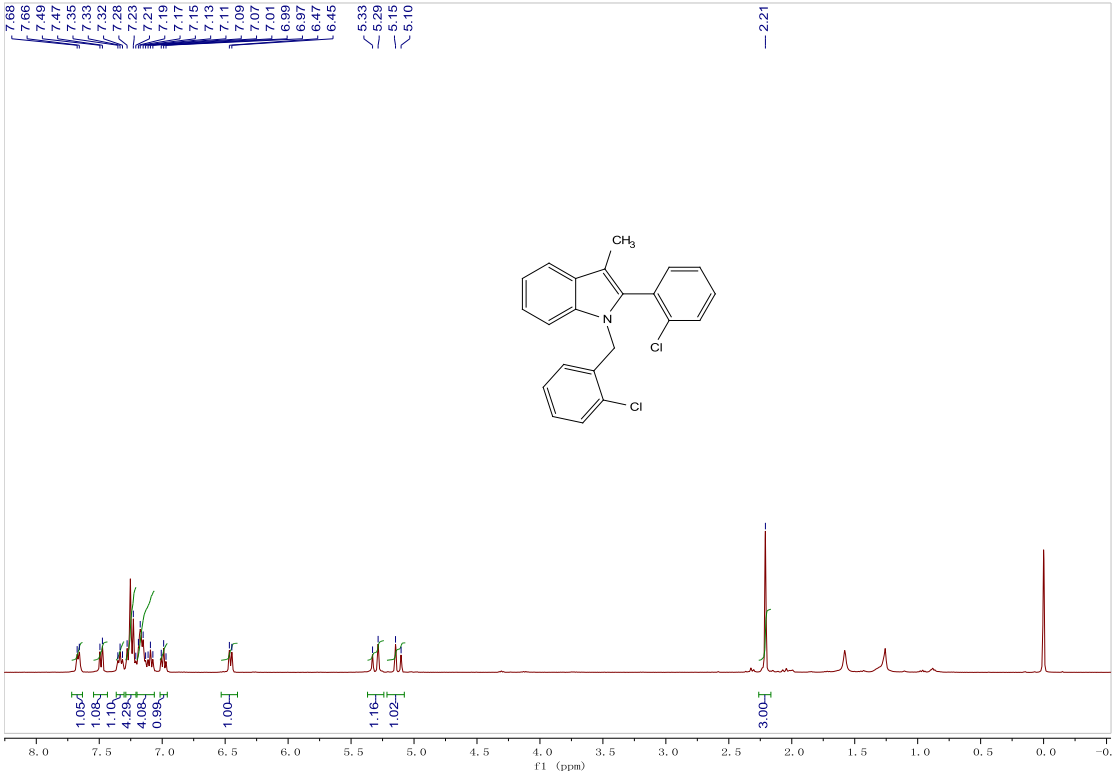


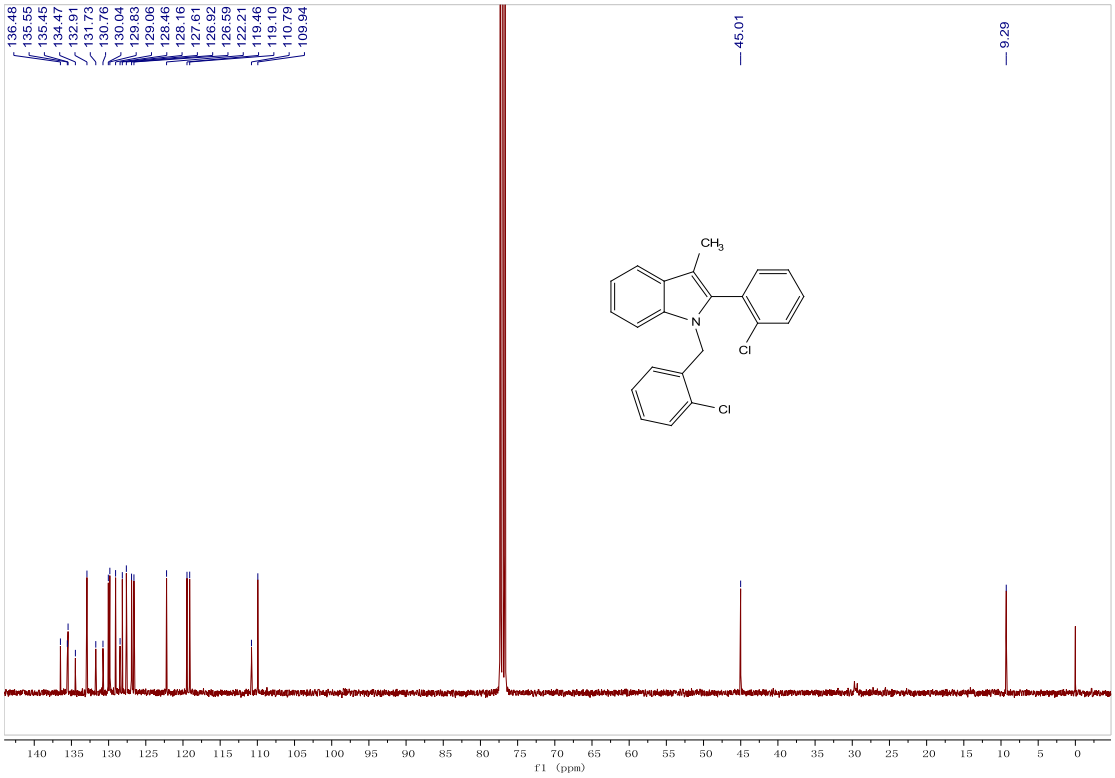
1-(3-chlorobenzyl)-2-(3-chlorophenyl)-3-methyl-1H-indole (**4g**)



