Electronic Supplementary Information for

Selective electrochemical acceptorless dehydrogenation reactions of tetrahydroisoquinoline derivatives

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Table of contents

1. General information

Reagents were purchased at the highest commercial quality grade and used without further purification, unless otherwise stated. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous material, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out on 0.25 mm E. Merck silica plates (60F-254), using UV light (254 nm) and TLC stain with anisaldehyde-sulfuric acid for visualization. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (b.p. 60-90 ^{o}C). ^{1}H and ^{13}C NMR data were recorded with Bruker (400 MHz) or Jeol (400 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ (ppm):) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts were reported relative to tetramethylsilane (0 ppm for ^{1}H), $CDCl_3$ (77.0 ppm for ^{13}C). The general preparation methods of all isoquinoline derivatives were synthesized according to the existing literature.[1]

2. Electrode materials and dimensions

The instrument for undivided electrolysis is IKA® ElectraSyn 2.0 with carousel. The electrodes used in IKA® ElectraSyn 2.0 were purchased from IKA Company. The anodic electrode was the carbon plate electrode (3.0 cm ×0.8 cm × 0.2 cm) (3.0 cm is the height of the electrode immersed in the solution) and the cathodic electrode was the carbon plate (3.0 cm × 0.8 cm × 0.2 cm).

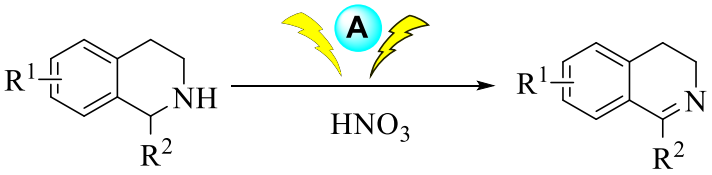
Figure S1. IKA® ElectraSyn 2.0

[1] B. L. Tran, J. L. Fulton and J. C. Linehan, *ACS Catalysis*, 2018, **8**, 8441-8449.

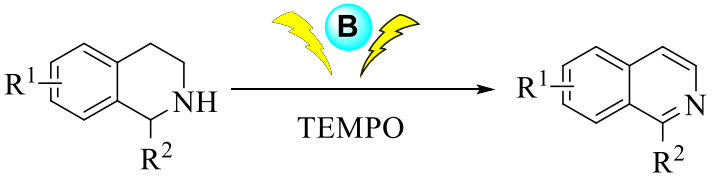
S. Kato, Y. Saga and M. Kojima, *J. Am. Chem. Soc.*, 2017, **139**, 2204–2207.

Cyclic voltammograms were recorded on an electrochemical workstation CS150H (CorrTest®). A steady glassy carbon disk electrode (3 mm in diameter) was used as the working electrode; a platinum plate was used as the counter electrode; the reference was an $Ag/AgNO_3$ electrode with (0.01 M) $AgNO_3$ in N,N-dimethylformamide.

3. General procedure for the electrochemical selective oxidation reaction



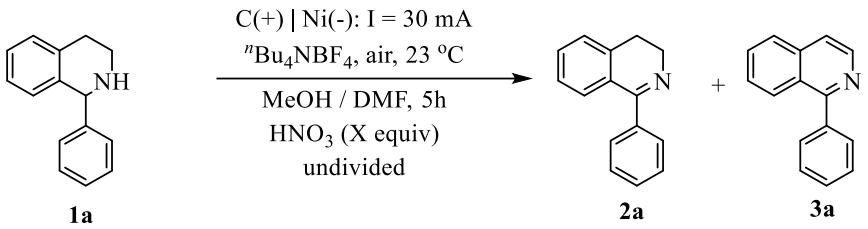
General procedure A: The electrolysis was carried out in the electrolysis cell of IKA® ElectraSyn 2.0. The anodic electrode was the carbon plate electrode (3.0 cm × 0.8 cm × 0.2 cm) and the cathodic electrode was the carbon plate (3.0 cm × 0.8 cm × 0.2 cm). Isoquinoline derivative (0.5 mmol), $^{n}Bu_4NIO_4$ (227 mg, 0.5 mmol), concentrated nitric acid (0.75 mmol) and MeOH : DMF = 3 mL:1 mL were added to an oven-dried undivided cell (6 mL) equipped with a stirring bar (the order of the addition did not affect the result). The reaction mixture was stirred and electrolyzed at a constant current of 30 mA at room temperature for 4 h. When the reaction was finished, the solvent was evaporated under vacuum and the crude material was purified by column chromatography or preparative TLC to furnish the desired product.



General procedure B: The electrolysis was carried out in the electrolysis cell of IKA® ElectraSyn 2.0. The anodic electrode was the carbon plate electrode (3.0 cm × 0.8 cm × 0.2 cm) and the cathodic electrode was the carbon plate (3.0 cm × 0.8 cm × 0.2 cm). Isoquinoline derivative (0.5 mmol), $^{n}Bu_4NIO_4$ (227 mg, 0.5 mmol), TEMPO (1 mmol) and MeOH : DMF : H_2O= 3 mL:1 mL:0.5 mL were added to an oven-dried undivided cell (6 mL) equipped with a stirring bar (the order of the addition did not affect the result). The reaction mixture was stirred and electrolyzed at a constant current of 30 mA at room temperature for 14 h. When the reaction was finished, the solvent was evaporated under vacuum and the crude material was purified by column chromatography or preparative TLC to furnish the desired product.

4. Optimization of reaction conditions

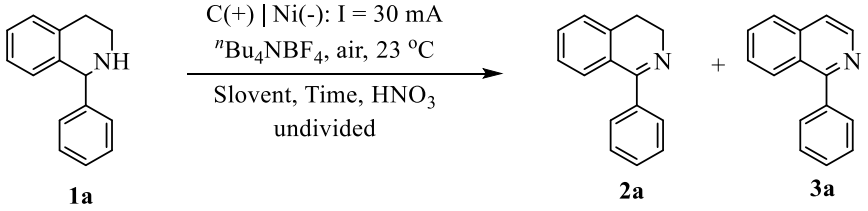
Table S1. Optimization of the nitric acid equivalent



Entry[a]	HNO_3 (X equiv.)	**2a**:**3a** Yield(%)[b]
1	0	27:14
2	0.25	45:32
3	0.5	49:30
4	0.75	65:16
5	1	73:9
6	1.5	85(79)[c]:<5
7	No electricity，1.5	No Reaction

[a]Standard conditions: **1a** (0.5 mmol), $^{n}Bu_4NBF_4$ (0.125 M), MeOH:DMF =2:2 mL, 5 h. [b]The crude nuclear magnetic yield was obtained by adding 0.1 mmol homometrimethoxybenzene as the internal standard compound. [c]chromatography separation yield.

Table S2. Optimization of the solvent

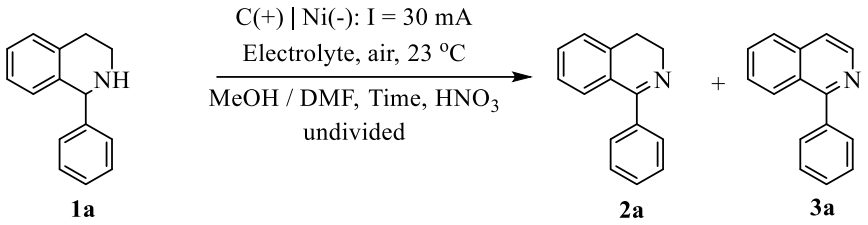


Entry[a]	Solvent (4 mL)	Time (h)	**2a**:**3a** Yield(%)[b]
1	MeOH	5	82:10
2	DMF	5	30:21
3	DMA	6	25:18
4	MeOH:DMF=2:2	5	70:12

5	MeOH:DMF=3:1	5	86(80)[c]:8
6	MeOH:DMF=1:3	6	44:20

[a] Standard conditions: **1a** (0.5 mmol), $^{n}Bu_4NBF_4$ (0.125 M), HNO_3 (0.75mmol). [b]The crude nuclear magnetic yield was obtained by adding 0.1 mmol homometrimethoxybenzene as the internal standard compound. [c]chromatography separation yield.

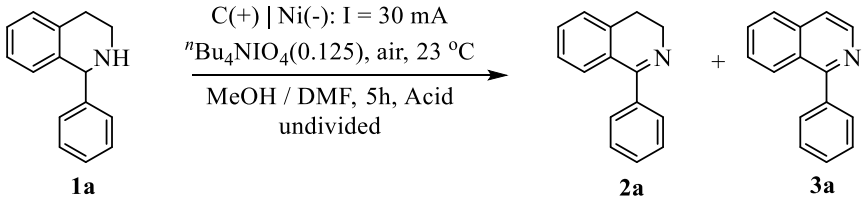
Table S3. Optimization of the electrolyte



Entry[a]	Electrolyte	Time (h)	**2a**:**3a** Yield(%)[b]
1	$^{n}Bu_4NBF_4$	5	85:8
2	$^{n}Bu_4NPF_6$	8.5	61:26
3	$^{n}Bu_4NBr$	5	70:13
4	$^{n}Bu_4NIO_4$	4	89(85)[c]:<5

[a] Standard conditions: **1a** (0.5 mmol), electrolyte (0.125 M), HNO_3 (0.75 mmol), MeOH:DMF =3:1 mL. [b] The crude nuclear magnetic yield was obtained by adding 0.1 mmol homometrimethoxybenzene as the internal standard compound. [c] chromatography separation yield.

Table S4. Optimization of the acid

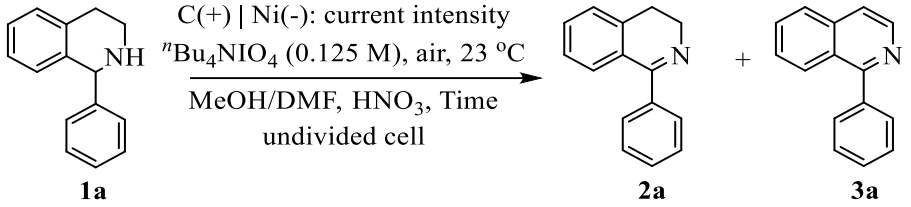


Entry[a]	Acid (1.5 equiv.)	**2a**:**3a** Yield(%)[a]
1	HCl	69:10
2	CH_3COOH	59:32
3	CF_3COOH	72:10

4	HNO_3		89(85)[c]:<5

[a] Standard conditions: **1a** (0.5 mmol), $^{n}Bu_4NIO_4$ (0.125 M), MeOH:DMF =3:1 mL. [b] The crude nuclear magnetic yield was obtained by adding 0.1 mmol homometrimethoxybenzene as the internal standard compound. [c] chromatography separation yield.

Table S5. Optimization of current intensity

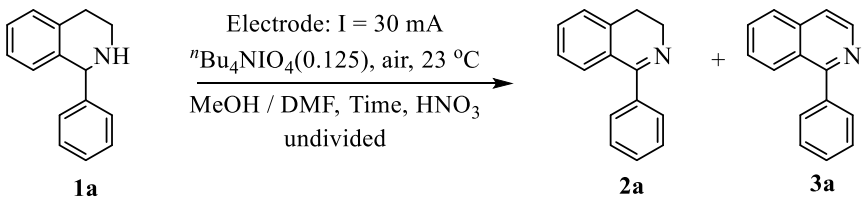


1a **2a** **3a**

Entry[a]	Current intensity (mA)	Time (h)	**2a**:**3a** Yield(%) [b]
1	10	5	84(80)[c]:9
2	20	5	85:11
3	30	5	89(85)[c]:<5
4	40	4	75:13

[a] Standard conditions: **1a** (0.5 mmol), $^{n}Bu_4NIO_4$ (0.125 M), HNO_3 (0.75 mmol), MeOH:DMF =3:1 mL. [b] The crude nuclear magnetic yield was obtained by adding 0.1 mmol homometrimethoxybenzene as the internal standard compound. [c] chromatography separation yield.

Table S6. Optimization of electrode

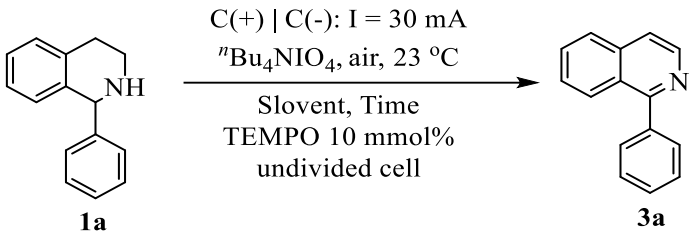


1a **2a** **3a**

Entry[a]	Electrode	Time (h)	**2a**:**3a** Yield(%)[b]
1	C(+) | SST(-)	6.5	72:<5
2	C(+) | C(-)	4	91(90)[c]:<5
3	C(+) | Pt(-)	5.5	60:<5

[a] Standard conditions: **1a** (0.5 mmol), $^{n}Bu_4NIO_4$ (0.125 M), HNO_3 (0.75 mmol), MeOH:DMF =3:1 mL. [b] The crude nuclear magnetic yield was obtained by adding 0.1 mmol homometrimethoxybenzene as the internal standard compound. [c] chromatography separation yield.

Table S7. Optimization of solvent

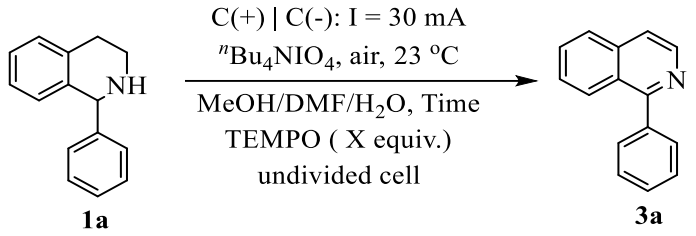


1a **3a**

Entry[a]	Slovent (mL)	Time (h)	**3a** Yield(%)[b]
1	MeOH:DMF=3:1	12	41
2	MeOH=4	12	30
3	DMF=4	12	23
4	MeOH:DMF:H_2O=3:1:0.1	16	55
5	MeOH:H_2O =4:0.1	16	40

[a] Standard conditions: **1a** (0.5 mmol), $^{n}Bu_4NIO_4$ (0.125 M), TEMPO 10 mmol%. [b] The crude nuclear magnetic yield was obtained by adding 0.1 mmol homometrimethoxybenzene as the internal standard compound.

Table S8. Optimization of TEMPO equivalent



1a **3a**

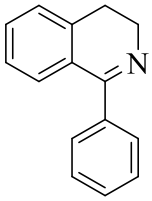
Entry[a]	TEMPO (X equiv.)	Time (h)	**3a** Yield(%)[b]
1	0.1	16	55
2	0.5	16	59
3	1	16	68
4	1.5	15	74

5	2	14	88(83)[c]
6	3	14	86

[a] Standard conditions: **1a** (0.5 mmol), $^{n}Bu_4NIO_4$ (0.125 M), HNO_3 (0.75 mmol), MeOH:DMF:H_2O =3:1:0.1 mL. [b] The crude nuclear magnetic yield was obtained by adding 0.1 mmol homometrimethoxybenzene as the internal standard compound. [c] chromatography separation yield.

5. Detail descriptions for products

1-phenyl-3,4-dihydroisoquinoline (2a)[2]



The starting 1-phenyl-1,2,3,4-tetrahydroisoquinoline (**1a**, 105 mg, 0.5 mmol) was reacted according to General Procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 5:1) to afford the title compound as a pale yellow oil in 90% yield (93 mg).

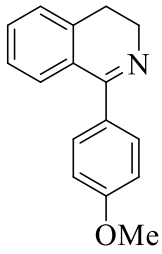
Rf (petroleum ether/ethyl acetate = 5:1): 0.2; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.68 – 7.59 (m, 2H), 7.51 – 7.37 (m, 4H), 7.28 (m, 3H), 3.96 – 3.81 (m, 2H), 2.83 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 167.3, 139.0, 138.9, 130.8, 129.4, 128.9, 128.8, 128.2, 128.0, 127.5, 126.6, 47.7, 26.4.

Procedure for gram-scale synthesis

The electrolysis was carried out in the electrochemical workstation CS150H (CorrTest®). The anodic electrode was the carbon plate electrode (3.0 cm × 0.8 cm × 0.2 cm) and the cathodic electrode was the carbon plate (3.0 cm × 0.8 cm × 0.2 cm). According to General Procedure, starting 1-phenyl-1,2,3,4-tetrahydroisoquinoline (**1a**, 2.09 g, 10.0 mmol) and concentrated nitric acid (0.96 mL, 15 mmol) were added to an oven-dried undivided cell (100 mL) in a mixed solvent of MeOH (60 mL) and DMF (20 mL) equipped with a stirring bar. The reaction mixture was stirred and electrolyzed at a constant current of 30 mA at room temperature for 26 h. Last, the reaction was able to be conducted in a gram scale, and 1.39 g of the desired product **2a** were isolated with 67% yield.

[2] G. S. Feng, Y. Ji, H. F. Liu, L. Shi and Y. G. Zhou, *Tetrahedron Letters*, 2016, **57**, 747–749.

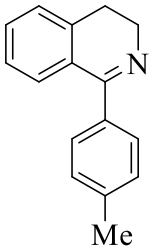
1-(4-methoxyphenyl)-3,4-dihydroisoquinoline (2b)[2]



The starting 1-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (**1b**, 120 mg, 0.5 mmol) was reacted according to General Procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 3:1) to afford the title compound as a light yellow liquid in 83% yield (100 mg).

Rf (petroleum ether/ethyl acetate = 3:1): 0.3; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.64 – 7.56 (m, 2H), 7.40 (m, 1H), 7.35 – 7.25 (m, 3H), 7.00 – 6.92 (m, 2H), 3.87 (s, 3H), 3.85 – 3.80 (m, 2H), 2.81 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 166.8, 160.7, 139.1, 131.2, 130.7, 130.4, 128.8, 128.1, 127.4, 126.6, 113.5, 55.4, 47.3, 26.4.

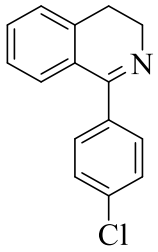
1-(*p*-tolyl)-3,4-dihydroisoquinoline (2c)[2]



The starting 1-(*p*-tolyl)-1,2,3,4-tetrahydroisoquinoline (**1c**, 112 mg, 0.5 mmol) was reacted according to General Procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 5:1) to afford the title compound as a white solid in 85% yield (95 mg).

Rf (petroleum ether/ethyl acetate = 5:1): 0.3; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.53 (d, *J* = 7.8 Hz, 2H), 7.41 (m, 1H), 7.33 – 7.23 (m, 5H), 3.92 – 3.81 (m, 2H), 2.82 (m, 2H), 2.44 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 167.2, 139.3, 139.0, 136.1, 130.6, 128.9, 128.8, 128.0, 127.4, 126.5, 47.6, 26.4, 21.4.

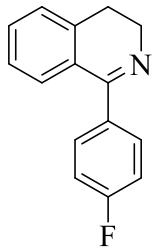
1-(4-chlorophenyl)-3,4-dihydroisoquinoline (2d)[2]



The starting 1-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline (**1d**, 122 mg, 0.5 mmol) was reacted according to General Procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 5:1) to afford the title compound as a white solid in 89% yield (108 mg).

Rf ((petroleum ether/ethyl acetate = 5:1): 0.3; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.67 – 7.54 (m, 2H), 7.42 (m, 3H), 7.33 – 7.22 (m, 3H), 3.95 – 3.79 (m, 2H), 2.83 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 166.3, 138.9, 137.4, 135.4, 131.0, 130.2, 128.5, 128.4, 127.7, 127.6, 126.7, 47.7, 26.3.

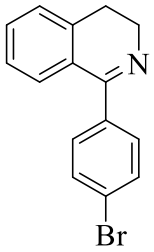
1-(4-fluorophenyl)-3,4-dihydroisoquinoline (2e)[2]



The starting 1-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (**1e**, 114 mg, 0.5 mmol) was reacted according to General Procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 5:1) to afford the title compound as a light yellow liquid in 88% yield (100 mg).

Rf (petroleum ether/ethyl acetate = 5:1): 0.3; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.70 – 7.55 (m, 2H), 7.42 (m, *J* = 8.2, 5.8, 2.8 Hz 1H), 7.33 – 7.21 (m, 3H), 7.19 – 7.04 (m, 2H), 4.00 – 3.73 (m, 2H), 2.82 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 166.3, 164.8 (d, *J* = 247 Hz), 138.9, 135.0 (d, *J* = 4 Hz), 130.9, 130.8, 130.7, 128.6, 127.8 (d, *J*= 23 Hz), 126.7, 115.3 (d, *J* = 20 Hz), 47.5, 26.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.92.

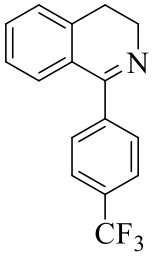
1-(4-bromophenyl)-3,4-dihydroisoquinoline (2f)[2]



The starting 1-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinoline (**1f**, 144 mg, 0.5 mmol) was reacted according to General Procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 5:1) to afford the title compound as a white solid in 97% yield (139 mg).

