Supporting Information

for

Highly Efficient Oxidative Carbon-Carbon Coupling with SBA-15-Support Iron Terpyridine Catalyst

Peng Liu[a], *Cong-Ying Zhou*[a], *Song Xiang*[a], *Chi-Ming Che*[a,*]

[a]Department of Chemistry and Open Laboratory of Chemical Biology of the Institute of Molecular Technology for Drug Discovery and Synthesis, The University of Hong Kong, Pokfulam Road, Hong Kong, China

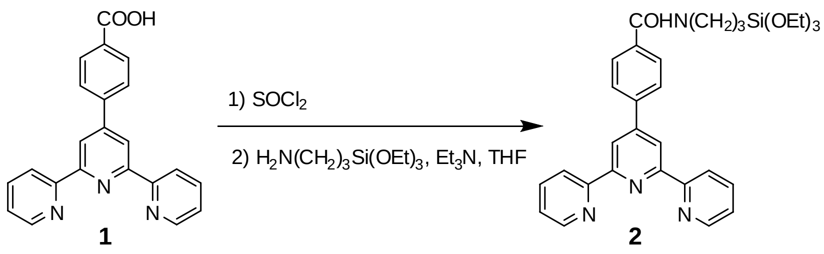
cmche@hku.hk

General Experimental Section: Reagents were obtained commercially and used without further purification unless indicated otherwise. Solvent was removed under reduced pressure and the residue obtained was chromatographed on a silica gel column (230-400 mesh) using a gradient solvent system (EtOAc / *n*-hexane as eluant unless specified otherwise). ^{1}H and ^{13}C NMR spectra were measured on Bruker DPX-500, DPX-400 or DPX-300 spectrometer. Chemical shifts (δ ppm) were determined with tetramethylsilane (TMS) as internal reference. Mass spectra were determined on a Finnigan MAT 95 mass spectrometer. Atomic absorption spectra were measured on Perkin Elmer 3110 atomic absorption spectrometer. Solid diffuse-reflectance UV/vis data were obtained from a Perkin Elmer Lambda 900 UV/vis/NIR integrating sphereattachment, which employs the diffuse-reflectance technique. X-ray powder diffraction (XRD) studies were performed using monochromatized Cu KR radiation and recorded over the 2 θ range from 1.5° to 30° in steps of 0.05°

Synthesis of SBA-15-Supported Iron Terpyridine complex 4

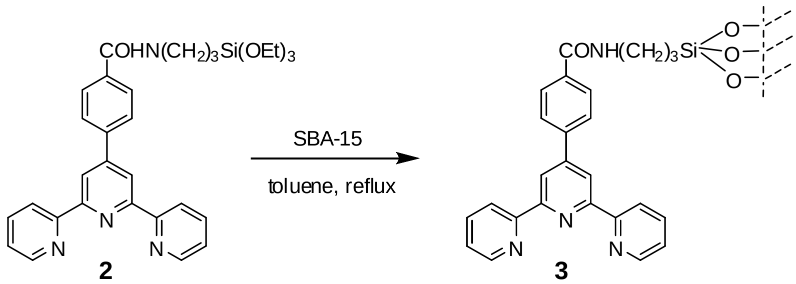
Compound **1** was prepared according to published procedures. [E. C. Constable, E. L. Dunphy, C. E. Housecroft, M. Neuburger, S. Schaffner, F. Schapera, and S. R. Batten, *Dalton. Trans.*, 2007, **38**, 4323.].

The material SBA-15 was prepared according to published procedures. [K. Feng, R.-Y. Zhang, L.-Z. Wu, B. Tu, M.-L. Peng, L.-P. Zhang, D. Zhao and C.-H. Tung, *J. Am. Chem. Soc.*, 2006, **128**, 14685.].



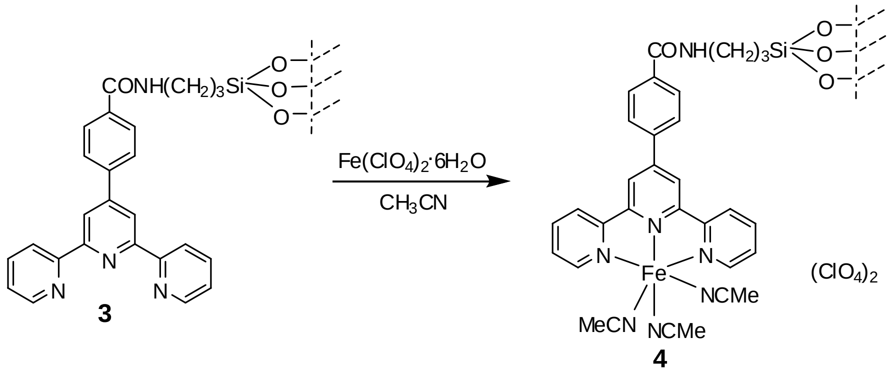
Compound **1** (353 mg, 1 mmol) was dissolved in $SOCl_2$ (15 mL), the mixture was stirred under reflux for 1 h under N_2, then the solvent was removed by distillation under reduced pressure. To the residue was added anhydrous THF (20 mL), Et_3N (2 mL) and $H_2N(CH_2)_3Si(OEt)_3$ (208 mg, 1.1 mmol) subsequently. The reaction mixture was stirred under reflux for 12 h. Then the reaction mixture was extracted with CH_2Cl_2 and washed by water and brine subsequently. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give product **2** in 478 mg (86% yield).

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 2H), 8.74 (d, *J* = 8.2 Hz, 2H), 8.68 (d, *J* = 8.2 Hz, 2H), 7.96-7.89 (m, 6H), 7.37 (m, 2H), 6.65 (t, *J* = 5.4 Hz, 1H), 3.81(q, *J* = 7.0 Hz, 6H), 3.52 (t, *J* = 8.0 Hz, 2H), 1.80 (m, 2H), 1.24 (t, *J* = 7.0 Hz, 9H), 0.75 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 166.8, 156.0, 156.0, 149.2, 149.1, 141.2, 136.9, 135.2, 127.5, 127.4, 123.9, 121.3, 118.8, 58.5, 42.2, 18.2, 7.8, 0.9; EIMS *m/z* 556 (M^+); HRMS (EI) for $C_{31}H_{36}N_4O_4Si$, calcd 556.2506, found 556.2496.



A mixture of compound **2** (420 mg, 0.8 mmol) and 500 mg of SBA-15 in toluene (10 mL) was stirred under reflux for 24 h. The precipitate was filtered and washed with CH_2Cl_2 more than five times to make sure that there was no unloaded compound **2**, then was dried under reduced pressure to give a white solid (630 mg, ligand loading: 0.39 mmol/g, 18.3 wt %).

IR (cm^{-1}): 2980, 2938, 1548, 1509, 1445, 1391.



The mixture of Ligand **3** (500 mg) and $Fe(ClO_4)_2{\bullet}6H_2O$ (100 mg) in MeCN (5 mL) was stirred at room temperature for 1 h. A purple precipitate was filtered, washed with MeCN and then dried under reduced pressure to give a purple solid (570 mg, iron loading: 0.34 mmol/g, 1.9 wt %).

UV-Vis (CH_3CN): λ_{max}/nm: 584; IR (cm^{-1}): 1545, 1508, 1481, 1400.

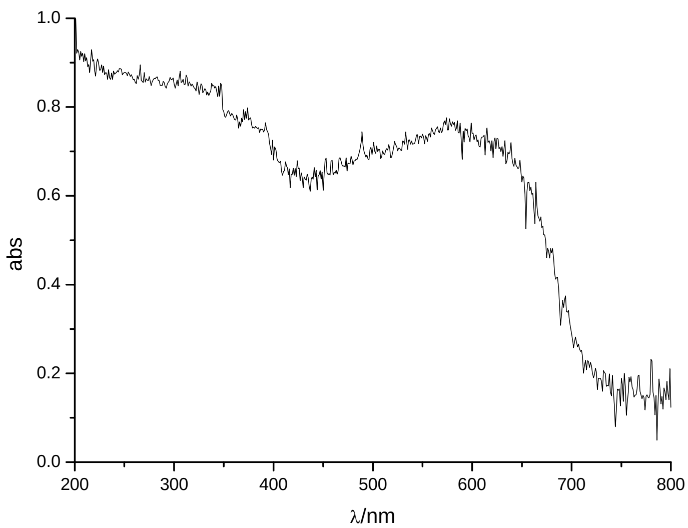


Figure S1, Solid diffuse-reflectance UV-vis spectrum of **4**

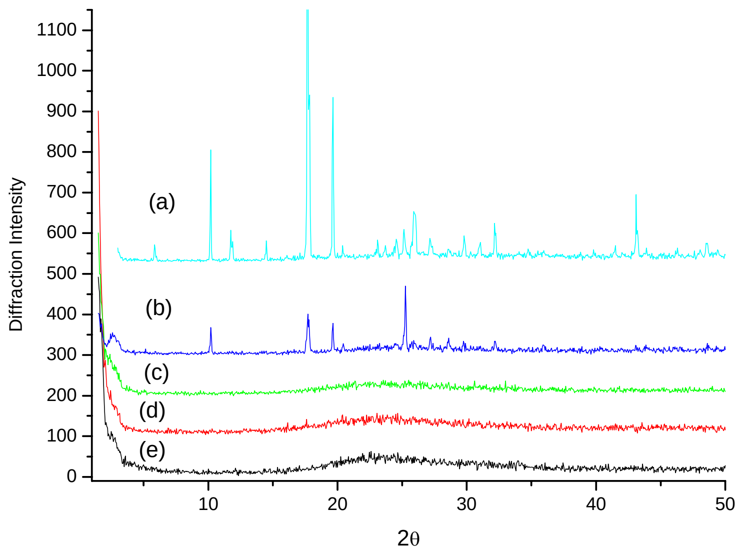
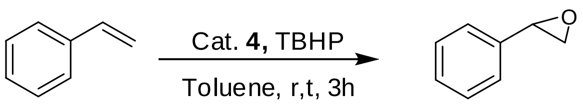


Figure S2, XRD patterns of (a) ligand **2**, (b) physical mixture of ligand **2** and SBA-15, (c) ligand **3**, (d) complex **4**, (e) SBA-15

General Procedure for Oxidative Coupling of Tertiary Amines with Nucleophiles

To a mixture of tertiary amine (0.2 mmol), nucleophile (0.24 mmol) and complex **4** (0.006 mmol, 3 mol %) in toluene (1 mL) was added TBHP (*tert*-butyl hydroperoxide) (0.6 mmol). The reaction mixture was stirred under reflux for 12 h. Then the reaction mixture was extracted with ethyl acetate and washed by water and brine subsequently. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The product was purified by flash column chromatography on silica gel using ethyl acetate-hexane as eluent.

