

## *Supporting Information*

### **$\alpha$ -Alkylation of Nitriles with Alcohols Catalyzed by NNN' Pincer Ru(II) Complexes Bearing Bipyridyl Imidazoline Ligands**

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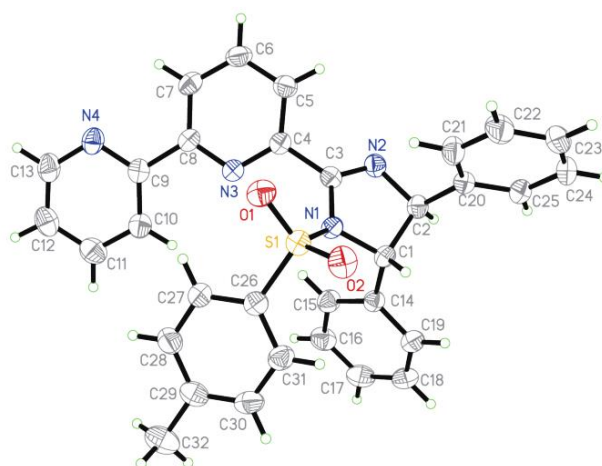
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## X-ray data of 1f, 1g and 2a

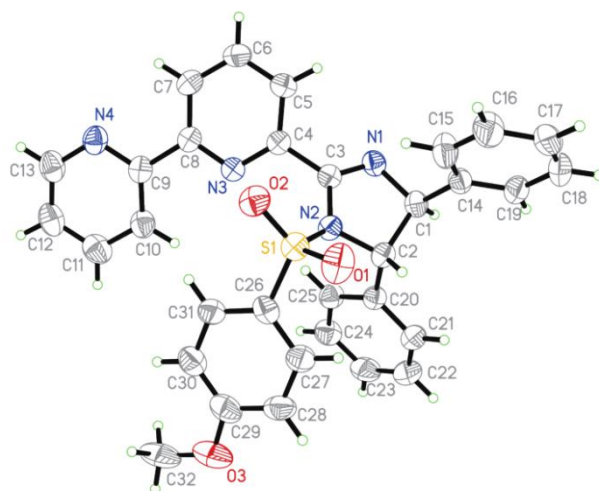
**Table S1.** Crystal data and structure refinement of **1f**, **1g** and **2a**.

Structure	<b>1f</b>	<b>1g</b>	<b>2a</b>
Identification code	20190101	20190102	201712284
Empirical formula	C <sub>32</sub> H <sub>26</sub> N <sub>4</sub> O <sub>2</sub> S	C <sub>32</sub> H <sub>26</sub> N <sub>4</sub> O <sub>3</sub> S	C <sub>42</sub> H <sub>41</sub> C <sub>12</sub> N <sub>4</sub> PRu
Formula weight	530.63	546.63	804.75
Temperature/K	293(2)	293(2)	293
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a/Å	10.0718(4)	10.0032(2)	10.9706(2)
b/Å	13.9361(4)	14.1704(3)	16.6015(4)
c/Å	19.3932(7)	19.5208(4)	20.7484(4)
$\alpha$ /°	90	90	90
$\beta$ /°	90	90	90
$\gamma$ /°	90	90	90
Volume/Å <sup>3</sup>	2722.05(17)	2767.08(10)	3778.88(15)
Z	4	4	4
$\rho_{\text{calc}}/\text{cm}^3$	1.295	1.312	1.414
$\mu/\text{mm}^{-1}$	1.347	1.369	5.330
F(000)	1112.0	1144.0	1656.0
Crystal size/mm <sup>3</sup>	0.18 × 0.15 × 0.12	0.16 × 0.15 × 0.13	0.2749 × 0.1933 × 0.1769
Radiation	CuK $\alpha$ ( $\lambda$ = 1.54184)	CuK $\alpha$ ( $\lambda$ = 1.54184)	CuK $\alpha$ ( $\lambda$ = 1.54184)
2 $\theta$ range for data collection/°	7.812 to 134.154	7.71 to 141.724	6.82 to 134.148
Index ranges	-11 ≤ h ≤ 12, -16 ≤ k ≤ 16, -22 ≤ l ≤ 23	-7 ≤ h ≤ 12, -17 ≤ k ≤ 12, -23 ≤ l ≤ 23	-8 ≤ h ≤ 13, -17 ≤ k ≤ 19, -24 ≤ l ≤ 15
Reflections collected	11232	10821	10200
Independent reflections	4858 [R <sub>int</sub> = 0.0299, R <sub>sigma</sub> = 0.0389]	5222 [R <sub>int</sub> = 0.0301, R <sub>sigma</sub> = 0.0380]	5980 [R <sub>int</sub> = 0.0362, R <sub>sigma</sub> = 0.0564]