Rf (petroleum ether/ethyl acetate = 5:1): 0.3; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.62 – 7.55 (m, 2H), 7.54 – 7.47 (m, 2H), 7.42 (m, 1H), 7.33 – 7.21 (m, 3H), 3.94 – 3.82 (m, 2H), 2.88 – 2.78 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 166.3, 138.9, 137.4, 135.4, 131.0, 130.2, 128.5, 128.4, 127.7, 127.6, 126.7, 47.7, 26.3.

1-(4-(trifluoromethyl)phenyl)-3,4-dihydroisoquinoline (2g)[2]

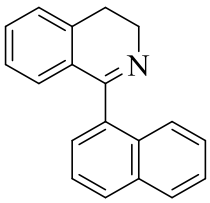


The starting 1-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinoline (**1g**, 139 mg, 0.5 mmol) was reacted according to General Procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 5:1) to afford the title compound as a white solid in 86% yield (119 mg).

Rf (petroleum ether/ethyl acetate = 3:1): 0.3; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.81 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.36 (m, 2H), 7.31 – 7.24 (m, 2H), 3.76 (q, *J* = 6.6 Hz, 2H), 2.97 (t, *J* = 6.9 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 166.2, 138.7, 128.8, 127.3, 126.7, 125.6 (q, *J* = 3.4 Hz), 123.6 (q, *J* = 270.1 Hz), 41.3, 35.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.94.

1-(naphthalen-1-yl)-3,4-dihydroisoquinoline (2h)[3]

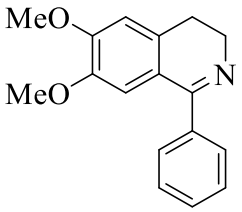
[3] J. M. Rosello, S. Staniland, N. J. Turner and J. Clayden, *Tetrahedron*, 2016, **72**, 5172-5177.



The starting 1-(naphthalen-1-yl)-1,2,3,4-tetrahydroisoquinoline (**1h**, 130 mg, 0.5 mmol) was reacted according to General Procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 5:1) to afford the title compound as a light yellow solid in 89% yield (113 mg).

Rf (petroleum ether/ethyl acetate = 5:1): 0.3; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 8.13 (d, *J* = 1.7 Hz, 1H), 8.01 – 7.85 (m, 3H), 7.78 (m, 1H), 7.61 – 7.49 (m, 2H), 7.45 (m, 1H), 7.39 – 7.27 (m, 3H), 4.13 – 3.77 (m, 2H), 2.95 – 2.79 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 167.4, 139.0, 136.3, 133.9, 133.0, 130.8, 128.9, 128.7, 128.6 (d, *J* = 1.4 Hz, 1H), 128.1, 127.9, 127.8, 127.5, 126.7 (d, *J* = 3.9 Hz), 126.3 (d, *J* = 2.7 Hz, 1H), 47.7, 26.4.

6,7-dimethoxy-1-phenyl-3,4-dihydroisoquinoline (2i)[4]



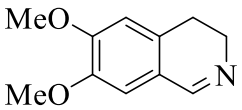
The starting 6,7-dimethoxy-1-phenyl-1,2,3,4-tetrahydroisoquinoline (**1i**, 135 mg, 0.5 mmol) was reacted according to General Procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 3:1) to afford the title compound as a light yellow solid in 93% yield (125 mg).

Rf (petroleum ether/ethyl acetate = 3:1): 0.3; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.62 (m, 2H), 7.45 (m, 3H), 6.81 (d, *J* = 4.9 Hz, 2H), 3.96 (s, 3H), 3.86 – 3.79 (m, 2H), 3.74 (s, 3H), 2.79 – 2.70 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 166.8, 150.9, 147.1, 139.2, 132.6, 129.3, 128.8, 128.2, 121.6, 111.6, 110.3, 56.2, 56.1, 47.7, 26.0.

6,7-dimethoxy-3,4-dihydroisoquinoline (2j)[5]

[4] L. Min, W.G. Yang, Y. X. Weng, W. P. Zheng and X. Y. Wang, *Org.Lett.*, 2019, **21**, 2574−2577.

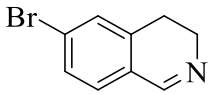
[5] D. Stubba, G. Lahm, M. Geffe, J. W. Runyon, A. Arduengo and T. Opatz, *Angew.Chem.Int.Ed.*, 2015, **54**, 14187–14189.



The starting 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (**1j**, 97 mg, 0.5 mmol) was reacted according to General Procedure. The crude product was purified by column chromatography (dichloromethane/methanol =15:1) to afford the title compound as a light yellow solid in 50% yield (48 mg).

Rf (dichloromethane/methanol = 15:1): 0.2; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 9.23 (m, 1H), 7.60 (s, 1H), 6.84 (s, 1H), 4.03 (s, 3H), 3.97 (s, 3H), 3.16 (t, *J* = 8.6 Hz, 2H), 2.77 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 177.4, 164.2, 157.5, 149.0, 133.1, 116.7, 115.7, 110.9, 56.7 (d, *J* = 2.9 Hz), 41.0, 29.6, 24.8.

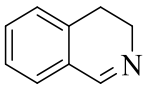
6-bromo-3,4-dihydroisoquinoline (2k)[6]



The starting 6-bromo-1,2,3,4-tetrahydroisoquinoline (**1k**, 106 mg, 0.5 mmol) was reacted according to General Procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 1:1) to afford the title compound as a pale yellow oily in 71% yield (74 mg).

Rf (petroleum ether/ethyl acetate = 1:1): 0.3; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 8.30 (s, 1H), 7.43 (m, 1H), 7.34 – 7.30 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 3.79 – 3.72 (m, 2H), 2.75 – 2.70 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 159.4, 138.3, 130.6, 130.3, 128.7, 125.2, 46.9, 29.8, 24.8.

3,4-dihydroisoquinoline (2l)[6]

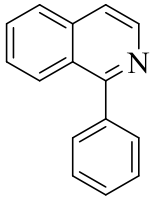


The starting 1,2,3,4-tetrahydroisoquinoline (**1l**, 67 mg, 0.5 mmol) was reacted according to General Procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 3:1) to afford the title compound as a light yellow liquid in 75% yield (50 mg).

[6] J. Zhang, S. Chen, F. F. Chen, W. S. Xu, G. J. Deng and H. Gong, *Adv. Synth. Catal.*, 10.1002/adsc.201700178.

Rf (petroleum ether/ethyl acetate = 3:1): 0.3; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 8.34 (s, 1H), 7.41 – 7.21 (m, 3H), 7.16 (d, *J* = 7.3 Hz, 1H), 3.78 (m, 2H), 2.75 (t, *J* = 7.7 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 160.4, 136.3, 131.1, 128.5, 127.4, 127.2, 127.1, 47.4, 25.0.

1-phenylisoquinoline (3a)[7]



The starting 1-phenyl-1,2,3,4-tetrahydroisoquinoline (**1a**,105 mg, 0.5 mmol) was reacted according to General Procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 7:1) to afford the title compound as a light yellow solid in 83% yield (87 mg).

Rf (petroleum ether/ethyl acetate = 7:1): 0.3; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 8.62 (d, *J* = 5.7 Hz, 1H), 8.14 – 8.07 (m, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.74 – 7.62 (m, 4H), 7.57 – 7.47 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 160.8, 142.3, 139.7, 136.9, 130.0, 128.6, 128.4, 127.6, 127.2, 127.0, 126.7, 120.0.

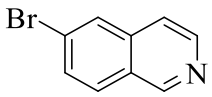
Procedure for gram-scale synthesis

The electrolysis was carried out in the electrochemical workstation CS150H (CorrTest®). The anodic electrode was the carbon plate electrode (3.0 cm × 0.8 cm × 0.2 cm) and the cathodic electrode was the carbon plate (3.0 cm × 0.8 cm × 0.2 cm). According to General Procedure, starting 1-phenyl-1,2,3,4-tetrahydroisoquinoline (1.05 g, 5.0 mmol) and TEMPO (1.56 g, 10 mmol) were added to an oven-dried undivided cell (100 mL) in a mixed solvent of MeOH (30 mL) and DMF (10 mL) and H_2O (0.5 mL) equipped with a stirring bar. The reaction mixture was stirred and electrolyzed at a constant current of 30 mA at room temperature for 48 h. Then the reaction mixture was evaporated under vacuum, and the crude material was purified by column chromatography (petroleum ether/ethyl acetate = 5:1) to afford the title compound as a pale yellow solid in 59% yield (0.61 g).

6-bromoisoquinoline (3b)[8]

[7] O. M. Kuzmina, A. K.Steib, S. Fernandez, W. Boudot, T. Markiewicz and P. Knochel, *Chem.Eur.J.*, 2015, **21**, 8242–8249.

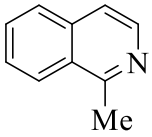
[8] C. Gene` s, S. Michel, F. Tillequin and F. H. Pore´e, *Tetrahedron,* 2009, **65**, 10009–10015.



The starting 6-bromo-1,2,3,4-tetrahydroisoquinoline (**1k**, 106 mg, 0.5 mmol) was reacted according to General Procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the title compound as a yellow solid in 82% yield (87 mg).

Rf (petroleum ether/ethyl acetate = 10:1): 0.3; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 8.85 (m, 1H), 7.96 – 7.92 (m, 1H), 7.91 (d, *J* = 9.0 Hz, 1H), 7.86 (d, *J* = 2.2 Hz, 1H), 7.69 (m, 1H), 7.32 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 150.7, 146.7, 135.0, 132.9, 131.2, 129.8, 129.2, 121.8, 120.4.

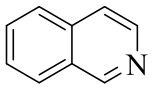
1-methylisoquinoline (3c)[9]



The starting 1-methyl-1,2,3,4-tetrahydroisoquinoline (**1m**, 76 mg, 0.5 mmol) was reacted according to General Procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 20:1) to afford the title compound as a yellow liquid in 46% yield (34 mg).

Rf (petroleum ether/ethyl acetate = 20:1): 0.3; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 8.46 – 8.24 (m, 1H), 8.12 – 7.92 (m, 1H), 7.82 – 7.33 (m, 4H), 2.99 – 2.82 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 158.5, 141.7, 135.8, 129.9, 127.1, 127.0, 125.6, 119.3, 22.3.

Isoquinoline (3d)[6]



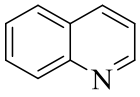
The starting 1,2,3,4-tetrahydroisoquinoline (**1l**, 66 mg, 0.5 mmol) was reacted according to General Procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 20:1) to afford the title compound as a reddish brown liquid in 78% yield (52 mg).

Rf (petroleum ether/ethyl acetate = 20:1): 0.3; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 9.14 (m, 1H), 8.43 (m,

[9] N. O. Balayeva, N. Zheng, R. Dillert and D. W. Bahnemann, *ACS Catal.*, 2019, **9**, 10694−10704.

1H), 7.86 – 7.77 (m, 1H), 7.66 (m, 1H), 7.58 – 7.39 (m, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 152.4, 142.9, 135.7, 130.3, 128.6, 127.5, 127.2, 126.4, 120.4.

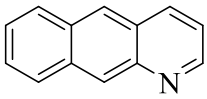
Quinoline (3e)[6]



The starting 1,2,3,4-tetrahydroquinoline (**1n**, 66 mg, 0.5 mmol) was reacted according to General Procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 100:1) to afford the title compound as a yellow liquid in 56% yield (37 mg).

Rf (petroleum ether/ethyl acetate = 100:1): 0.3; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 8.88 (m, 1H), 8.12 – 8.01 (m, 2H), 7.80 – 7.61 (m, 2H), 7.49 (m, 1H), 7.32 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 152.4, 142.9, 135.7, 130.3, 128.6, 127.5, 127.2, 126.4, 120.4.

benzo*[g]*quinoline (3f)[10]



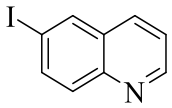
The starting 1,2,3,4-tetrahydrobenzo*[g]*quinoline (**1o**, 92 mg, 0.5 mmol) was reacted according to General Procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the title compound as a brown solid in 74% yield (64 mg).

Rf (petroleum ether/ethyl acetate = 10:1): 0.3; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 9.40 – 9.30 (m, 1H), 9.01 (m, 1H), 8.12 (m, 1H), 7.90 (m, 1H), 7.81 – 7.74 (m, 2H), 7.70 (m, 1H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.48 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 148.8, 146.6, 135.8, 133.7, 131.6, 128.2, 127.9, 127.8, 127.1, 126.4, 125.4, 124.4, 121.8.

6-iodoquinoline (3g)[11]

[10] O. Akio, *J. Org. Chem*., 1982, **47**, 3497-3503.

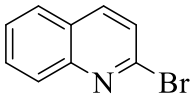
[11] K. D. Kim and J. H. Lee, *Org. Lett*., 2018, **20**, 7712−7716.



The starting 6-iodo-1,2,3,4-tetrahydroquinoline (**1p**, 130 mg, 0.5 mmol) was reacted according to General Procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the title compound as a yellow solid in 62% yield (79 mg).

Rf (petroleum ether/ethyl acetate = 10:1): 0.3; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 8.89 (m, 1H), 8.17 (d, *J* = 2.0 Hz, 1H), 8.00 (m, 1H), 7.92 (m, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.38 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 150.9, 147.2, 138.2, 136.5, 134.9, 131.2, 129.9, 121.8, 92.2.

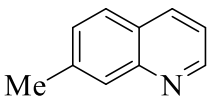
2-bromoquinoline (3h)[12]



The starting 2-bromo-3,4-dihydroquinoline (**1q**, 106 mg, 0.5 mmol) was reacted according to General Procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the title compound as a purple solid in 66% yield (69 mg).

Rf (petroleum ether/ethyl acetate = 10:1): 0.3; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 8.02 (m, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.76 (m, 1H), 7.70 (m, 1H), 7.53 (m, 1H), 7.47 (d, *J* = 8.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 148.4, 141.8, 138.5, 130.6, 128.5, 127.7, 127.2, 127.0, 125.8.

7-methylquinoline (3i)[13]



The starting 7-methyl-1,2,3,4-tetrahydroquinoline (**1r**, 74 mg, 0.5 mmol) was reacted according to General Procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 100:1) to afford the title compound as a yellow liquid in 46% yield (33 mg).

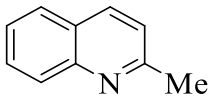
Rf (petroleum ether/ethyl acetate = 100:1): 0.2; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 8.85 (m, 1H), 8.07

[12] D. Wang, Y. Wang, J. Zhao, L. Li, L. Miao, D. Wang and P. Yu, *Tetrahedron*, 2016, **72**, 5762e5768.

[13] S. Rousseaux, B. Liegault and K. Fagnou, *Chem. Sci*., 2012, **3**, 244–248.

(m, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.70 – 7.44 (m, 2H), 7.36 (m, 1H), 2.54 (d, *J* = 0.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 149.6, 136.4, 135.4, 131.8, 129.1, 128.4, 126.6, 121.1, 21.6.

2-methylquinoline (3j)[6]

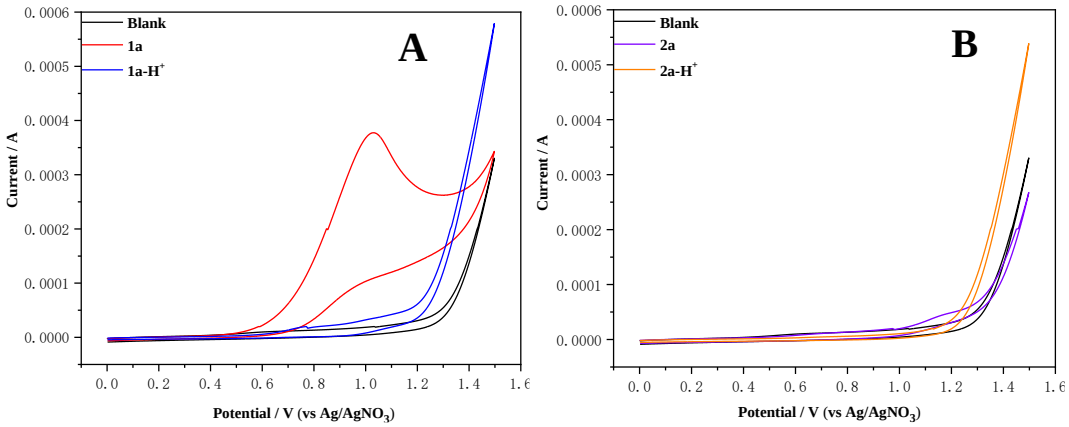


The starting 2-methyl-1,2,3,4-tetrahydroquinoline (**1s**, 74 mg, 0.5 mmol) was reacted according to General Procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 100:1) to afford the title compound as a yellow liquid in 39% yield (28 mg).

Rf (petroleum ether/ethyl acetate = 100:1): 0.2; **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 8.03 – 7.95 (m, 1H), 7.90 (m, 1H), 7.72 – 7.51 (m, 2H), 7.38 (m, 1H), 7.14 (m, 1H), 2.78 – 2.56 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 158.9, 147.8, 136.1, 129.4, 128.6, 127.5, 126.4, 125.6, 122.0, 25.4.

6. Cyclic voltammetry (CV) graphs

Cyclic voltammetry was performed in a three-electrode cell under air at room temperature. A-C: A steady glassy carbon disk electrode (3 mm in diameter) was used as the working electrode; a platinum plate was used as the counter electrode; the reference was an $Ag/AgNO_3$ electrode with (0.01 M) $AgNO_3$ in 8 mL DMF solvent containing (0.01 M). 8 mL DMF solvent containing (0.0625 M) $^{n}Bu_4NBF_4$ was used as the blank. The spectrums were recorded with the scan rate of 100 mV s-1 (starting from 0 V). The CV of background, 1a, 1a-H^+, 2a, 2a-H^+, CH_3OH. D: 8 mL DMF solvent containing (0.01 M) $^{n}Bu_4NBF_4$ was used as the blank. The spectrums were recorded with the scan rate of 100 mV s-1 (starting from 0 V). The CV of background, TEMPO, 1-methyl-1,2,3,4-tetrahydroisoquinoline, 1-methyl-1,2,3,4-tetrahydroisoquinoline + TEMPO.



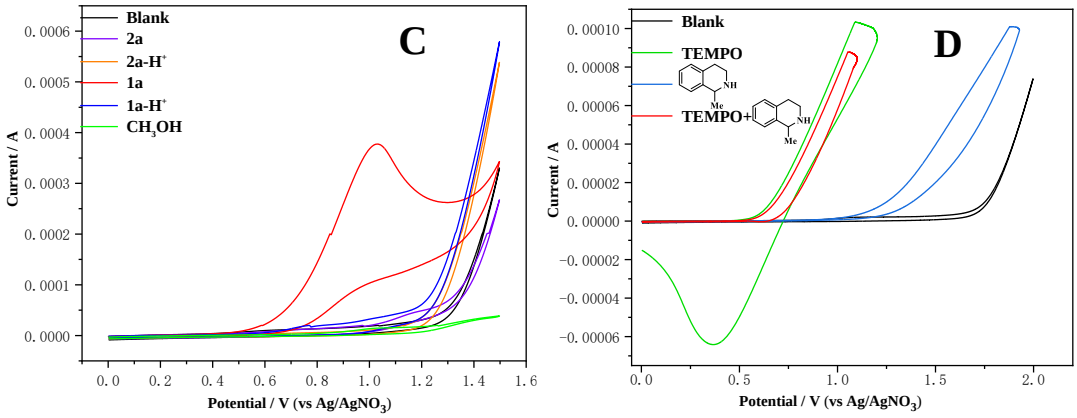


Figure S2. Cyclic Voltammograms recorded in $^{n}Bu_4NBF_4$-DMF solution (0.0625 M, as blank solution): scan rate: 100 mV s^{-1}; starting potential: 0 V; glass carbon (3 mm diameter, Working Electrode); platinum plate (Counter Electrode); $Ag/AgNO_3$ (0.01 M) $AgNO_3$ in MeCN (Reference Electrode). **A-C: 1a**, **2a** (0.5 mmol / 8 ml DMF), **1a-H$^+$**, **2a-H$^+$** (0.5 mmol + 0.75 mmol HNO_3 / 8 ml DMF), CH_3OH (8 ml) **D:** Cyclic Voltammograms recorded in $^{n}Bu_4NBF_4$-DMF solution (0.01 M, as blank solution), TEMPO, 1-methyl-1,2,3,4-tetrahydroisoquinoline (0.08 mmol / 8 ml DMF), 1-methyl-1,2,3,4-tetrahydroisoquinoline + TEMPO (0.08 mmol + 0.16 mmol TEMPO / 8 ml DMF).