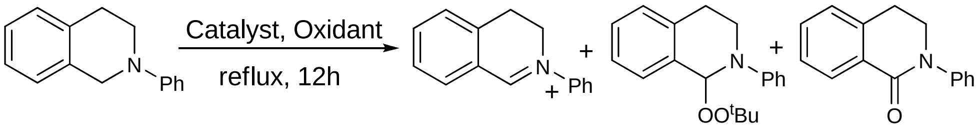
Epoxidation of Styrene with TBHP Catalyzed by Complex 4



To a solution of styrene (0.2 mmol) in toluene (2 mL) was added complex **4** (17 mg, 3 mol %)

and TBHP (0.3 mmol). The reaction mixture was stirred at room temperature for 3 h. The conversion of styrene and yield were determined by GC-analysis (conversion: 72%; yield: 73%).

Oxidation of Tetrahydroisoquinoline with TBHP Catalyzed by Complex 4



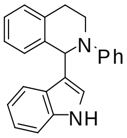
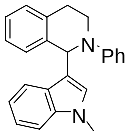
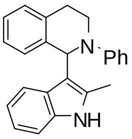
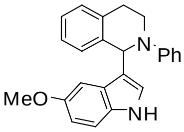
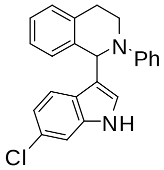
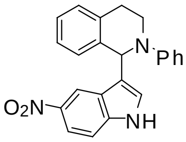
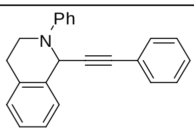
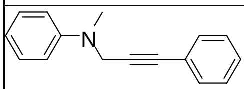
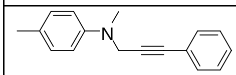
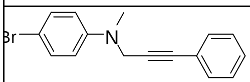
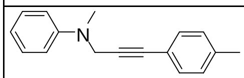
a **b** **c**

To a solution of tetrahydroisoquinoline (0.2 mmol) in toluene(1 mL) was added complex **4** (17 mg, 3 mol %) and TBHP (0.3 mmol). The reaction mixture was stirred under reflux for 12 h. After cooled down, the reaction mixture was extracted with dichloromethane. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give three products (conversion: 100%; yield: **a** 60%, **b** 15%, **c** 12%).

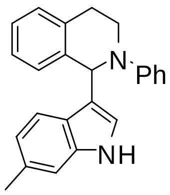
General Procedure for Recycling Silica Supported Ligand 3

To a suspended solution of SBA-15 supported ligand **3** (0.006 mmol) in toluene (1 mL) was added $Fe(ClO_4)_2{\cdot}6H_2O$ (0.006 mmol). The mixture was stirred at room temperature for 10 min. To the mixture was added tetrahydroisoquinoline **6a** (0.2 mmol) and indole **5a** (0.24 mmol). The reaction mixture was stirred under reflux for 12 h. Upon completion of the reaction, the initial purple complex **4** turned white, revealing that demetalation took place. The SBA-15 supported ligand **3** could be recycled simply by filtration. The recycled ligand reacted with a new batch of $Fe(ClO_4)_2{\cdot}6H_2O$ (3 mmol%) to regenerate complex **4** *in situ*, which was used for consecutive reactions.

Literature References for Indoles 7a-7g and Propargylamines 13a-13e

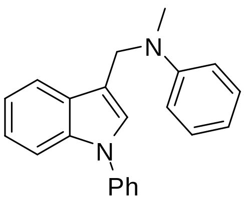
 **7a**	Zhiping Li and Chao-Jun Li, *J. Am. Chem. Soc.*, 2005, **127**, 6968.
 **7b**	Zhiping Li and Chao-Jun Li, *J. Am. Chem. Soc.*, 2005, **127**, 6968.
 **7c**	Zhiping Li and Chao-Jun Li, *J. Am. Chem. Soc.*, 2005, **127**, 6968.
 **7e**	Zhiping Li and Chao-Jun Li, *J. Am. Chem. Soc.*, 2005, **127**, 6968.
 **7f**	Zhiping Li and Chao-Jun Li, *J. Am. Chem. Soc.*, 2005, **127**, 6968.
 **7g**	Zhiping Li and Chao-Jun Li, *J. Am. Chem. Soc.*, 2005, **127**, 6968.
 **13a**	Zhiping Li, D. Scott Bohle and Chao-Jun Li, *PNAS*, 2006, **103**, 8928.
 **13b**	Zhiping Li and Chao-Jun Li, *J. Am. Chem. Soc.*, 2004, **126**, 11810.
 **13c**	Zhiping Li and Chao-Jun Li, *J. Am. Chem. Soc.*, 2004, **126**, 11810.
 **13d**	Zhiping Li and Chao-Jun Li, *J. Am. Chem. Soc.*, 2004, **126**, 11810.
 **13e**	Zhiping Li and Chao-Jun Li, *J. Am. Chem. Soc.*, 2004, **126**, 11810.

Characterization Data



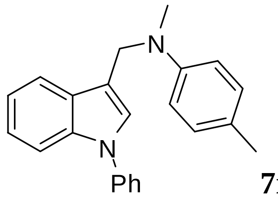
7d

White solid; analytical TLC (silica gel 60) (10 % EtOAc in hexane) R_f = 0.47; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.28-7.11 (m, 6H), 7.08 (s, 1H), 7.01 (d, *J* = 7.9 Hz, 2H), 6.84 (d, *J* = 8.2 Hz, 1H), 6.76 (dd, *J* = 5.2, 1.2 Hz, 1H), 6.53 (d, *J* = 1.2 Hz, 1H), 6.13 (s, 1H), 3.62-3.58 (m, 2H), 3.05 (ddd, *J* = 16.0, 7.6, 7.6 Hz, 1H), 2.80 (ddd, *J* = 16.0, 4.4, 4.4 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 149.9, 137.6, 137.1, 135.6, 132.0, 129.3, 128.8, 128.1, 126.7, 125.8, 124.4, 123.6, 121.5, 119.8, 119.1, 118.1, 115.9, 111.1, 56.8, 42.4, 26.8, 21.7; EIMS *m/z* 338 (M^+); HRMS (EI) for $C_{24}H_{22}N_2$, calcd 338.1783, found 338.1763.



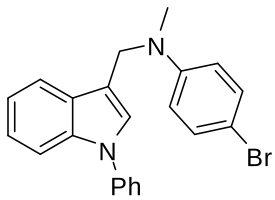
7h

Yellow oil; analytical TLC (silica gel 60) (5 % EtOAc in hexane) R_f = 0.51; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.51-7.41 (m, 4H), 7.31-7.29 (m, 1H), 7.26-7.22 (m, 3H), 7.20-7.18 (m, 2H), 6.88 (d, *J* = 7.9 Hz, 2H), 6.73 (t, *J* = 7.2 Hz, 1H), 4.73 (s, 2H), 3.03 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 140.1, 136.8, 130.4, 130.0, 129.6, 128.6, 126.5, 124.6, 124.5, 123.9, 123.1, 120.6, 119.8, 114.3, 113.7, 110.1, 49.4, 30.1; EIMS *m/z* 312 (M^+); HRMS (EI) for $C_{22}H_{20}N_2$, calcd 312.1626, found 312.1621.



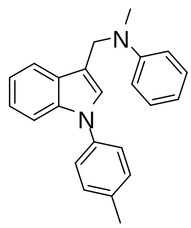
7i

Yellow oil; analytical TLC (silica gel 60) (5 % EtOAc in hexane) $R_f = 0.52$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.47-7.45 (m, 4H), 7.24-7.15 (m, 4H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 4.67 (s, 2H), 2.97 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 148.2, 139.7,136.3, 129.7, 129.5, 128.3, 126.2, 126.0, 124.2, 122.6, 120.1, 119.5, 118.2, 114.5, 113.5, 110.6, 49.1, 38.2, 20.3; EIMS *m/z* 326 (M^+); HRMS (EI) for $C_{23}H_{22}N_2$, calcd 326.1783, found 326.1786.