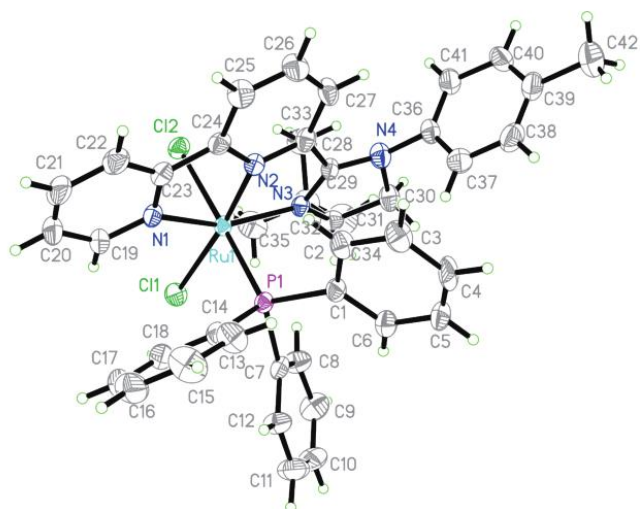
Data/restraints/parameters	4858/0/353	5222/2/388	5980/0/455
Goodness-of-fit on $F^2$	1.021	1.034	1.036
Final R indexes [ $I \geq 2\sigma$ (I)]	$R_1 = 0.0409$ , $wR_2 = 0.1032$	$R_1 = 0.0452$ , $wR_2 = 0.1139$	$R_1 = 0.0508$ , $wR_2 = 0.1270$
Final R indexes [all data]	$R_1 = 0.0471$ , $wR_2 = 0.1088$	$R_1 = 0.0530$ , $wR_2 = 0.1228$	$R_1 = 0.0562$ , $wR_2 = 0.1326$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.12/-0.20	0.12/-0.21	0.98/-0.95



