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Efficient cyclization of tertiary amines and alkenes promoted by KO*t*-Bu/DMF

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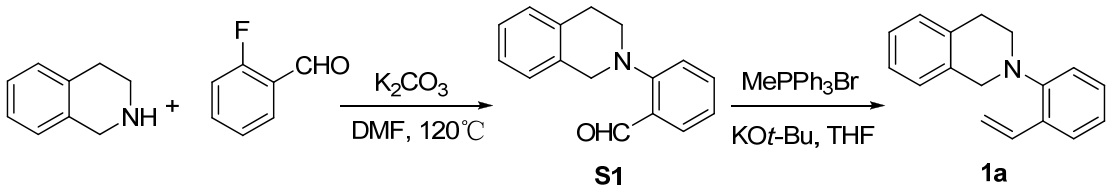
1. General Information

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE 400 spectrometer. Chemical shifts of protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CDCl_3$: δ 7.26). Chemical shifts of carbon are referenced to the carbon resonances of the solvent ($CDCl_3$: δ 77.0). Peaks are labeled as singlet（s）, broad singlet (br), doublet (d), triplet (t), double doublet (dd), multiplet (m). Melting points were measured on a WRS-2A melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Bruker Tensor 37 spectrophotometer. Data are represented as frequency of absorption (cm^{-1}). All products were further characterized by HRMS (high resolution mass spectra). Copies of their ^{1}H NMR and ^{13}C NMR spectra were provided. GC spectra were taken on an Agilent-6890A instrument. The normal and 99.99% purity KO*t*-Bu were purchased from Alfa Aesar chemical company and Sigma-Aldrich chemical company respectively and used without further purification. THF, toluene, DMF, dichloromethane, 1,4-dioxane were dried and redistilled according to standard methods. DMSO, DMA (*N,N*-dimethylacetamide), *t*-BuOH, dichloroethane were dried over 4Å molecular sieves.

2. General Procedures

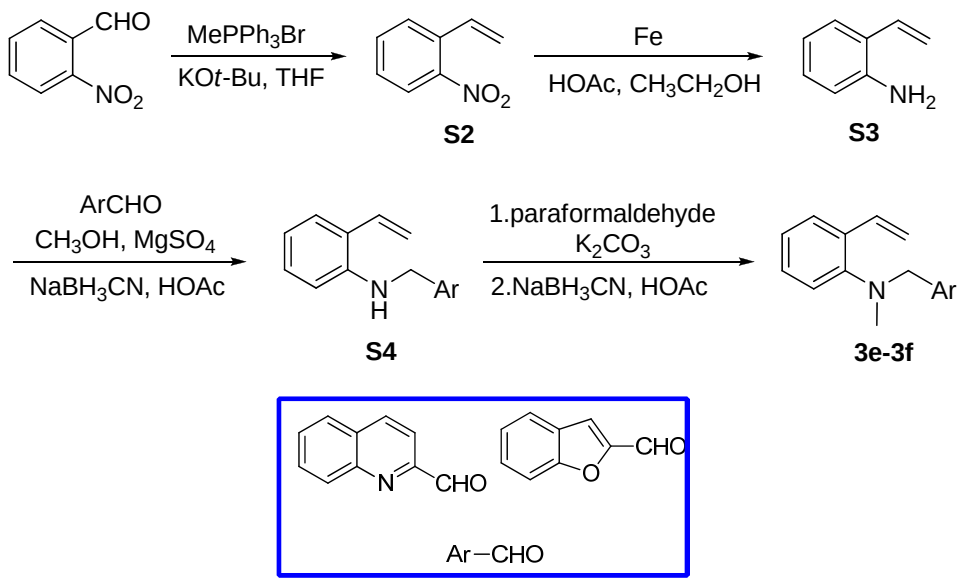
(I) Preparation of substrates (1a–1j, 3a–3d, 3h–3i)



Compound **S1** was synthesized according to a known procedure.[1] To a solution of potassium carbonate (5 mmol) in DMF (20 mL), was added 1,2,3,4-tetrahydroisoquinoline (5.5 mmol) and 2-fluoro benzaldehyde (5 mmol). The reaction mixture was stirred at 120 °C for 24 h. After the complete consumption of 2-fluoro benzaldehyde as shown by TLC, water (50 mL) was added to dilute the reaction mixture. The organic layer was extracted with CH_2Cl_2 (30 mL × 2), The combined organic layer was washed with water (30 mL × 2), dried with anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash chromatography to give **S1**.

Compound **1a** was synthesized according to a known procedure.[2] A mixture of $R_3CH_2PPh_3Br$ (3.6 mmol) and KO*t*-Bu (3.9 mmol) in dry THF (30 mL) was stirred at 0℃ for 1 h. After the addition of **S1** (3 mmol) at 0℃, the reaction mixture was stirred overnight at rt. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography over silica gel to give **1a** as a colorless oil.

(II) Preparation of 3e–3f



S2 was synthesized according to a known procedure. A mixture of CH_3PPh_3Br (18 mmol) and KO*t*-Bu (19.5 mmol) in dry THF (30 mL) was stirred at rt for 1 h. The reaction mixture was cooled to 0℃ and 2-nitrobenzaldehyde (15 mmol) was added. The reaction mixture was stirred overnight at rt. Then the solvent was evaporated under reduced pressure. The residue was purified by column chromatography to give **S2** as a brown oil (yield: 73%).

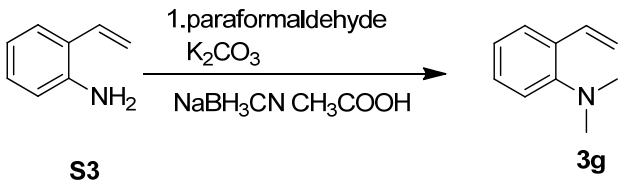
The reduction of **S2** was conducted according to a known procedure.[3] A mixture of **S2** (1.3 g, 8.7 mmol) and iron powder (1.95 g, 35 mmol) in ethanol and glacial acetic acid (15 mL/15 mL) were heated at 55℃ for 2 h. Aqueous sodium carbonate (30 mL) was added. The reaction mixture was extracted with dichloromethane (30 mL × 2). The combined organic layer was dried with anhydrous Na_2SO_4 and evaporated under vacuum. The crude product was purified by column chromatography to give 2-vinylaniline **S3** as a yellow oil (yield: 58%).

A mixture of 2-vinylaniline **S3** (2.5 mmol), the corresponding aldehyde (2.5 mmol) and $MgSO_4$ (3.75 mmol) in MeOH (15 mL) was stirred at rt for 1 h. The sodium cyanoborohydride（3

mmol) and acetic acid (1 mL) was added. The reaction mixture was stirred at rt overnight. The reaction was quenched with saturated aqueous sodium bicarbonate (15 mL). The reaction mixture was extracted with CH_2Cl_2 (30 mL × 3). The combined organic layer was dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The crude product was purified by column chromatography to give **S4** (yield: 65–63%).

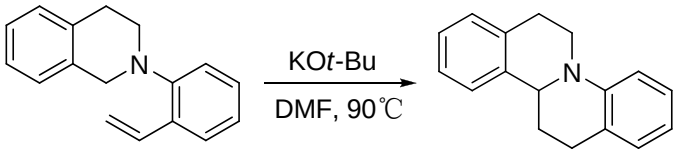
To a solution of **S4** (1 mmol) and paraformaldehyde (2 mmol) in MeCN (20 mL), was added K_2CO_3 (1.5 mmol). The reaction mixture was stirred at rt for 2h. Sodium cyanoborohydride (1.3 equiv) and acetic acid (1 mL) was added. The reaction mixture was stirred at rt overnight. The reaction was quenched with saturated aqueous sodium bicarbonate (15 mL). The reaction mixture was extracted with CH_2Cl_2 (30 mL × 3). The combined organic layer was dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The crude product was purified by column chromatography to give product **3e** or **3f**.

(III) Preparation of 3g



To a solution of 2-Vinylaniline **S3** (2 mmol) and paraformaldehyde (4 mmol) in 15 mL CH_3CN, was added K_2CO_3 (4 mmol). The reaction mixture was stirred at rt for 1 h. Sodium cyanoborohydride（4 mmol) and acetic acid (1 mL) was added. The reaction mixture was stirred at rt overnight. The reaction was quenched with saturated aqueous sodium bicarbonate (15 mL). The reaction mixture was extracted with CH_2Cl_2 (30 mL × 3). The combined organic layer was dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The crude product was purified by column chromatography to give **3g** (yield: 90 %).

(IV) General procedure for the cyclization of substrates 1a-1j and 3a-3i promoted by KO*t*-Bu/DMF



1a **2a**

To a dried 10 mL reaction tube was added **1a** (23.5 mg, 0.1 mmol), KO*t*-Bu (16.8 mg, 0.15 mmol) and DMF (1.2 mL). The mixture was stirred at 90 °C for 4 h under an argon atmosphere. After being cooled down to room temperature, the reaction mixture was diluted with CH_2Cl_2 (10 mL) and washed with water (10 mL × 2). The solvent was evaporated under vacuum. The residue was purified by flash chromatography over silica gel (petroleum ether/ethyl acetate=70:1). **2a** was obtained as a yellow oil (17.8 mg, 76%).

(V) General procedure for the screening of bases and reaction solvents

1a (0.1 mmol), base (0.3 mmol) and DMF (1.2 mL) was added into a dried test tube. Then the reaction mixture was stirred at 90 °C for 4 h under an argon atmosphere. After cooling down, the reactive mixture was analyzed by GC.

Table 1. Screening of bases.

entry	base	yield (%)[a]
1	KO*t*-Bu	67 (64)
2	NaO*t*-Bu	63 (55)
3	LiO*t*-Bu	0
4	NaOMe	10
5	KOH	0
6	NaH	0
7	DBU	0
8	n-BuLi[b]	0
9	KHMDS[c]	56

[a] Yields were determined by GC with *n*-dodecane as the internal standard. [b] **1a** (0.1 mmol), n-BuLi (0.3 mmol), THF (2 mL), -30 °C, 4h. [c] KHMDS (Potassium hexamethyldisilazide).

1a (0.1 mmol), KO*t*-Bu and solvent (1.2 mL) was added into a dried test tube. Then the reaction mixture was stirred at 90 °C for 4 h under an argon atmosphere. After cooling down, the reactive mixture was tested by GC.

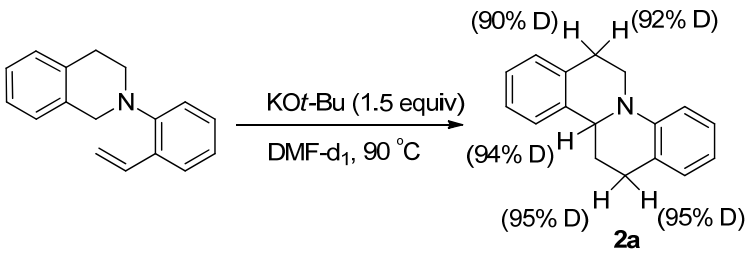
Table 2. Screening of reaction solvents.

entry	solvent	KO*t*-Bu	yield (%)[a]
1	DMF	3.0 equiv	67 (64)
2	DMSO	3.0 equiv	62
3	DMA	3.0 equiv	11
4	*t*-BuOH	3.0 equiv	0
5	Toluene	3.0 equiv	0
6	DMC[b]	3.0 equiv	0
7	1,4-Dioxane	3.0 equiv	0
8	DME[c]	3.0 equiv	0
9	DMF	1.5 equiv	82(76)
11[d]	DMF	0.5 equiv	78(65)

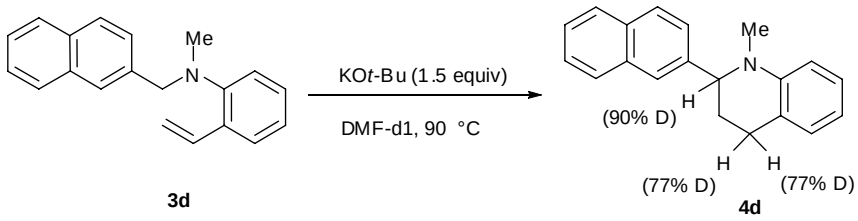
[a] Yields were determined by GC with *n*-dodecane as the internal standard. [b] DMC (1, 2-dichloroethane). [c] DME (dimethoxyethane). [d] **1a** (0.3 mmol), KO*t*-Bu (0.15 mmol), and DMF (1.2 mL) were used.

3. Study of Reaction Mechanism

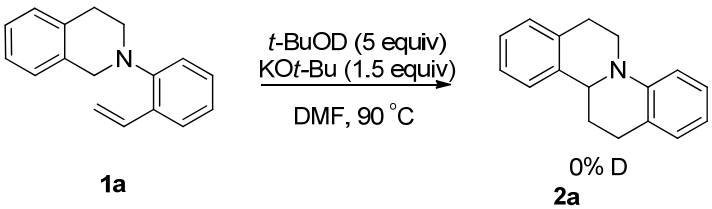
(I) Deuterium-labeling experiments



To a dried 10 mL reaction tube was added **1a** (23.5 mg, 0.1 mmol), KO*t*-Bu (16.8 mg, 0.15 mmol) and DMF-d_1 (1.2 mL). The mixture was stirred at 90 °C for 4 h under an argon atmosphere. After being cooled down to room temperature, the reaction mixture was diluted with CH_2Cl_2 (10 mL) and washed with water (10 mL × 2). The solvent was evaporated under vacuum. The residue was purified by flash chromatography over silica gel (petroleum ether/ethyl acetate=70:1). Deuterated **2a** was obtained as a yellow oil (15.8 mg, 66%).

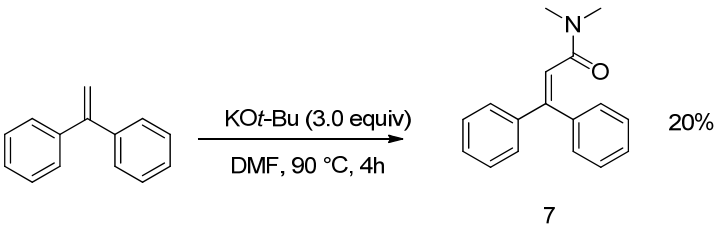


To a dried 10 mL reaction tube was added **3d** (27.3 mg, 0.1 mmol), KO*t*-Bu (16.8 mg, 0.15 mmol) and DMF-d_1 (1.2 mL). The mixture was stirred at 90 °C for 2.5 h under an argon atmosphere. After being cooled down to room temperature, the reaction mixture was diluted with CH_2Cl_2 (10 mL) and washed with water (10 mL × 2). The solvent was evaporated under vacuum. The residue was purified by flash chromatography over silica gel (petroleum ether/ethyl acetate=70:1). Deuterated **4d** was obtained as a yellow oil (17.3 mg, 63%).



To a dried 10 mL reaction tube was added **1a** (23.5 mg, 0.1 mmol), KO*t*-Bu (16.8 mg, 0.15 mmol), *t*-BuOD (0.5 mmol) and DMF (1.2 mL). The mixture was stirred at 90 °C for 4 h under an argon atmosphere. After being cooled down to room temperature, the reaction mixture was diluted with CH_2Cl_2 (10 mL) and washed with water (10 mL × 2). The solvent was evaporated under vacuum. The residue was purified by flash chromatography over silica gel (petroleum ether/ethyl acetate=70:1). **2a** was obtained as a yellow oil (10.1 mg, 43%).

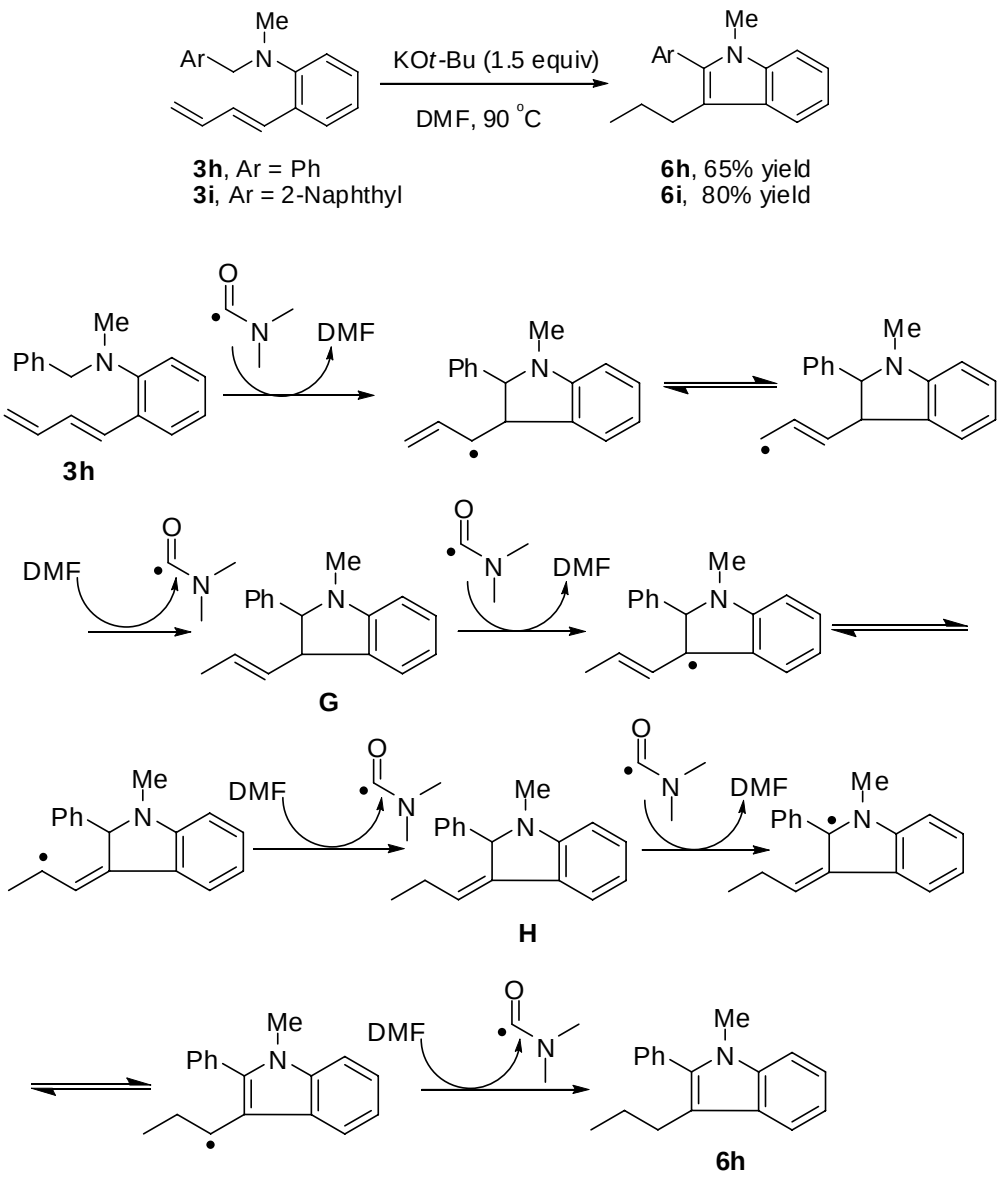
(II) Trapping of the radical intermediate with 1,1-diphenylethylene



To a dried 10 mL reaction tube was added 1,1-Diphenylethylene (0.5 mmol), KO*t*-Bu (1.5 mmol) and DMF (2 mL). The mixture was stirred at 90 °C for 4 h under an argon atmosphere. After being cooled down to room temperature, the reaction mixture was diluted with CH_2Cl_2 (10

mL) and washed with water (10 mL × 2). The solvent was evaporated under vacuum. The residue was purified by flash chromatography to give *N,N*-dimethyl-3,3-diphenylacrylamide **7** as a yellow oil (25 mg, 20%).

4. Tentative mechanism for the generation of products 6h and 6j



Initially the 5-*exo*-*trig* radical cyclization provides an allyl radical intermediate. The rearrangement of double bond and the hydrogen abstraction from DMF give 3-propenyl-indoline **G**. After the abstraction of 3-H of the indoline by a carbamoyl radical, second rearrangement of the allyl radical and the hydrogen abstraction provide 3-propylideneindoline **H**. Then the abstraction of 2-H of the indoline and subsequent rearrangement of the double bond give an

indolylmethyl radical intermediate. The final product **6h** is obtained after the abstraction of a hydrogen atom from DMF.

5. References

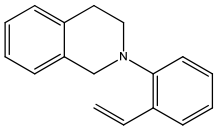
[1] M. Sandip, D. Indubhusan, Z. Chen, S. Daniel, *J. Am. Chem. Soc.* **2009,** *131*, 13226.

[2] A. K. Zulfiqar, I. Michio, W. Thomas, *Tetrahedron* **2010**, *66*, 6639.

[3] G. Christian, G. A. Helmut, *J. Mol. Catal. A: Chem.* **2007,** *273*, 118.

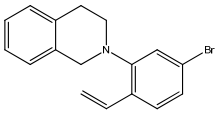
6. Characterization Data

2-(2-Vinylphenyl)-1,2,3,4-tetrahydroisoquinoline (1a)



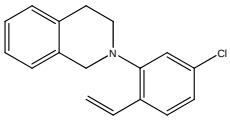
Yield: 75%. Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.53（d, *J* = 7.5 Hz, 1H）, 7.28–7.24 (br, 1H), 7.18–7.16 (br, 3H), 7.13–7.05 (m, 4H), 5.71 (d, *J* = 17.8 Hz, 1H), 5.23 (d, *J* = 11.0 Hz, 1H), 4.16 (s, 2H), 3.28 (t, *J* = 5.8 Hz, 2H), 3.01 (t, *J* = 5.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.6, 135.2, 134.6, 134.4, 132.5, 128.9, 128.5, 126.8, 126.4, 126.3, 125.8, 123.0, 118.9, 113.6, 54.5, 50.7, 29.5. **IR** (KBr) v/cm^{-1}: 3063, 3025, 2920, 2806, 1624, 1595, 1484, 1450, 1381, 1270, 1146, 1096, 1004, 935, 908, 753. **HRMS** (ESI) calculated for $C_{17}H_{18}N$ $(M+H)^+$: 236.1434, found: 236.1440.

2-(5-Bromo-2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline (1b)



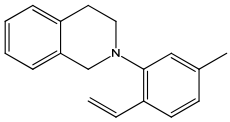
Yield: 67%. Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.2 Hz, 1H), 7.20–7.18 (m, 5H), 7.08–7.07 (m, 1H) , 6.96 (dd, *J* = 17.8, 11.0 Hz, 1H), 5.70 (dd, *J* = 17.7, 1.3 Hz, 2H), 5.25 (dd, *J* = 11.0, 1.3 Hz, 2H), 4.13 (s, 2H), 3.25 (t, *J* = 5.8 Hz, 2H), 3.01 (t, *J* = 5.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 151.7, 134.6, 134.3, 133.6, 131.3, 128.9, 128.2, 126.5, 126.4, 125.9, 125.8, 122.2, 122.0, 114.2, 54.1, 50.6, 29.5. **IR** (KBr) v/cm^{-1}: 3022, 2921, 2811, 1625, 1558, 1482, 1459, 1401, 1380, 1265, 1214, 1089, 1019, 934, 911, 843, 817, 740. **HRMS** (ESI) calculated for $C_{17}H_{17}BrN$ $(M+H)^+$: 314.0539, found: 314.0539.

2-(5-Chloro-2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline (1c)



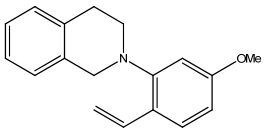
Yield: 57%. Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.2 Hz, 1H), 7.22–7.15 (m, 3H), 7.09–7.02 (m, 3H), 6.97 (dd, *J* = 17.8, 11.0 Hz, 1H), 5.69 (d, *J* = 17.7 Hz, 1H), 5.25 (d, *J* = 11.0 Hz, 1H), 4.14 (s, 2H), 3.26 (t, *J* = 5.8 Hz, 2H), 3.01 (t, *J* = 5.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 151.5, 134.6, 134.3, 133.9, 133.5, 130.8, 128.9, 127.9, 126.4, 126.4, 125.9, 122.9, 119.2, 114.0, 54.1, 50.6, 29.4. **IR** (KBr) ν/cm^{-1}: 2923, 2811, 1624, 1588, 1484, 1459, 1414, 1381, 1265, 1216, 1112, 1093, 1020, 954, 912, 848, 820, 740. **HRMS** (ESI) calculated for $C_{17}H_{17}ClN$ $(M+H)^+$: 270.1044, found: 270.1035.

2-(5-Methyl-2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline (1d)



Yield: 70%. Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42(d, *J* = 7.7 Hz, 1H), 7.18–7.15 (br, 3H), 7.09–7.08 (br, 1H), 7.03 (dd, *J* = 17.8, 11.0 Hz, 1H), 6.91 (s, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 5.67 (d, *J* = 17.7 Hz, 1H), 5.17 (d, *J* = 11.0 Hz, 1H), 4.14 (s, 2H), 3.26 (t, *J* = 5.8 Hz, 2H), 3.01 (t, *J* = 5.7 Hz, 2H), 2.35 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.5, 138.4, 135.3, 134.6, 134.2, 129.6, 128.9, 126.6, 126.4, 126.2, 125.7, 123.8, 119.5, 112.7, 54.5, 50.8, 29.7, 21.5. **IR** (KBr) ν/cm^{-1}: 2920, 1605, 1497, 1415, 1380, 1266, 1236, 1025, 935, 905, 818, 740. **HRMS** (ESI) calculated for $C_{18}H_{20}N$ $(M+H)^+$: 250.1590, found: 250.1597.

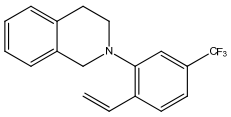
2-(5-Methoxy-2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline (1e)



Yield: 63%. Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.5 Hz, 1H), 7.17 (m, 3H), 7.09–7.07 (br, 1H), 6.99 (dd, *J* = 17.7, 11.1 Hz, 1H), 6.66–6.61 (m, 2H), 5.60 (d, *J* = 17.7 Hz, 1H), 5.13 (d, *J* = 11.0 Hz, 1H), 4.15 (s, 2H), 3.81 (s, 3H), 3.28 (t, *J* = 5.7 Hz, 2H), 3.01 (t, *J* = 5.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.1, 151.9, 135.0, 134.5, 133.9, 128.9, 127.7, 126.4, 126.3,

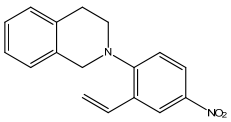
125.8, 125.3, 111.6, 107.5, 105.5, 55.3, 54.3, 50.6, 29.5. **IR** (KBr) ν/cm^{-1}: 2929, 2834, 1602, 1569, 1496, 1462, 1443, 1380, 1248, 1196, 1166, 1104, 975, 901, 851, 741. **HRMS** (ESI) calculated for $C_{18}H_{20}NO$ $(M+H)^+$: 266.1539, found: 266.1532.

2-(5-(Trifluoromethyl)-2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline (1f)



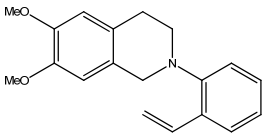
Yield: 64%. Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.59 (d, J = 7.9 Hz, 1H), 7.31–7.29 (m, 2H), 7.19 (m, 3H), 7.1–7.08 (m, 1H), 7.04 (dd, J = 17.8, 11.0 Hz, 1H), 5.79 (d, J = 17.8 Hz, 1H), 5.34 (d, J = 11.0 Hz, 1H), 4.17 (s, 2H), 3.30 (t, J = 5.8 Hz, 2H), 3.04 (t, J = 5.7 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.8, 135.8, 134.5, 134.2, 133.6, 130.3 (q, $^2J_{CF3}$ = 31 Hz), 129.0, 127.3, 126.5, 126.4, 125.9, 119.5 (q, $^3J_{CF3}$ = 4 Hz), 115.8, 115.5 (q, $^3J_{CF3}$ = 4 Hz), 54.1, 50.6, 29.6. **IR** (KBr) ν/cm^{-1}: 2925, 1573, 1500, 1427, 1382, 1336, 1312, 1166, 1123, 1081, 959, 833, 737. **HRMS** (ESI) calculated for $C_{18}H_{17}F_3N$ $(M+H)^+$: 304.1308, found: 304.1308.

2-(5-Nitro-2-vinylphenyl)-1, 2, 3, 4-tetrahydroisoquinoline (1g)



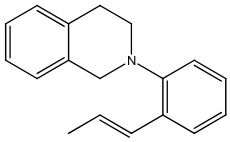
Yield: 92%. Yellow solid. M. p. 64.0–65.2 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.34 (d, J = 2.6 Hz, 1H), 8.11 (dd, J = 8.9, 2.6 Hz, 1H), 7.23–7.17 (m, 3H), 7.16–7.10 (m, 1H), 7.08 (d, J = 8.9 Hz, 1H), 6.89 (dd, J = 17.6, 10.9 Hz, 1H), 5.86 (d, J = 17.6 Hz, 1H), 5.42 (d, J = 10.9 Hz, 1H), 4.34 (s, 2H), 3.46 (t, J = 5.8 Hz, 2H), 3.02 (t, J = 5.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.7, 142.1, 134.0, 133.7, 133.6, 131.5, 129.0, 126.8, 126.4, 126.2, 124.0, 123.3, 117.8, 115.9, 53.2, 50.2, 29.0. **IR** (KBr) ν/cm^{-1}: 2923, 1601, 1579, 1549, 1511, 1462, 1382, 1335, 1274, 1222, 1084, 934, 825, 798, 745. **HRMS** (ESI) calculated for $C_{17}H_{17}N_2O_2$ $(M+H)^+$: 281.1285, found: 281.1289.

6,7-Dimethoxy-2-(2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline (1h)



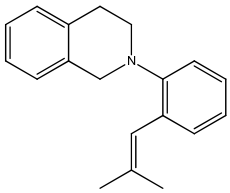
Yield: 62%. Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 7.6 Hz, 1H), 7.28–7.24 (m, 1H), 7.13–7.04 (m, 3H), 6.67 (s, 1H), 6.58 (s, 1H), 5.72 (d, *J* = 17.8 Hz, 1H), 5.24 (d, *J* = 11.0 Hz, 1H), 4.09 (s, 2H), 3.88 (s, 3H), 3.86 (s, 3H), 3.26 (t, *J* = 5.4 Hz, 2H), 2.91 (t, *J* = 5.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.6, 147.7, 147.4, 134.4, 132.4, 128.5, 127.0, 126.7, 126.5, 123.0, 118.9, 113.5, 111.7, 109.3, 56.0, 55.9, 54.0, 50.7, 29.0. **IR** (KBr) *ν*/cm^{-1}: 2933, 2833, 1595, 1517, 1484, 1450, 1376, 1257, 1228, 1116, 1023, 909, 855, 738. **HRMS** (ESI) calculated for $C_{19}H_{22}NO_2$ $(M+H)^+$: 296.1645, found: 296.1655.

2-(2-(Prop-1-en-1-yl) phenyl)-1,2,3,4-tetrahydroisoquinoline (1i)



Yield: 63%. Yellow oil. **Z:E**=3.3:1, **Z**-isomer **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.32 (d, *J* = 7.5 Hz, 1H), 7.25–7.13 (m, 4H), 7.09–7.03 (m, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.56 (d, *J* = 11.6 Hz, 1H), 5.78 (dq, *J* = 11.7, 7.0 Hz, 1H), 4.19 (s, 2H), 3.28 (t, *J* = 5.7 Hz, 2H), 2.97 (t, *J* = 5.7 Hz, 2H), 1.91–1.88 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 151.1, 135.3, 134.7, 131.4, 130.5, 129.0, 128.4, 127.6, 126.4, 126.2, 125.7, 125.2, 121.8, 118.2, 53.7, 50.4, 29.6, 14.8. **E**-isomer **^{1}H NMR** (400 MHz, $CDCl_3$): 7.45 (d, *J* = 7.6 Hz,0.3H), 7.25–7.13 (m, 1.5H), 7.09–7.03 (m, 0.6H), 6.75 (d, *J* = 16.2 Hz, 0.3H), 6.20 (dq, *J* = 15.6，6.6 Hz，0.3H), 4.16 (s, 2H), 3.28 (m, 0.6H), 3.01 (d, *J* = 5.8 Hz, 0.6H), 1.91–1.88 (m, 0.9). **IR** (KBr) *ν*/cm^{-1}: 3021, 2920, 1594, 1485, 1448, 1382, 1265, 1147, 936, 739, 703. **HRMS** (ESI) calculated for $C_{18}H_{20}N$ $(M+H)^+$: 250.1590, found: 250.1603.

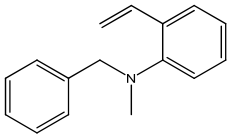
2-(2-(2-Methylprop-1-en-1-yl) phenyl)-1,2,3,4-tetrahydroisoquinoline (1j)



Yield: 90%. Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.25–7.16 (m, 5H), 7.09–7.04 (m, 2H), 7.02–6.98 (m, 1H), 6.32 (s, 1H), 4.20 (s, 2H), 3.24 (t, *J* = 5.7, 2H), 2.96 (t, *J* = 5.5, 2H), 1.91 (s, 3H), 1.87 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.9, 135.4, 134.8, 133.6, 132.4, 130.8, 128.9, 126.9, 126.5, 126.1, 125.7, 123.8, 121.7, 117.7, 53.2, 50.5, 29.6, 26.4, 19.6. **IR** (KBr) *ν*/cm^{-1}: 3024,

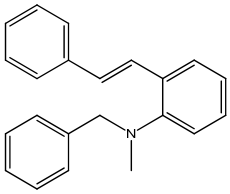
2924, 1595, 1485, 1447, 1383, 1270, 1220, 1099, 985, 911, 740, 657. **HRMS** (ESI) calculated for $C_{19}H_{22}N$ $(M+H)^+$: 264.1747, found: 264.1750.

***N*-Benzyl-*N*-methyl-2-vinylaniline (3a)**



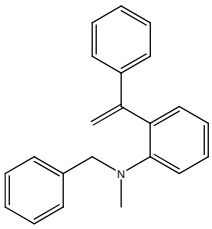
Yield: 43%. Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.0, 1H), 7.33–7.30 (m, 4H), 7.27 (m, 1H), 7.26–7.20 (m, 2H), 7.05–7.02 (m, 2H), 5.69 (d, *J* = 17.7 Hz, 1H), 5.25 (d, *J* = 11.0 Hz, 1H), 4.11 (s, 2H), 2.62 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 151.2, 138.7, 134.6, 132.4, 128.4, 128.4, 128.3, 127.0, 126.8, 122.8, 119.6, 113.5, 61.0, 41.0. **IR** (KBr) ν/cm^{-1}: 3063, 3028, 2797, 1625, 1595, 1484, 1451, 1412, 1362, 1266, 1222, 1083, 1002, 945, 908, 758, 697. **HRMS** (ESI) calculated for $C_{16}H_{18}N$ $(M+H)^+$: 224.1434, found: 224.1437.

***N*-Benzyl-*N*-methyl-2-styrylaniline (3b)**



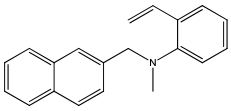
Yield: 52%. Yellow oil. **Z/E** isomer，**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.64–7.60 (m, 1H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.36–7.27 (m, 10H), 7.24–7.13 (m, 6H), 7.08–7.02 (m, 3H), 6.84–6.81 (m, 2H), 6.56 (d, *J* = 12.2 Hz, 1H), 4.24 (s, 2H), 4.16 (s, 1H), 2.70 (s, 1.5H), 2.69 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 151.9, 151.5, 138.9, 138.7, 138.0, 137.2, 131.7, 131.1, 130.5, 129.3, 128.7, 128.6, 128.4, 128.3, 128.3, 128.2, 128.1, 128.1, 127.2, 127.0, 126.9, 126.7, 126.5, 126.5, 122.7, 121.6, 119.5, 118.8, 61.3, 60.8, 40.8, 40.4. **IR** (KBr) ν/cm^{-1}: 3061, 3026, 2847, 2796, 1594, 1494, 1483, 1450, 1360, 1227, 1172, 1120, 1073, 1028, 944, 756, 696. **HRMS** (ESI) calculated for $C_{22}H_{22}N$ $(M+H)^+$: 300.1747, found: 300.1748.

***N*-Benzyl-*N*-methyl-2-(1-phenylvinyl) aniline (3c)**



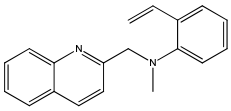
Yield: 39%. White solid. M. p. 48.6–49.8 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.33–7.27 (m, 6H), 7.13–7.04 (m, 6H), 6.66 (d, *J* = 6.5 Hz, 2H), 5.64 (br, 1H), 5.38 (br, 1H), 3.98 (s, 2H), 2.41 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 151.6, 150.8, 141.5, 138.8, 135.9, 132.4, 128.8, 128.3, 128.1, 128.0, 127.4, 126.7, 126.5, 122.1, 119.6, 115.2, 59.3, 40.5. **IR** (KBr) ν/cm^{-1}: 2921, 1594, 1494, 1445, 1323, 1266, 1130, 946, 740, 699, 599. **HRMS** (ESI) calculated for $C_{22}H_{22}N$ $(M+H)^+$: 300.1747, found: 300.1749.

***N*-Methyl-*N*-(naphthalen-2-ylmethyl)-2-vinylaniline (3d)**



Yield: 80%. Yellow solid. M. p. 37.4–38.5℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 7.7 Hz, 1H), 7.86 (d, *J* = 7.4 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7. 58 (d, *J* = 6.7 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.49–7.43 (m, 3H), 7.28–7.21 (m, 2H), 7.10-7.07 (m, 2H), 5.64 (d, *J* = 17.7 Hz, 1H), 5.12 (d, *J* = 11.0 Hz, 1H), 4.57 (s, 2H), 2.61 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 151.7, 134.6, 134.4, 134.0, 132.8, 132.2, 128.6, 128.5, 127.9, 126.8, 126.7, 125.8, 125.6, 125.2, 124.2, 123.0, 119.8, 113.6, 58.4, 42.3. **IR** (KBr) ν/cm^{-1}: 3061, 2950, 2844, 2795, 1653, 1595, 1558, 1508, 1485, 1450, 1397, 1264, 1164, 1058, 1003, 938, 908, 855, 793, 759. **HRMS** (ESI) calculated for $C_{20}H_{20}N$ $(M+H)^+$: 274.1590, found: 274.1600.