7j

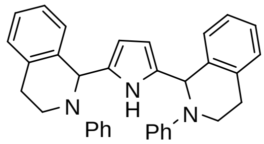
White solid; analytical TLC (silica gel 60) (10 % EtOAc in hexane) $R_f = 0.52$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.55 (m, 2H), 7.51-7.44 (m, 4H), 7.31-7.24 (m, 5H), 7.13 (s, 1H), 6.97 (d, *J* = 8.1 Hz, 2H), 4.69 (s, 2H), 3.00 (s, 3H); 13C NMR (400 MHz, CDCl3) δ 149.1, 136.5, 131.9, 129.7, 128.1, 126.5, 126.2, 124.4, 122.9, 120.4, 119.4, 114.6, 114.1, 113.9, 110.8, 108.6, 48.8, 38.3; EIMS *m/z* 390 (M^+); HRMS (EI) for $C_{22}H_{19}N_2Br$, calcd 390.0732, found 390.0735.



7k

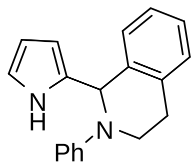
White solid; analytical TLC (silica gel 60) (10 % EtOAc in hexane) $R_f = 0.57$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.23-7.38 (m, 7H), 7.21-7.18

(m, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.77 (t, *J* = 7.2 Hz, 1H), 4.75 (s, 2H), 3.05 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 150.3, 136.6, 135.3, 130.2, 129.3, 128.2, 126.4, 124.4, 124.2, 122.6, 120.1, 119.5, 116.8, 114.1, 113.2, 110.8, 48.8, 38.1, 21.2; EIMS *m/z* 326 (M^+); HRMS (EI) for $C_{23}H_{22}N_2$, calcd 326.1783, found 326.1781.



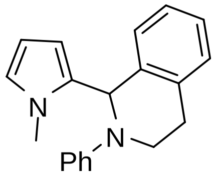
11a (mixture of diastereomers)

Yellow oil; analytical TLC (silica gel 60) (10% EtOAc in hexane) R_f = 0.43; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.24-7.18 (m, 10H), 7.09 (d, *J* = 6.4 Hz, 2H), 6.90-6.85 (m, 4H), 6.78 (d, *J* = 7.2 Hz, 2H), 5.76 (s, 1H), 5.74 (s, 0.8 H), 5.48 (d, *J* = 2.6 Hz, 0.8 H), 5.42 (d, *J* = 2.6 Hz, 1H), 3.48-3.42 (m, 2H), 3.31-3.23 (m, 2H), 2.93-2.87 (m, 2H), 2.70-2.62 (m, 2H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 150.2, 150.2, 135.9, 135.9, 135.2, 135.2, 132.8, 132.7, 129.5, 129.4, 128.8, 128.8, 127.9, 127.1, 125.9, 125.9, 119.3, 119.2, 116.5, 116.4, 107.8, 107.7, 58.1, 58.0, 42.9, 42.6, 27.4(2), 27.4(0); EIMS *m/z* 481 (M^+); HRMS (EI) for $C_{34}H_{31}N_3$, calcd 481.2518, found 481.2511.



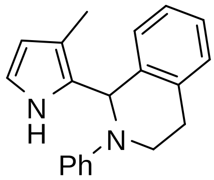
11b

Yellow oil; analytical TLC (silica gel 60) (10% EtOAc in hexane) R_f = 0.41; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.30-7.27 (m, 2H), 7.26-7.24 (m, 3H), 7.15 (m, 1H), 6.98 (d, *J* = 7.8 Hz, 2H), 6.82 (t, *J* = 7.6 Hz, 1H), 6.65 (d, *J* = 1.6 Hz, 1H), 6.06 (m, 1H), 5.89 (s, 1H), 5.69 (d, *J* = 1.6 Hz, 1H), 3.59-3.53 (m, 1H), 3.49-3.47 (m, 1H), 2.96 (ddd, *J* = 16.0, 7.6, 7.6 Hz, 1H), 2.77 (ddd, *J* = 16.0, 4.4, 4.4 Hz, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 150.0, 136.0, 135.5, 133.6, 129.6, 128.9, 127.9, 127.3, 126.1, 118.9, 117.2, 115.7, 108.4, 107.7, 57.8, 43.1, 27.3; EIMS *m/z* 274 (M^+); HRMS (EI) for $C_{19}H_{18}N_2$, calcd 274.1470, found 274.1463.



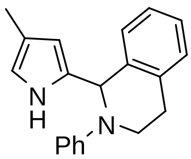
11c

Yellow oil; analytical TLC (silica gel 60) (10% EtOAc in hexane) $R_f = 0.46$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.21 (m, 5H), 7.07 (d, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 7.8 Hz, 2H), 6.82 (t, *J* = 7.6 Hz, 1H), 6.59 (d, *J* = 1.8 Hz, 1H), 5.94 (m, 1H), 5.77 (s, 1H), 5.42 (d, *J* = 1.8 Hz, 1H), 3.62-3.58 (m, 2H), 3.56 (s, 3H), 2.92 (ddd, *J* = 16.0, 7.6, 7.6 Hz, 1H), 2.59 (ddd, *J* = 16.0, 4.4, 4.4 Hz, 1H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 149.8, 135.8, 135.6, 134.1, 129.4, 129.2, 128.7, 126.9, 125.7, 123.0, 119.7, 117.8, 111.2, 106.0, 55.8, 43.0, 34.4, 25.3; EIMS *m/z* 288 (M^+); HRMS (EI) for $C_{20}H_{20}N_2$, calcd 288.3862, found 288.3868.



11d

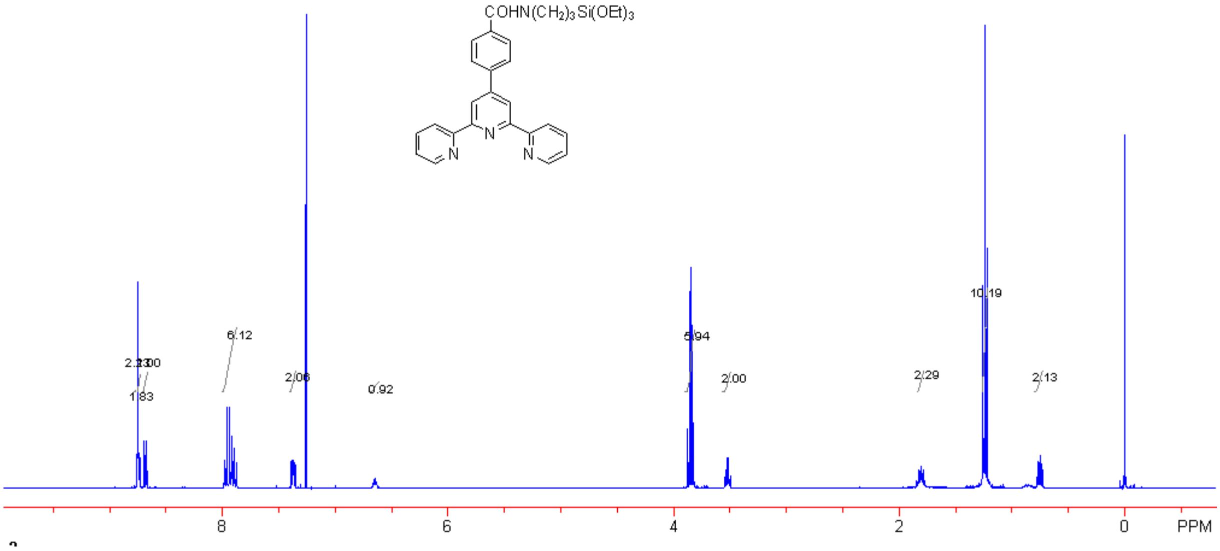
Yellow oil; analytical TLC (silica gel 60) (10% EtOAc in hexane) $R_f = 0.41$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.23-7.17 (m, 6H), 6.93 (d, *J* = 7.8 Hz, 2H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.50 (m, 1H), 5.93 (m, 1H), 5.79 (s, 1H), 3.56-3.52 (m, 2H), 3.06-2.87 (m, 2H), 1.89 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 150.4, 136.6, 135.6, 129.4, 129.3, 129.0, 128.9, 128.2, 127.1, 126.4, 119.7, 117.4, 115.9, 110.9, 57.6, 44.9, 28.1, 11.5; EIMS *m/z* 288 (M^+); HRMS (EI) for $C_{20}H_{20}N_2$, calcd 288.3862, found 288.3864.



