

## Supporting Information

# Ru<sup>II</sup>-Complexes of Heteroditopic Chelating NHC Ligands: Effective Catalysts for the $\beta$ -alkylation of Secondary Alcohols and the Synthesis of 2-alkylaminoquinoline Derivatives Following Dehydrogenative Protocol

Vivek Kumar Singh, S. N. R. Donthireddy, Vipin K. Pandey, and Arnab Rit\*

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India

\*To whom correspondence should be addressed. E-mail: [arnabrit@iitm.ac.in](mailto:arnabrit@iitm.ac.in)

### Table of contents:

General experimental details

General procedure for the  $\beta$ -alkylation reaction

General procedure for one-pot sequential synthesis of 2-alkylaminoquinolines

Procedure for the calculation of TON for  $\beta$ -alkylation reaction

Optimization studies

Comparison of TON values with the selected complexes

NMR characterization data of the isolated compounds

<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of isolated compounds from catalytic reactions

Mechanistic studies

## General experimental details

All manipulations were performed under an argon/dinitrogen atmosphere using either standard Schlenk line or glovebox techniques. All glassware was oven-dried at 130 °C overnight prior to use. The solvents used were dried, distilled, and degassed by standard methods and stored over 4 Å molecular sieves. NMR measurements were performed on Bruker 400 and 500 MHz FT-NMR spectrometers. The chemical shifts in the  $^1\text{H}$  NMR spectra were referenced to the residual proton signals of the deuterated solvents ( $\text{CDCl}_3$ ,  $^1\text{H}$  7.26 ppm and  $^{13}\text{C}\{^1\text{H}\}$  77.16 ppm) and reported relative to tetramethylsilane. The coupling constants are expressed in hertz. Both primary and secondary alcohols were synthesized according to the literature procedures.<sup>1,2</sup> All other chemicals were purchased from commercial sources and used as received without further purification.

**General procedure for  $\beta$ -alkylation reaction:** An oven dried Schlenk tube was charged with the catalyst stock solution, prepared in  $\text{CH}_3\text{CN}$  (0.01 mol%), and after that the volatiles were removed in vacuum. To this, secondary alcohol (0.5 mmol), primary alcohol (0.5 mmol), and KOH (0.25 mmol, 50 mol%) followed by toluene (1 mL) were added. The reaction tube was then kept in oil bath (bath temperature 120 °C) and heated for the specified time. After the completion of reaction, the reaction mixture was cooled to room temperature and the pure products were isolated *via* column chromatography using hexane/ethyl acetate as eluent.

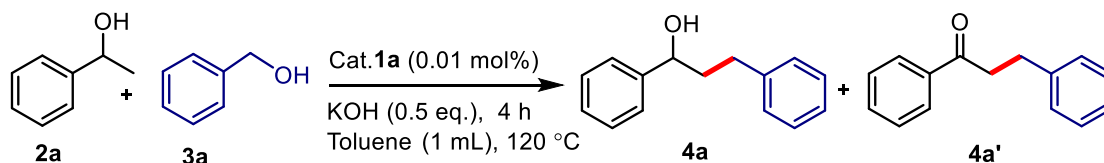
**General procedure for one-pot sequential synthesis of 2-alkylaminoquinolines:** An oven dried Schlenk tube was charged with 2-aminobenzyl alcohol (0.6 mmol), aryl acetonitrile (0.5 mmol), **1a** (1.5 mol%), and KOH (0.05 mmol, 10 mol%) followed by toluene (1 mL). Next, the reaction tube was kept in oil bath (bath temperature 120 °C) and heated for 12 h before the addition of primary alcohol (0.6 mmol) and KOH (0.5 mmol). Then the reaction mixture was further heated for 24 h and the pure products were isolated *via* column chromatography using hexane/ethyl acetate as eluent.

**Procedure for the calculation of TON for  $\beta$ -alkylation reaction:** The catalyst stock solution was prepared by dissolving **1a** in  $\text{CH}_3\text{CN}$ . An oven dried Schlenk tube was charged with **1a** (0.0001 mol%) and all the volatiles were removed in vacuum. To this, 1-phenylethanol (**2a**, 20 mmol), benzyl alcohol (**3a**, 20 mmol), and KOH (10 mmol) followed by toluene (10 mL) were added. The

reaction tube was then kept in oil bath (bath temperature 120 °C) and heated for 24 h. After that the reaction mixture was cooled to room temperature and dodecane was added before subjecting to GC-MS analysis. The average data based on the GC-MS analysis shows 42% conversion of **2a** and the formation of **4a** in 39.6% yield which provides TON of 396000.

### Optimization studies

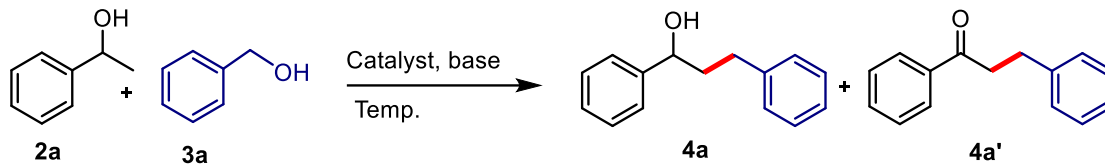
**Table S1.** Optimization of the reaction conditions for the  $\beta$ -alkylation of secondary alcohols using primary alcohols<sup>a</sup>



Entry	Catalyst (0.01 mol%)	Base	Conversion of <b>2a</b> (%)	<b>4a</b> : <b>4a'</b> (molar ratio)
1	<b>1a</b>	KOH	91	96 : 4
2	<b>1b</b>	KOH	74	89 : 11
3	<b>1c</b>	KOH	83	88 : 12
4	<b>1a</b>	NaOH	87	88 : 12
5	<b>1a</b>	NaO <sup>t</sup> Bu	89	92 : 8
6	<b>1a</b>	KO <sup>t</sup> Bu	92	93 : 7
7	<b>1a</b>	K <sub>3</sub> PO <sub>4</sub>	15	27 : 73
8	<b>1a</b>	Cs <sub>2</sub> CO <sub>3</sub>	3	0 : 100
<b>9<sup>b</sup></b>	<b>1a</b>	KOH	<b>100</b>	<b>98 : 2 (93%)</b>
10	<b>1a</b>	-	-	-
11 <sup>3</sup>	-	KOH	9%	-

<sup>a</sup>Reaction conditions: 1-phenylethanol (0.5 mmol), benzyl alcohol (0.5 mmol), cat. (0.01 mol%) KOH (0.25 mmol), and toluene (1 mL). Conversion was determined by GC-MS analysis using dodecane as internal standard. <sup>b</sup>6 h, Isolated yield is given in parenthesis.

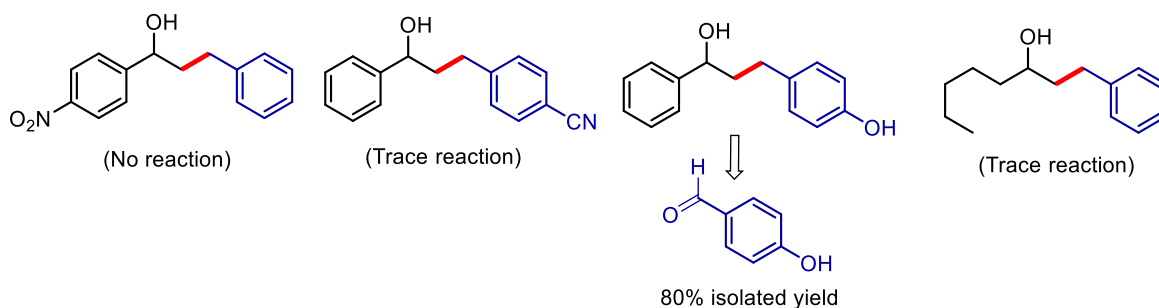
**Table S2. Comparison of TON values with selected complexes:**



Entry	Complex	Loading/Time	Base (equiv.)	Temp.	Yield of 4a	TON	Ref.
1		1 mol%/3 h	KOH (1.0)	110 °C	10%	10	8
2		1 mol%/9 h	Cs <sub>2</sub> CO <sub>3</sub> (1.5)	110 °C	81%	81	7
3		1 mol%/6 h	KOH (0.2)	110 °C	90%	90	10
4		1 mol%/2 h	KOH (1.0)	110 °C	92%	92	9
5		0.5 mol%/1 h	<sup>t</sup> BuOK (0.5)	Toluene reflux	91%	182	4
6		0.05 mol%/0.5 h	KOH (0.1)	130 °C	90%	1800	5

7		0.01 mol%/12 h	KOH (0.2)	120 °C	88%	8800	11
8		0.00025 mol% (w.r.t <b>2a</b> + <b>3a</b> ) /20 h  *(total mol % = <b>0.0005</b> (w.r.t <b>2a/3a</b> ))	NaOH (0.025 w.r.t <b>2a</b> + <b>3a</b> )	140 °C	73%	372000* (TON for the formation of <b>4a</b> + <b>4a'</b> + <b>acetophen one</b> )	6
9		0.00016 mol%/24 h	Na <sup>i</sup> OPr (0.4)	125 °C	48%	288000	12
10		0.0001 mol%/24 h	NaOH (0.2)	135 °C	91%	910000	3b
11	<p>R = 2,4,6-trimethyl</p>	0.0001 mol%/24 h	KOH (0.5)	120 °C	39.6%	<b>396000</b>	<b>This work</b>

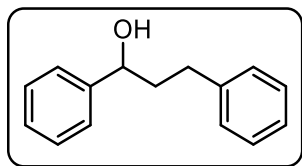
**Figure S1.** Unsuccessful substrates



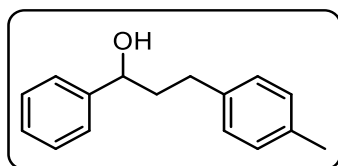
## References

1. S. N. R. Donthireddy, P. M. Illam, and A. Rit, *Inorg. Chem.*, 2020, **59**, 1835–1847.
2. Y. Pan, Y. Gong, Y. Song, W. Tong, and H. Gong, *Org. Biomol. Chem.*, 2019, **17**, 4230–4233.
3. (a) X.-B. Lan, Z. Ye, J. Liu, M. Huang, Y. Shao, X. Cai, Y. Liu, and Z. Ke, *ChemSusChem*, 2020, **13**, 2557-2563; (b) S. Genç, B. Arslan, S. Gülcemal, S. Günnaz, B. Çetinkaya, and D. Gülcemal, *J. Org. Chem.*, 2019, **84**, 6286–6297; (c) M.-J. Zhang, H.-X. Li, D. J. Young, H.-Y. Li, J.-P. Lang, *Org. Biomol. Chem.* 2019, **17**, 3567-3574.
4. C. Zhang, J.-P. Zhao, B. Hu, J. Shi, and D. Chen, *Organometallics* 2019, **38**, 654-664.
5. M. Kaur, N. O. D. Reshi, K. Patra, A. Bhattacherya, S. Kunnikuruvaan, and J. K. Bera, *Chem. Eur. J.*, 2021, **27**, 10737–10748.
6. K. Das, E. Yasmin, B. Das, H. K. Srivastava, A. Kumar, *Catal. Sci. Technol.*, 2020, **10**, 8347–8358.
7. M. V. Jiménez, J. Fernández-Tornos, F. J. Modrego, J. J. Pérez-Torrente, and L. A. Oro, *Chem. Eur. J.*, 2015, **21**, 17877–17889.
8. D. Gnanamgari, E. L. O. Sauer, N. D. Schley, C. Butler, C. D. Incarvito, and R. H. Crabtree, *Organometallics* 2009, **28**, 321–325.
9. X. Gong, H. Zhang, and X. Li, *Tetrahedron Lett.*, 2011, **52**, 5596–5600.
10. Q. Wang, K. Wu, and Z. Yu, *Organometallics* 2016, **35**, 1251–1256.
11. V. K. Singh, S. N. R. Donthireddy, P. M. Illam, and A. Rit, *Dalton Trans.*, 2020, **49**, 11958-11970.
12. S. Shee, B. Paul, D. Panja, B. C. Roy, K. Chakrabarti, K. Ganguli, A. Das, G. K. Das, and S. Kundu, *Adv. Synth. Catal.*, 2017, **359**, 3888–3893.
13. M.-J. Zhang, H.-X. Li, D. J. Young, H.-Y. Li and J.-P. Lang, *Org. Biomol. Chem.*, 2019, **17**, 3567-3574.
14. S. Shee, K. Ganguli, K. Jana and S. Kundu, *Chem. Commun.*, 2018, **54**, 6883-6886.
15. W. Lv, B. Xiong, H. Jiang and M. Zhang, *Adv. Synth. Catal.*, 2017, **359**, 1202-1207.
16. K. Das, A. Mondal, D. Pal and D. Srimani, *Org. Lett.*, 2019, **21**, 3223-3227.

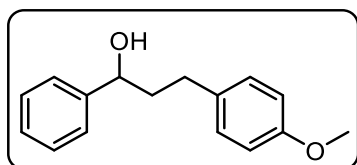
## NMR characterization data of isolated compounds



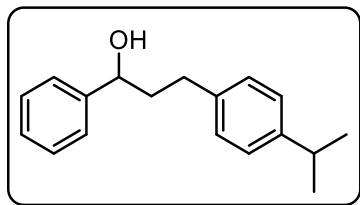
**1,3-diphenylpropan-1-ol (4a).**<sup>5,10</sup> The title compound was prepared according to the general procedure and isolated as colorless liquid (99 mg, 93% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.35 (d, 4H), 7.31-7.24 (m, 3H), 7.20-7.16 (m, 3H), 4.68 (t, 1H), 2.75-2.62 (m, 2H), 2.18-2.08 (m, 1H), 2.07-1.98 (m, 1H), 1.93 (s, 1H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 144.7, 141.9, 128.7, 128.6, 128.5, 127.8, 126.1, 126.0, 74.0, 40.6, 32.2 ppm.



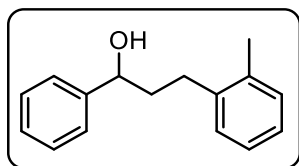
**3-(4-methylphenyl)-1-phenylpropan-1-ol (4b).**<sup>5,10</sup> The title compound was prepared according to the general procedure and isolated as colorless liquid (96 mg, 85% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.34-7.31 (m, 4H), 7.30-7.24 (m, 1H), 7.08 (s, 4H), 4.66 (t, 1H), 2.73-2.58 (m, 2H), 2.31 (s, 3H), 2.15-1.95 (m, 2H), 1.92 (s, 1H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 144.7, 138.8, 135.4, 129.2, 128.6, 128.4, 127.7, 126.1, 74.0, 40.7, 31.7, 21.1 ppm.



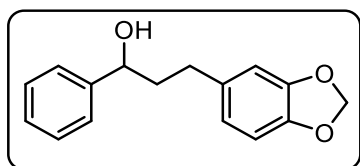
**3-(4-methoxyphenyl)-1-phenylpropan-1-ol (4c).**<sup>5,10</sup> The title compound was prepared according to the general procedure and isolated as colorless liquid (107 mg, 88% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.35-7.32 (m, 4H), 7.30-7.27 (m, 1H), 7.10 (d, 2H), 6.82 (d, 2H), 4.67 (t, 1H), 3.78 (s, 3H), 2.72-2.57 (m, 2H), 2.14-2.05 (m, 1H), 2.03-1.95 (m, 1H), 1.91 (m, 1H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>) δ 157.9, 144.8, 133.9, 129.5, 128.6, 127.8, 126.1, 114.0, 74.0, 55.4, 40.8, 31.3 ppm.



**3-(4-isopropylphenyl)-1-phenylpropan-1-ol (4d).**<sup>3b</sup> The title compound was prepared according to the general procedure and isolated as colorless liquid (109 mg, 86% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.25 (d, 4H), 7.19-7.17 (m, 1H), 7.06-7.01 (m, 4H), 4.59-4.57 (dd, 1H), 2.83-2.74 (m, 1H), 2.65-2.59 (m, 1H), 2.57-2.51 (m, 1H), 2.06-1.99 (m, 1H), 1.97-1.89 (m, 1H), 1.80 (s, 1H), 1.15 (d, 6H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  146.5, 144.8, 139.2, 128.6, 128.5, 127.7, 126.5, 126.1, 74.1, 40.6, 33.8, 31.7, 24.2 ppm.

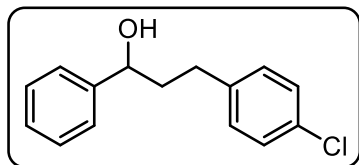


**1-phenyl-3-(o-tolyl)propan-1-ol (4e).**<sup>10</sup> The title compound was prepared according to the general procedure and isolated as colorless liquid (108 mg, 95% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36-7.33 (m, 4H), 7.31-7.24 (m, 1H), 7.14-7.08 (m, 4H), 4.74-4.70 (m, 1H), 2.79-2.72 (m, 1H), 2.65-2.58 (m, 1H), 2.26 (s, 3H), 2.12-2.03 (m, 1H), 2.02-1.94 (m, 1H), 1.91 (s, 1H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  144.7, 140.1, 136.1, 130.3, 128.9, 128.7, 127.8, 126.1, 126.1, 126.0, 74.4, 39.4, 29.6, 19.4 ppm.

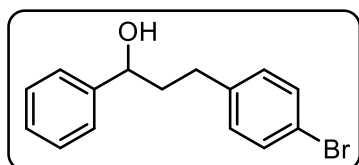


**3-(benzo[d][1,3]dioxol-5-yl)-1-phenylpropan-1-ol (4f).**<sup>10,12</sup> The title compound was prepared according to the general procedure and isolated as white solid (104 mg, 81% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.38-7.35 (m, 4H), 7.32-7.27 (m, 1H), 6.73 (d, 1H), 6.69 (s, 1H), 6.64 (d, 1H), 5.91 (s, 2H), 4.68-4.65 (m, 1H), 2.71-2.56 (m, 2H), 2.13-1.95 (m, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  147.7, 145.7, 144.7, 135.7, 128.6, 127.8, 126.0, 121.3, 109.0, 108.3, 100.9, 73.8, 40.8, 31.9 ppm.

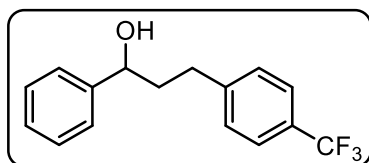




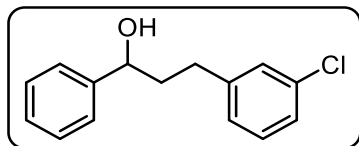
**3-(4-chlorophenyl)-1-phenylpropan-1-ol (4g).**<sup>5,10</sup> The title compound was prepared according to the general procedure and isolated as colorless liquid (111 mg, 90% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.38-7.33 (m, 4H), 7.30-7.28 (m, 1H), 7.25-7.23 (m, 2H), 7.11 (d, 2H), 4.66 (t, 1H), 2.75-2.60 (m, 2H), 2.15-2.06 (m, 1H), 2.03-1.94 (m, 1H), 1.88 (s, 1H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 144.5, 140.4, 131.7, 129.9, 128.7, 128.6, 127.9, 126.0, 73.9, 40.5, 31.5 ppm.



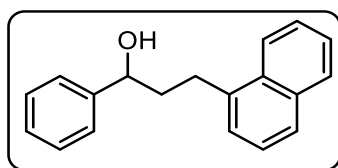
**3-(4-bromophenyl)-1-phenylpropan-1-ol (4h).**<sup>3b,5</sup> The title compound was prepared according to the general procedure and isolated as colorless liquid (136 mg, 93% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.40-7.32 (m, 6H), 7.30-7.27 (m, 1H), 7.06 (d, 2H), 4.69-4.64 (m, 1H), 2.74-2.59 (m, 2H), 2.15-1.94 (m, 2H), 1.89 (s, 1H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 144.5, 140.9, 131.6, 130.4, 128.7, 127.9, 126.0, 119.7, 73.8, 40.4, 31.6 ppm.



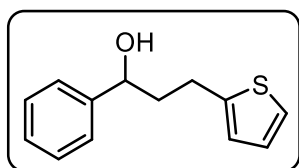
**1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-ol (4i).**<sup>3b</sup> The title compound was prepared according to the general procedure and isolated as colorless liquid (100 mg, 75% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.44 (d, 2H), 7.29-7.16 (m, 7H), 4.58 (q, 1H), 2.76-2.60 (m, 2H), 2.09-1.85 (m, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 146.1, 144.4, 128.9, 128.7, 128.4 (q, *J*(C,F) = 32 Hz), 127.9, 126.0, 125.5 (q, *J*(C,F) = 3.6 Hz), 124.5 (q, *J*(C,F) = 271.6 Hz) 73.8, 40.2, 32.0 ppm.



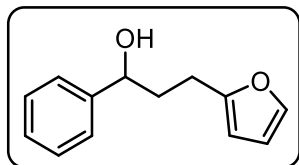
**3-(3-chlorophenyl)-1-phenylpropan-1-ol (4j).**<sup>10,12</sup> The title compound was prepared according to the general procedure and isolated as colorless liquid (111 mg, 90% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.38-7.33 (m, 4H), 7.30-7.27 (m, 1H), 7.22-7.15 (m, 3H), 7.08-7.05 (m, 1H), 4.69-4.65 (m, 1H), 2.77-2.61 (m, 2H), 2.16-2.06 (m, 1H), 2.04-1.95 (m, 1H), 1.89 (s, 1H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 144.5, 144.0, 134.3, 129.8, 128.7, 127.9, 126.8, 126.2, 126.1, 126.0, 73.8, 40.3, 31.9 ppm.



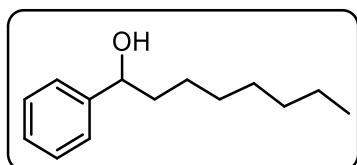
**3-(naphthalen-1-yl)-1-phenylpropan-1-ol (4k).**<sup>10,12</sup> The title compound was prepared according to the general procedure and isolated as colorless liquid (79 mg, 60% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.97 (d, 1H), 7.84 (d, 1H), 7.70 (d, 1H), 7.49-7.43 (m, 2H), 7.40-7.32 (m, 6H), 7.31-7.27 (m, 1H), 4.79 (t, 1H), 3.28-3.20 (m, 1H), 3.13-3.06 (m, 1H), 2.30-2.10 (m, 2H), 1.98 (s, 1H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 144.7, 138.1, 134.0, 132.0, 128.9, 128.7, 127.8, 126.8, 126.1, 125.9, 125.7, 125.6, 123.9, 74.3, 40.0, 29.3 ppm.



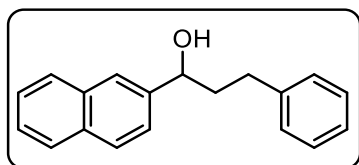
**1-phenyl-3-(thiophen-2-yl)propan-1-ol (4l).**<sup>3b,5</sup> The title compound was prepared according to the general procedure and isolated as colorless liquid (66 mg, 60% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.40-7.35 (m, 4H), 7.33-7.27 (m, 1H), 7.14 (d, 1H), 6.94 (t, 1H), 6.83 (s, 1H), 4.73 (t, 1H), 3.01-2.88 (m, 2H), 2.24-2.05 (m, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 144.7, 144.4, 128.7, 127.8, 126.9, 126.0, 124.4, 123.2, 73.6, 40.8, 26.3 ppm.



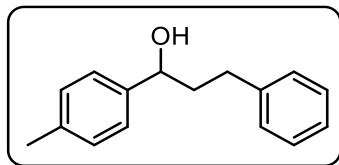
**3-(furan-2-yl)-1-phenylpropan-1-ol (4m).**<sup>3b,10</sup> The title compound was prepared according to the general procedure and isolated as colorless liquid (52 mg, 51% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.27-7.25 (m, 4H), 7.21-7.17 (m, 2H), 6.19 (s, 1H), 5.91 (s, 1H), 4.59 (t, 1H), 2.67-2.58 (m, 2H), 2.05-1.93 (m, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  155.7, 144.5, 141.1, 128.6, 127.8, 126.0, 110.2, 105.2, 73.8, 37.2, 24.5 ppm.



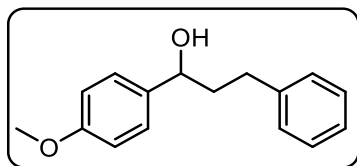
**1-phenyloctan-1-ol (4n).**<sup>5,10</sup> The title compound was prepared according to the general procedure and isolated as colorless liquid (54 mg, 52% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.27-7.23 (m, 4H), 7.21-7.16 (m, 1H), 4.56 (t, 1H), 1.87 (s, 1H), 1.75-1.56 (m, 2H), 1.33-1.13 (m, 10H), 0.83-0.76 (m, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  145.1, 128.5, 127.6, 126.0, 74.8, 39.2, 31.9, 29.6, 29.3, 26.0, 22.8, 14.2 ppm.



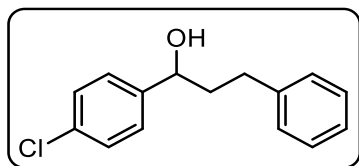
**1-(naphthalen-2-yl)-3-phenylpropan-1-ol (4o).**<sup>10,12</sup> The title compound was prepared according to the general procedure and isolated as colorless liquid (112 mg, 85% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.85-7.78 (m, 4H), 7.50-7.45 (m, 3H), 7.30-7.25 (m, 2H), 7.21-7.17 (m, 3H), 4.86 (t, 1H), 2.81-2.66 (m, 2H), 2.27-2.08 (m, 2H), 2.01 (s, 1H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  142.0, 141.9, 133.4, 133.2, 128.6, 128.6, 128.1, 127.8, 126.3, 126.0, 124.8, 124.2, 74.1, 40.5, 32.2 ppm.



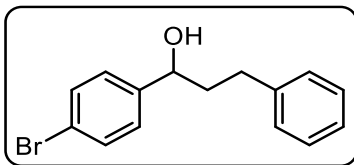
**3-phenyl-1-(p-tolyl)propan-1-ol (4p).**<sup>5,12</sup> The title compound was prepared according to the general procedure and isolated as colorless liquid (97 mg, 86% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.30-7.15 (m, 9H), 4.63 (t, 1H), 2.77-2.60 (m, 2H), 2.35 (s, 3H), 2.19-1.95 (m, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 142.0, 141.7, 137.4, 129.3, 128.6, 128.5, 126.0, 125.9, 73.8, 40.5, 32.2, 21.2 ppm.



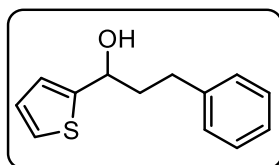
**1-(4-methoxyphenyl)-3-phenylpropan-1-ol (4q).**<sup>5,10</sup> The title compound was prepared according to the general procedure and isolated as colorless liquid (103 mg, 85% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.29-7.25 (m, 4H), 7.19-7.17 (m, 3H), 6.88 (d, 2H), 4.62 (t, 1H), 3.80 (s, 3H), 2.75-2.59 (m, 2H), 2.17-1.95 (m, 2H), 1.86 (s, 1H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 159.2, 142.0, 136.8, 128.6, 128.5, 127.3, 126.0, 114.0, 73.6, 55.4, 40.5, 32.3 ppm.



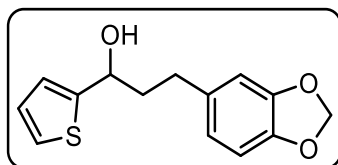
**1-(4-chlorophenyl)-3-phenylpropan-1-ol (4r).**<sup>5,10</sup> The title compound was prepared according to the general procedure and isolated as colorless liquid (106 mg, 86% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.33-7.26 (m, 6H), 7.21-7.17 (m, 3H), 4.69-4.65 (m, 1H), 2.77-2.62 (m, 2H), 2.15-1.94 (m, 2H), 1.90 (s, 1H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 143.1, 141.6, 133.4, 128.8, 128.6, 128.6, 127.4, 126.1, 73.3, 40.6, 32.1 ppm.



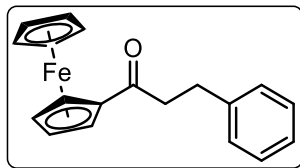
**1-(4-bromophenyl)-3-phenylpropan-1-ol (4s).**<sup>10,12</sup> The title compound was prepared according to the general procedure and isolated as colorless liquid (131 mg, 90% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.48-7.46 (m, 2H), 7.31-7.28 (m, 2H), 7.23-7.18 (m, 5H), 4.65 (t, 1H), 2.76-2.63 (m, 2H), 2.13-2.06 (m, 1H), 2.03-1.95 (m, 2H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>) δ 143.7, 141.6, 131.7, 128.6, 128.5, 127.8, 126.1, 121.5, 73.3, 40.6, 32.0 ppm.



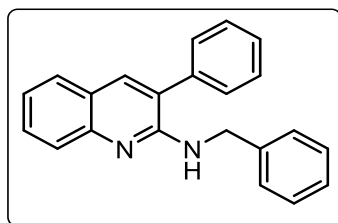
**3-phenyl-1-(thiophen-2-yl)propan-1-ol (4t).**<sup>13</sup> The title compound was prepared according to the general procedure and isolated as colorless liquid (70 mg, 64% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.29-7.22 (m, 3H), 7.20-7.16 (m, 3H), 6.96-6.94 (m, 2H), 4.89 (t, 1H), 2.79-2.65 (m, 2H), 2.24-2.07 (m, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 148.6, 141.6, 128.6, 128.5, 126.8, 126.1, 124.8, 124.0, 69.6, 40.8, 32.1 ppm.



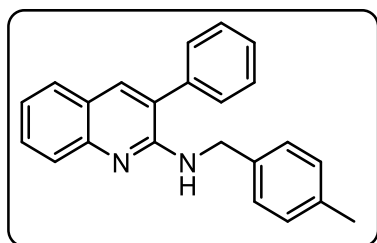
**3-(benzo[d][1,3]dioxol-5-yl)-1-(thiophen-2-yl)propan-1-ol (4u).** The title compound was prepared according to the general procedure and isolated as colorless liquid (67 mg, 51% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.17 (m, 1H), 6.89-6.87 (m, 2H), 6.65-6.61 (m, 2H), 6.56 (d, 1H), 5.82 (s, 2H), 4.83-4.80 (m, 1H), 2.64-2.51 (m, 2H), 2.13-1.95 (m, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 148.6, 147.7, 145.8, 135.4, 126.8, 124.8, 124.0, 121.3, 109.1, 108.3, 100.9, 69.4, 41.0, 31.8 ppm. HRMS (ESI): m/z = 263.0740, calcd. for C<sub>14</sub>H<sub>14</sub>O<sub>3</sub>SH [M + H]<sup>+</sup> : 263.0742.



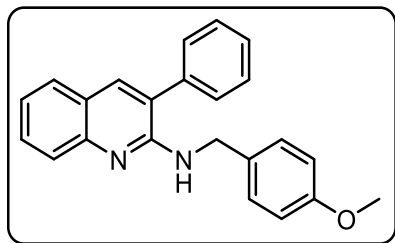
**1-(ferrocene)-3-phenylpropan-1-one (4v')**.<sup>13</sup> The title compound was prepared according to the general procedure and isolated as red solid (121 mg, 76% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.25-7.20 (m, 4H), 7.16-7.11 (m, 1H), 4.67 (s, 2H), 4.38 (s, 2H), 3.98 (s, 5H), 2.97-2.92 (m, 4H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 203.1, 141.7, 128.7, 128.6, 126.2, 79.1, 72.3, 69.7, 69.3, 41.6, 30.2 ppm.