7. DFT study

In order to understand the cause of selective oxidative dehydrogenation of tetrahydroisoquinoline derivatives, density functional theory (DFT) was used to calculate the representative substrates 1-phenyl-1,2,3,4-tetrahydroisoquinoline (**1a**) and 1-phenyl-3,4-dihydroisoquinoline (**2a**) and their protonated structures using Gaussian 09 program.[14] The geometry of the minimum energy structure is optimized at the level of B3-LYP theory, and 6-31G (d, p) bases are implicitly set in CH_3CN, and harmonic vibration frequency calculations are performed to confirm that they are local minima. The Molecular orbitals of the structure were analyzed by

[14] Frischi, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucii, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Jr., Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision D.01.

Multiwfn (Multifunctional Wavefunction Analyzer)[15] and VMD (Visual Molecular Dynamics) software[16], and the corresponding HOMO orbital energy level diagram was drawn.

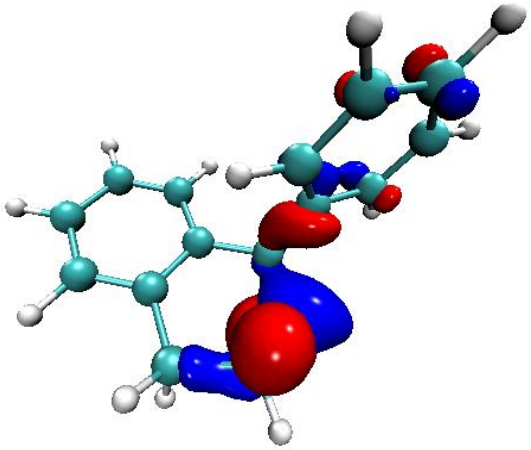


Figure. S3 1-phenyl-1,2,3,4-tetrahydroisoquinoline (**1a**)

HOMO orbital 56, energy level -5.9050 eV

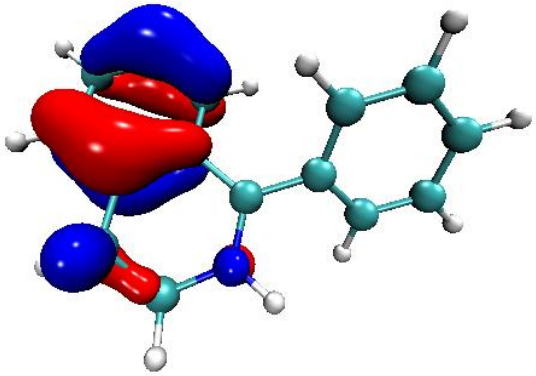


Figure. S4 Protonated 1-phenyl-1,2,3,4-tetrahydroisoquinoline (**1a-H**$^+$)

HOMO orbital 56, energy level -6.7505 eV

[15] T. Lu and F. Chen, *Journal of Computational Chemistry*, 2012, **33** 580-592.

[16] W. Humphrey, A Dalke and K Schulten, *Journal of Molecular Graphics*, 1996, **14** 33-38.

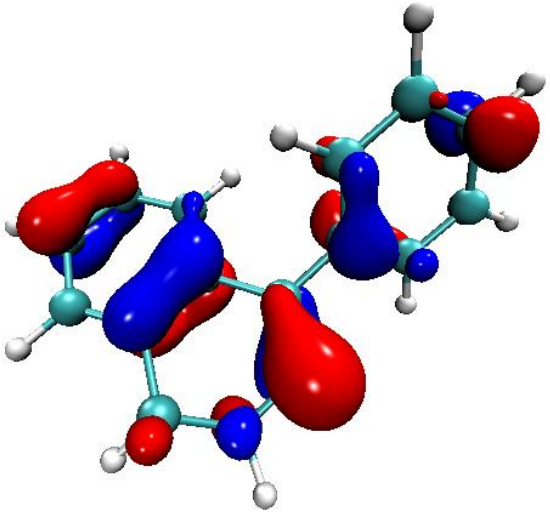


Figure. S5 1-phenyl-3,4-dihydroisoquinoline (**2a**)

HOMO orbital 55, energy level -6.2333 eV

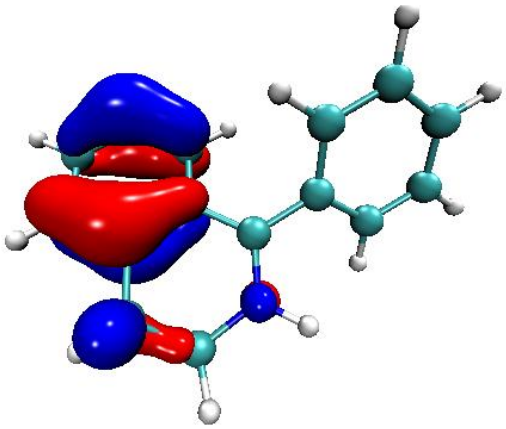


Figure. S6 Protonated 1-phenyl-3,4-dihydroisoquinoline (**2a-H**$^{+}$)

HOMO orbital 55, energy level -7.0805 eV

CH_3OH

HOMO orbital 9, energy level -7.0526 eV

B3-LYP Geometries for All the Optimized Species

1a

0 1

C	0.46185500	2.41089900	0.42263200
C	1.90326200	1.94260800	0.61506900
C	2.07887500	0.48239900	0.24541000
C	1.12119300	-0.18426700	-0.53882000
C	-0.14265000	0.51668300	-1.02121800
H	3.96248700	0.29740200	1.27027600
H	-0.16959200	2.02383400	1.24026800
H	2.56287200	2.55127300	-0.01841000
C	3.22275600	-0.21814500	0.66182600
C	1.32979000	-1.52783700	-0.88683900
H	-0.24688800	0.30553600	-2.09283400
C	2.46936800	-2.21138700	-0.47096100
C	3.42303500	-1.55099400	0.31111200
H	0.58501200	-2.03783400	-1.49339600
H	2.61506500	-3.24994700	-0.75445900
H	4.31524900	-2.07351200	0.64486800
H	0.40973900	3.50309200	0.46712300

H	2.22361700	2.10823000	1.65014000
N	0.01028500	1.98323000	-0.90503200
H	-0.88655200	2.41480600	-1.11727100
C	-1.42336900	-0.00604300	-0.35478100
C	-2.61557200	-0.00462100	-1.09645900
C	-1.47318200	-0.42787400	0.98259800
C	-3.82318200	-0.40314900	-0.52127100
H	-2.59316400	0.30930600	-2.13776600
C	-2.68160000	-0.82299700	1.56312400
H	-0.56197300	-0.46440700	1.57124500
C	-3.86037100	-0.81159200	0.81462600
H	-4.73240500	-0.40065800	-1.11634700
H	-2.69892300	-1.14637900	2.60040700
H	-4.79779500	-1.12544900	1.26508500

1a-pro-tion

1 1

C	0.51371100	2.40489600	0.55859800
C	1.94055700	1.89605000	0.67707400
C	2.08356400	0.44360300	0.26889200
C	1.11804300	-0.19483700	-0.52588700
C	-0.15667400	0.49529100	-0.98296500
H	3.97436800	0.21812500	1.26830900

H	-0.14898700	1.97000600	1.30805300
H	2.59751200	2.51700000	0.05338500
C	3.22661700	-0.27520900	0.65268200
C	1.31133300	-1.52686300	-0.92343900
H	-0.25630800	0.38287600	-2.06560200
C	2.44894500	-2.22718000	-0.53569300
C	3.41223900	-1.59694900	0.25934600
H	0.55875300	-2.01155600	-1.53958900
H	2.58555300	-3.25710900	-0.85126300
H	4.30281900	-2.13546500	0.56981700
H	0.45536000	3.49200400	0.61679700
H	2.27284400	2.03528200	1.71005800
N	-0.02970700	2.00412300	-0.78452300
H	-0.94855700	2.43406000	-0.93342400
C	-1.44433600	-0.00033200	-0.33688600
C	-2.63812700	0.08414100	-1.06966400
C	-1.47585900	-0.52878700	0.96052100
C	-3.84374600	-0.34084600	-0.51140400
H	-2.61907000	0.47830700	-2.08274200
C	-2.68328800	-0.95334900	1.51842700
H	-0.55777300	-0.61874800	1.53190600
C	-3.86812500	-0.85999700	0.78540100

H	-4.75980100	-0.27491100	-1.09085500
H	-2.69549900	-1.36126500	2.52479300
H	-4.80495700	-1.19672200	1.21960600
H	0.58256600	2.38145900	-1.51761600

2a

0 1

C	1.37218900	2.56882900	-0.14719100
C	2.37600400	1.76286100	0.67755800
C	2.30756800	0.31512200	0.26111600
C	1.04293400	-0.19583000	-0.10607700
C	-0.11944600	0.73856200	-0.06226600
H	4.39657700	-0.12274100	0.50690000
H	1.33409200	3.60605000	0.19991700
H	3.38835700	2.15887400	0.55207600
C	3.42613100	-0.51862300	0.21871700
C	0.93919800	-1.52470400	-0.54689900
C	2.06601800	-2.34572000	-0.59539900
C	3.30916700	-1.84559800	-0.20267200
H	-0.02102300	-1.91628000	-0.86420400
H	1.97271300	-3.37138600	-0.93984900
H	4.18866200	-2.48240500	-0.23537600
H	1.68848500	2.59933500	-1.20162300

H	2.12253900	1.85828700	1.74362700
N	0.01345900	2.02073800	-0.08926700
C	-1.51809800	0.20956800	0.00108900
C	-2.53759300	0.86536500	-0.70917600
C	-1.85780900	-0.89073900	0.80536400
C	-3.85787000	0.42648400	-0.62775200
H	-2.28064600	1.71920200	-1.32758100
C	-3.18264900	-1.32212900	0.89591100
H	-1.08920800	-1.40015300	1.37747400
C	-4.18546700	-0.66908200	0.17659500
H	-4.63204800	0.93820700	-1.19255200
H	-3.42970300	-2.16798500	1.53111300
H	-5.21466200	-1.01037300	0.24144000

2a--pro-tion

1 1

C	1.41012500	2.58511100	-0.13060200
C	2.41962400	1.74663500	0.64121700
C	2.31360200	0.29908500	0.22661300
C	1.03867600	-0.22327200	-0.10886100
C	-0.12137800	0.66437000	-0.04533000
H	4.39820700	-0.15538900	0.44822700
H	1.32469100	3.59440200	0.27144600

H	3.42656200	2.12767400	0.45572600
C	3.41991700	-0.54590000	0.18406000
C	0.91132300	-1.56469500	-0.51873200
C	2.03076900	-2.38788200	-0.56824100
C	3.28163300	-1.88043200	-0.20714200
H	-0.05515300	-1.95113200	-0.81931100
H	1.93006000	-3.41865000	-0.89150800
H	4.15704500	-2.52198800	-0.24250200
H	1.67449900	2.65196600	-1.19248700
H	2.22857000	1.83811700	1.71877900
N	0.08079100	1.95942100	-0.02997200
C	-1.51347200	0.18260100	0.00531200
C	-2.51123700	0.84220500	-0.73724000
C	-1.86339800	-0.90466300	0.82685600
C	-3.83338000	0.41341100	-0.66247200
H	-2.24650000	1.66310400	-1.39674300
C	-3.19207500	-1.31460700	0.90830100
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C	-4.17630700	-0.66133300	0.16245400
H	-4.59473000	0.91456000	-1.25172500
H	-3.45822400	-2.14421000	1.55554500
H	-5.20929000	-0.99053000	0.22157000

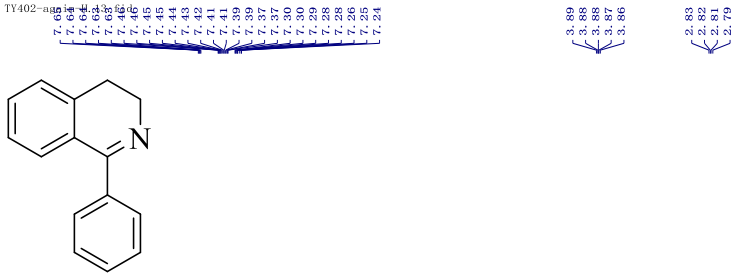
H	-0.72283500	2.57570200	0.05595100

CH_3OH

0 1

C	0.66389700	-0.01864100	0.00000000
H	1.09050200	0.98874800	-0.00000100
H	1.03503900	-0.54587000	-0.89108100
H	1.03503900	-0.54586800	0.89108300
O	-0.75223900	0.12303100	0.00000000
H	-1.12605300	-0.76941400	0.00000000

8. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra



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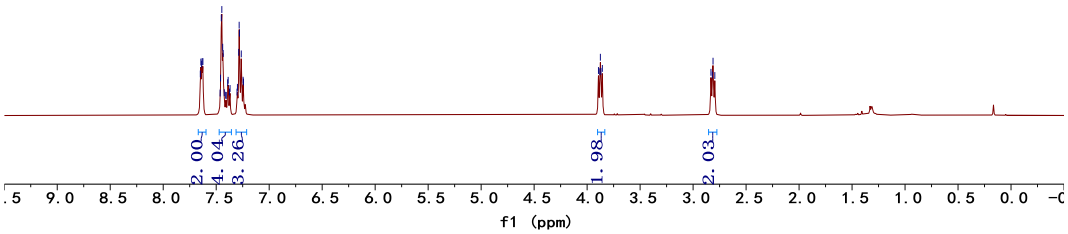

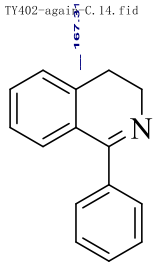

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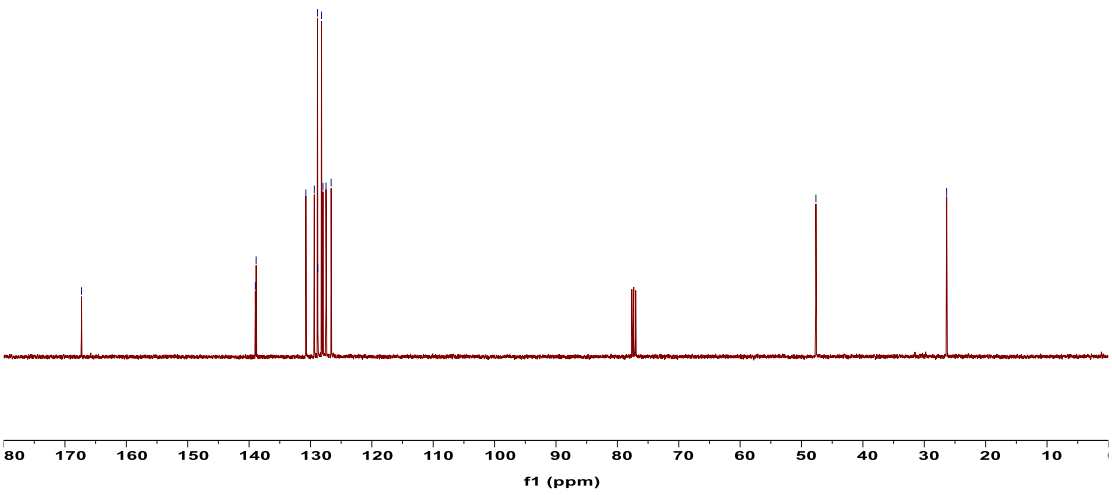

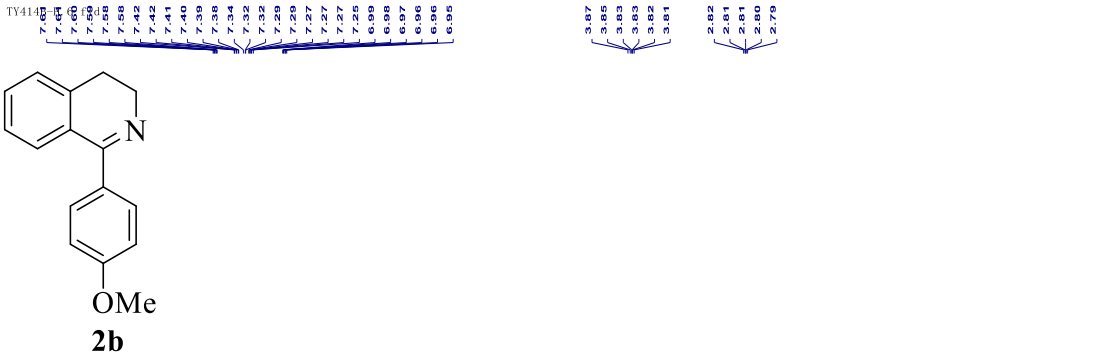

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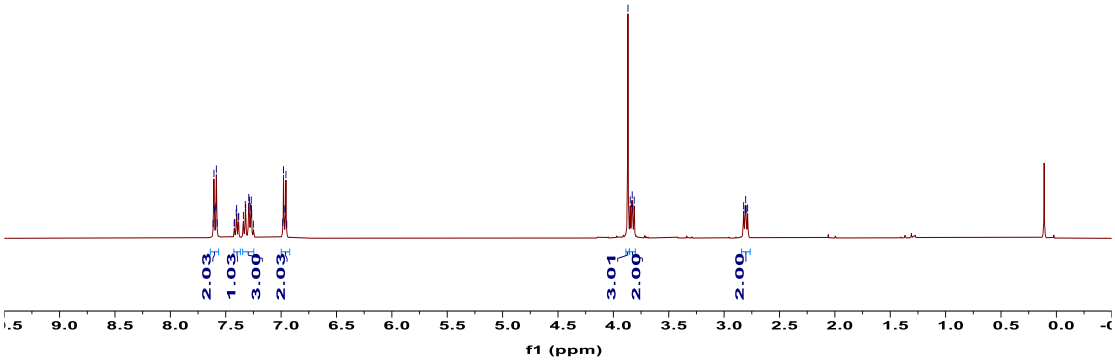

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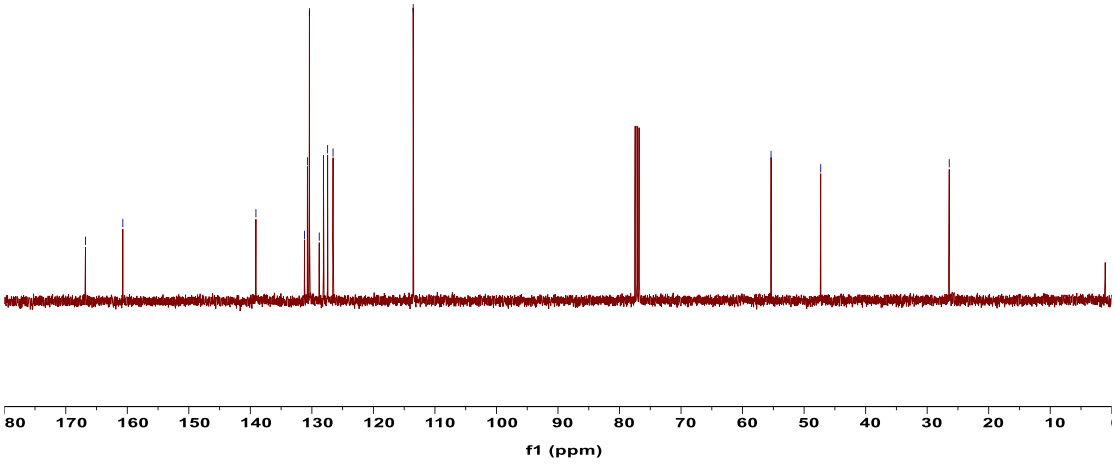