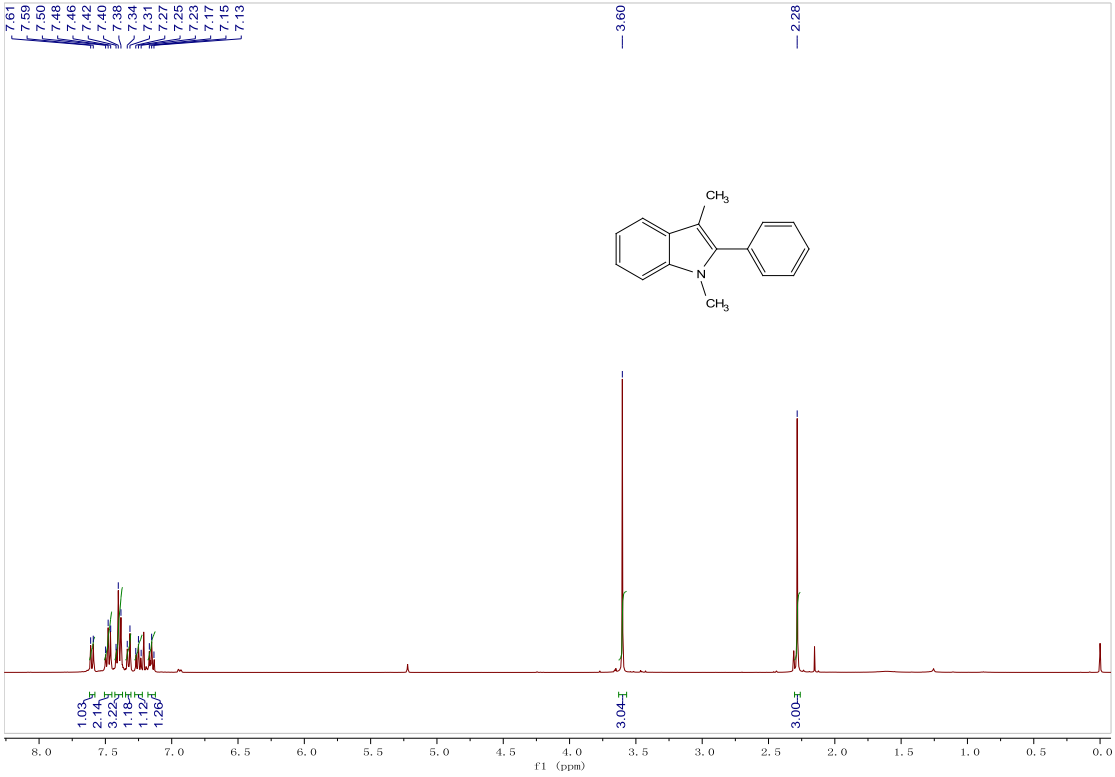


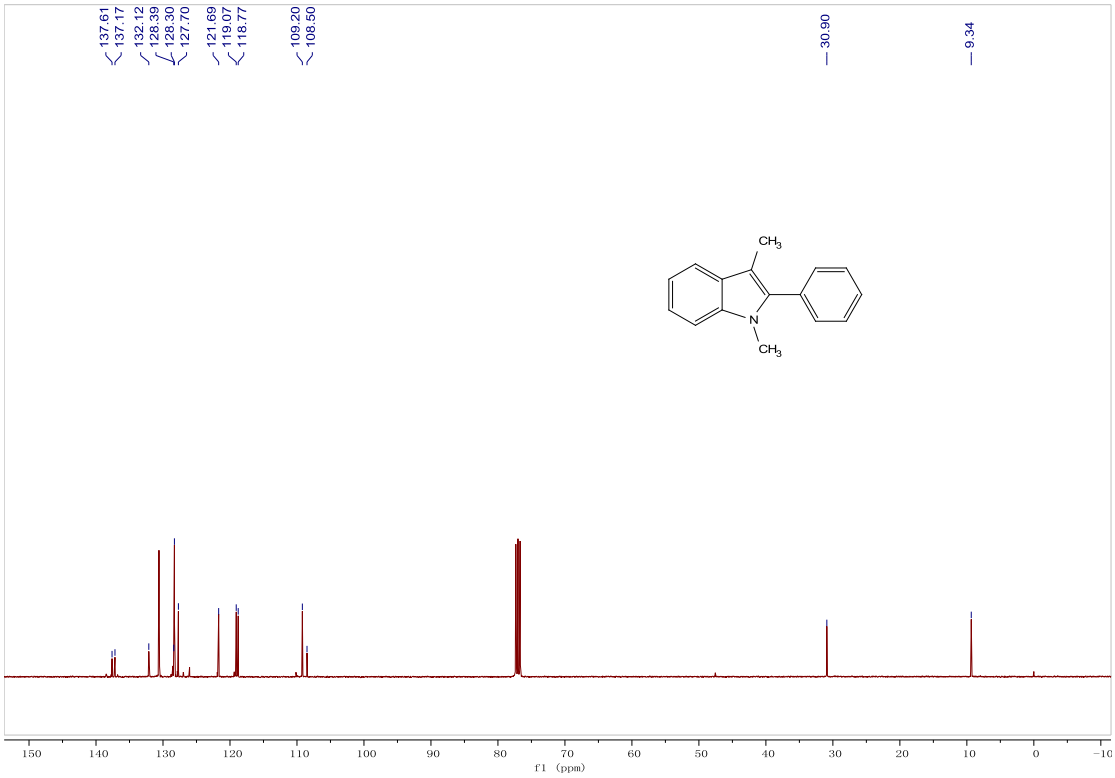
1-(2-chlorobenzyl)-2-(2-chlorophenyl)-3-methyl-1H-indole (**4h**)