11e

Yellow oil; analytical TLC (silica gel 60) (10% EtOAc in hexane) $R_f = 0.41$; ^{1}H NMR (300 MHz,

$CDCl_3$) δ 7.82 (s, 1H), 7.28-7.20 (m, 5H), 7.15 (m, 1H), 6.97 (d, *J* = 7.8 Hz, 2H), 6.80 (t, *J* = 7.3 Hz, 1H), 6.40 (s, 1H), 5.85 (s, 1H), 5.53 (s, 1H), 3.58-3.48 (m, 2H), 2.94 (ddd, *J* = 16.0, 7.6, 7.6 Hz, 1H), 2.77 (ddd, *J* = 16.0, 4.4, 4.4 Hz, 1H), 2.00 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 150.0, 136.2, 135.5, 133.5, 131.0, 129.5, 128.8, 127.9, 127.2, 126.0, 118.7, 115.5, 114.9, 109.2, 57.7, 43.0, 27.3, 12.1; EIMS *m/z* 288 (M^+); HRMS (EI) for $C_{20}H_{20}N_2$, calcd 288.3862, found 288.3858..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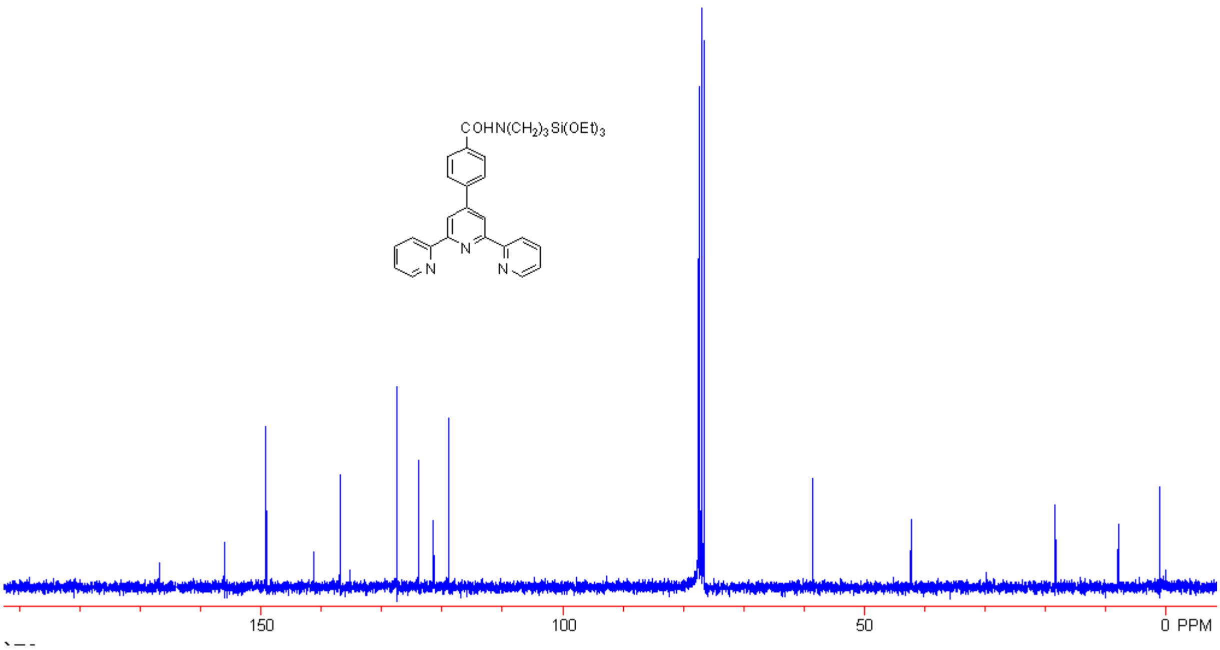
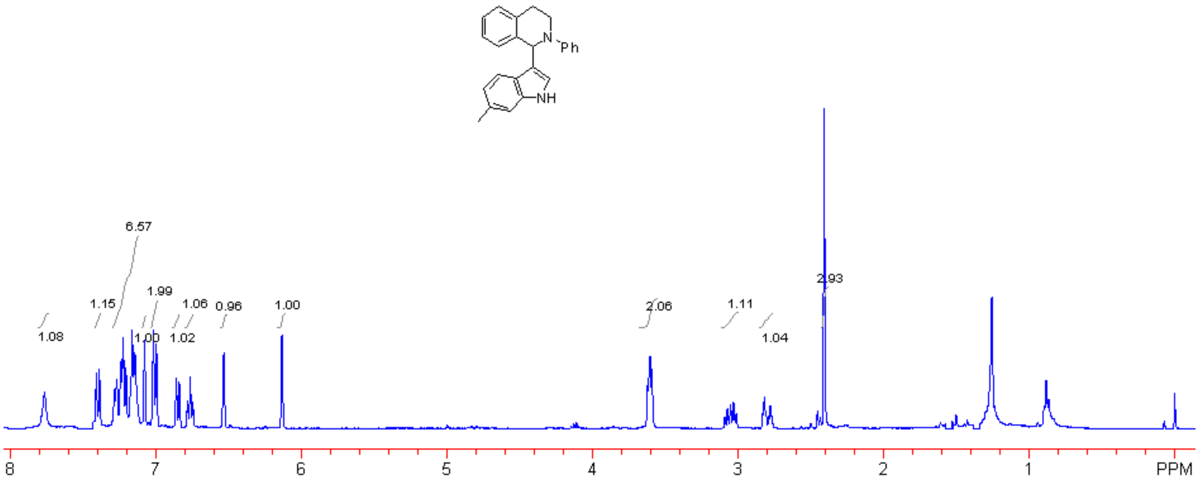
N
N
N
2.13
1.00
1.83
6.12
2.06
0.92
5.94
2.00
2.29
10.19
2.13
8
6
4
2
0
PPM


COHN(CH2)3Si(OEt)3
N
N
N
150
100
50
0 PPM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Ph
NH
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1.06
0.96
1.00
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1.11
1.04
2.93
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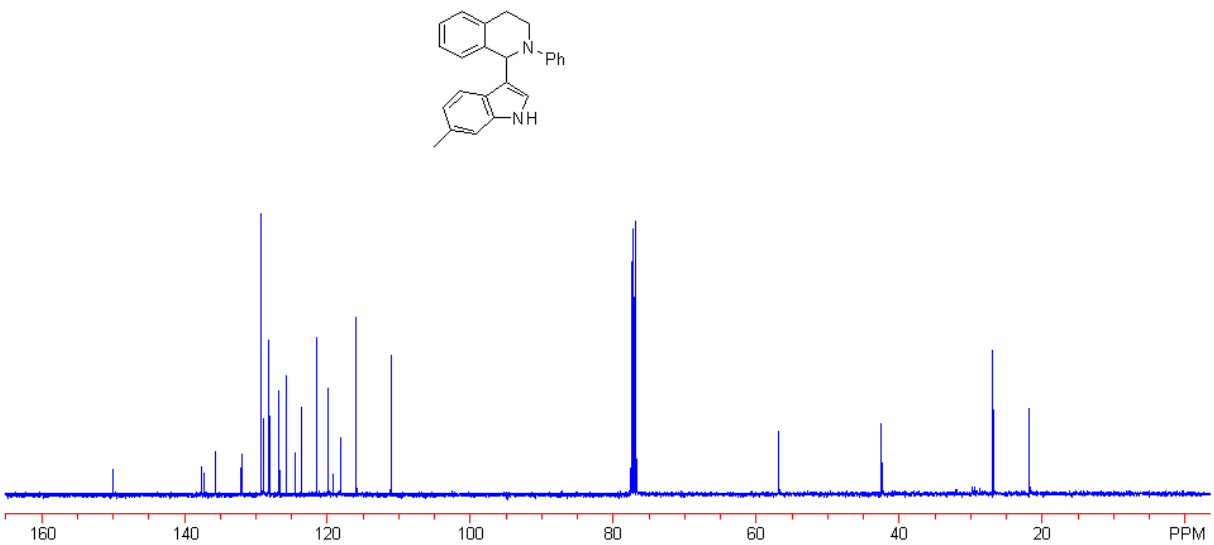
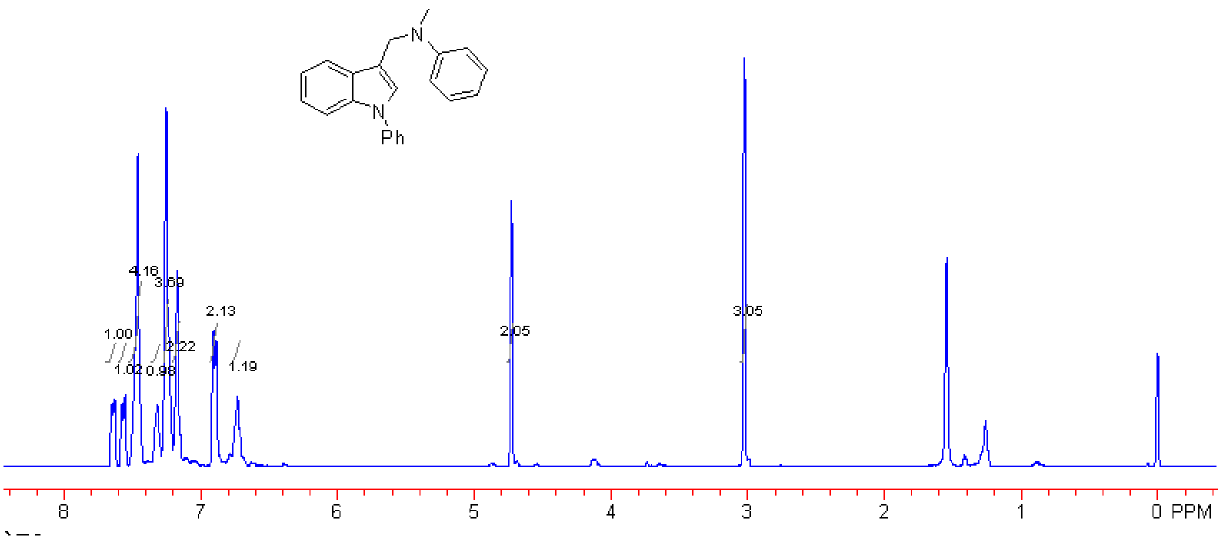
7
6
5
4
3
2
1
PPM