**Figure S1.** ORTEP views of the molecular structures of **1f** with ellipsoids drawn at the 30% probability level.

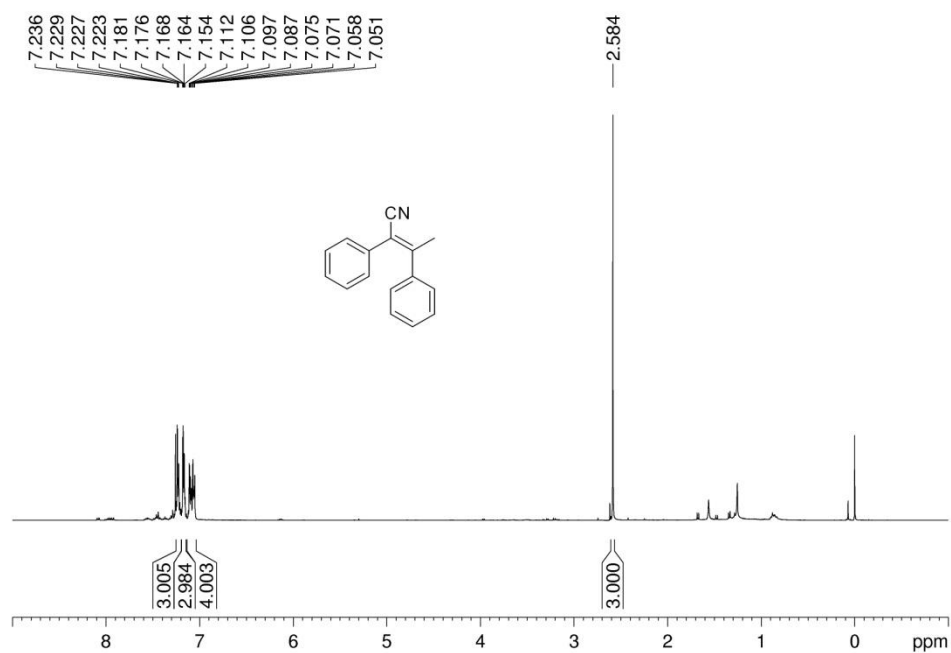


**Figure S2.** ORTEP views of the molecular structures of **1g** with ellipsoids drawn at the 30% probability level.

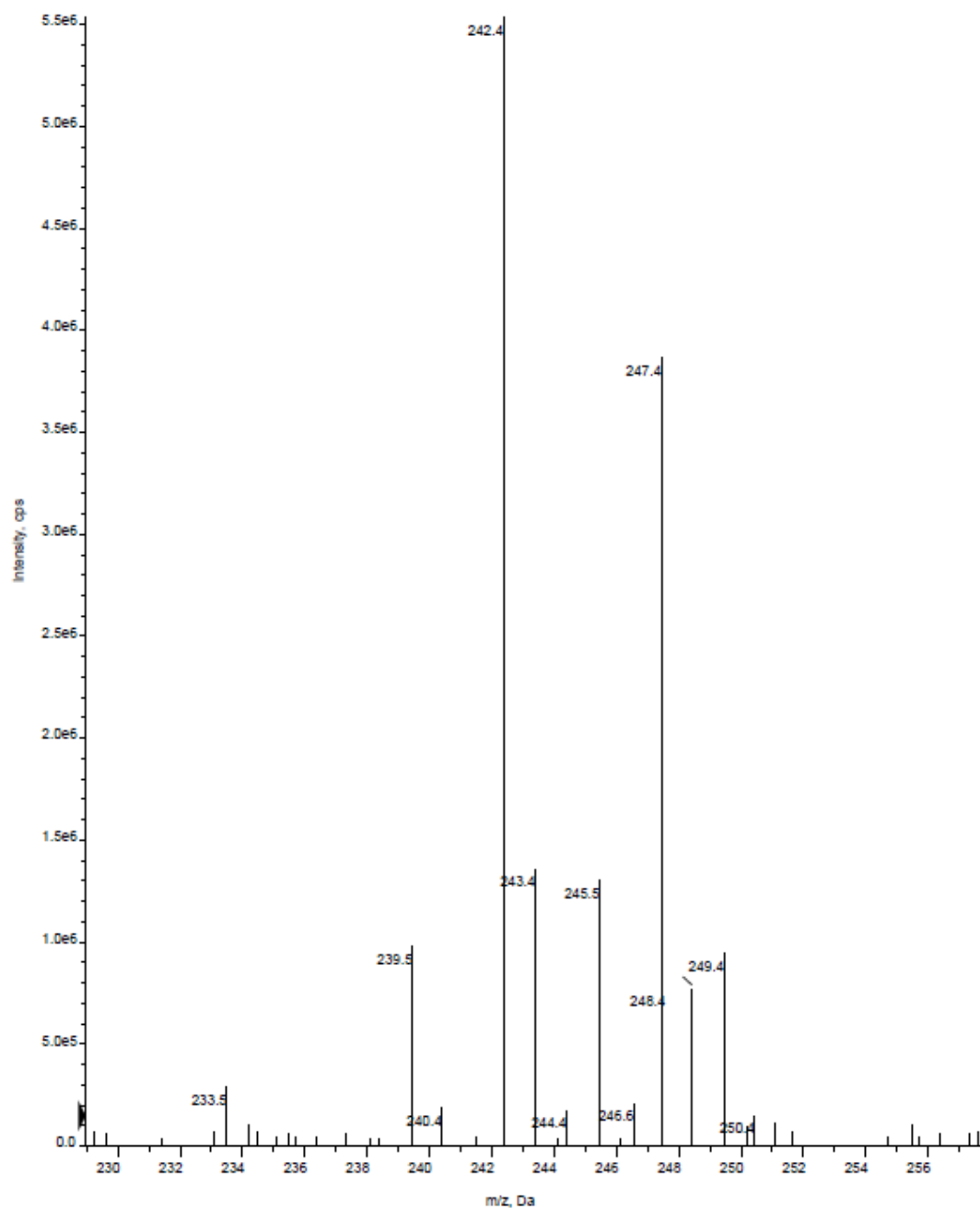


**Figure S3.** ORTEP views of the molecular structures of **2a** with ellipsoids drawn at the 30% probability level.

## Characterization of vinyl nitrile: 2,3-diphenylbut-2-enitrile



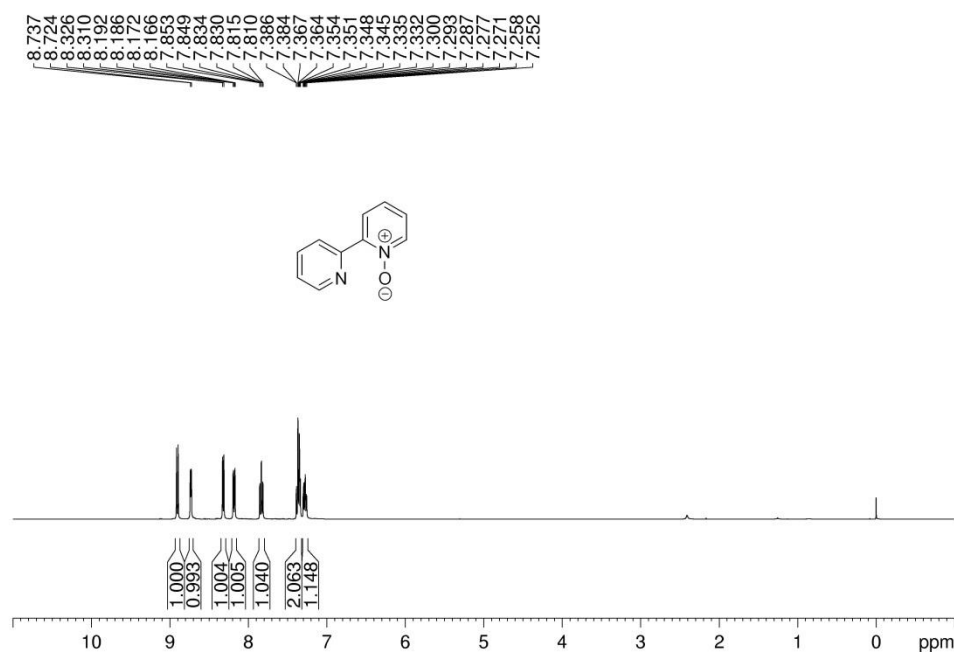
**Figure S4.**  $^1\text{H}$  NMR spectrum of 2,3-diphenylbut-2-enitrile