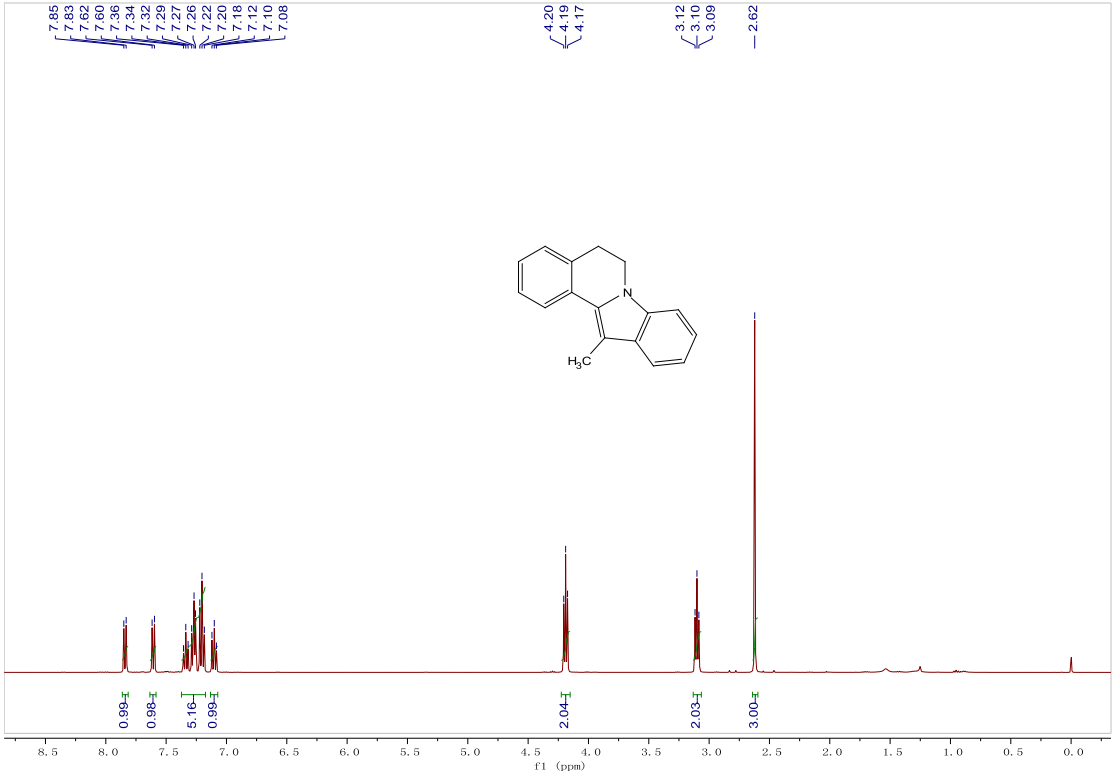


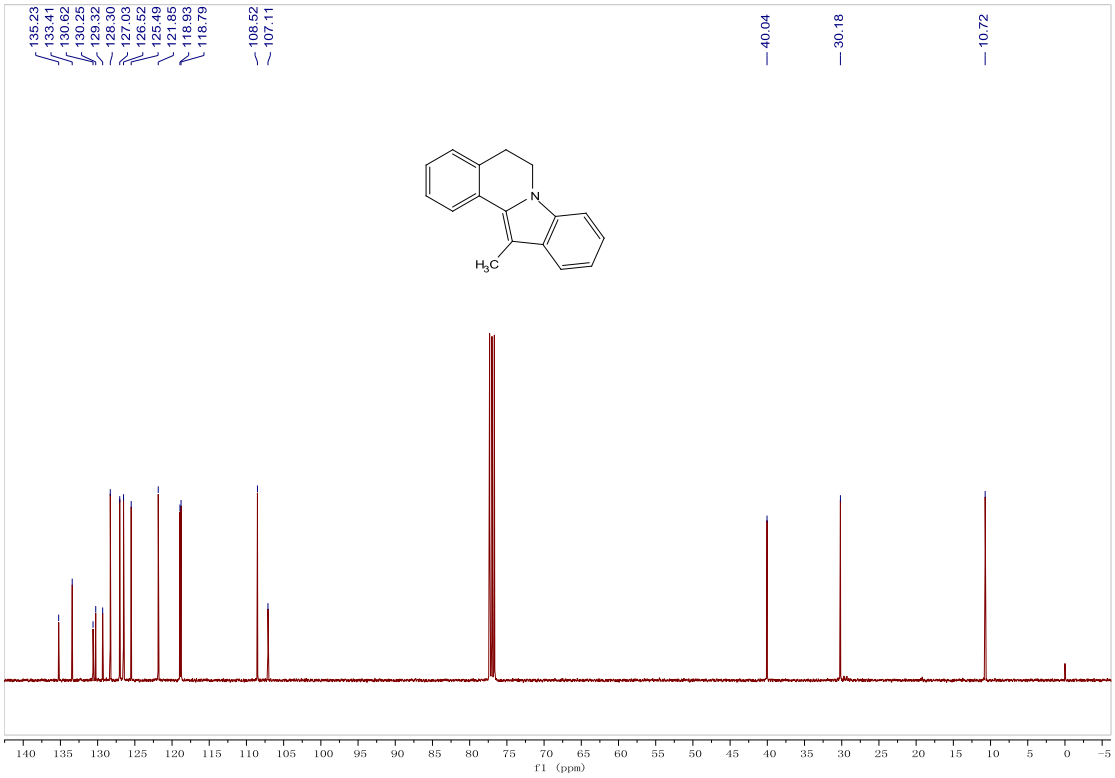
1,3-dimethyl-2-phenyl-1H-indole (**4i**)