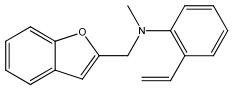
***N*-Methyl-*N*-(quinolin-2-ylmethyl)-2-vinylaniline (3e)**



Yield: 95%. Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.7 Hz, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.73–7.69 (m, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.54–7.50 (m, 2H), 7.27 (dd, *J* = 17.8, 11.0 Hz, 1H), 7.24–7.21 (m, 1H), 7.14 (d, *J* = 7.3 Hz, 1H), 7.05 (t, *J* = 7.3 Hz, 1H), 5.72 (dd, *J* = 17.7, 1.3 Hz, 1H), 5.28 (dd, *J* = 11.0, 1.3 Hz, 1H), 4.48 (s, 2H), 2.72 (s, 3H).

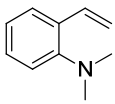
^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 150.9, 147.6, 136.6, 134.5, 132.4, 129.5, 128.9, 128.5, 127.6, 127.4, 126.9, 126.2, 123.0, 120.3, 119.7, 113.9, 63.0, 42.4. **IR** (KBr) ν/cm^{-1}: 3061, 2848, 2800, 1623, 1596, 1505, 1485, 1451, 1426, 1358, 1301, 1224, 1090, 1058, 1000, 937, 910, 829, 758, 740. **HRMS** (ESI) calculated for $C_{19}H_{19}N_2$ $(M+H)^+$: 275.1543, found: 275.1555.

***N*-(Benzofuran-2-ylmethyl)-*N*-methyl-2-vinylaniline (3f)**



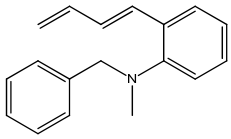
Yield: 85%. Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ ppm 7.53–7.50 (m, 2H), 7.45 (d, J = 8.2 Hz, 1H), 7.30–7.26 (m, 1H), 7.25–7.18 (m, 3H), 7.07–7.03 (m, 2H), 6.54 (s, 1H), 5.72 (d, J = 17.7 Hz, 1H), 5.30 (d, J = 11.0 Hz, 1H), 4.23 (s, 2H), 2.80 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.7, 154.9, 150.2, 134.6, 132.4, 128.4, 128.3, 126.9, 123.7, 123.0, 122.6, 120.7, 119.5, 113.9, 111.2, 104.7, 54.4, 40.8. **IR** (KBr) ν/cm^{-1}: 1596, 1484, 1453, 1254, 1123, 1068, 1000, 952, 863, 830, 750. **HRMS** (ESI) calculated for $C_{18}H_{18}NO$ $(M+H)^+$: 264.1383, found: 264.1394.

***N*, *N*-Dimethyl-2-vinylaniline (3g)**



Yield: 77%. Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.47 (d, J = 7.6 Hz, 1H), 7.25–7.19 (m, 1H), 7.10–6.98 (m, 3H), 5.67 (dd, J = 17.7, 1.8 Hz, 1H), 5.24 (d, J = 11.0 Hz, 1H), 2.72 (t, J = 4.5 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 151.8, 134.9, 131.9, 128.3, 126.8, 122.3, 118.0, 113.1, 44.6.

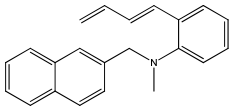
***N*-Benzyl-2-(buta-1,3-dien-1-yl)-*N*-methylaniline (3h)**



Yield: 78%. Coroless oil. **Z/E** isomer **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.52 (d, J = 7.9 Hz, 0.2H), 7.35–7.24 (m, 6.4H), 7.24–7.17(m, 1.6H), 7.10–6.98 (m, 2.8H), 6.91–6.78 (m, 1.4H), 6.73 (d, J = 11.2 Hz, 1H), 6.58–6.49 (m, 0.4H), 6.38 (t, J = 11.0 Hz, 1H), 5.33 (d, J = 16.5 Hz, 1H), 5.28 (m, 0.2H), 5.17 (d, J = 10.1 Hz, 1H), 5.12 (d, J = 9.9 Hz, 0.2H), 4.11 (s, 2.4H), 2.62 (s, 3.6H). **^{13}C**

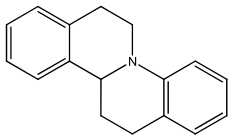
NMR (100 MHz, $CDCl_3$): δ 151.9, 151.4, 138.8, 138.6, 138.0, 133.9, 131.6, 131.3, 131.1, 130.5, 129.8, 129.5, 129.4, 128.5, 128.4, 128.3, 128.2, 128.1, 127.1, 127.1, 126.7, 122.8, 121.7, 119.8, 119.0, 118.6, 116.8, 61.2, 60.7, 41.1, 40.4. **IR** (KBr) ν/cm^{-1}: 3026, 2796, 1593, 1484, 1450, 1362, 1311, 1221, 1107, 1006, 904, 758, 733, 698, 610. **HRMS** (ESI) calculated for $C_{18}H_20N$ $(M+H)^+$: 250.1590, found: 250.1598.

2-(Buta-1, 3-dien-1-yl)-*N*-methyl-*N*-(naphthalen-2-ylmethyl) aniline (3i)



Yield: 68%. Coroless oil, a mixture of *Z*- and *E*-isomer. **^{1}H NMR** (400 MHz, $CDCl_3$)：δ 8.08 (d, *J* = 7.7 Hz, 0.2H), 8.03 (d, *J* = 7.9 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1.2H), 7.67 (d, *J* = 11.7, 7.6 Hz, 0.2H), 7.56 (d, *J* = 6.9 Hz, 1H), 7.53 (m, 0.2H), 7.48 – 7.40 (m, 3.8H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.29 – 7.24 (m, 1.2H), 7.21 (m, 0.2H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 0.2H), 7.03 (t, *J* = 7.3 Hz, 1H), 6.95 (m, 0.2H), 6.91 – 6.82 (m, 1H), 6.71 (dd, *J* = 15.9, 10.5 Hz, 0.2H), 6.63 (d, *J* = 11.3 Hz, 1H), 6.35 (dt, *J* = 16.9, 10.3 Hz, 0.2H), 6.15 (t, *J* = 11.3 Hz, 1H), 5.28 (d, *J* = 16.9 Hz, 1H), 5.22 (d, *J* = 17.2Hz, 1H), 5.14 (d, *J* = 10.2 Hz, 1H), 5.03 (d, *J* = 10.1 Hz, 0.2H), 4.58 (s, 2H), 4.55 (s, 0.4H), 2.61 (s, 3H), 2.60 (s, 0.6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.37, 151.96, 137.99, 134.38, 133.97, 133.87, 132.23, 131.40, 130.47, 129.69, 129.55, 129.44, 128.65, 128.42, 128.27, 128.06, 127.94, 126.86, 126.65, 125.84, 125.71, 125.67, 125.33, 125.28, 124.40, 124.17, 123.20, 121.84, 120.17, 119.13, 118.66, 116.74, 58.46, 58.01, 42.59, 41.75. **IR** (KBr) ν/cm^{-1}: 3059, 2924, 2848, 2796, 1635, 1559, 1508, 1484, 1449, 1365, 1311, 1264, 1090, 1048, 1006, 939, 905, 792, 760. **HRMS** (ESI) calculated for $C_{22}H_{22}N$ $(M+H)^+$: 300.1747, found：300.1748.

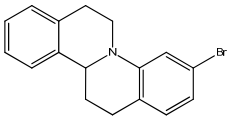
7,11b,12,13-Tetrahydro-6H-isoquinolino [2, 1-a] quinolone (2a)



Yield: 76%. Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$)：δ 7.27–7.08 (m, 5H), 6.99 (d, *J* = 7.3 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.67 (t, *J* = 7.3 Hz, 1H), 4.46 (dd, *J* = 9.2, 2.6 Hz, 1H), 3.95 (dt, *J* = 12.5, 4.5 Hz, 1H), 3.29–3.23 (m, 1H), 3.11–3.03 (m, 1H), 2.96–2.90 (m, 1H), 2.82–2.77 (br, 2H),

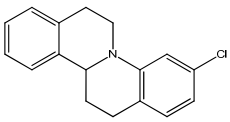
2.48–2.41 (m, 1H), 2.16–2.06 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): 146.1, 138.8, 135.5, 129.1, 128.6, 127.0, 126.2, 125.4, 124.4, 117.3, 112.9, 56.5, 44.8, 28.8, 28.7, 27.0. **IR** (KBr) ν/cm^{-1}: 2924, 1642, 1602, 1492, 1453, 1383, 1215, 1112, 987, 888, 744. **HRMS** (ESI) calculated for $C_{17}H_{18}N$ $(M+H)^+$: 236.1434, found: 236.1438.

3-Bromo-7,11b,12,13-tetrahydro-6H-isoquinolino[2, 1-a]quinolone (2b)



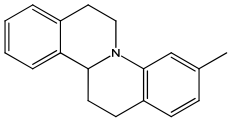
Yield: 68%. Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.25–7.13 (m, 4H), 6.93 (s, 1H), 6.83 (d, J = 7.9 Hz, 1H), 6.75 (d, J = 7.9 Hz, 1H), 4.48 (dd, J = 9.1, 3.1 Hz, 1H), 3.88 (dt, J = 12.5, 4.6 Hz, 1H), 3.31–3.24 (m, 1H), 3.11–3.03 (m, 1H), 2.89–2.71 (m, 3H), 2.50–2.43 (m, 1H), 2.11–2.02 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$)**:** δ 147.2, 138.4, 135.4, 130.1, 128.5, 126.4, 126.3, 125.1, 122.9, 120.5, 119.5, 114.9, 56.1, 44.7, 28.6, 28.5, 26.4. **IR** (KBr) ν/cm^{-1}: 2924, 1593, 1487, 1420, 1265, 1118, 982, 882, 748. **HRMS** (ESI) calculated for $C_{17}H_{17}NBr$ $(M+H)^+$: 314.0539, found: 314.0554.

3-Chloro-7,11b,12,13-tetrahydro-6H-isoquinolino [2, 1-a] quinolone (2c)



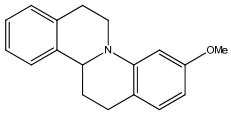
Yield: 75%. Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.26–7.12 (m, 4H), 6.87 (d, J = 7.9 Hz, 1H), 6.76 (s, 1H), 6.59 (d, J = 7.9 Hz, 1H), 4.47 (dd, J = 9.2, 3.4 Hz, 1H), 3.87 (dt, J = 12.5, 4.6 Hz, 1H), 3.30–3.23 (m, 1H), 3.11–3.03 (m, 1H), 2.90–2.85 (m, 1H), 2.83–2.72 (m, 2H), 2.50–2.43 (m, 1H), 2.11–2.01 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.9, 138.4, 135.4, 132.3, 129.7, 128.6, 126.4, 126.3, 125.1, 122.4, 116.6, 112.0, 56.1, 44.6, 28.6, 28.4, 26.4. **IR** (KBr) ν/cm^{-1}: 2924, 1598, 1565, 1489, 1423, 1379, 1203, 1119, 1097, 880, 831, 792, 746, 590. **HRMS** (ESI) calculated for $C_{17}H_{17}ClN$ $(M+H)^+$: 270.1044, found : 270.1035.

3-Methyl-7, 11b, 12, 13-tetrahydro-6H-isoquinolino [2, 1-a] quinolone (2d)



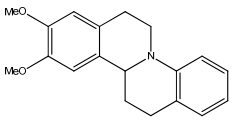
Yield: 57%. Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.18–7.03 (m, 4H), 6.80 (d, *J* = 7.5 Hz, 1H), 6.60 (s, 1H), 6.42 (d, *J* = 7.5 Hz, 1H), 4.35 (dd, *J* = 9.4, 2.9 Hz, 1H), 3.87 (dt, *J* = 12.4, 4.6 Hz, 1H), 3.19–3.13 (m, 1H), 3.02–2.94 (m, 1H), 2.86–2.78 (m, 1H), 2.75–2.66 (m, 2H), 2.38–2.31 (m, 1H), 2.21 (s, 3H), 2.05–1.95 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.0, 138.8, 136.5, 135.5, 129.0, 128.6, 126.2, 125.5, 121.4, 118.2, 113.7, 56.6, 44.8, 29.0, 28.8, 26.7, 21.7. **IR** (KBr) ν/cm^{-1}: 3021, 2922, 2841, 1611, 1575, 1507, 1429, 1376, 1318, 1265, 1237, 1162, 1123, 1038, 882, 796, 737. **HRMS** (ESI) calculated for $C_{18}H_{20}N$ $(M+H)^+$: 250.1590, found: 250.1594.

3-Methoxy-7,11b,12,13-tetrahydro-6H-isoquinolino [2,1-a]quinolone (2e)



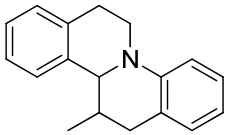
Yield: 52%. Orange oil, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30–7.10 (m, 4H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.40 (d, *J* = 2.0 Hz, 1H), 6.24 (dd, *J* = 8.2, 2.3 Hz, 1H), 4.45 (dd, *J* = 9.2, 3.0 Hz, 1H), 3.91 (dt, *J* = 12.5, 4.6 Hz, 1H), 3.78 (s, 3H), 3.36–3.19 (m, 1H), 3.07 (ddd, *J* = 15.2, 10.1, 4.9 Hz, 1H), 2.81 (m, 3H), 2.50–2.36 (m, 1H), 2.08 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.2, 146.9, 138.7, 135.5, 129.4, 128.6, 126.2, 125.3, 117.0, 101.8, 99.4, 56.4, 55.3, 44.8, 29.0, 28.6, 26.2. **IR** (KBr) ν/cm^{-1}: 2926, 1613, 1579, 1503, 1452, 1381, 1265, 1114, 1017, 898, 748. **HRMS** (ESI) calculated for $C_{18}H_{20}NO$ $(M+H)^+$: 266.1539, found : 266.1548.

9, 10-Dimethoxy-7,11b,12,13-tetrahydro-6H-isoquinolino [2, 1-a] quinolone (2h)



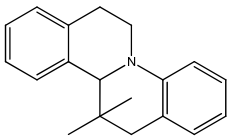
Yield: 72%. Orange oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.10 (t, *J* = 7.7 Hz, 1H), 7.00 (d, *J* = 7.3 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 6.75 (s, 1H), 6.68 (t, *J* = 7.4 Hz, 1H), 6.61 (s, 1H), 4.39 (d, *J* = 8.6 Hz, 1H), 4.01–3.95 (m, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.29–3.15 (m, 1H), 3.06 –2.87 (m, 2H), 2.86–2.74 (m, 1H), 2.71 (d, *J* = 15.8 Hz, 1H), 2.40 (m, 1H), 2.16–2.01 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.6, 146.4, 130.5, 129.1, 127.6, 127.0, 124.4, 117.4, 113.1, 111.4, 108.8, 56.4, 56.1, 55.9, 44.9, 29.0, 28.2, 26.9. **IR** (KBr) ν/cm^{-1}: 2918, 2850, 1603, 1513, 1494, 1454, 1379, 1254, 1208, 1105, 1022, 860, 825, 740.

12-Methyl-7,11b,12,13-tetrahydro-6H-isoquinolino [2, 1-a] quinolone (2i)



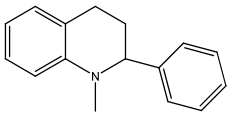
Yield: 85%. Yellow oil, a mixture of *cis*- and *trans*-isomers (*cis*/*trans*=3:2). C*is*-isomer, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.29–7.06 (m, 5H), 7.04 (d, *J* = 7.3 Hz, 1H), 6.80 (d, *J* = 8.3 Hz, 1H), 6.67 (t, *J* = 7.3 Hz, 1H), 4.49 (br, 1H), 4.05 (m, 1H), 3.37 (dd, *J* = 16.3, 6.3 Hz, 1H), 3.00 (m, 2H), 2.86–2.70 (m, 1H), 2.64 (d, *J* = 16.4 Hz, 1H), 2.59–2.51 (m, 1H), 0.69 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.9, 137.4, 135.8, 130.4, 128.3, 126.7, 126.2, 126.0, 125.8, 121.5, 116.8, 110.9, 60.1, 41.9, 35.9, 33.3, 30.3, 13.2. **IR** (KBr) ν/cm^{-1}: 2923, 1642, 1574, 1492, 1453, 1382, 1262, 1220, 1108, 899, 749. **HRMS** (ESI) calculated for $C_{18}H_{20}N$ $(M+H)^+$: 250.1590, found: 250.1601. *Trans*-isomer, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.29 (d, *J* = 7.6 Hz, 1H), 7.22–7.04 (m, 4H), 6.93 (t, *J* = 7.0 Hz, 2H), 6.66 (t, *J* = 7.3 Hz, 1H), 4.27 (d, *J* = 3.5 Hz, 1H), 4.17 (ddd, *J* = 13.4, 5.4, 2.6 Hz, 1H), 3.39 (ddd, *J* = 13.3, 11.7, 4.0 Hz, 1H), 3.22–3.09 (m, 1H), 2.84 (dd, *J* = 15.7, 5.0 Hz, 1H), 2.73 (m, 1H), 2.65 (m, 1H), 2.38 (dd, *J* = 15.7, 3.9 Hz, 1H), 1.20 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): 144.6, 139.0, 136.4, 129.7, 129.0, 127.0, 126.4, 126.3, 124.8, 123.4, 117.4, 113.1, 62.0, 46.4, 31.7, 29.0, 26.7, 19.3. **IR** (KBr) ν/cm^{-1}: 2925, 1601, 1493, 1455, 1381, 1266, 1114, 1019, 921, 745. **HRMS** (ESI) calculated for $C_{18}H_{20}N$ $(M+H)^+$: 250.1590, found m/z 250.1583.

12,12-Dimethyl-7,11b,12,13-tetrahydro-6H-isoquinolino [2, 1-a] quinolone (2j)

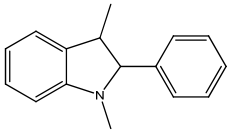


Yield: 84%. White solid, M.p. 104.8–105.7 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ ppm 7.22–7.15 (m, 4H), 7.11 (t, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.69–6.64 (m, 2H), 4.24 (s, 1H), 3.91–3.87 (m, 1H), 3.15–3.09 (m, 1H), 3.07–2.99 (m, 1H), 2.94 (d, *J* = 16.7 Hz, 1H), 2.74–2.70 (m, 1H), 2.59–2.55 (d, *J* = 16.7 Hz, 1H), 1.04 (s, 3H), 0.71 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.4, 137.3, 134.4, 129.6, 129.5, 128.2, 126.6, 126.4, 124.9, 121.9, 116.4, 111.4, 65.3, 44.5, 43.0, 34.4, 31.4, 29.0, 21.4. **IR** (KBr) ν/cm^{-1}: 2929, 2832, 1601, 1576, 1492, 1456, 1382, 1358, 1265, 1101, 895, 743. **HRMS** (ESI) calculated for $C_{19}H_{22}N$ $(M+H)^+$: 264.1747, found : 264.1755.

1-Methyl-2-phenyl-1,2,3,4-tetrahydroquinoline (4a)

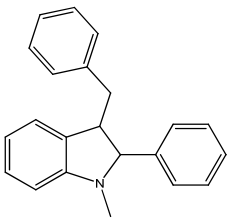


1,3-Dimethyl-2-phenylindoline (5a)



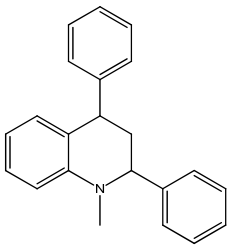
Yield: 84%. White solid, a mixture of compound **4a** and **5a** (**4a**/**5a**=5:12, *cis*-**5a**/*trans*-**5a**=1:5). The configurations of *cis*-**5a**/*trans*-**5a** were assigned by the comparison of the coupling constant $J_{2,3}$ with the reported data of *cis*- and *trans*-isomers of 3-methyl-2-phenylindoline (*J. Org. Chem.* **1997**, *62*, 8600-8603). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.47–7.44 (m, 1.7H), 7.40 – 7.28 (m, 4.9H), 7.25–7.24 (m, 0.2H), 7.22–7.20 (m, 0.2H), 7.19–7.12 (m, 2.9H), 7.07 (d, *J* = 7.3 Hz, 0.2H), 7.04 (d, *J* = 7.2 Hz, 1H), 6.97 (d, *J* = 6.8 Hz, 0.5H), 6.77 (t, *J* = 7.4 Hz, 1H), 6.75–6.74 (m, 0.2H), 6.67 (d, *J* = 8.1 Hz, 0.5H), 6.62 (t, *J* = 7.3 Hz,0.5H), 6.57 (m, 0.2H), 4.50–4.46 (m, 0.7H), 3.78 (d, *J* = 10.8 Hz, 1H), 3.41 (qd, *J* = 7.8,7.2, Hz, 0.2H), 3.10 (dq, *J* = 13.4, 6.7 Hz, 1H), 2.86 (s, 1.5H), 2.66 (s, 0.6H), 2.59 (s, 4H), 2.21–2.15 (m, 0.5H), 2.04–1.97 (m, 0.5H), 1.32 (d, *J* = 6.7 Hz, 3H), 0.74 (d, *J* = 7.3 Hz, 0.6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 152.8, 152.7, 146.2, 144.3, 141.6, 138.5, 134.9, 133.5, 128.6, 128.5, 128.5, 128.3, 128.1, 127.9, 127.8, 127.7, 127.4, 127.3, 126.9, 126.6, 123.7, 122.7, 122.6, 118.4, 115.7, 110.0, 107.5, 107.4, 81.1, 75.0, 63.3, 45.7, 40.9, 37.8, 34.5, 34.4, 30.2, 24.3, 17.1, 16.1. **IR** (KBr) ν/cm^{-1}: 3026, 2925, 2853, 1605, 1484, 1452, 1308, 1267, 1219, 1132, 974, 748, 710, 620. **HRMS** (ESI) calculated for $C_{16}H_{18}N$ $(M+H)^+$: 224.1434, found: 224.1434

3-Benzyl-1-methyl-2-phenylindoline (5b)



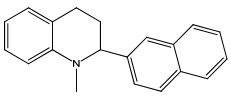
Yield: 82%. White solid, a mixture of *cis*- and *trans*-isomers (*cis*/*trans*=1:10), m.p. 68.8–71.1 °C. The configurations of *cis*-**5b**/*trans*-**5b** were assigned by the comparison of the coupling constant $J_{2,3}$ with the reported data of *cis*- and *trans*-isomers of 3-methyl-2-phenylindoline (*J. Org. Chem.* **1997**, *62*, 8600-8603). *Trans*-isomer, **^{1}H NMR** (400 MHz, $CDCl_3$)：δ 7.28–7.27 (m, 2H), 7.26–7.08 (m, 9H), 6.77 (d, *J* = 7.3 Hz, 1H), 6.62 (t, *J* = 7.4 Hz, 1H), 6.50 (d, *J* = 7.8 Hz, 1H), 4.01 (d, *J* = 9.2 Hz, 1H), 3.56 (dt, *J* = 8.1, 7.7 Hz, 1H), 3.04 (d, *J* = 7.2 Hz, 2H), 2.58 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 152.6, 141.9, 139.5, 131.6, 129.3, 128.4, 128.3, 128.0, 127.7, 127.6, 126.2, 123.8, 117.7, 106.7, 77.6, 51.4, 39.3, 33.8. **IR** (KBr) ν/cm^{-1}: 3027, 2853, 1605, 1484, 1453, 1354, 1266, 1112, 1023, 743, 699. **HRMS** (ESI) calculated for $C_{22}H_{22}N$ $(M+H)^+$: 300.1747, found : 300.1754.

1-Methyl-2,4-diphenyl-1, 2, 3, 4-tetrahydroquinoline (4c)



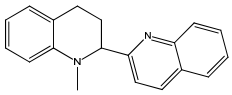
Yield: 82%. Yellow solid, a mixture of *cis*- and *trans*-isomers (*cis*/*trans*=1:3). The configurations were assigned by the NOE experiments of 2-H and 4-H. The *cis*-isomer showed stronger NOE than the *trans*-isomer. **^{1}HNMR** (400 MHz, $CDCl_3$)：δ 7.32–7.28 (m, 4.6H), 7.25–7.09 (m, 7.6H), 7.19–7.14 (m, 2H), 6.78–6.73 (m, 1.3H), 6.66 (d, *J*=7.4 Hz, 1H), 6.59–6.53 (m, 1.6H), 4.49 (dd, *J* = 11.0, 4.6 Hz, 0.3H), 4.42–4.39 (t, *J*= 5.1 Hz, 1H), 4.16 (dd, *J* = 12.2, 4.3 Hz, 0.3H), 3.85 (dd, *J* = 9.6, 4.4 Hz, 1H), 2.89 (s, 3H), 2.75 (s, 0.9H), 2.45–2.33 (m, 1.3H), 2.26–2.20 (m, 1.3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.6, 146.3, 145.0, 144.2, 144.0, 129.0, 128.7, 128.6, 128.5, 128.4, 128.1, 127.9, 127.7, 127.5, 127.2, 127.0, 126.9, 126.6, 126.3, 125.4, 116.5, 115.8, 112.3, 110.4, 64.9, 61.8, 44.2, 43.0, 40.1, 38.9, 38.0, 37.8. **IR** (KBr) ν/cm^{-1}: 1636, 1497, 1418, 1264, 1104, 987, 896, 748, 710, 619. **HRMS** (ESI) calculated for $C_{22}H_{22}N$ $(M+H)^+$: 300.1747, found : 300.1753.

1-Methyl-2-(naphthalen-2-yl)-1,2,3,4-tetrahydroquinoline (4d)



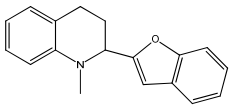
Yield: 70%. White solid, m.p. 154.4–155.3 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 8.3 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.56–7.48 (m, 2H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.27 (s, 1H), 7.19 (t, *J* = 7.7 Hz, 1H), 6.99 (d, *J* = 7.2 Hz, 1H), 6.72 (d, *J* = 8.2 Hz, 1H), 6.66 (t, *J* = 7.3 Hz, 1H), 5.33 (t, *J* = 4.3 Hz, 1H), 2.92 (s, 3H), 2.65–2.48 (m, 2H), 2.34–2.21 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.1, 138.5, 134.2, 130.4, 129.2, 128.5, 127.5, 127.4, 126.1, 125.4, 125.3, 124.3, 122.8, 122.2, 115.5, 109.6, 60.0, 37.8, 27.9, 24.3. **IR** (KBr) ν/cm^{-1}: 3050, 2927, 1603, 1502, 1443, 1352, 1265, 1221, 1098, 986, 810, 781, 742, 704. **HRMS** (ESI) calculated for $C_{20}H_{20}N$ $(M+H)^+$: 274.1590, found : 274.1590.

1-Methyl-1,2,3,4-tetrahydro-2,2'-biquinoline (4e)



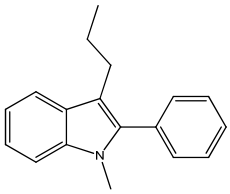
Yield: 77%. Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.31 (d, *J* = 8.5 Hz, 1H), 7.19 (t, *J* = 7.7 Hz, 1H), 7.01 (d, *J* = 7.3 Hz, 1H), 6.74 (d, *J* = 8.2 Hz, 1H), 6.68 (t, *J* = 7.3 Hz, 1H), 4.78 (d, *J* = 5.0 Hz, 1H), 2.92 (s, 3H), 2.72 (dt, *J* = 15.7, 5.0 Hz, 1H), 2.61–2.53 (m, 1H), 2.32–2.27 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.5, 147.9, 145.7, 136.8, 129.7, 128.8, 128.6, 127.6, 127.5, 127.4, 126.2, 122.9, 118.9, 116.2, 110.5, 65.9, 38.0, 28.8, 24.8. **IR** (KBr) ν/cm^{-1}: 3061, 2926, 1619, 1601, 1500, 1429, 1373, 1340, 1268, 1224, 1003, 925, 833, 745. **HRMS** (ESI) calculated for $C_{19}H_{18}N_2$ $(M+H)^+$: 275.1543, found: 275.1535.

2-(Benzofuran-2-yl)-1-methyl-1,2,3,4-tetrahydroquinoline (4f)



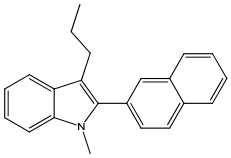
Yield: 41%. Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44 (t, *J* = 6.8 Hz, 2H), 7.24–7.10 (m, 3H), 6.97 (d, *J* = 7.1 Hz, 1H), 6.69–6.64 (m, 2H), 6.38 (s, 1H), 4.65 (t, *J* = 4.0 Hz, 1H), 3.01 (s, 3H), 2.70–2.65 (m, 2H), 2.43–2.29 (m, 1H), 2.27–2.08 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.5, 154.9, 144.9, 128.6, 128.5, 127.3, 123.6, 122.7, 122.3, 120.7, 116.3, 111.0, 110.3, 103.6, 58.1, 38.0, 26.2, 24.3. **IR** (KBr) ν/cm^{-1}: 1604, 1502, 1454, 1254, 1104, 1003, 897, 748. **HRMS** (ESI) calculated for $C_{18}H_{18}NO$ $(M+H)^+$: 264.1383, found : 264.1394.

1-Methyl-2-phenyl-3-propyl-1H-indole (6h)



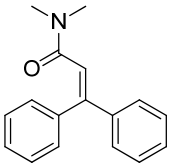
Yield: 65%. White solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 7.8 Hz, 1H), 7.49–7.37 (m, 5H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.24–7.22 (m, 1H), 7.13 (t, *J* = 7.7 Hz, 1H), 3.56 (s, 3H), 2.66 (t, *J* = 7.6 Hz, 2H), 1.68–1.59 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 137.8, 137.2, 132.4, 130.7, 128.3, 127.9, 127.8, 121.6, 119.2, 119.0, 113.8, 109.3, 30.8, 26.8, 24.4, 14.3.

1-Methyl-2-(naphthalen-2-yl)-3-propyl-1H-indole (6i)



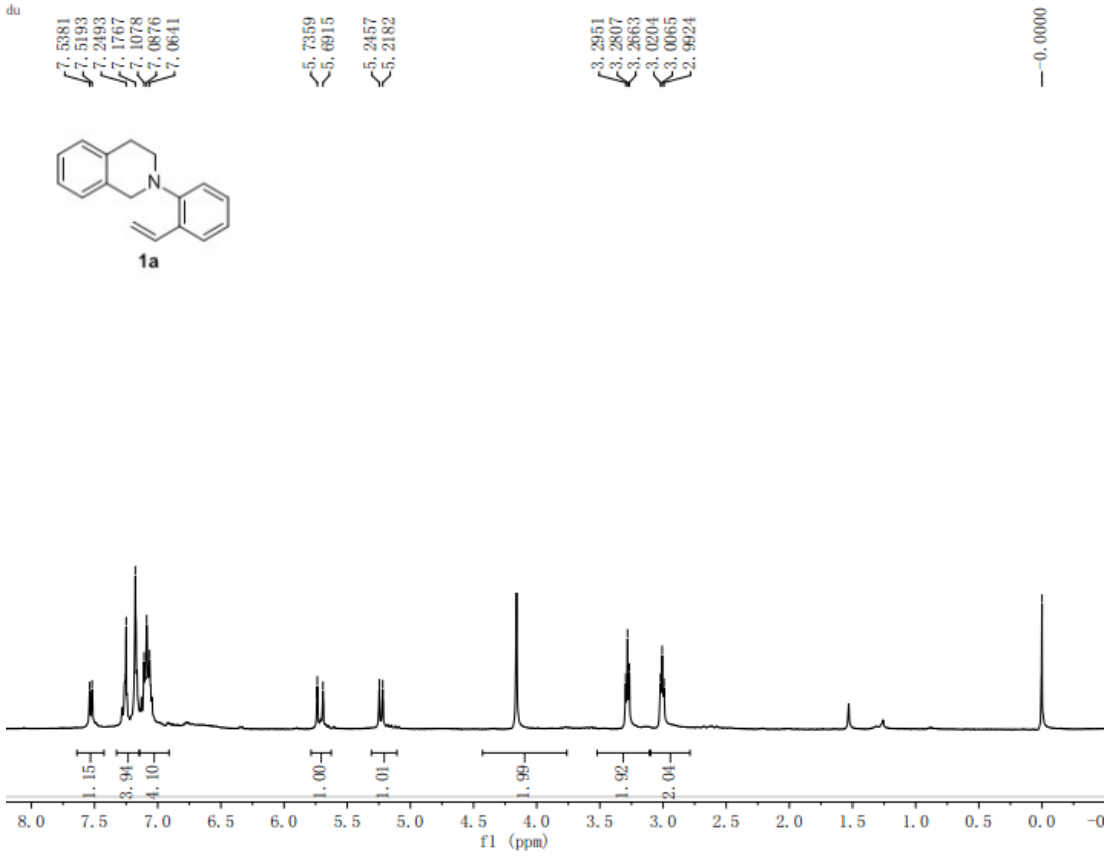
Yield: 80%. White solid, m.p. 79.7–81.0 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.58 (t, *J* = 7.1 Hz, 1H), 7.52–7.49 (br, 3H), 7.41–7.36 (m, 2H), 7.30–7.26 (m, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 3.37 (s, 3H), 2.67–2.45 (m, 2H), 1.59–1.51 (m, 3H), 0.76 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 137.1, 135.9, 133.6, 133.5, 130.1, 129.5, 128.9, 128.2, 127.9, 126.5, 126.1, 126.0, 125.2, 121.4, 119.2, 118.9, 114.9, 109.2, 30.4, 26.9, 24.1, 14.2. **IR** (KBr) ν/cm^{-1}: 2957, 1642, 1580, 1469, 1412, 1384, 1265, 1106, 986, 895, 800, 777, 740, 700. **HRMS** (ESI) calculated for $C_{22}H_{22}N$ $(M+H)^+$: 300.1747, found : 300.1754.

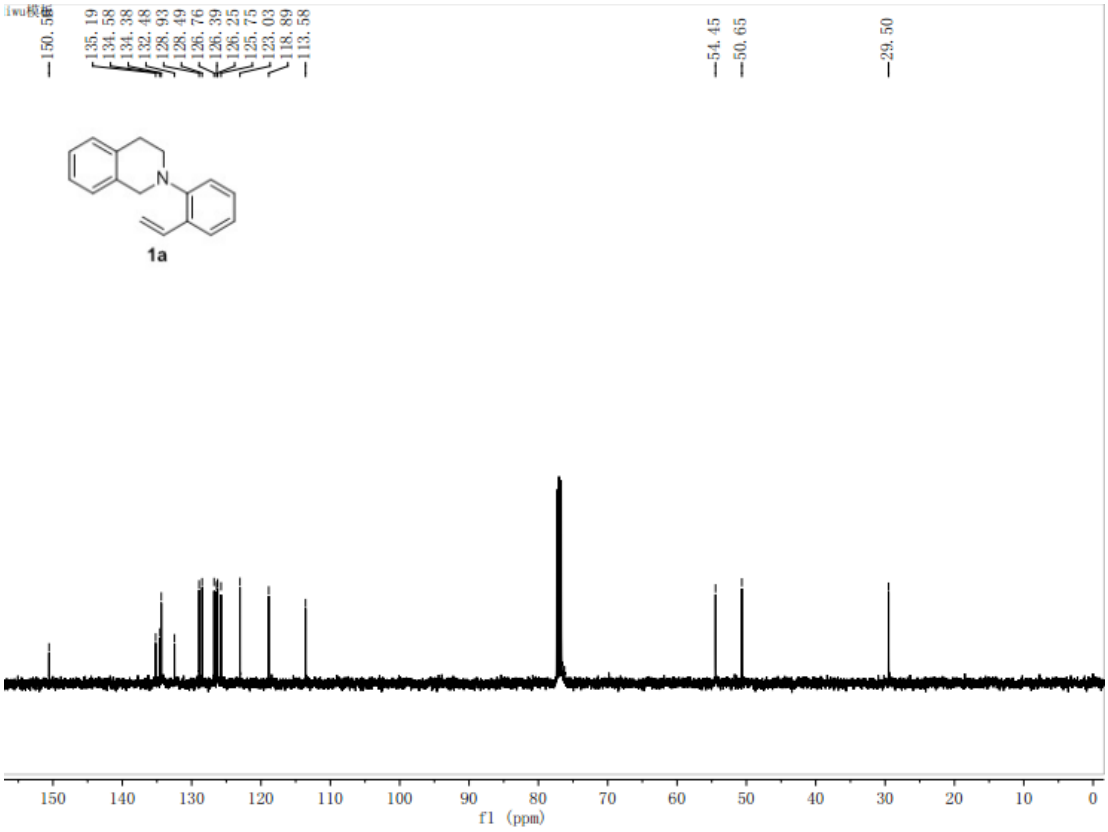
N, N-dimethyl-3,3-diphenylacrylamide(7)

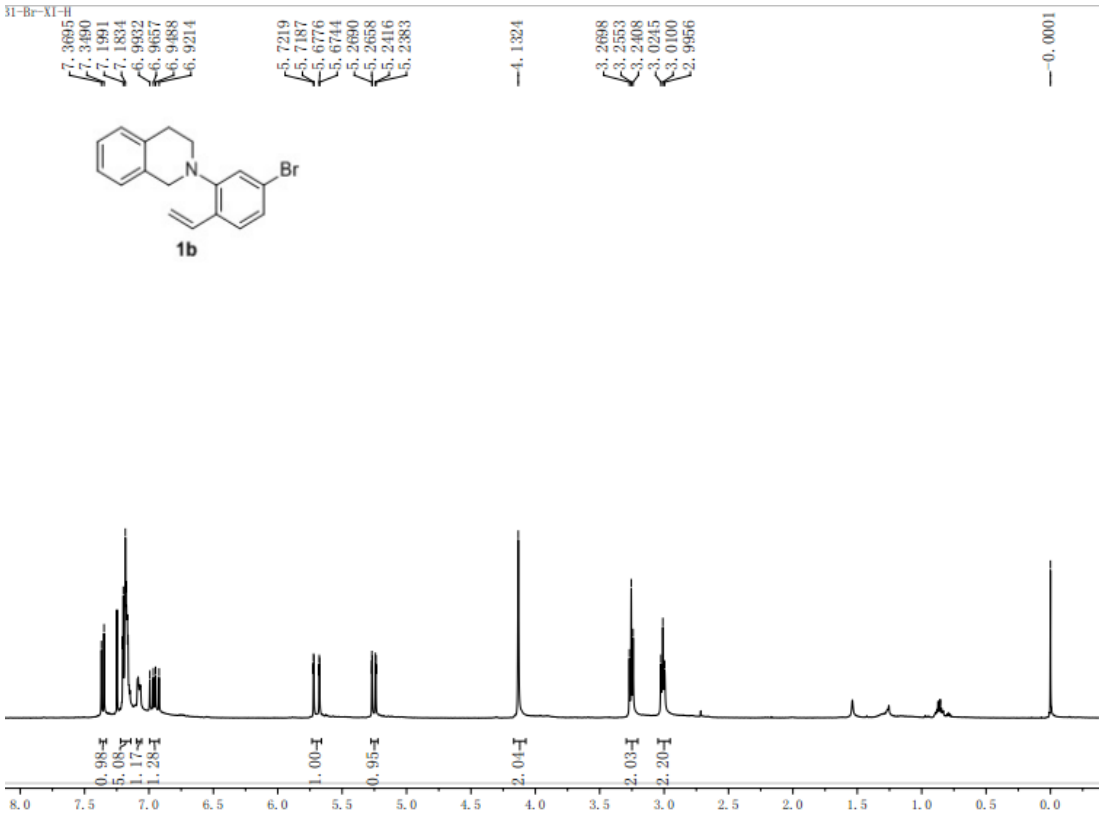


Yield: 20%. Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.32-7.27 (m, 10H), 6.35 (s, 1H), 2.83 (s, 3H), 2.76 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 168.4, 147.4, 141.2, 139.0, 129.3, 128.5, 128.4, 128.3, 128.1, 121.4, 37.7, 34.3.