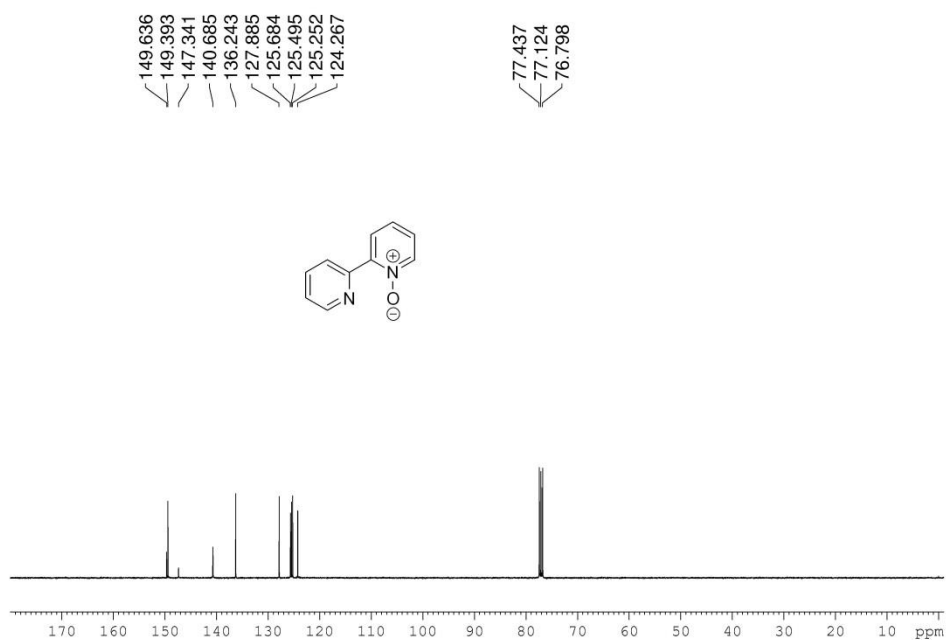
Calculated mass for  $C_{16}H_{13}N$ : 219.3. Observed mass in MS-ESI: 242.3  $[M+Na]^+$