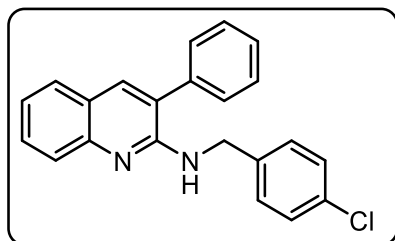
**N-benzyl-3-phenylquinolin-2-amine (7a)**.<sup>14,15</sup> The title compound was prepared according to the general procedure and isolated as yellow liquid (110 mg, 71% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.67 (d, 1H), 7.57 (s, 1H), 7.51-7.41 (m, 2H), 7.38-7.32 (m, 4H), 7.29-7.23 (m, 3H), 7.18 (t, 2H), 7.11 (t, 2H), 5.00 (s, 1H), 4.71 (d, 2H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 154.3, 147.7, 140.0, 137.6, 136.5, 129.4, 129.3, 129.2, 128.6, 128.3, 127.8, 127.5, 127.1, 126.4, 125.7, 123.8, 122.4, 45.5 ppm.



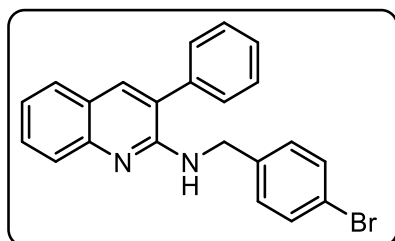
**N-(4-methylbenzyl)-3-phenylquinolin-2-amine (7b)**.<sup>14</sup> The title compound was prepared according to the general procedure and isolated as yellow liquid (128 mg, 79% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.67 (d, 1H), 7.54 (s, 1H), 7.47 (d, 1H), 7.41 (t, 1H), 7.39-7.32 (m, 4H), 7.28-7.23 (m, 1H), 7.13-7.09 (m, 3H), 6.98 (d, 2H), 4.95 (s, 1H), 4.65 (d, 2H), 2.18 (s, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 154.4, 147.7, 137.6, 136.9, 136.8, 136.5, 129.4, 129.3, 129.3, 129.2, 128.3, 127.9, 127.5, 126.4, 125.7, 123.8, 122.3, 45.4, 21.2 ppm.



**N-(4-methoxybenzyl)-3-phenylquinolin-2-amine (7c).**<sup>16</sup> The title compound was prepared according to the general procedure and isolated as yellow liquid (119 mg, 70% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.72 (d, 1H), 7.59 (s, 1H), 7.52 (d, 1H), 7.46 (t, 1H), 7.39-7.35 (m, 4H), 7.33-7.28 (m, 1H), 7.20 (d, 2H), 7.14 (t, 1H), 6.75 (d, 2H), 4.97 (s, 1H), 4.66 (d, 2H), 3.68 (s, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 158.9, 154.3, 137.5, 136.6, 131.9, 129.5, 129.4, 129.2, 129.2, 128.4, 127.5, 127.5, 126.2, 125.7, 123.7, 122.4, 114.0, 55.4, 45.2 ppm.

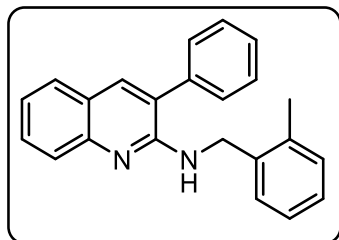


**N-(4-chlorobenzyl)-3-phenylquinolin-2-amine (7d).** The title compound was prepared according to the general procedure and isolated as yellow liquid (104 mg, 60% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.67 (d, 1H), 7.59 (s, 1H), 7.50 (d, 1H), 7.44 (t, 1H), 7.38-7.34 (m, 4H), 7.33-7.29 (m, 1H), 7.20-7.11 (m, 5H), 5.01 (s, 1H), 4.66 (d, 2H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 154.0, 147.4, 138.6, 137.4, 136.7, 132.8, 129.5, 129.4, 129.2, 129.2, 128.7, 128.4, 127.5, 126.3, 125.6, 123.8, 122.6, 44.8 ppm. HRMS (ESI): m/z = 345.1158, calcd. for C<sub>22</sub>H<sub>17</sub>N<sub>2</sub>ClH [M + H]<sup>+</sup> : 345.1159.

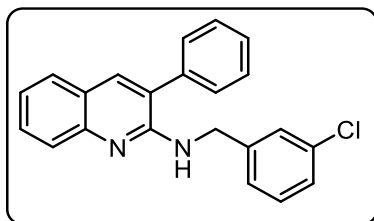


**N-(4-bromobenzyl)-3-phenylquinolin-2-amine (7e).** The title compound was prepared according to the general procedure and isolated as yellow liquid (107 mg, 55% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.61 (s, 1H), 7.52 (d, 1H), 7.45 (t, 1H), 7.41-7.35 (m, 4H), 7.33-7.28 (m, 3H),

7.17-7.14 (m, 3H), 5.04 (s, 1H), 4.67 (d, 2H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  154.0, 139.1, 137.4, 136.7, 131.7, 129.6, 129.4, 129.2, 128.7, 128.5, 127.9, 127.5, 126.3, 125.6, 123.8, 122.7, 120.9, 44.9 ppm. HRMS (ESI):  $m/z = 389.0655$ , calcd. for  $\text{C}_{22}\text{H}_{17}\text{N}_2\text{BrH}$   $[\text{M} + \text{H}]^+$  : 389.0653.

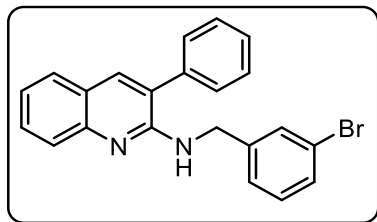


**N-(2-methylbenzyl)-3-phenylquinolin-2-amine (7f).** The title compound was prepared according to the general procedure and isolated as yellow liquid (100 mg, 61% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (d, 1H), 7.60 (s, 1H), 7.52 (d, 1H), 7.46 (t, 1H), 7.37 (d, 4H), 7.33-7.28 (m, 1H), 7.19 (d, 1H), 7.15 (t, 1H), 7.09-7.02 (m, 3H), 4.87 (s, 1H), 4.71 (d, 2H), 2.28 (s, 3H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  154.2, 137.5, 137.4, 136.7, 130.5, 129.6, 129.4, 129.1, 128.5, 128.4, 127.5, 127.4, 126.1, 125.7, 123.7, 122.5, 44.0, 19.3 ppm. HRMS (ESI):  $m/z = 325.1675$ , calcd. for  $\text{C}_{23}\text{H}_{20}\text{N}_2\text{H}$   $[\text{M} + \text{H}]^+$  : 325.1705.

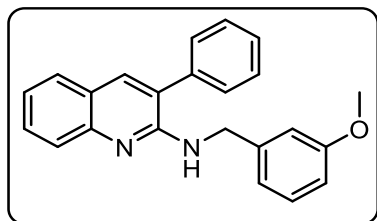


**N-(3-chlorobenzyl)-3-phenylquinolin-2-amine (7g).** The title compound was prepared according to the general procedure and isolated as yellow liquid (88 mg, 51% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 (d, 1H), 7.60 (s, 1H), 7.51 (d, 1H), 7.44 (t, 1H), 7.40-7.36 (m, 4H), 7.34 (m, 1H), 7.25 (s, 1H), 7.16-7.10 (m, 4H), 5.05 (s, 1H), 4.69 (d, 2H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  154.0, 147.4, 142.2, 137.4, 136.7, 134.4, 129.8, 129.6, 129.4, 129.2, 128.5, 128.0, 127.5, 127.3, 126.3, 125.9, 125.6, 123.8, 122.6, 45.0 ppm. HRMS (ESI):  $m/z = 345.1160$ , calcd. for  $\text{C}_{22}\text{H}_{17}\text{N}_2\text{ClH}$   $[\text{M} + \text{H}]^+$  : 345.1159.

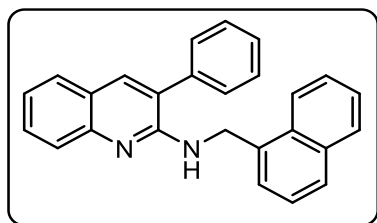




**N-(3-bromobenzyl)-3-phenylquinolin-2-amine (7h).** The title compound was prepared according to the general procedure and isolated as yellow liquid (107 mg, 55% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (d, 1H), 7.57 (s, 1H), 7.48 (d, 1H), 7.42-7.37 (m, 2H), 7.36-7.33 (m, 4H), 7.31-7.27 (m, 1H), 7.22 (d, 1H), 7.16 (d, 1H), 7.11 (t, 1H), 7.01 (t, 1H), 5.02 (s, 1H), 4.66 (d, 2H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  154.0, 147.5, 139.1, 137.4, 136.5, 131.6, 129.6, 129.5, 129.4, 129.3, 129.1, 128.4, 127.8, 127.5, 126.4, 125.6, 123.8, 122.5, 120.8, 44.8 ppm. HRMS (ESI):  $m/z = 389.0652$ , calcd. for  $\text{C}_{22}\text{H}_{17}\text{N}_2\text{BrH}$   $[\text{M} + \text{H}]^+$  : 389.0653.

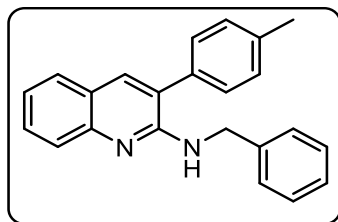


**N-(3-methoxybenzyl)-3-phenylquinolin-2-amine (7i).** The title compound was prepared according to the general procedure and isolated as yellow liquid (94 mg, 55% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (d, 1H), 7.69 (s, 1H), 7.60 (d, 1H), 7.54 (t, 1H), 7.50-7.45 (m, 4H), 7.42-7.38 (m, 1H), 7.24-7.19 (m, 2H), 6.91 (d, 2H), 6.77 (d, 1H), 5.09 (s, 1H), 4.79 (d, 2H), 3.76 (s, 3H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.9, 154.3, 147.7, 141.7, 137.6, 136.5, 129.6, 129.5, 129.4, 128.4, 127.5, 126.4, 125.7, 123.8, 122.4, 120.1, 113.5, 112.6, 55.3, 45.5 ppm. HRMS (ESI):  $m/z = 341.1651$ , calcd. for  $\text{C}_{23}\text{H}_{20}\text{N}_2\text{OH}$   $[\text{M} + \text{H}]^+$  : 341.1654.

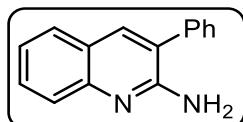


**N-(naphthalen-1-ylmethyl)-3-phenylquinolin-2-amine (7j).** The title compound was prepared according to the general procedure and isolated as yellow liquid (94 mg, 52% yield).  $^1\text{H}$  NMR

(400 MHz, CDCl<sub>3</sub>)  $\delta$  8.02 (d, 1H), 7.73 (t, 2H), 7.61 (d, 1H), 7.56 (s, 1H), 7.49-7.42 (m, 2H), 7.37-7.32 (m, 3H), 7.31-7.15 (m, 6H), 7.11 (t, 1H), 5.13 (d, 2H), 4.97 (s, 1H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  154.1, 147.7, 137.4, 136.6, 135.0, 133.9, 131.9, 129.5, 129.3, 129.1, 128.8, 128.2, 128.2, 127.5, 126.4, 126.3, 126.3, 125.9, 125.7, 125.5, 124.0, 123.8, 122.4, 43.9 ppm. HRMS (ESI):  $m/z = 361.1697$ , calcd. for C<sub>26</sub>H<sub>20</sub>N<sub>2</sub>H [M + H]<sup>+</sup>: 361.1705.

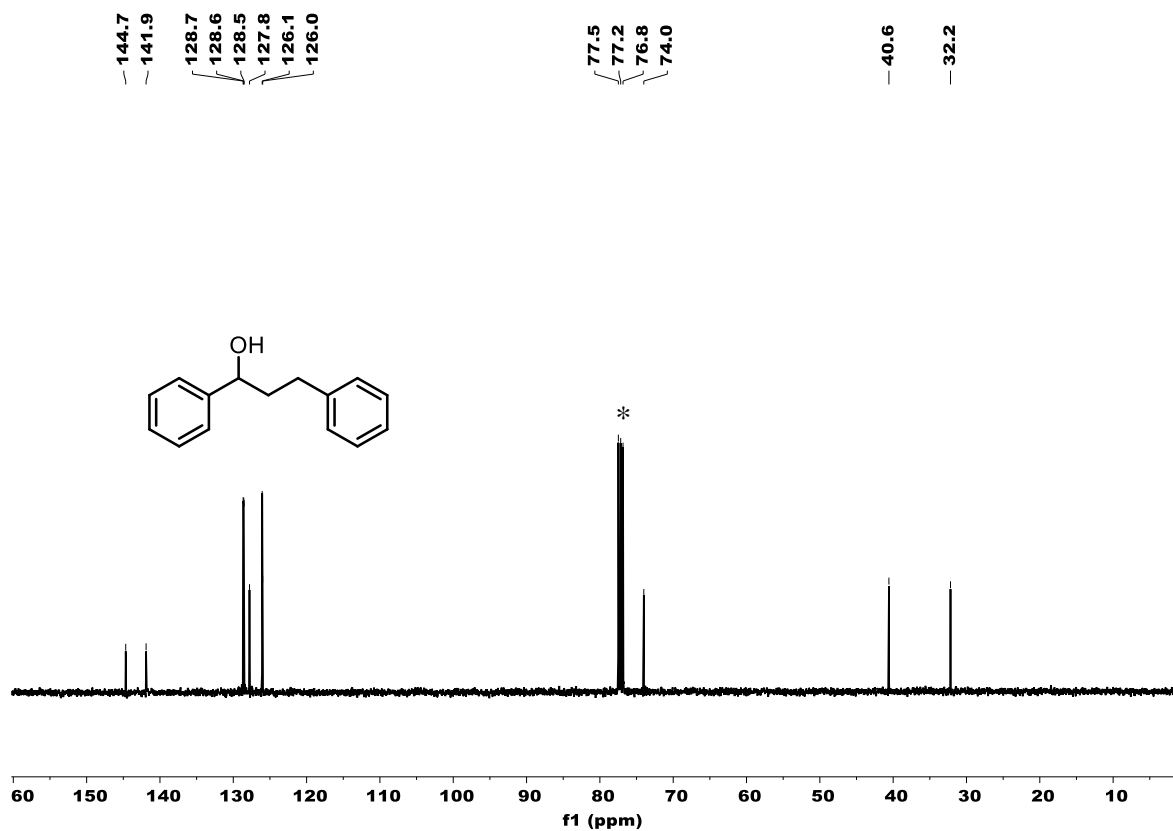
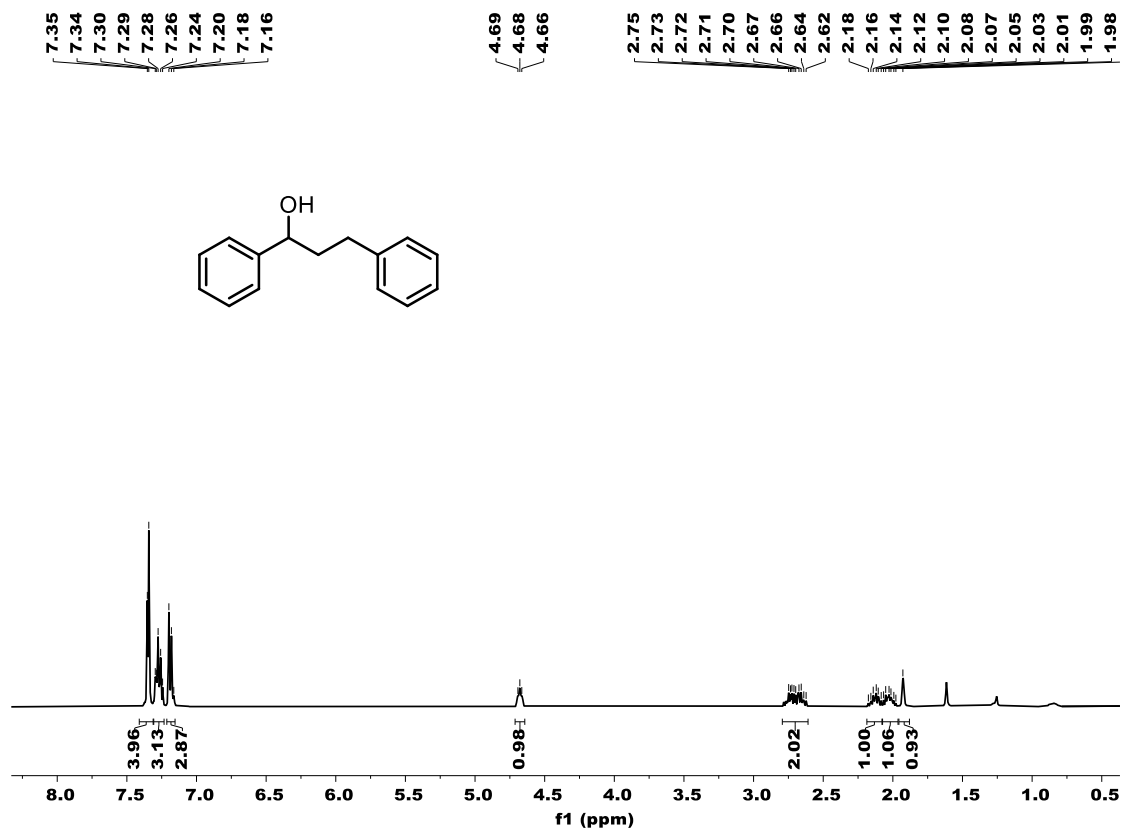


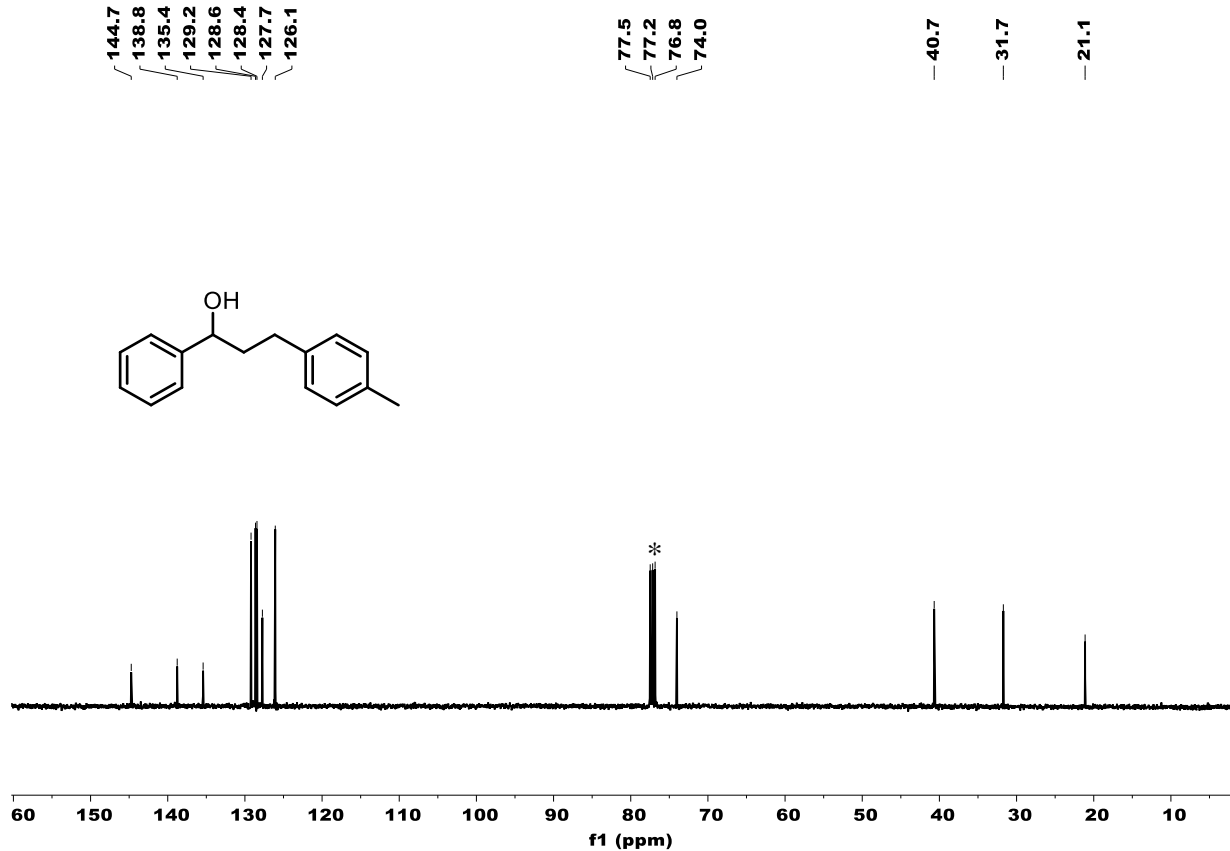
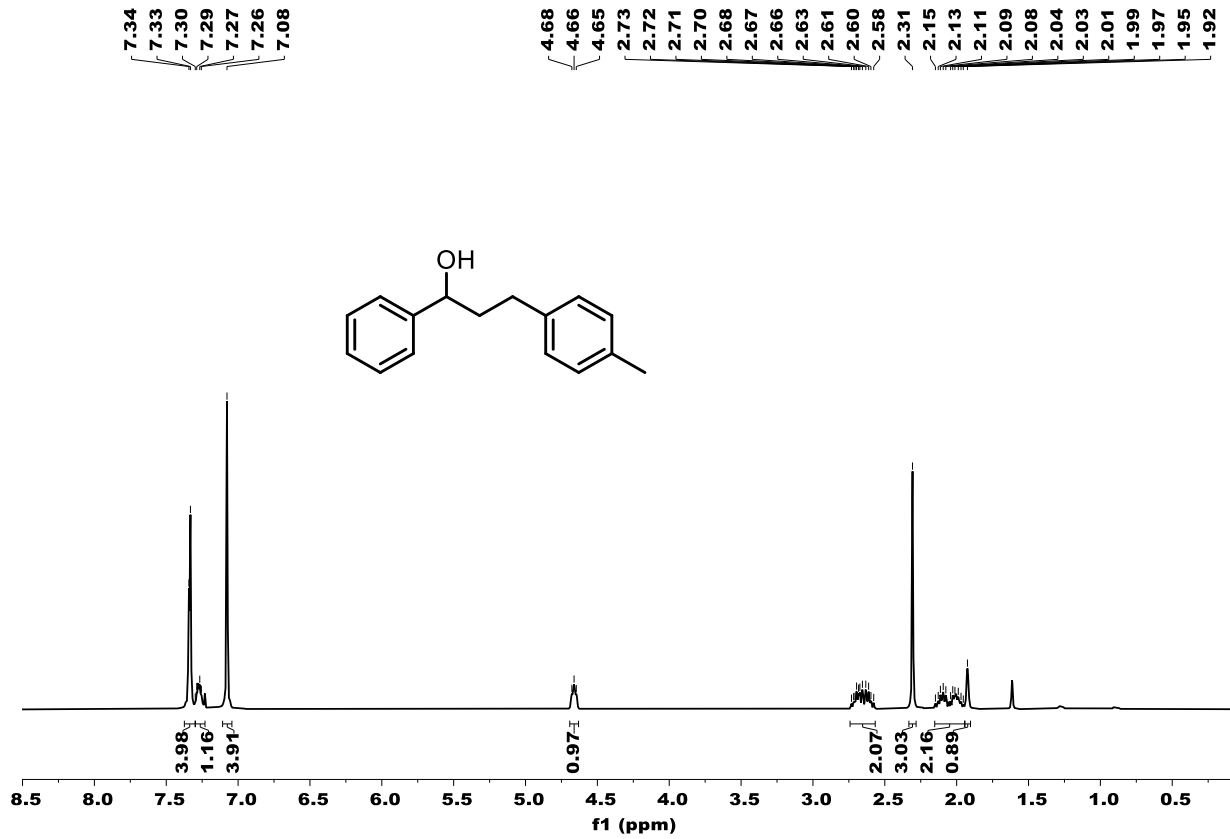
**N-benzyl-3-(p-tolyl)quinolin-2-amine (7k).**<sup>15</sup> The title compound was prepared according to the general procedure and isolated as yellow liquid (99 mg, 61% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.67 (d, 1H), 7.56 (s, 1H), 7.49 (d, 1H), 7.43 (t, 1H), 7.28-7.23 (m, 4H), 7.22-7.09 (m, 6H), 5.03 (s, 1H), 4.72 (d, 2H), 2.29 (s, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  154.5, 147.6, 140.0, 138.2, 136.4, 134.5, 130.0, 129.3, 129.0, 128.6, 127.9, 127.4, 127.1, 126.3, 125.7, 123.9, 122.3, 45.6, 21.3 ppm.

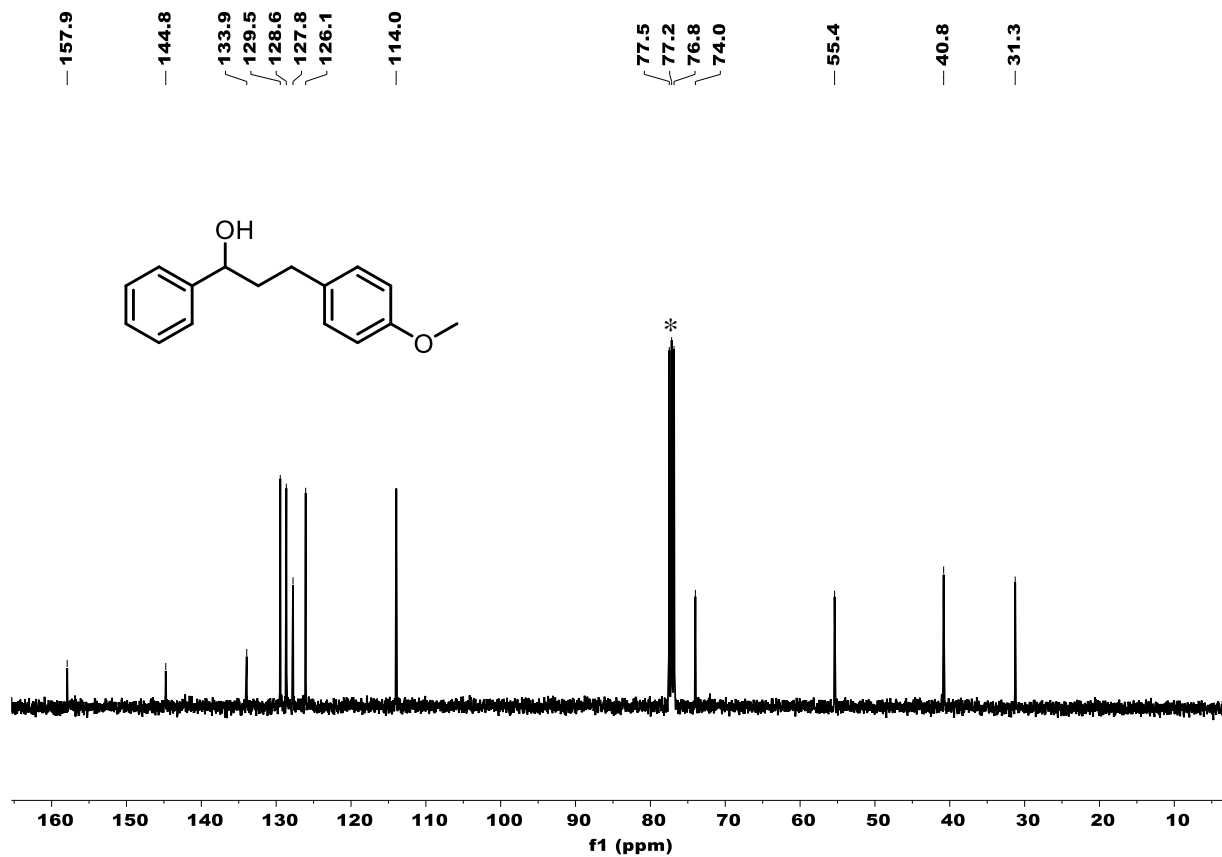
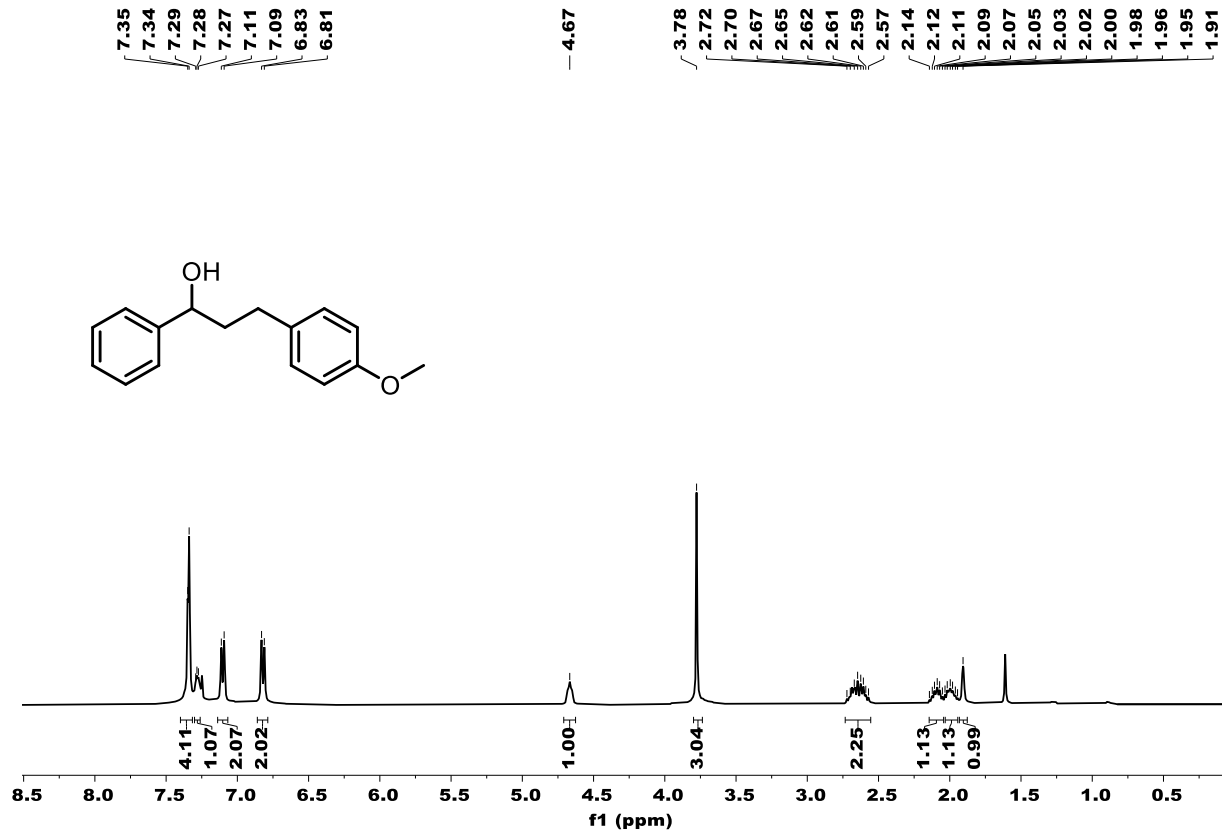