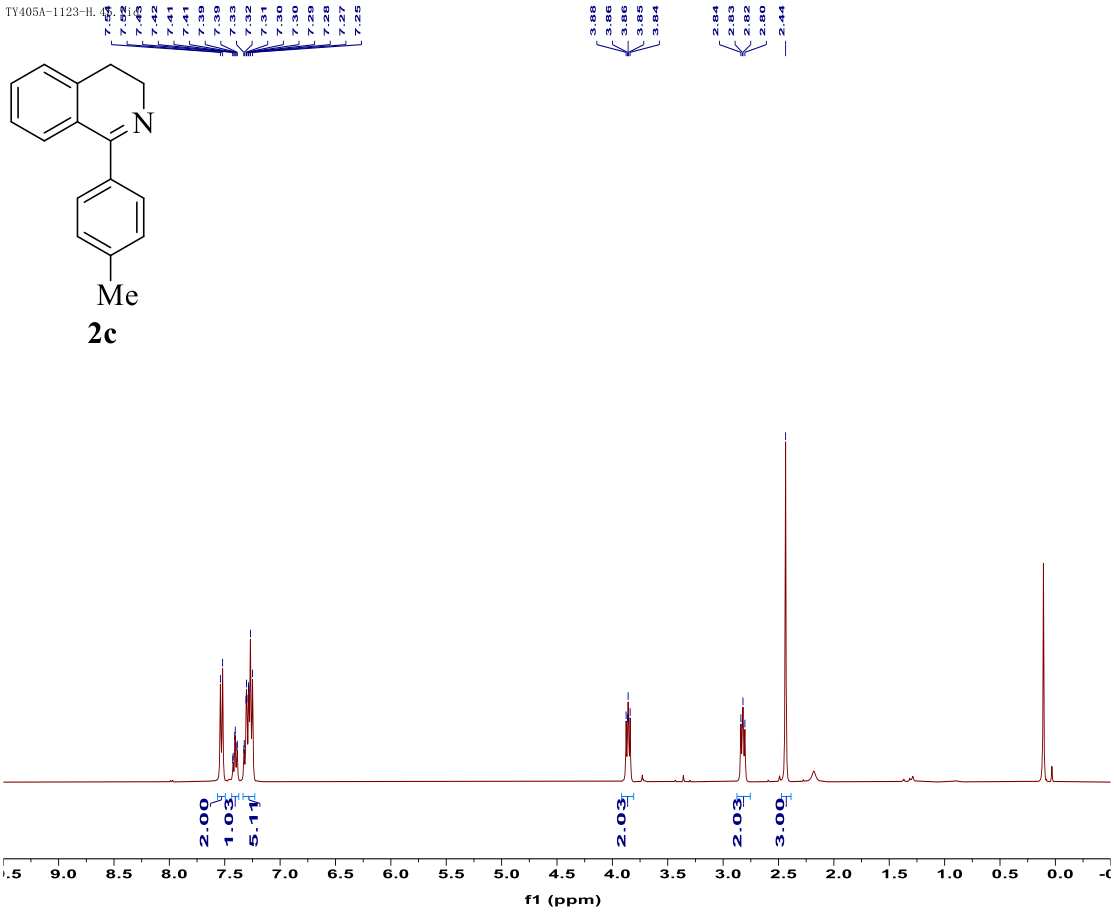
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Me
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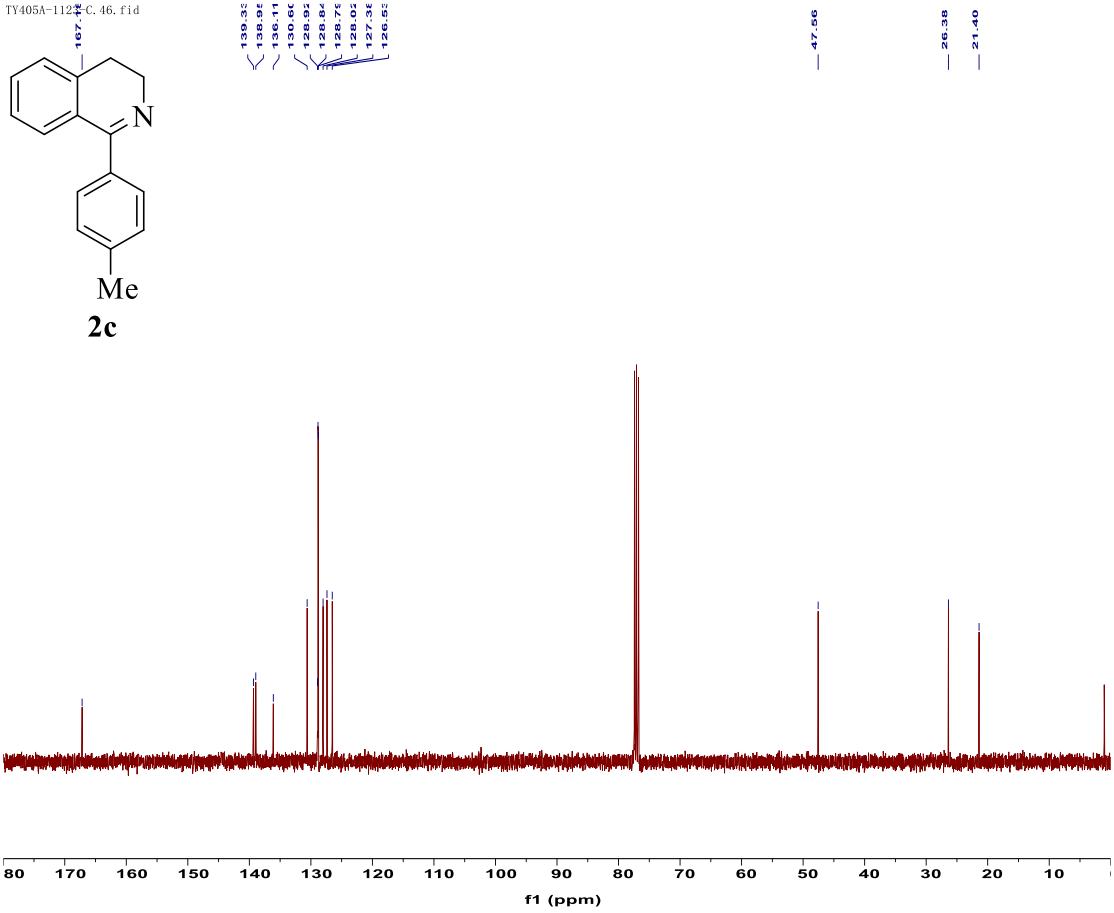
1.03
5.11
2.03
2.03
3.00
f1 (ppm)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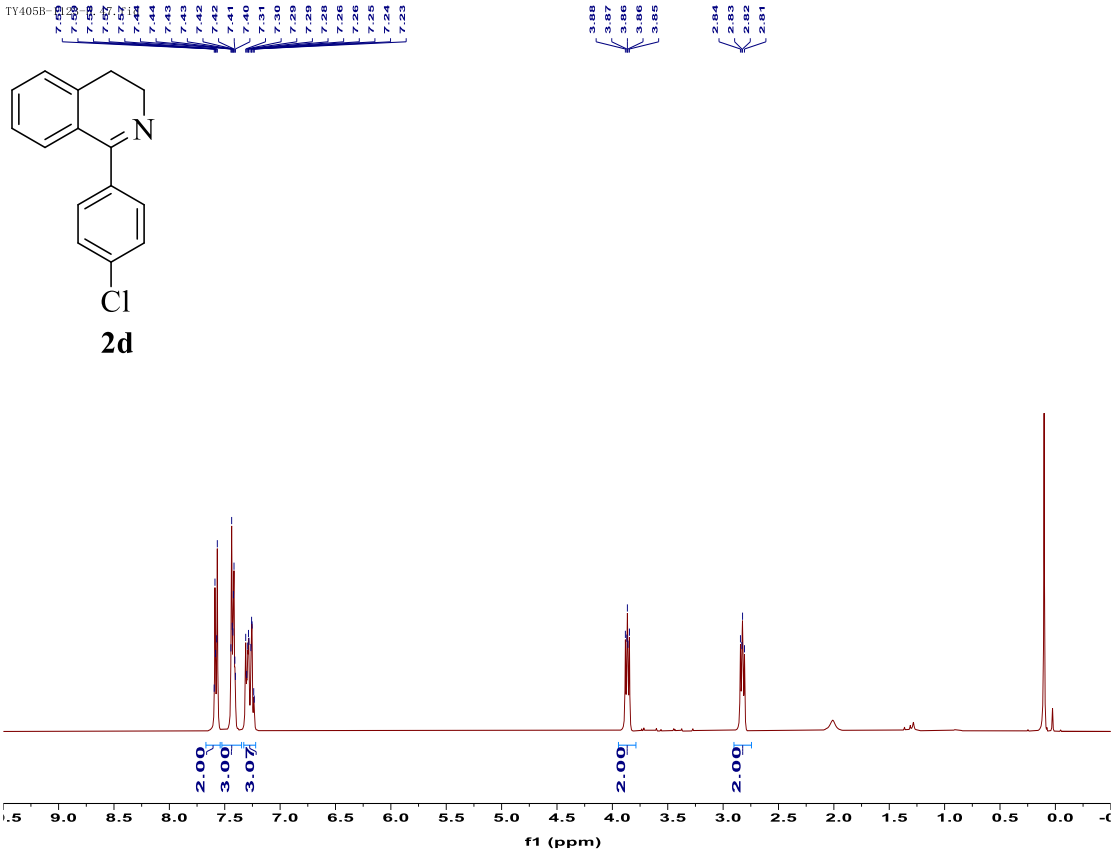

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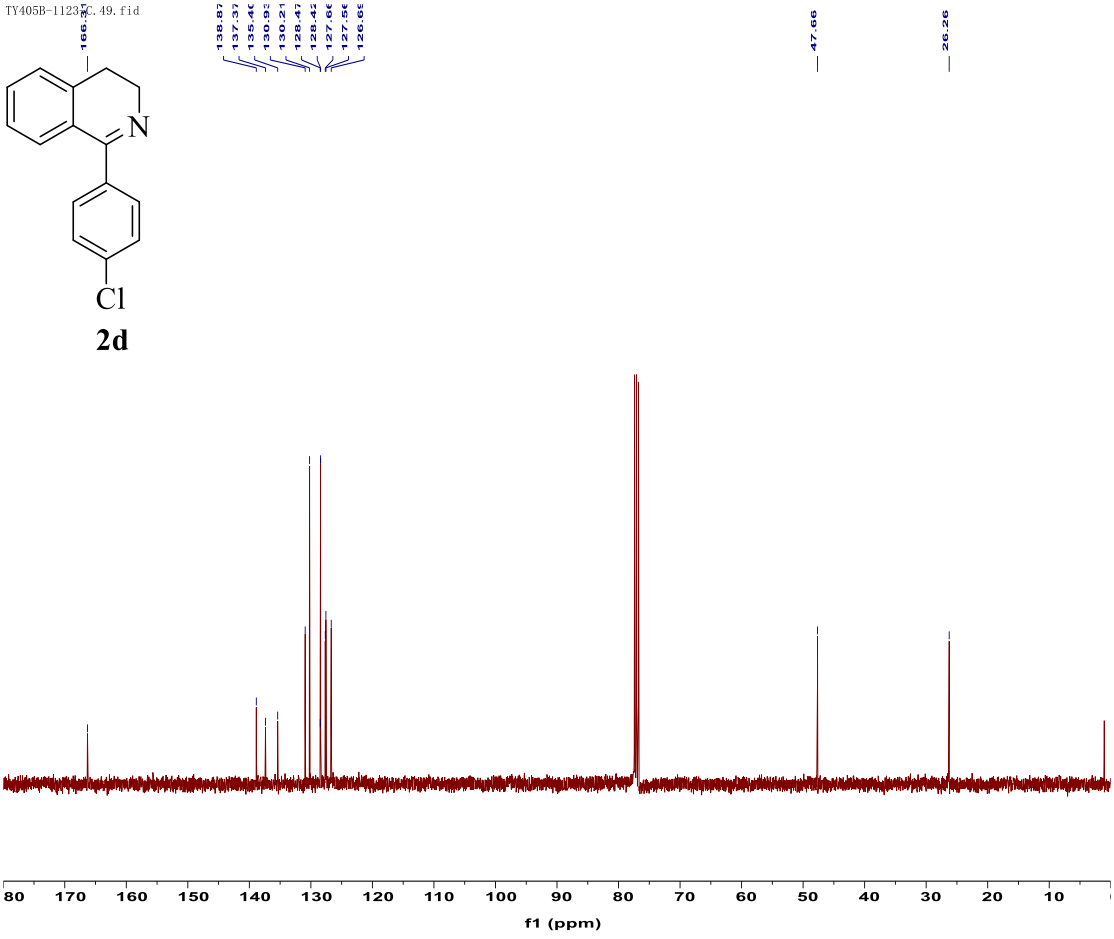

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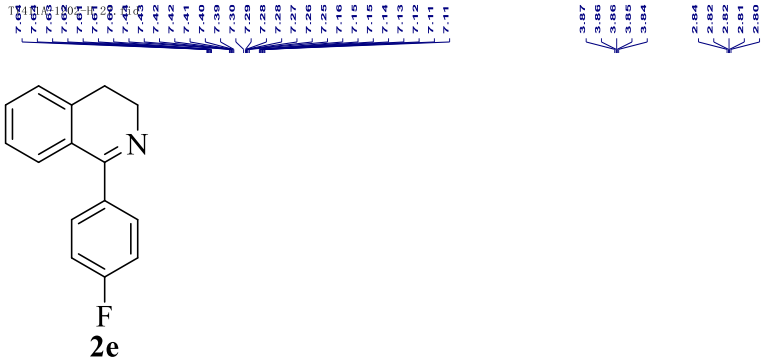

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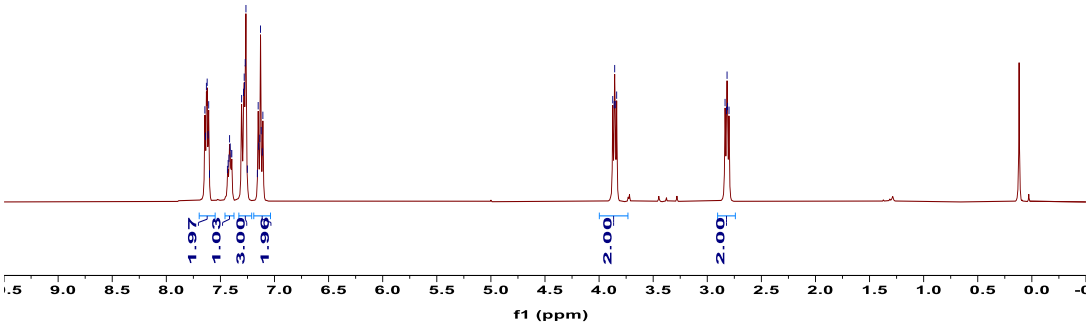

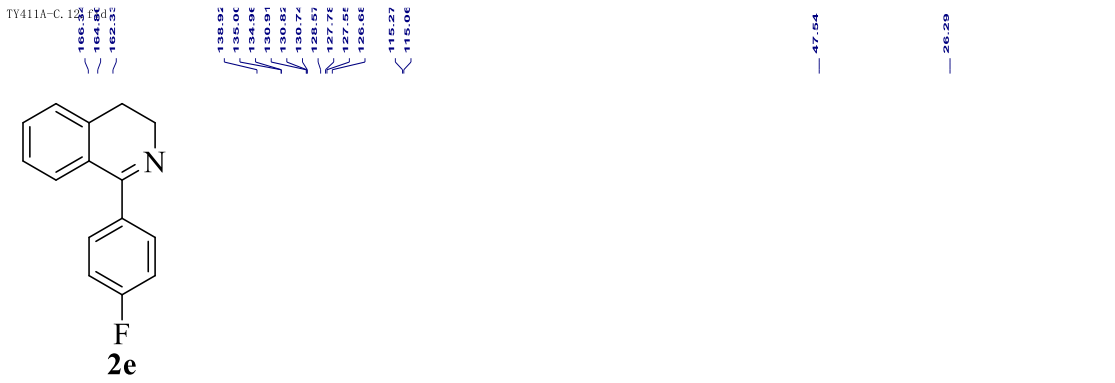

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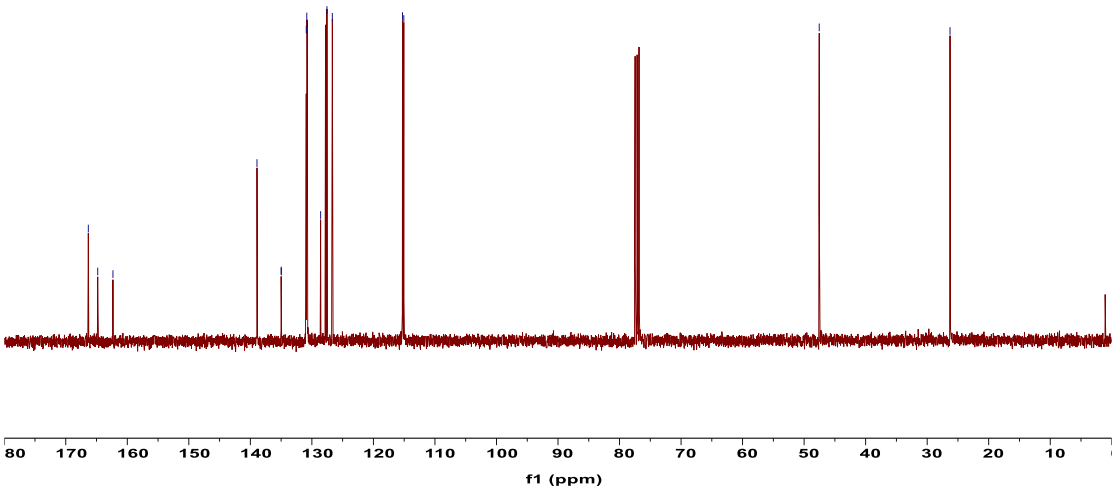

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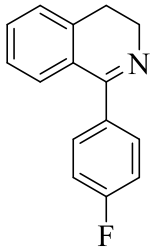

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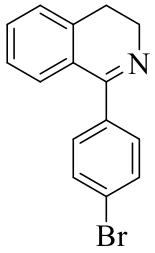

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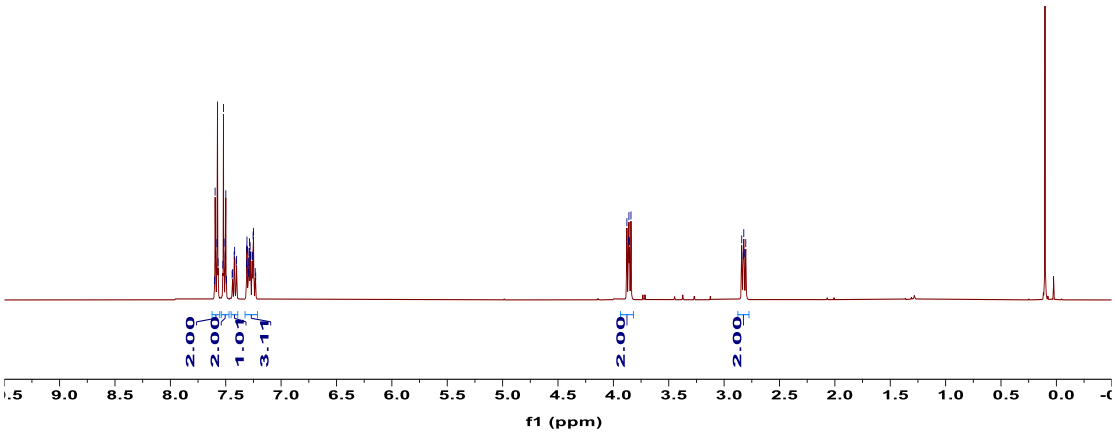