**Figure S5.** Mass spectroscopy of 2,3-diphenylbut-2-enenitrile

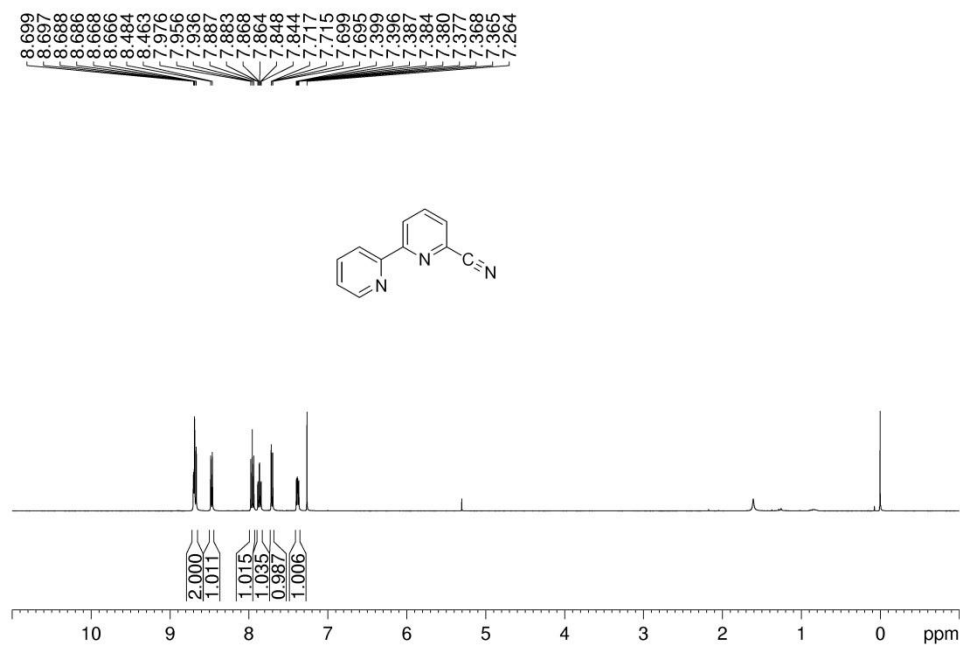
## NMR spectra of synthesized compounds



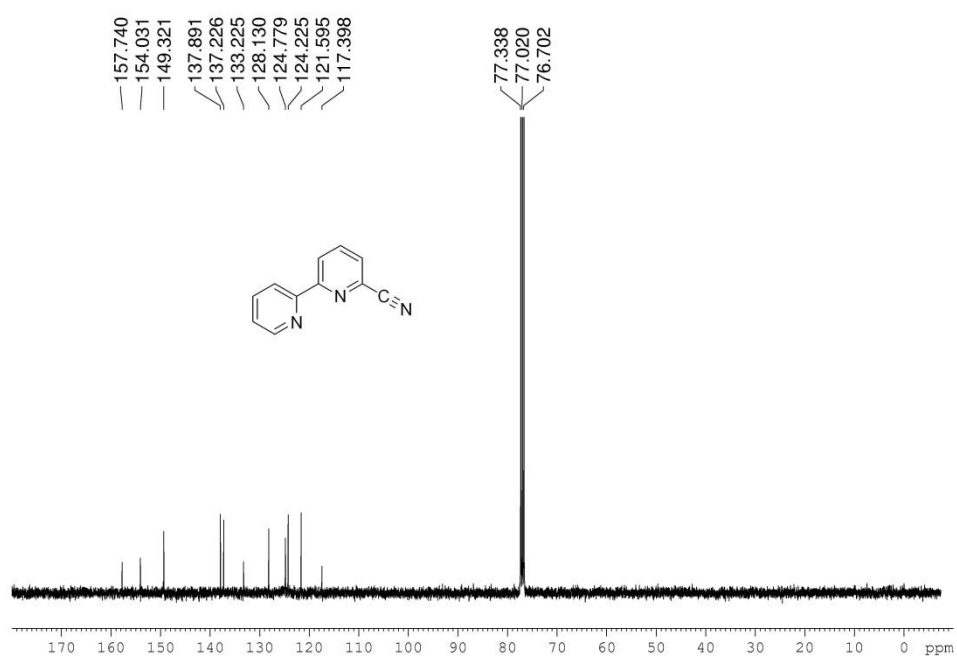
**Figure S6.** <sup>1</sup>H NMR of 2,2'-bipyridine-*N*-oxide in CDCl<sub>3</sub>.