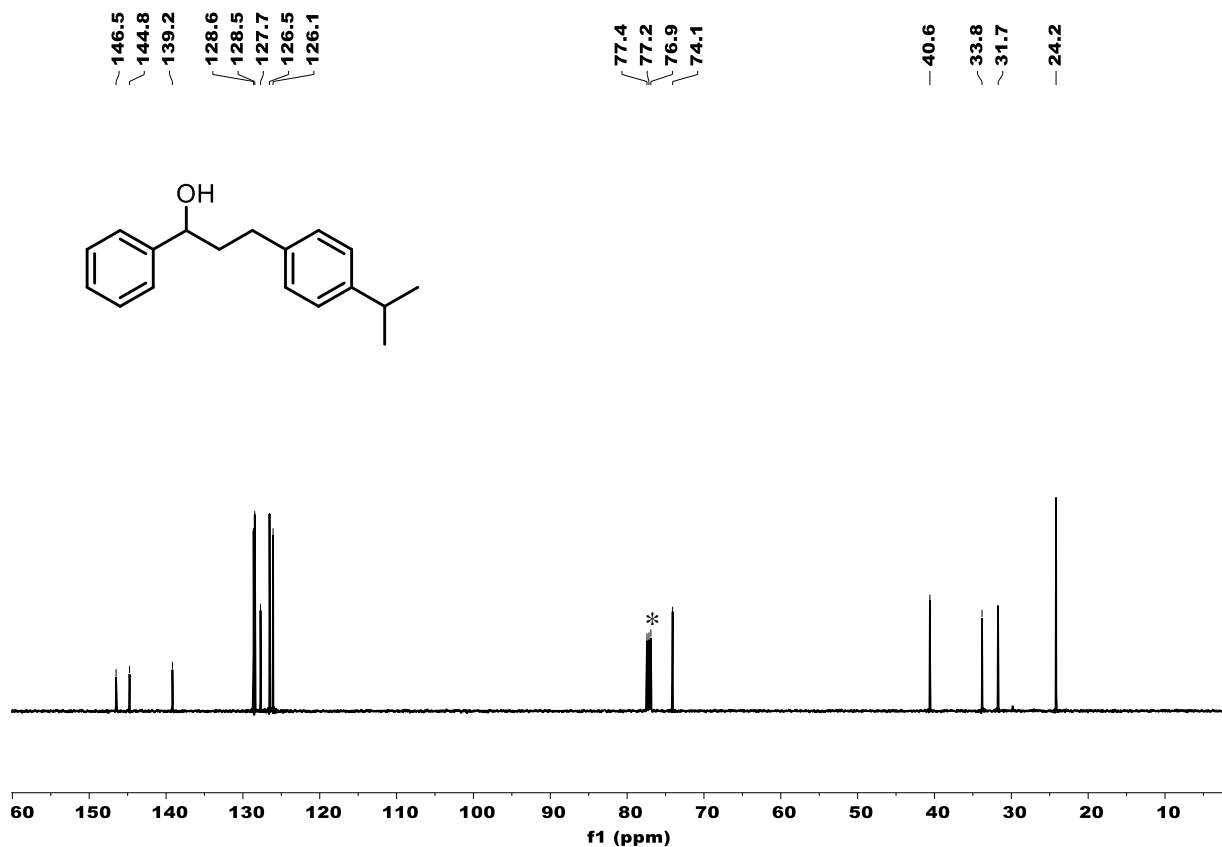
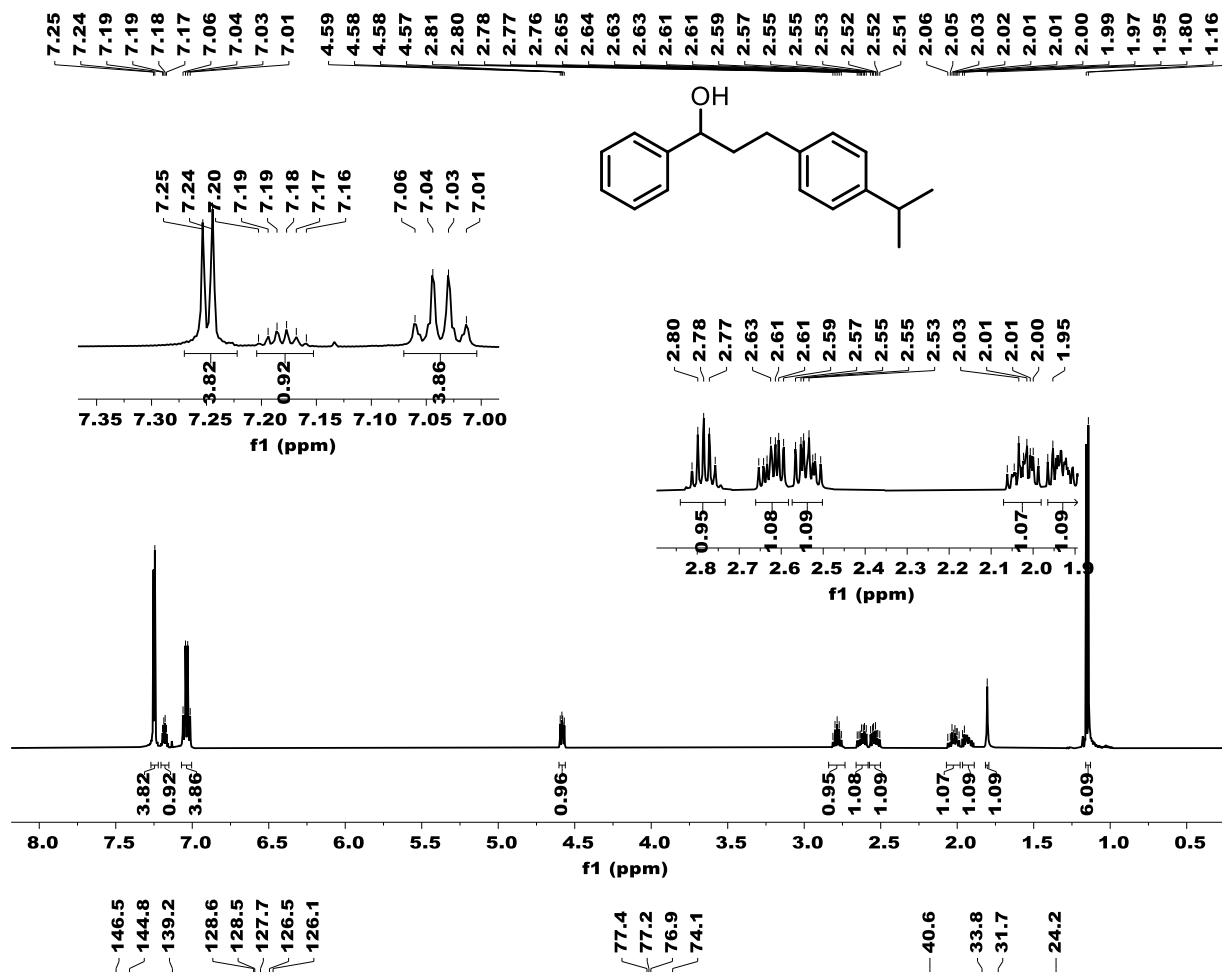
**3-phenylquinolin-2-amine.**<sup>15,16</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.81 (s, 1H), 7.70 (dd, 2H), 7.60 (t, 1H), 7.57-7.41 (m, 5H), 7.30 (t, 1H), 5.15 (s, 2H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  155.3, 146.8, 137.6, 137.6, 130.0, 129.4, 129.1, 128.5, 127.7, 125.5, 125.3, 124.3, 123.1 ppm.

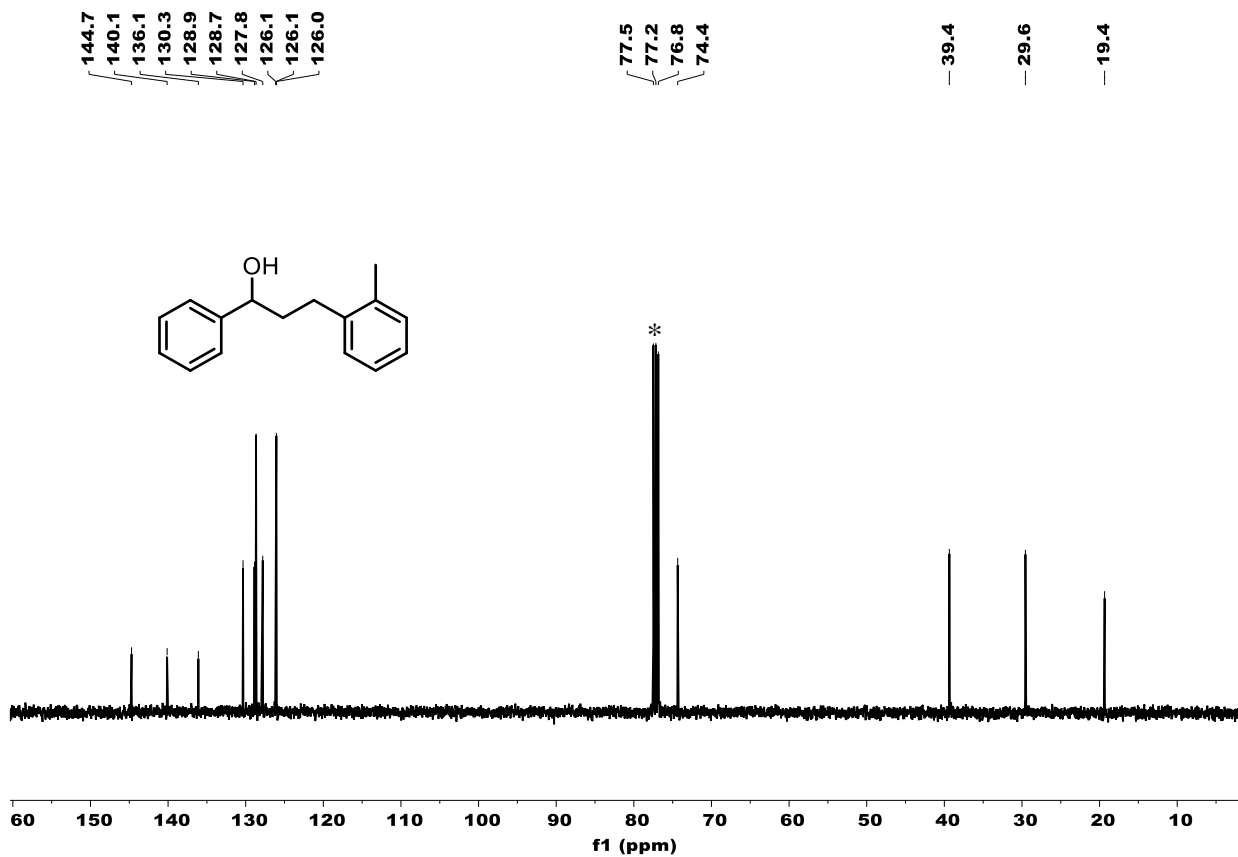
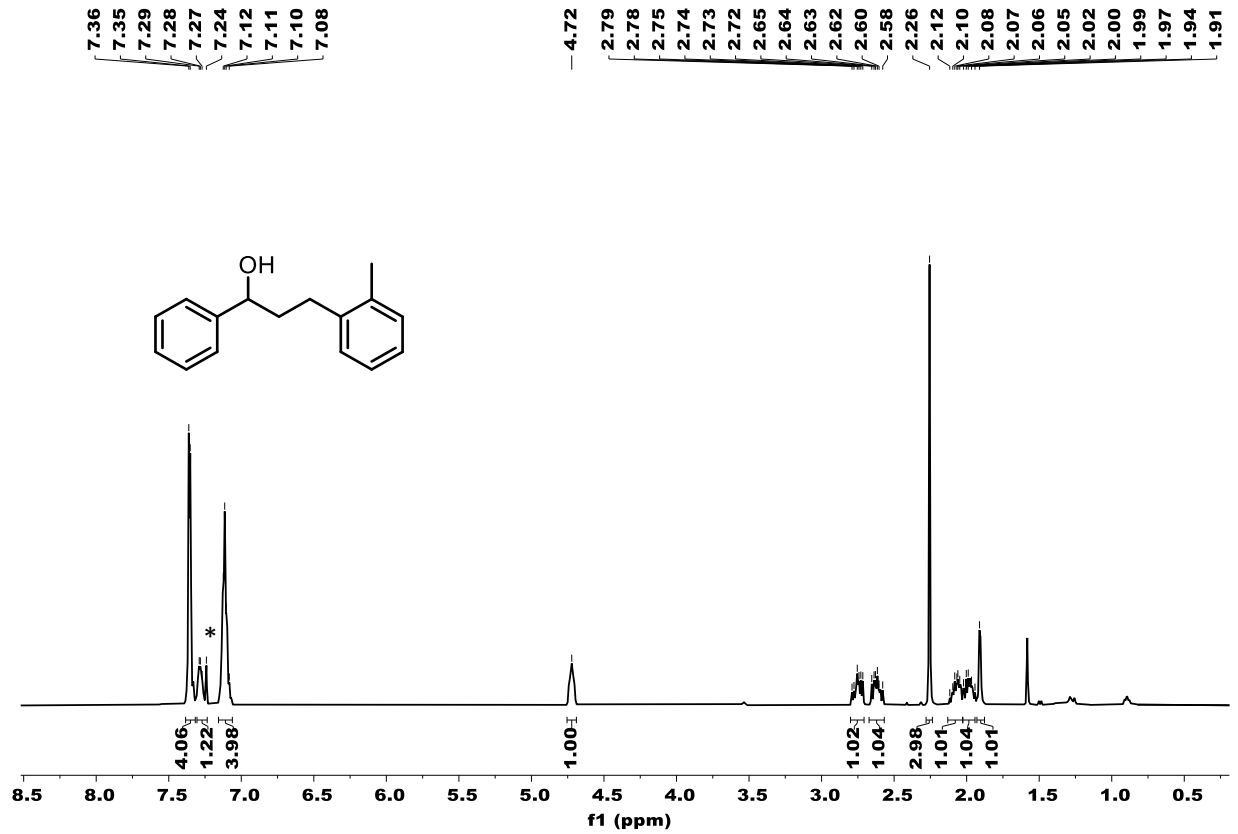
**<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of isolated compounds in CDCl<sub>3</sub>(\*)**

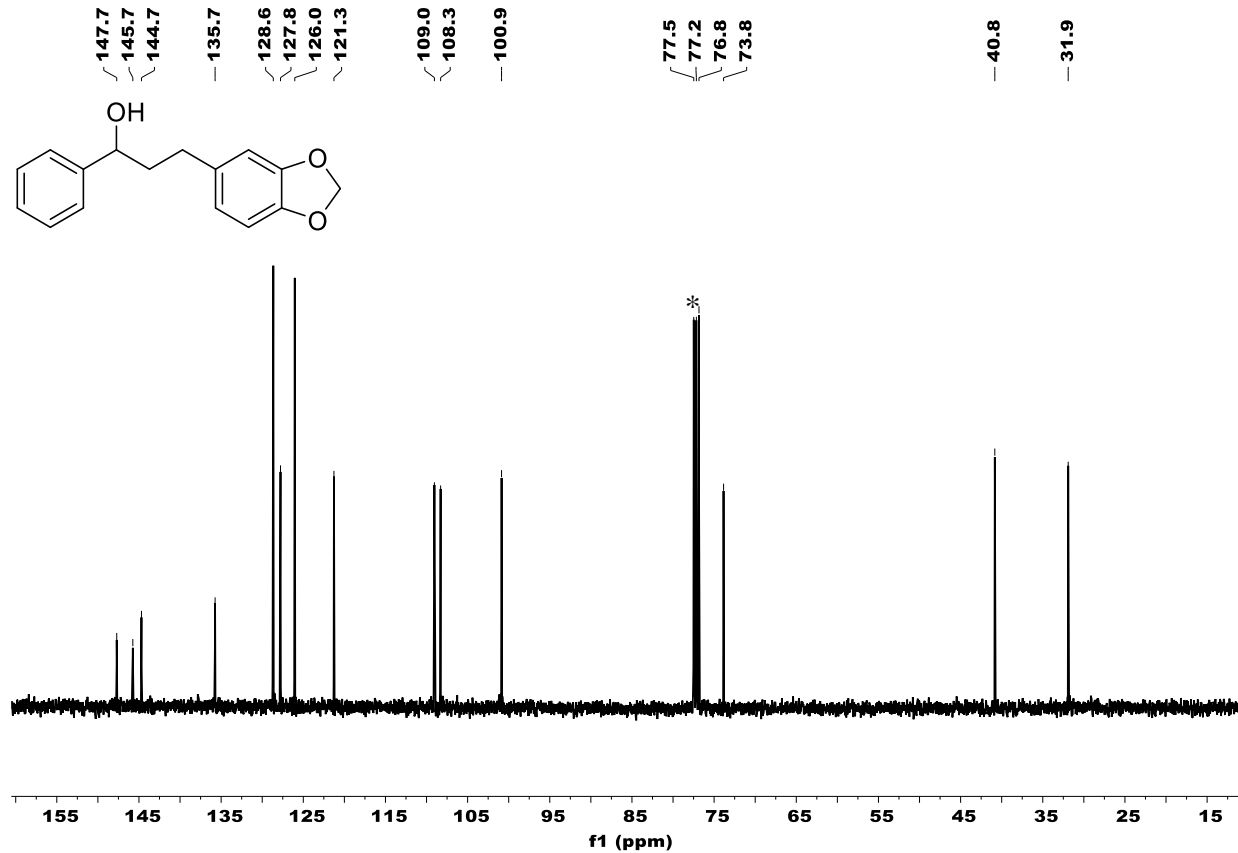
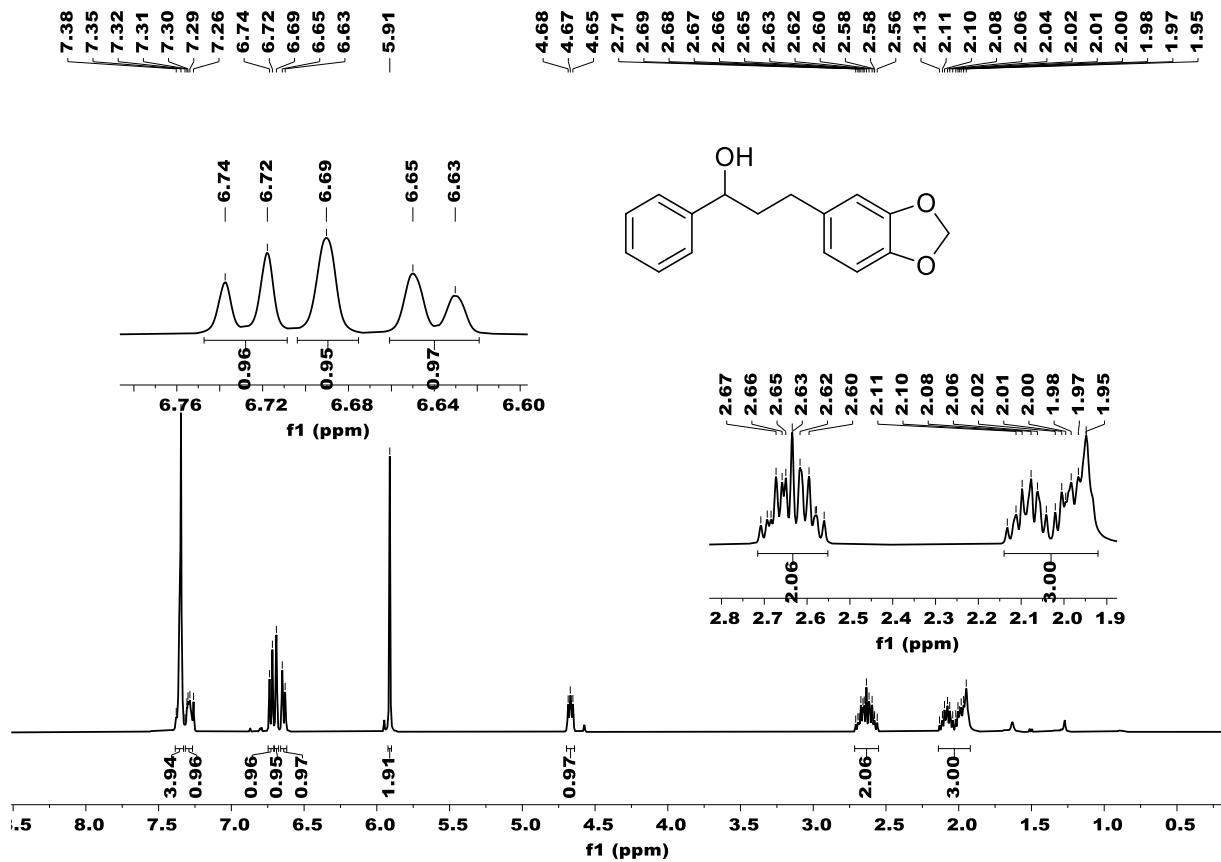




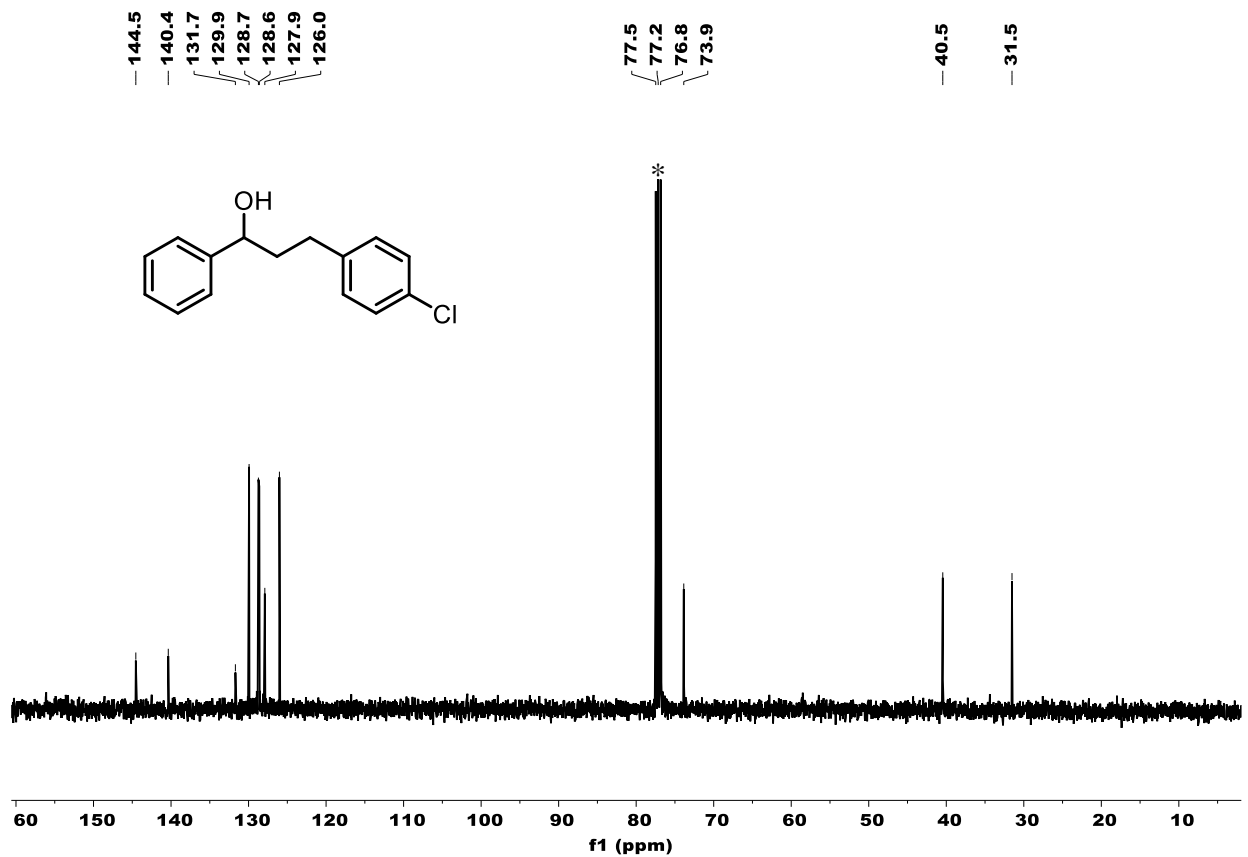
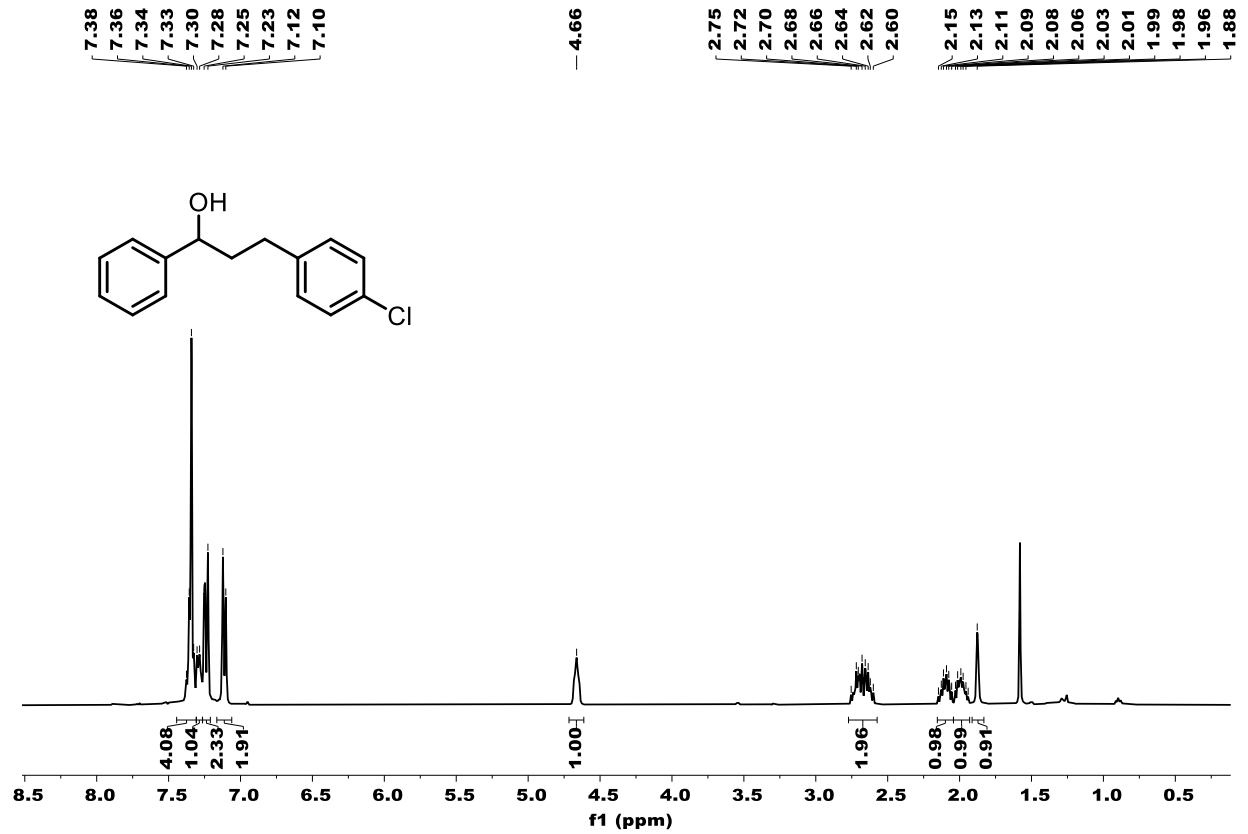


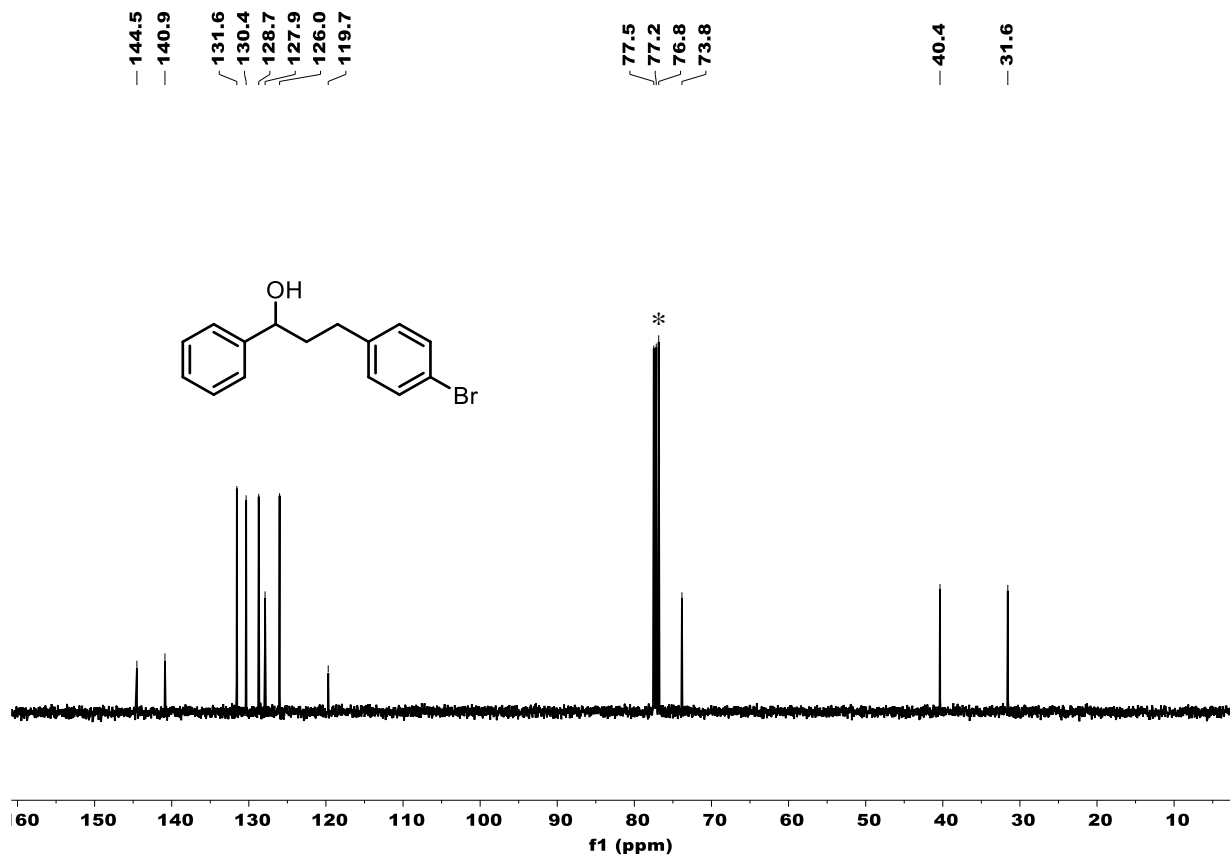
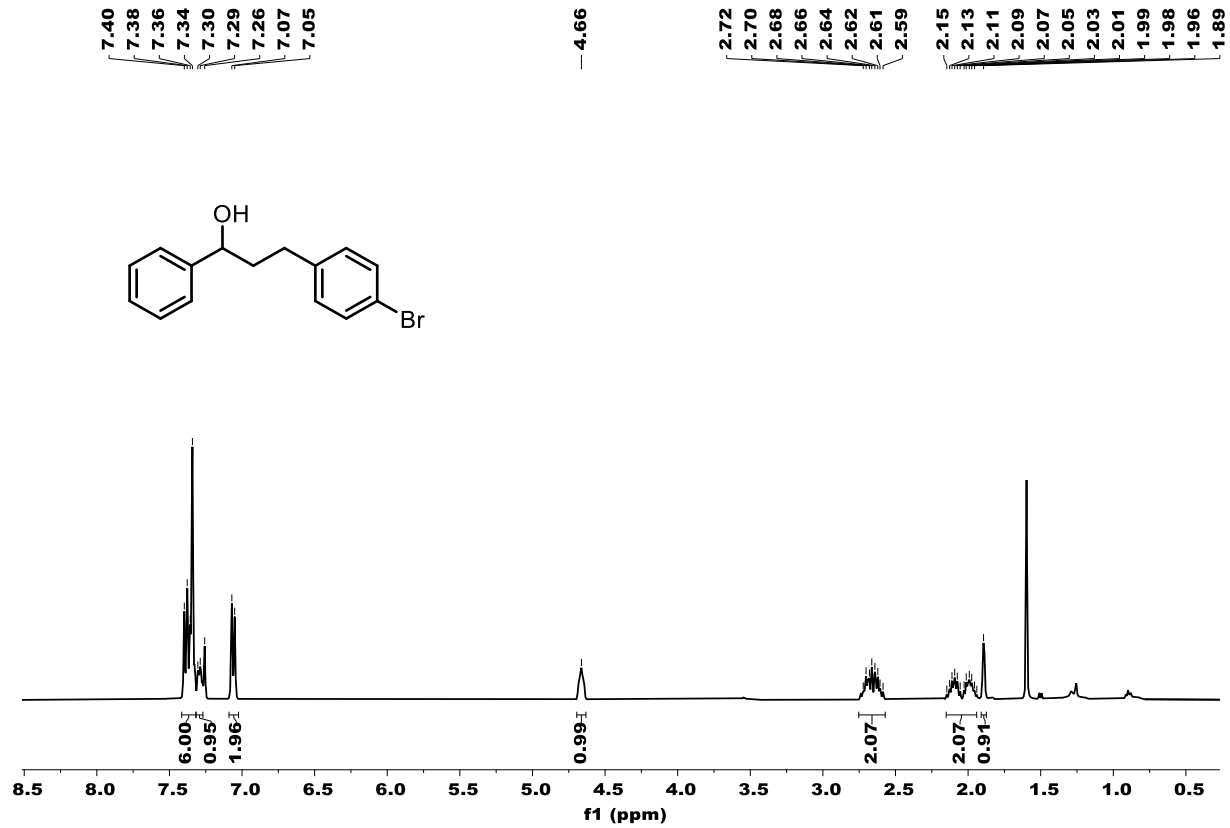