N
Ph
NH
160
140
120
100
80
60
40
20
PPM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N
Ph
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1.19
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3.05
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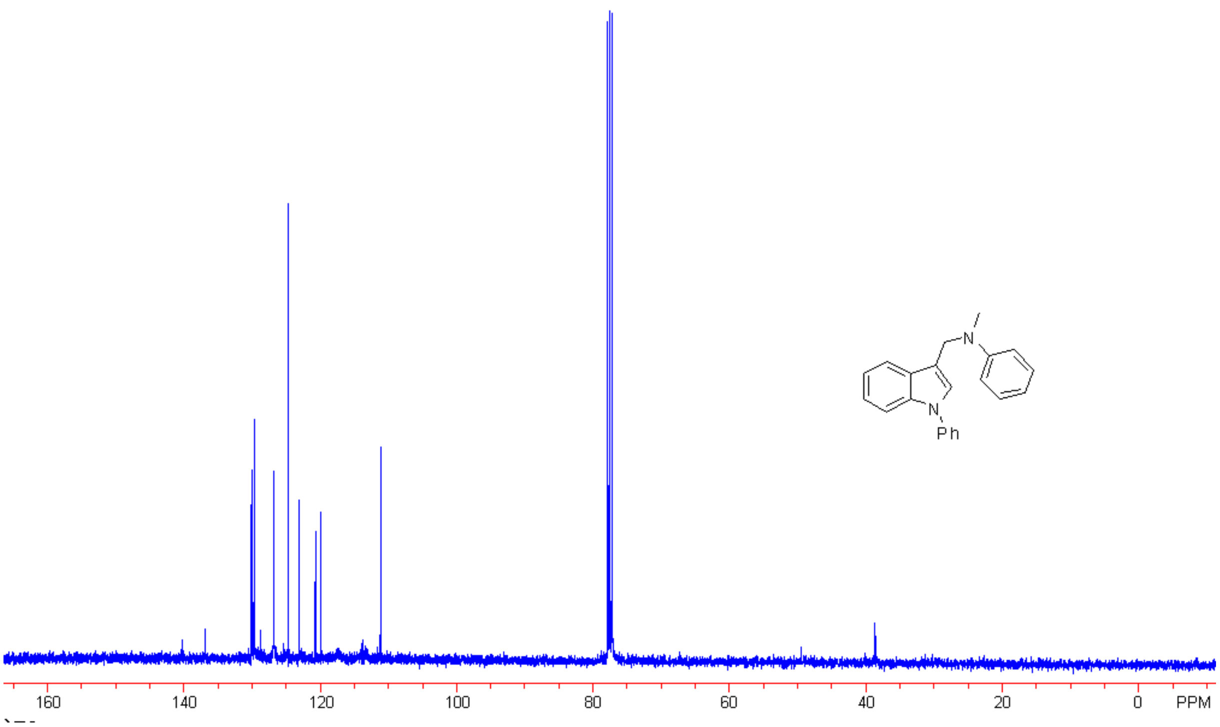
4
3
2
1
0 PPM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Ph
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100
80
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40
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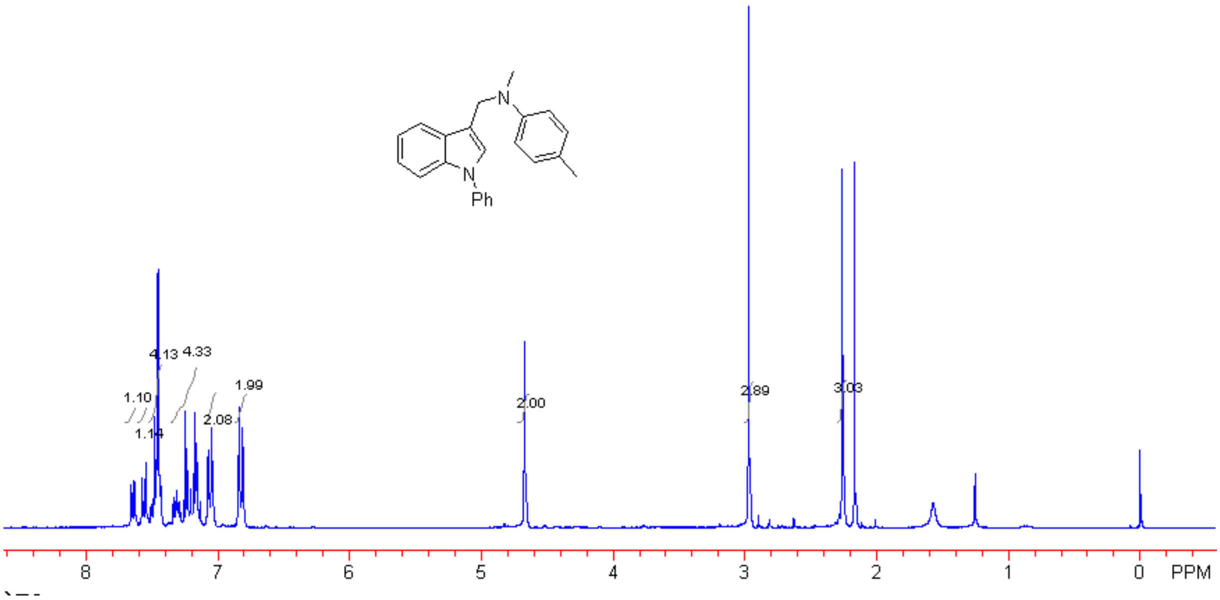
0
PPM