7. NMR Spectra



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6.9488
6.9214
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5.6776
5.6744
5.2690
5.2658
5.2416
5.2383
4.1324
3.2698
3.2553
3.2408
3.0245
3.0100
2.9956
0.0001
Br
N
1b
0.98
5.08
1.17
1.28
1.00
0.95
2.04
2.03
2.20
8.0
7.5
7.0
6.5
6.0
5.5
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2.0
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1.0
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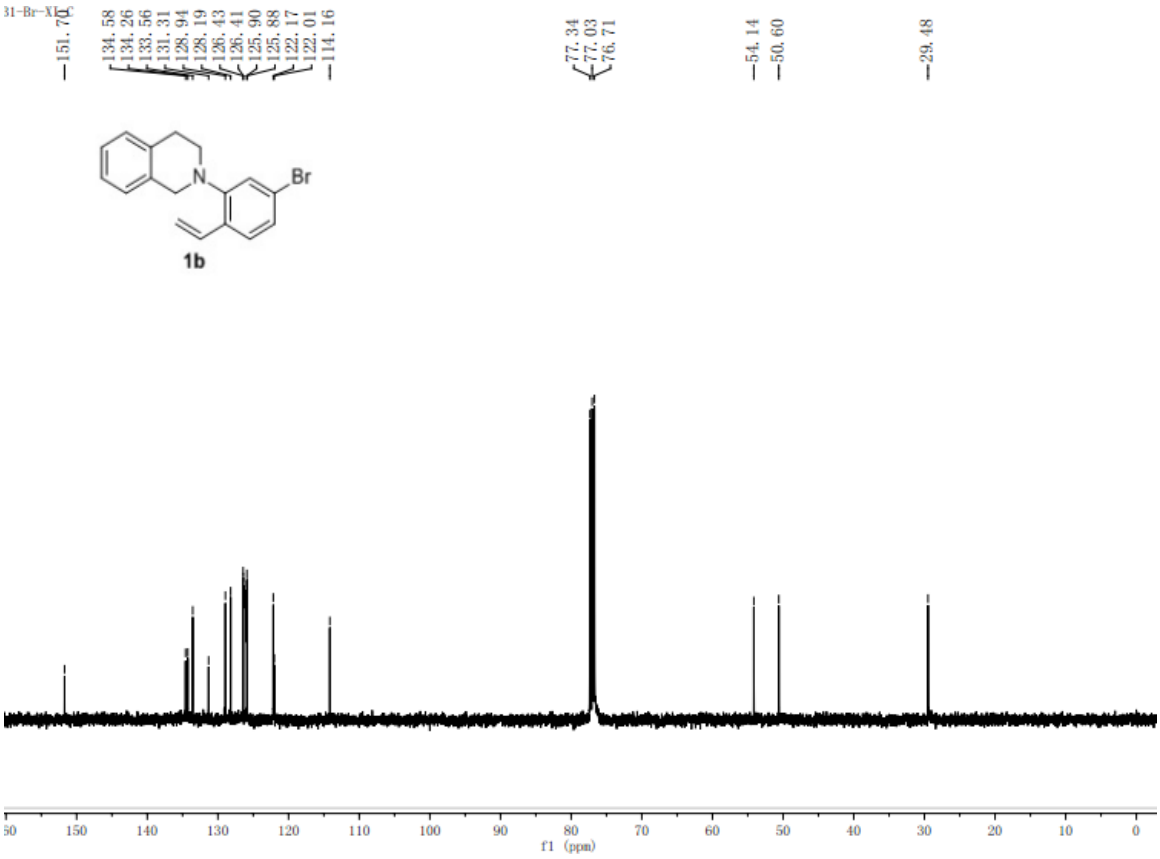
0.0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125.88
122.17
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114.16
77.34
77.03
76.71
54.14
50.60
29.48
Br
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50
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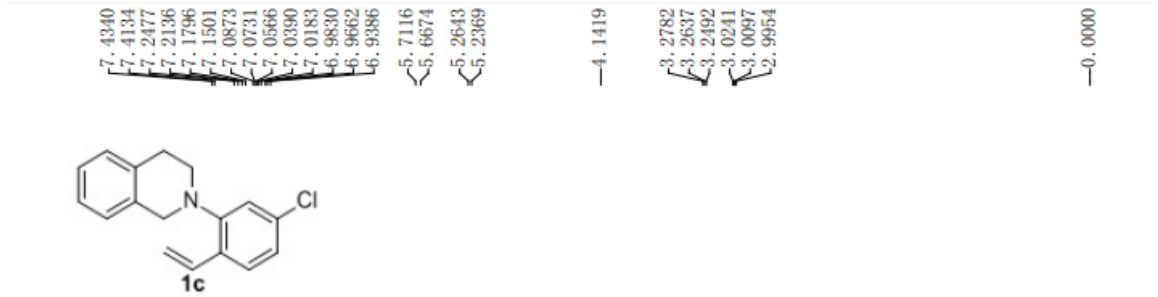
f1 (ppm)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6.9830
6.9662
6.9386
5.7116
5.6674
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5.2369
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3.2782
3.2637
3.2492
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0.0000
N
Cl
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2.95
3.13
0.93
0.96
0.94
1.99
1.96
1.97
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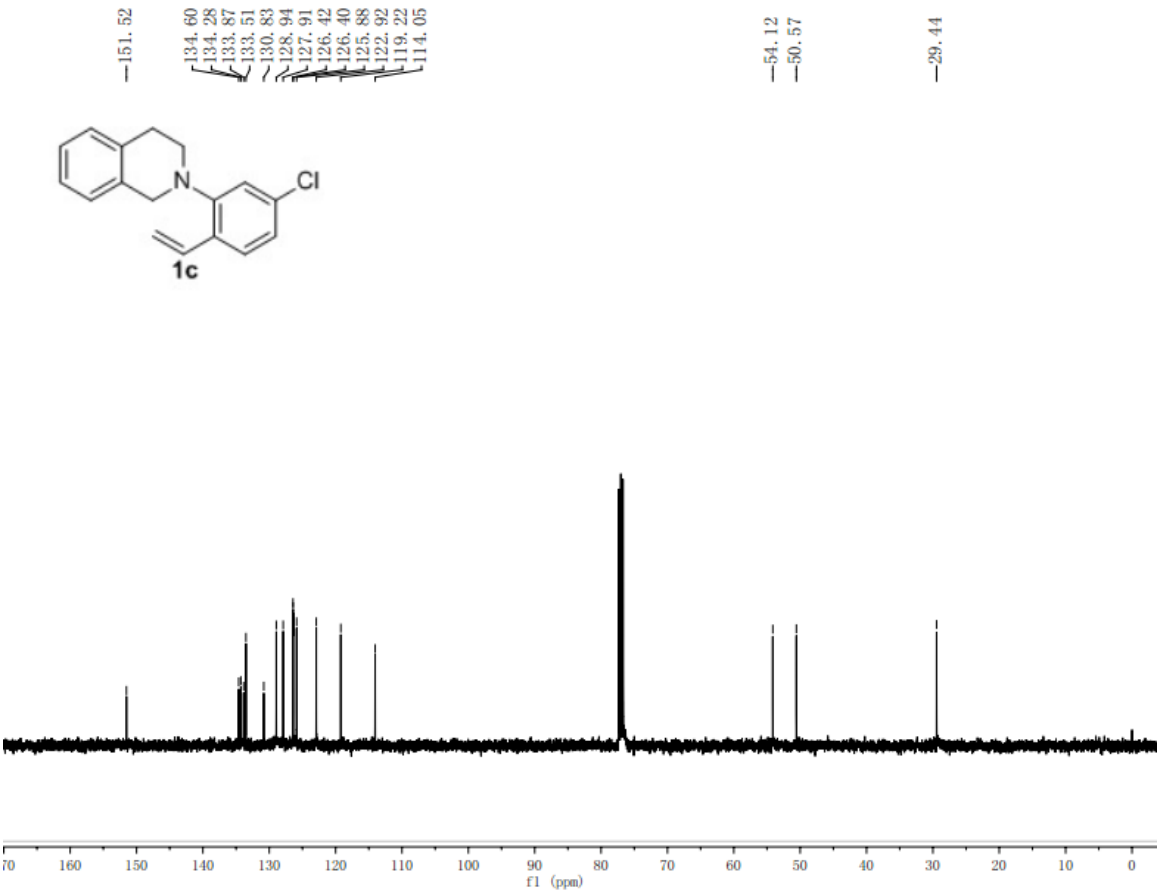
f1 (ppm)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Cl
1c
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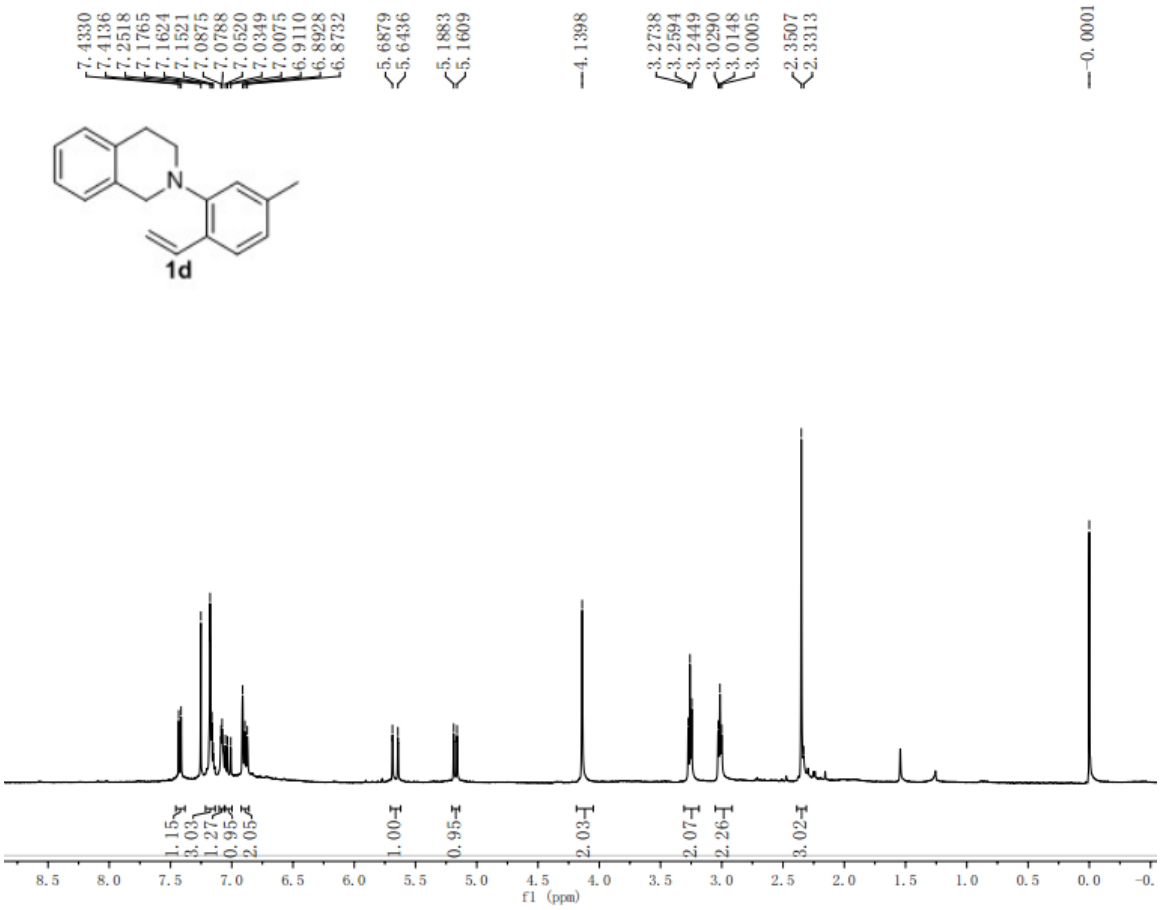
f1 (ppm)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7.0075
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6.8928
6.8732
5.6879
5.6436
5.1883
5.1609
4.1398
3.2738
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3.2449
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3.0148
3.0005
2.3507
2.3313
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1d
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2.05
1.00
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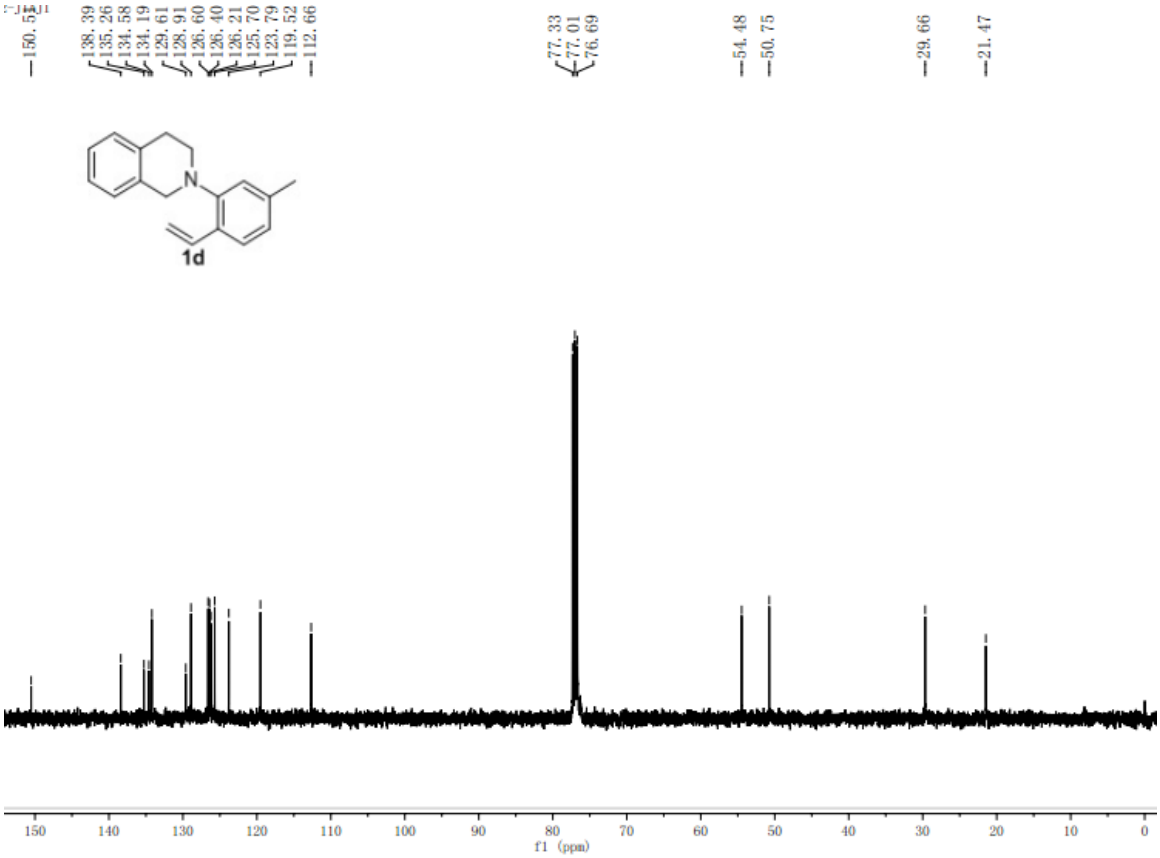
2.07
2.26
3.02
f1 (ppm)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77.01
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29.66
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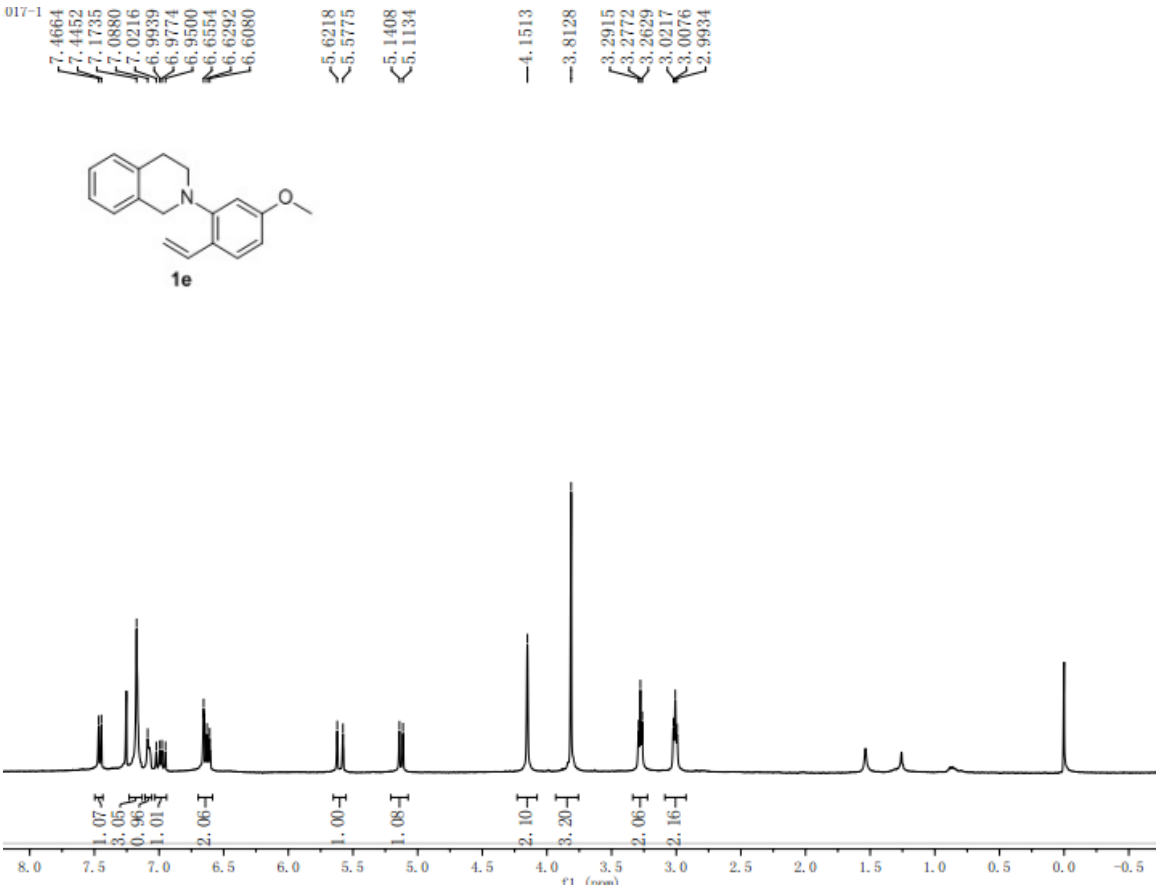
1d
f1 (ppm)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5.1134
4.1513
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3.2915
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2.06
1.00
1.08
2.10
3.20
2.06
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6.0
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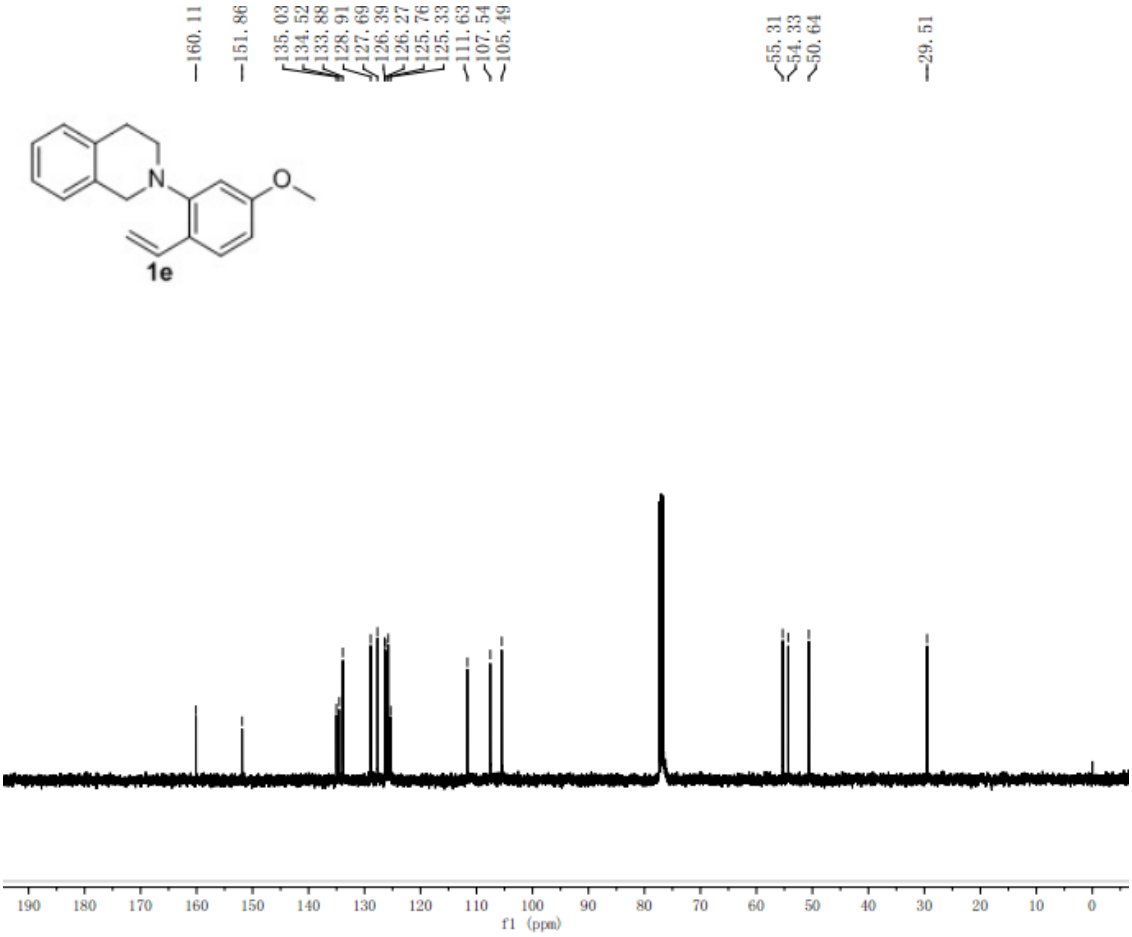
f1 (ppm)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29.51
190
180
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50
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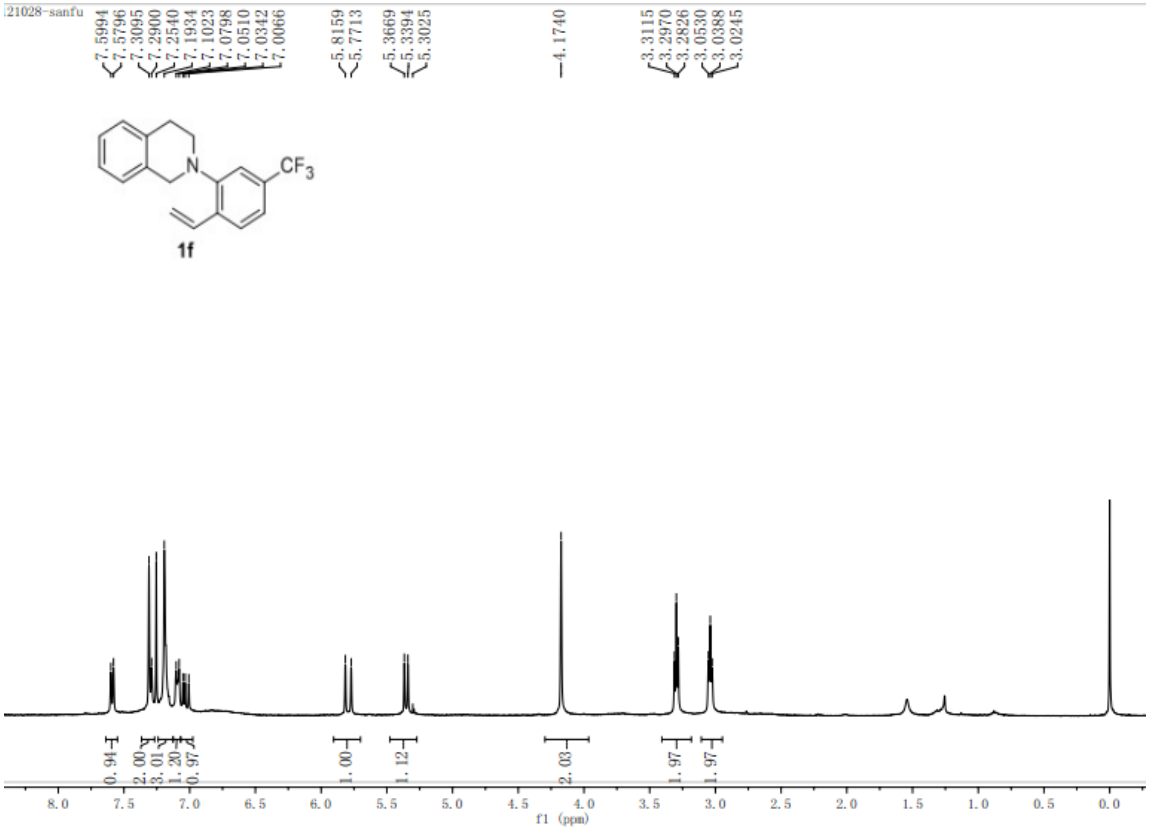
f1 (ppm)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7.0066
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5.3669
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3.3115
3.2970
3.2826
3.0530
3.0388
3.0245
CF3
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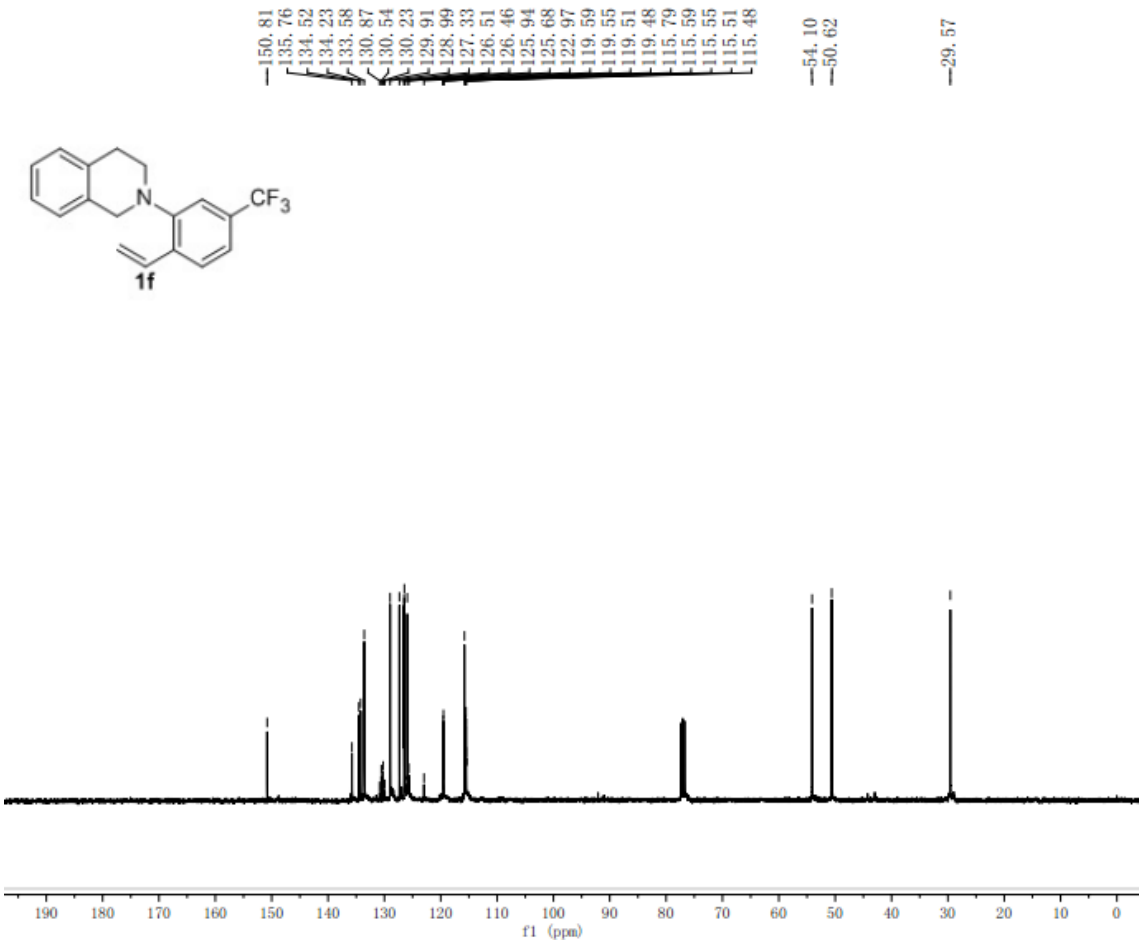
f1 (ppm)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CF3
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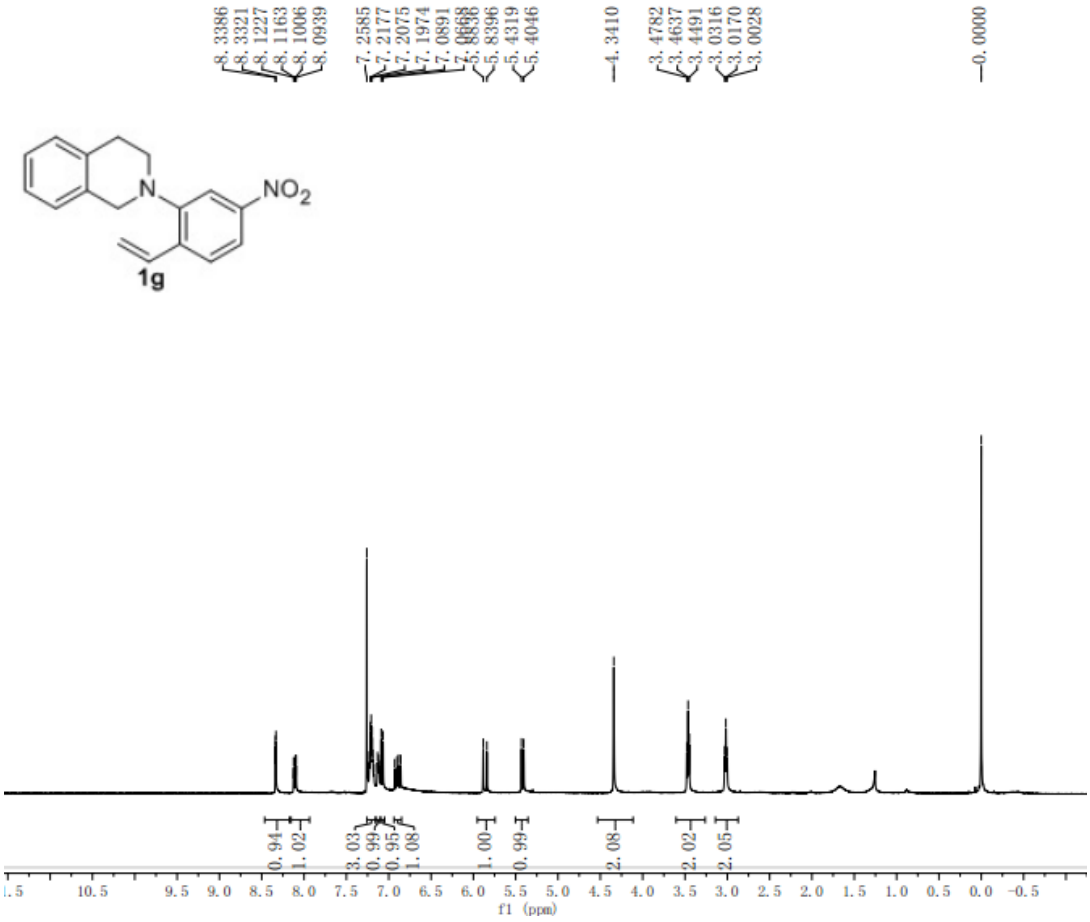
f1 (ppm)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7.2075
7.1974
7.0891
5.8396
5.4319
5.4046
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3.4637
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3.0170
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NO2
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1.00
0.99
2.08
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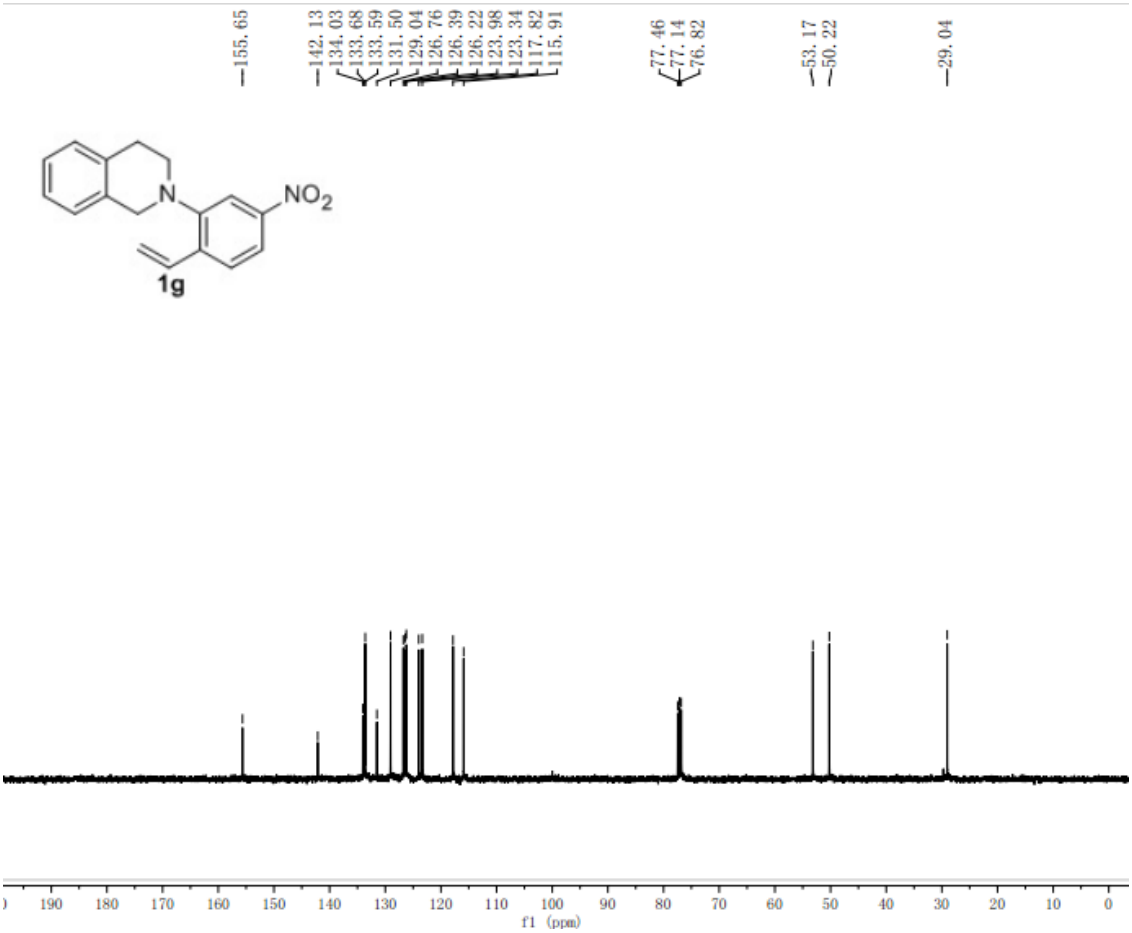
2.05
f1 (ppm)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123.98
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77.14
76.82
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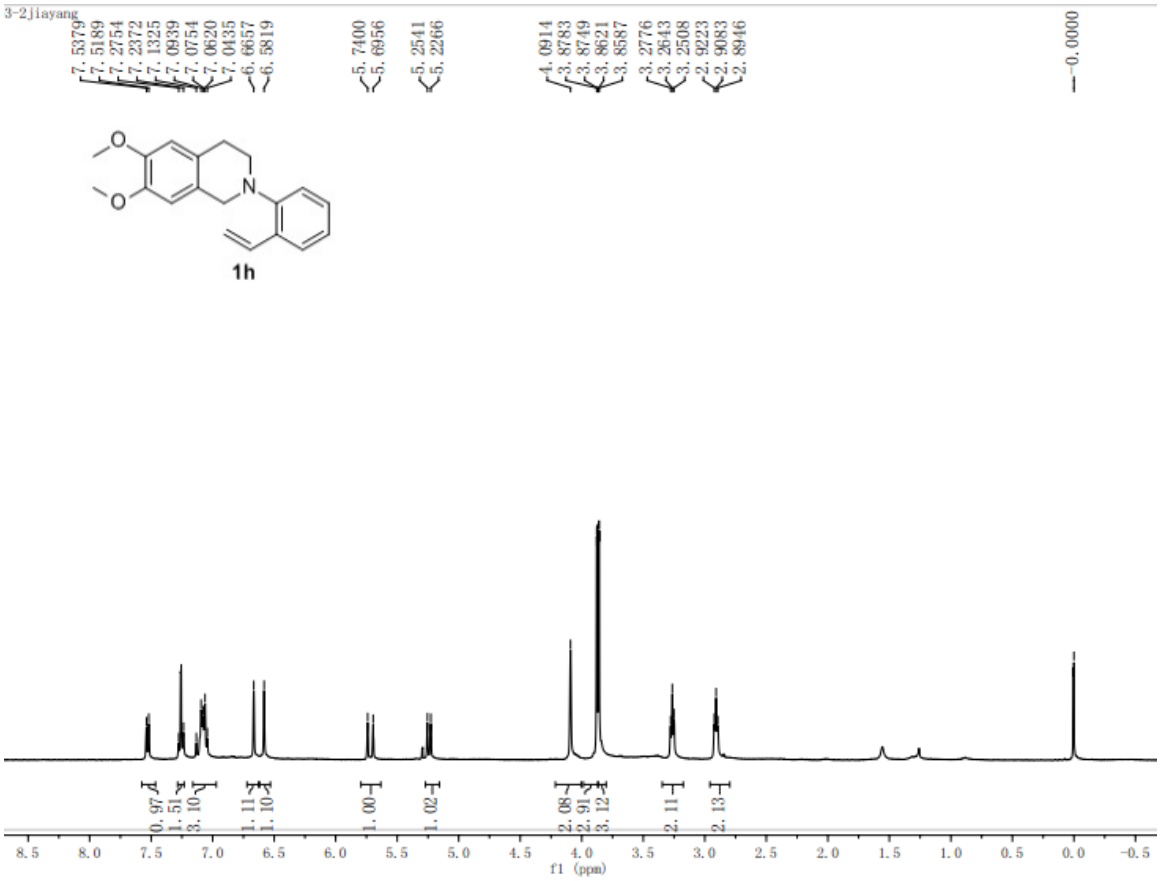
29.04
N
NO2
1g