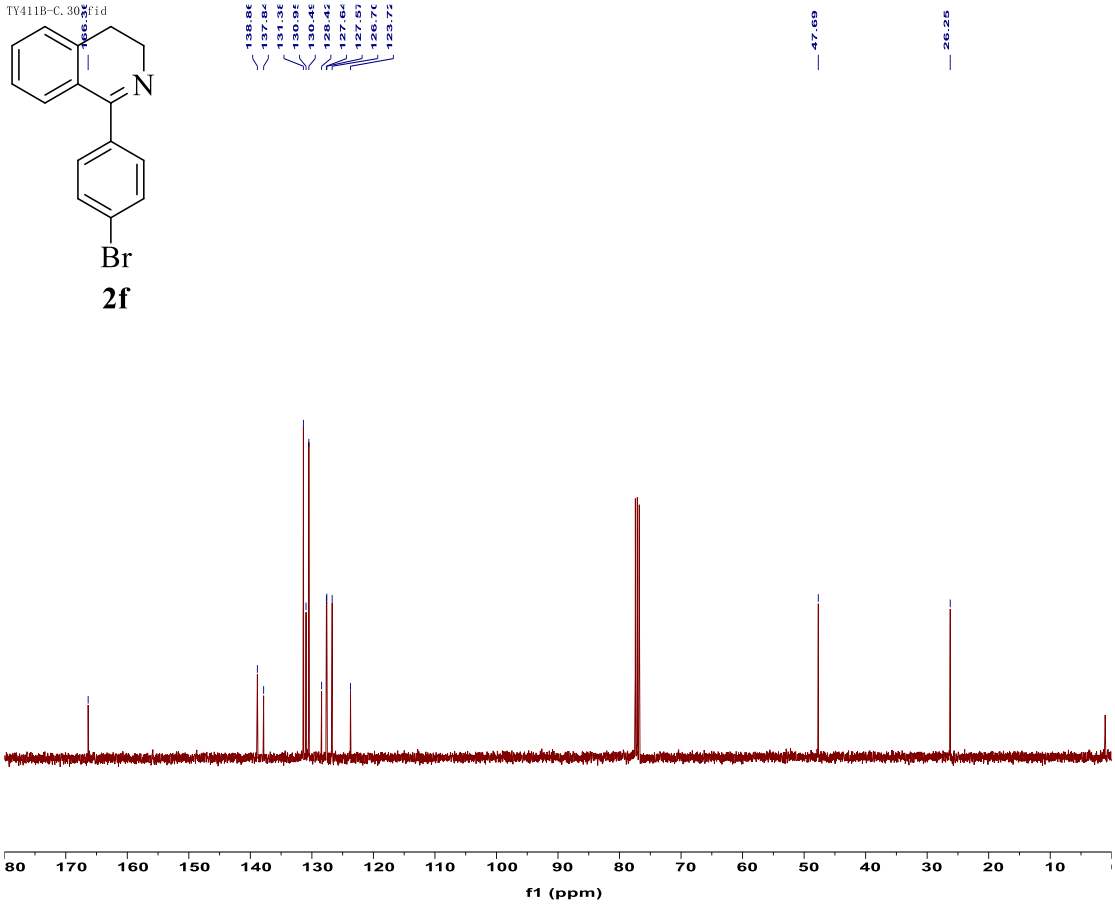
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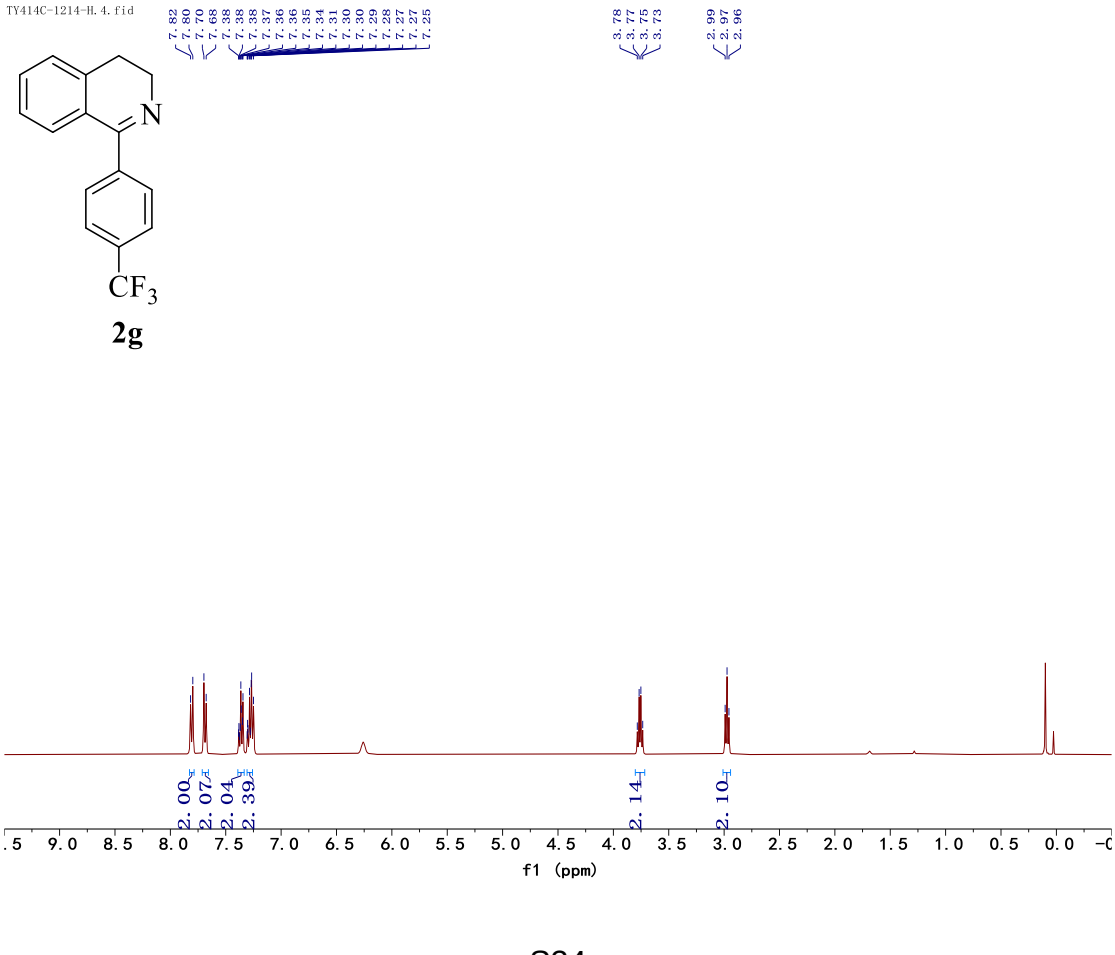
47.69
26.25
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

2f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CF3
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7.80
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7.68
7.38
7.38
7.38
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7.36
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7.34
7.31
7.30
7.30
7.29
7.28
7.27
7.27
7.25
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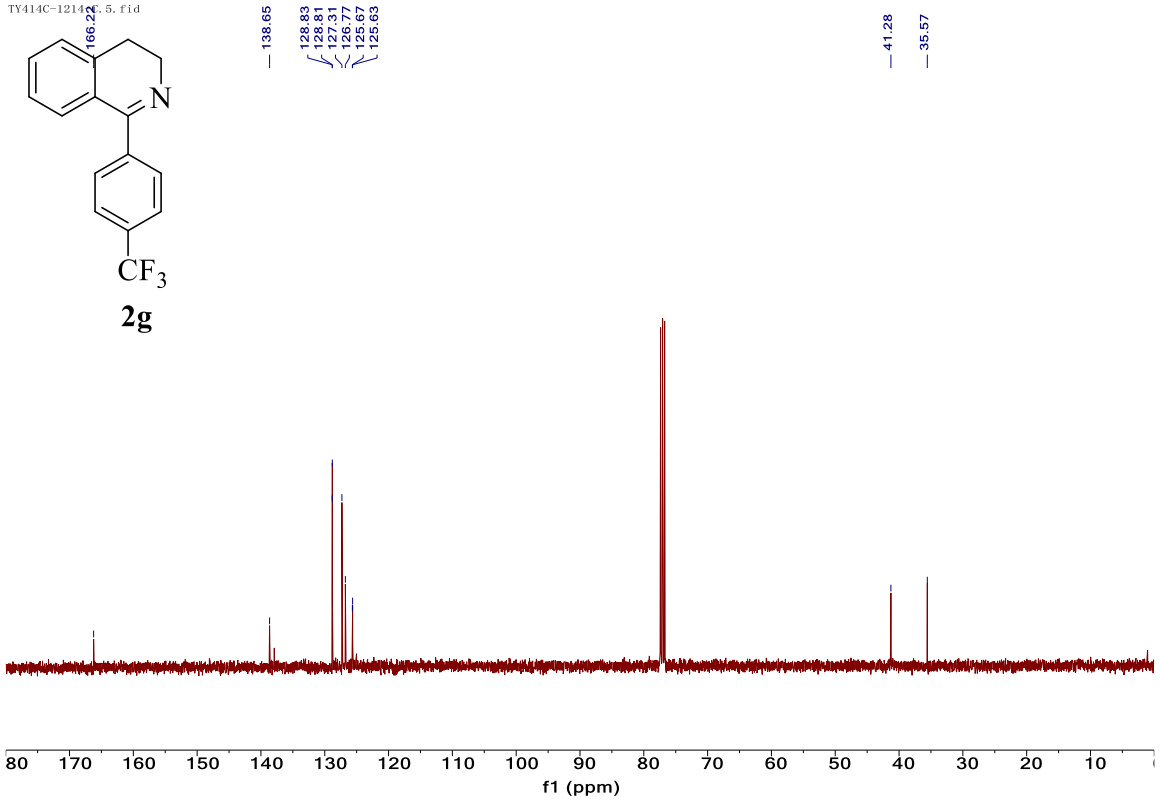
3.77
3.75
3.73
2.99
2.97
2.96
2.00
2.07
2.04
2.39
2.14
2.10
.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

2g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128.83
128.81
127.31
126.77
125.67
125.63
41.28
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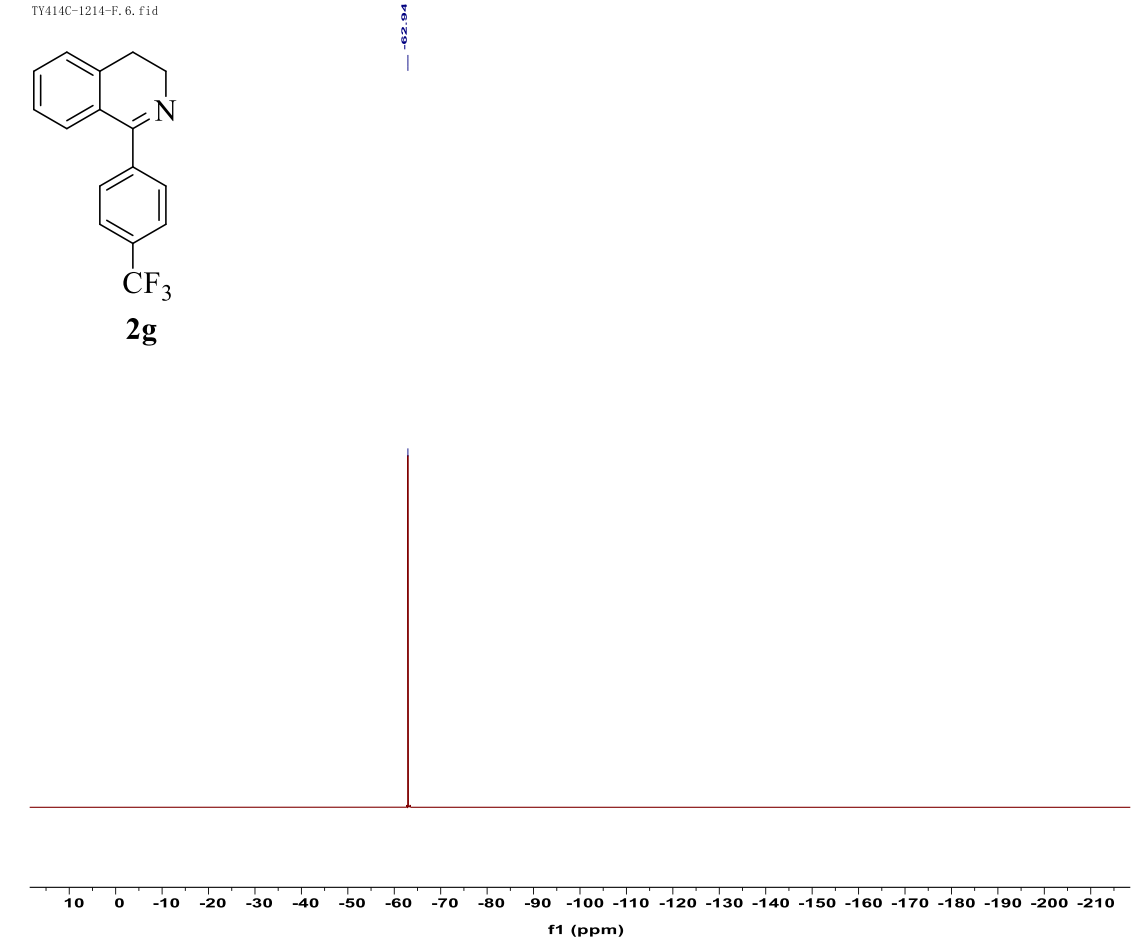
N
CF3
2g
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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N
CF3
2g
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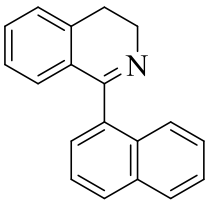
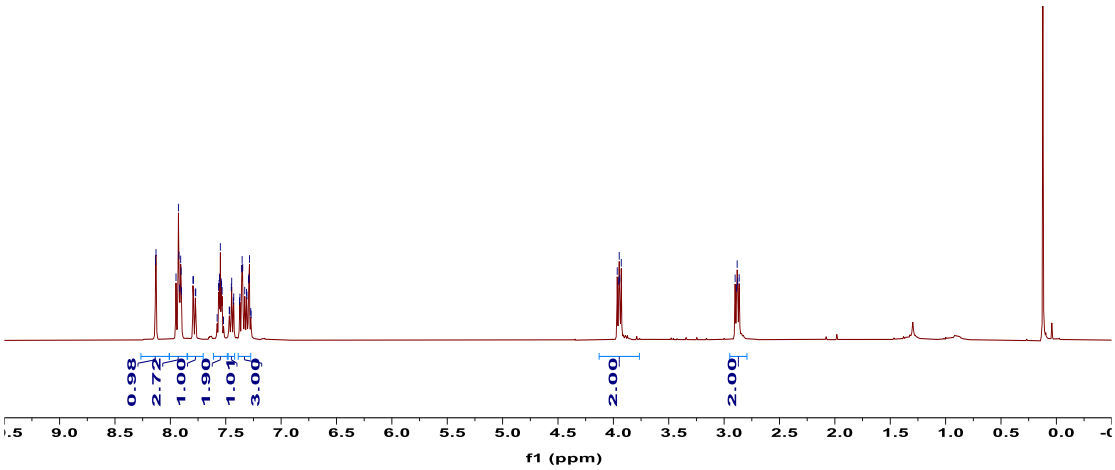
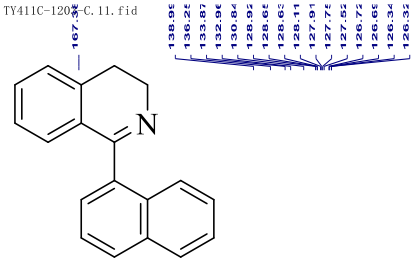
f1 (ppm)