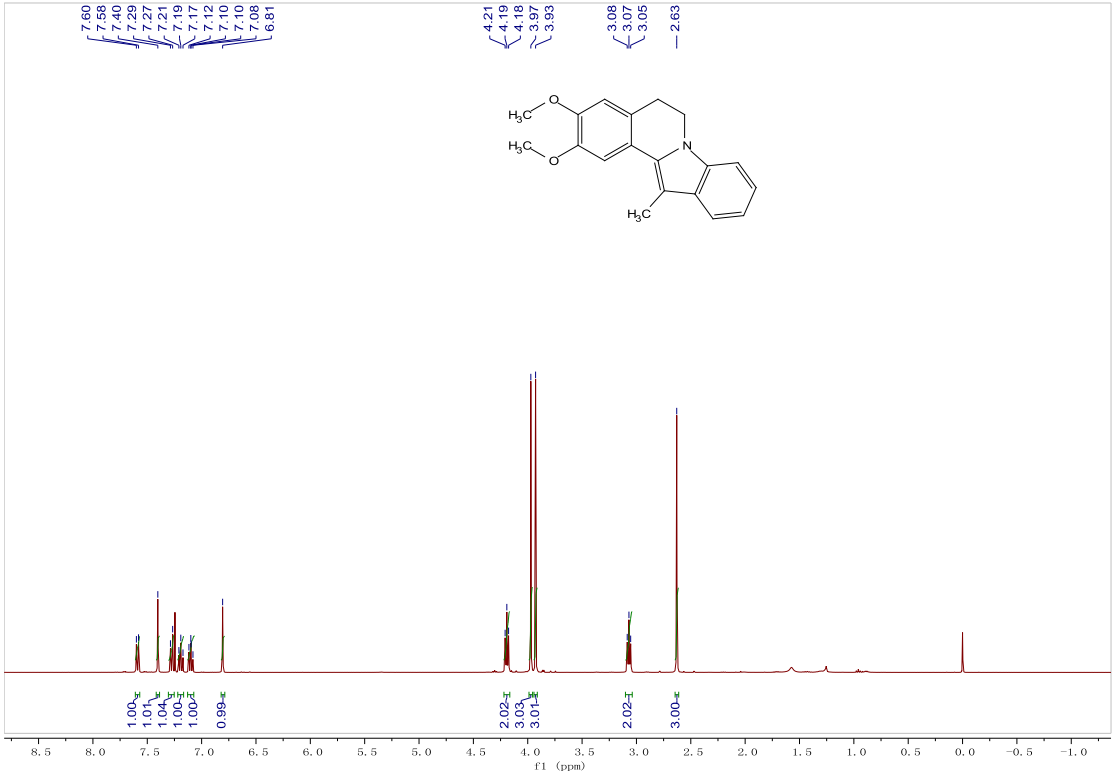


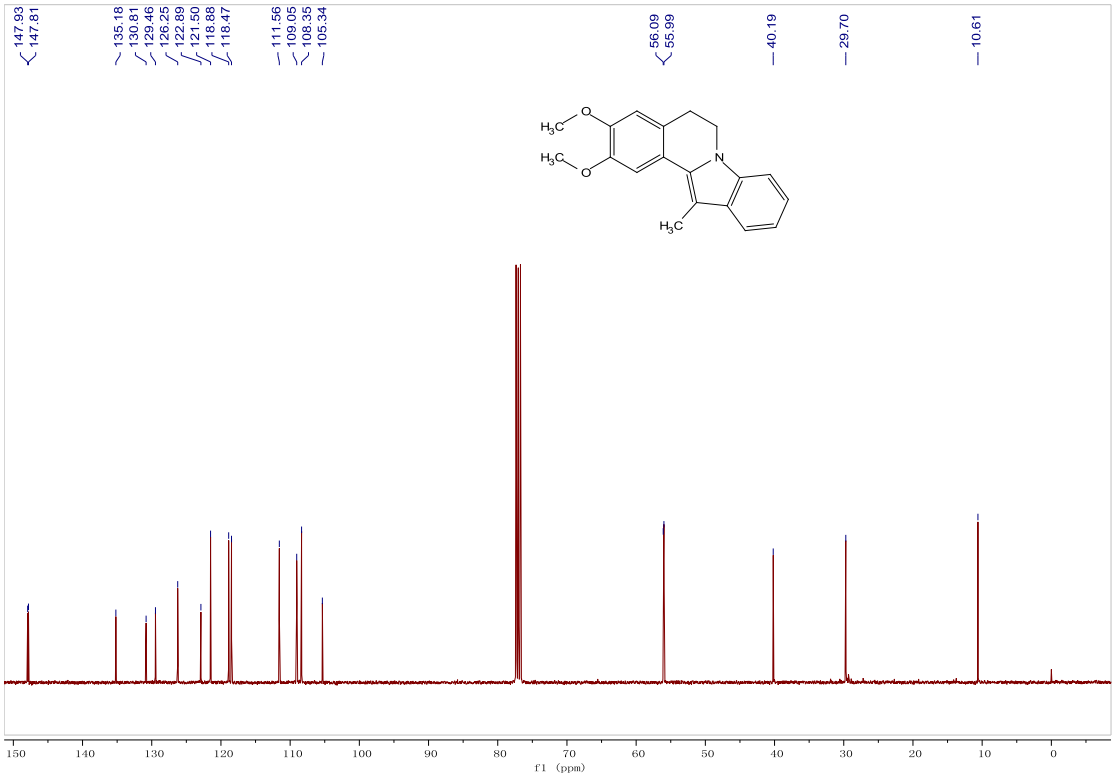
12-methyl-5,6-dihydroindolo[2,1-a]isoquinoline (**4j**)





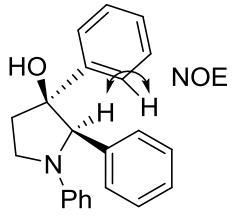
2,3-dimethoxy-12-methyl-5,6-dihydroindolo[2,1-a]isoquinoline (**4k**)