**Figure S7.** <sup>13</sup>C NMR of 2,2'-bipyridine-*N*-oxide in CDCl<sub>3</sub>.

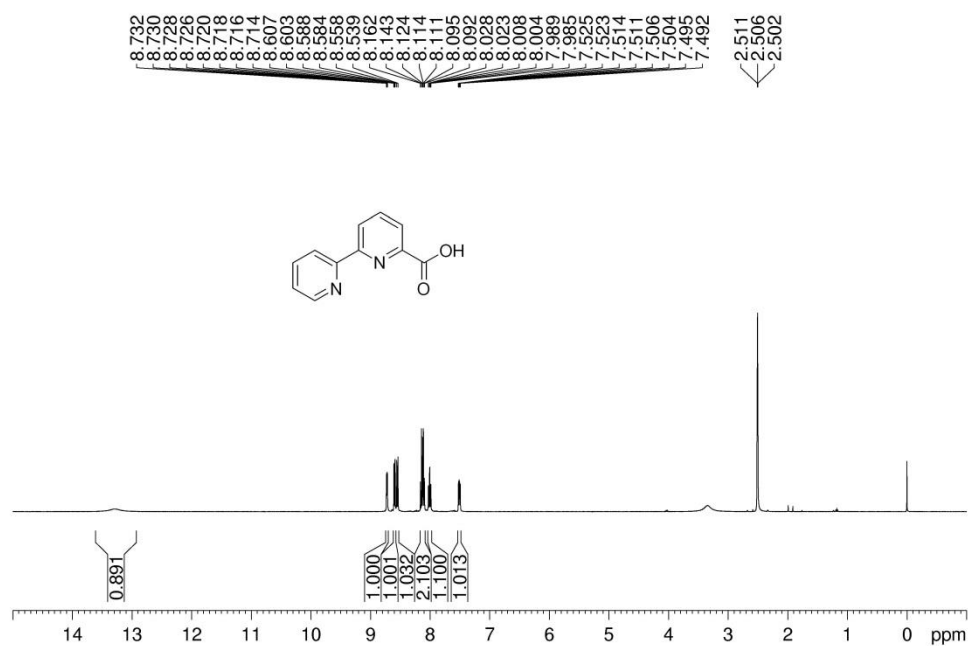


**Figure S8.** <sup>1</sup>H NMR of 2,2'-bipyridyl-6-carbonitrile in CDCl<sub>3</sub>.

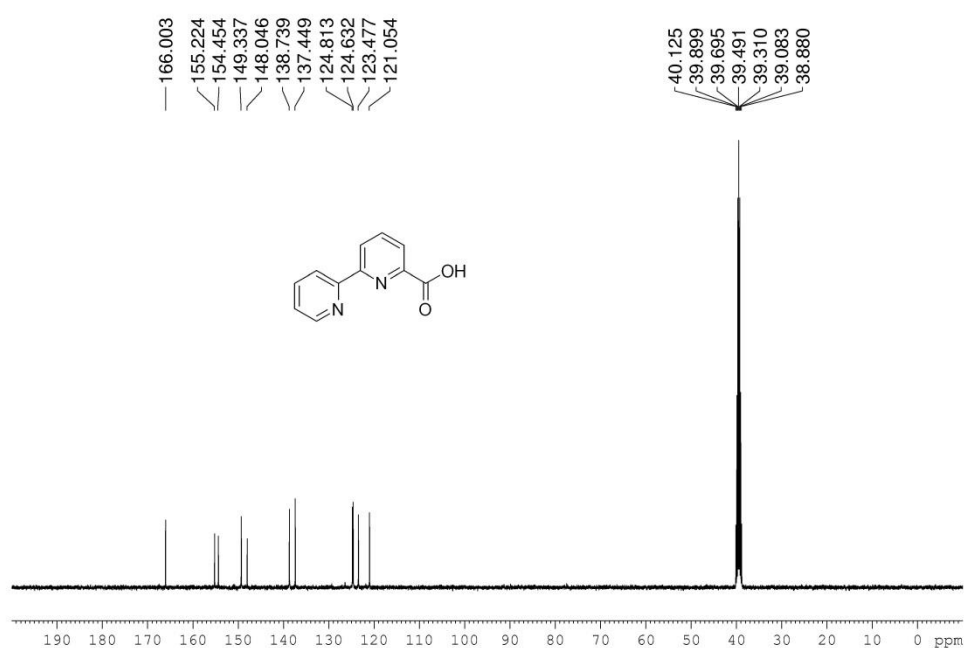


**Figure S9.** <sup>13</sup>C NMR of 2,2'-bipyridyl-6-carbonitrile in CDCl<sub>3</sub>.

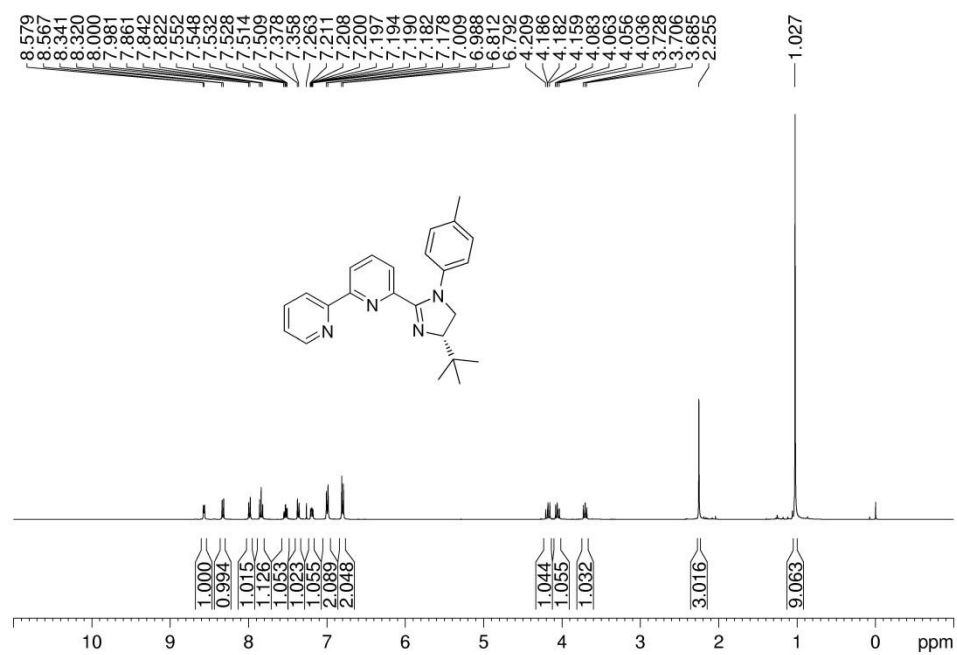




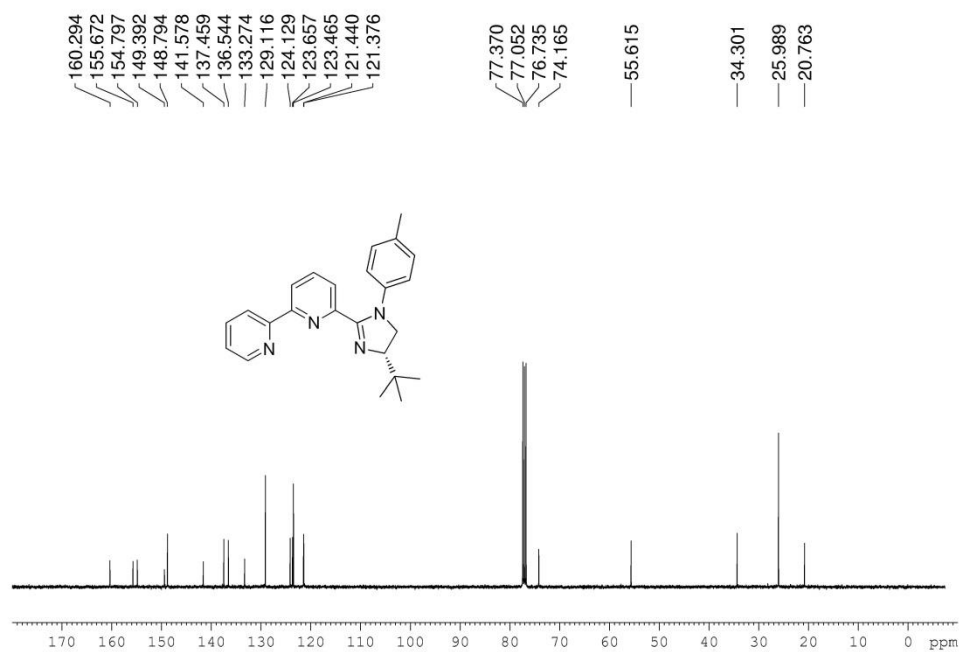
**Figure S10.** <sup>1</sup>H NMR of 2,2'-bipyridine-6-carboxylic acid in *d*<sub>6</sub>-DMSO.