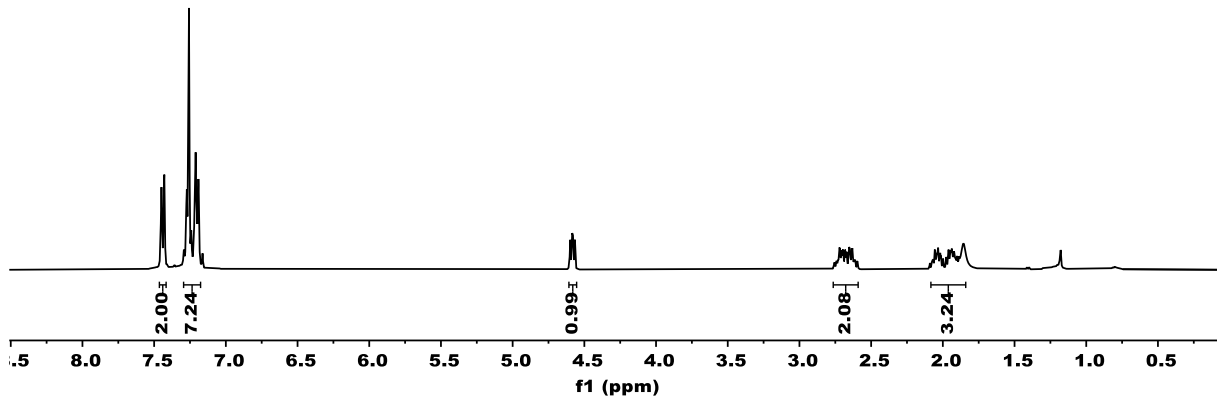
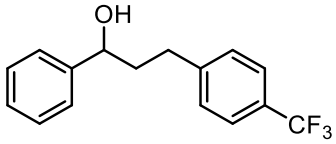




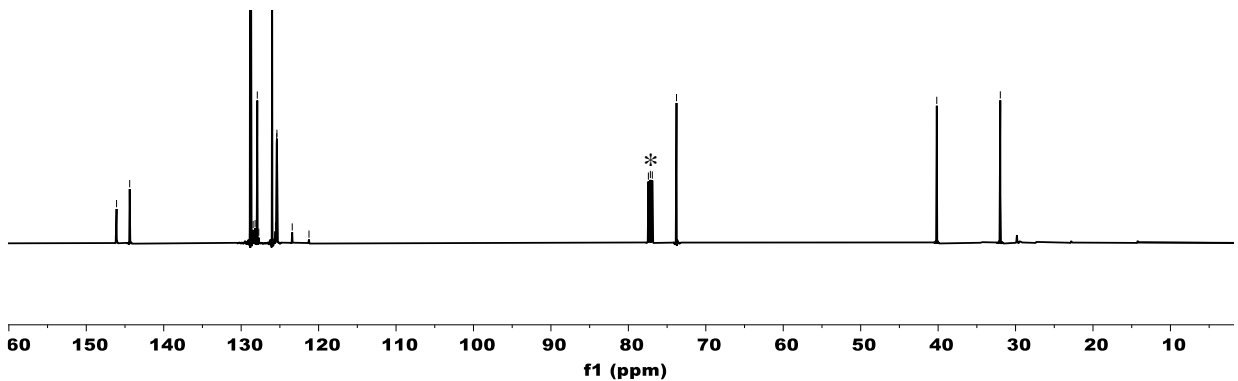
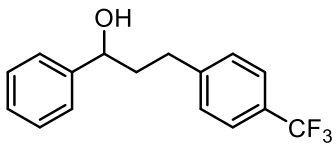


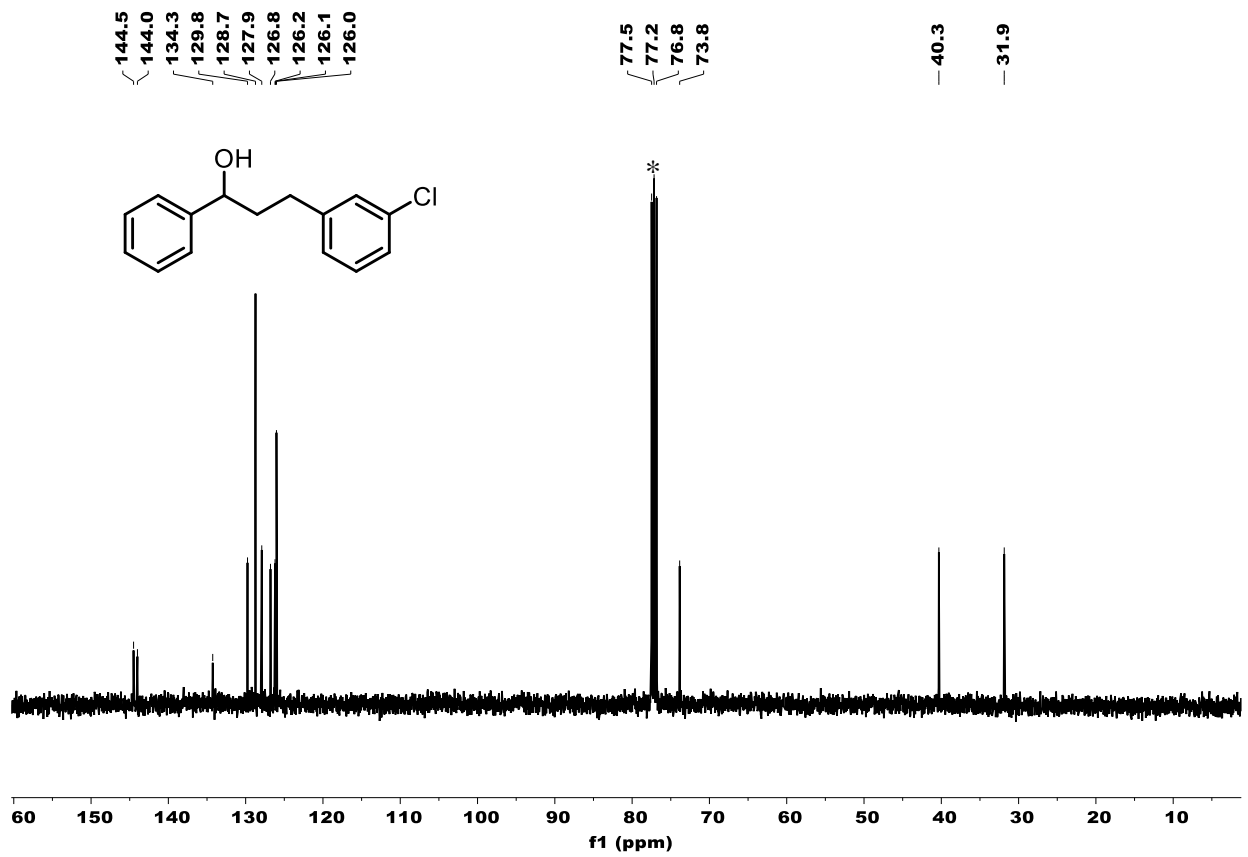
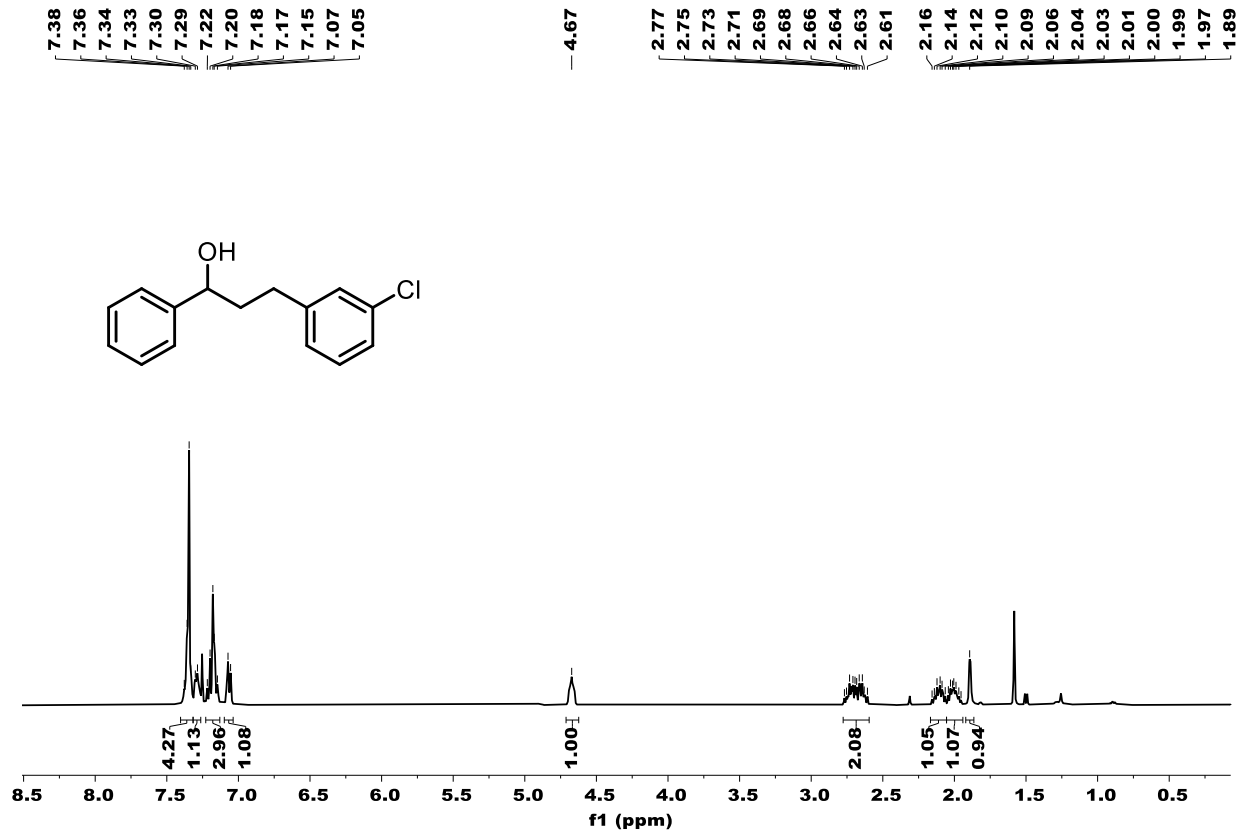


7.45 7.43 7.29 7.28 7.27 7.27 7.26 7.26 7.24 7.24 7.22 7.21 7.20 7.19 7.16 4.60 4.59 4.58 4.57 2.73 2.72 2.71 2.70 2.68 2.67 2.65 2.65 2.63 2.62 2.61 2.07 2.06 2.04 2.03 2.02 2.01 2.00 1.98 1.96 1.95 1.93 1.92 1.92 1.91 1.90 1.89 1.85



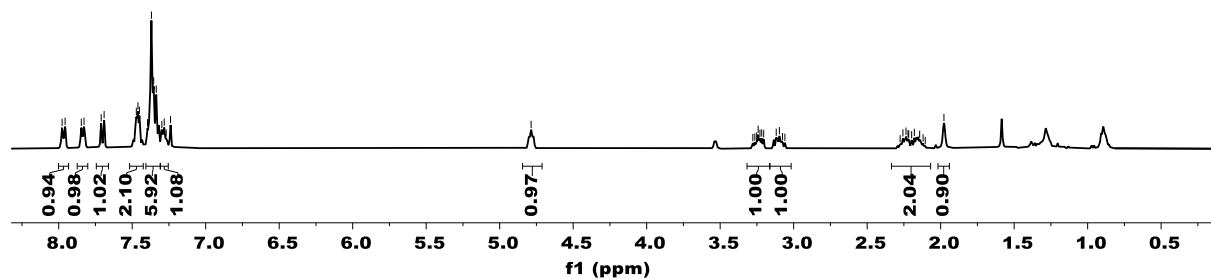
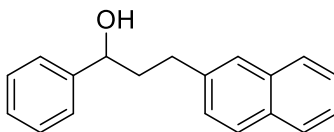
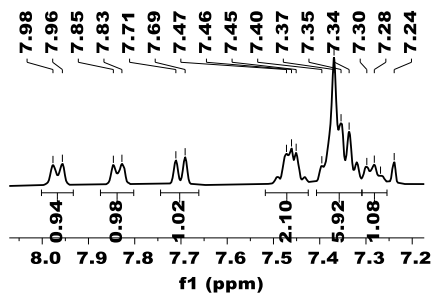
146.1 144.4 128.9 128.7 128.5 128.2 127.9 127.7 126.0 125.6 125.4 125.4 125.4 125.4 123.4 121.2 77.4 77.2 76.9 73.8 40.2 32.0





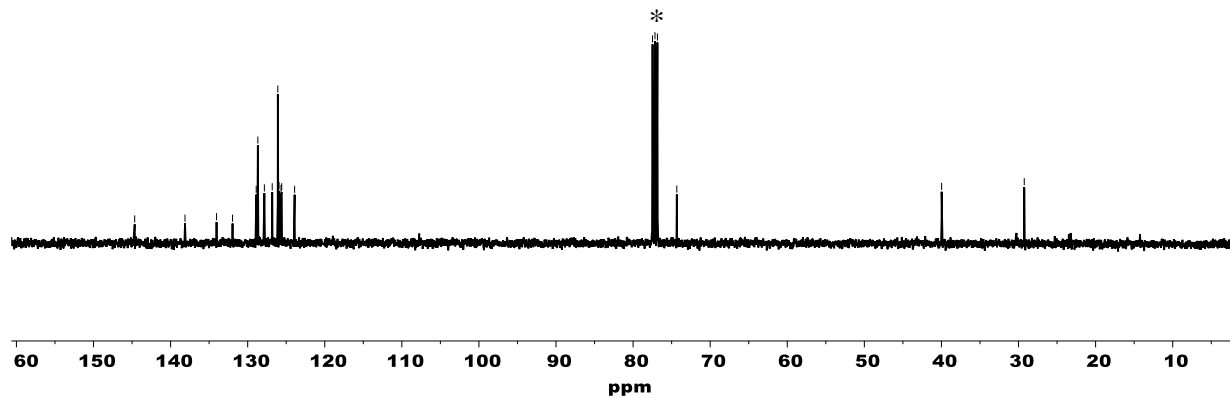
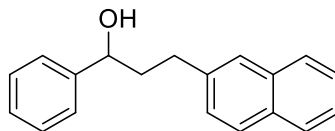
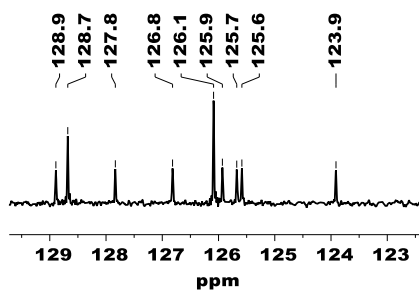
7.96  
7.85  
7.83  
7.71  
7.69  
7.47  
7.46  
7.45  
7.40  
7.37  
7.35  
7.34  
7.30  
7.28  
7.27  
7.24

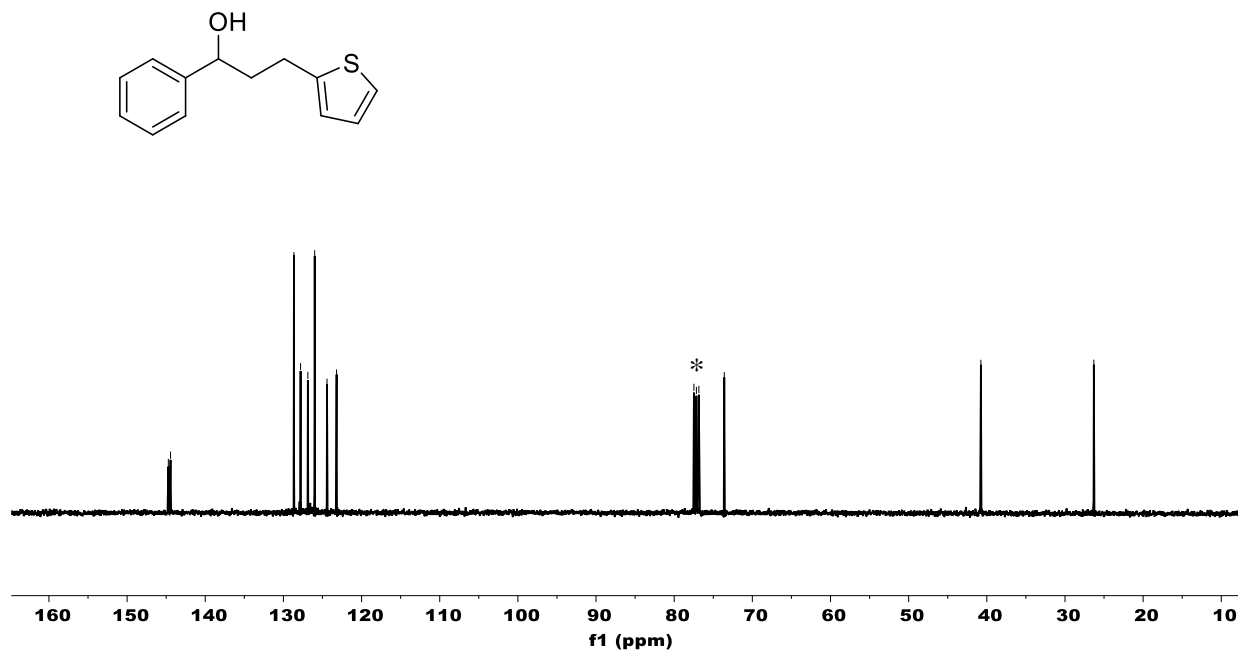
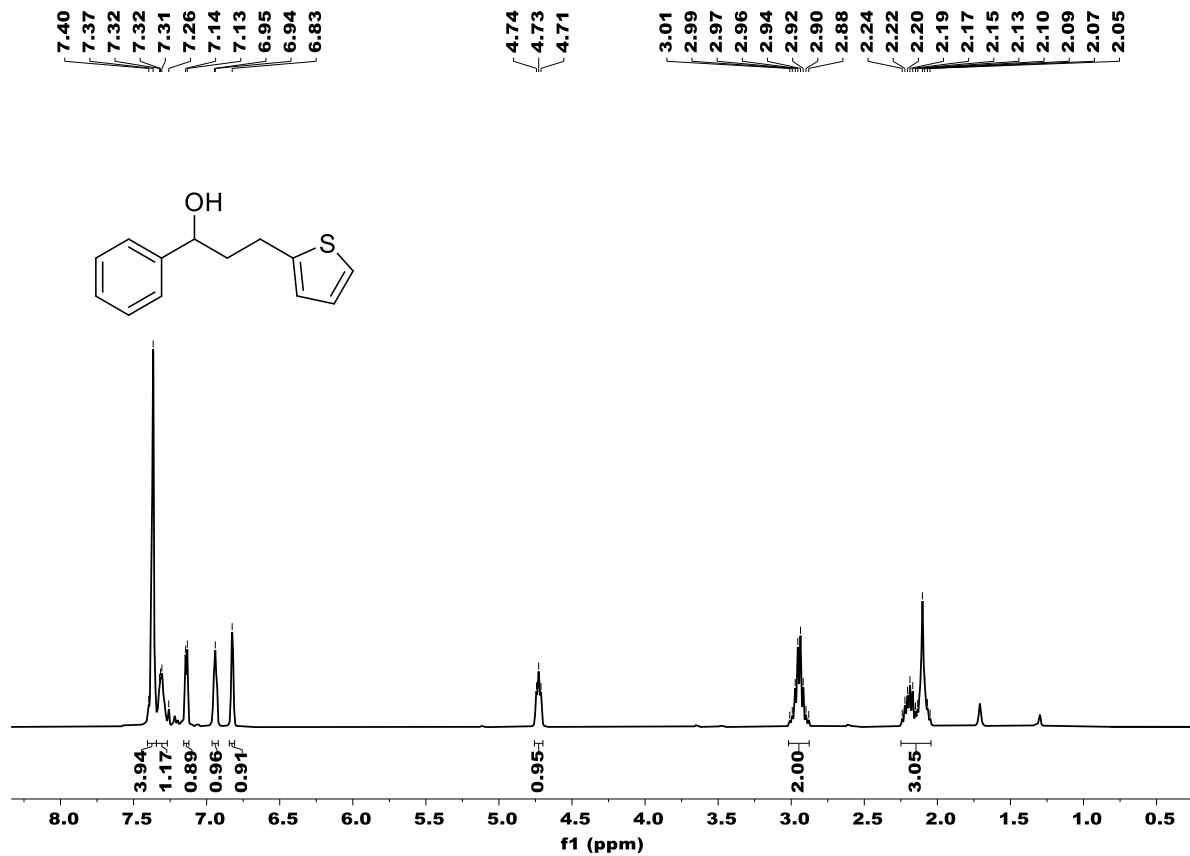
4.79  
3.28  
3.26  
3.25  
3.24  
3.23  
3.22  
3.20  
3.12  
3.10  
3.08  
3.06  
2.28  
2.26  
2.24  
2.22  
2.22  
2.20  
2.18  
2.14  
2.12  
2.10  
1.98

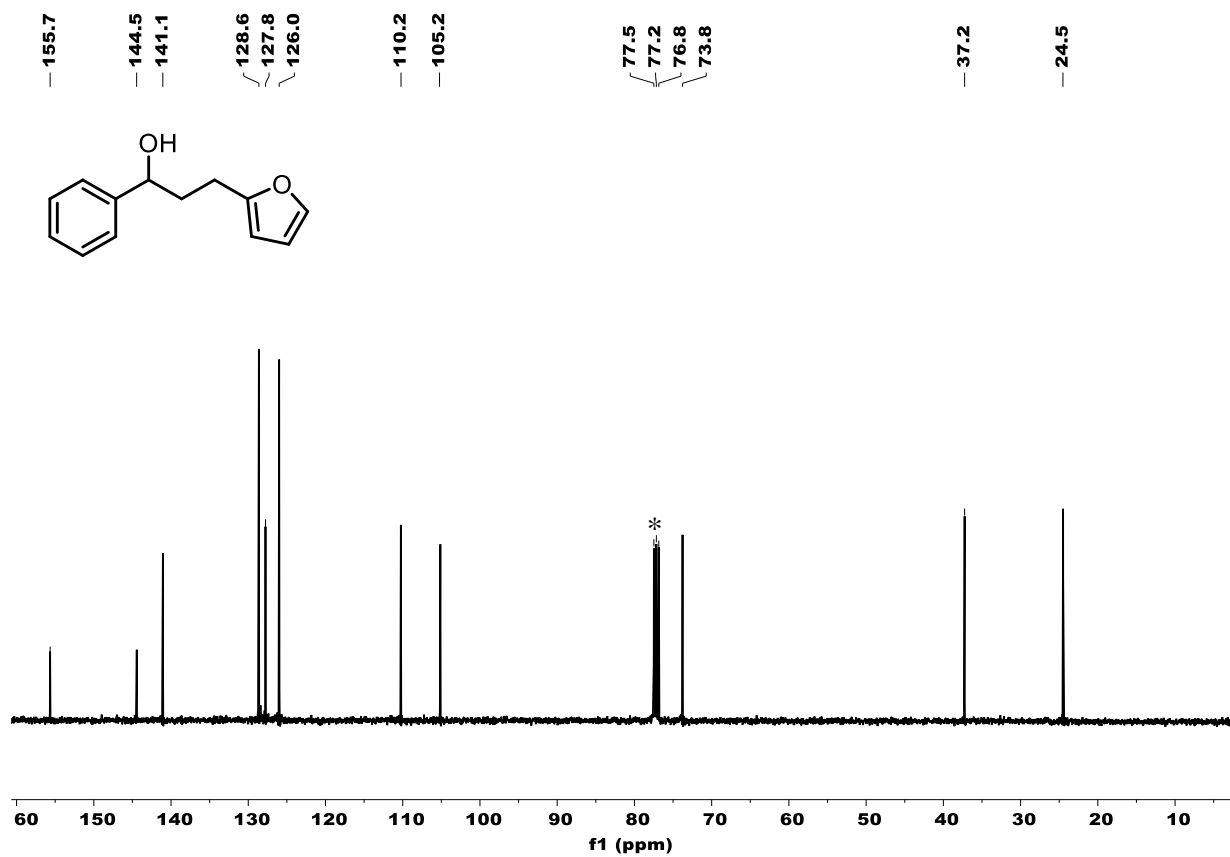
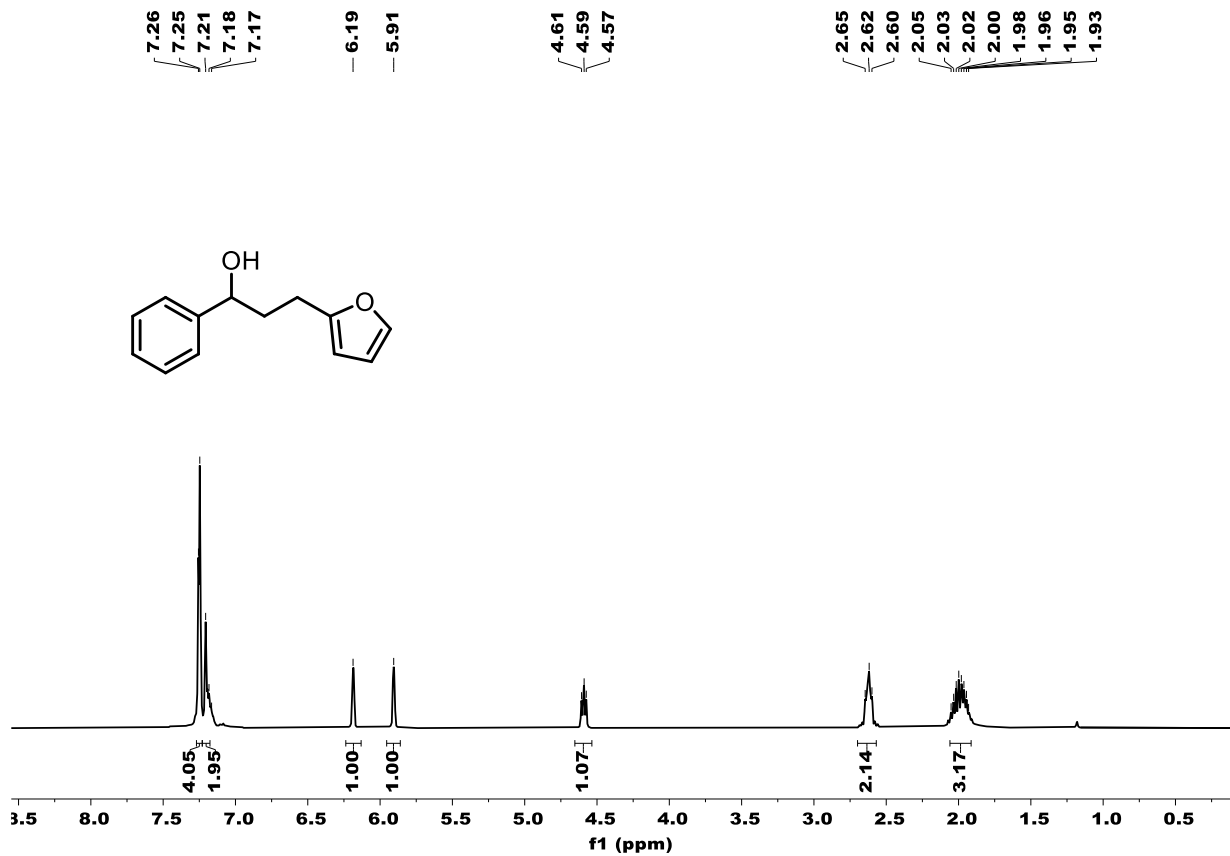


144.7  
138.1  
134.0  
132.0  
128.9  
128.7  
127.8  
126.8  
126.1  
125.9  
125.7  
125.6  
123.9