f1 (ppm)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1.10
1.00
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3.12
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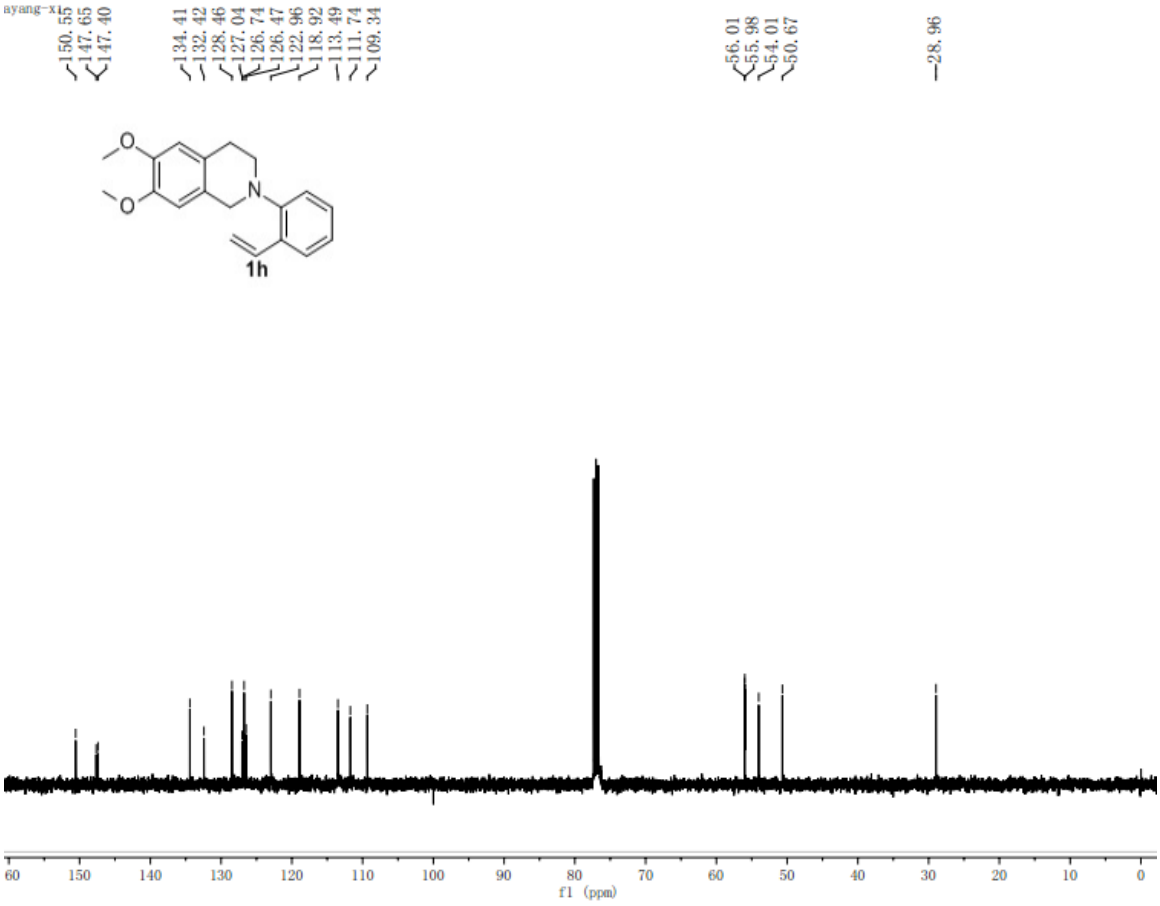
2.13
f1 (ppm)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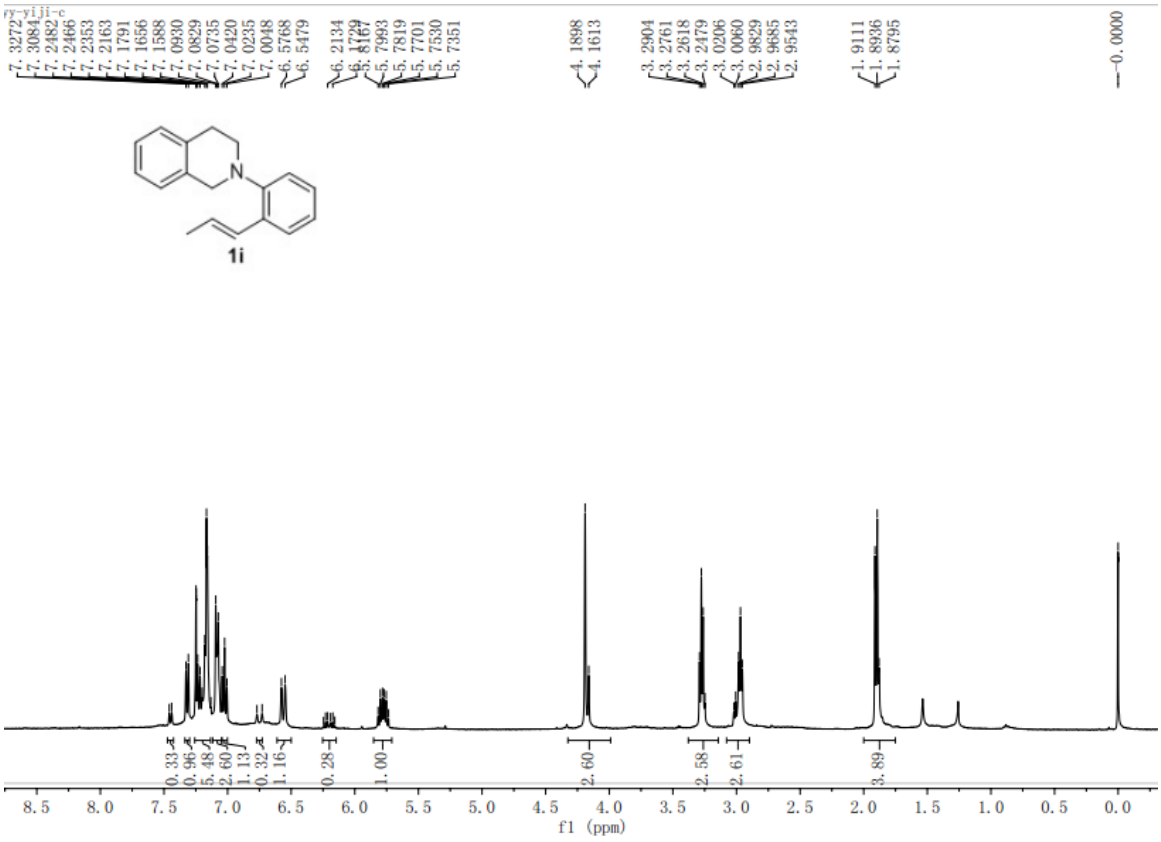
f1 (ppm)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6.5768
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6.2134
6.1729
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5.7530
5.7351
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4.1613
3.2904
3.2761
3.2618
3.2479
3.0206
3.0060
2.9829
2.9685
2.9543
1.9111
1.8936
1.8795
0.0000
N
1i
0.33
0.96
5.48
2.60
1.13
0.32
1.16
0.28
1.00
2.60
2.58
2.61
3.89
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
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1.0
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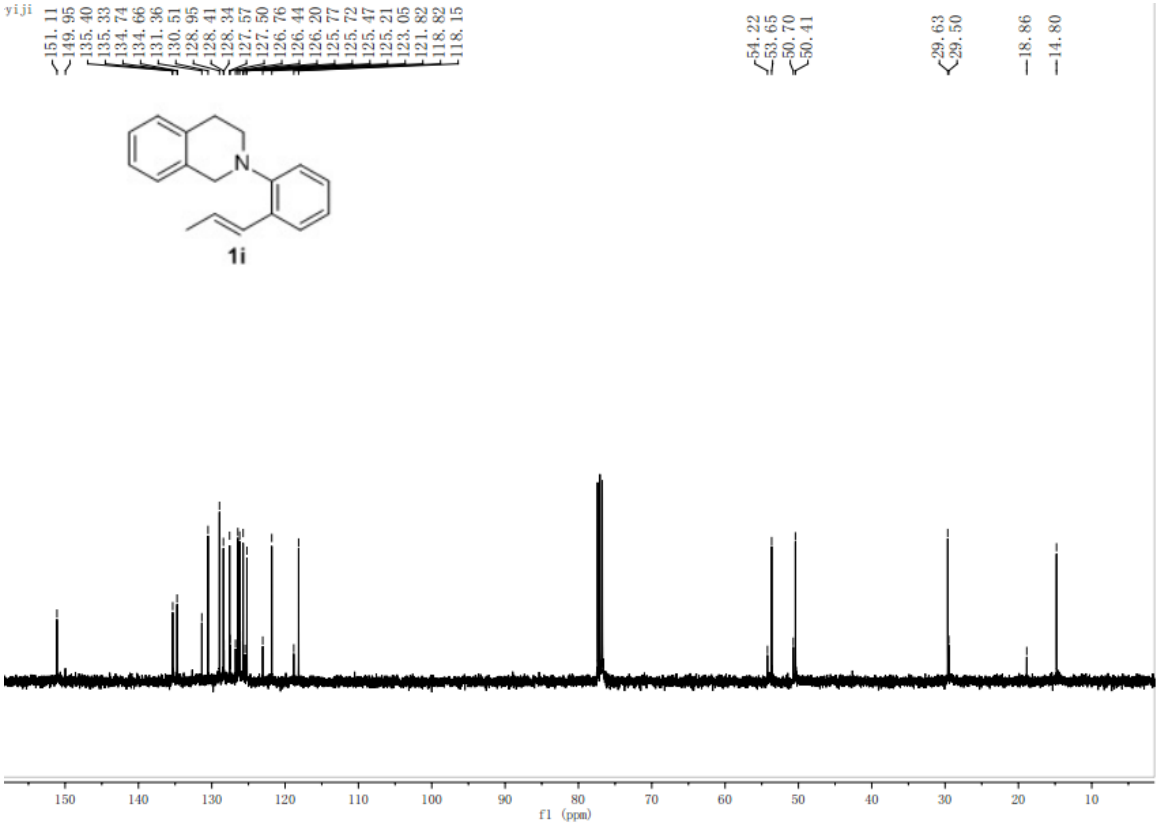
f1 (ppm)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127.57
127.50
126.76
126.44
126.20
125.77
125.72
125.47
125.21
123.05
121.82
118.82
118.15
54.22
53.65
50.70
50.41
29.63
29.50
18.86
14.80
N
1i
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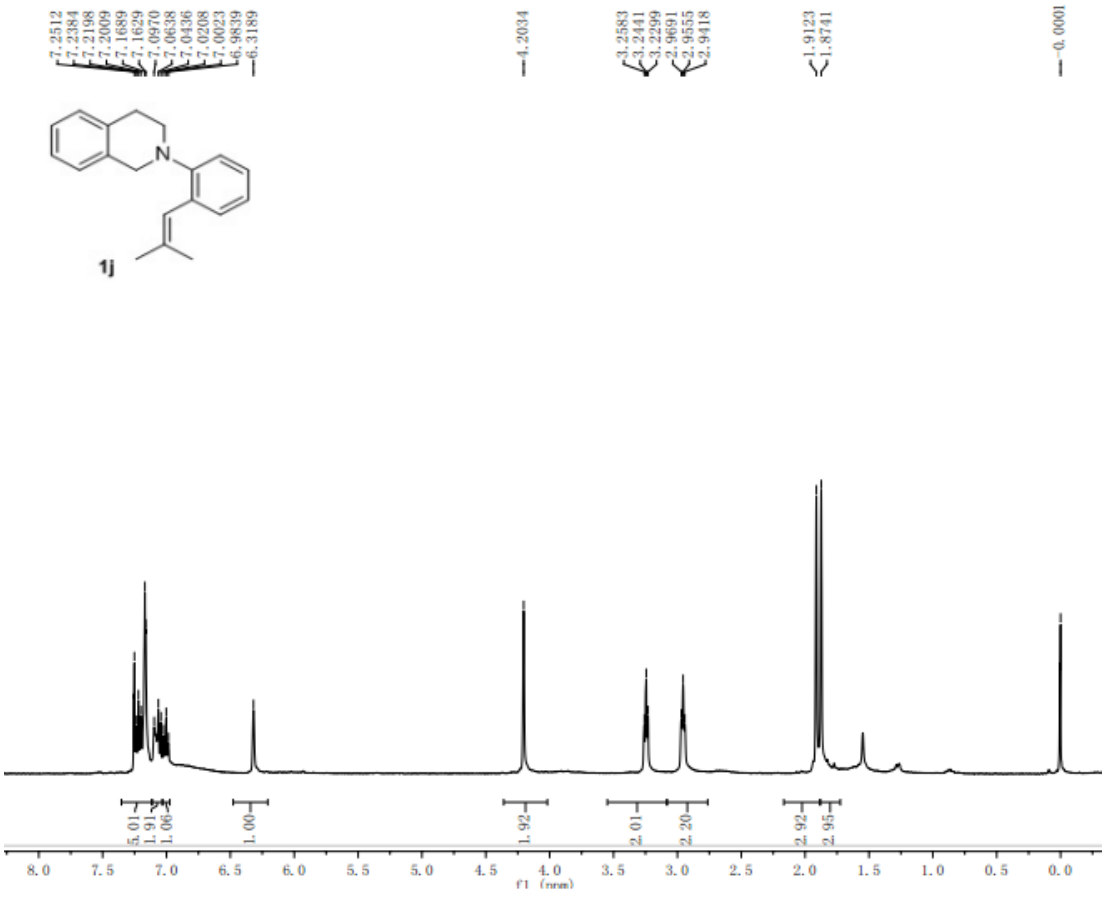
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.0023
6.9839
6.3189
4.2034
3.2583
3.2441
3.2299
2.9691
2.9555
2.9418
1.9123
1.8741
0.0001
N
1j
5.01
1.91
1.06
1.00
1.92
2.01
2.20
2.92
2.95
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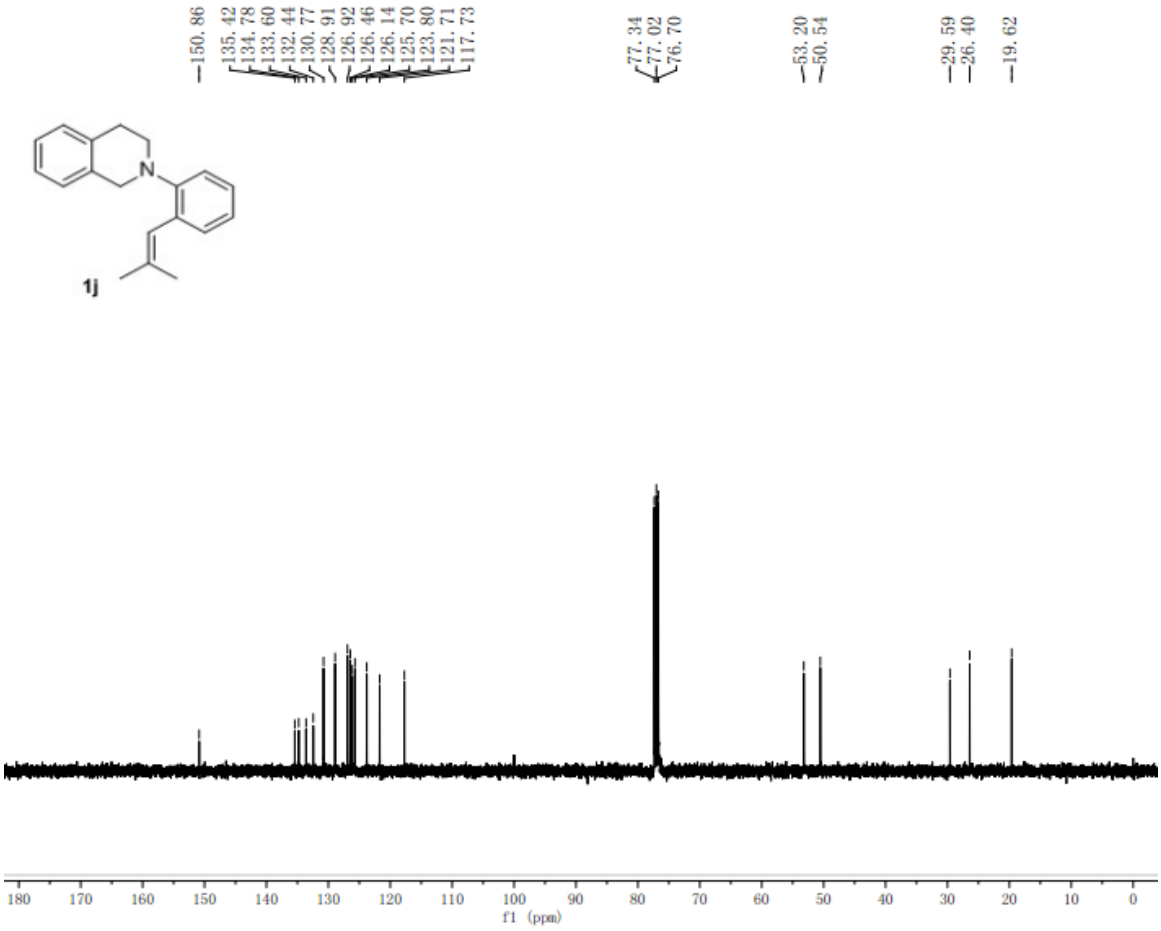
f1 (ppm)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126.92
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126.14
125.70
123.80
121.71
117.73
77.34
77.02
76.70
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50.54
29.59
26.40
19.62
N
1j
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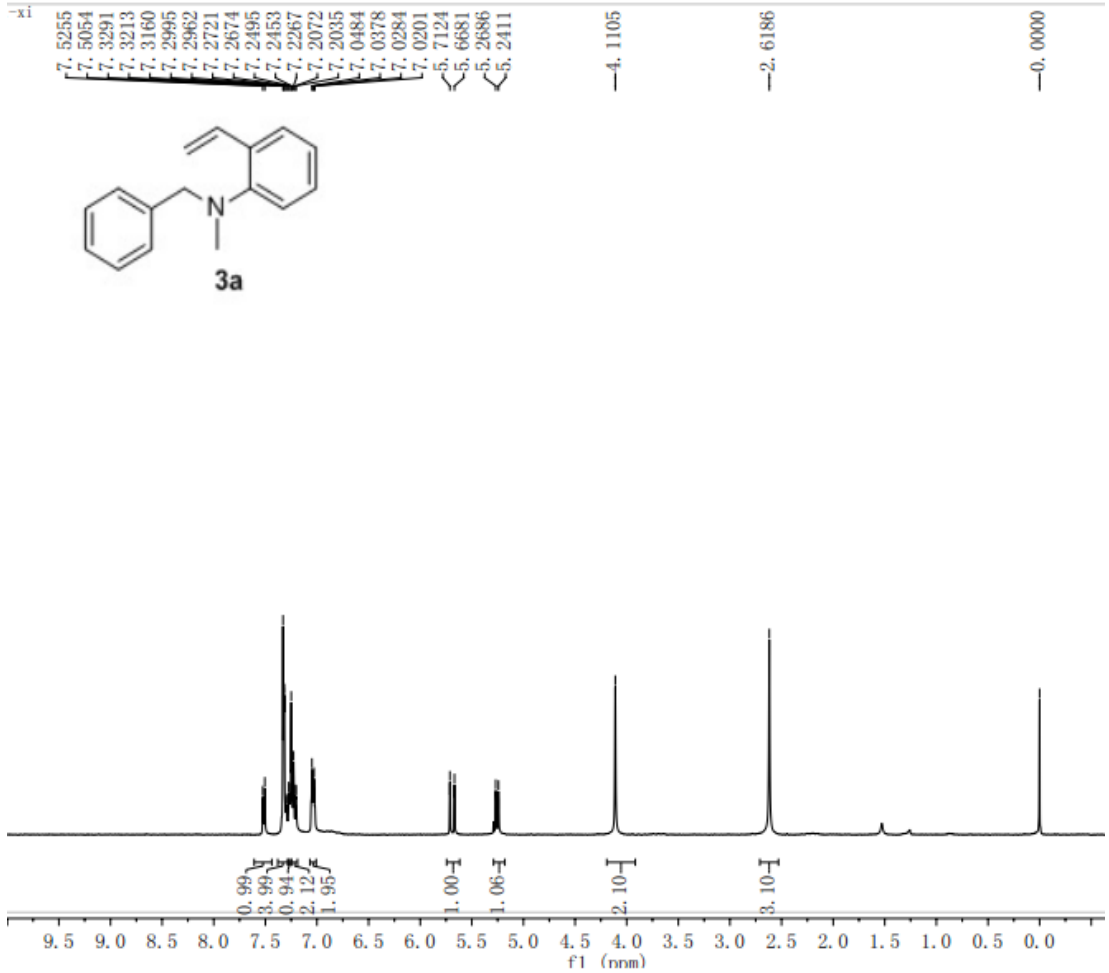
f1 (ppm)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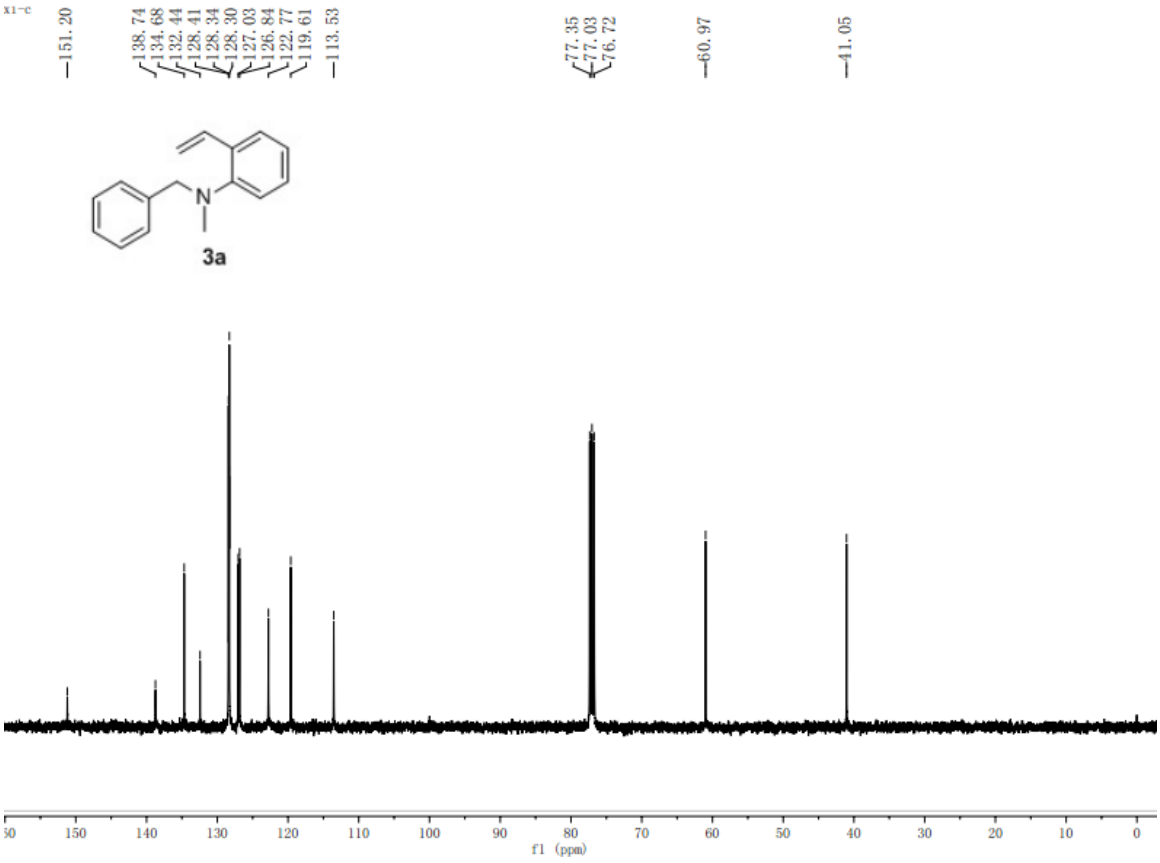
7.2267
7.2072
7.2035
7.0484
7.0378
7.0284
7.0201
5.7124
5.6681
5.2686
5.2411
4.1105
2.6186
0.0000
N
3a
0.99
3.99
0.94
2.12
1.95
1.00
1.06
2.10
3.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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122.77
119.61
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76.72
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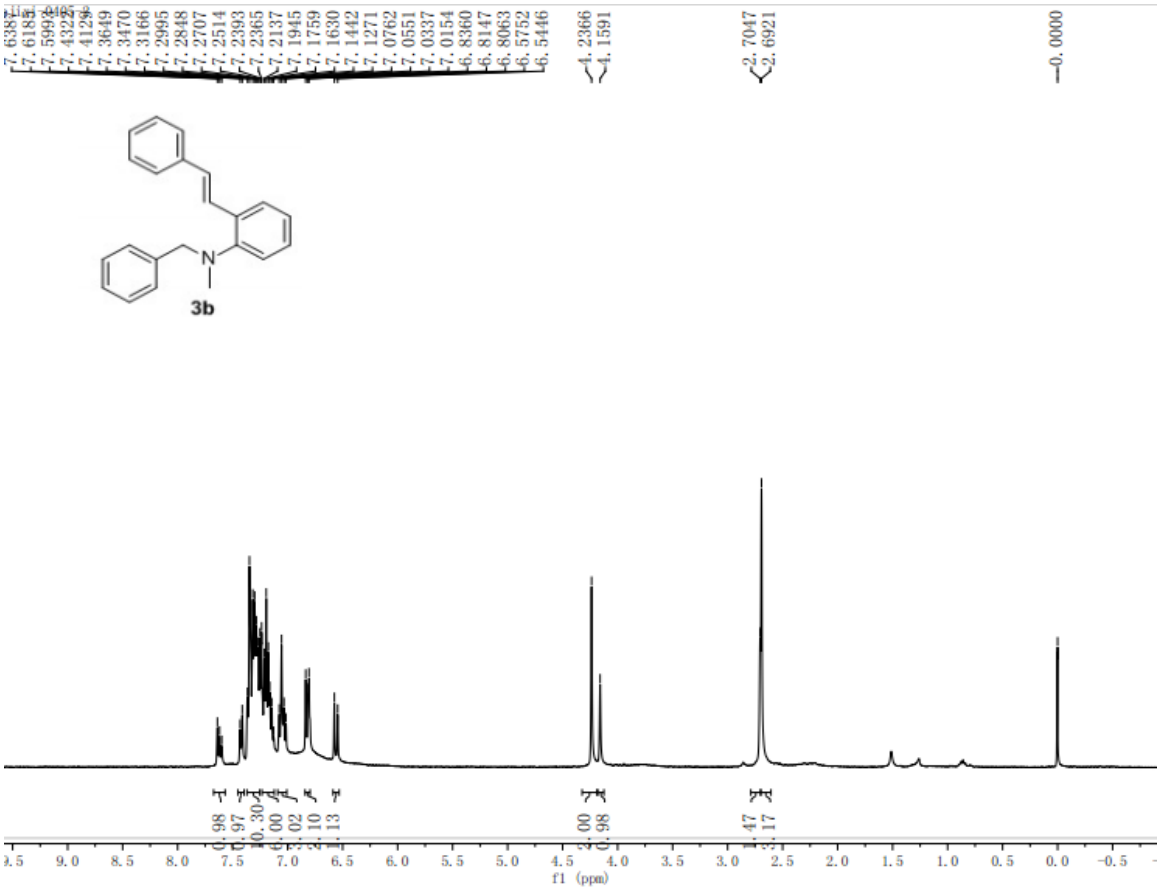
f1 (ppm)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7.2707
7.2514
7.2393
7.2365
7.2137
7.1945
7.1759
7.1630
7.1442
7.1271
7.0762
7.0551
7.0337
7.0154
6.8360
6.8147
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6.5752
6.5446
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4.1591
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2.6921
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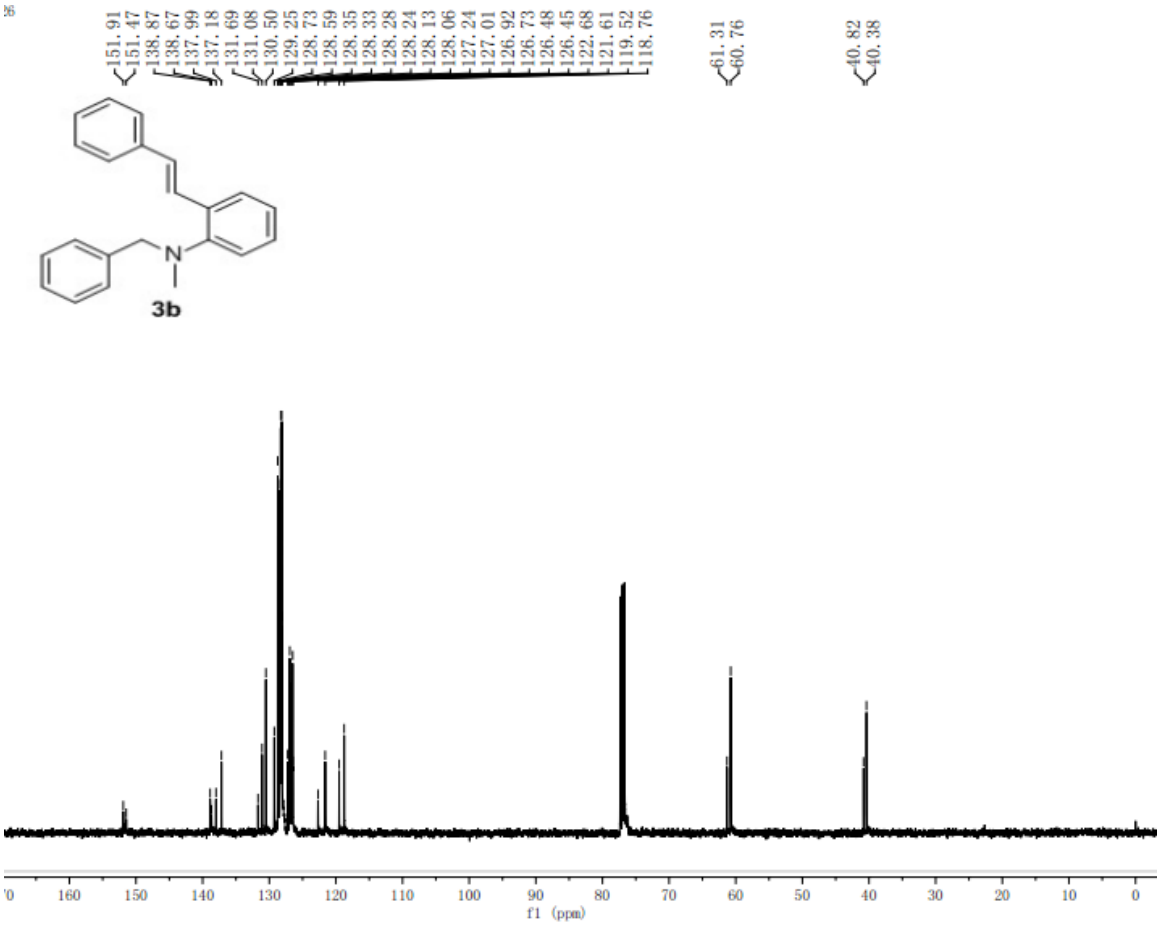
N
3b
f1 (ppm)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131.08
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129.25
128.73
128.59
128.35
128.33
128.28
128.24
128.13
128.06
127.24
127.01
126.92
126.73
126.48
126.45
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121.61
119.52
118.76
61.31
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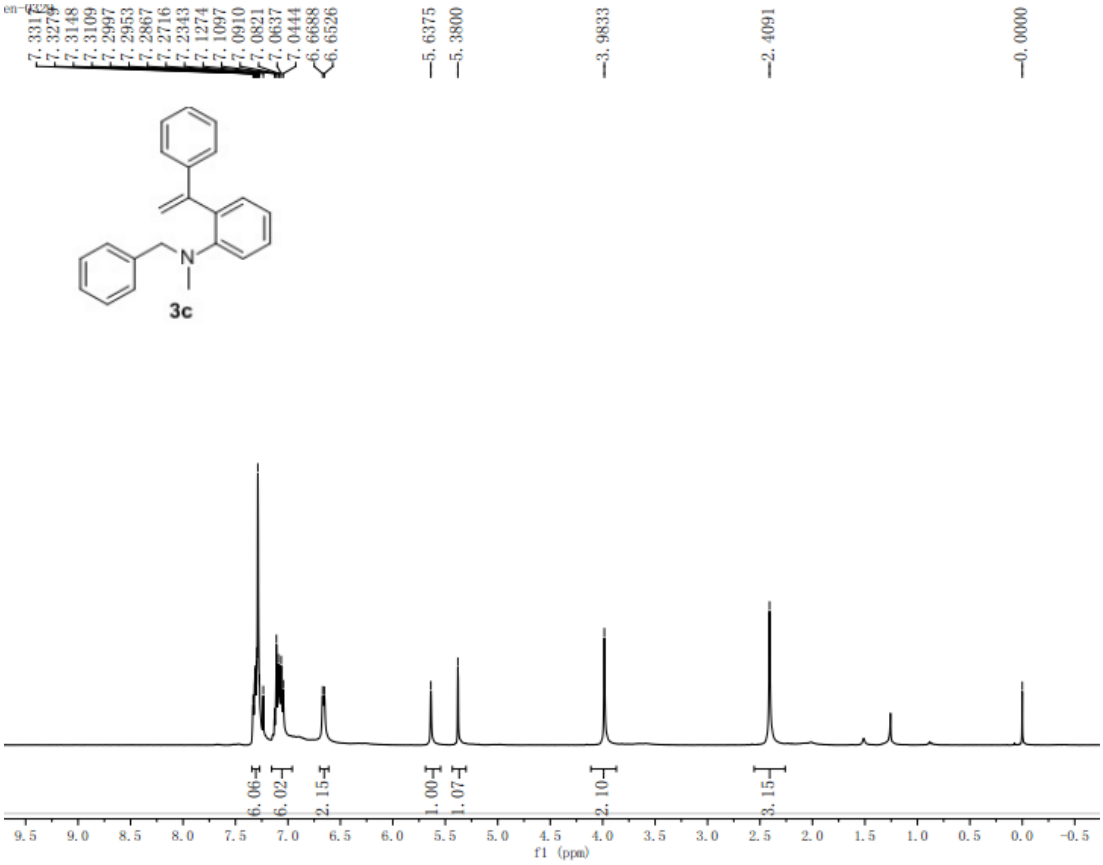
40.82
40.38
N
3b
f1 (ppm)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7.3148
7.3109
7.2997
7.2953
7.2867
7.2716
7.2343
7.1274
7.1097
7.0910
7.0821
7.0637
7.0444
6.6688
6.6526
5.6375
5.3800
3.9833
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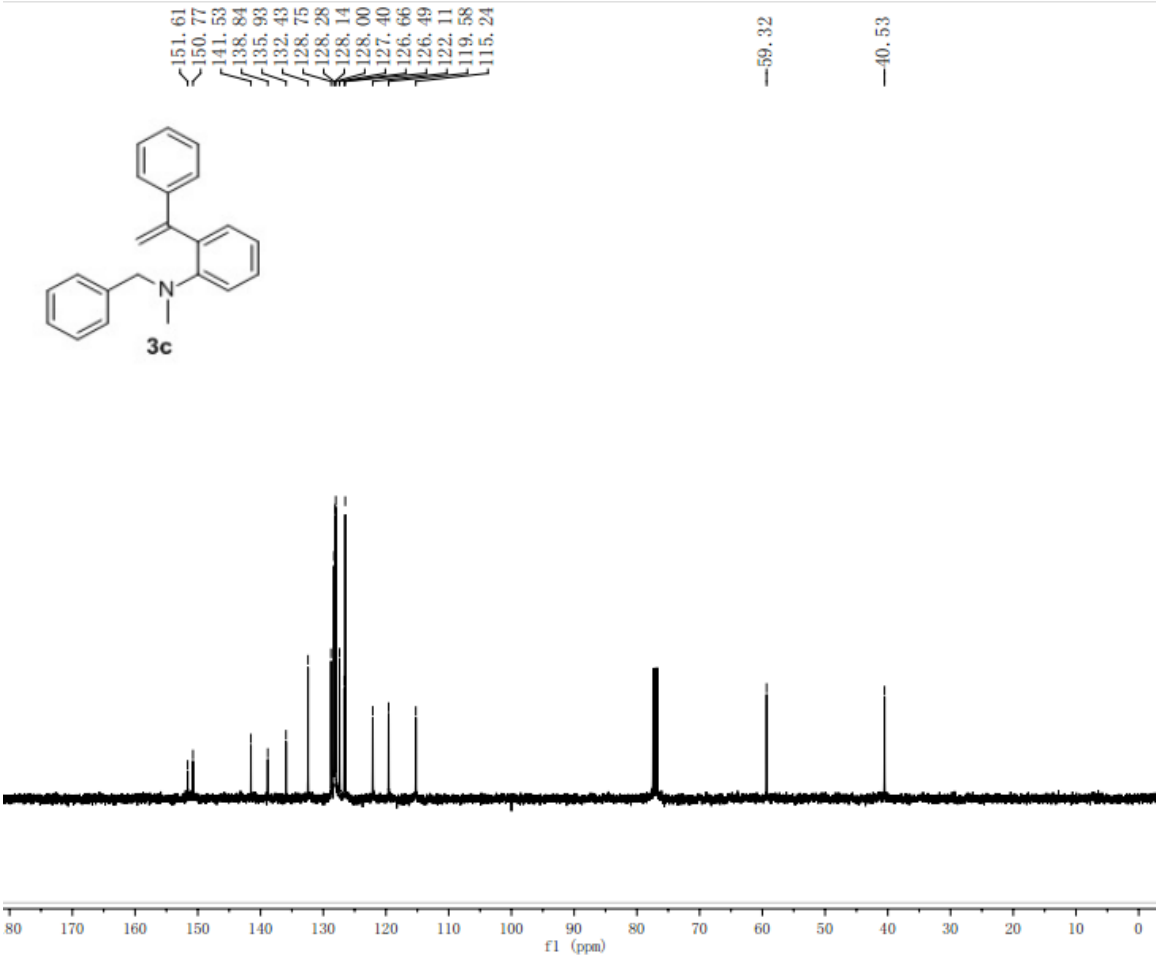
3c
6.06
6.02
2.15
1.00
1.07
2.10
3.15
f1 (ppm)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132.43
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128.28
128.14
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126.49
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119.58
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59.32
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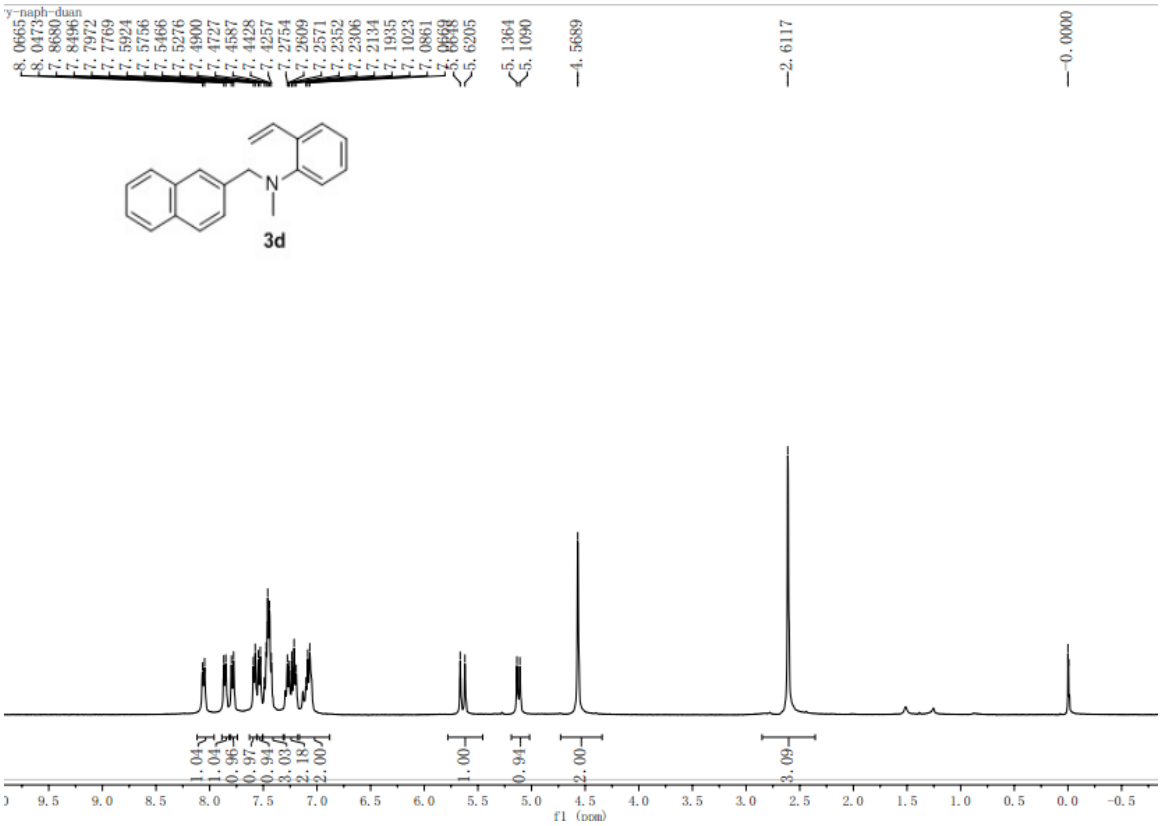
N
3c
f1 (ppm)