N
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Ph
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4
3
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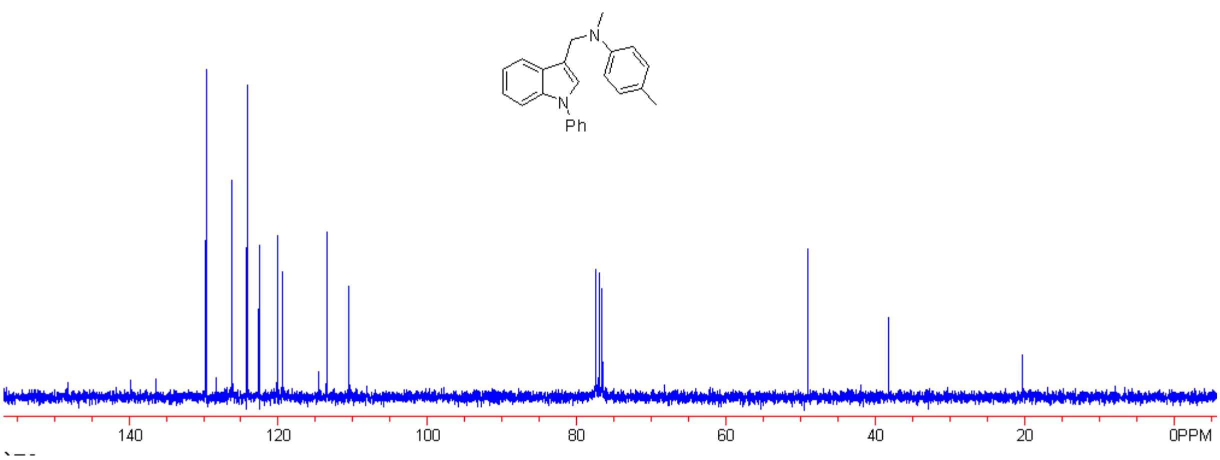
1
0
PPM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Ph
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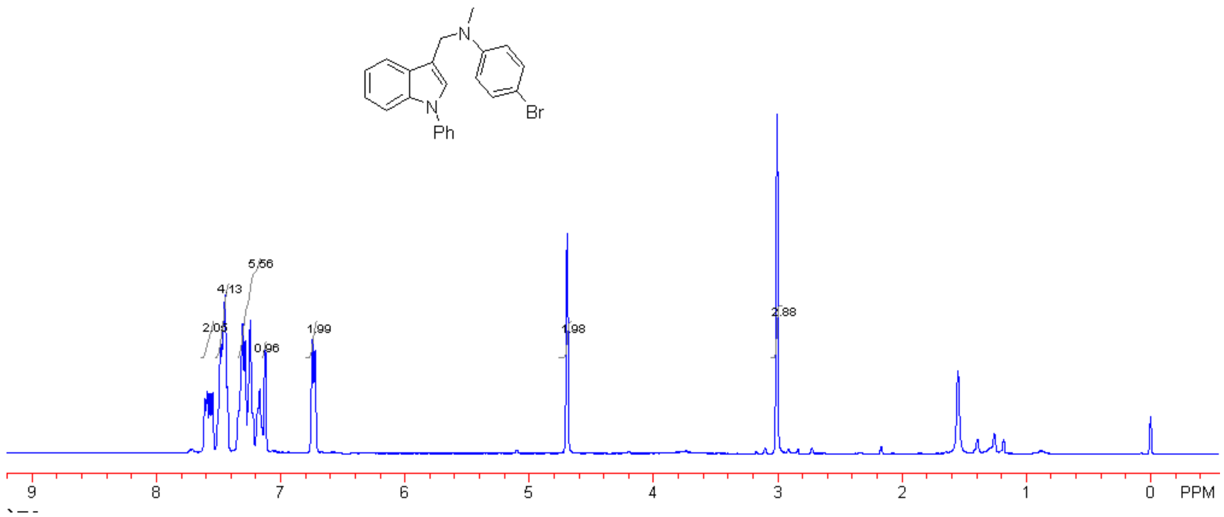
120
100
80
60
40
20
0PPM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Ph
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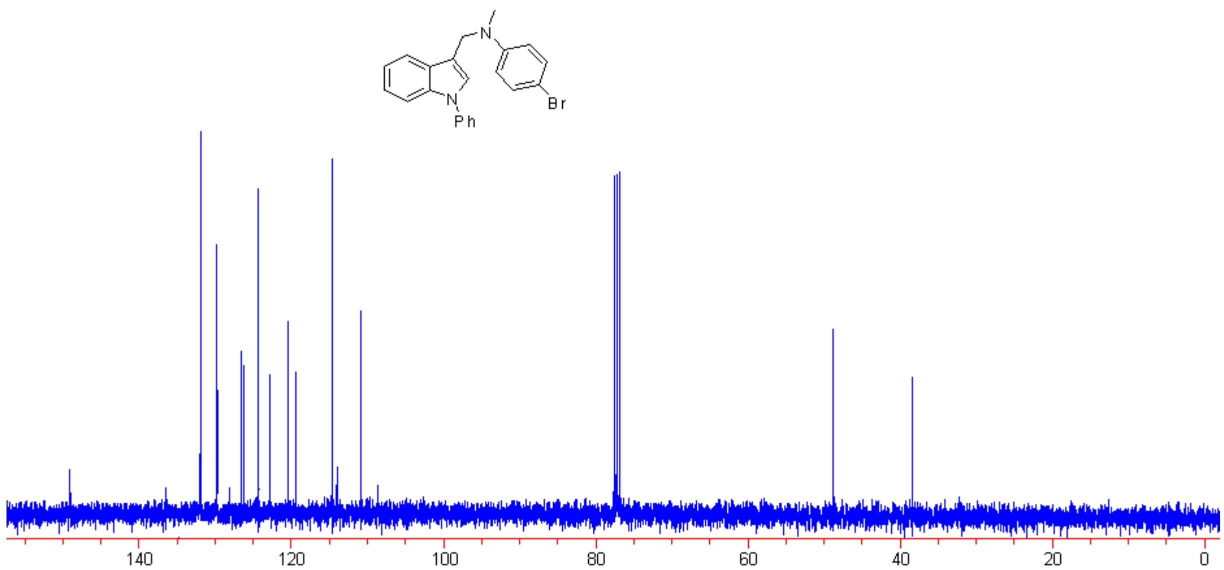
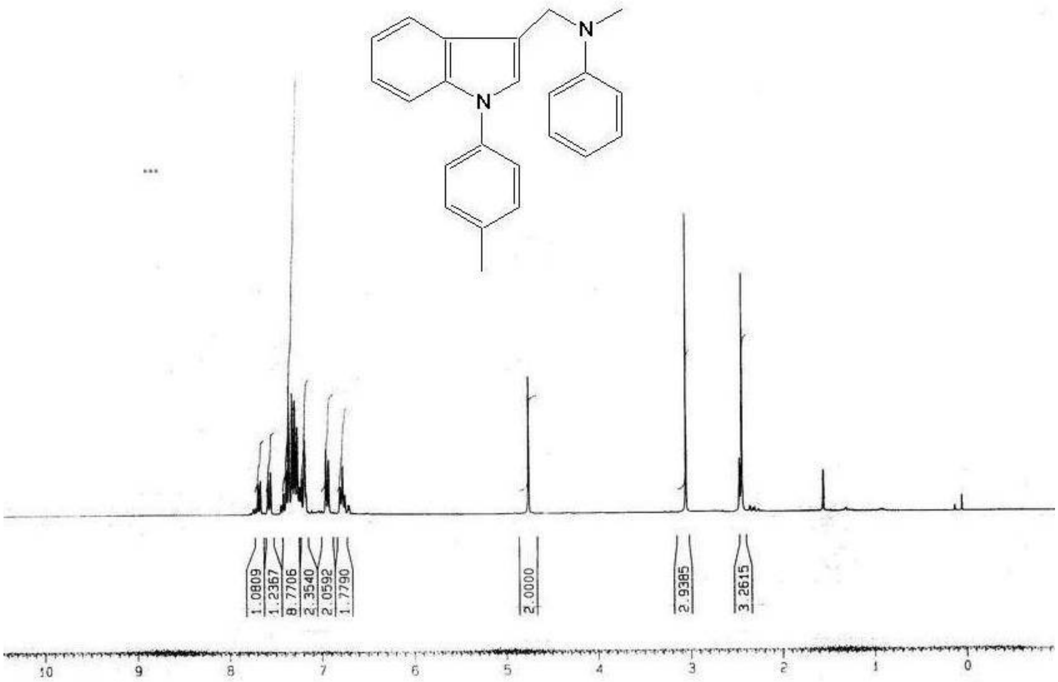
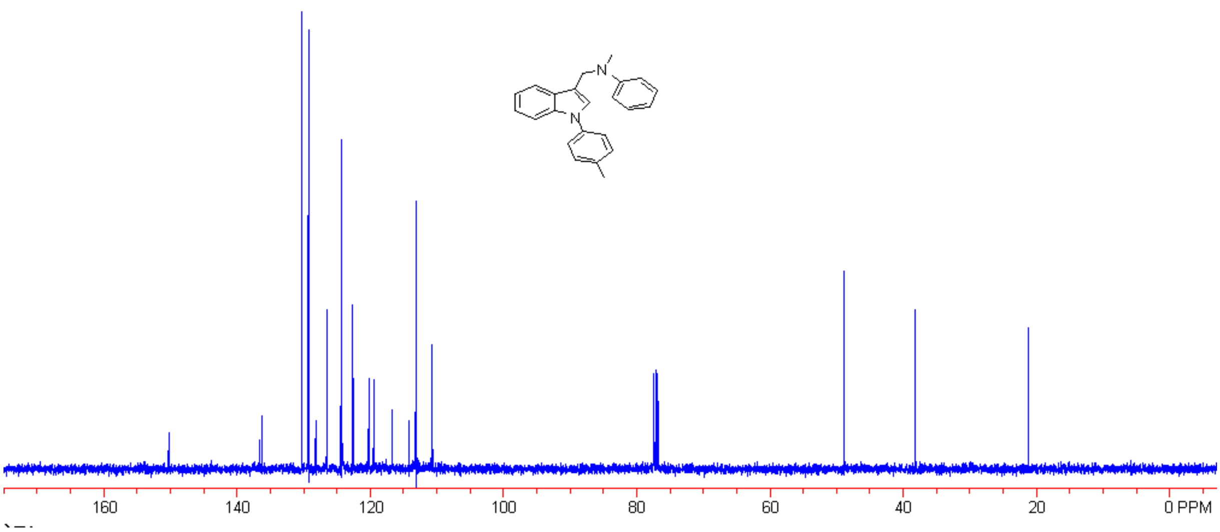
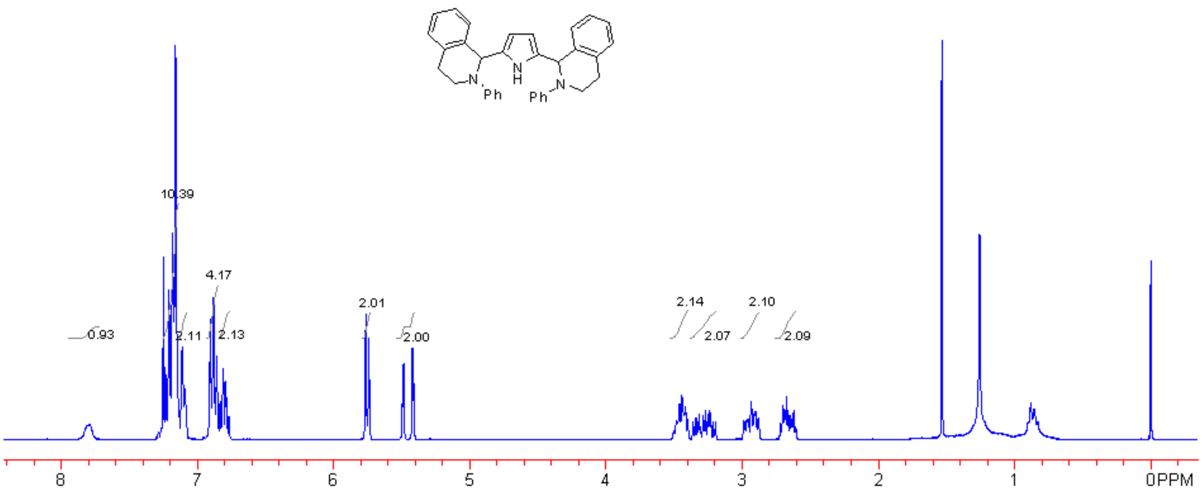
6
5
4
3
2
1
0
PPM