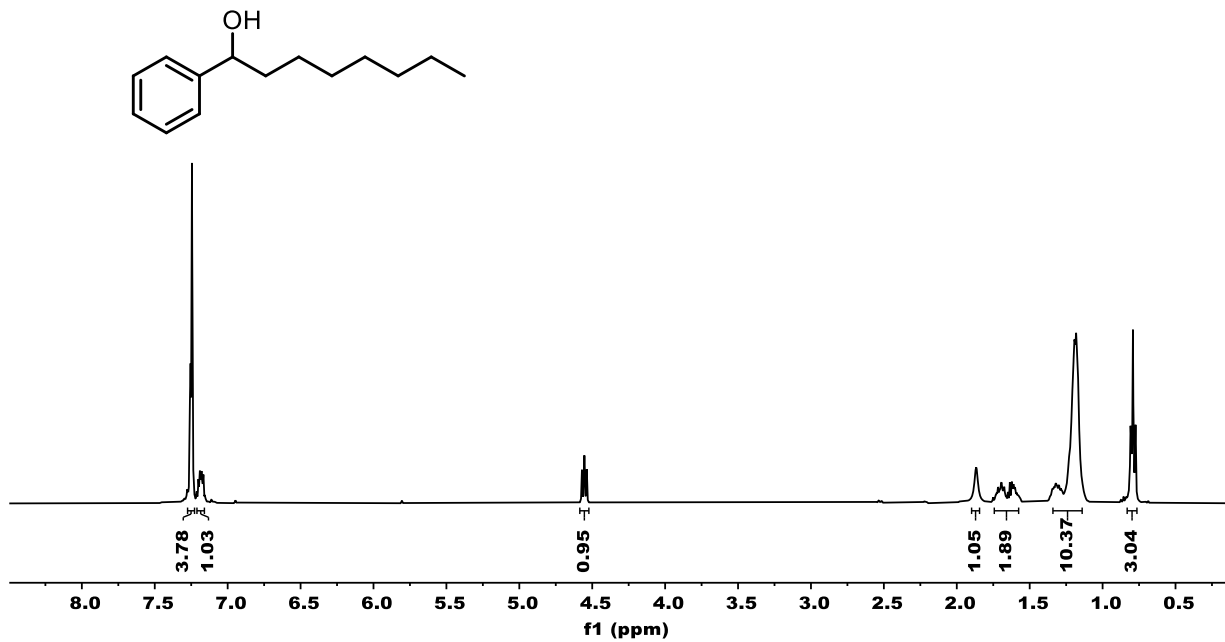
77.5  
77.2  
76.8  
74.3  
40.0  
29.3



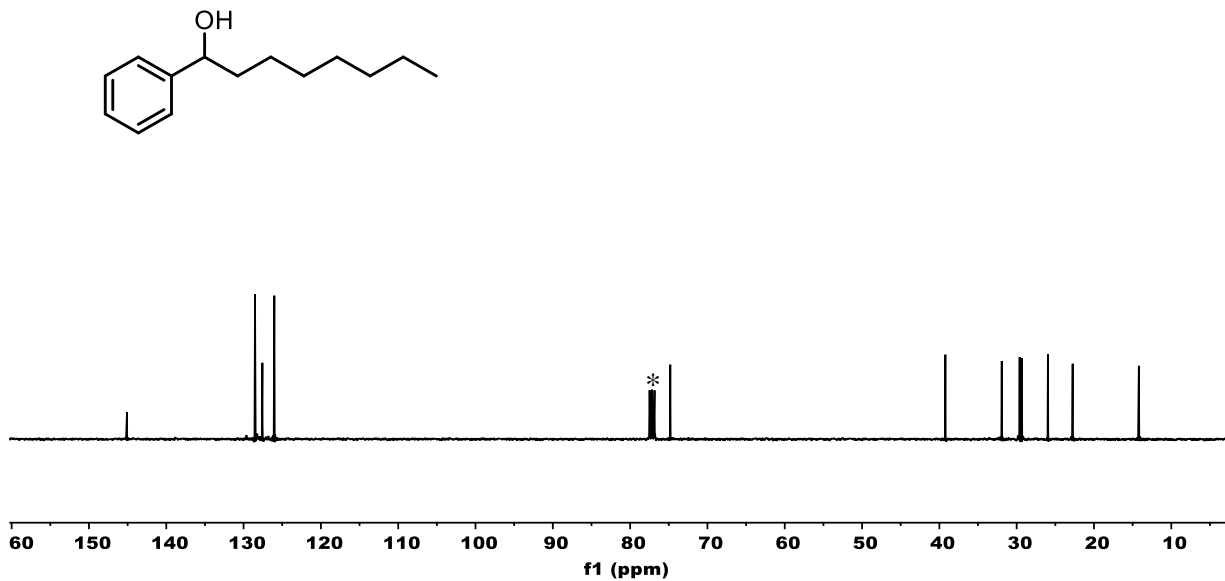




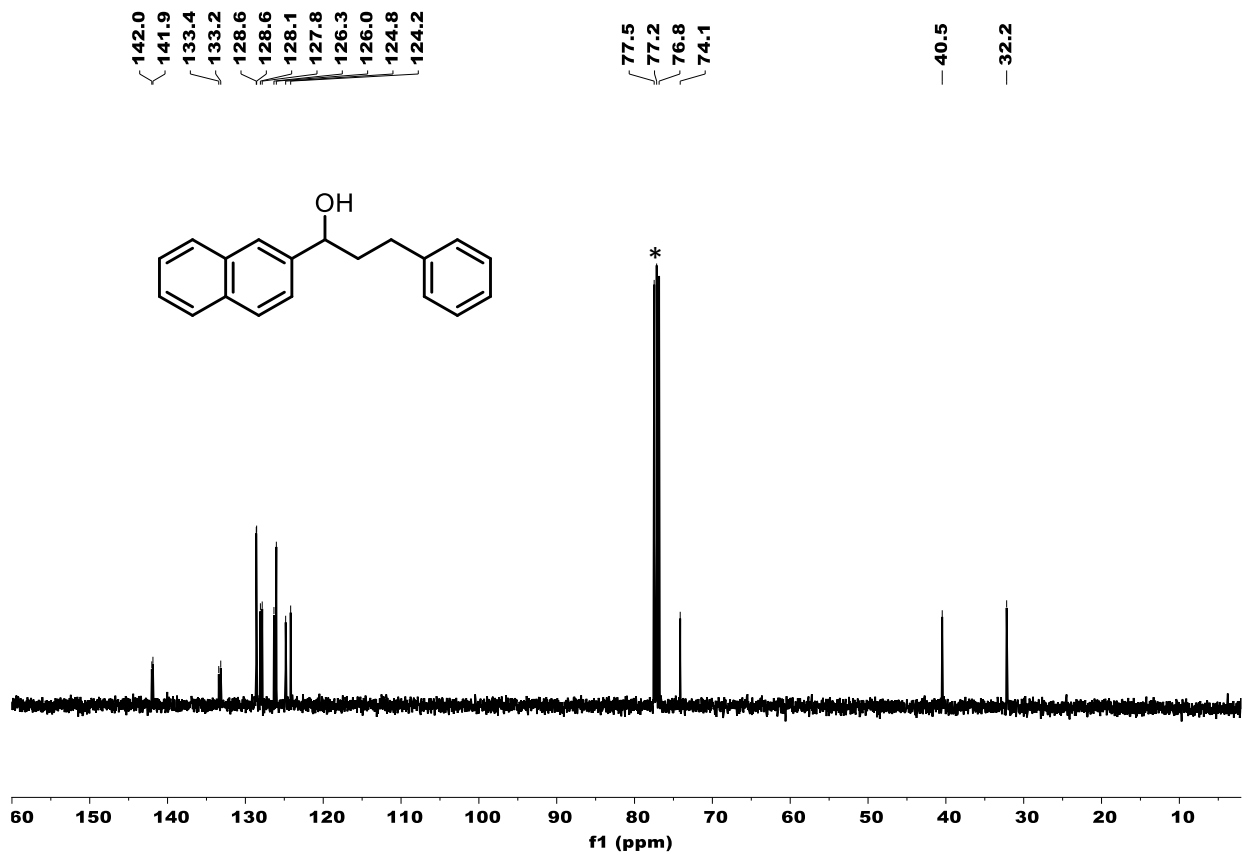
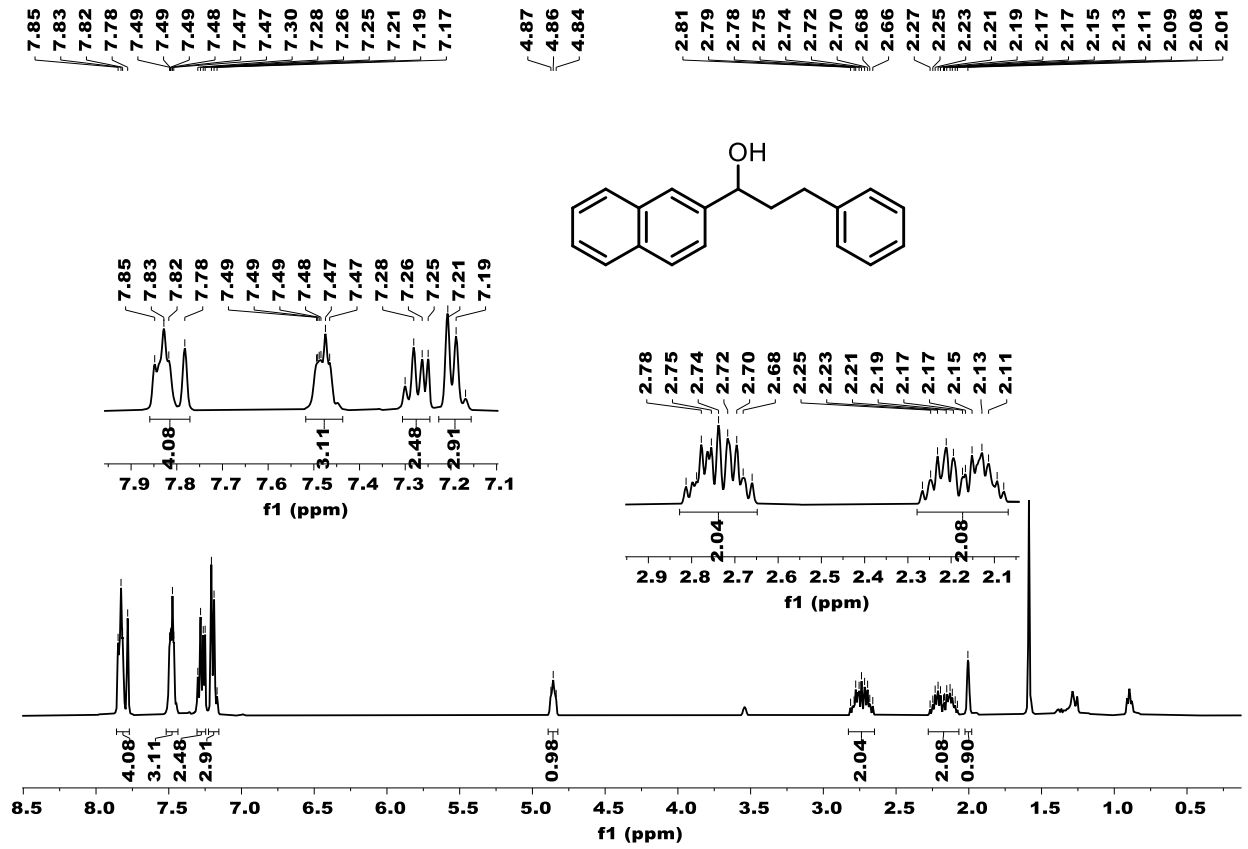
7.27  
7.26  
7.25  
7.24  
7.23  
7.21  
7.20  
7.19  
7.18  
7.18  
7.17  
7.17  
4.57  
4.56  
4.54  
1.87  
1.72  
1.71  
1.70  
1.69  
1.69  
1.67  
1.65  
1.64  
1.62  
1.62  
1.60  
1.35  
1.33  
1.32  
1.31  
1.30  
1.29  
1.24  
1.23  
1.22  
1.20  
1.18  
1.17  
1.17  
1.15  
1.13  
0.82  
0.81  
0.79  
0.77

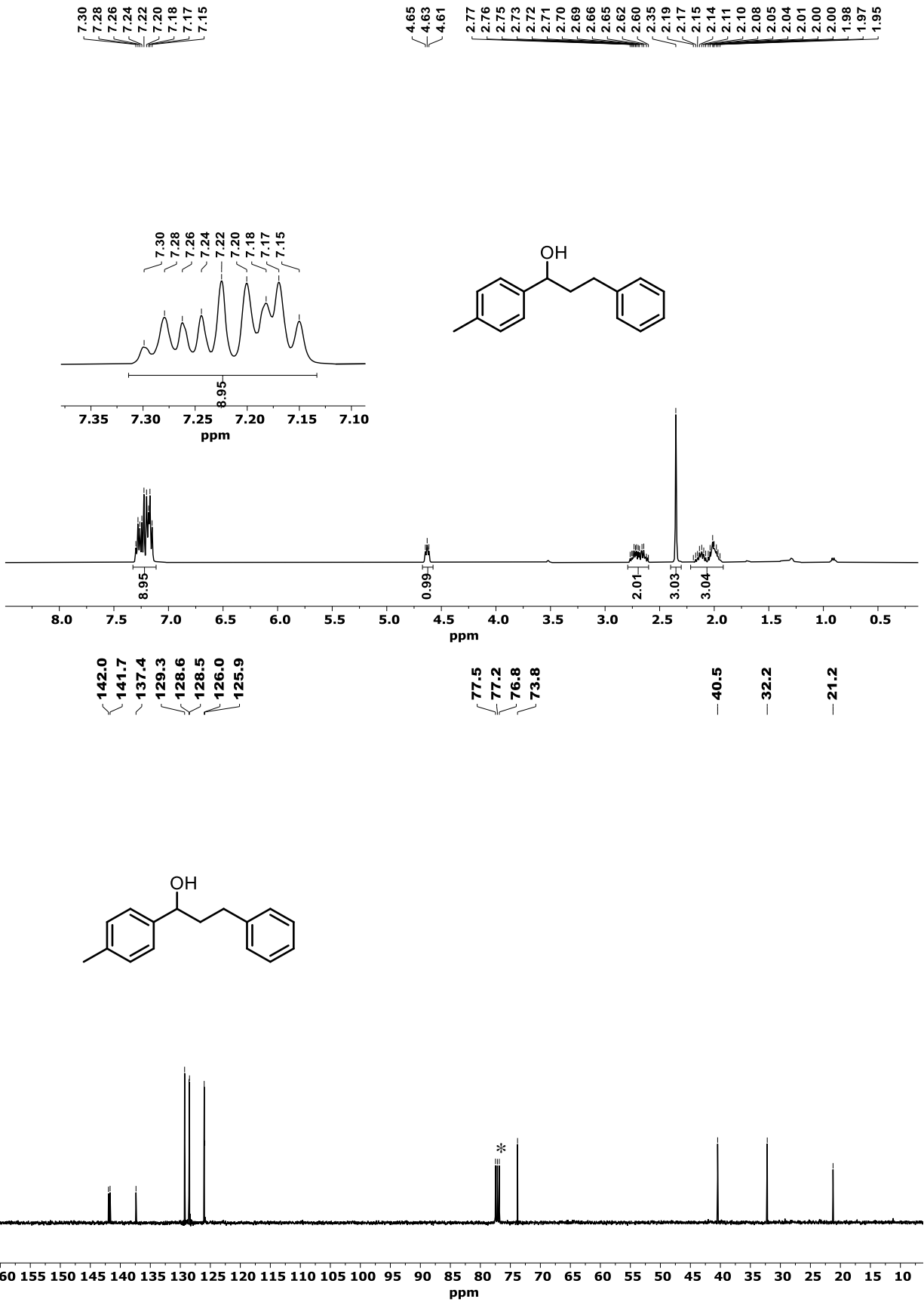


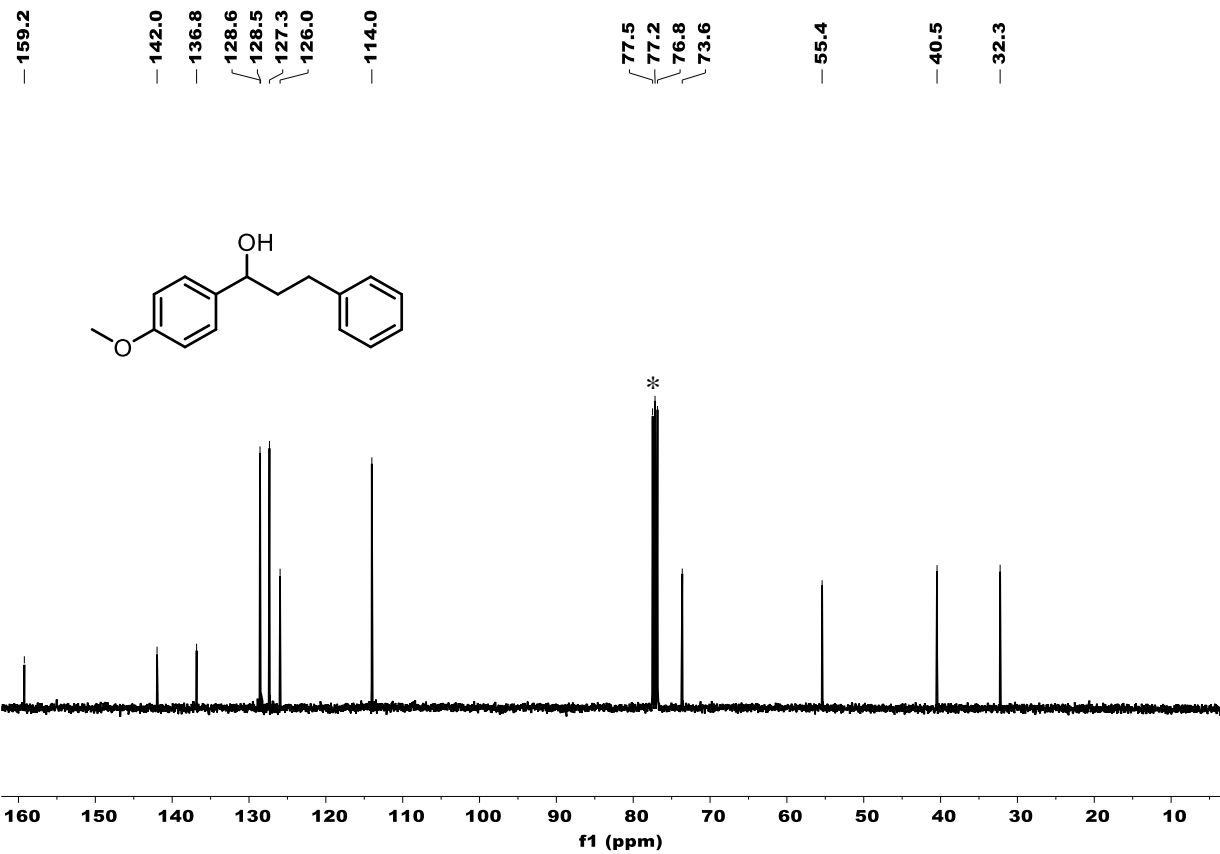
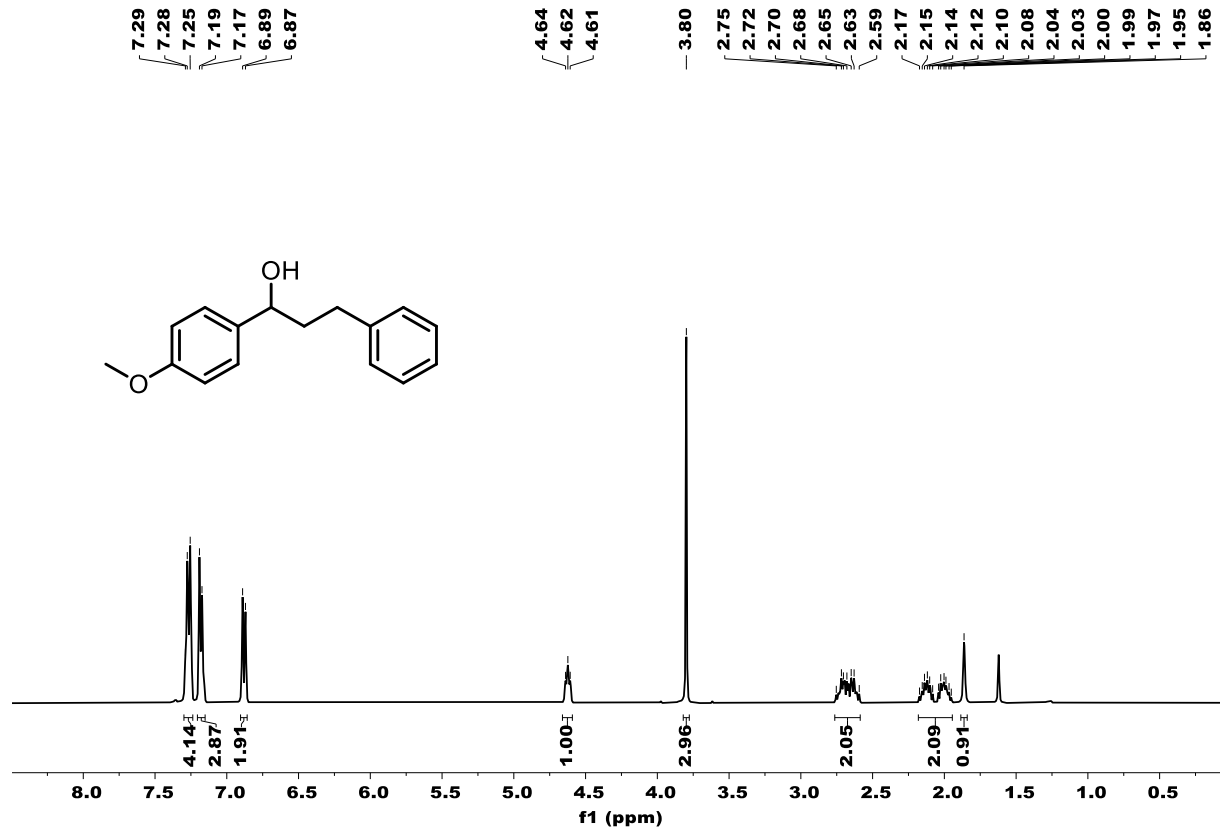
145.1  
128.5  
127.6  
126.0  
77.5  
77.2  
76.8  
74.8  
39.2  
31.9  
29.6  
29.3  
26.0  
22.8  
14.2

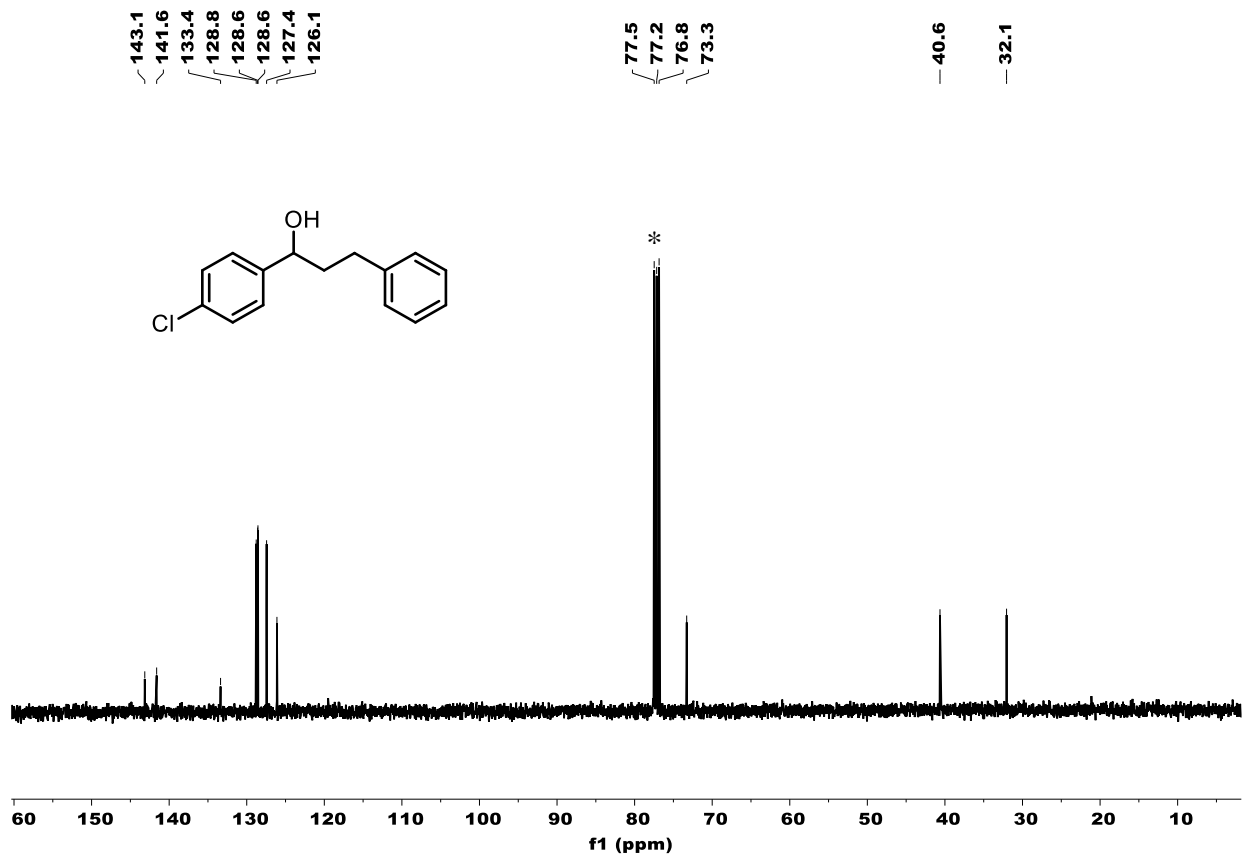
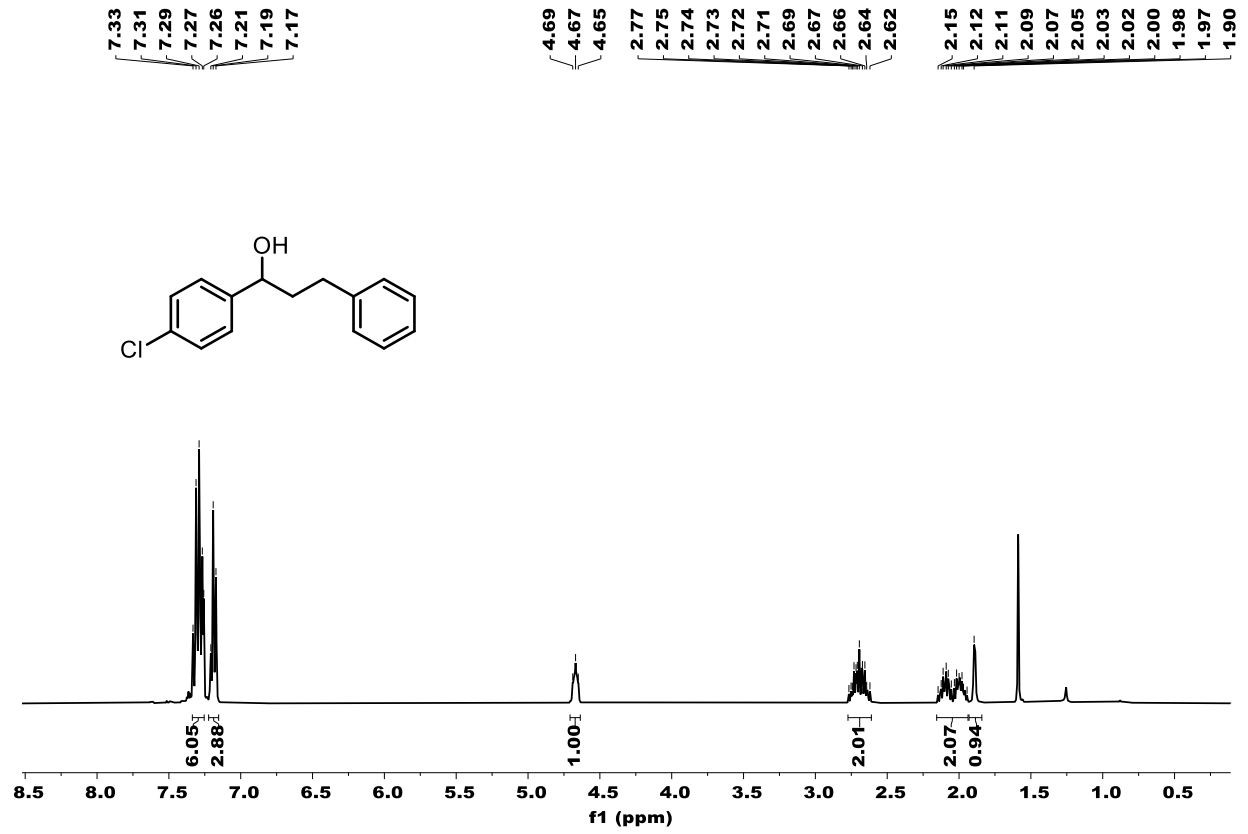


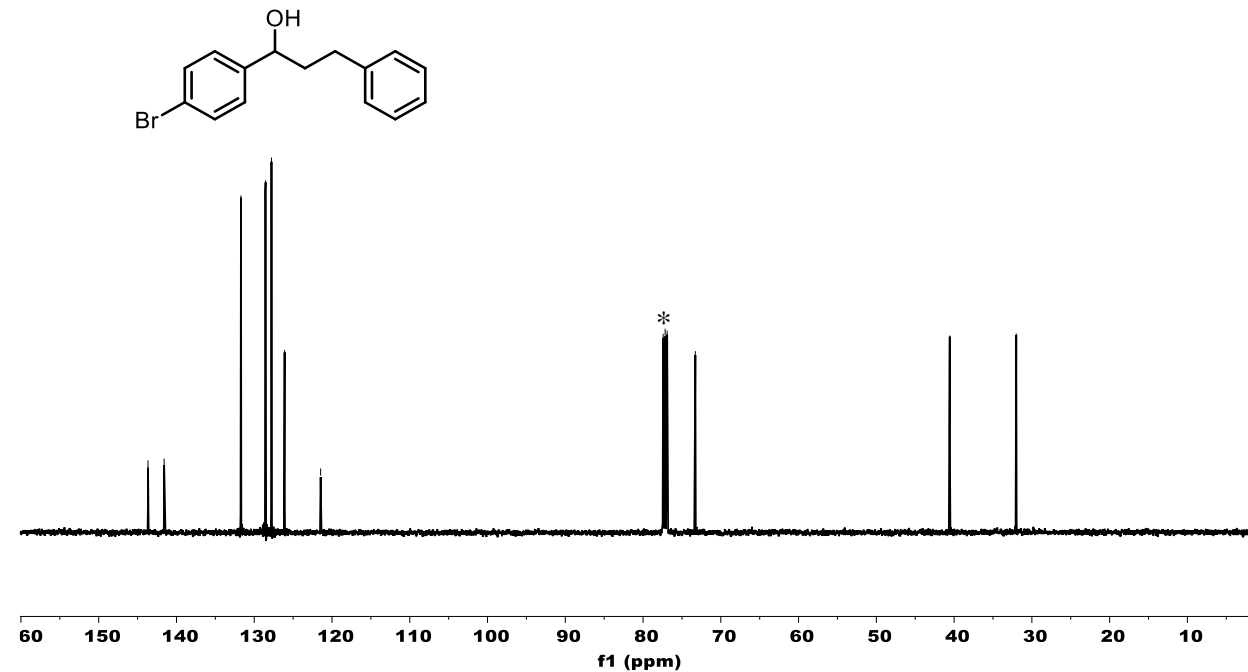
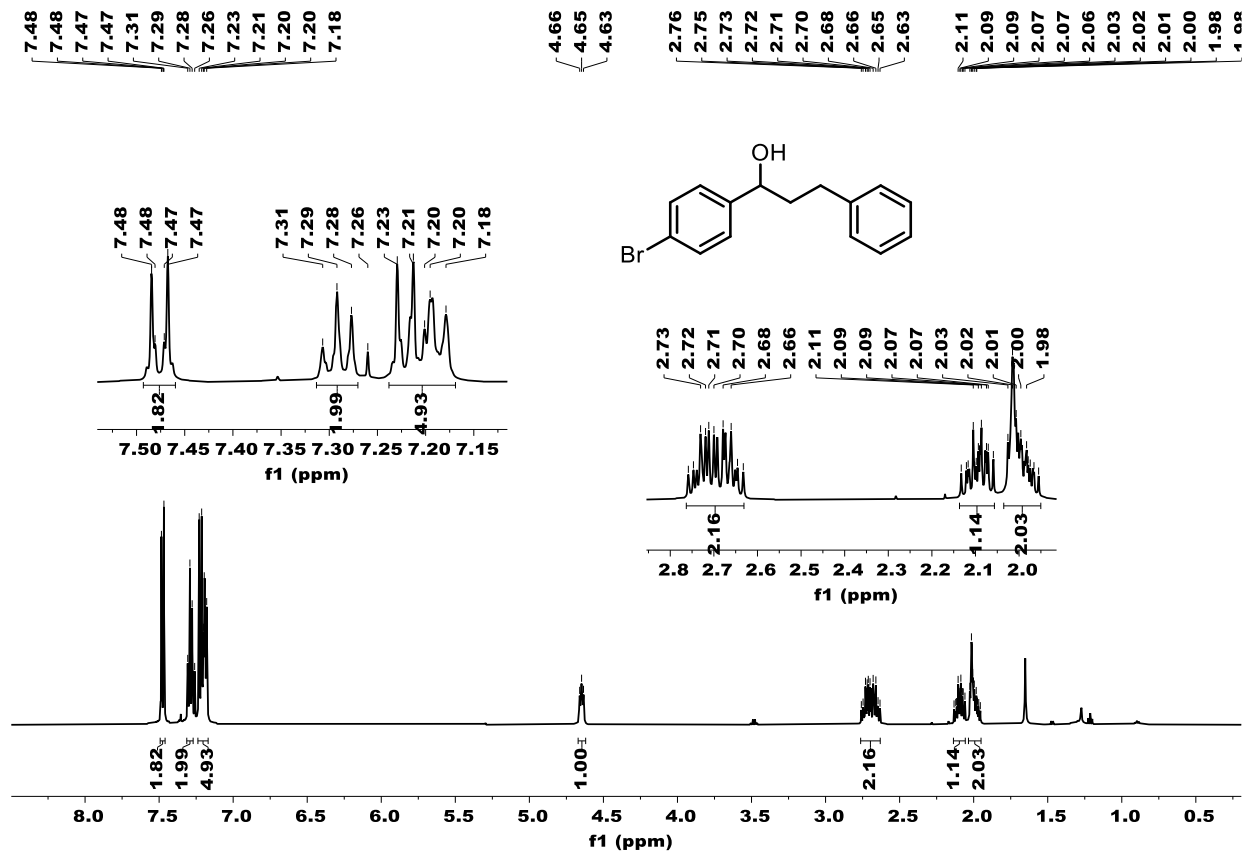