y-naph-duan
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7.7769
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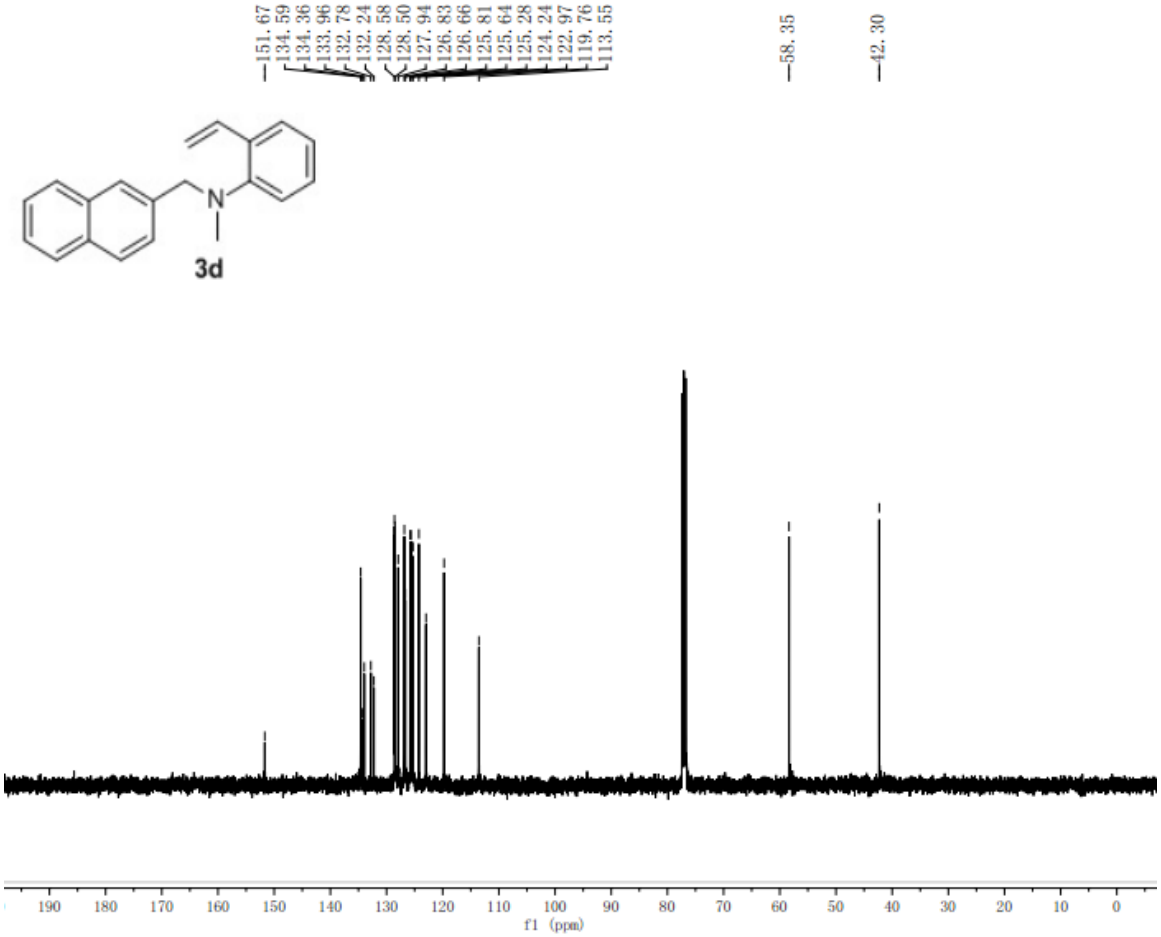
7.5756
7.5466
7.5276
7.4900
7.4727
7.4587
7.4428
7.4257
7.2754
7.2609
7.2571
7.2352
7.2306
7.2134
7.1935
7.1023
7.0861
5.6205
5.1364
5.1090
4.5689
2.6117
0.0000
N
3d
1.04
1.04
0.96
0.97
0.94
3.03
2.18
2.00
1.00
0.94
2.00
3.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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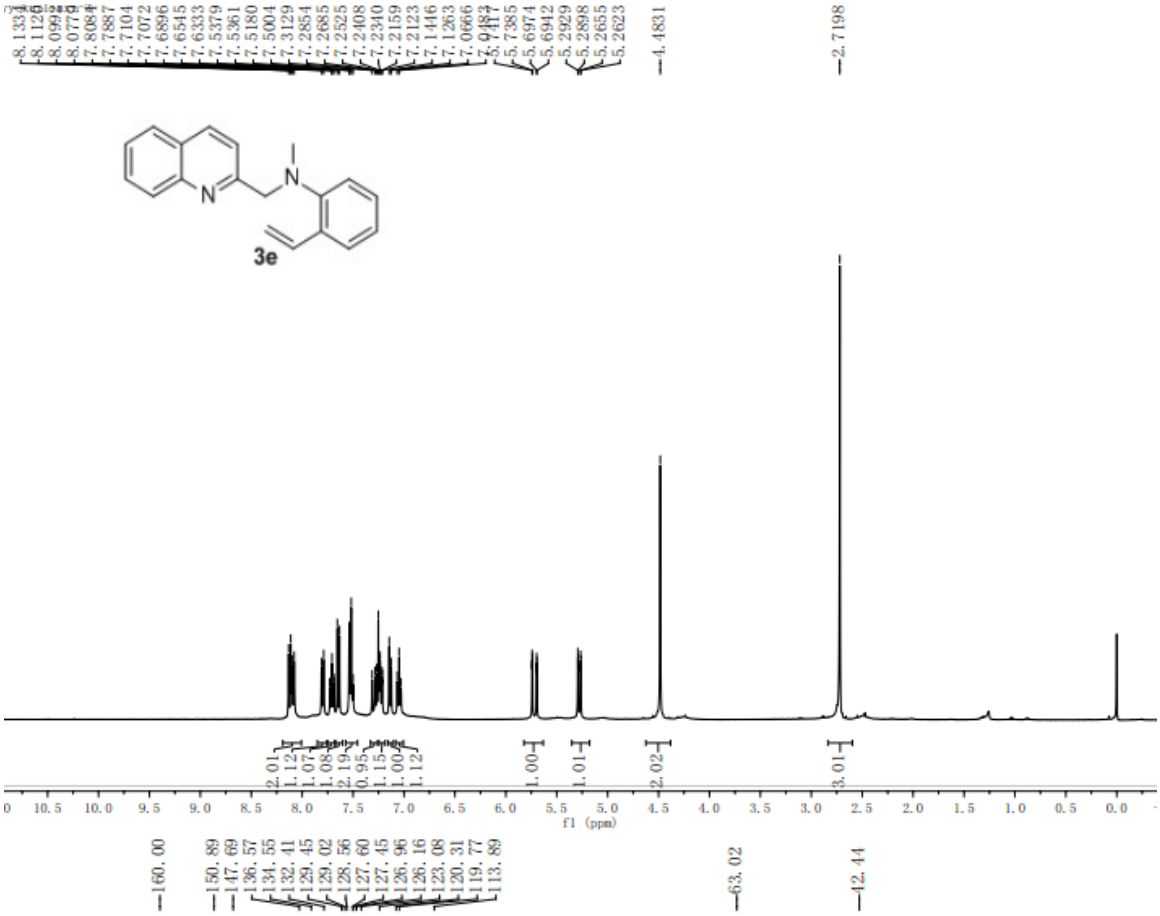
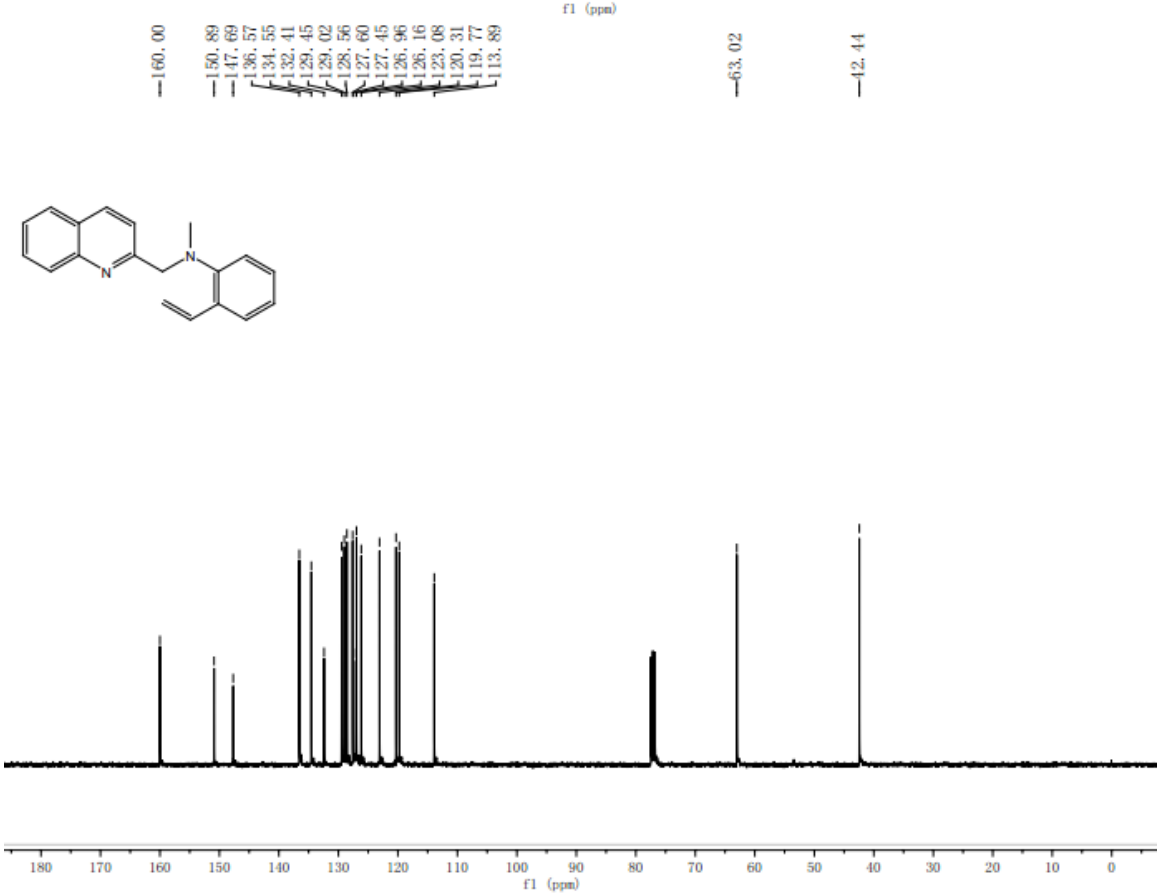
133.96
132.78
132.24
128.58
128.50
127.94
126.83
126.66
125.81
125.64
125.28
124.24
122.97
119.76
113.55
58.35
42.30
N
3d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)





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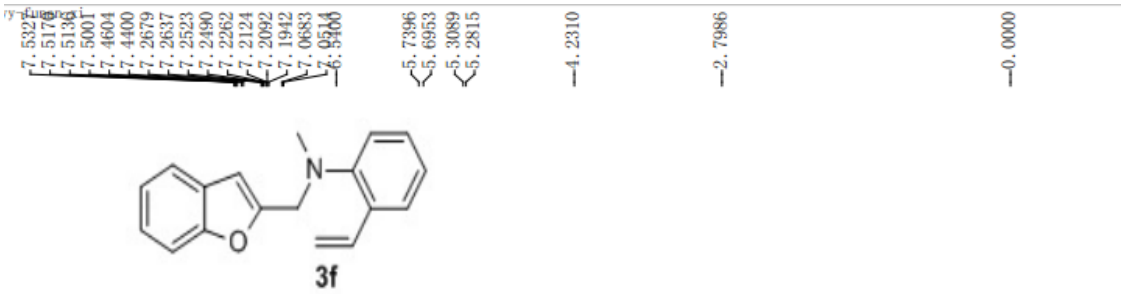
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7.4604
7.4400
7.2679
7.2637
7.2523
7.2490
7.2262
7.2124
7.2092
7.1942
7.0683
7.0514
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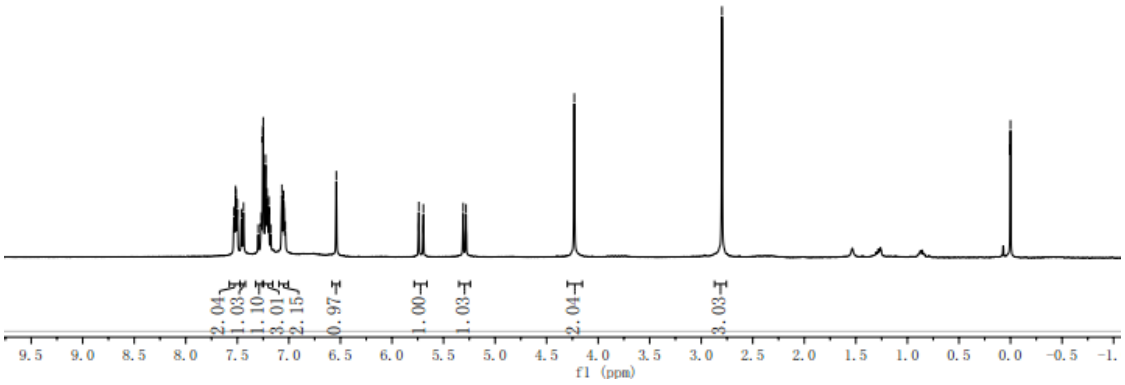
5.6953
5.3089
5.2815
4.2310
2.7986
0.0000
N
O
3f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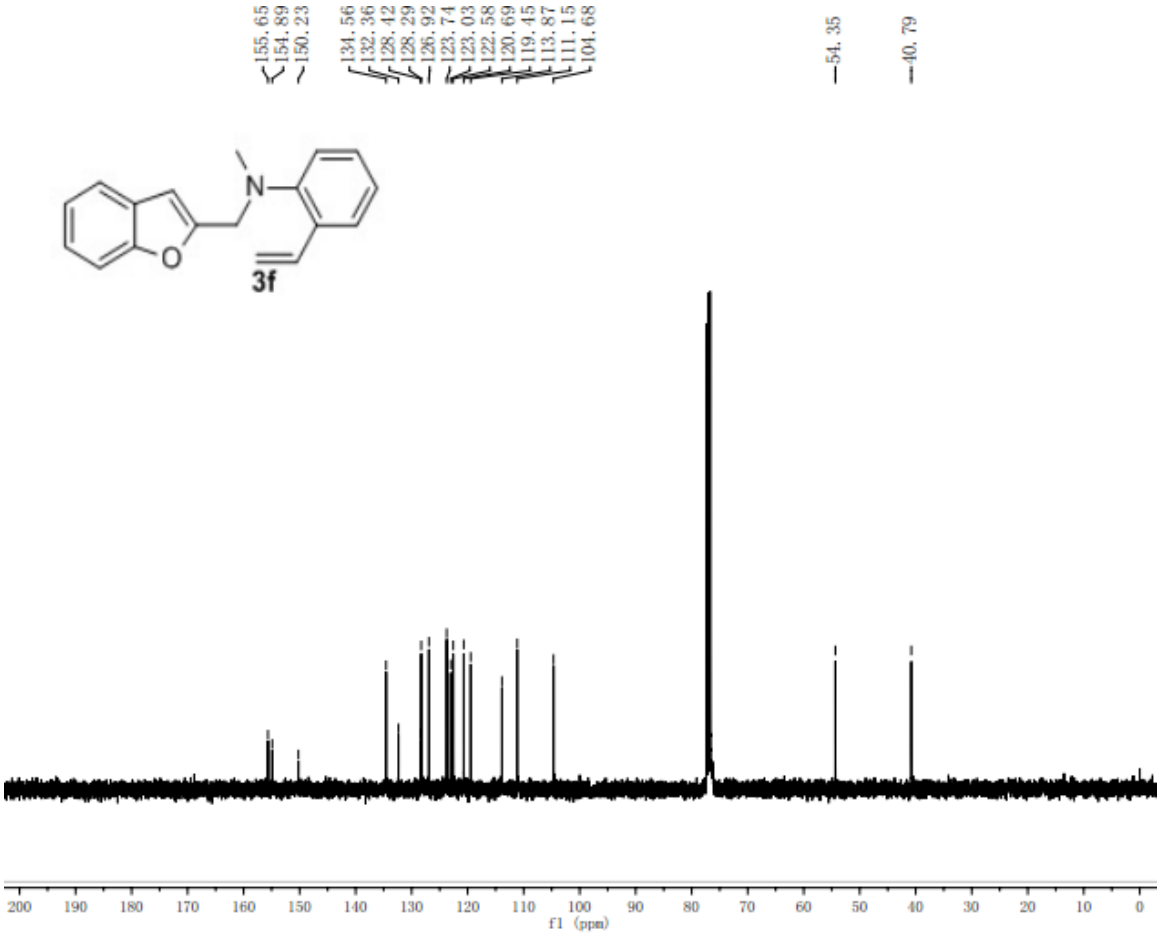
1.03
1.10
3.01
2.15
0.97
1.00
1.03
2.04
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)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128.29
126.92
123.74
123.03
122.58
120.69
119.45
113.87
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54.35
40.79
N
O
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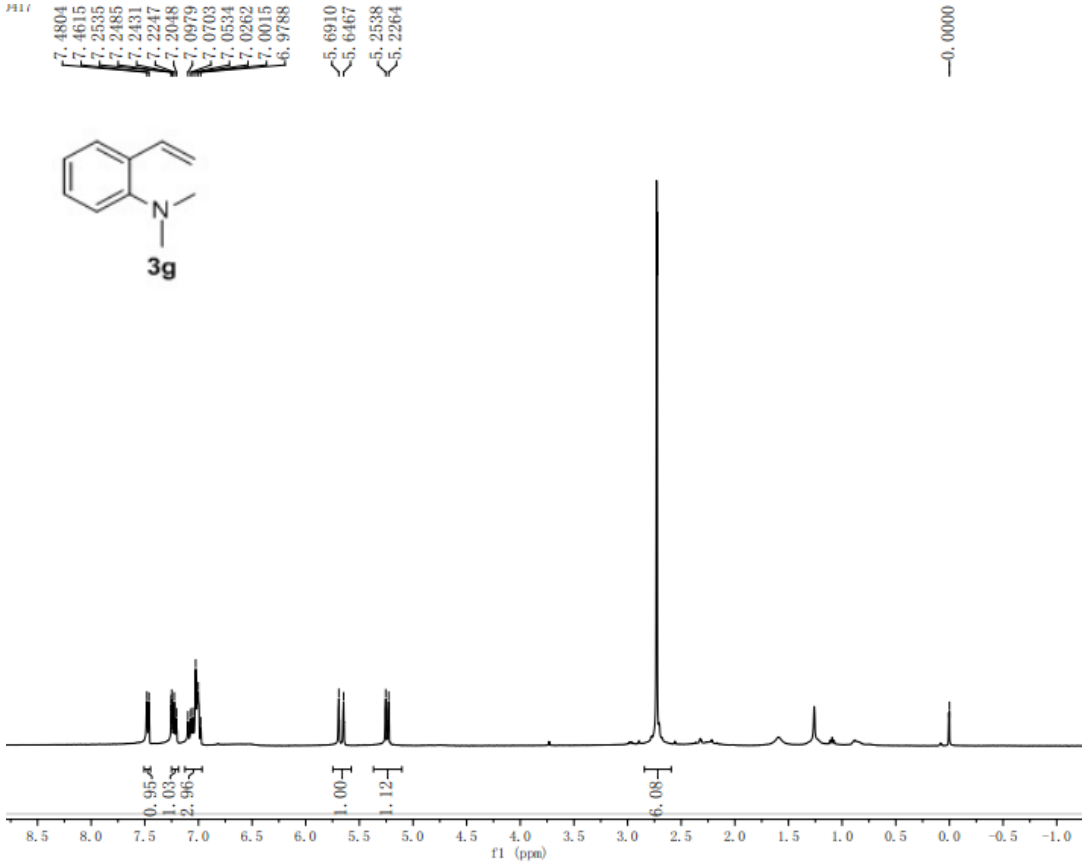
f1 (ppm)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7.2048
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7.0703
7.0534
7.0262
7.0015
6.9788
5.6910
5.6467
5.2538
5.2264
0.0000
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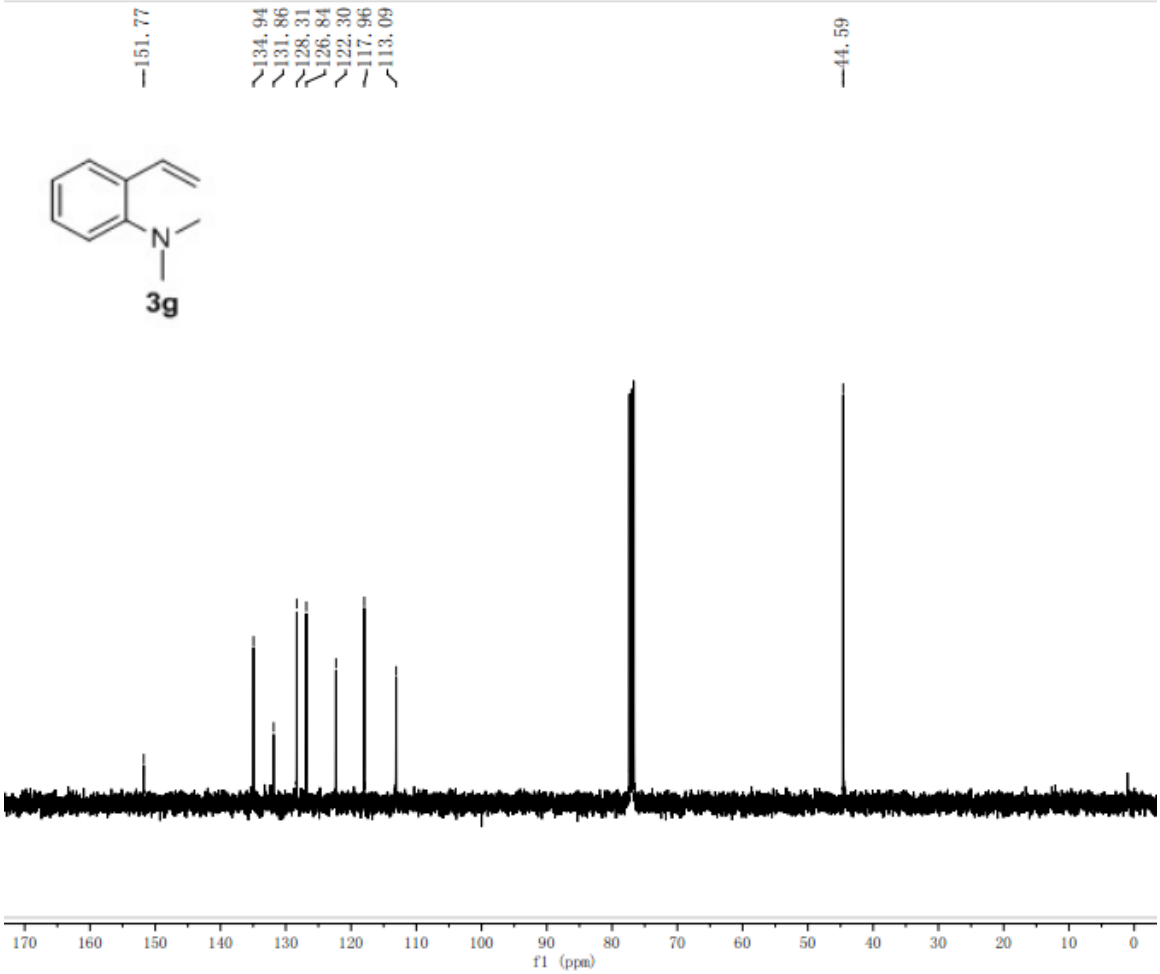
3g
0.95
1.03
2.96
1.00
1.12
6.08
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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113.09
44.59
N
3g
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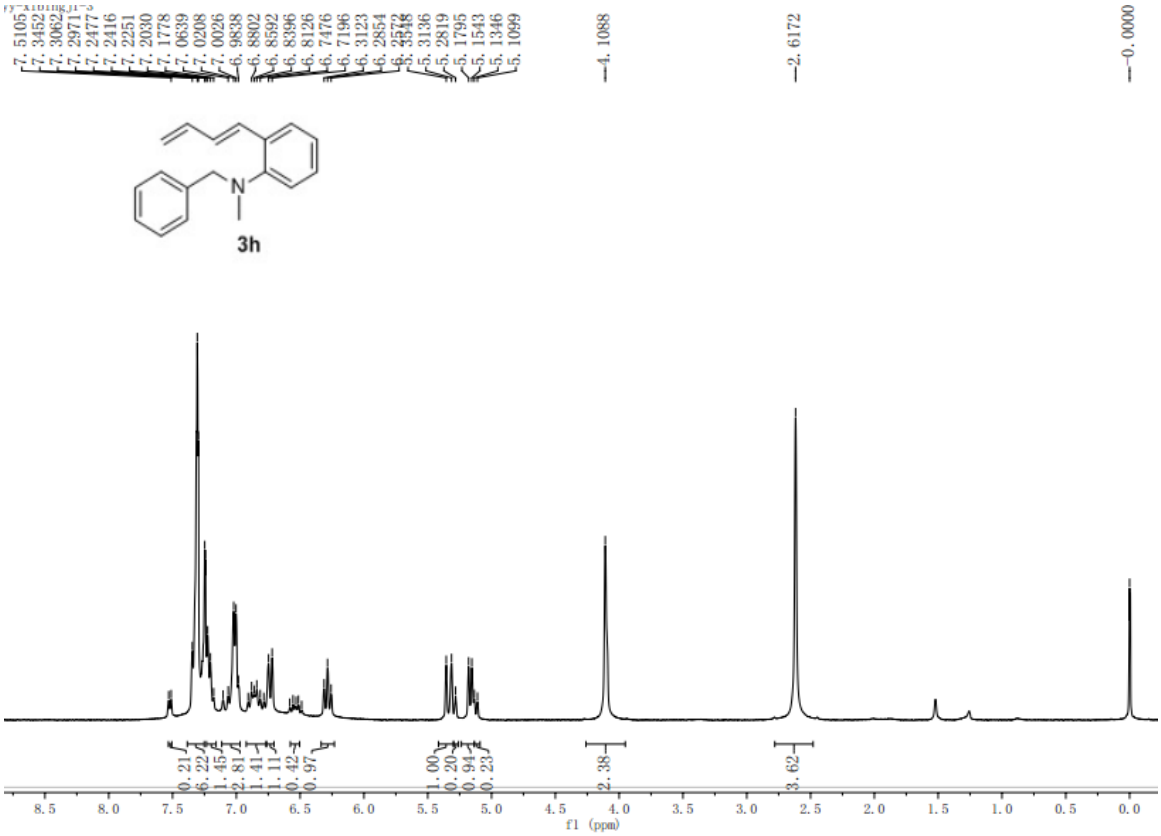
f1 (ppm)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7.1778
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7.0208
7.0026
6.9838
6.8802
6.8592
6.8396
6.8126
6.7476
6.7196
6.3123
6.2854
5.3136
5.2819
5.1795
5.1543
5.1346
5.1099
4.1088
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3h
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6.22
1.45
2.81
1.41
1.11
0.42
0.97
1.00
0.20
0.94
0.23
2.38
3.62
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
2.0
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1.0
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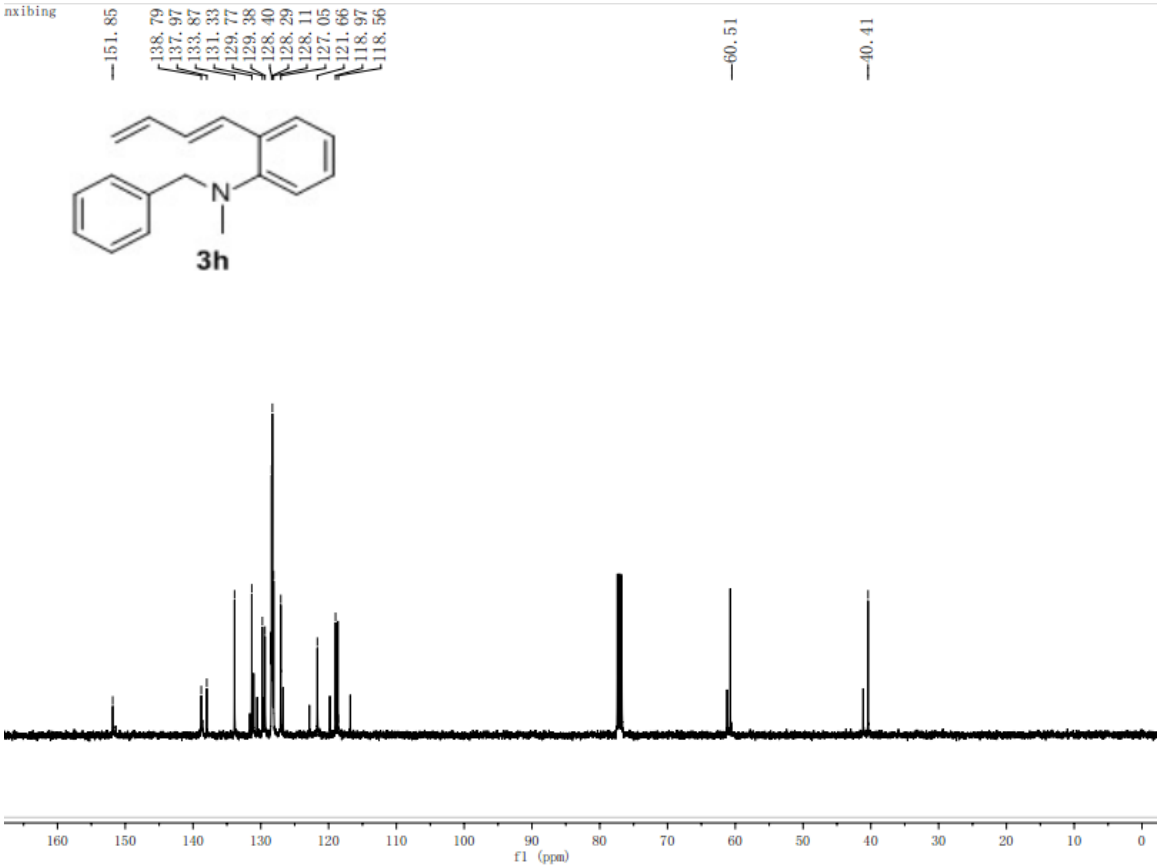
0.0
f1 (ppm)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127.05
121.66
118.97
118.56
60.51
40.41
N
3h
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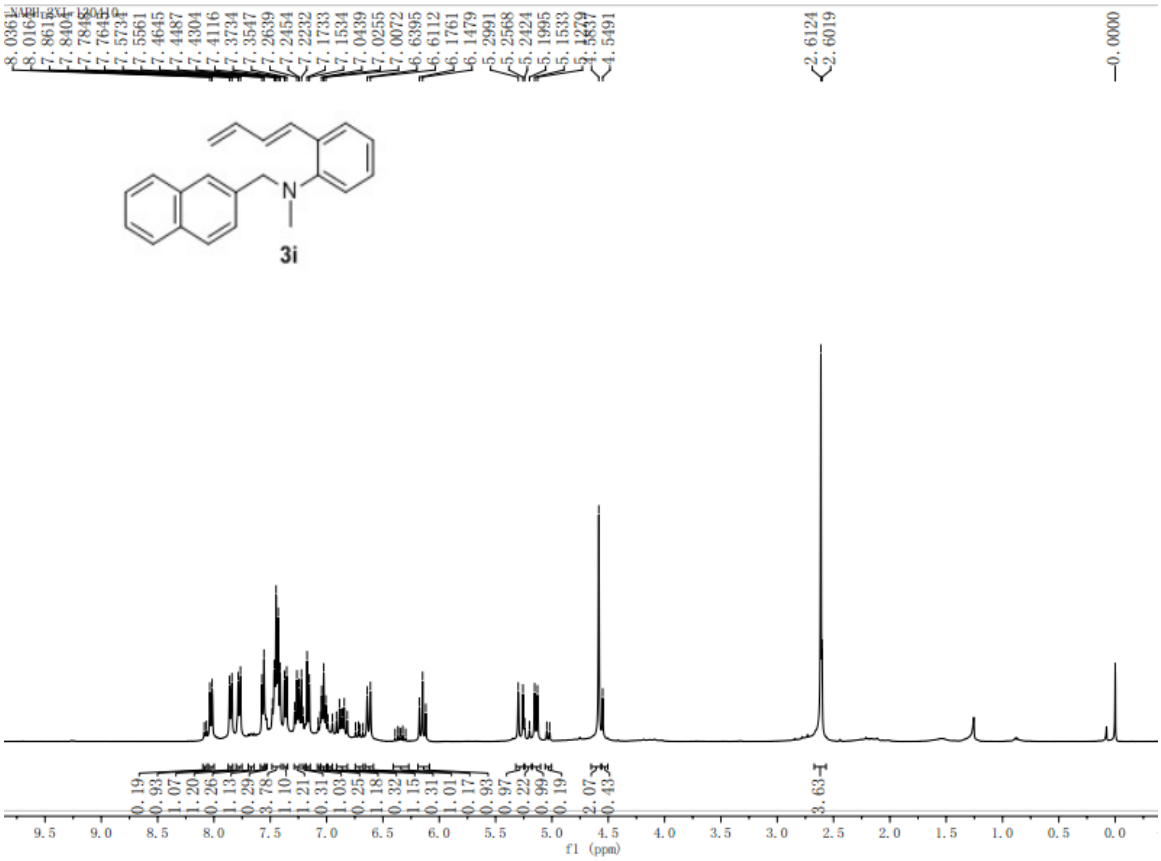
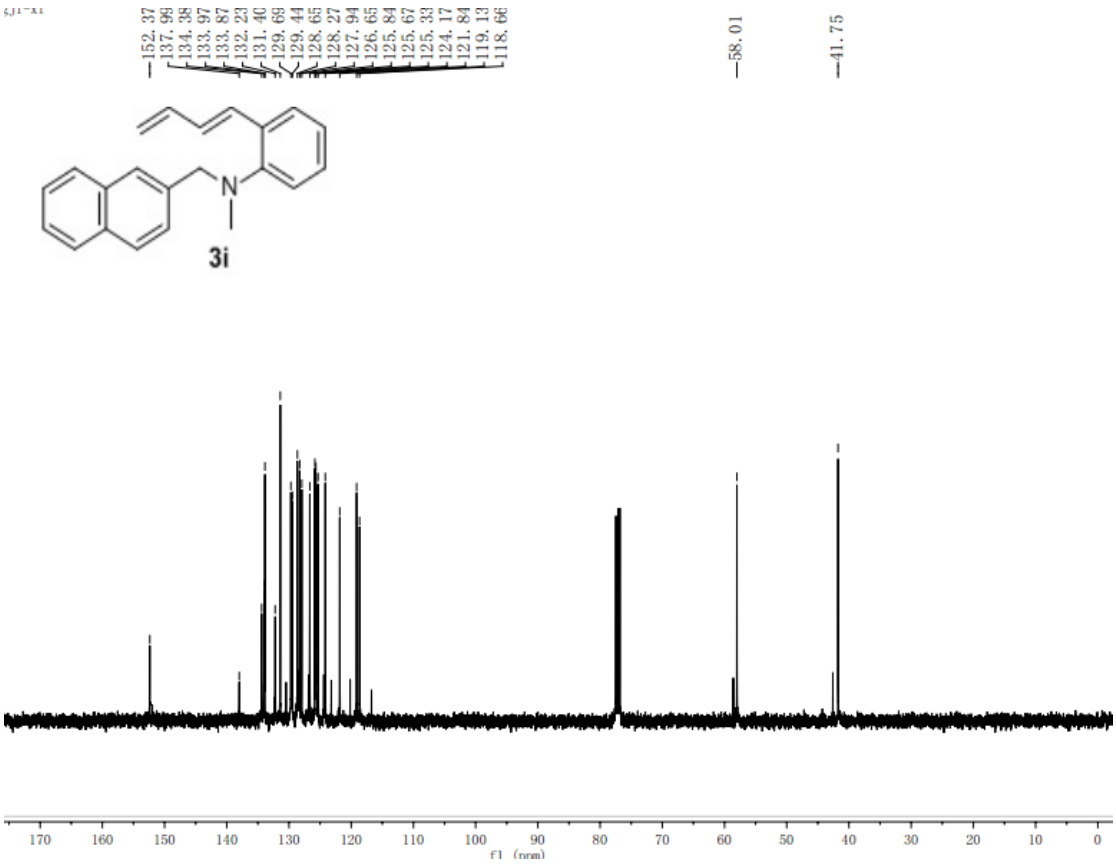
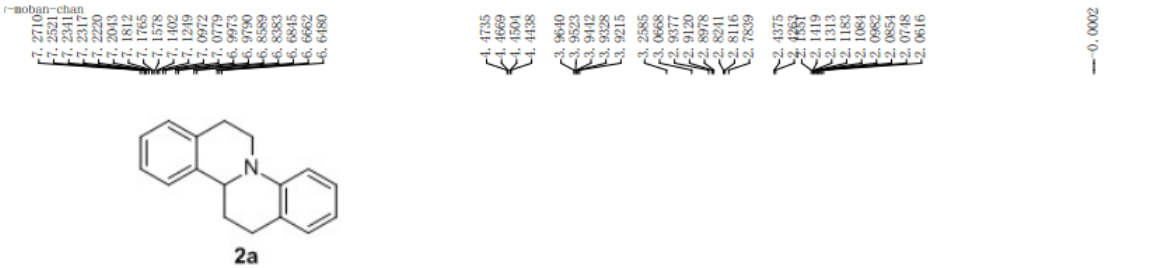
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