Br
N
Ph
140
120
100
80
60
40
20
0

Supplementary Material (ESI) for Chemical Communications



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2.14
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2.10
2.09
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7
6
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4
3
2
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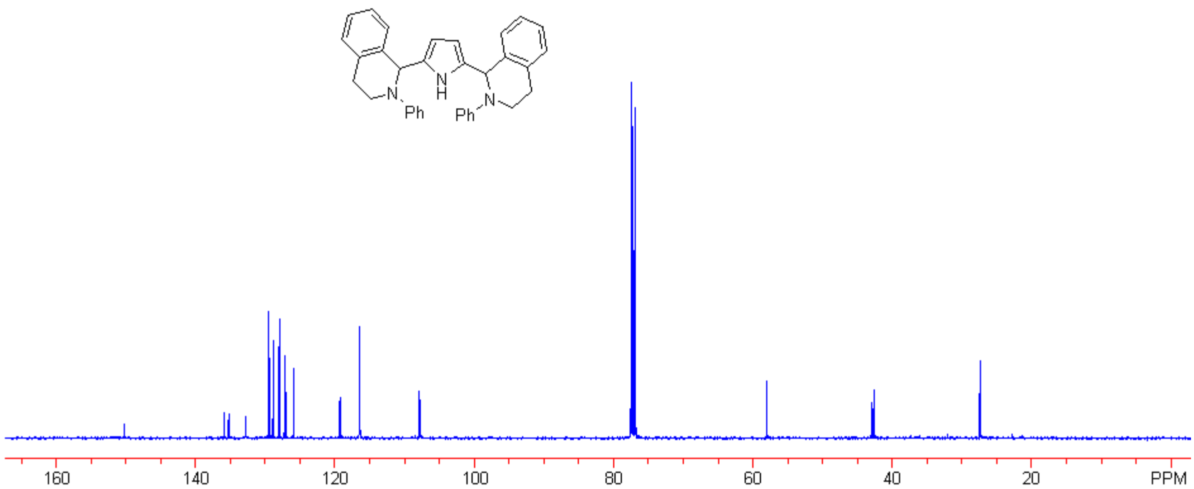
0PPM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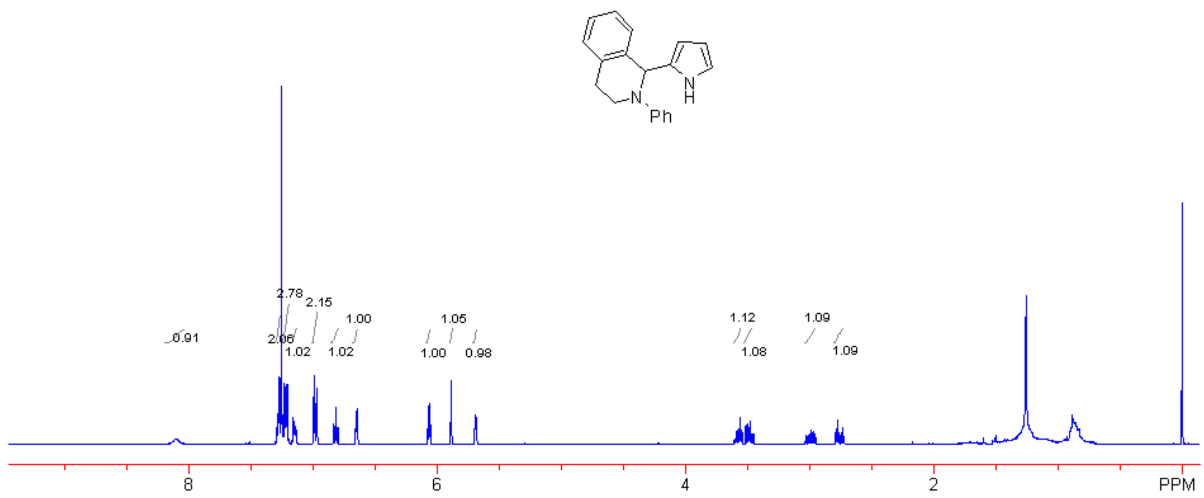
140
120
100
80
60
40
20
PPM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H
N
Ph
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1.05
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1.12
1.08
1.09
1.09
8
6
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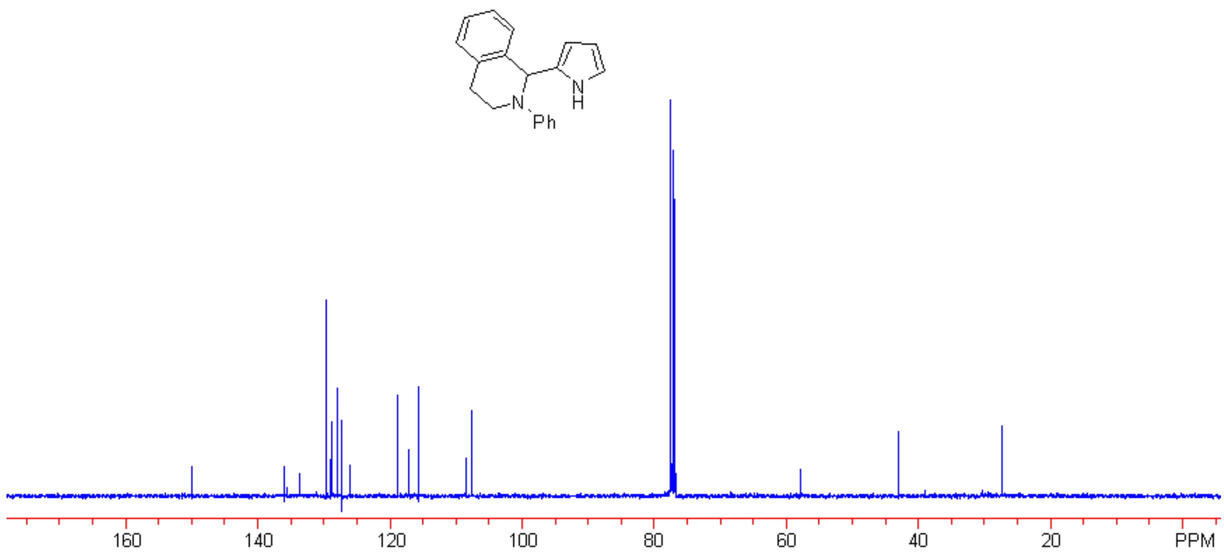
2
PPM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H
N
Ph
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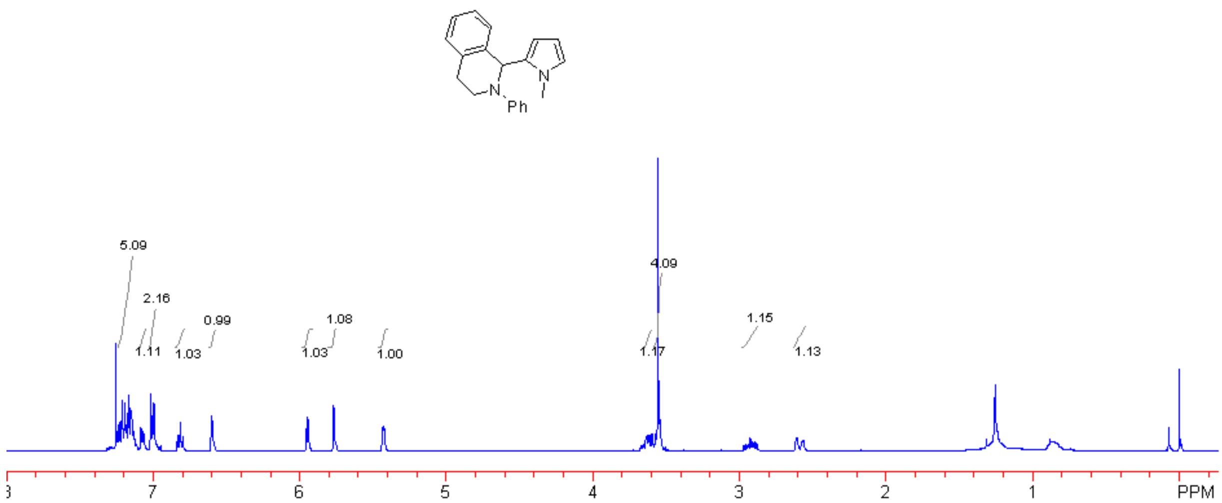
80
60
40
20
PPM


N
Ph
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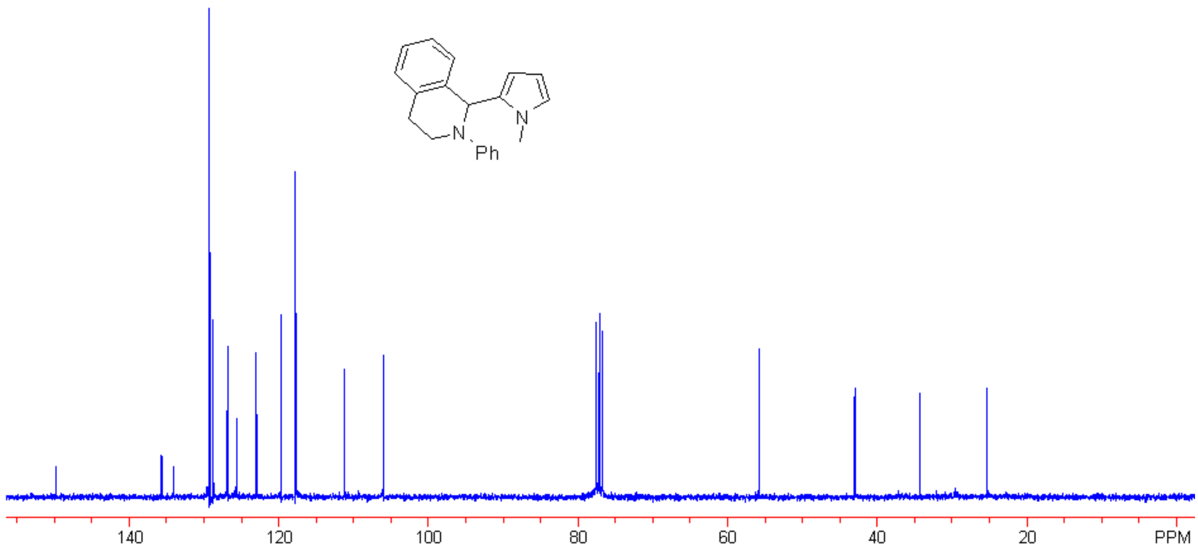
2.16
1.11
1.03
0.99
1.08
1.03
1.00
4.09
1.17
1.15
1.13
7
6
5
4
3
2
1
PPM