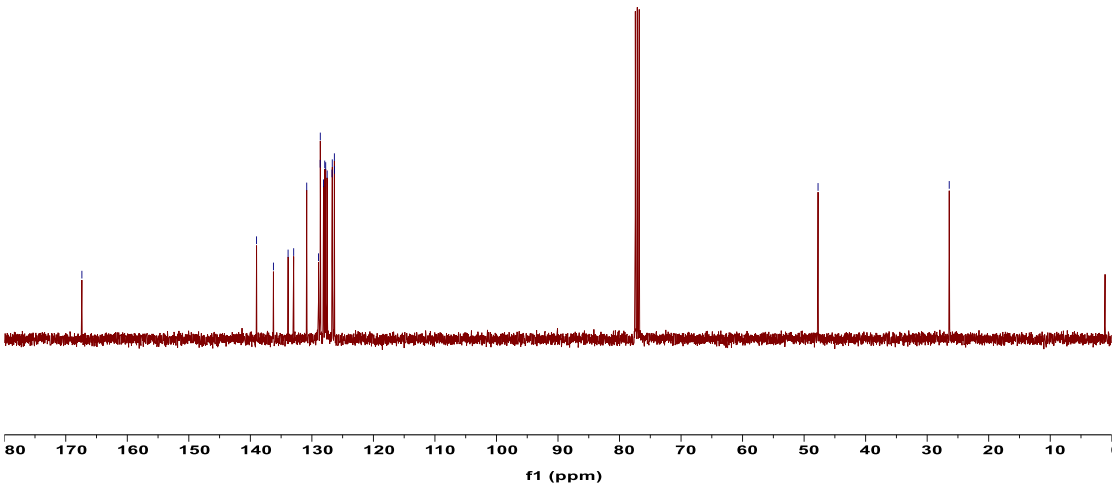


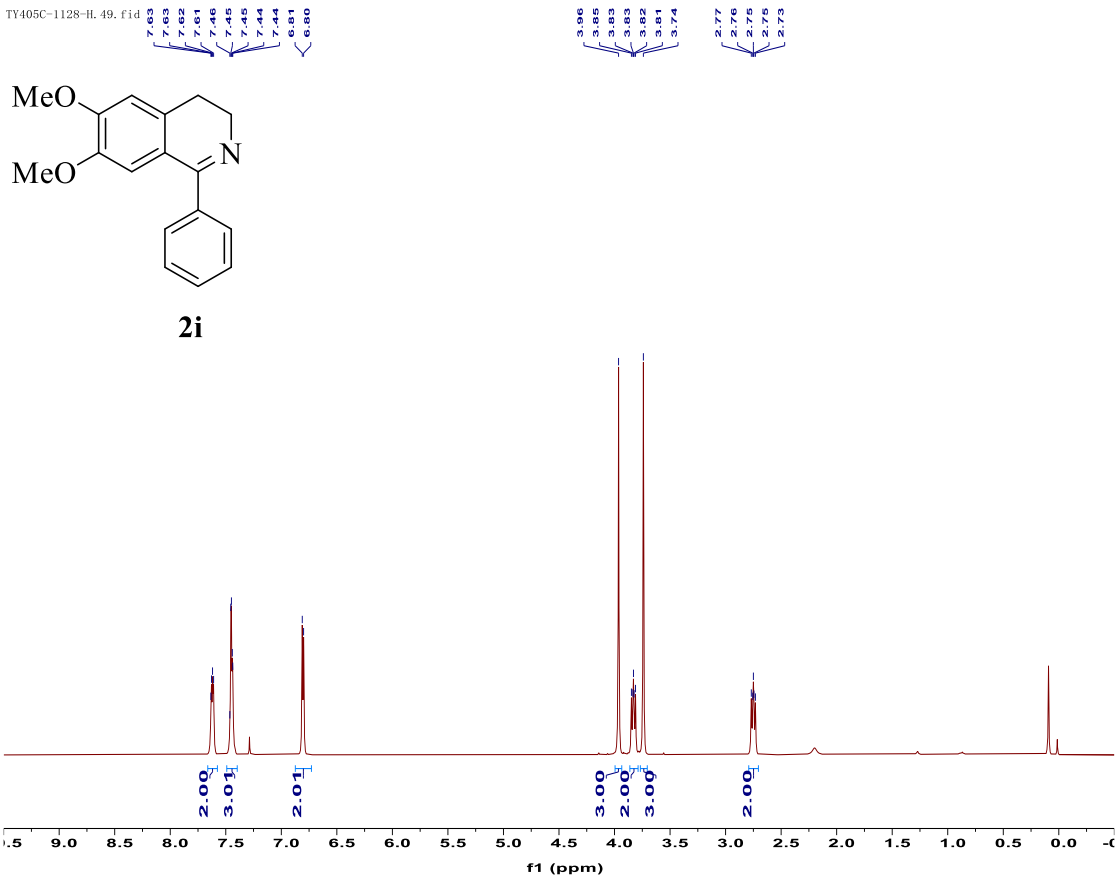
2h

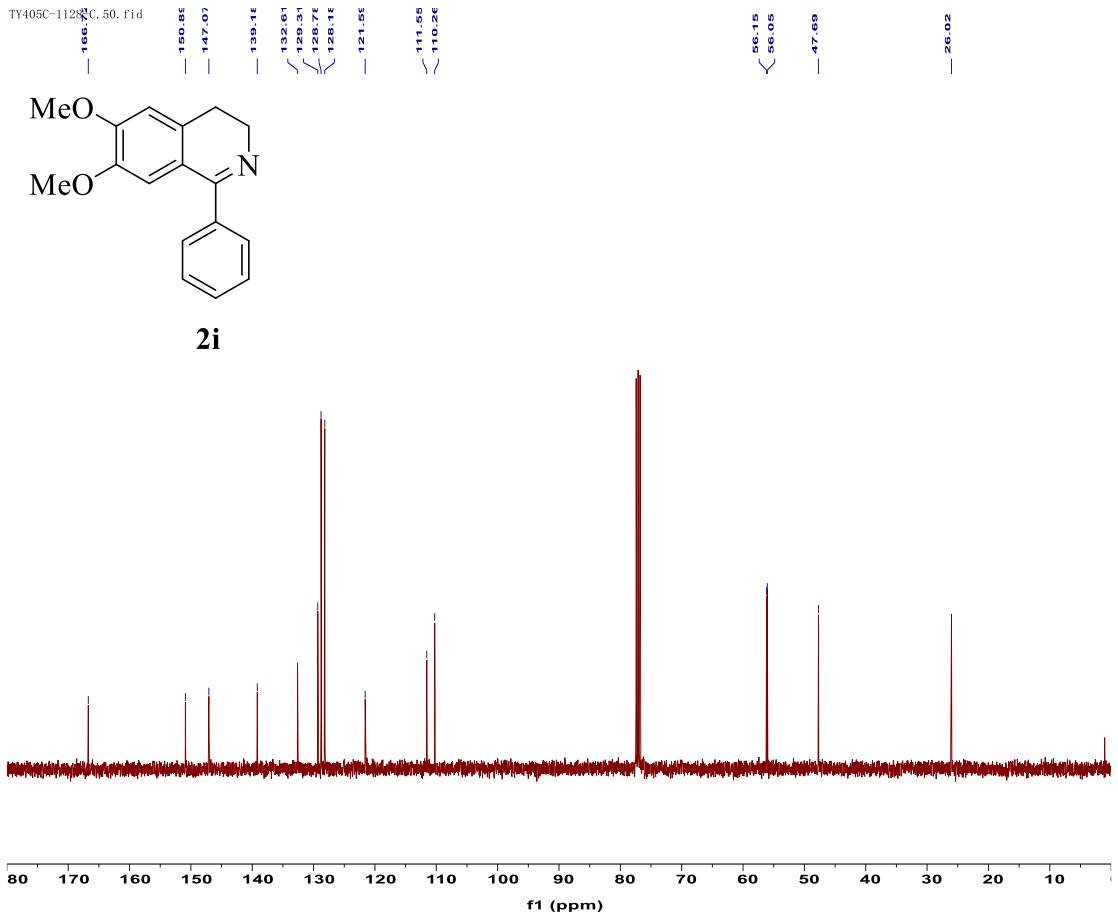


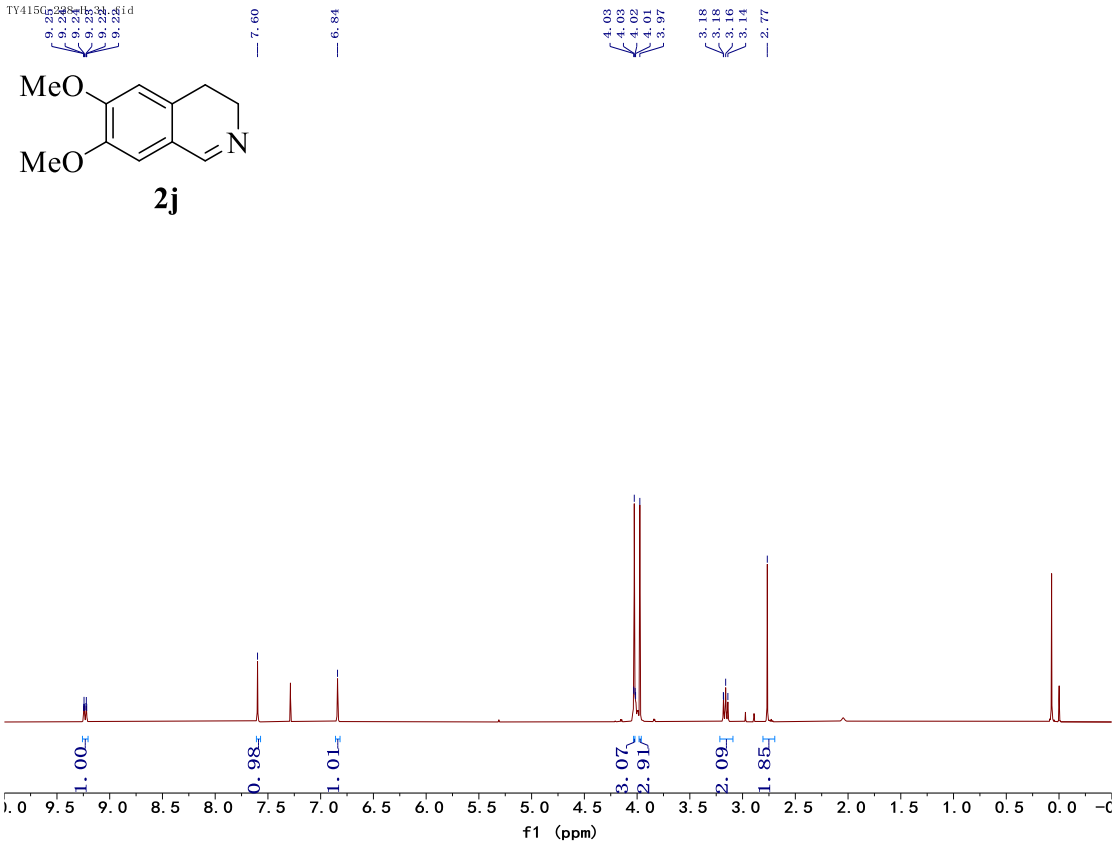


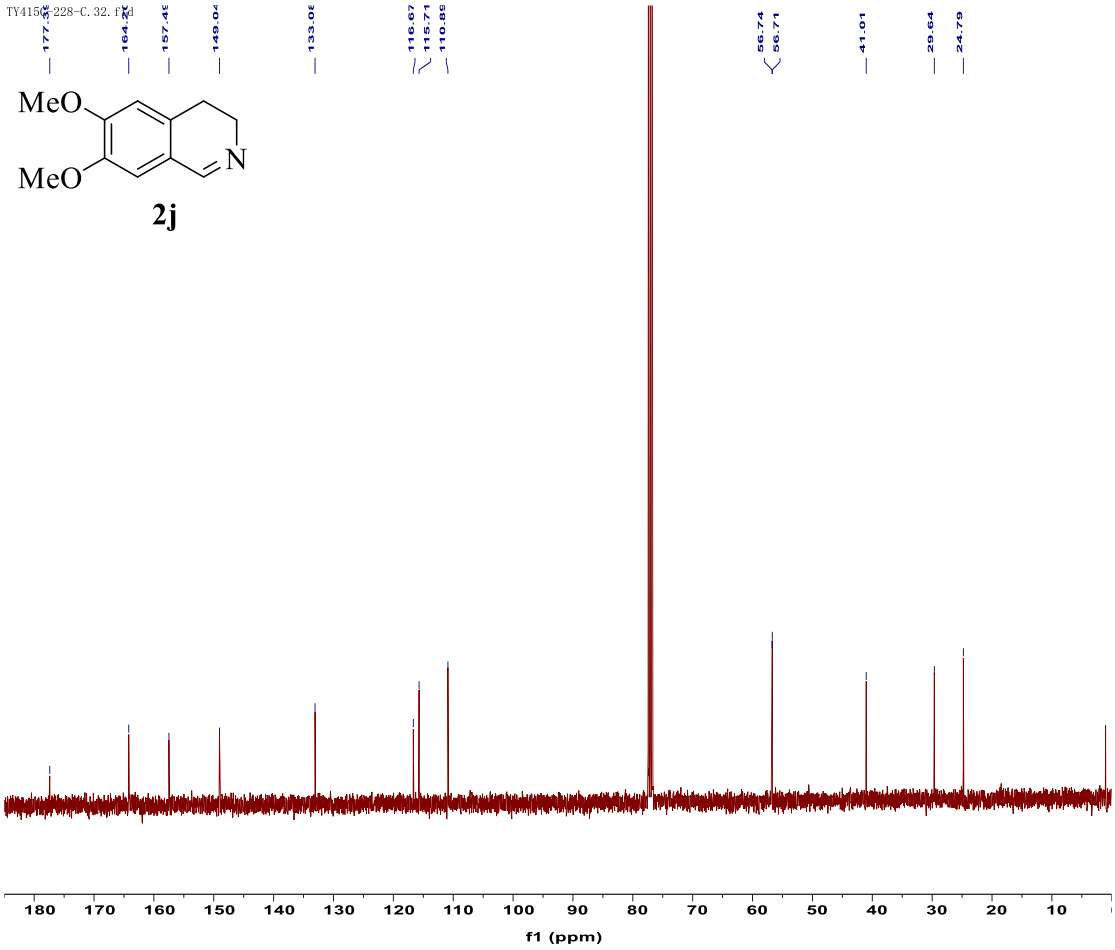
2h

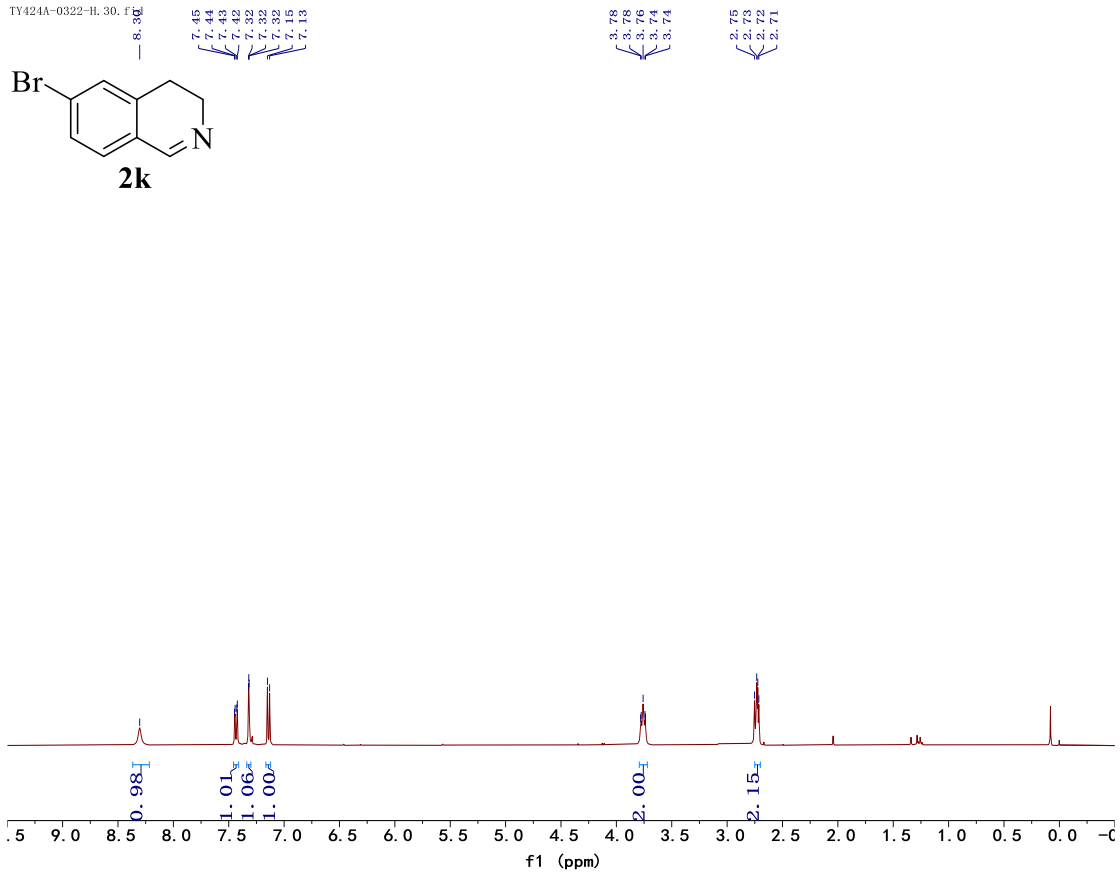


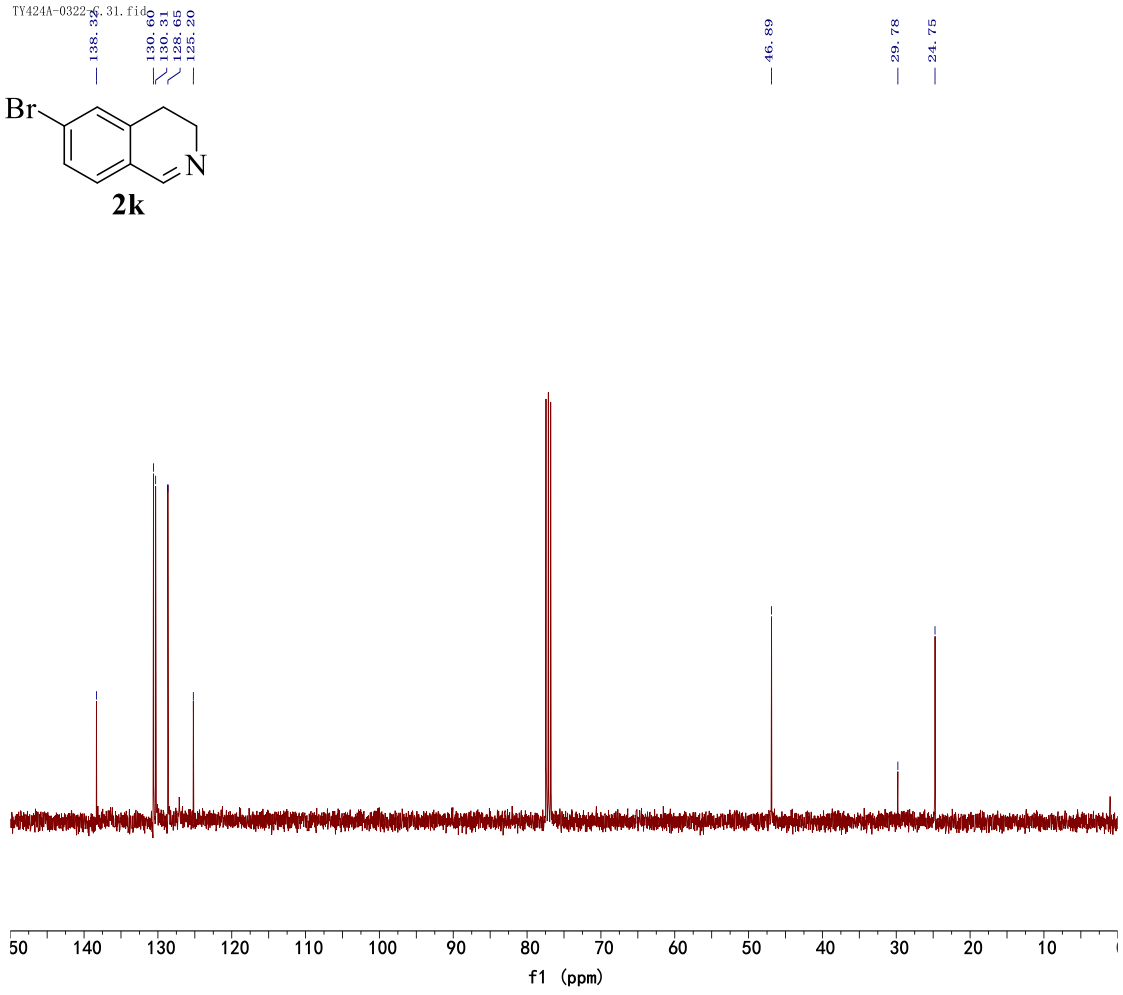

TY405C-1128-H.49.fid
MeO
MeO
N
2i
f1 (ppm)

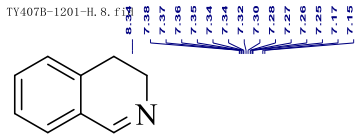

TY405C-1128C.50.fid
MeO
MeO
N
2i
f1 (ppm)


MeO
MeO
N
2j
f1 (ppm)

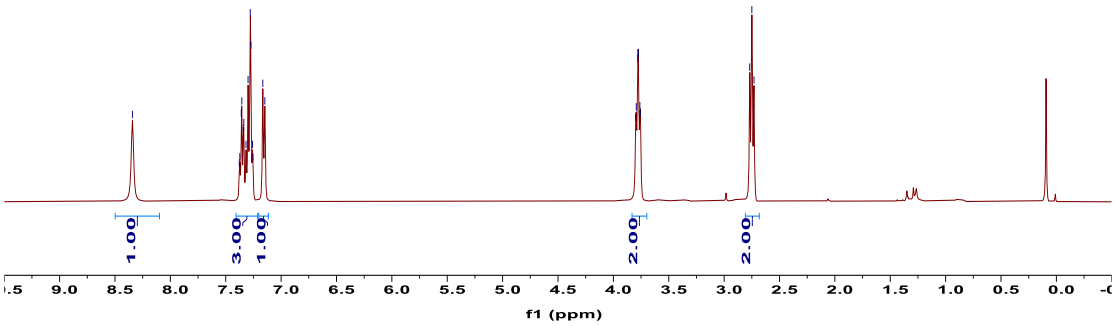

MeO
MeO
N
2j
f1 (ppm)


TY424A-0322-H.30.fid
8.30
7.45
7.44
7.43
7.42
7.32
7.32
7.32
7.15
7.13
3.78
3.78
3.76
3.74
3.74
2.75
2.73
2.72
2.71
Br
N
2k
0.98
1.01
1.06
1.00
2.00
2.15
f1 (ppm)

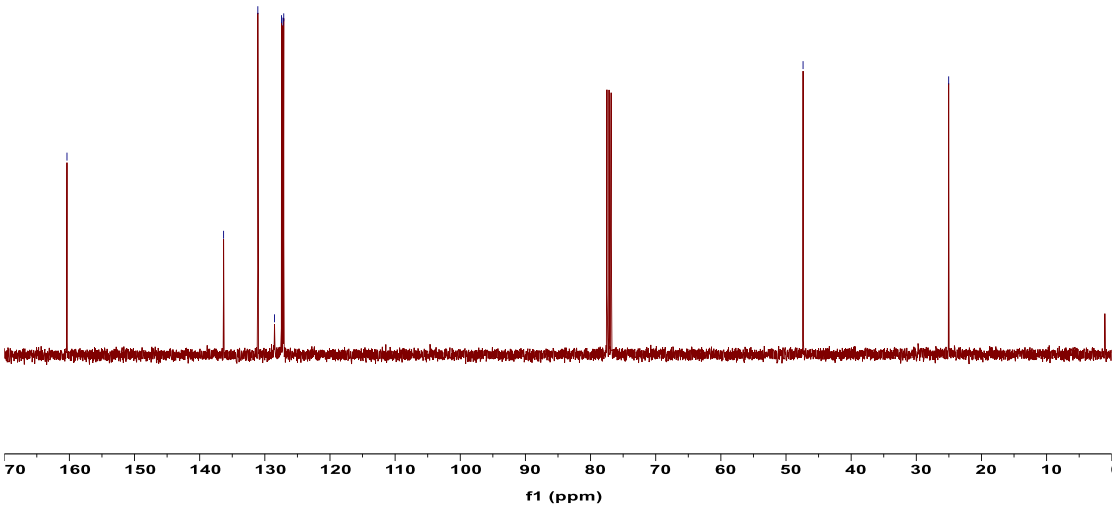

TY424A-0322-C.31.fid
138.32
130.60
130.31
128.65
125.20
46.89
29.78
24.75
Br
N
2k
f1 (ppm)