3i
f1 (ppm)


3i
f1 (ppm)


r-moban-chan
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7.1402
7.1249
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7.0779
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6.8383
6.6845
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6.6480
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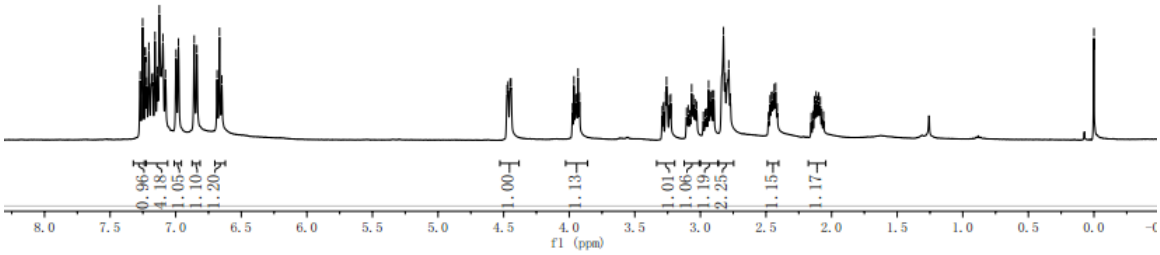
N
2a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1.13
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1.06
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2.25
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1.17
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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3.5
3.0
2.5
2.0
1.5
1.0
0.5
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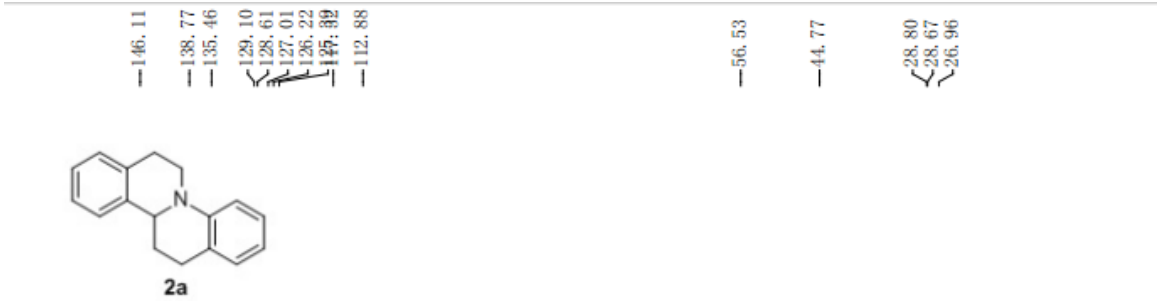
f1 (ppm)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126.22
112.88
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44.77
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26.96
N
2a
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10
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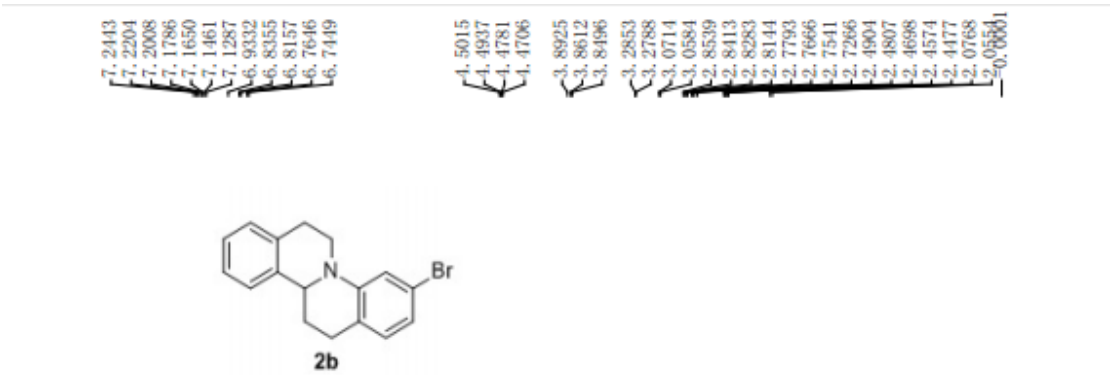
f1 (ppm)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2.7541
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2.4698
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2.0768
2.0554
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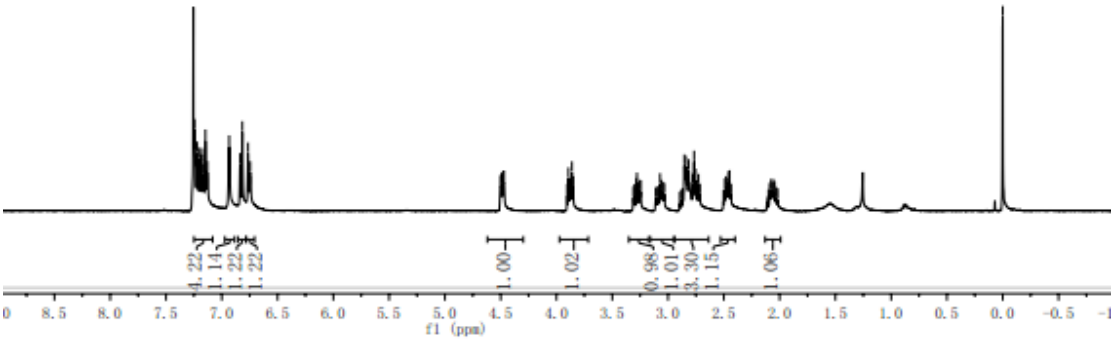
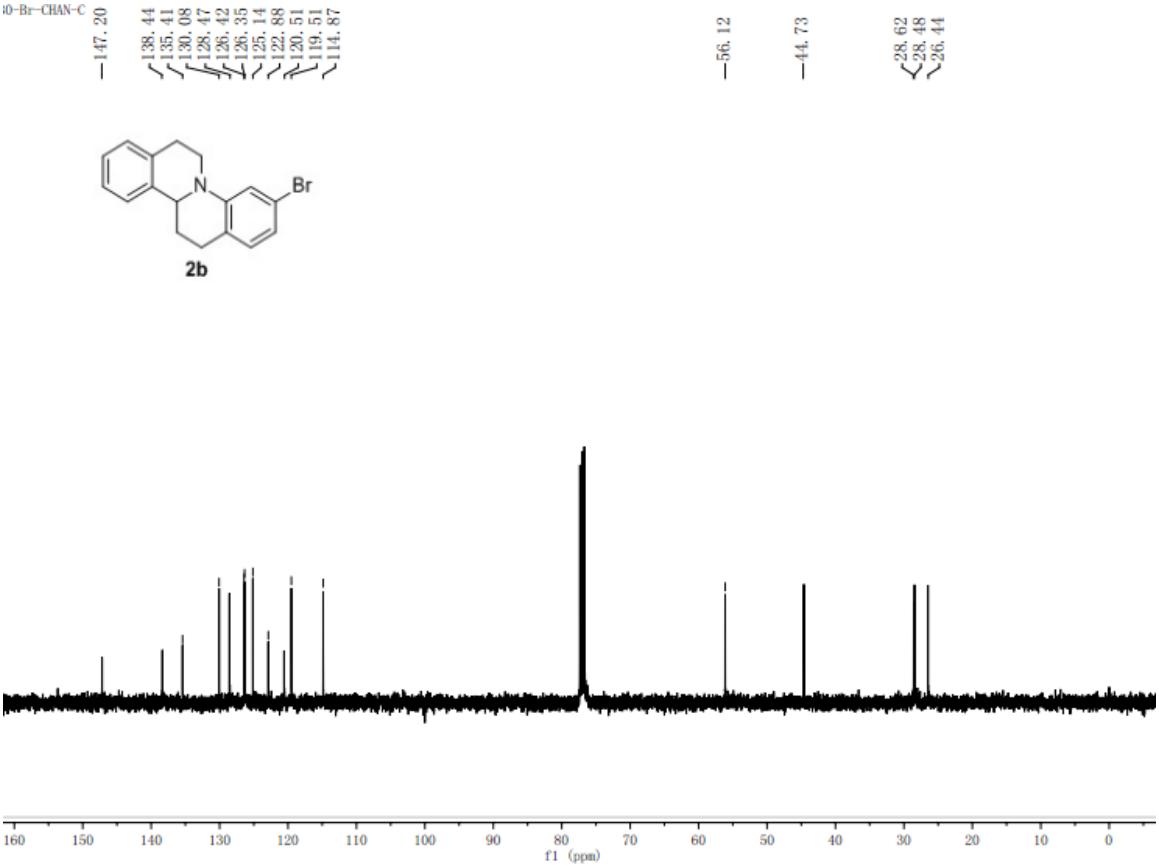
N
Br
2b


4.22
1.14
1.22
1.22
1.22
1.00
1.02
0.98
1.01
3.30
1.15
1.06
f1 (ppm)


0-Br-CHAN-C
147.20
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135.41
130.08
128.47
126.42
126.35
125.14
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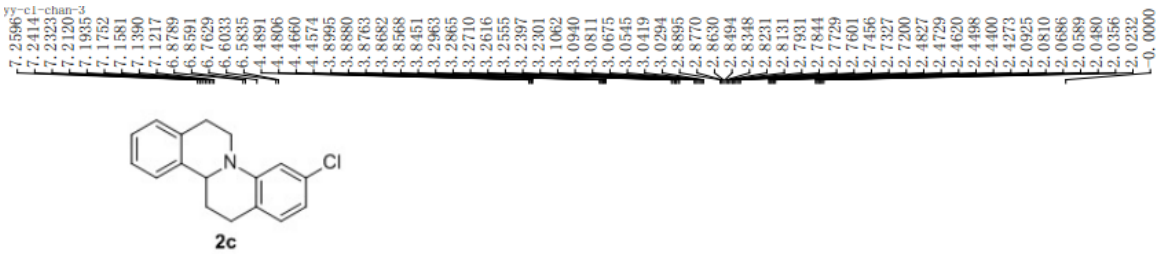
120.51
119.51
114.87
56.12
44.73
28.62
28.48
26.44
N
Br
2b
f1 (ppm)


yy-c1-chan-3
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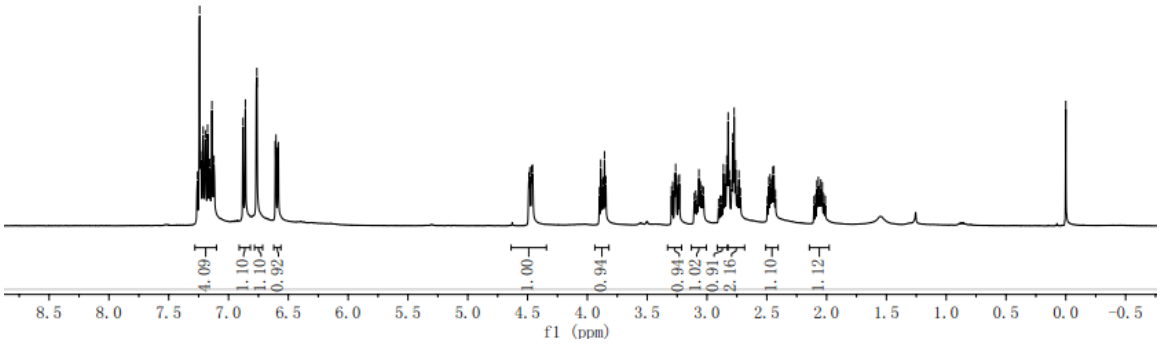
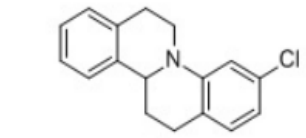
Cl

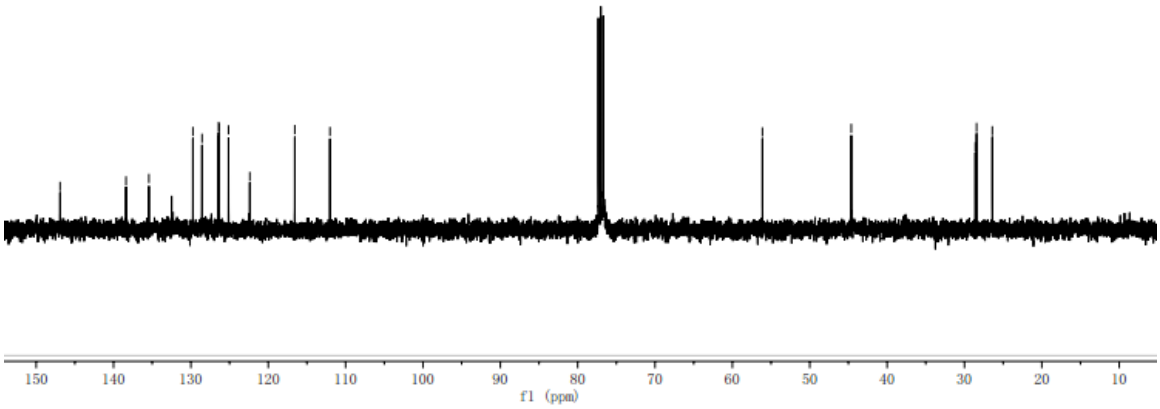
2c


4.09
1.10
1.10
0.92
1.00
0.94
0.94
1.02
0.91
2.16
1.10
1.12
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

146.91
138.39
135.43
132.28
129.74
128.56
126.41
126.34
125.14
122.38
116.57
112.02
56.12
44.63
28.60
28.43
26.40


N
Cl

2c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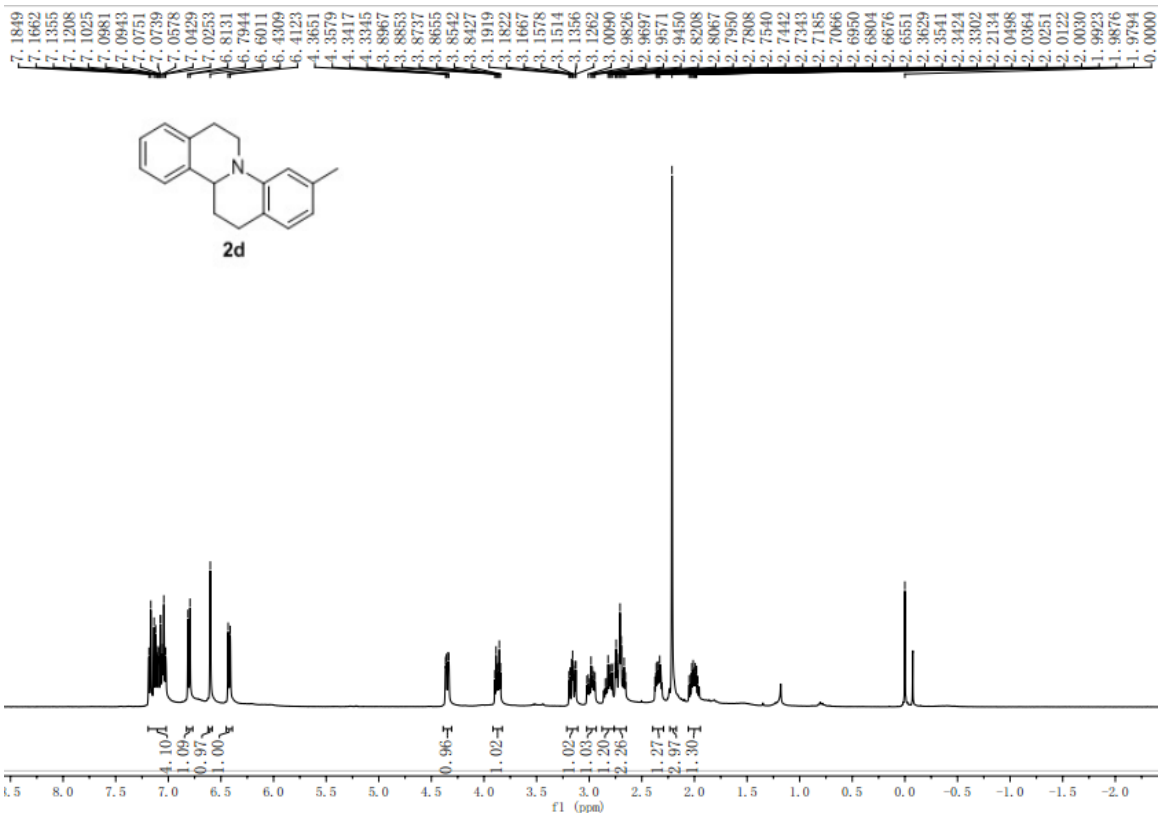
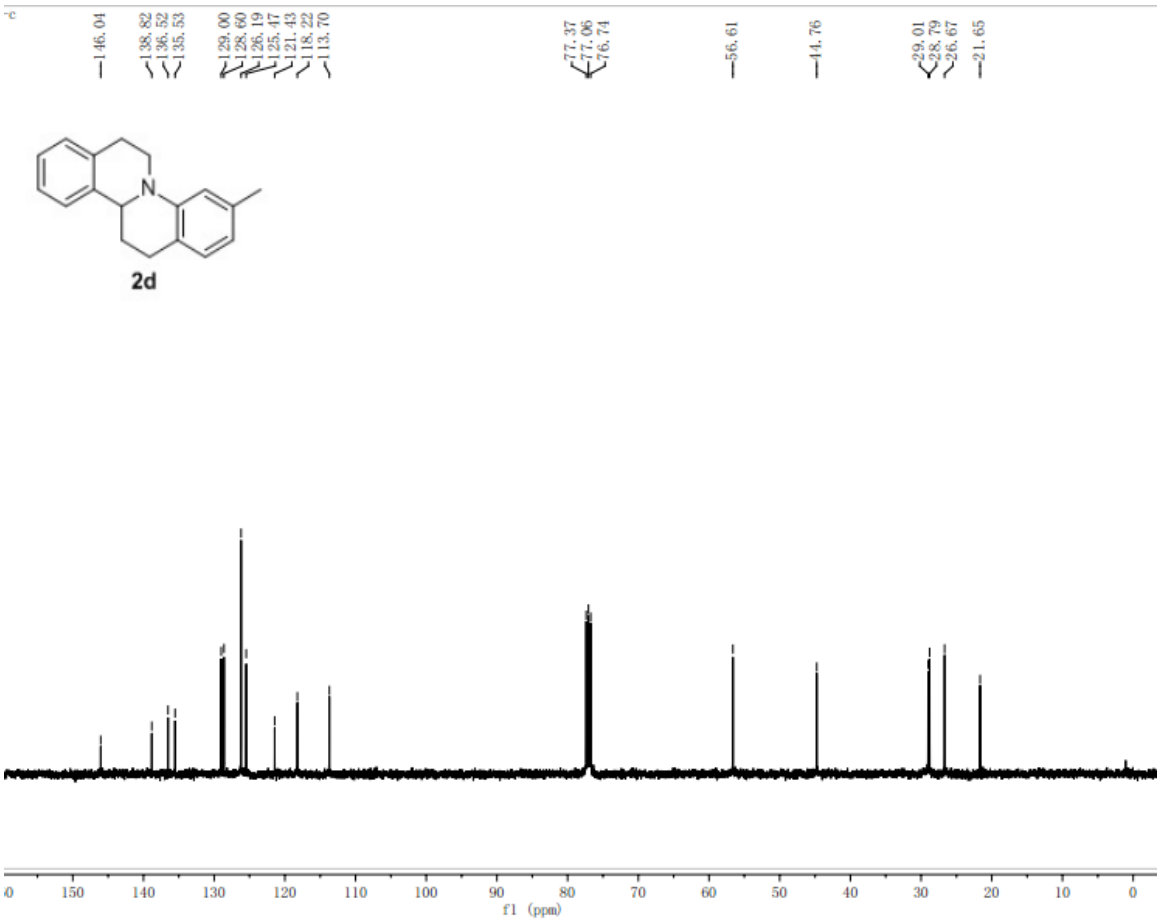
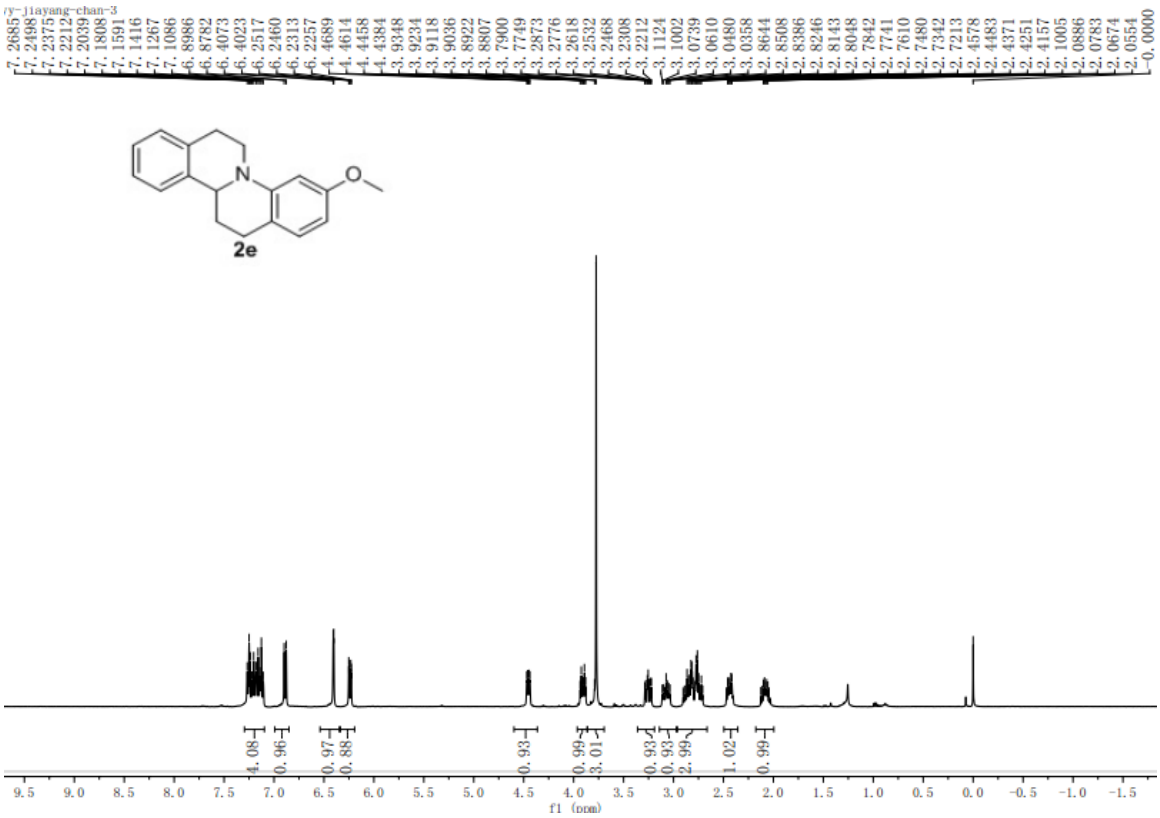
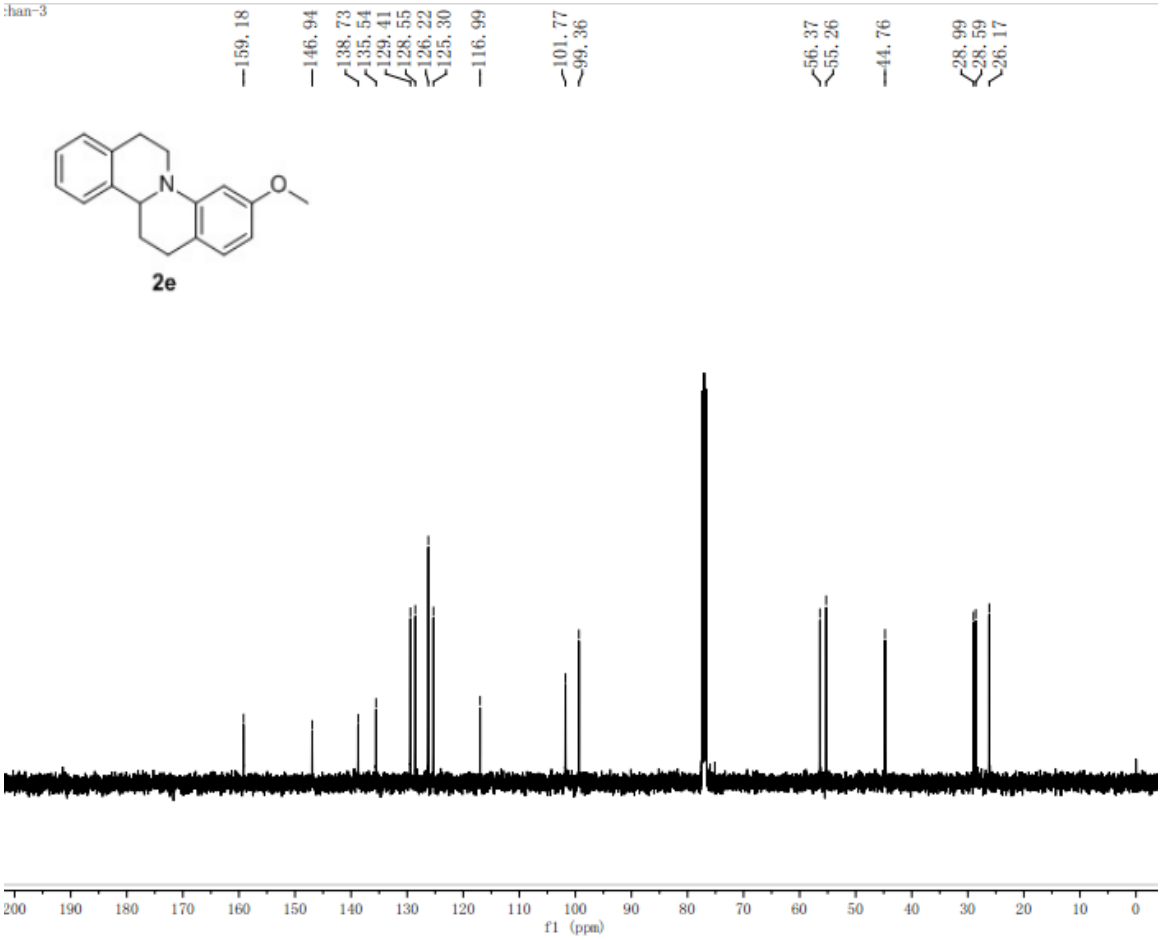
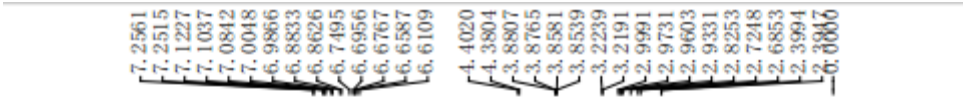
f1 (ppm)


2d
f1 (ppm)


2d
f1 (ppm)


2e
f1 (ppm)


2e
f1 (ppm)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7.1037
7.0842
7.0018
6.9866
6.8833
6.8626
6.7495
6.6956
6.6767
6.6587
6.6109
4.4020
4.3804
3.8807
3.8765
3.8581
3.8539
3.2239
3.2191
2.9991
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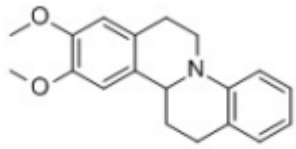
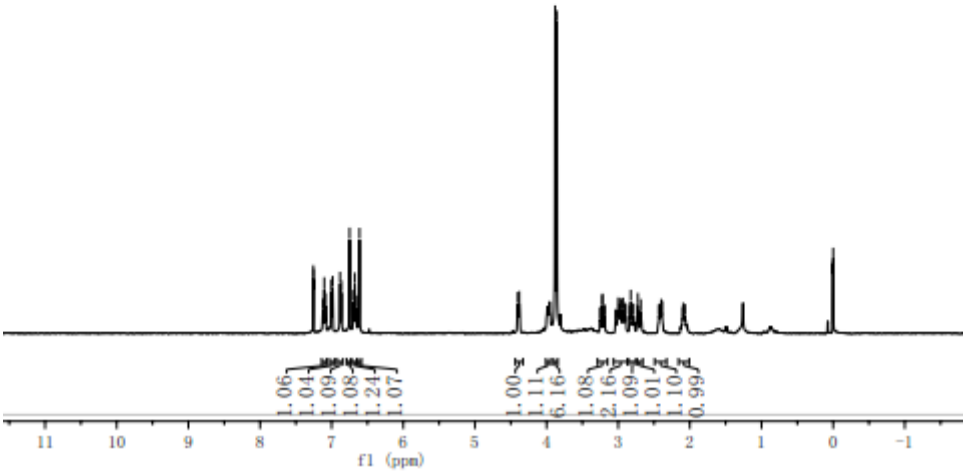
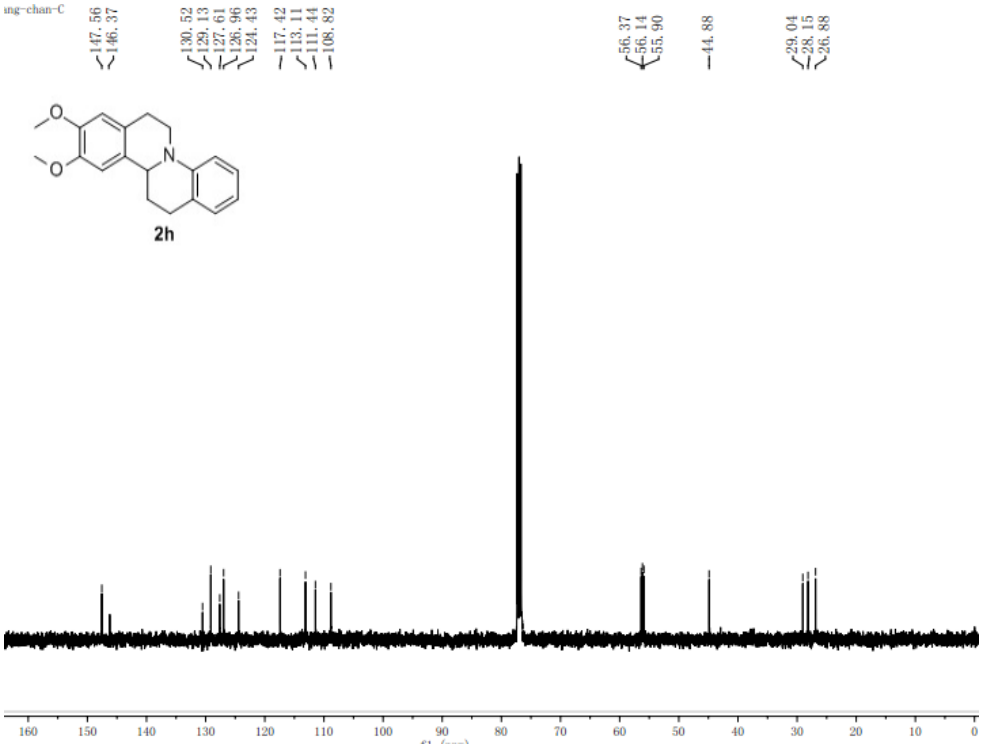
2.9603
2.9331
2.8253
2.7218
2.6853
2.3994
2.3847
0.0000