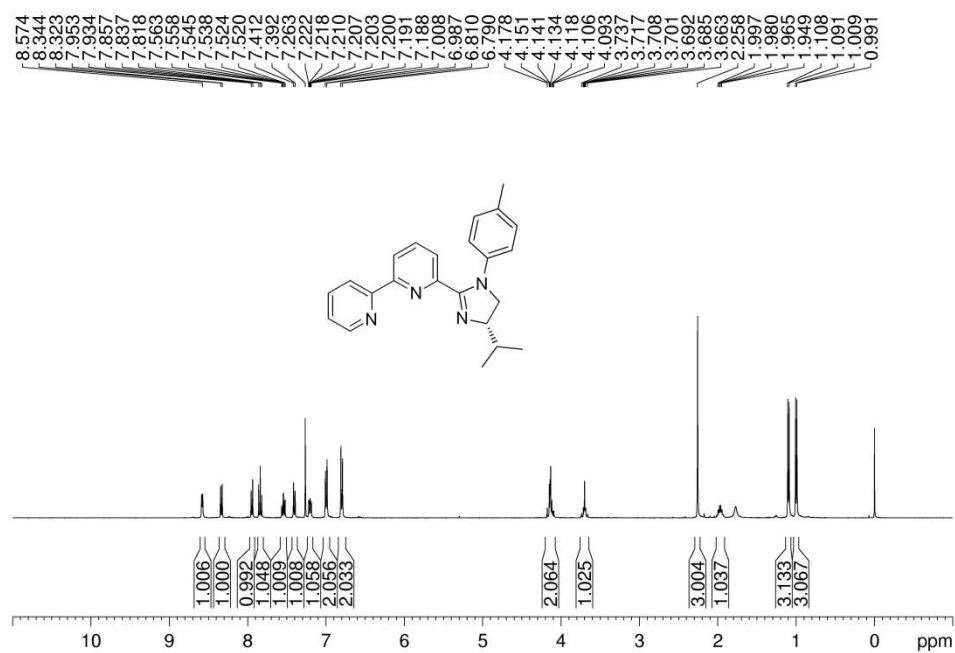
**Figure S11.** <sup>13</sup>C NMR of 2,2'-bipyridine-6-carboxylic acid in *d*<sub>6</sub>-DMSO.



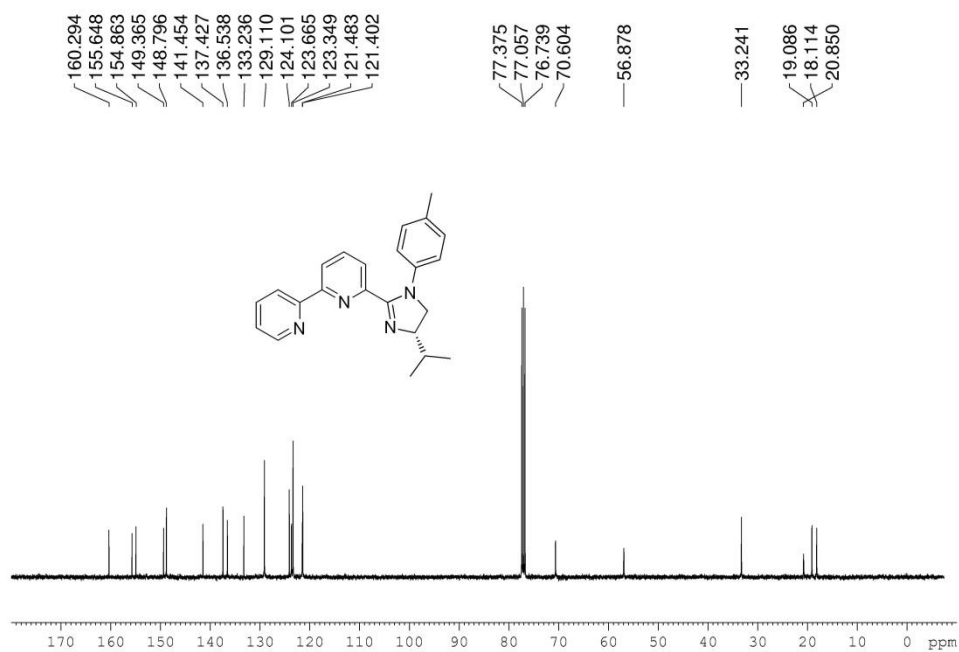
**Figure S12.** <sup>1</sup>H NMR of compound **1a** in CDCl<sub>3</sub>.