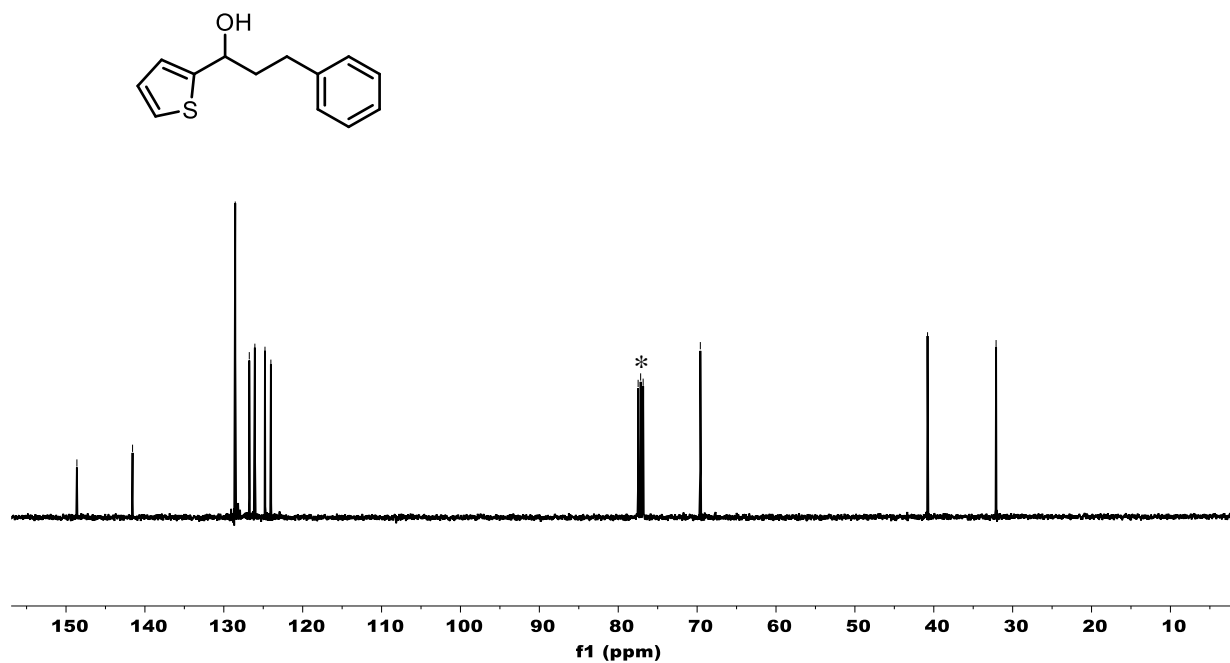
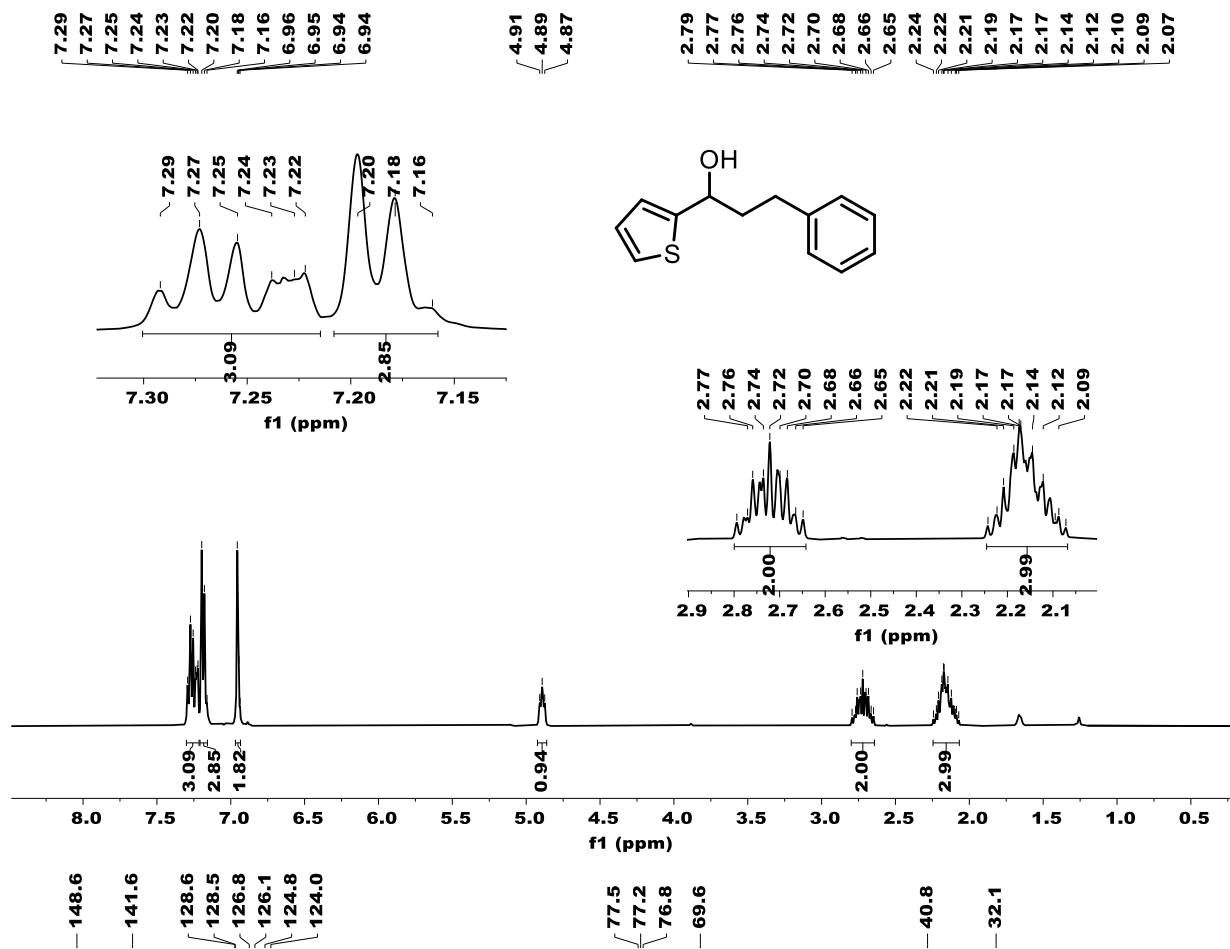


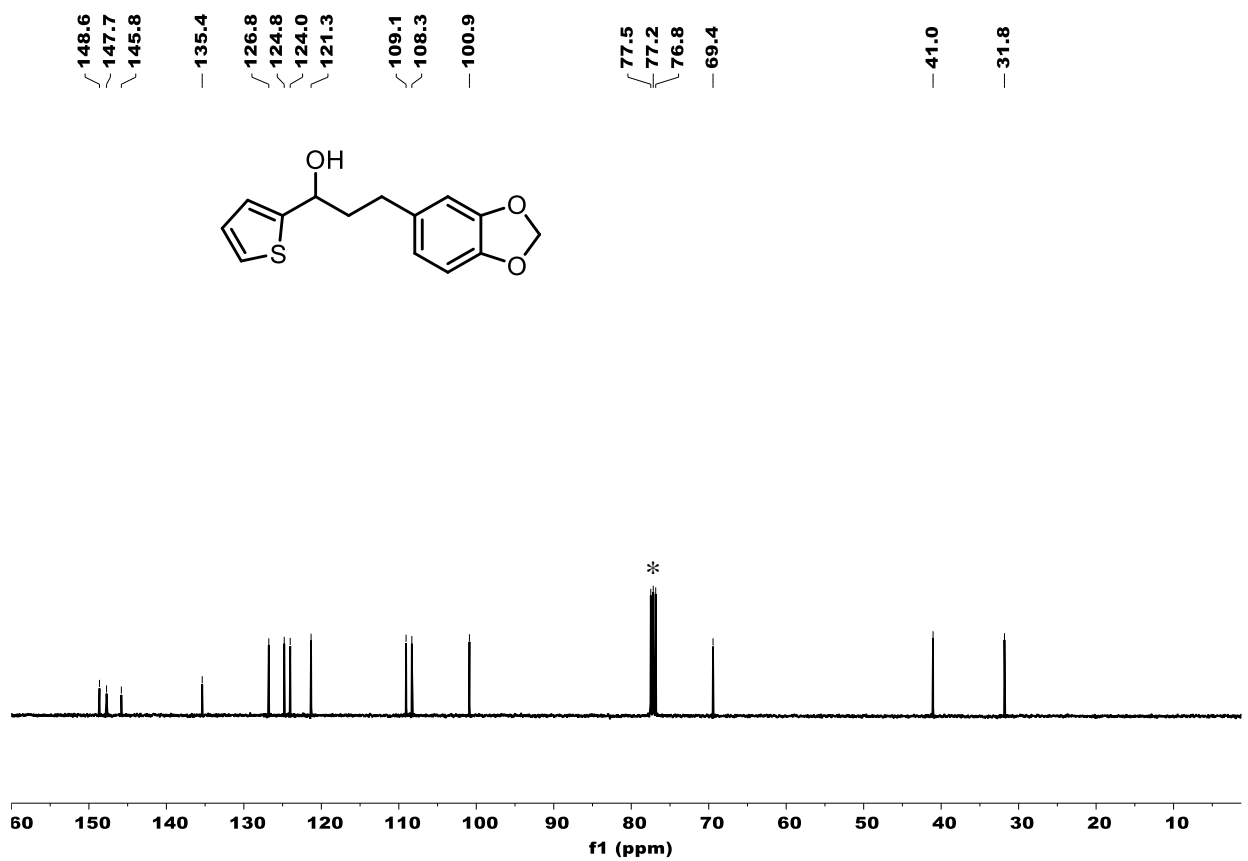
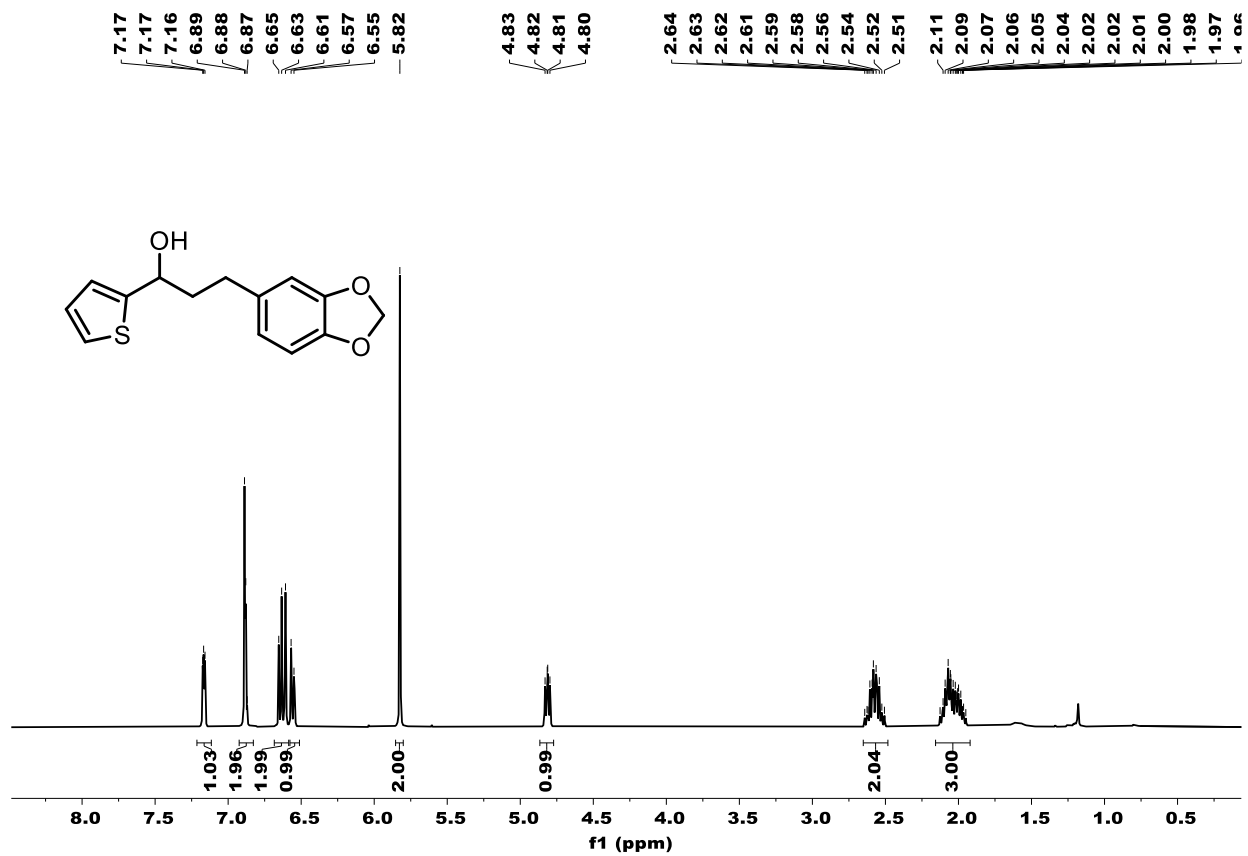


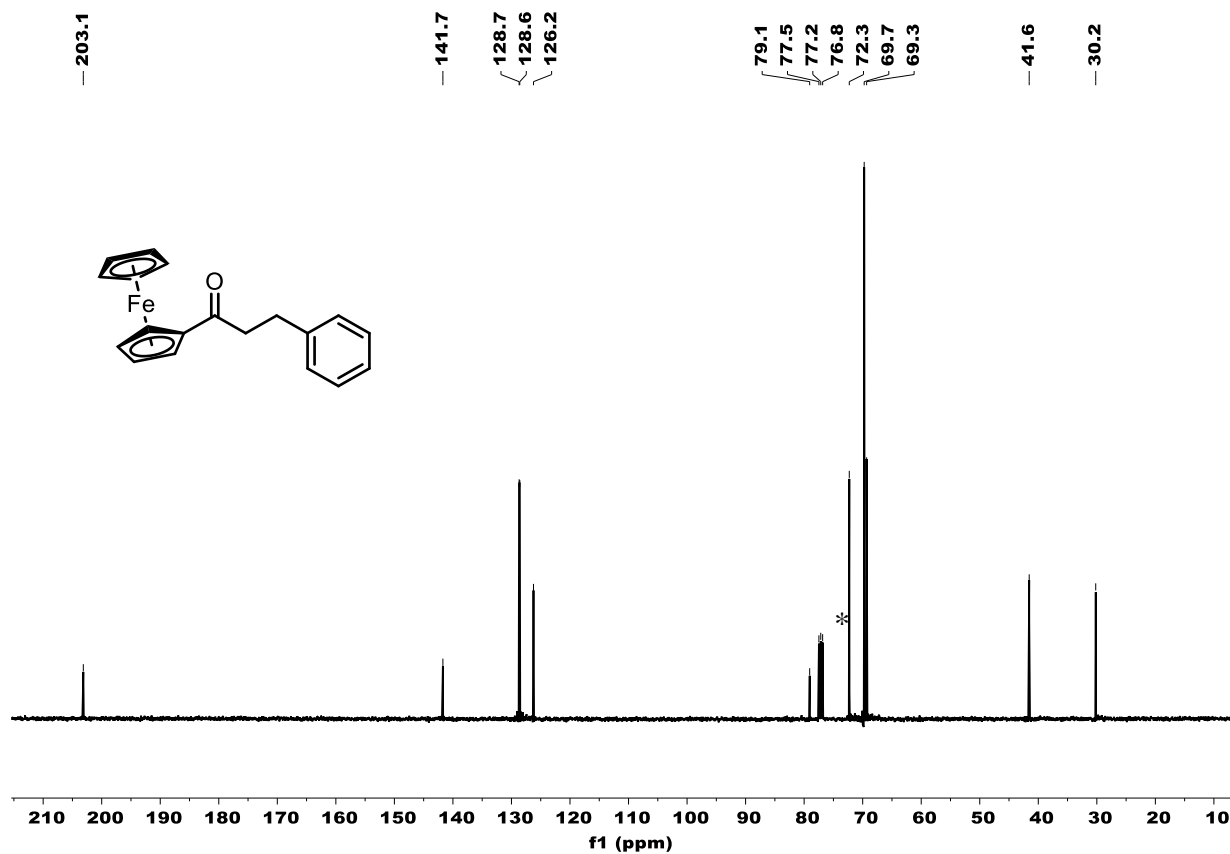
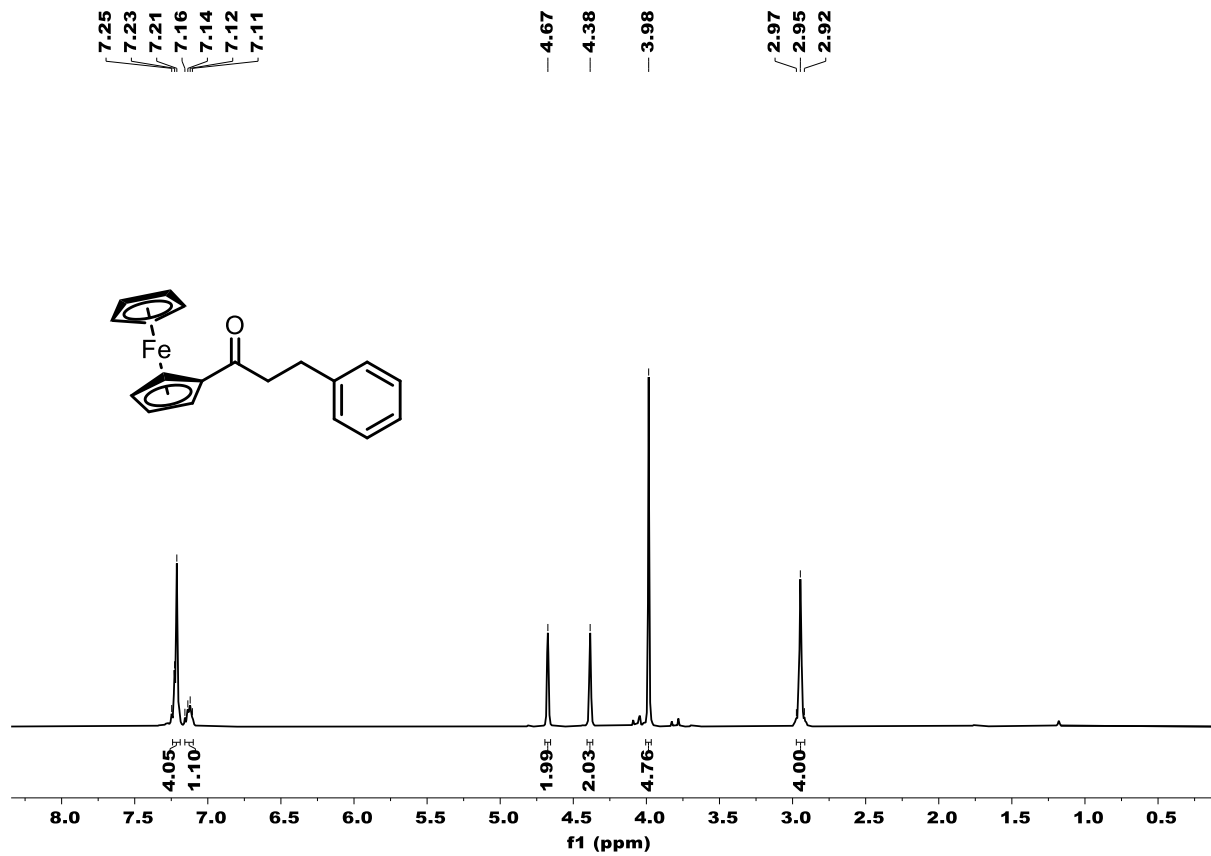






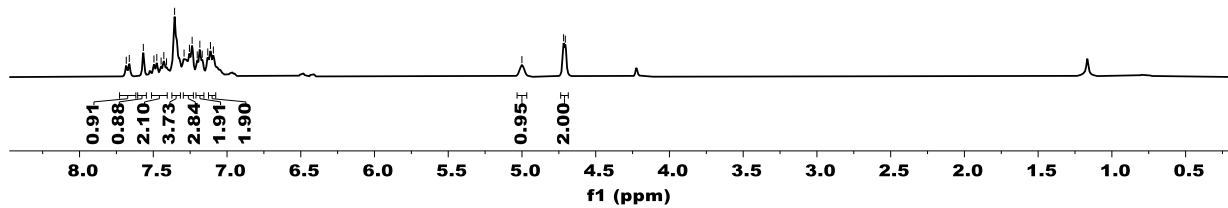
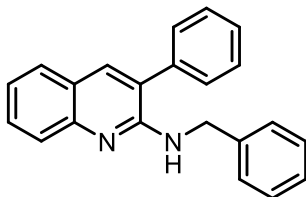




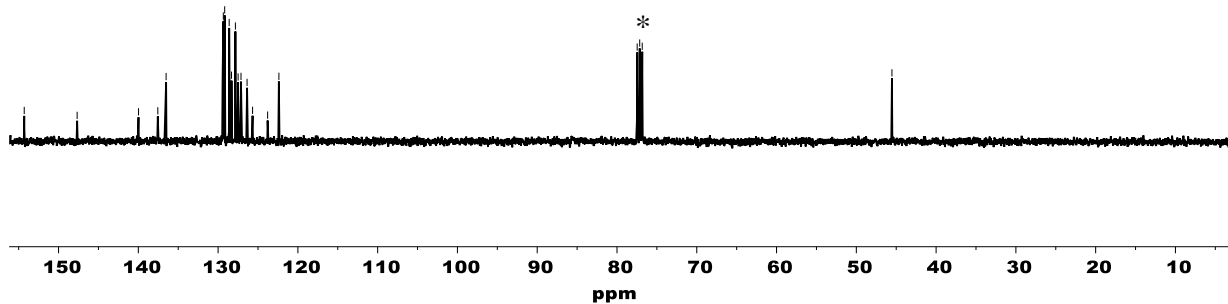
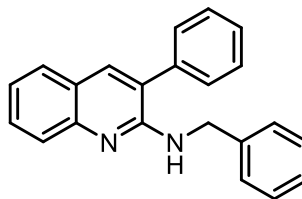
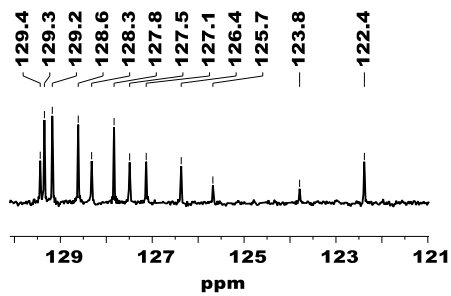




7.68  
7.66  
7.57  
7.50  
7.48  
7.45  
7.43  
7.41  
7.36  
7.29  
7.25  
7.24  
7.20  
7.18  
7.17  
7.13  
7.11  
7.09  
5.00  
4.72  
4.71



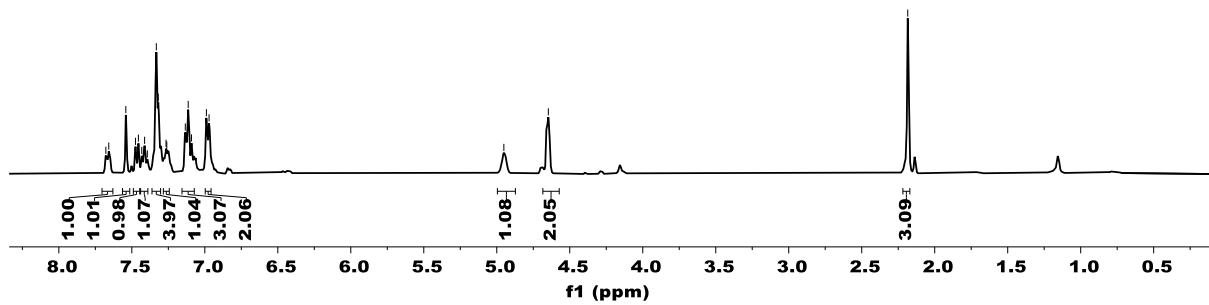
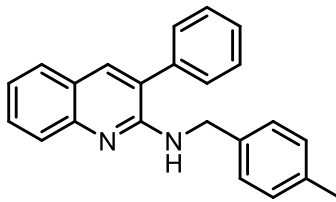
154.3  
147.7  
140.0  
137.6  
136.5  
129.4  
129.3  
129.2  
128.6  
128.3  
127.8  
127.5  
127.1  
126.4  
125.7  
123.8  
122.4  
77.5  
77.2  
76.8  
45.5



7.66  
7.54  
7.47  
7.46  
7.43  
7.41  
7.39  
7.33  
7.32  
7.27  
7.26  
7.13  
7.11  
7.09  
6.99  
6.97

— 4.95  
— 4.65

— 2.18

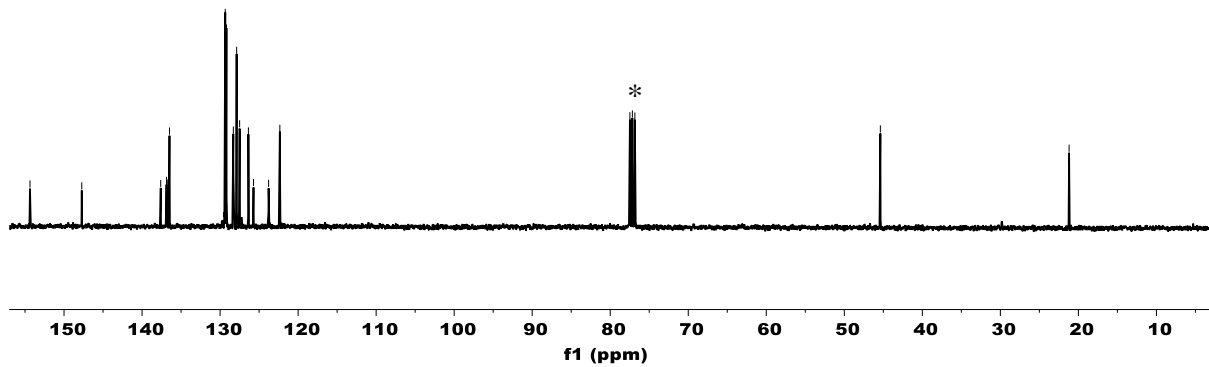
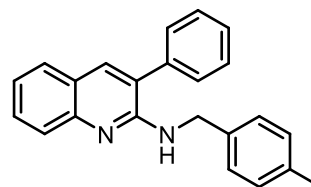
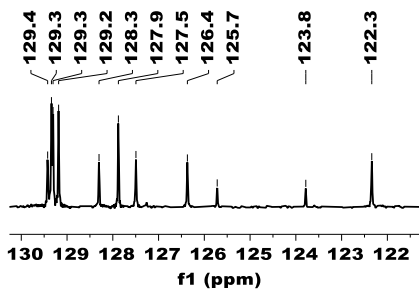


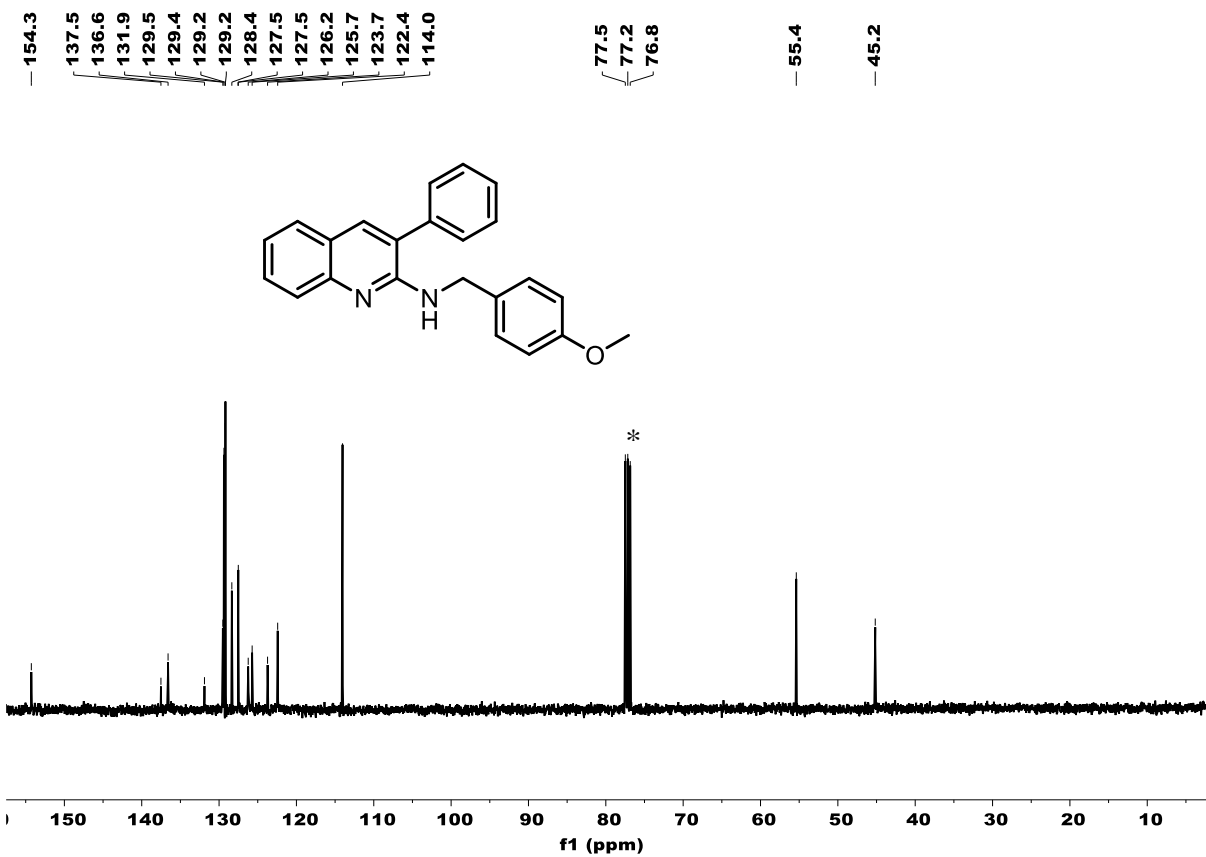
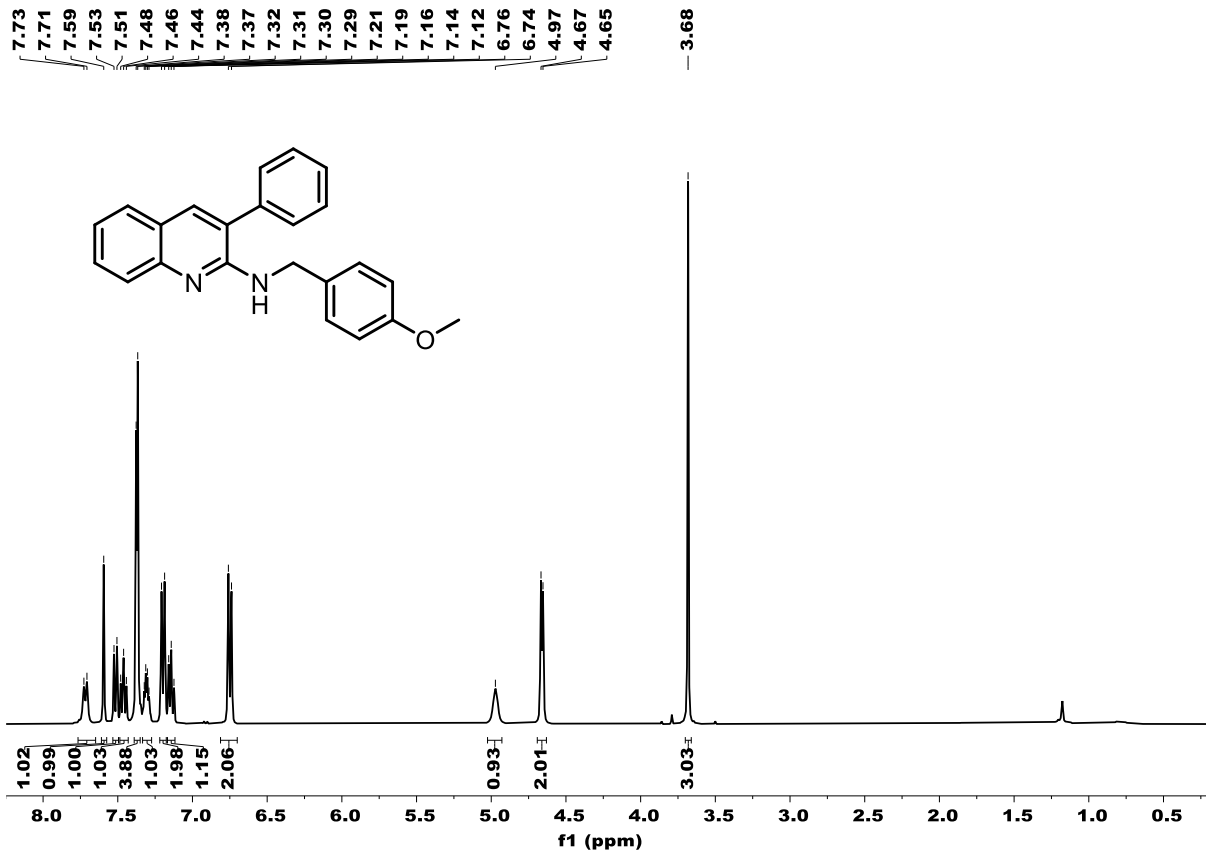
154.4  
147.7  
137.6  
136.9  
136.8  
136.5  
129.4  
129.3  
129.3  
129.2  
128.3  
127.9  
127.5  
126.4  
125.7  
123.8  
122.3