2h


1.06
1.04
1.09
1.08
1.24
1.07
1.00
1.11
6.16
1.08
2.16
1.09
1.01
1.10
0.99
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


ang-chan-C
147.56
146.37
130.52
129.13
127.61
126.96
124.43
117.42
113.11
111.44
108.82
56.37
56.14
55.90
44.88
29.04
28.15
26.88
160
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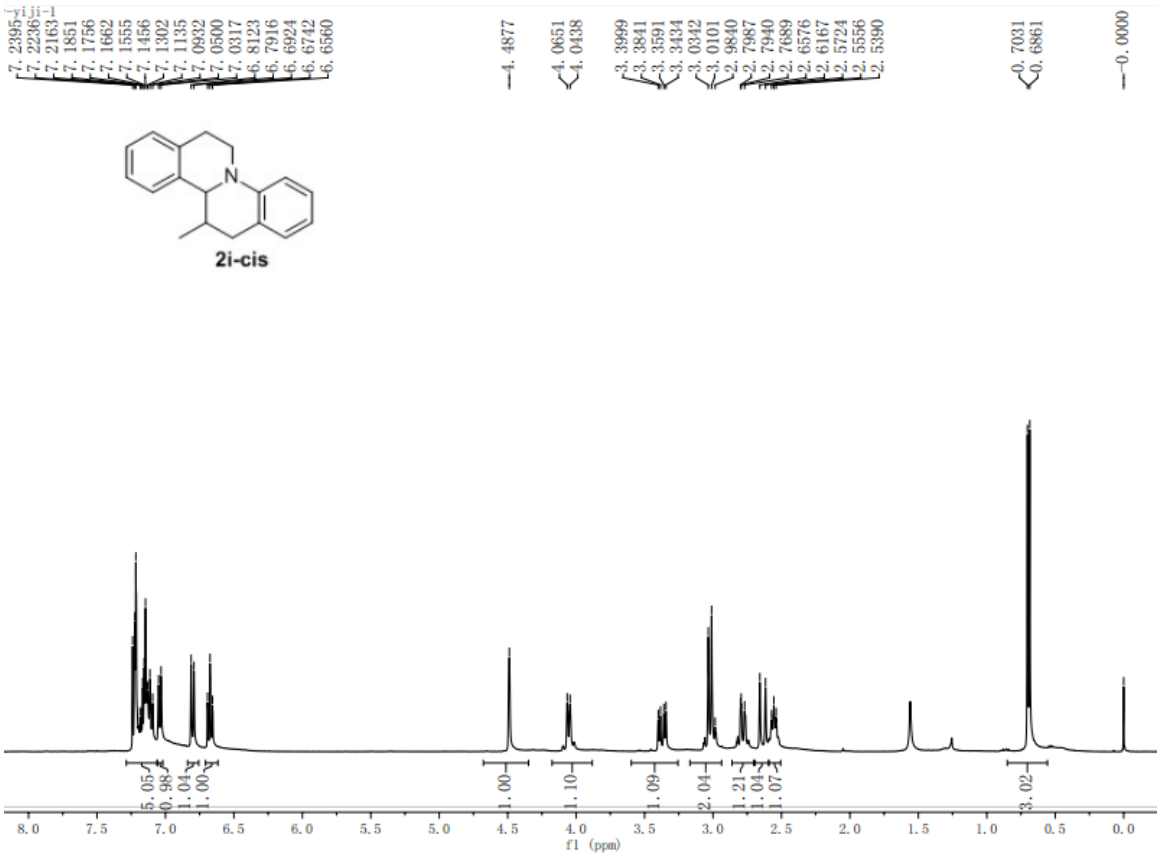
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

2h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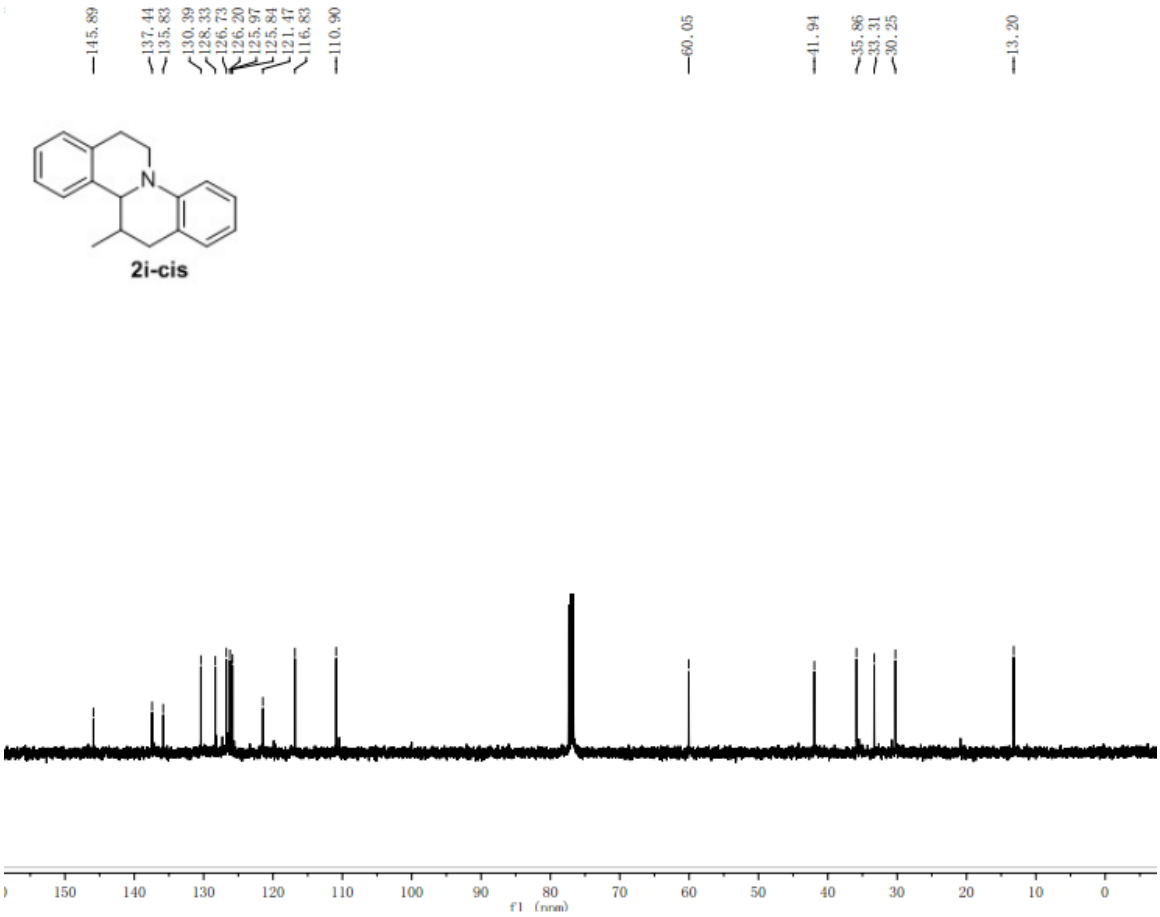
7.2236
7.2163
7.1851
7.1756
7.1662
7.1555
7.1456
7.1302
7.1135
7.0932
7.0500
7.0317
6.8123
6.7916
6.6924
6.6742
6.6560
4.4877
4.0651
4.0438
3.3999
3.3841
3.3591
3.3434
3.0342
3.0101
2.9840
2.7987
2.7940
2.7689
2.6576
2.6167
2.5724
2.5556
2.5390
0.7031
0.6861
0.0000
N
2i-cis
5.05
0.98
1.04
1.00
1.00
1.10
1.09
2.04
1.21
1.04
1.07
3.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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135.83
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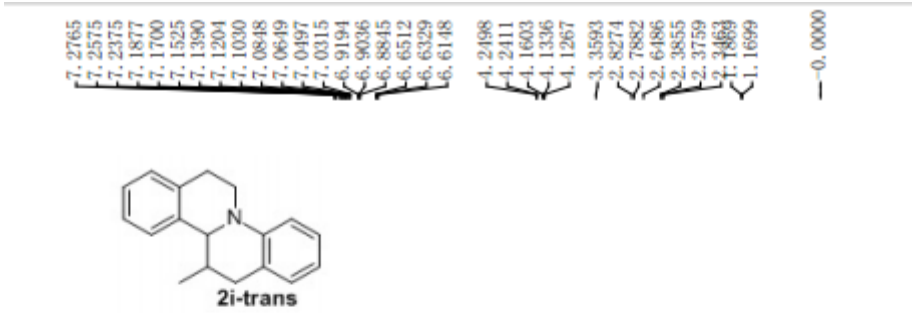
128.33
126.73
126.20
125.97
125.84
121.47
116.83
110.90
60.05
41.94
35.86
33.31
30.25
13.20
N
2i-cis
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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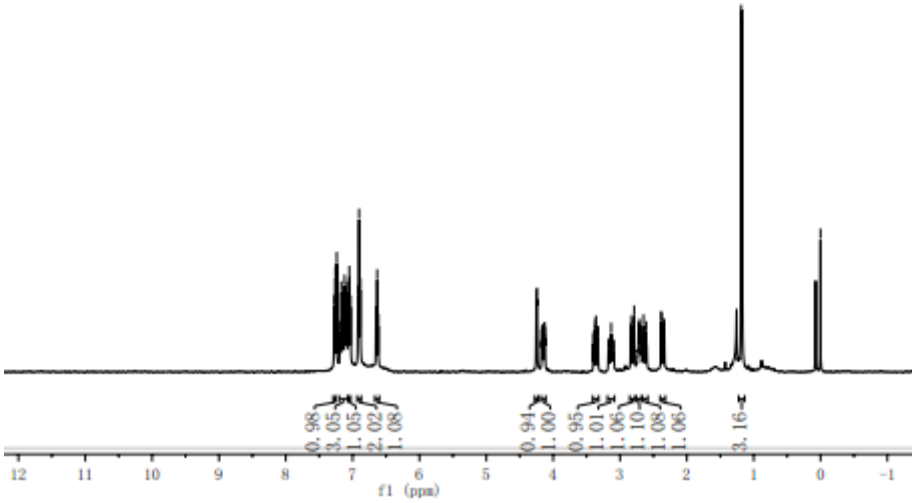
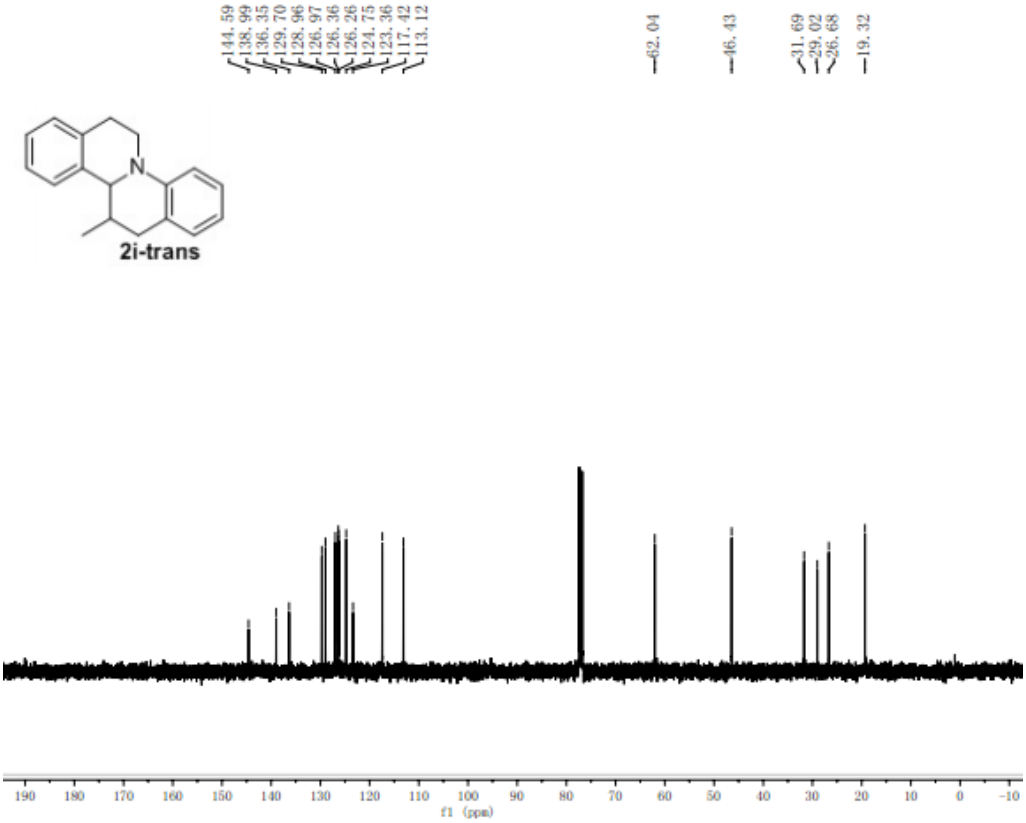
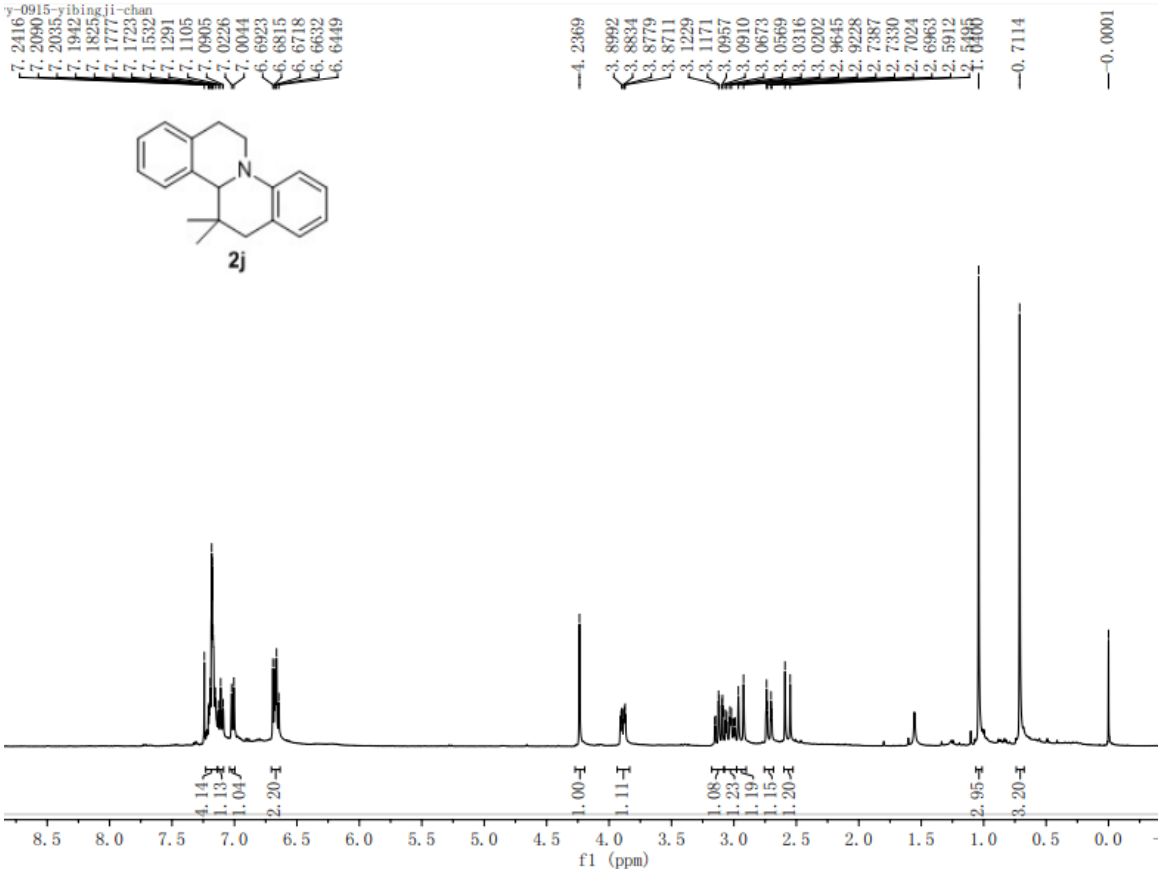
7.2375
7.1877
7.1700
7.1525
7.1390
7.1204
7.1030
7.0848
7.0649
7.0497
7.0315
6.9194
6.9036
6.8845
6.6512
6.6329
6.6148
4.2498
4.2411
4.1603
4.1336
4.1267
3.3593
2.8274
2.7882
2.6486
2.3855
2.3759
1.1699
-0.0000
N
2i-trans


0.98
3.05
1.05
2.02
1.08
0.94
1.00
0.95
1.01
1.06
1.10
1.08
1.06
3.16
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


144.59
138.99
136.35
129.70
128.96
126.97
126.36
126.26
124.75
123.36
117.42
113.12
62.04
46.43
31.69
29.02
26.68
19.32
N
2i-trans
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


y-0915-yibingji-chan
7.2416
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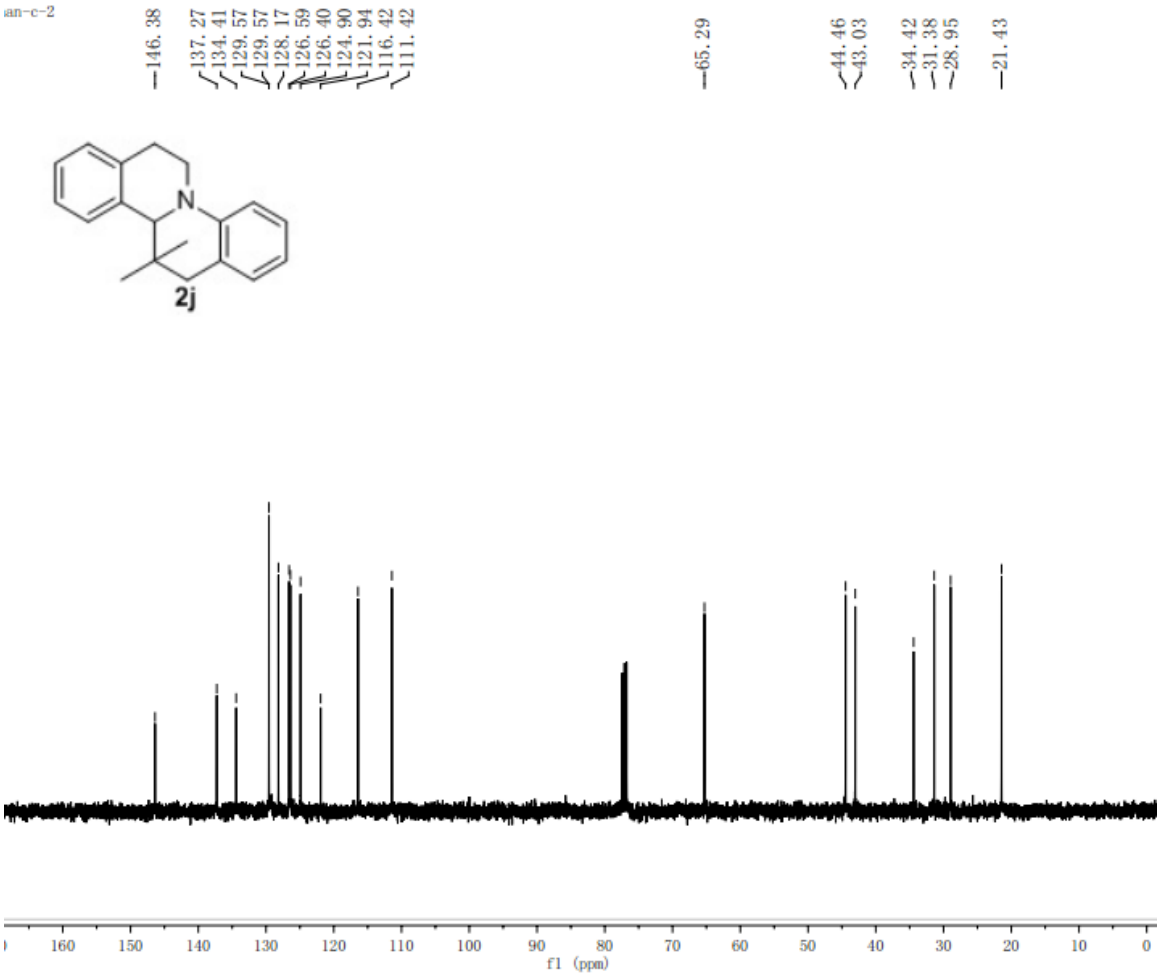
7.2035
7.1942
7.1825
7.1777
7.1723
7.1532
7.1291
7.1105
7.0905
7.0226
7.0044
6.6923
6.6815
6.6718
6.6632
6.6449
4.2369
3.8992
3.8834
3.8779
3.8711
3.1229
3.1171
3.0957
3.0910
3.0673
3.0569
3.0316
3.0202
2.9645
2.9228
2.7387
2.7330
2.7024
2.6963
2.5912
0.7114
0.0001
N
2j
4.14
1.13
1.04
2.20
1.00
1.11
1.08
1.23
1.19
1.15
1.20
2.95
3.20
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


an-c-2
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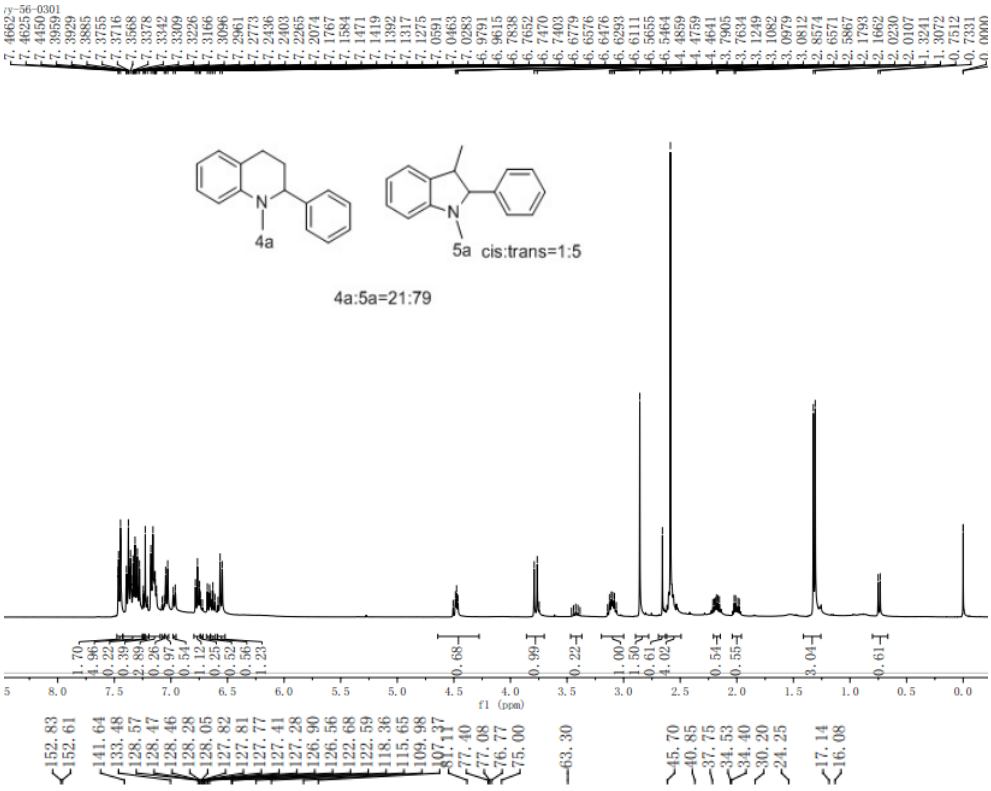
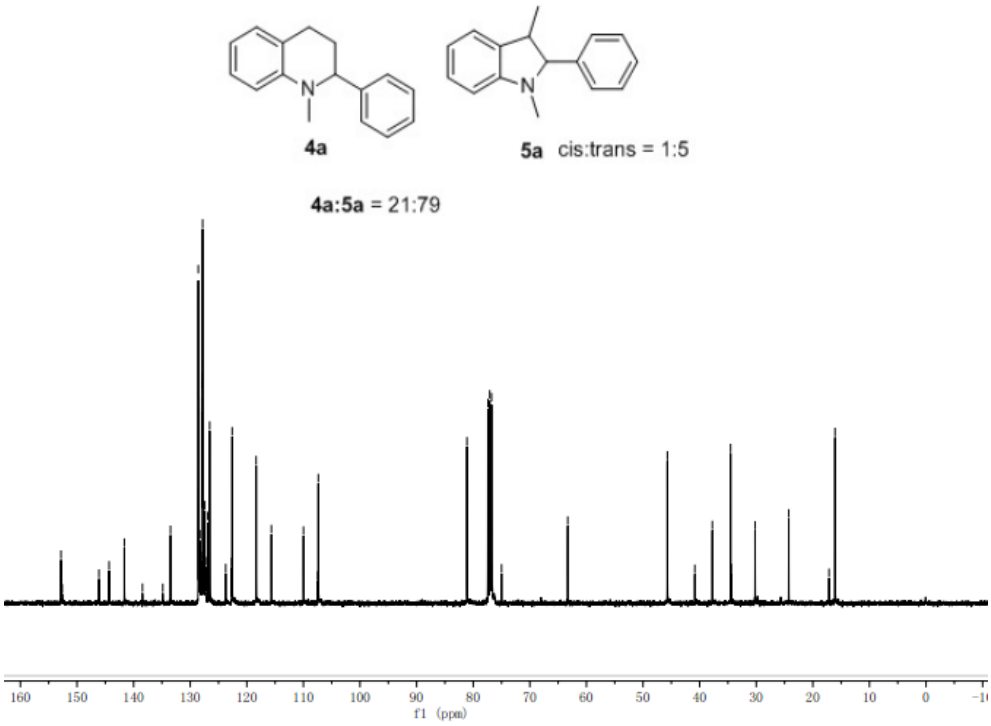
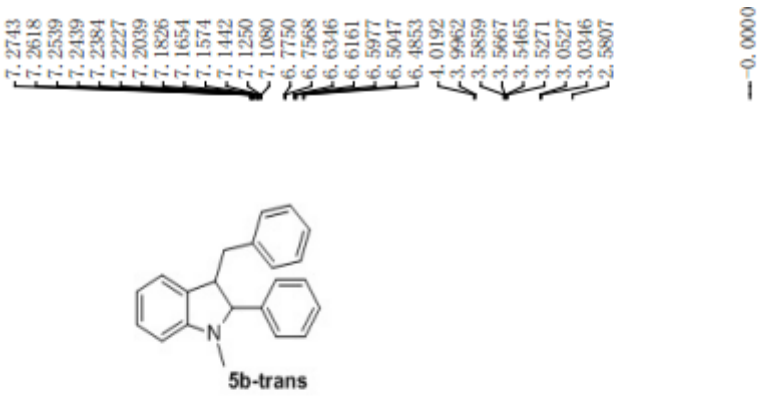
134.41
129.57
129.57
128.17
126.59
126.40
124.90
121.94
116.42
111.42
65.29
44.46
43.03
34.42
31.38
28.95
21.43
N
2j
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


4a
5a cis:trans=1:5
4a:5a=21:79
f1 (ppm)


4a
5a cis:trans = 1:5
4a:5a = 21:79
f1 (ppm)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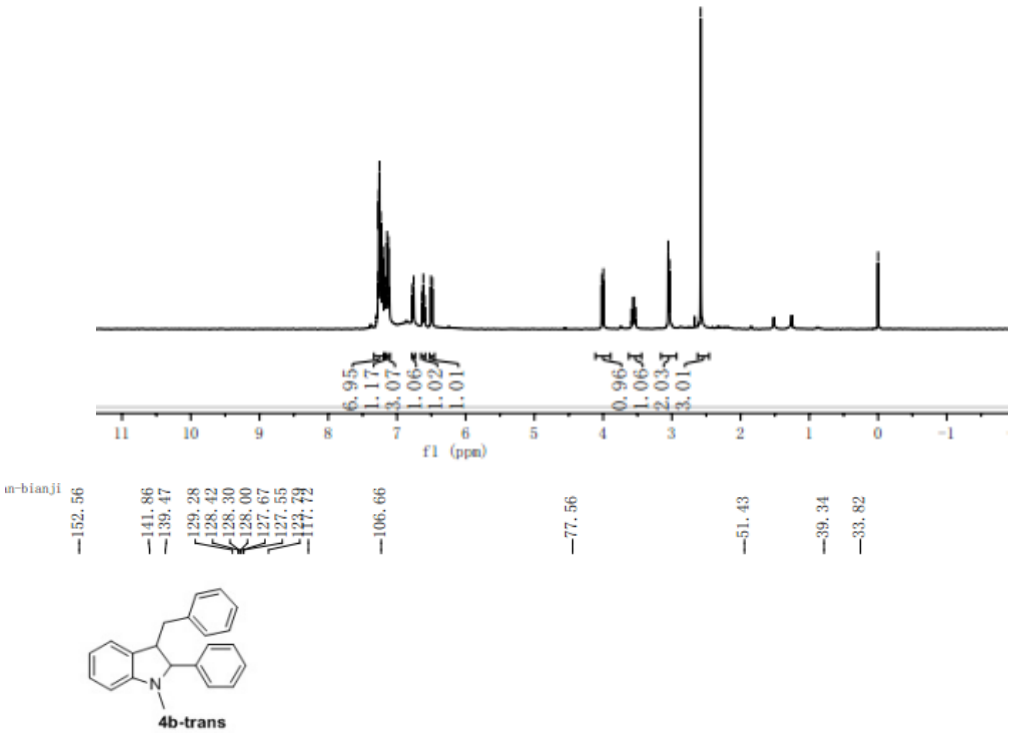
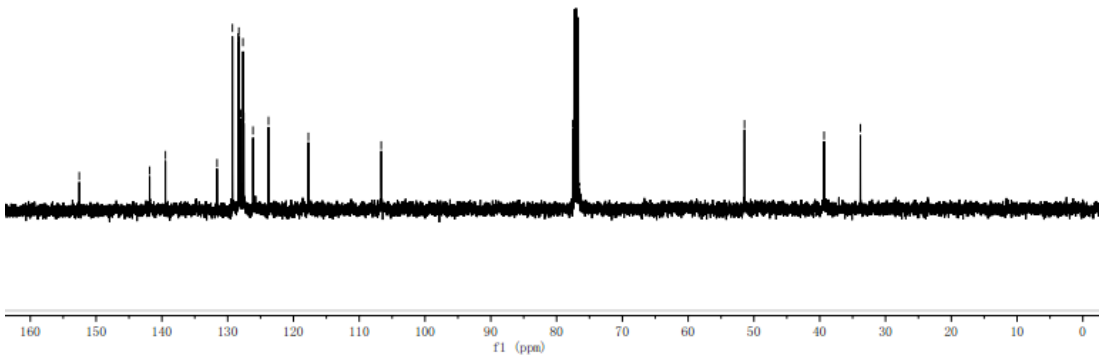
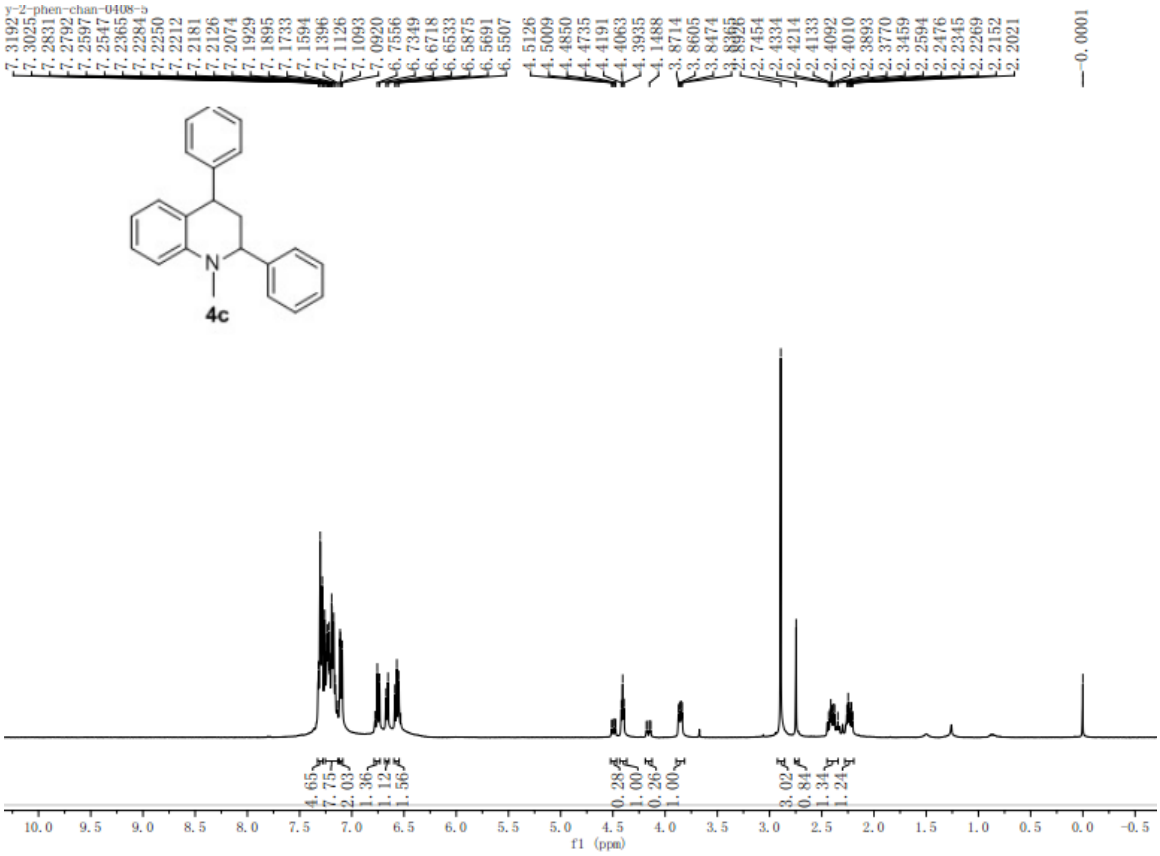
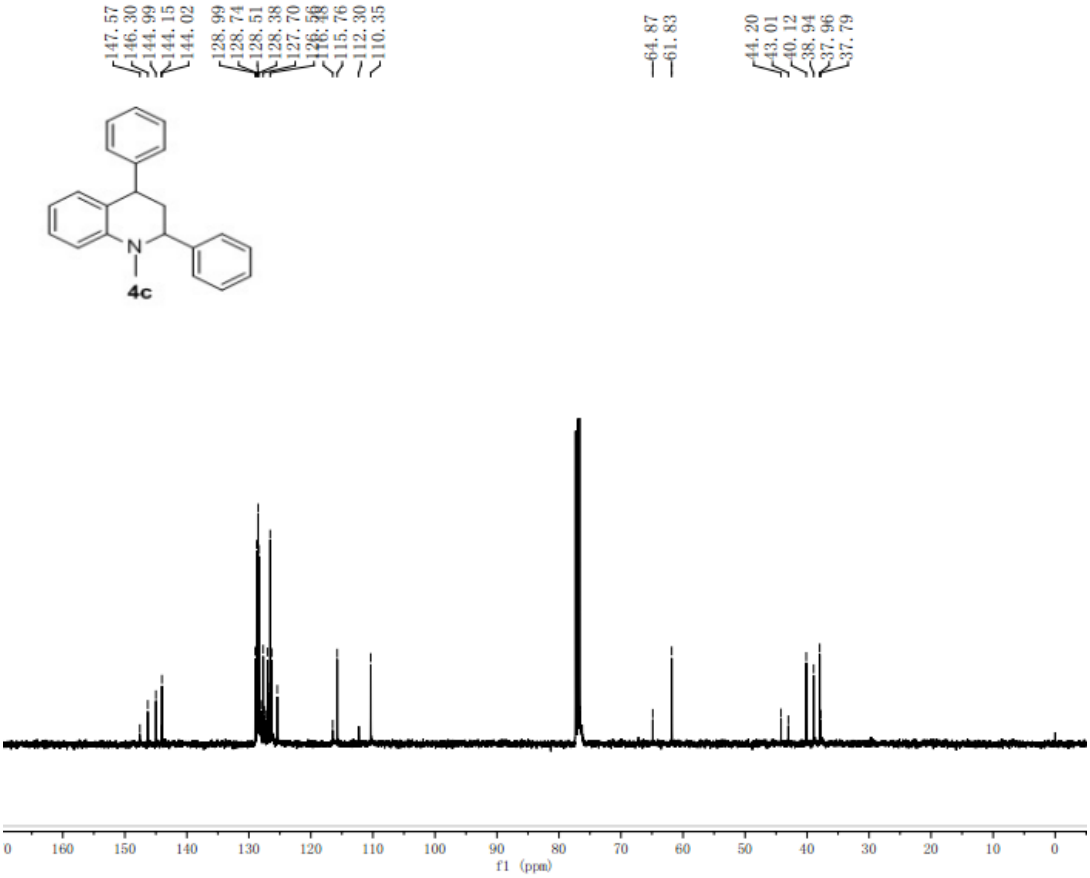
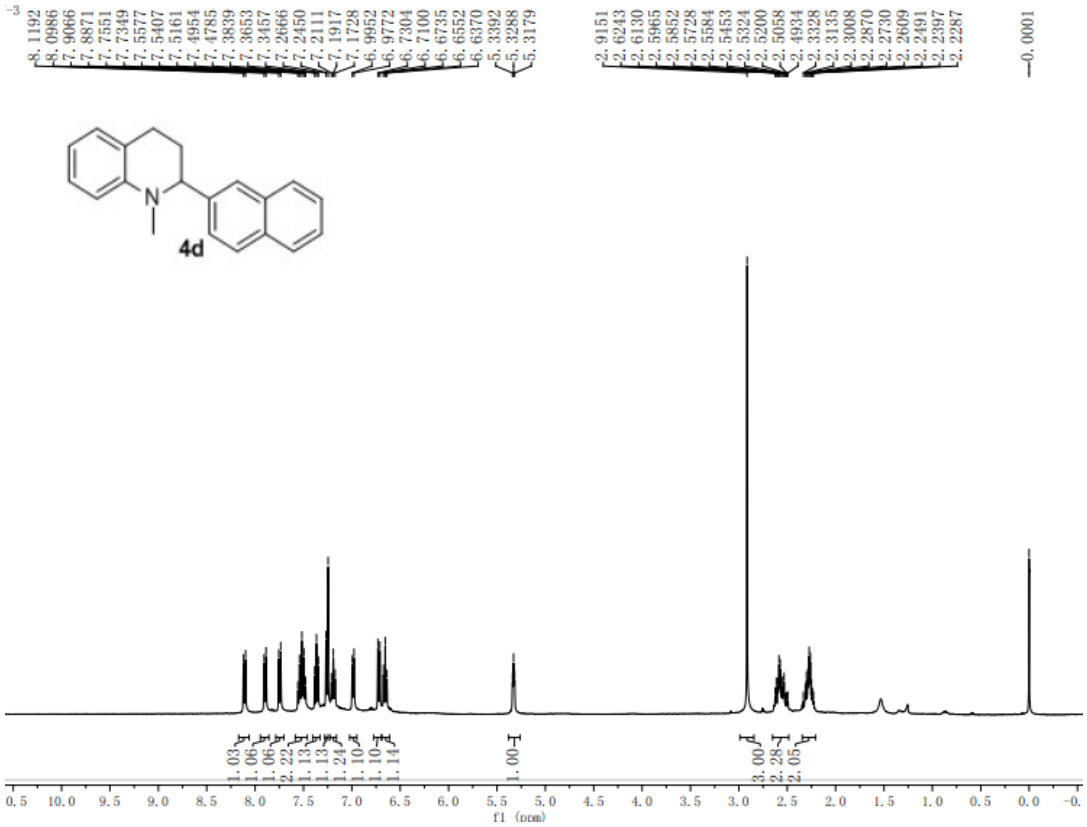
7.2539
7.2439
7.2384
7.2227
7.2039
7.1826
7.1654
7.1574
7.1442
7.1250
7.1080
6.7750
6.7568
6.6346
6.6161
6.5977
6.5047
6.4853
4.0192
3.9962
3.5859
3.5667
3.5465
3.5271
3.0527
3.0346
2.5807
0.0000
N
5b-trans