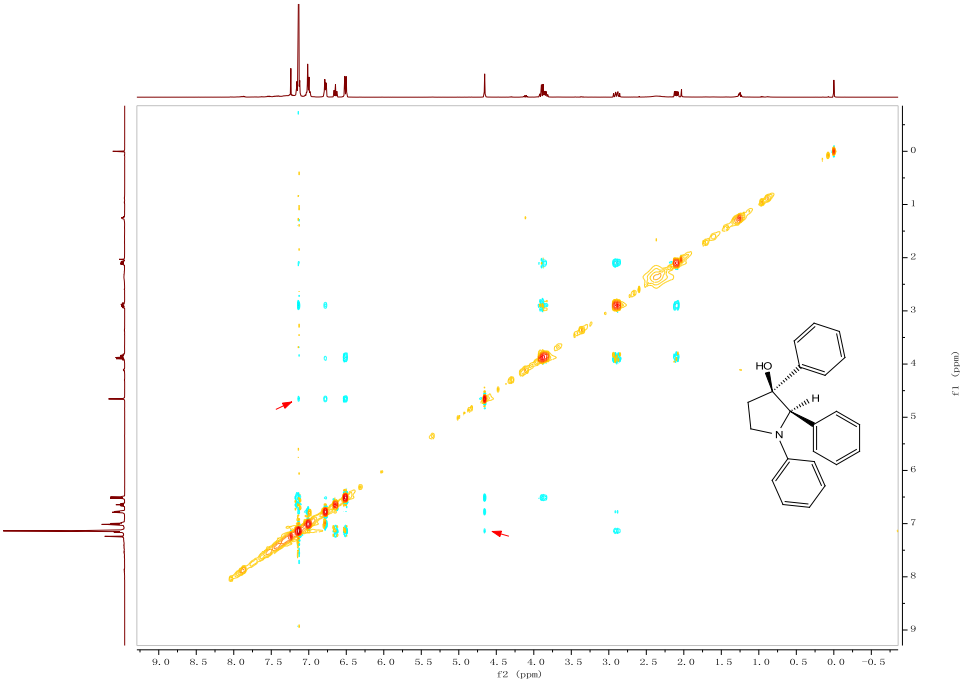


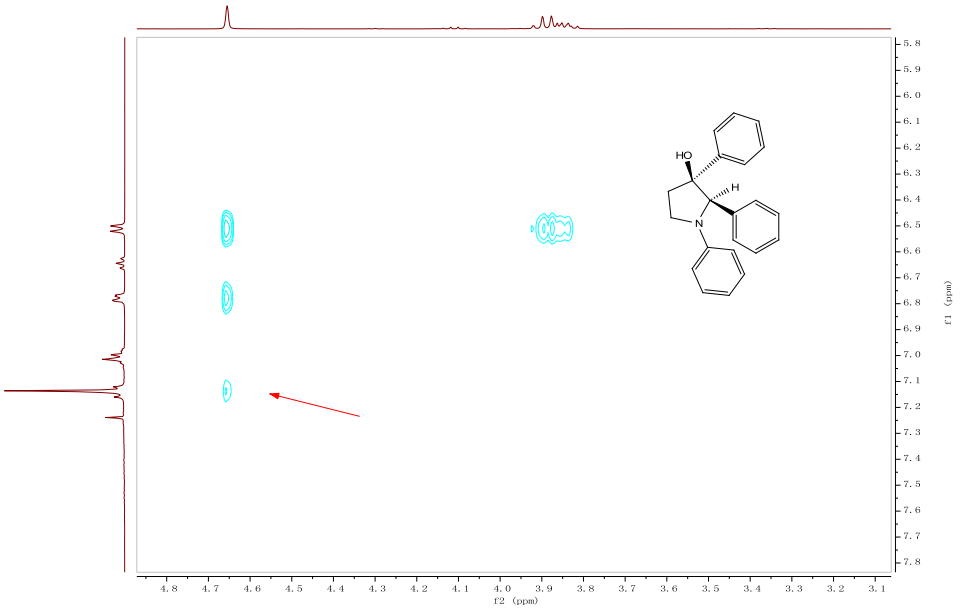
8. NOESY spectra

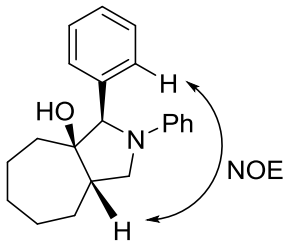
NOESY spectra of product **2a**