77.5  
77.2  
76.8

45.4

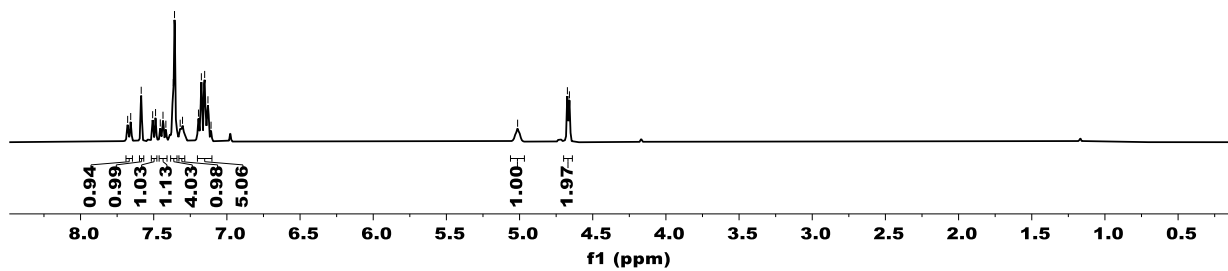
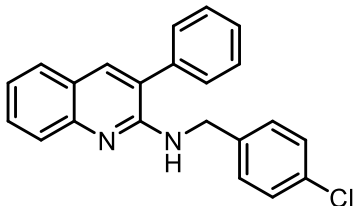
21.2





7.68  
7.66  
7.59  
7.51  
7.49  
7.46  
7.44  
7.42  
7.37  
7.36  
7.32  
7.30  
7.19  
7.17  
7.15  
7.13  
7.11

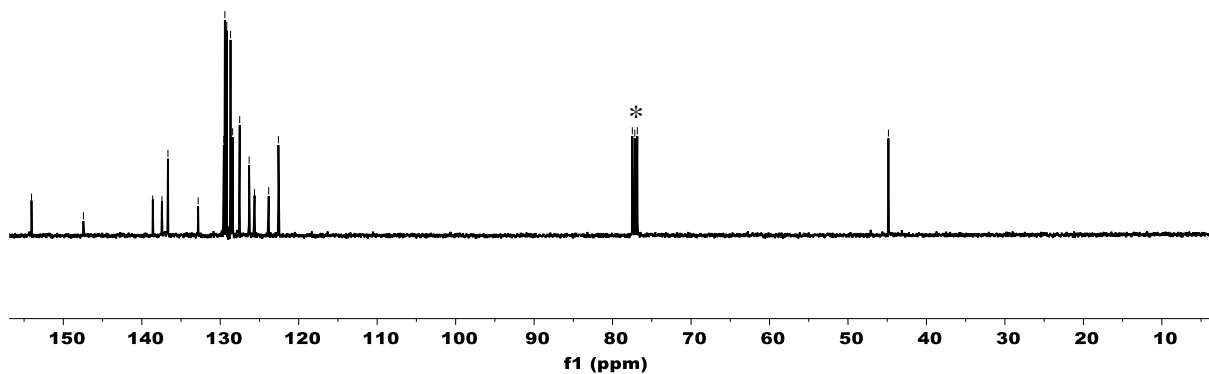
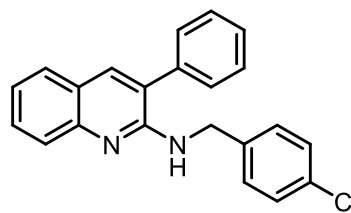
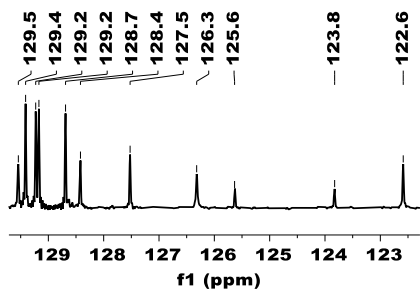
5.01  
4.67  
4.66

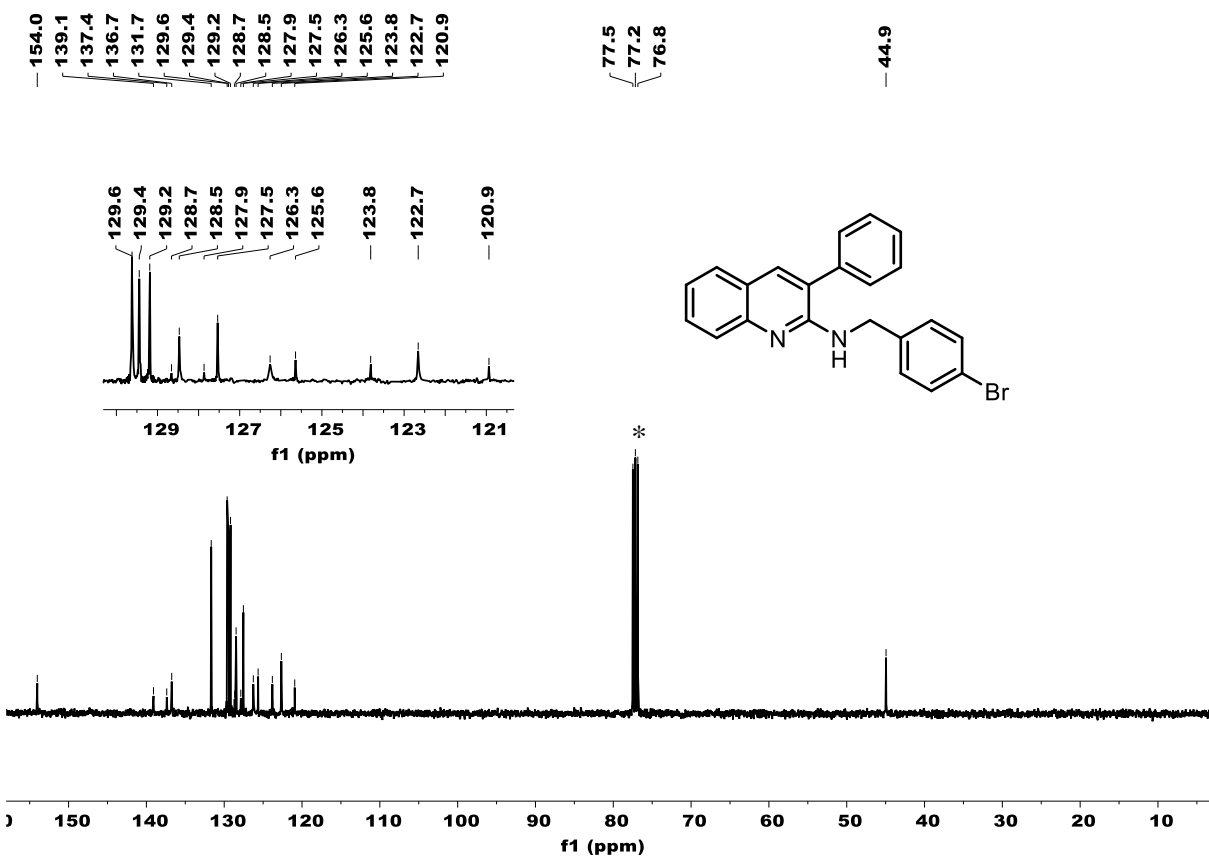
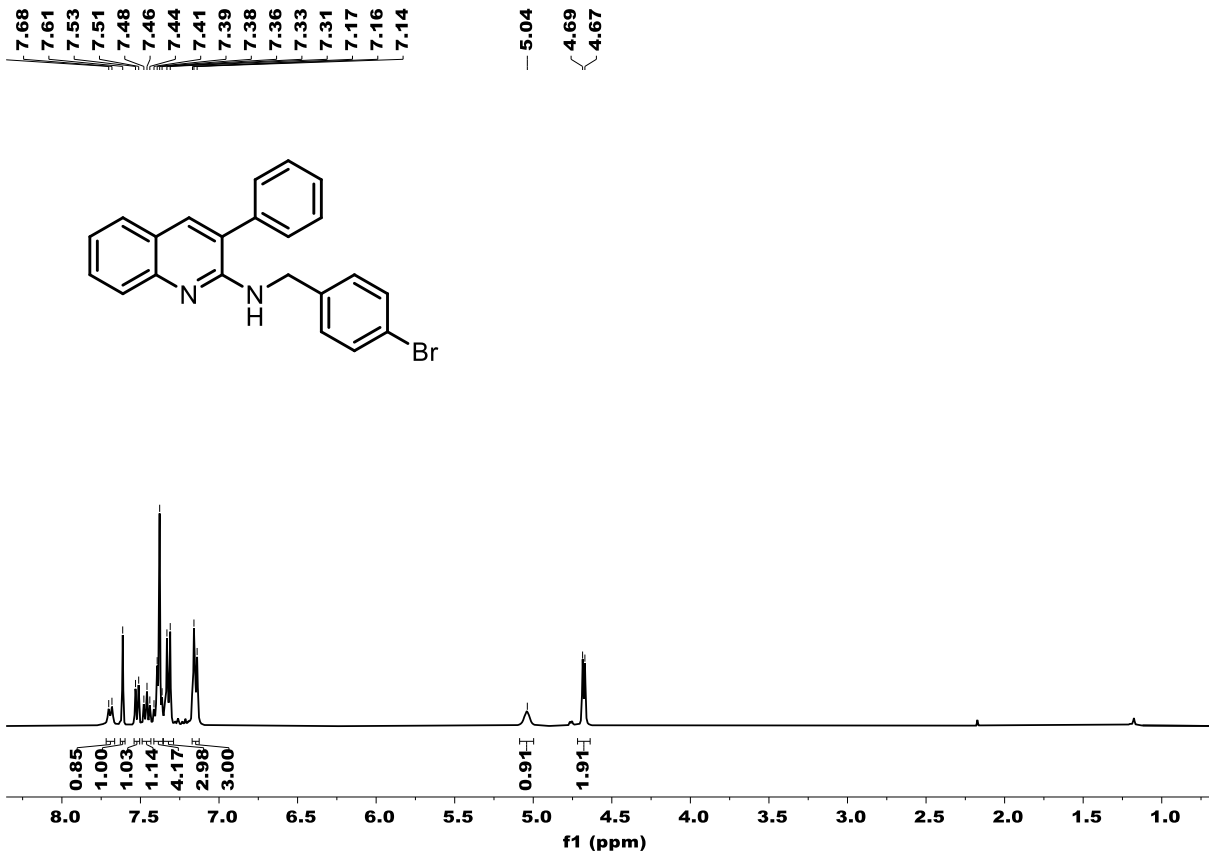


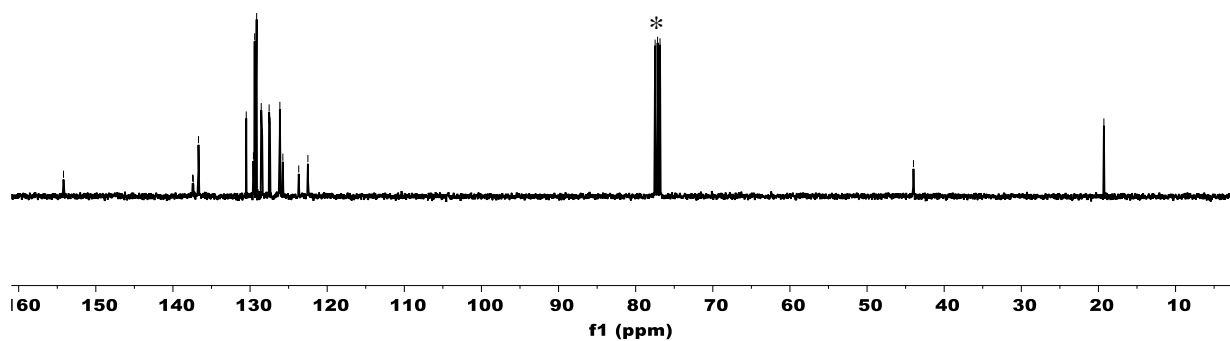
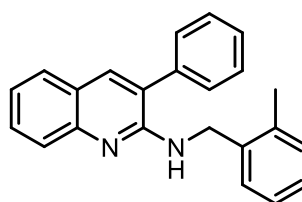
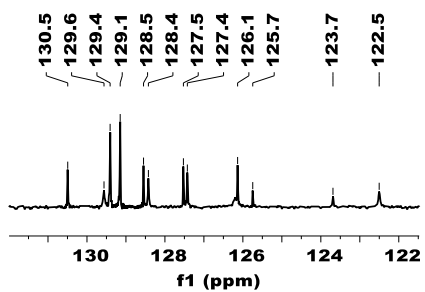
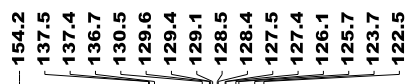
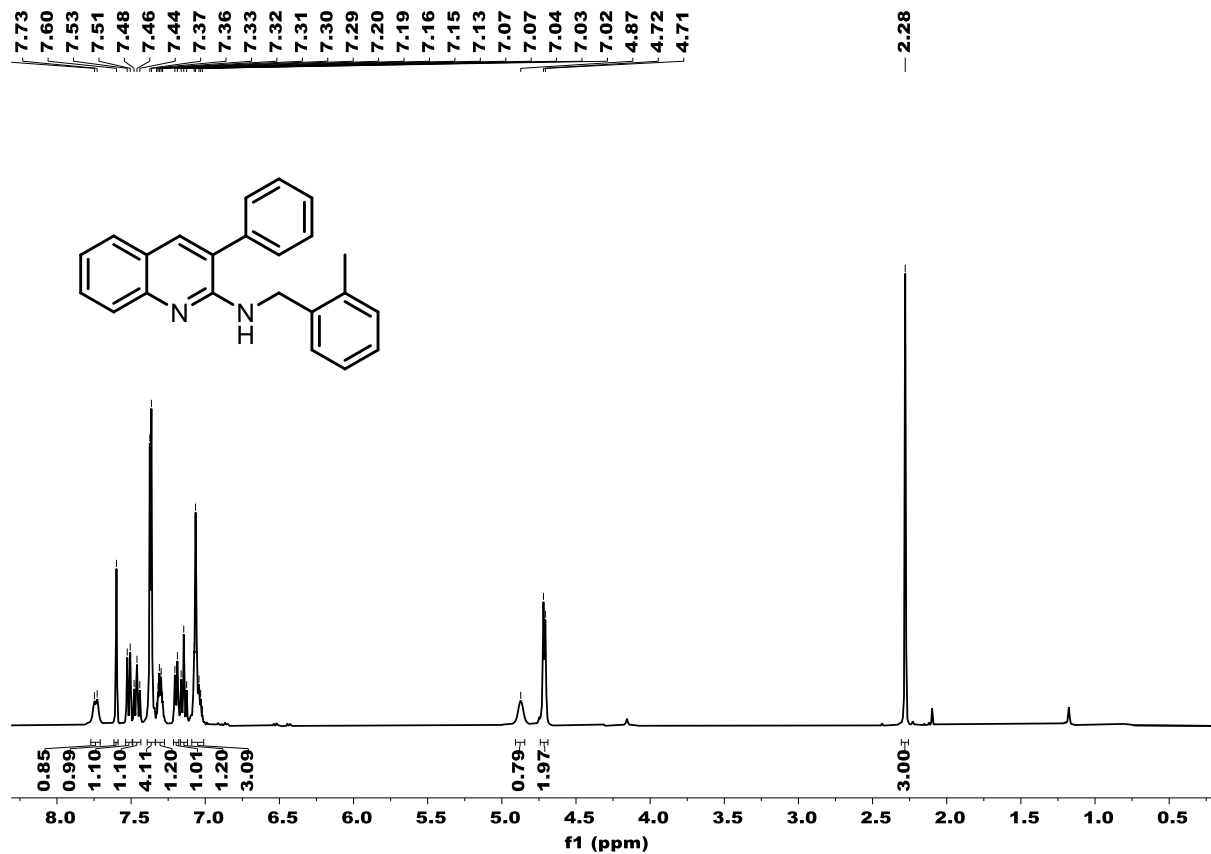
154.0  
147.4  
138.6  
137.4  
136.7  
132.8  
129.5  
129.4  
129.2  
129.2  
128.7  
128.4  
127.5  
126.3  
125.6  
123.8  
122.6

77.5  
77.2  
76.8

44.8

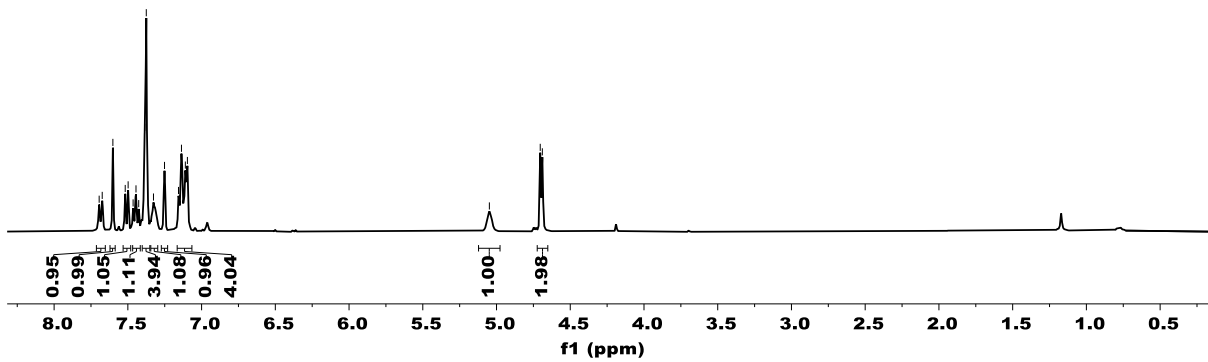
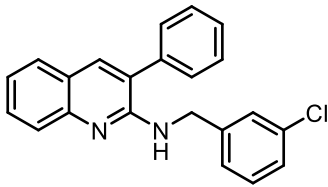






7.67  
7.60  
7.52  
7.50  
7.46  
7.44  
7.43  
7.39  
7.37  
7.33  
7.25  
7.16  
7.14  
7.11  
7.10

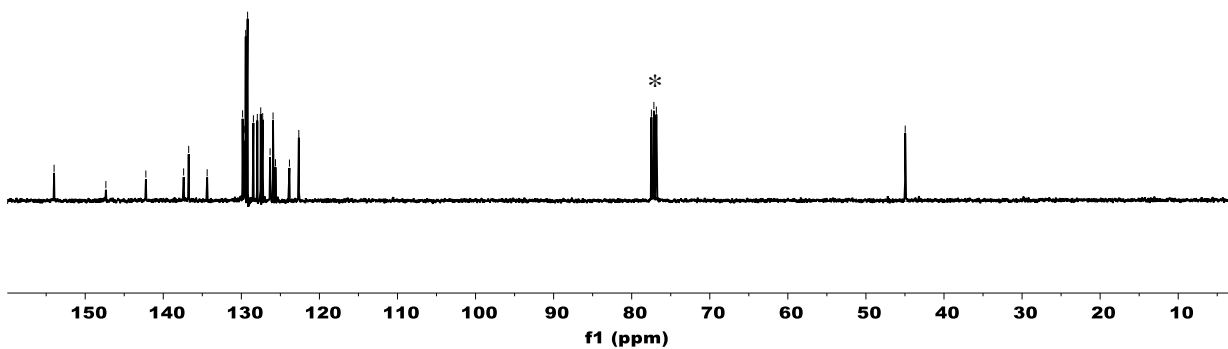
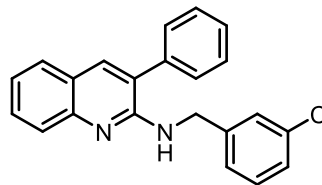
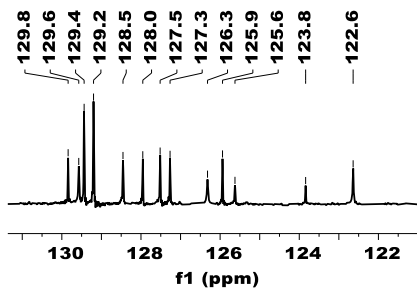
— 5.05  
4.70  
4.69



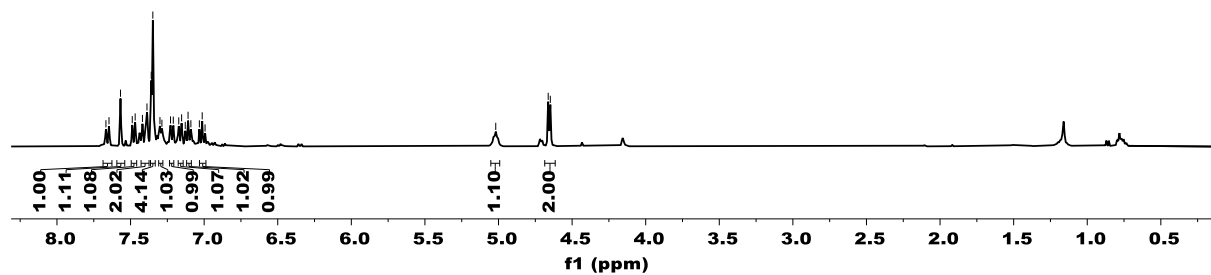
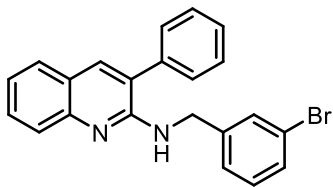
154.0  
147.4  
142.2  
137.4  
136.7  
134.4  
129.8  
129.6  
129.4  
129.2  
128.5  
128.0  
127.5  
127.3  
126.3  
125.9  
125.6  
123.8  
122.6

77.5  
77.2  
76.8

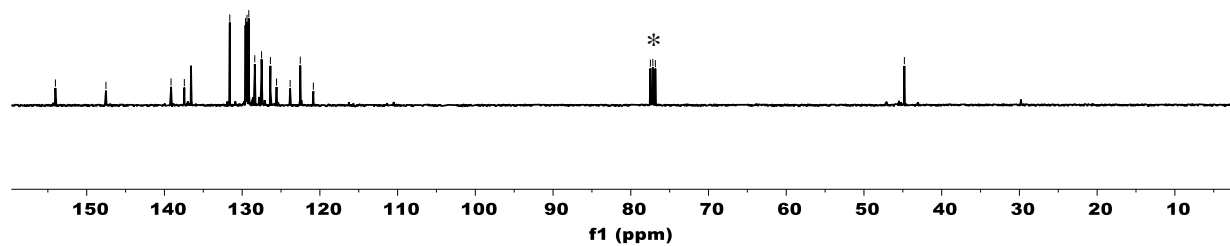
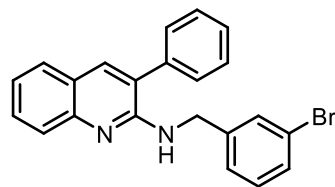
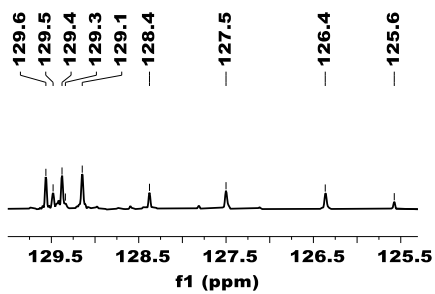
— 45.0



7.67  
7.65  
7.57  
7.49  
7.47  
7.42  
7.39  
7.36  
7.35  
7.30  
7.29  
7.23  
7.21  
7.17  
7.15  
7.13  
7.11  
7.09  
7.03  
7.01  
5.02  
4.86  
4.65



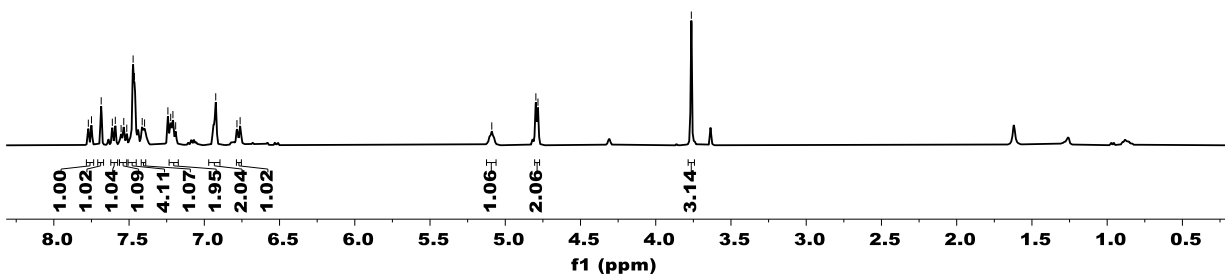
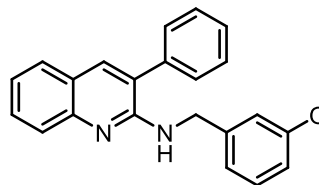
154.0  
147.5  
139.1  
137.4  
136.5  
131.6  
129.6  
129.5  
129.4  
129.3  
129.1  
128.4  
127.5  
126.4  
125.6  
123.8  
122.5  
120.8  
77.5  
77.2  
76.8  
44.8





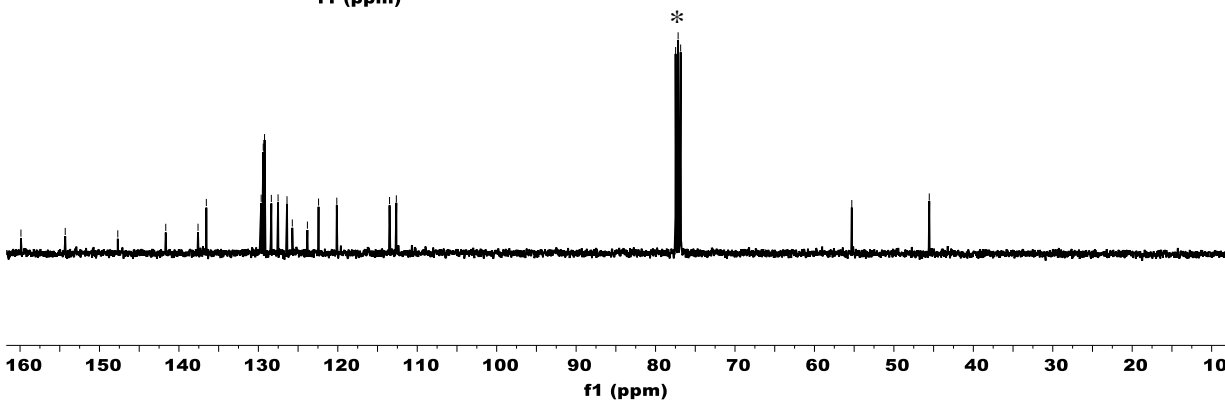
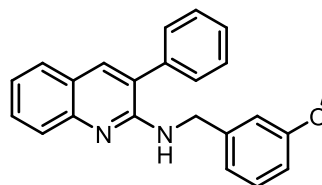
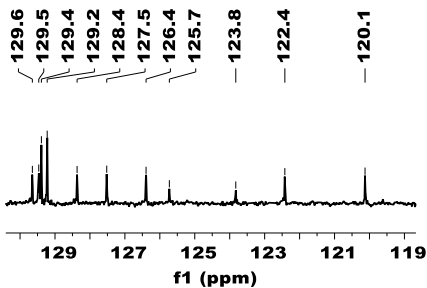
7.75  
7.69  
7.61  
7.59  
7.55  
7.54  
7.52  
7.47  
7.46  
7.41  
7.40  
7.24  
7.22  
7.21  
7.19  
6.92  
6.78  
6.76  
5.09  
4.80  
4.78

3.76

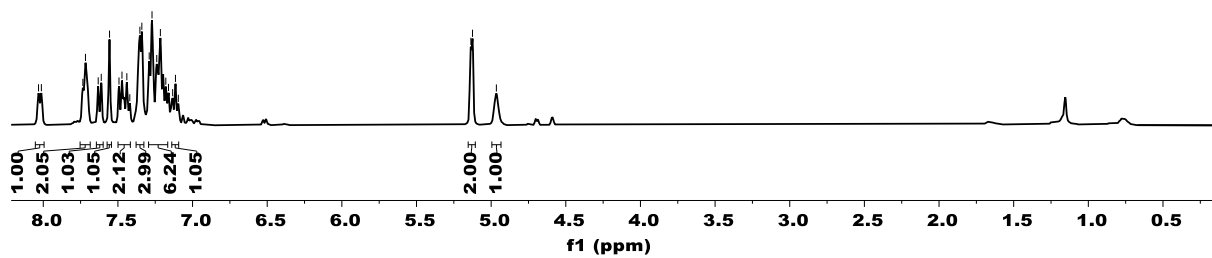
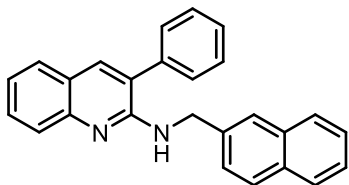


159.9  
154.3  
147.7  
141.7  
137.6  
136.5  
129.6  
129.5  
129.4  
129.2  
128.4  
127.5  
126.4  
125.7  
123.8  
123.8  
122.4  
122.4  
120.1  
113.5  
112.6

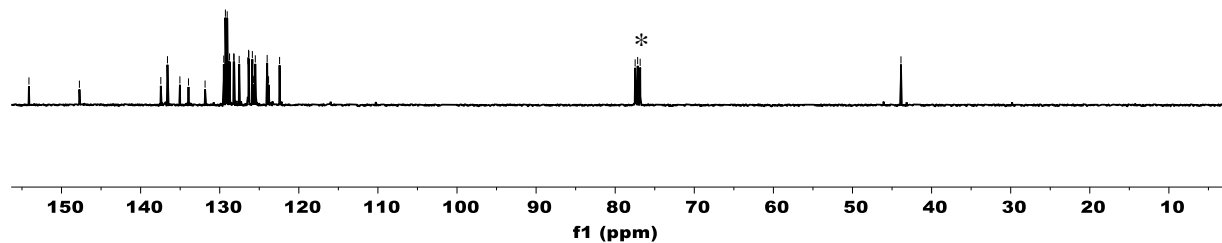
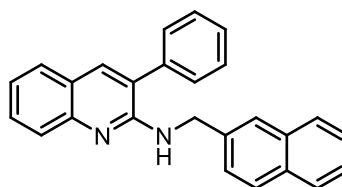
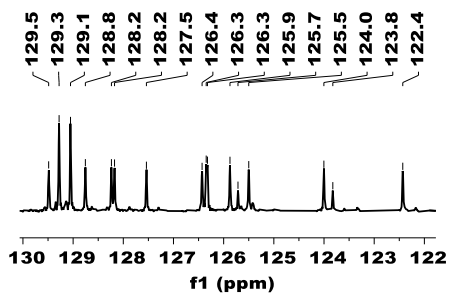
77.5  
77.2  
76.8  
55.3  
45.5