6.95
1.17
3.07
1.06
1.02
1.01
0.96
1.06
2.03
3.01
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)
m-bianji
152.56
141.86
139.47
129.28
128.42
128.30
128.00
127.67
127.55
123.79
117.72
106.66
77.56
51.43
39.34
33.82
N
4b-trans


160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


y-2-phen-chan-0408-5
4c
f1 (ppm)


4c
f1 (ppm)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7.7551
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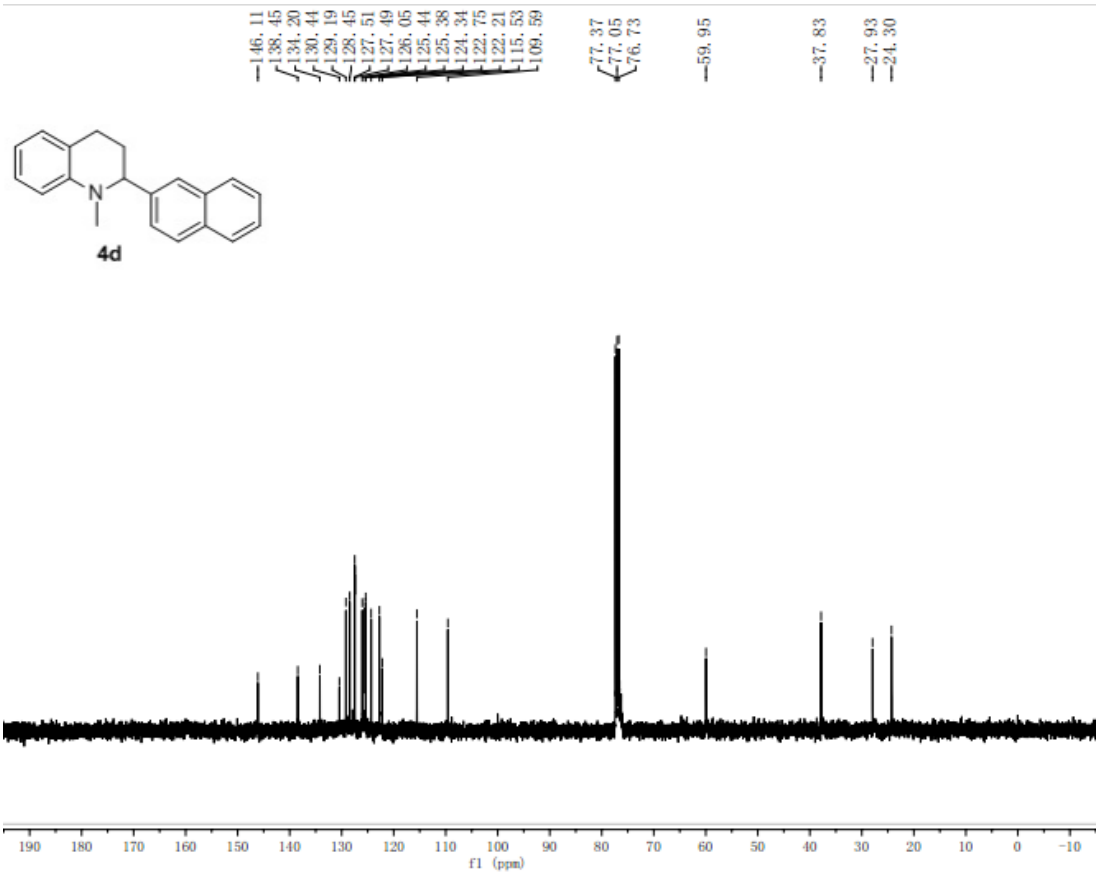
7.5577
7.5407
7.5161
7.4954
7.4785
7.3839
7.3653
7.3457
7.2666
7.2450
7.2111
7.1917
7.1728
6.9952
6.9772
6.7304
6.7100
6.6735
6.6552
6.6370
5.3392
5.3288
5.3179
2.9151
2.6243
2.6130
2.5965
2.5852
2.5728
2.5584
2.5453
2.5324
2.5200
2.5058
2.4934
2.3328
2.3135
2.3008
2.2870
2.2730
2.2609
2.2491
2.2397
2.2287
0.0001
N
4d
1.03
1.06
1.06
2.22
1.13
1.13
1.24
1.10
1.10
1.14
1.00
3.00
2.28
2.05
f1 (ppm)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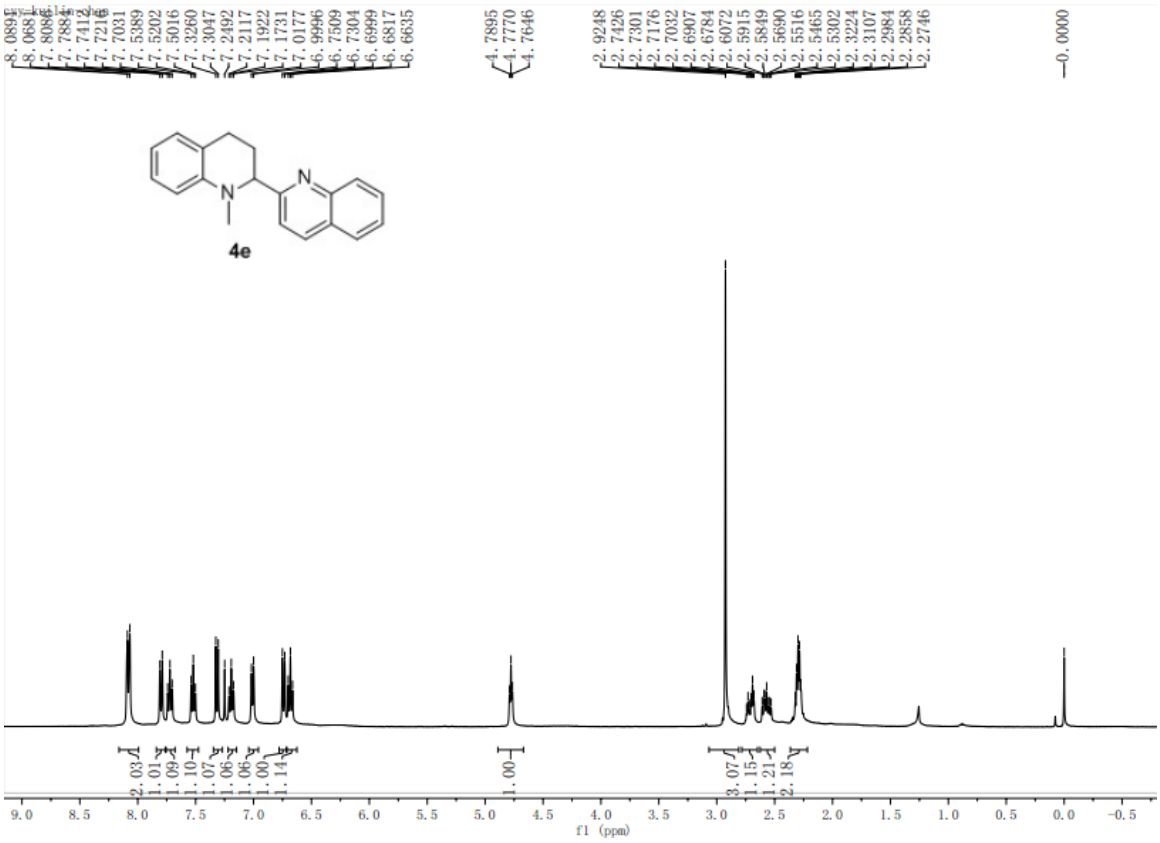
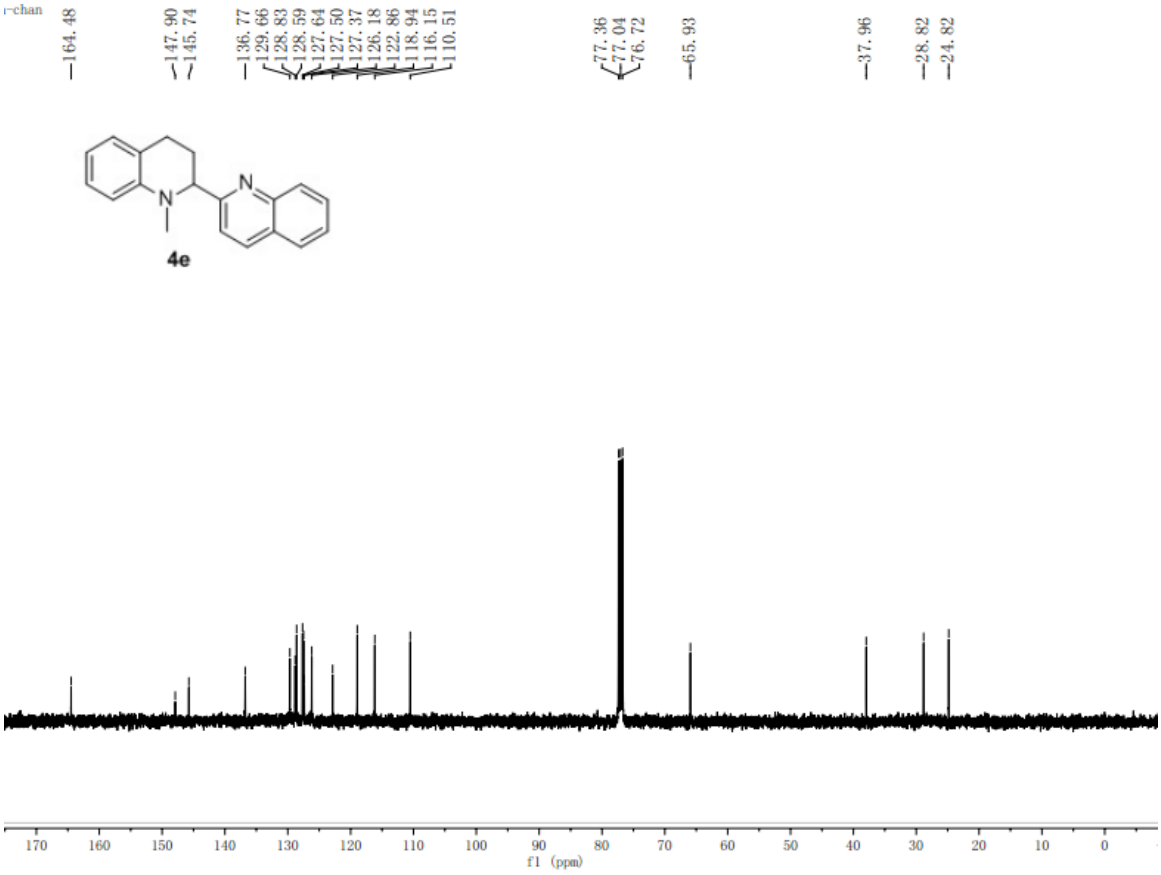
126.05
125.44
125.38
124.34
122.75
122.21
115.53
109.59
77.37
77.05
76.73
59.95
37.83
27.93
24.30
N
4d
f1 (ppm)


4e
f1 (ppm)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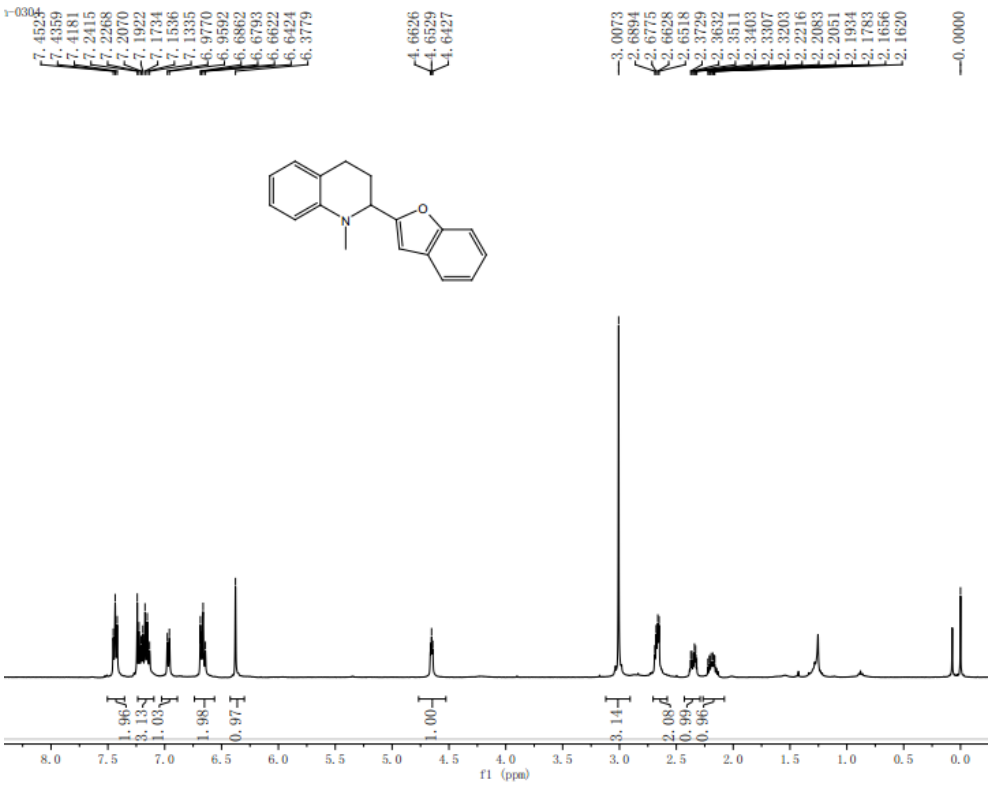
f1 (ppm)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7.1922
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7.1536
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6.9770
6.9592
6.6862
6.6793
6.6622
6.6424
6.3779
4.6626
4.6529
4.6427
3.0073
2.6894
2.6775
2.6628
2.6518
2.3729
2.3632
2.3511
2.3403
2.3307
2.3203
2.2216
2.2083
2.2051
2.1934
2.1783
2.1656
2.1620
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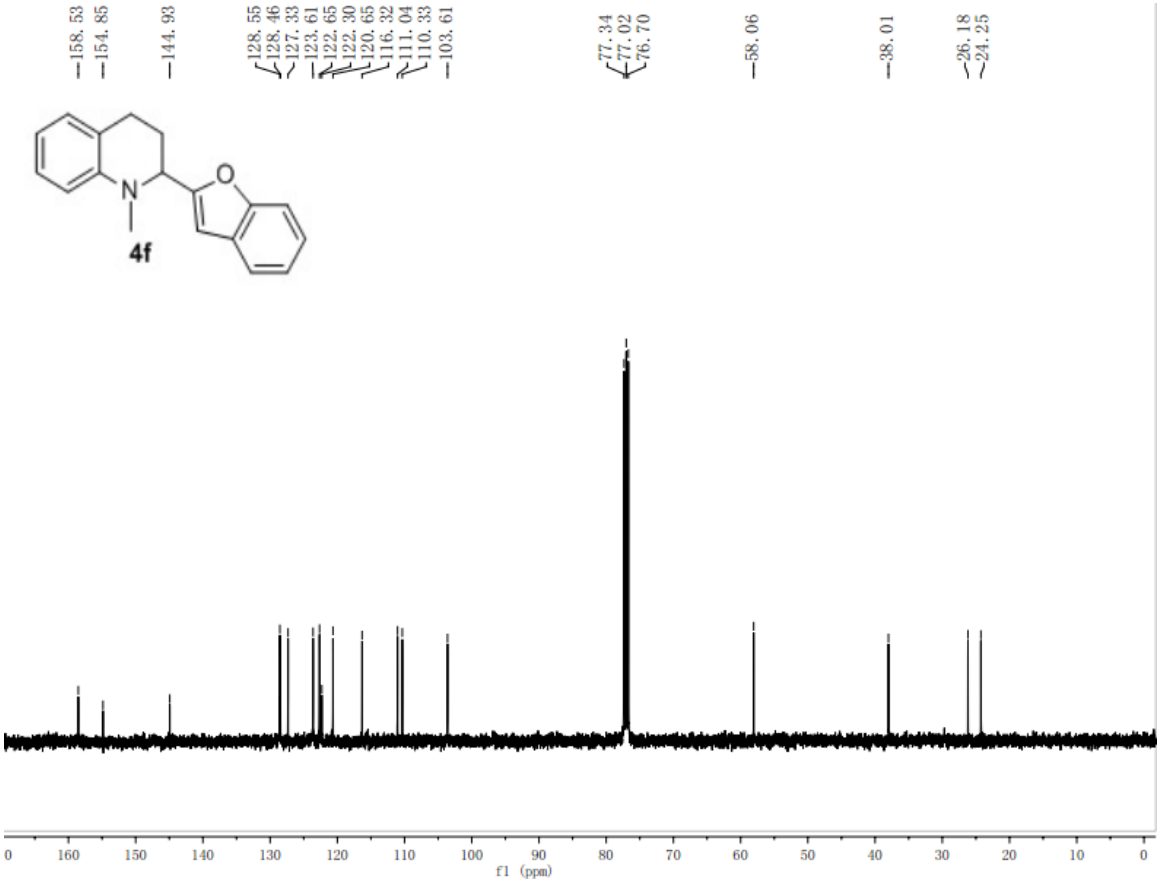
1.03
1.98
0.97
1.00
3.14
2.08
0.99
0.96
f1 (ppm)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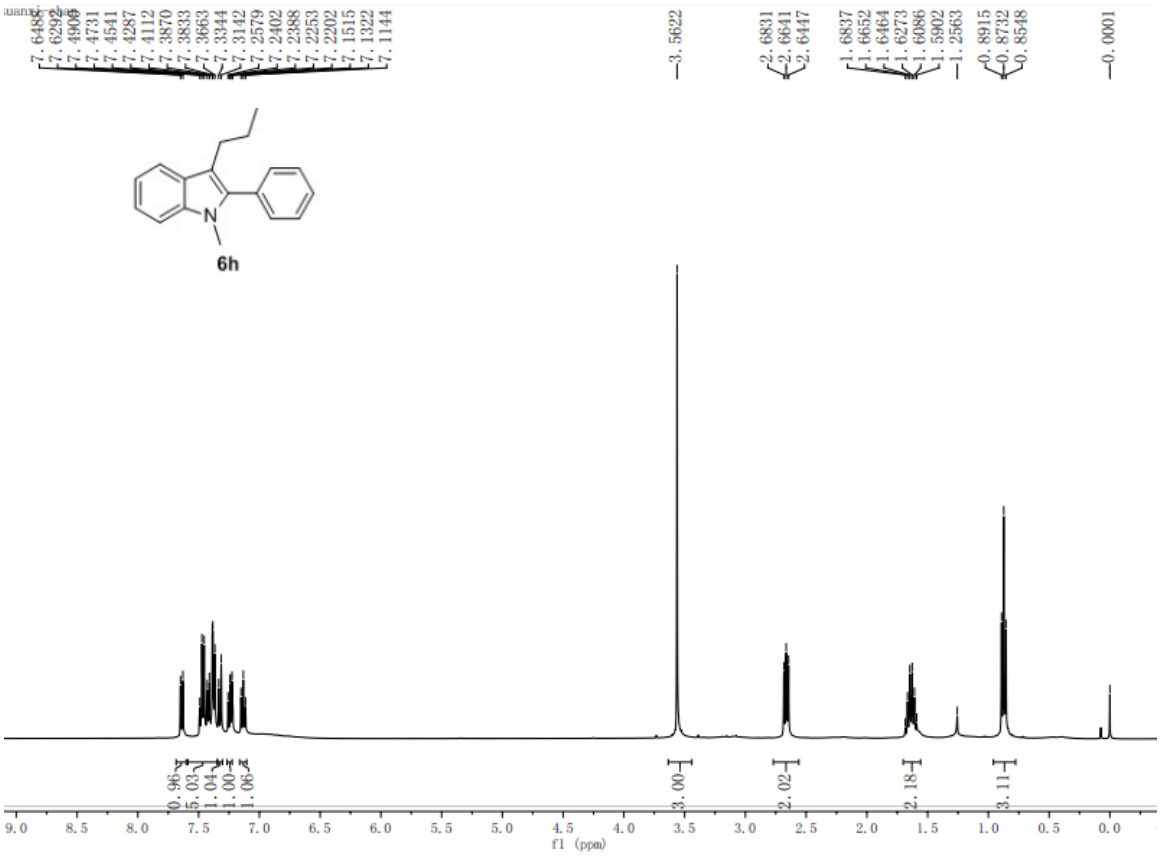
128.55
128.46
127.33
123.61
122.65
122.30
120.65
116.32
111.04
110.33
103.61
77.34
77.02
76.70
58.06
38.01
26.18
24.25
4f
f1 (ppm)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7.4731
7.4541
7.4287
7.4112
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7.3833
7.3663
7.3344
7.3142
7.2579
7.2402
7.2388
7.2253
7.2202
7.1515
7.1322
7.1144
3.5622
2.6831
2.6641
2.6447
1.6837
1.6652
1.6464
1.6273
1.6086
1.5902
1.2563
0.8915
0.8732
0.8548
0.0001
6h
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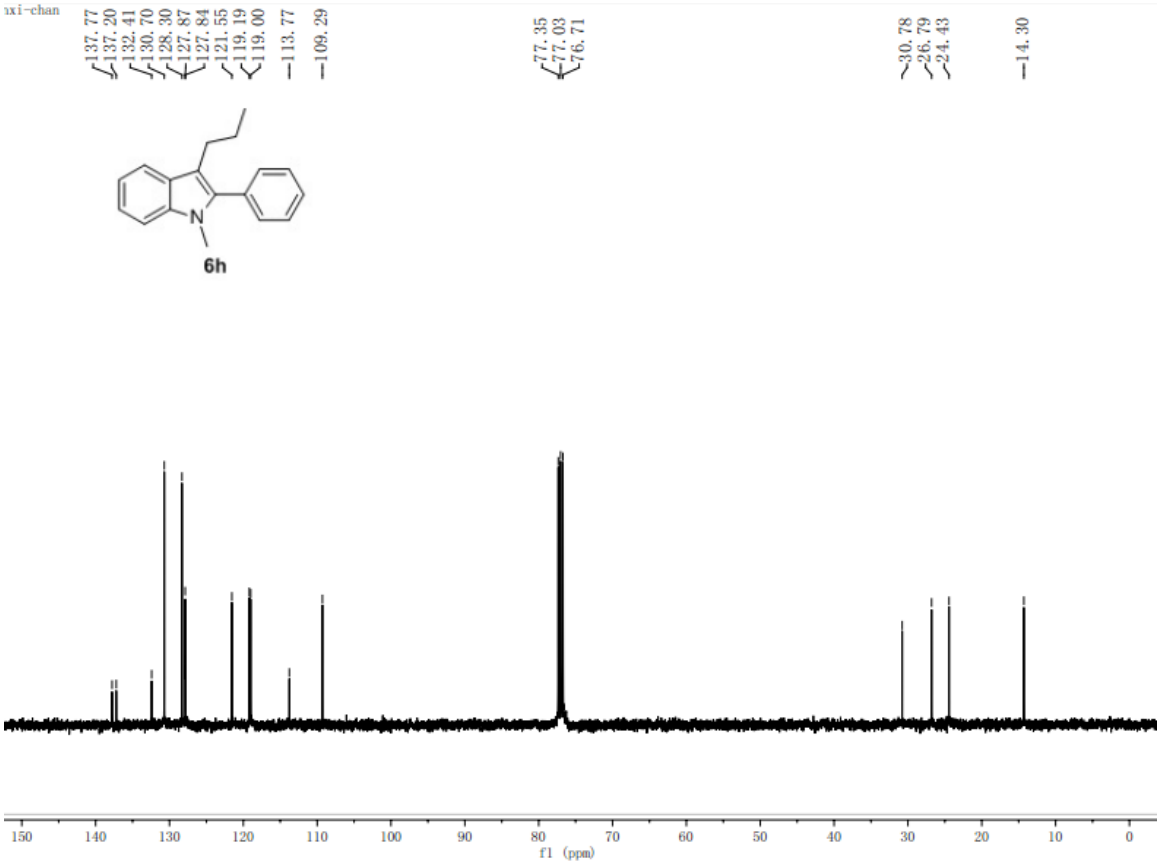
5.03
1.04
1.00
1.06
3.00
2.02
2.18
3.11
f1 (ppm)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127.84
121.55
119.19
119.00
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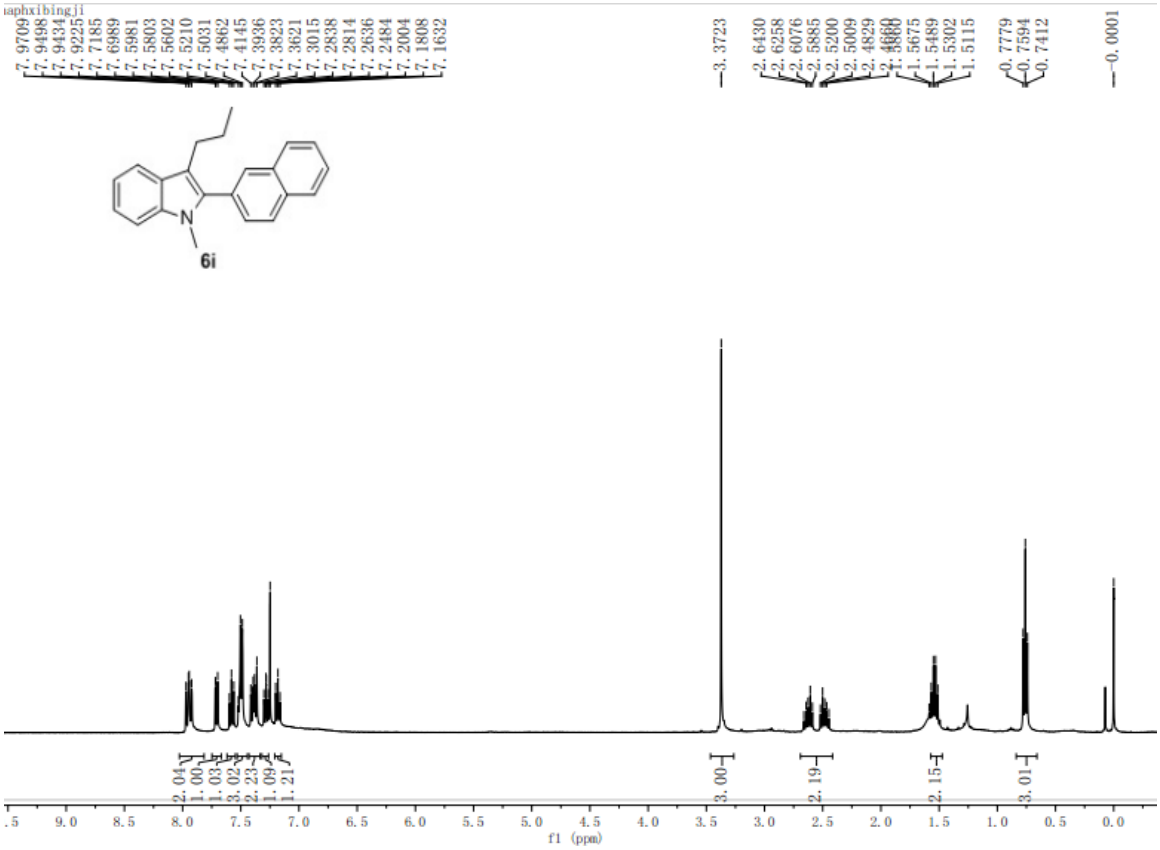
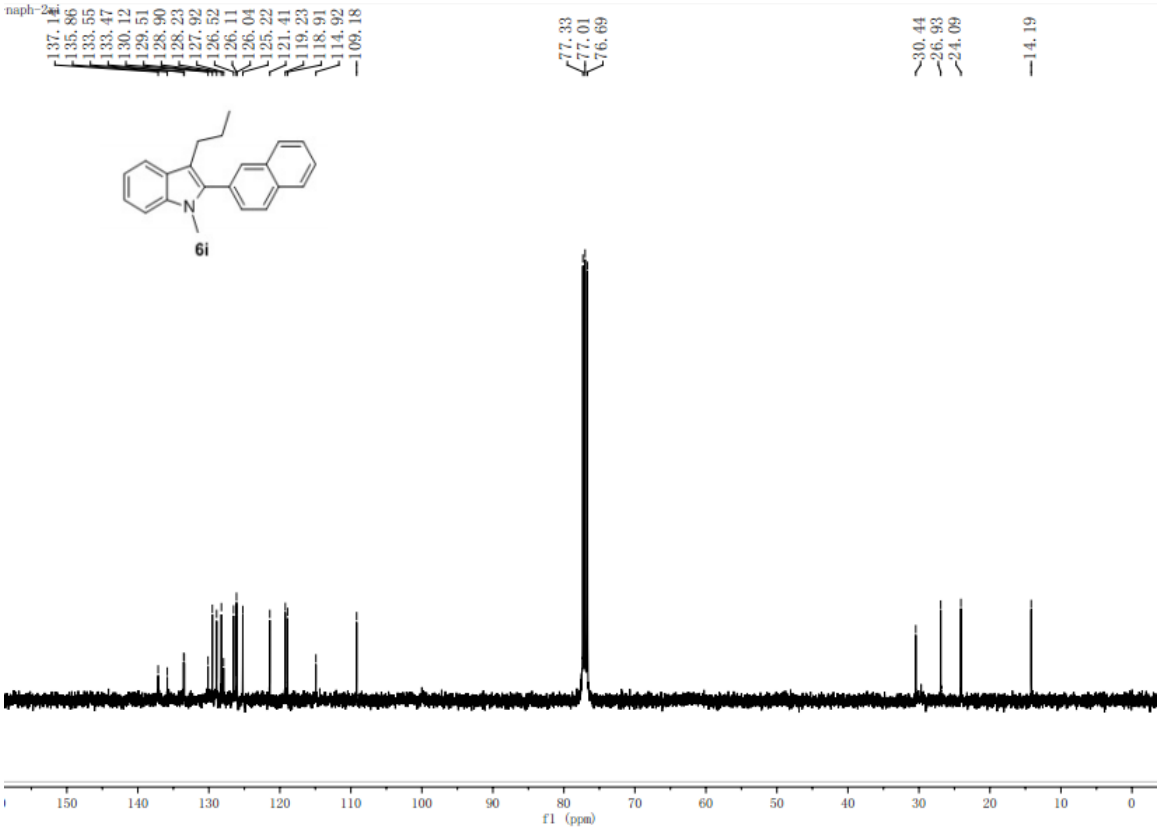
77.35
77.03
76.71
30.78
26.79
24.43
14.30
6h
f1 (ppm)


6i
f1 (ppm)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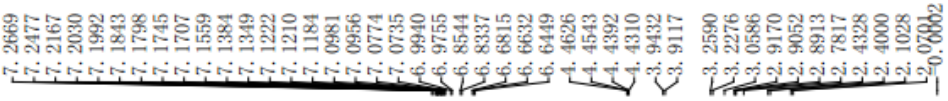
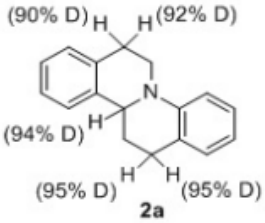
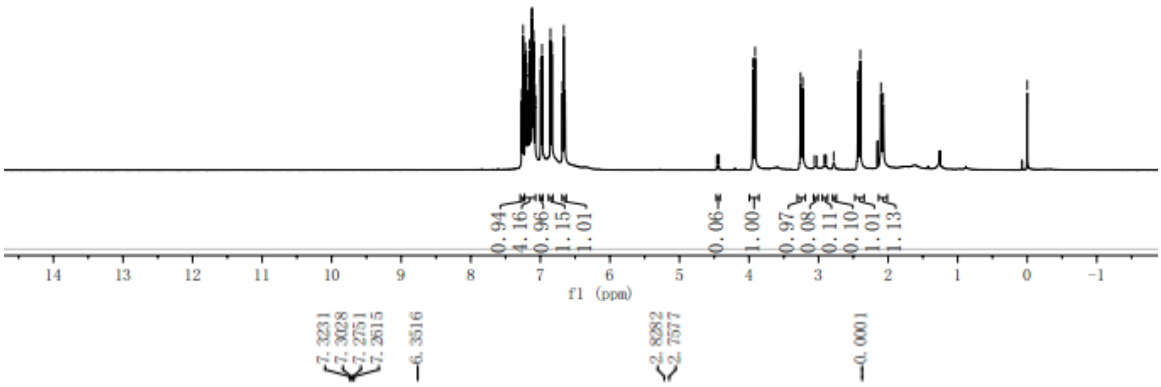
f1 (ppm)




(90% D)
(92% D)
(94% D)
(95% D)
(95% D)
2a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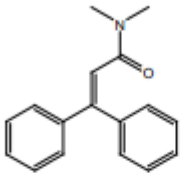
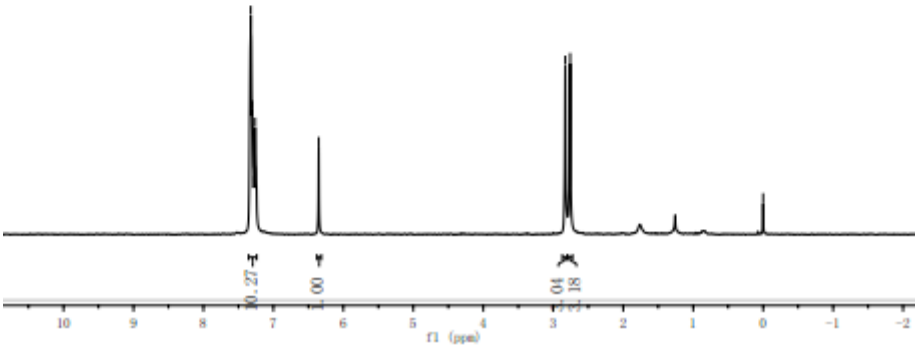
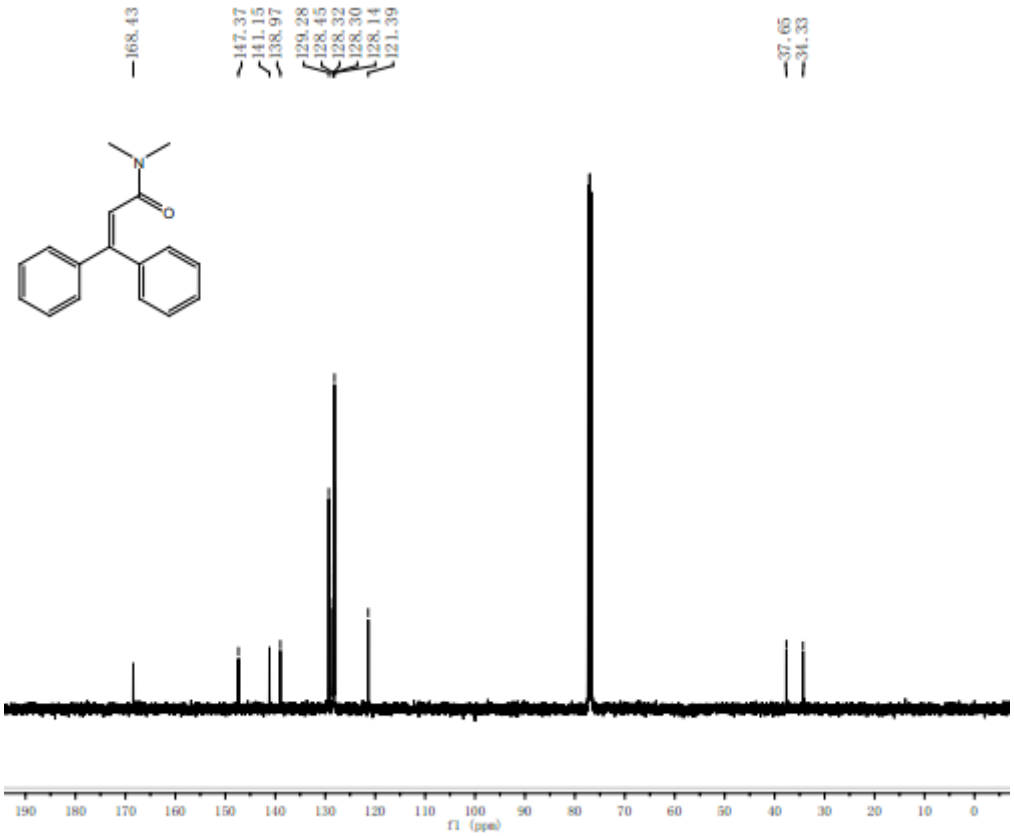



f1 (ppm)


168.43
147.37
141.15
138.97
129.28
128.45
128.32
128.30
128.14
121.39
37.65
34.33
N
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)