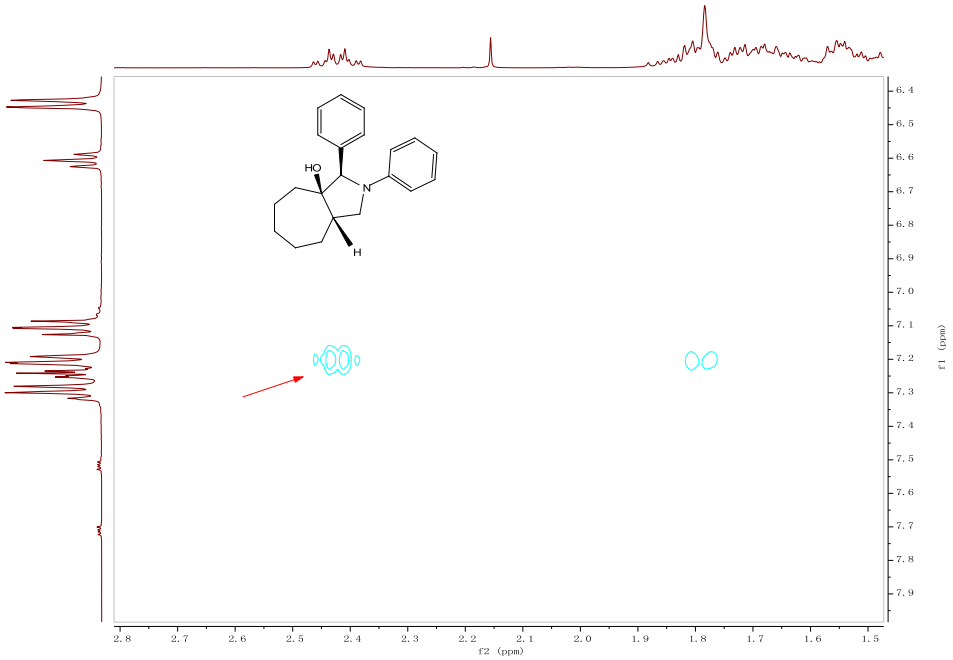
2a: trans

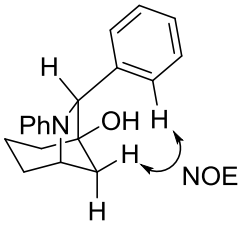




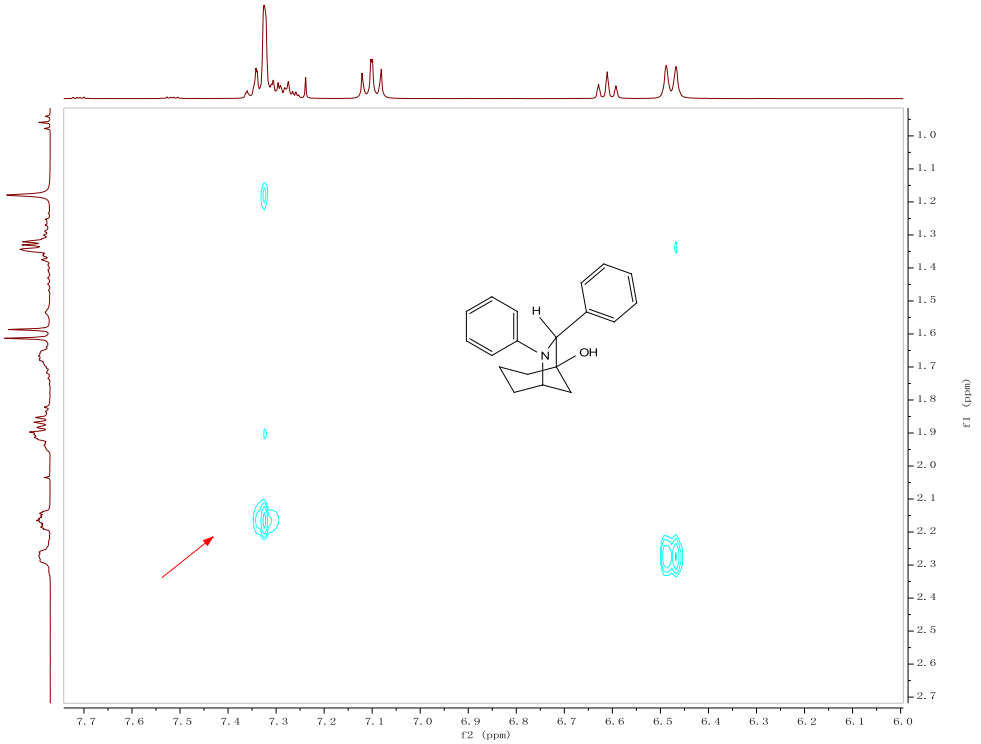


2w





2x


H
N
OH
f2 (ppm)
f1 (ppm)