N
Ph
140
120
100
80
60
40
20
PPM

Supplementary Material (ESI) for Chemical Communications
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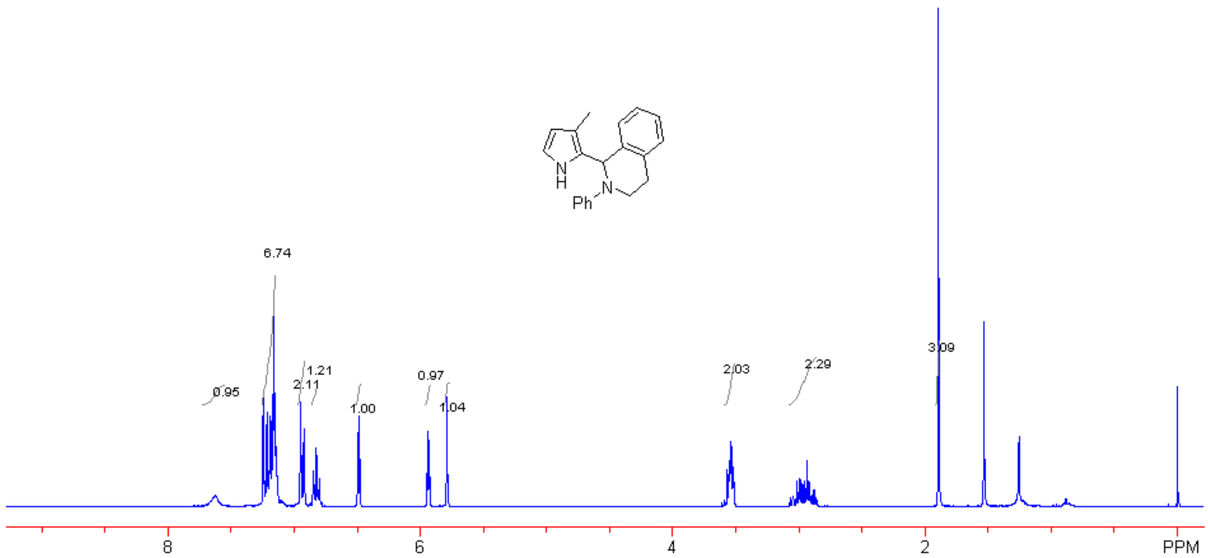

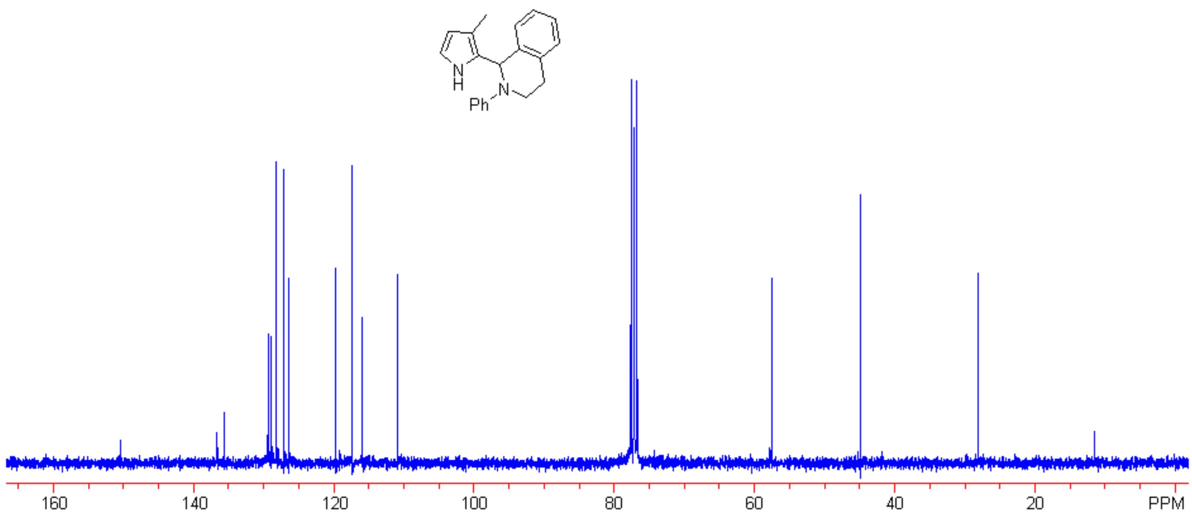

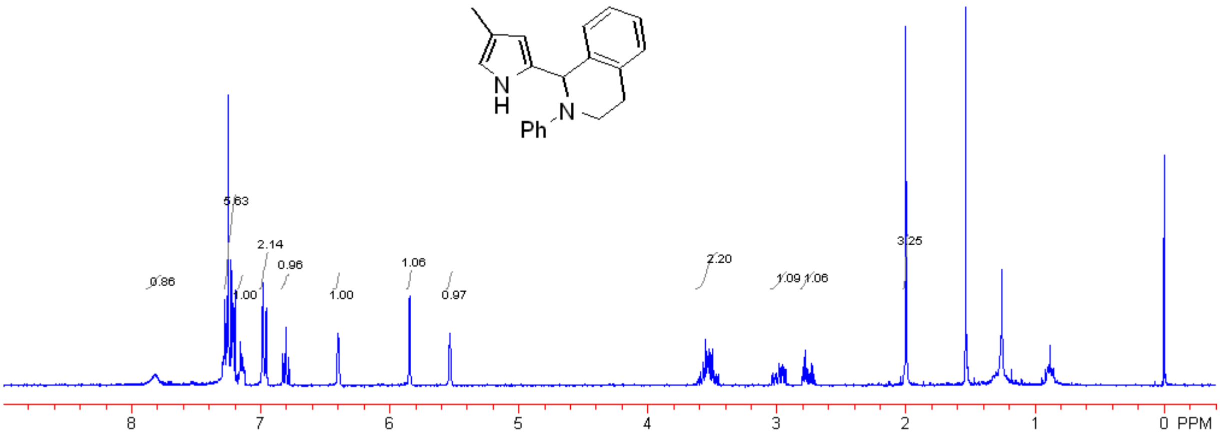
H
N
Ph
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1.00
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1.06
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8
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6
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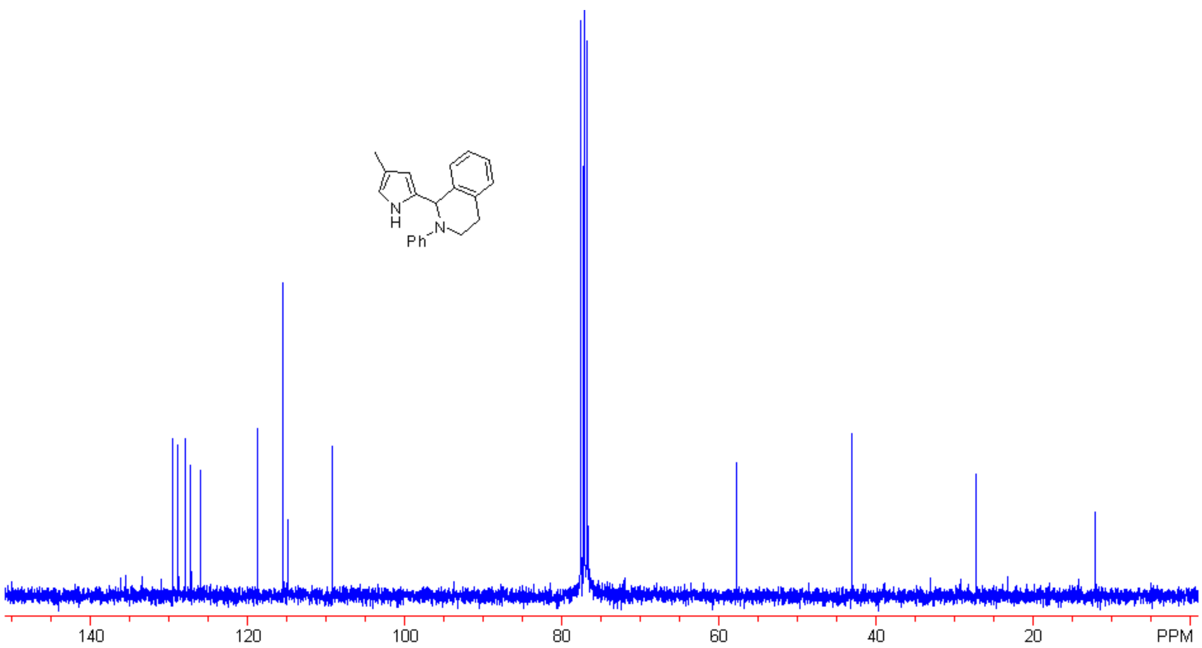
4
3
2
1
0 PPM


H
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Ph
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120
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80
60
40
20
PPM