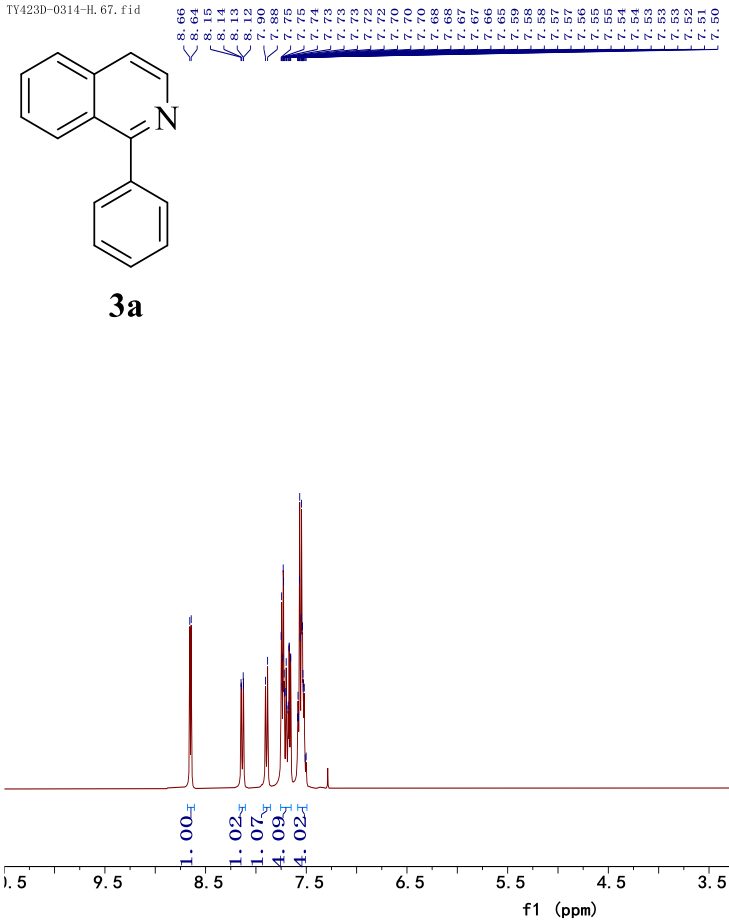


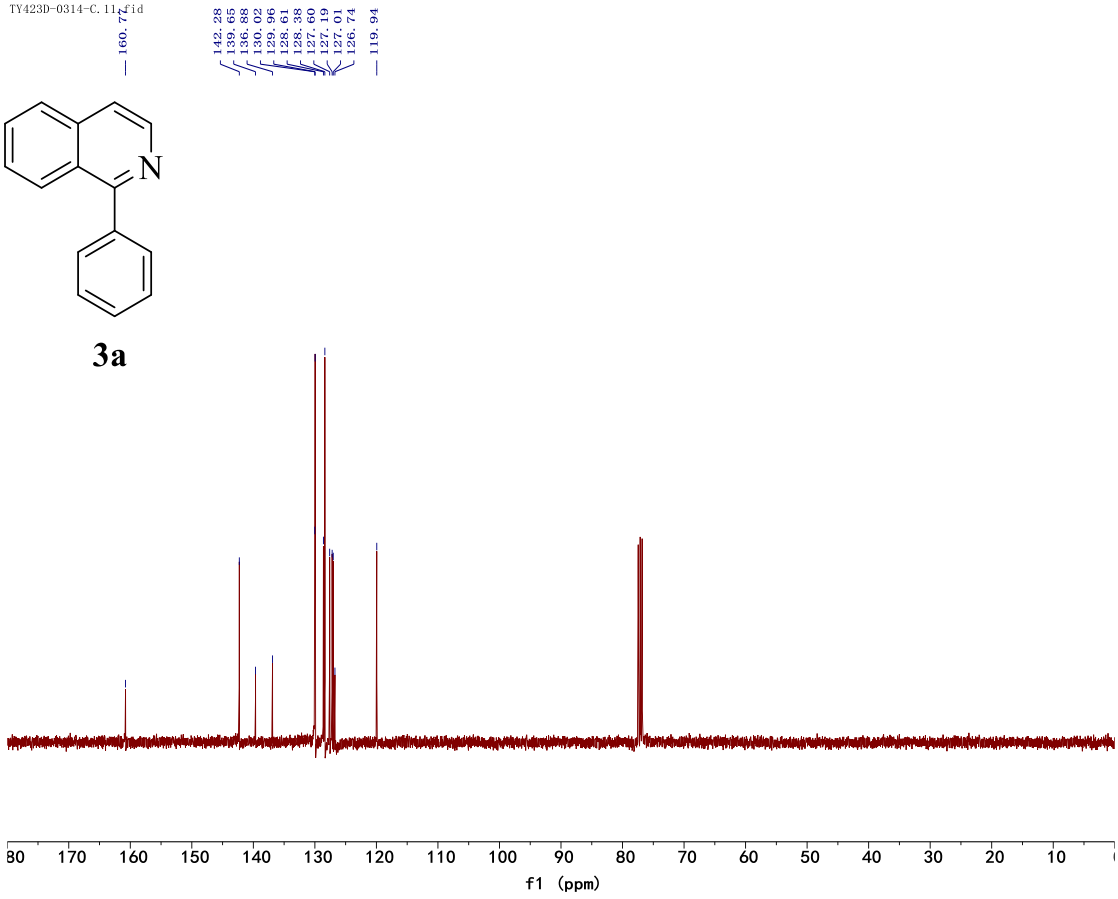
2l

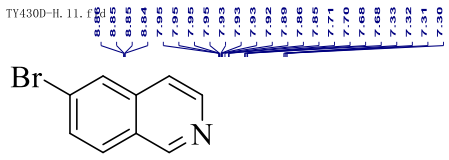


2l



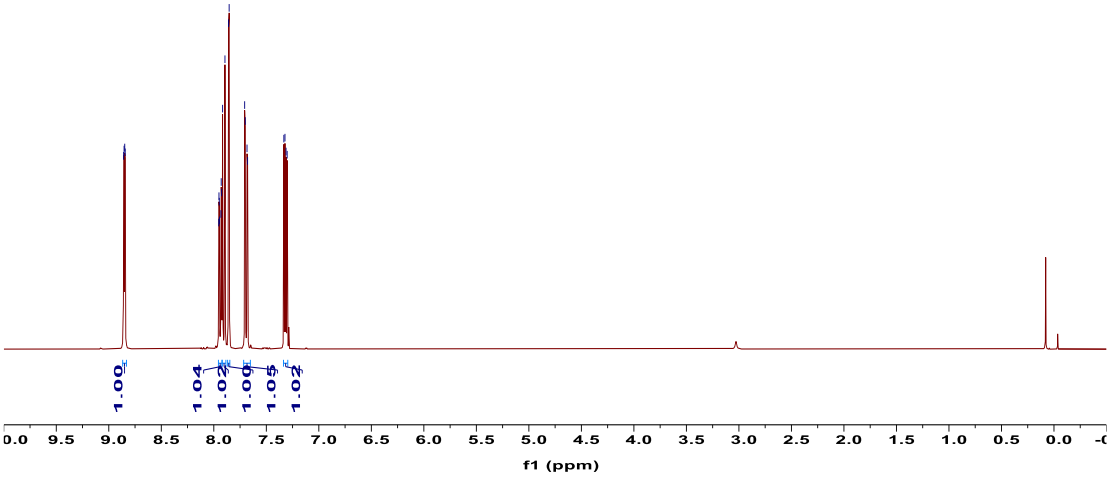

TY423D-0314-H.67.fid
8.66
8.64
8.15
8.14
8.13
8.12
7.90
7.88
7.75
7.75
7.74
7.73
7.73
7.73
7.72
7.72
7.70
7.70
7.70
7.68
7.68
7.67
7.67
7.66
7.65
7.59
7.58
7.58
7.57
7.57
7.56
7.55
7.55
7.54
7.54
7.53
7.53
7.53
7.52
7.51
7.50
N
3a
1.00
1.02
1.07
4.09
4.02
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


TY423D-0314-C.11.fid
160.77
142.28
139.65
136.88
130.02
129.96
129.61
128.38
127.60
127.19
127.01
126.74
119.94
N
3a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

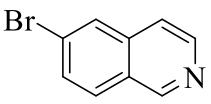

TY430D-H. 11. fid
8.85
8.85
8.84
7.95
7.95
7.95
7.93
7.93
7.92
7.89
7.86
7.85
7.71
7.70
7.68
7.33
7.32
7.31
7.30

Br
N

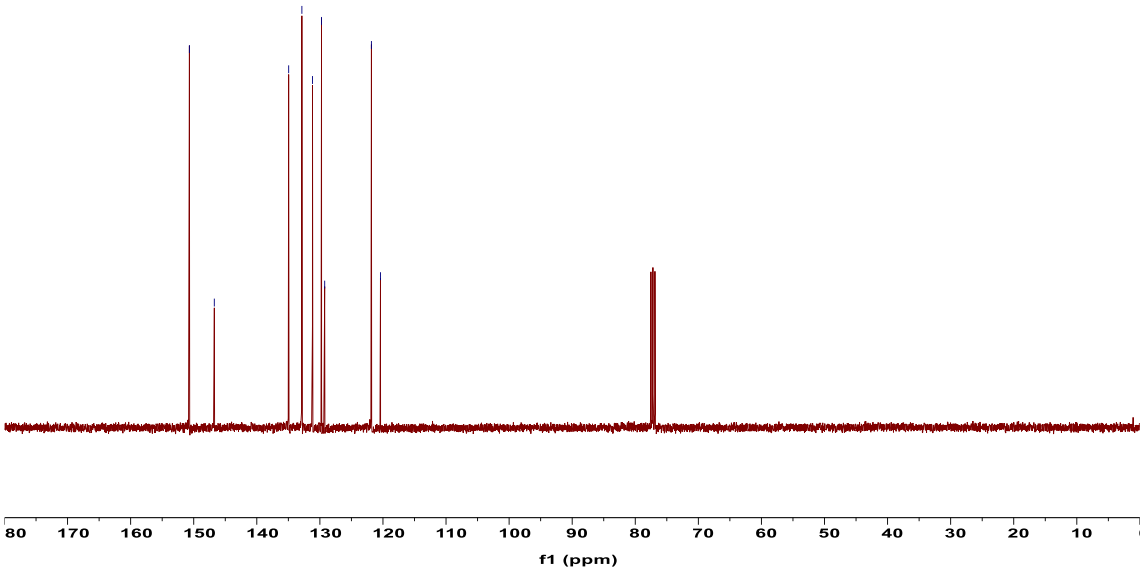
3b

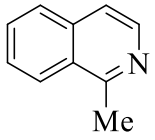

1.00
1.04
1.02
1.00
1.05
1.02
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


TY430D-C. 12. fid
150.65
146.74
134.95
132.85
131.11
129.74
129.24
121.83
120.46

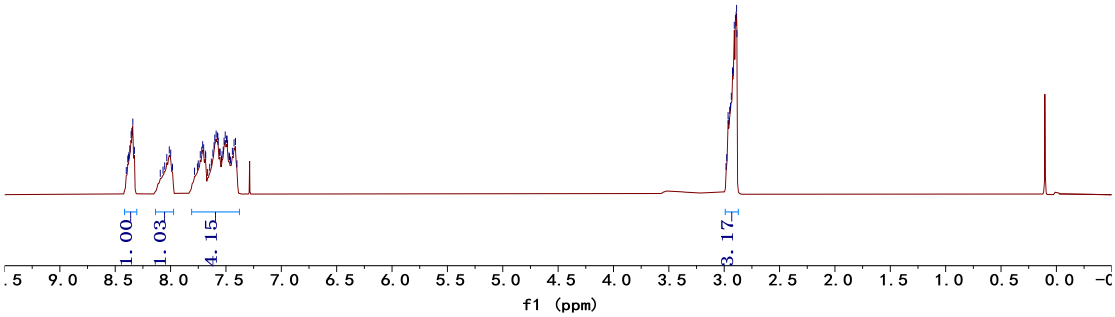

Br
N

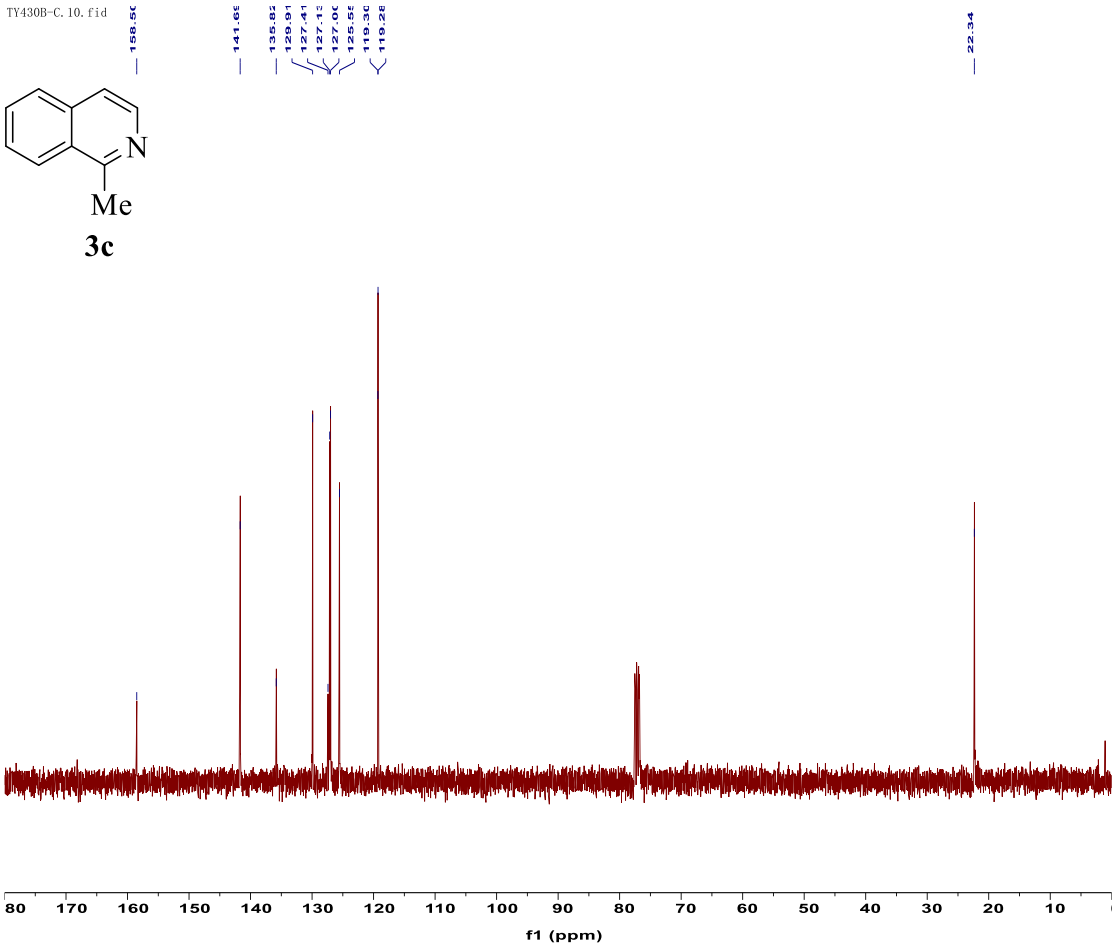
3b


80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


N
Me

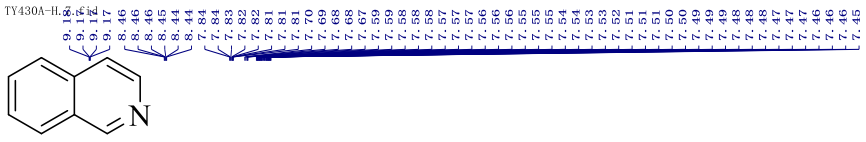
3c


1.00
1.03
4.15
3.17
f1 (ppm)

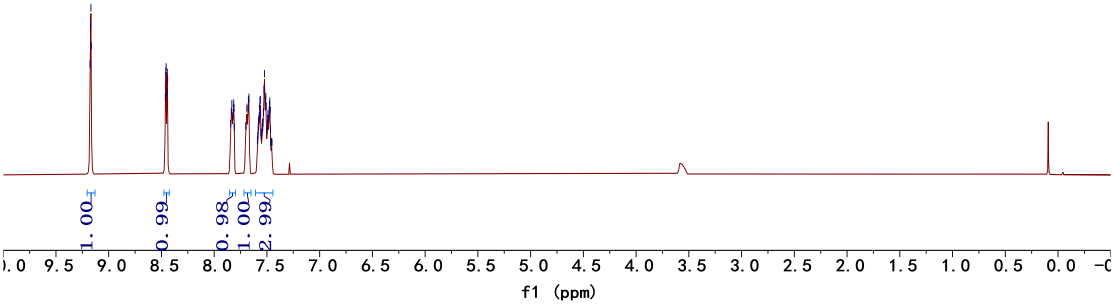

TY430B-C.10.fid
158.56
141.65
135.85
129.91
127.41
127.12
127.06
125.55
119.36
119.28
22.34
f1 (ppm)

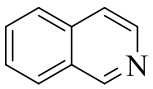
N
Me

3c

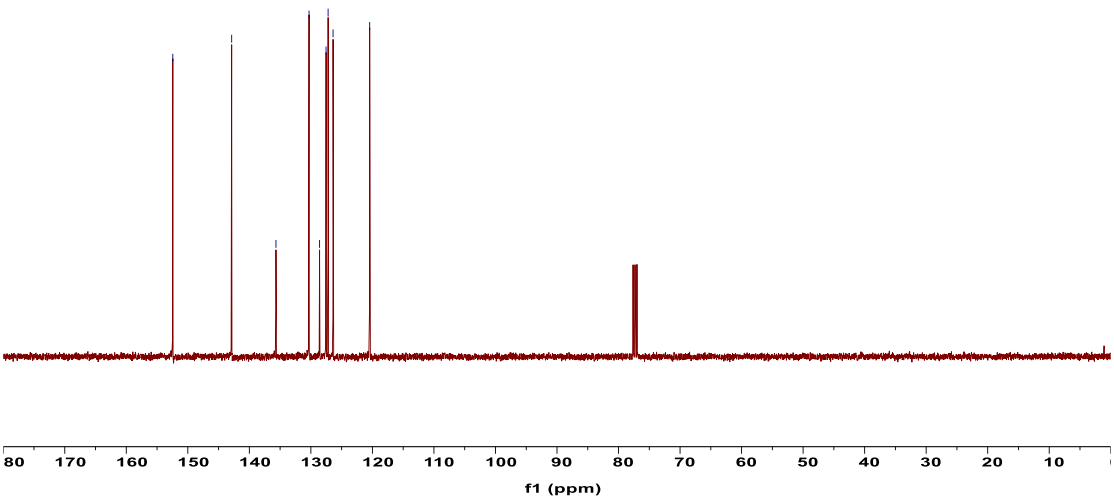


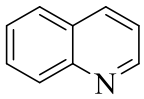
3d



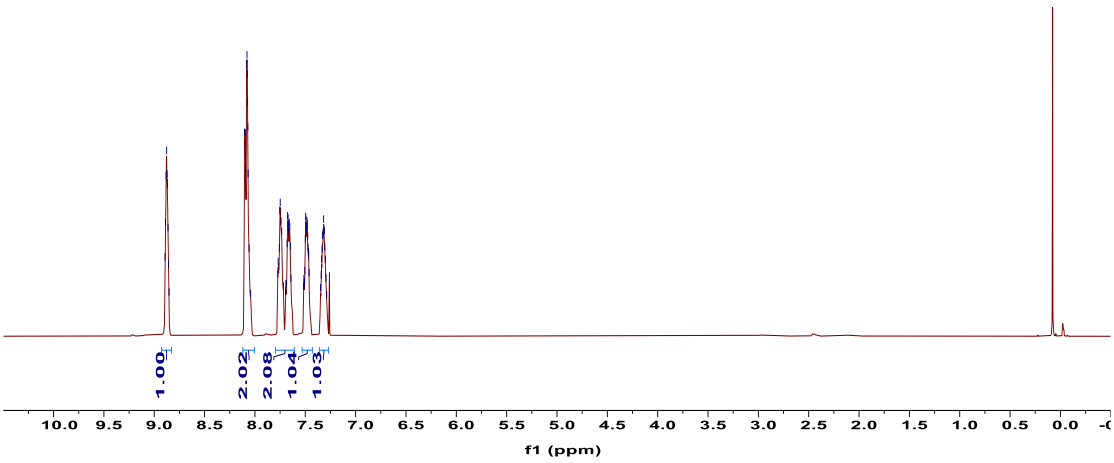


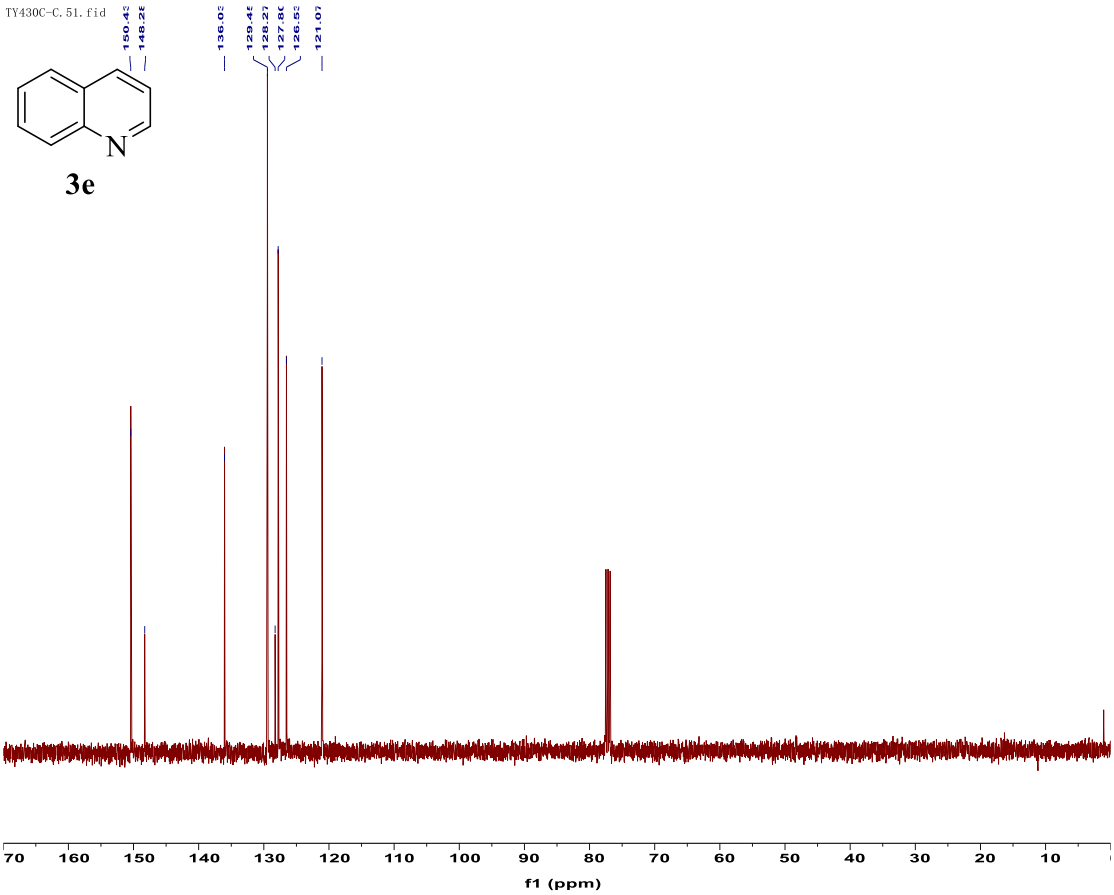
3d



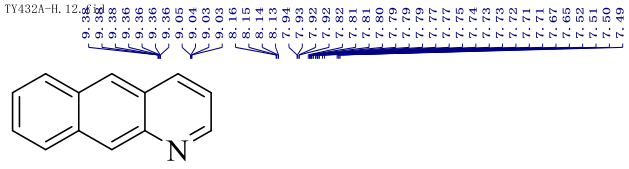


3e

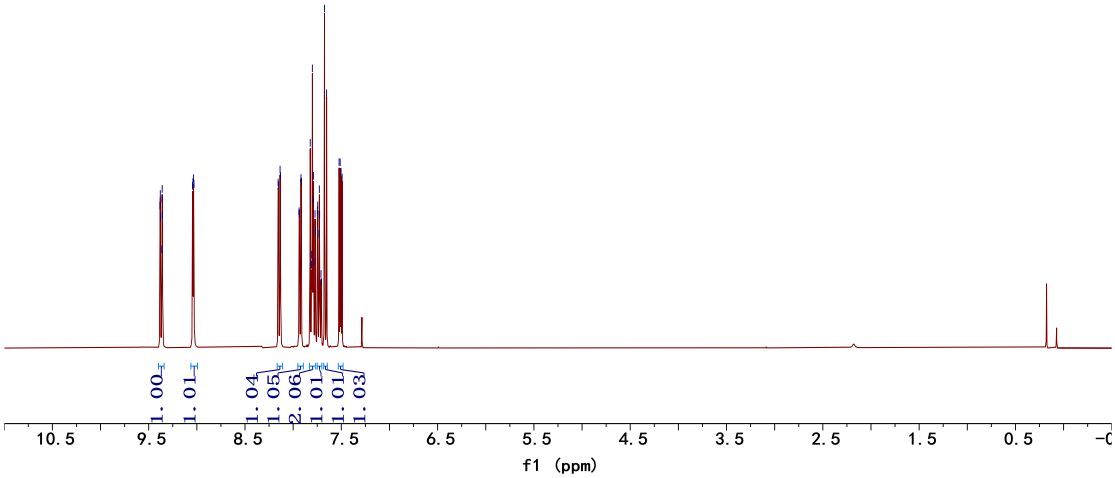

1.00
2.02
2.08
1.04
1.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

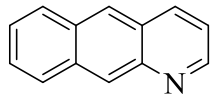

TY430C-C.51.fid
150.43
148.28
136.03
129.45
128.27
127.80
126.52
121.07
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