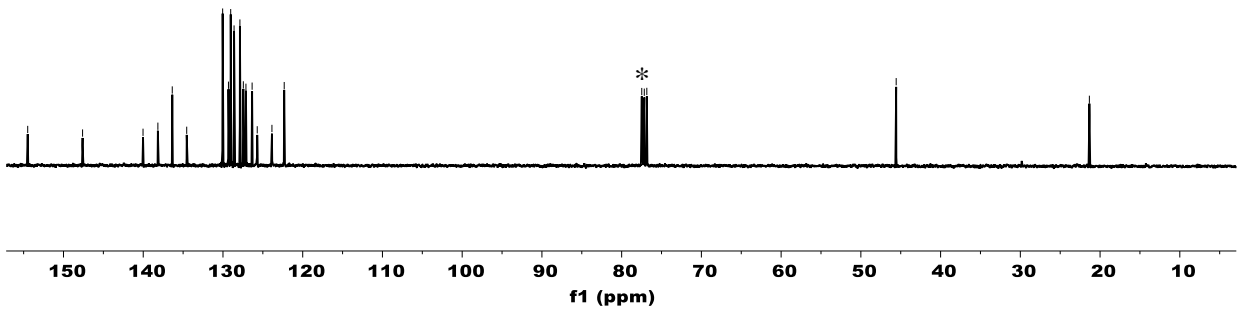
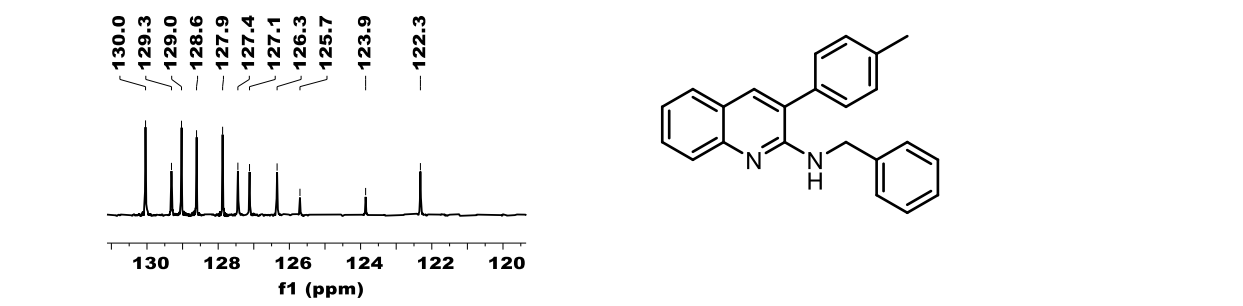
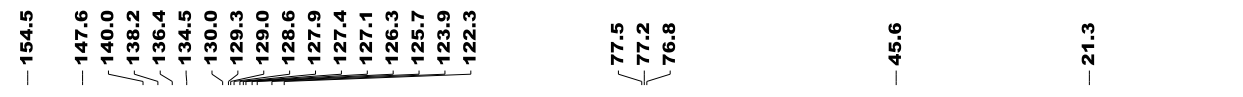
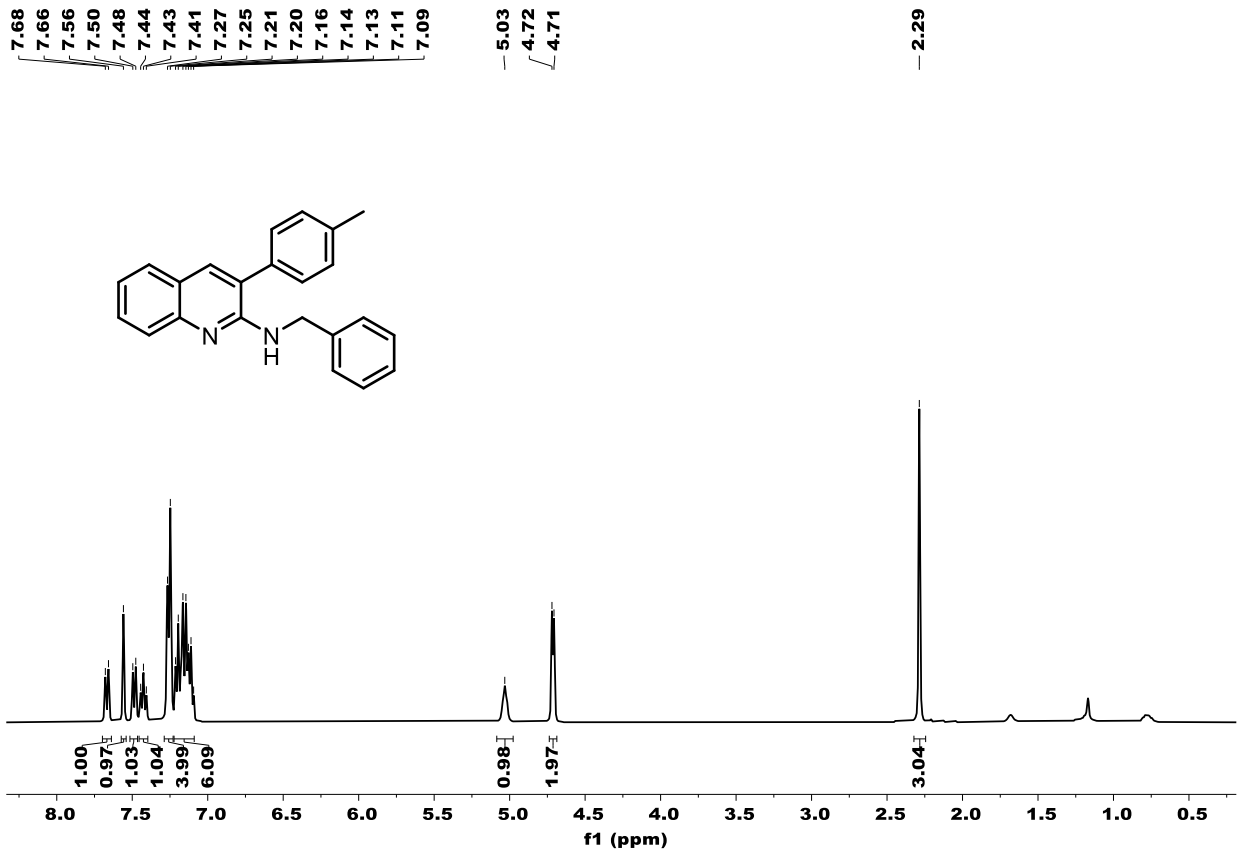


8.01  
7.73  
7.72  
7.63  
7.61  
7.56  
7.49  
7.47  
7.44  
7.42  
7.35  
7.34  
7.29  
7.27  
7.24  
7.22  
7.18  
7.16  
7.13  
7.11  
7.10  
5.14  
5.12  
4.97

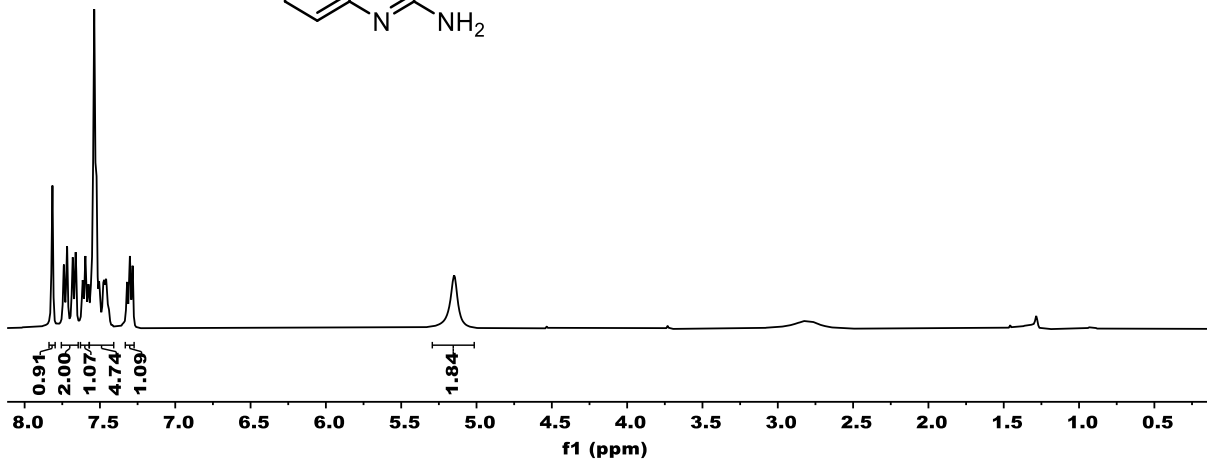
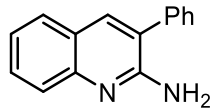


154.1  
147.7  
137.4  
136.6  
135.0  
133.9  
131.9  
129.5  
129.3  
129.1  
128.8  
128.2  
128.2  
127.5  
126.4  
126.3  
126.3  
125.9  
125.7  
125.5  
124.0  
123.8  
122.4  
77.5  
77.2  
76.8  
43.9



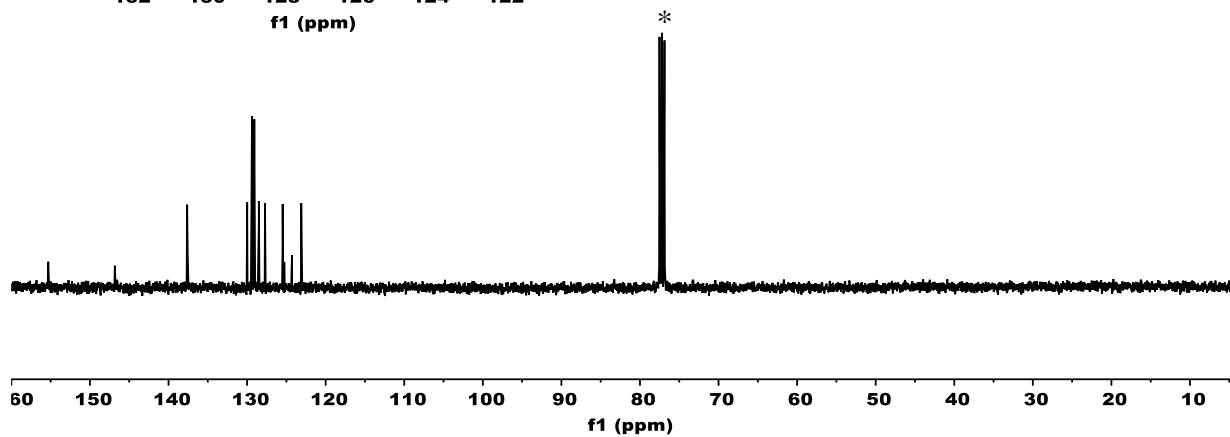
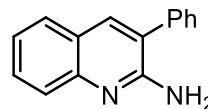
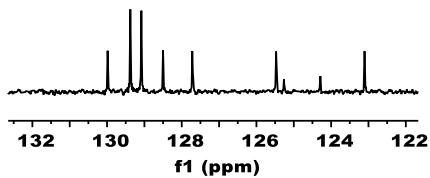


7.81  
7.74  
7.72  
7.68  
7.66  
7.61  
7.60  
7.58  
7.54  
7.52  
7.50  
7.48  
7.46  
7.44  
7.41  
7.32  
7.30  
7.28  
5.15

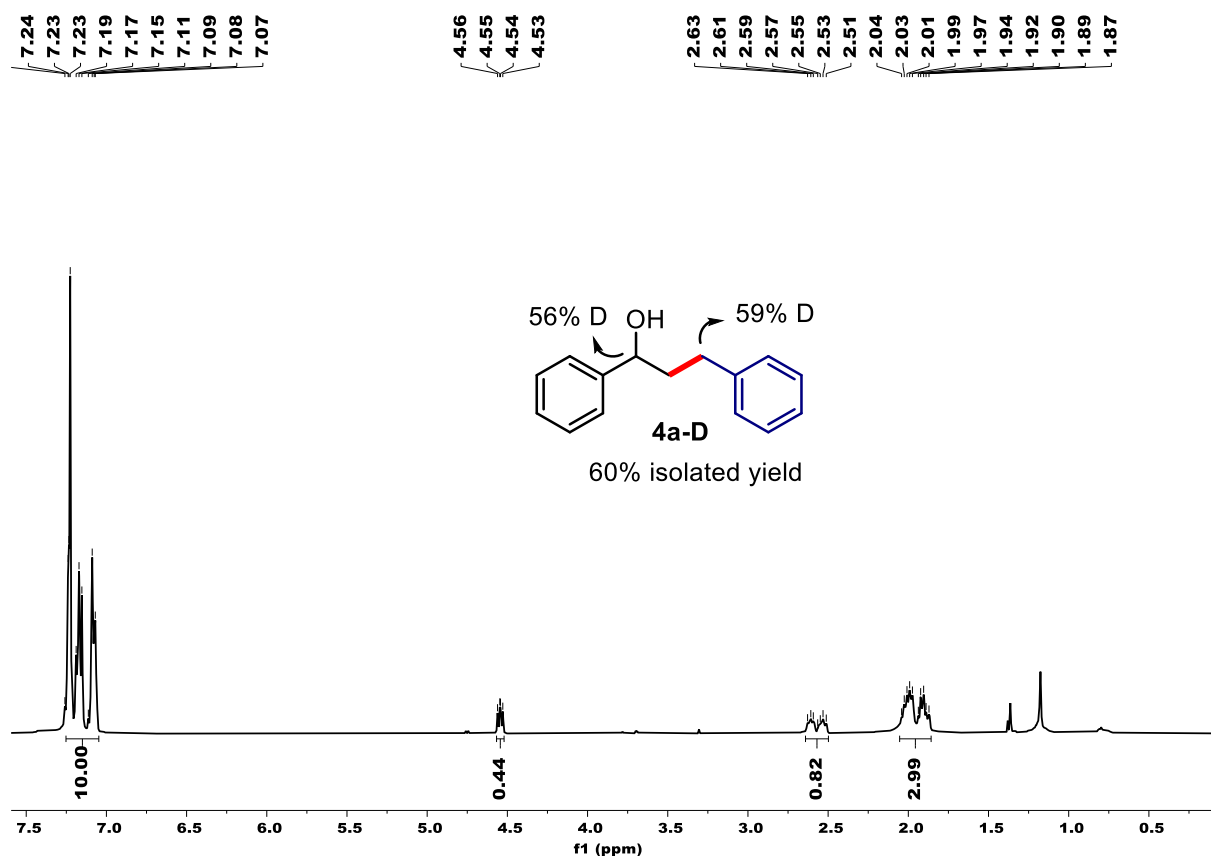


155.3  
146.8  
137.6  
137.6  
130.0  
129.4  
129.1  
128.5  
127.7  
127.7  
125.5  
125.3  
124.3  
123.1  
77.5  
77.2  
76.9

130.0  
129.4  
129.1  
128.5  
127.7  
125.5  
125.3  
124.3  
123.1



**Procedure for the  $\beta$ -alkylation of 1-phenylethanol with benzyl alcohol- $d_2$ :** An oven dried Schlenk tube was charged with a catalyst stock solution (prepared in  $CH_3CN$ , 0.01 mol%) and after that all the volatiles were removed in vacuum. To this, secondary alcohol (0.5 mmol), benzyl alcohol- $d_2$  (0.5 mmol), and KOH (0.25 mmol, 50 mol%) followed by toluene (1 mL) were added. Next, the reaction tube was kept in oil bath (bath temperature 120 °C) and heated for 6 h. After the completion of reaction, the reaction mixture was cooled to room temperature and subjected to column chromatography using hexane/ethyl acetate eluent system. The obtained isolated product (60% yield) was analyzed from  $^1H$  NMR to find out deuterium incorporation percentage.



**Figure S2.**  $^1H$  NMR spectrum of 4a-D in  $CDCl_3$ .

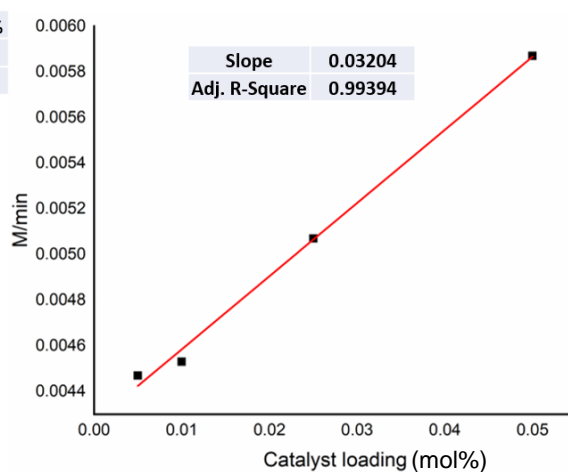
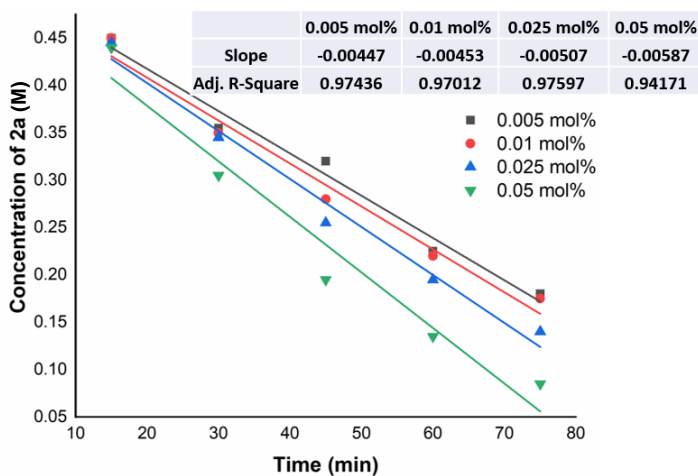
#### Determination of order of reaction:

The order of the reaction with respect to the catalyst concentration was determined by employing the initial rate method. Accordingly, four different sets of reactions were conducted by varying the catalyst concentration (0.005–0.05 mol%) keeping other factors constant and the concentration of

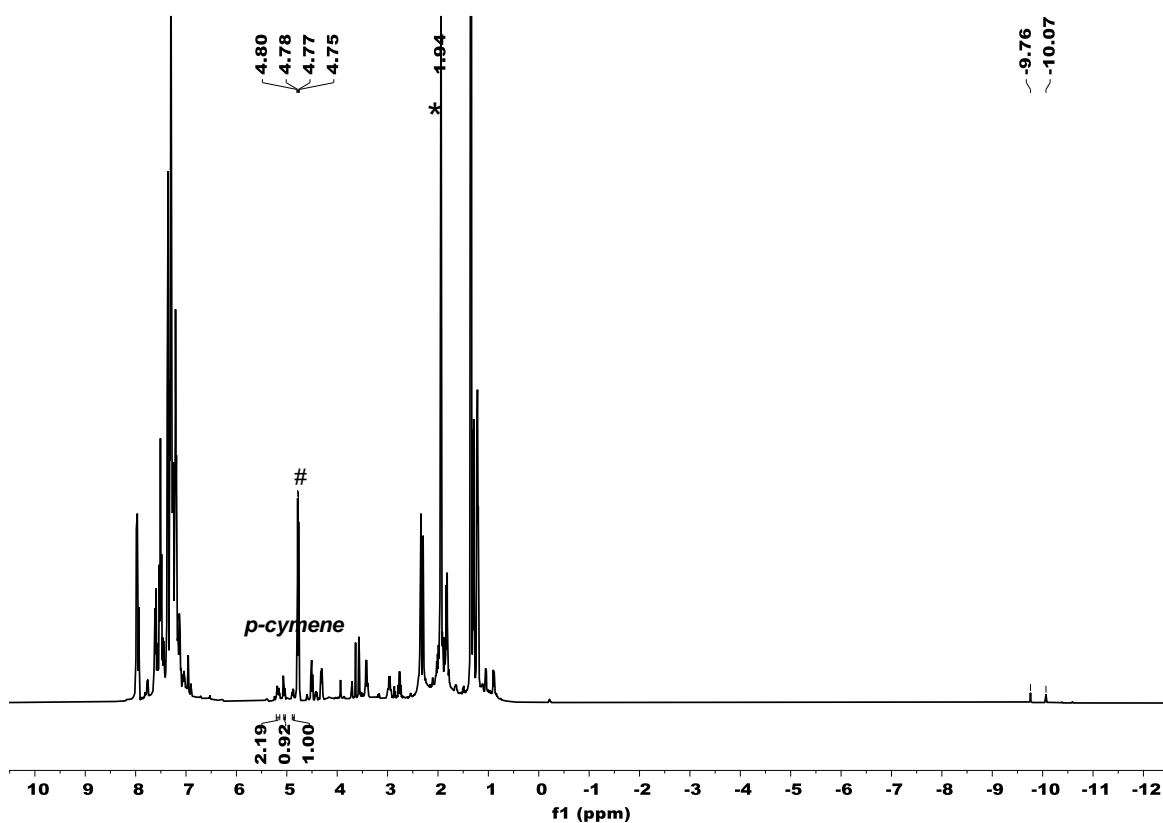
the reactant **2a** (upto 75 min) was noted (from the GC-MS analysis) in each case. Initial rates were then calculated from the plots of **2a** concentration vs time. After that the initial rates were plotted against the catalyst concentration. The straight line nearly passing through the origin implies that the reaction is of first order with respect to the concentration of **1a**.

Entry	2a (mmol)	1a (mol%)	KOH (mmol)	Toluene (mL)
1	0.5	0.005	0.25	1.0
2	0.5	0.01	0.25	1.0
3	0.5	0.025	0.25	1.0
4	0.5	0.05	0.25	1.0

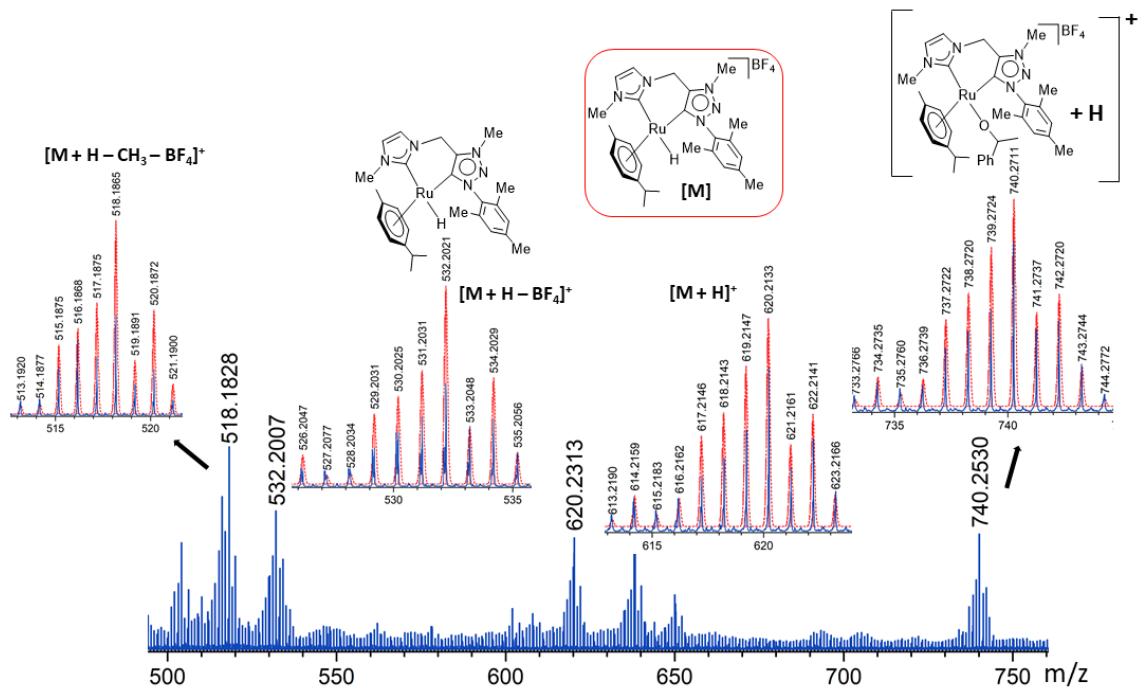
Entry	Time (min)	Concentration of 2a (M)			
		0.005 mol%	0.01 mol%	0.025 mol%	0.05 mol%
1	15	0.450	0.450	0.445	0.440
2	30	0.355	0.350	0.345	0.305
3	45	0.320	0.280	0.255	0.195
4	60	0.225	0.220	0.195	0.135
5	75	0.180	0.175	0.140	0.085



**General procedure for the detection of Ruthenium hydride species:** An oven dried Schlenk tube was charged with the catalyst **1a** (20 mg, 0.031 mmol), 1-phenylethanol (0.5 mmol), and KOH (0.25 mmol, 50 mol%) followed by toluene (1 mL). The reaction tube was then kept in oil bath (bath temperature 120 °C) and heated for 120 min. After that, the reaction mixture was cooled to room temperature and all the volatiles were removed in high vacuum. The obtained reaction mixture was then dissolved in CD<sub>3</sub>CN and the <sup>1</sup>H-NMR was recorded. HRMS analysis was also performed with a small portion of the reaction mixture.



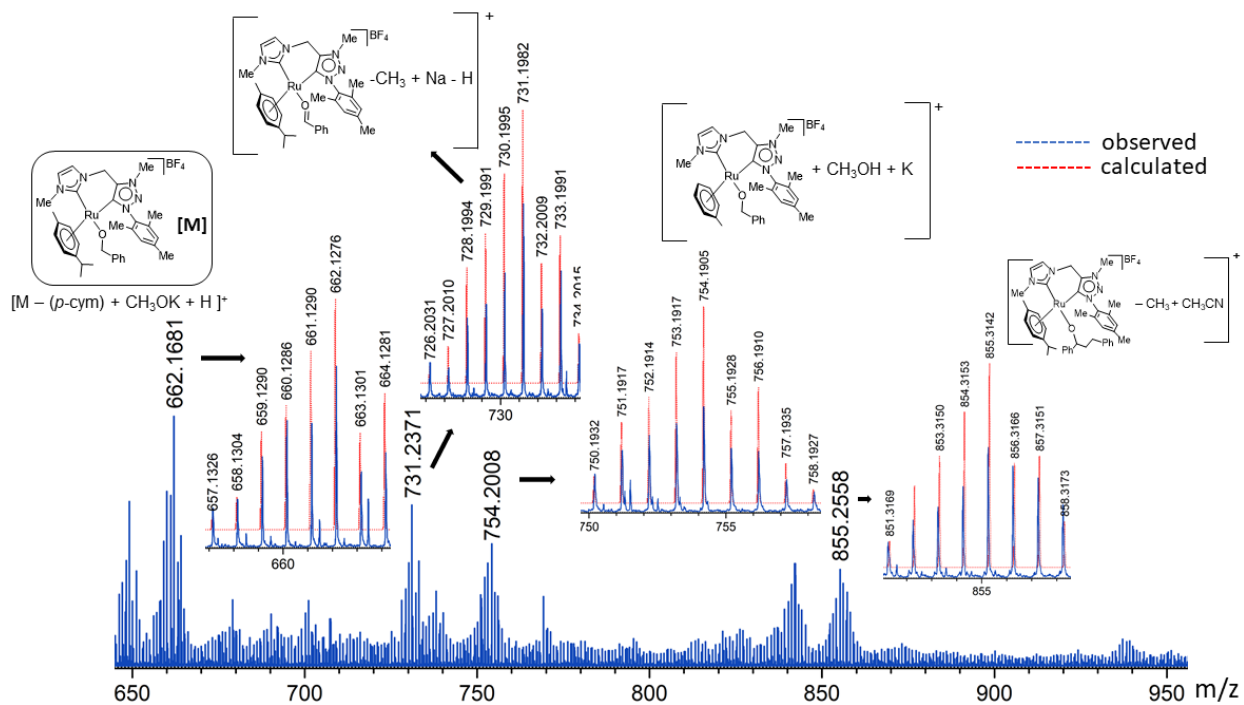
**Figure S3.** <sup>1</sup>H-NMR spectrum of the reaction mixture of complex **1a** and 1-phenylethanol (# and \* represents CH<sub>3</sub>CHOH, CH<sub>3</sub>CHOH peaks of 1-phenylethanol respectively).



**Figure S4.** ESI-Mass spectrum of the reaction mixture of complex **1a** and 1-phenylethanol showing the formation of ruthenium hydride species.

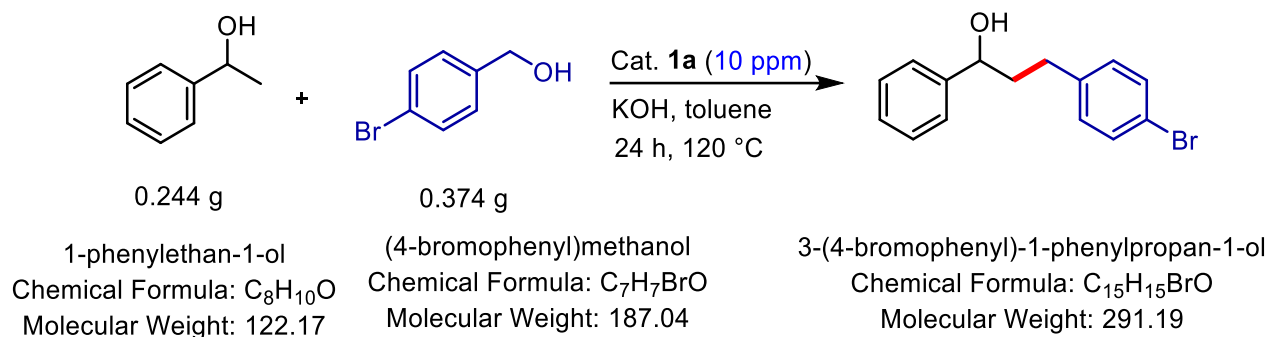


**General procedure for the HRMS analysis of reaction mixture:** An oven dried Schlenk tube was charged with the catalyst **1a** (1 mol%, 0.005 mmol), secondary alcohol (0.5 mmol), primary alcohol (0.5 mmol), and KOH (0.25 mmol) followed by toluene (1 mL). The Schlenk tube was then kept in oil bath (bath temperature 120 °C) and heated for 30 min. After that, the reaction mixture was cooled to room temperature and the HRMS analysis of the sample was performed immediately.



**Figure S5.** ESI-Mass spectrum (in CH<sub>3</sub>CN) of the reaction between **2a** and **3a** catalyzed by **1a** in toluene.

### Calculation of Green metrics:



Total: 122.17 + 187.04 = 309.21

Product yield: 90%

Reactant 1	1-phenylethan-1-ol	0.244 g	FW 122.17
Reactant 2	4-bromobenzyl alcohol	0.374 g	FW 187.04
Base	KOH	0.056 g	FW 56.11
Solvent	Toluene	0.867 g	-
Auxiliary	-	-	-
Product	3-(4-bromophenyl)-1-phenylpropan-1-ol	0.524 g	FW 291.19
Byproduct	Water	0.036 g	FW 18.01

Product yield = 90%

Atom economy:  $291.19/309.21 = 94.2\%$

Atom efficiency:  $90 \times (94.2/100) = 84.8\%$

Carbon efficiency:  $(15/15) \times 100 = 100\%$

Reaction mass efficiency:  $[0.524 \text{ g} / (0.244 \text{ g} + 0.374 \text{ g})] \times 100 = 88.7\%$