3e

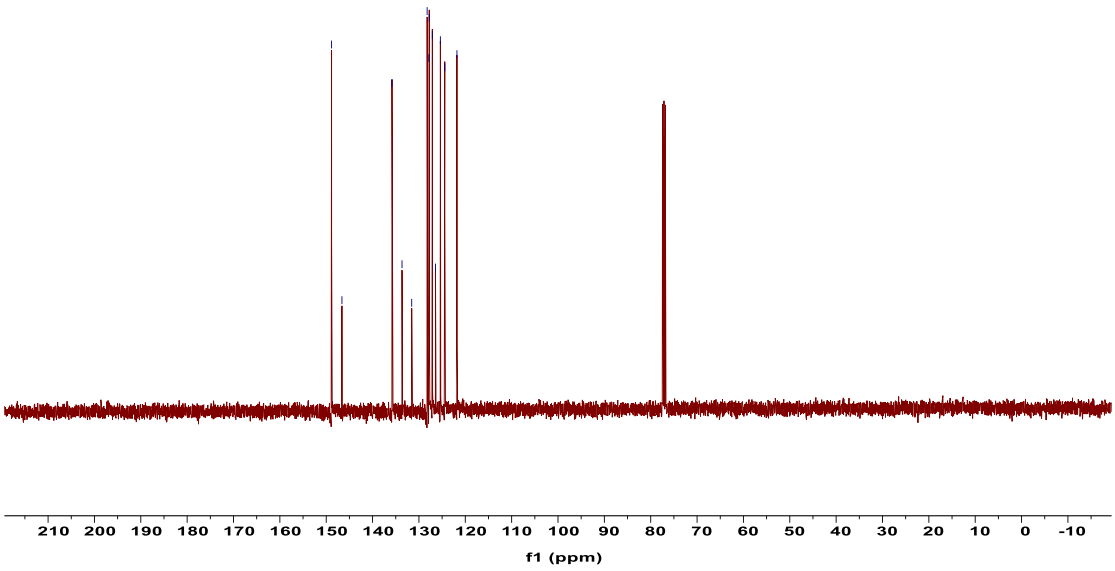


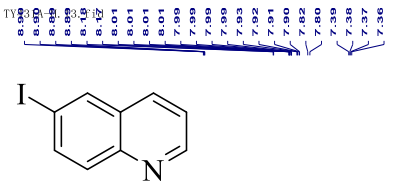
3f


1.00
1.01
1.04
1.05
2.06
1.01
1.01
1.03
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

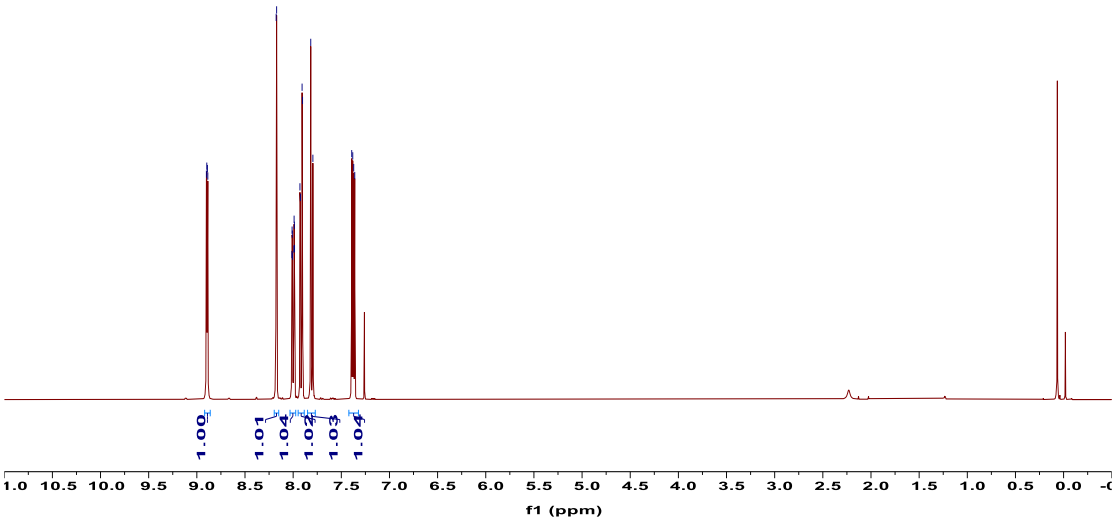


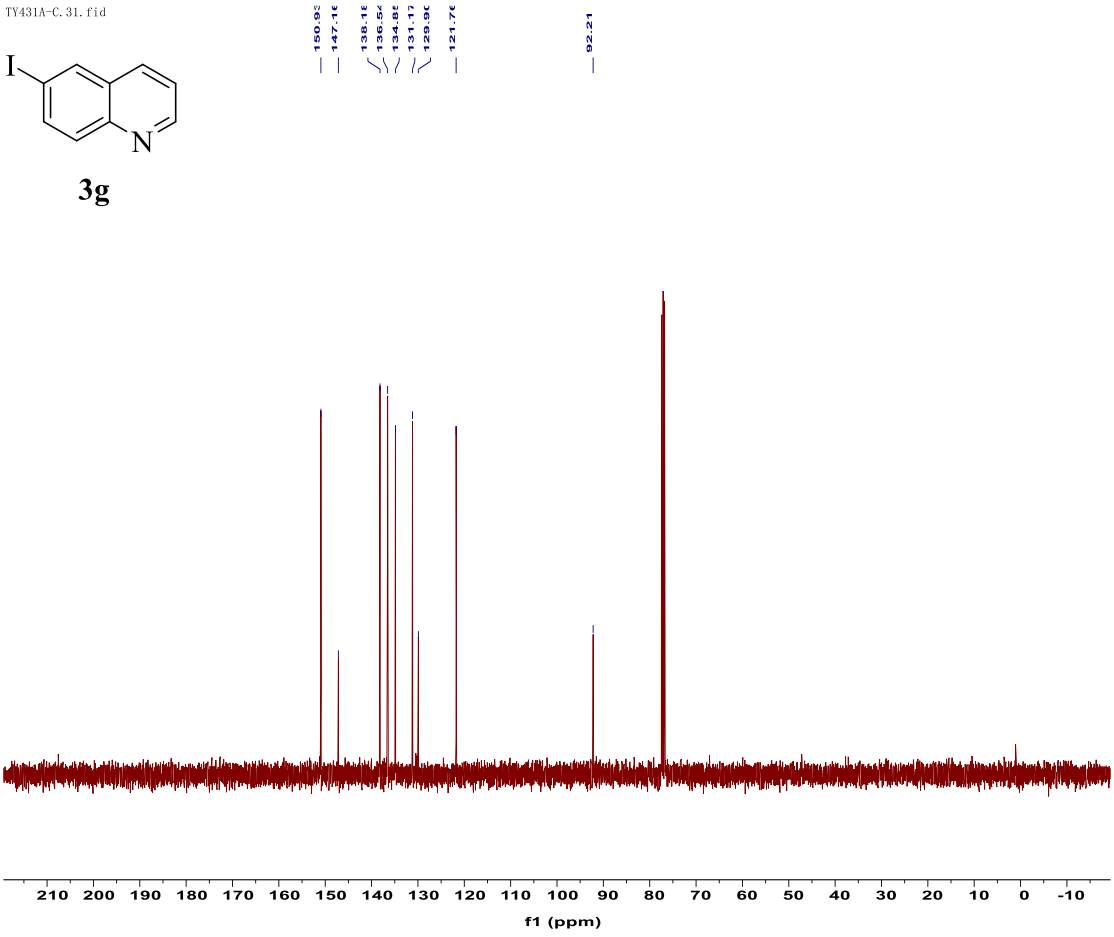
3f


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



3g





3g


TY432B-H. 14. fid
8.03
8.03
8.03
8.01
8.01
8.01
7.95
7.93
7.77
7.77
7.75
7.75
7.72
7.72
7.70
7.70
7.69
7.68
7.68
7.55
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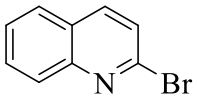
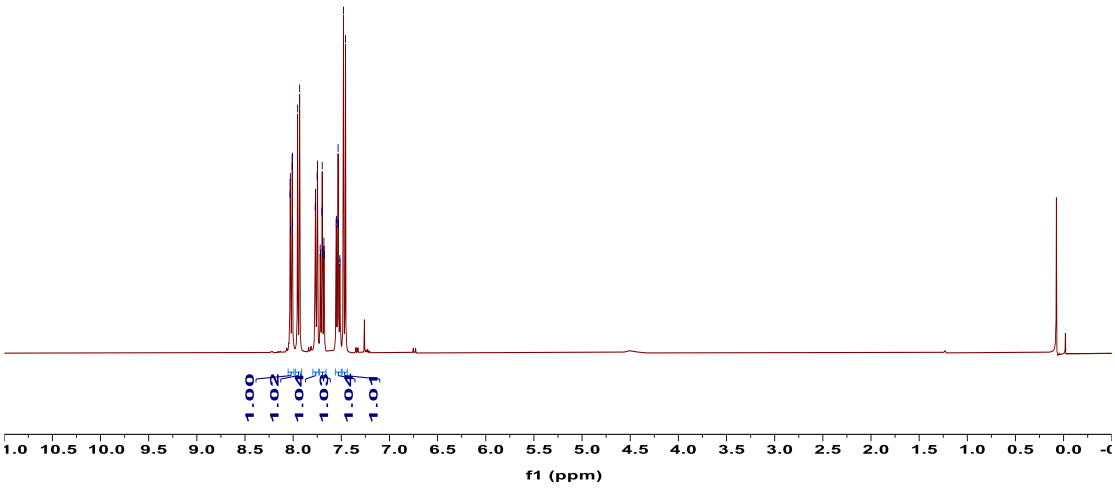
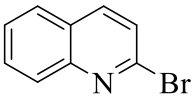
7.54
7.53
7.53
7.52
7.51
7.48
7.46


N
Br

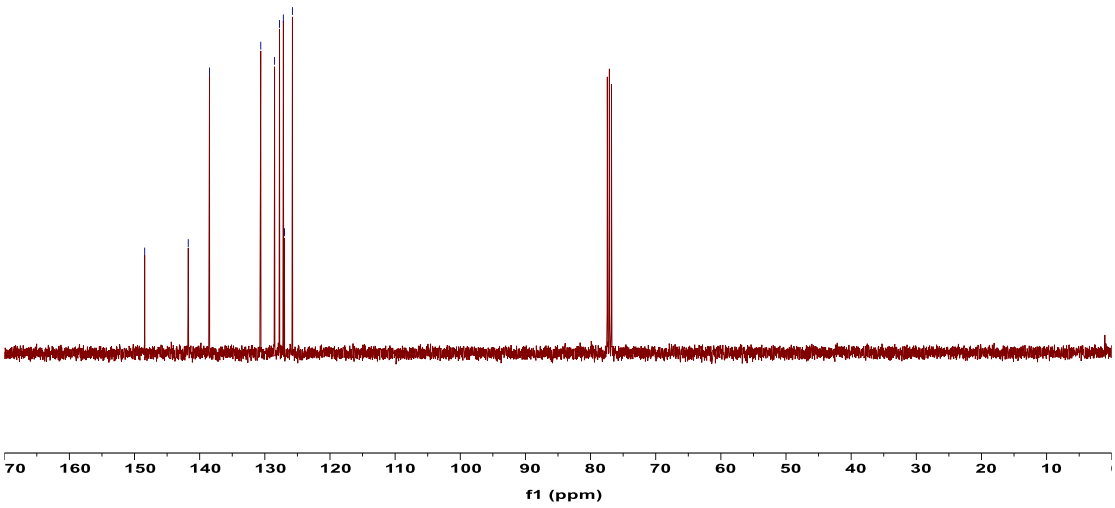
3h

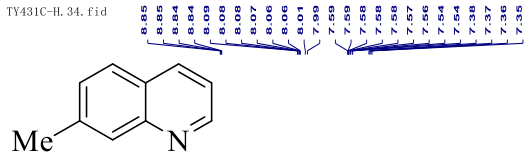

1.00
1.02
1.02
1.03
1.04
1.01
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


TY432B-C. 15. fid
148.44
141.7
138.45
130.65
128.5
127.74
127.1
126.9
125.7

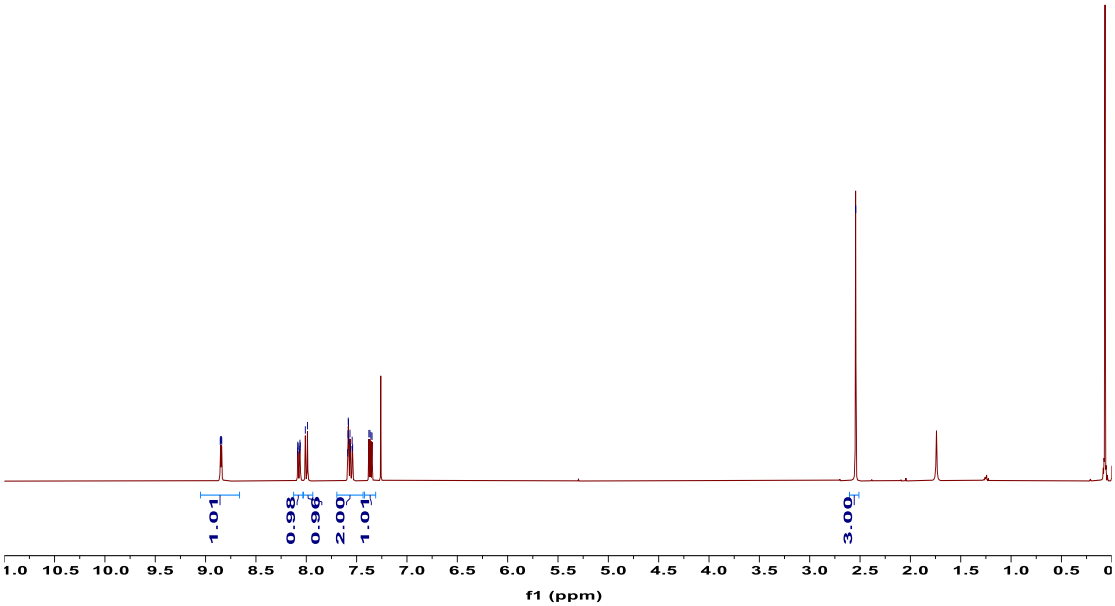

N
Br

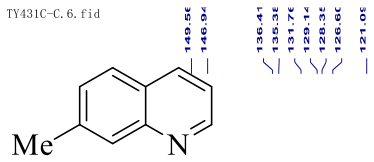
3h


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

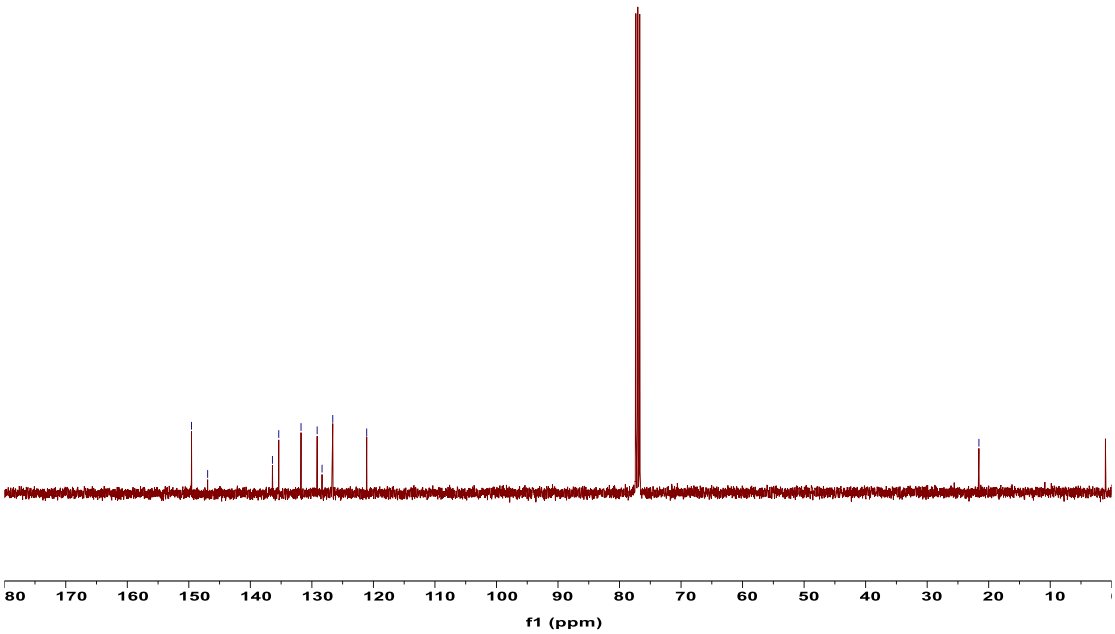

TY431C-H. 34. fid
8.85
8.85
8.84
8.84
8.09
8.08
8.08
8.07
8.06
8.06
8.01
7.99
7.59
7.59
7.58
7.58
7.58
7.57
7.56
7.54
7.54
7.38
7.37
7.36
7.35
2.54
2.54
Me
N

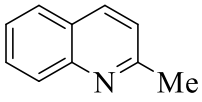
3i


1.01
0.98
0.96
2.00
1.01
3.00
1.0 10.5 10.0 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
f1 (ppm)


TY431C-C. 6. fid
149.56
146.94
136.41
135.38
131.76
129.14
128.31
126.66
121.06
21.59
Me
N

3i


80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



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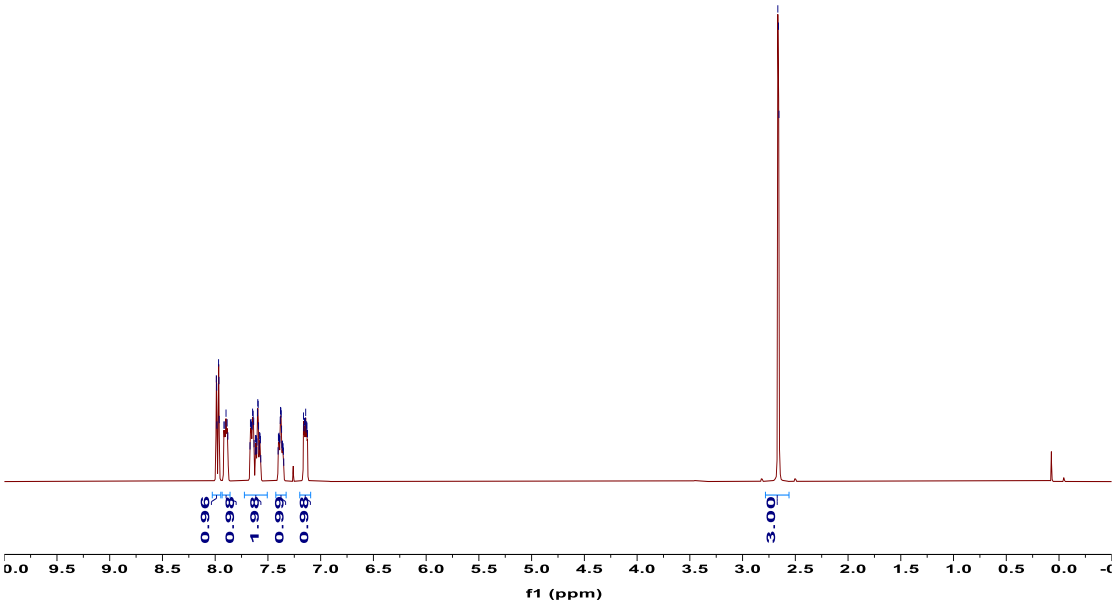

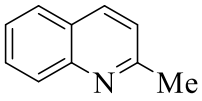

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