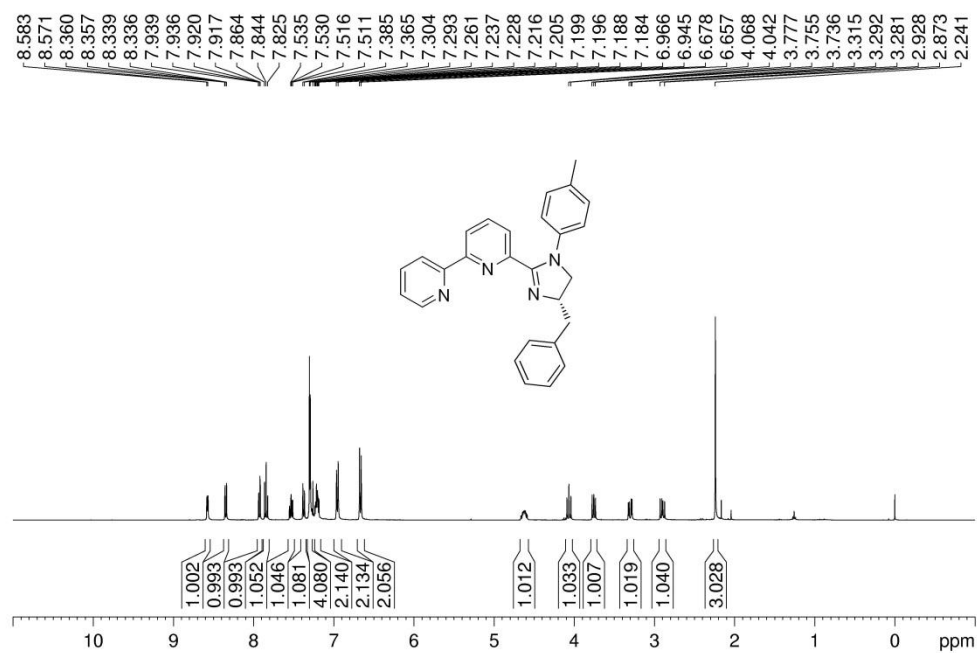
**Figure S13.** <sup>13</sup>C NMR of compound **1a** in CDCl<sub>3</sub>.



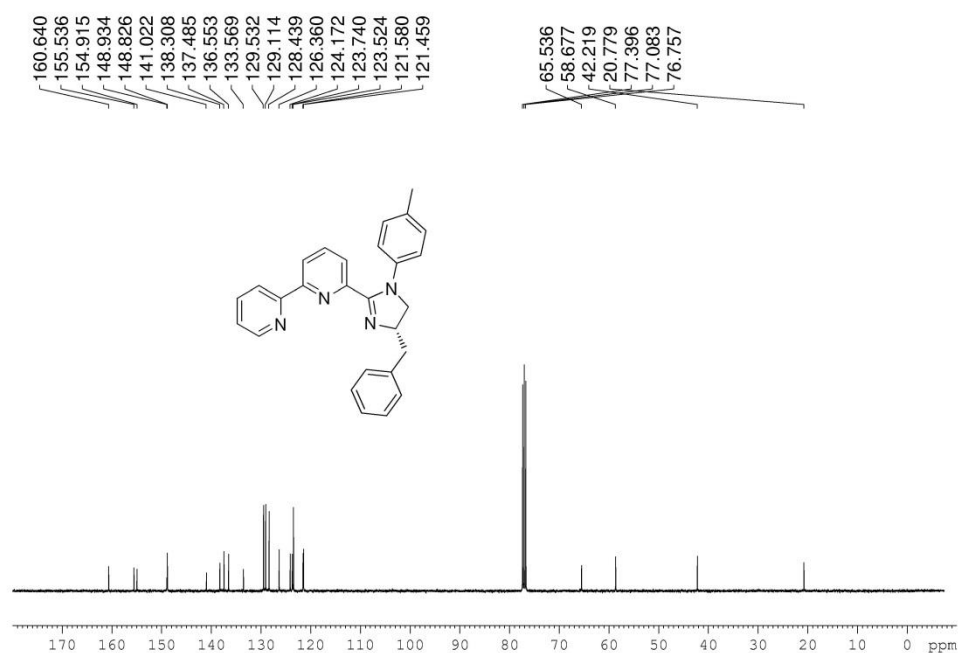
**Figure S14.** <sup>1</sup>H NMR of compound **1b** in CDCl<sub>3</sub>.



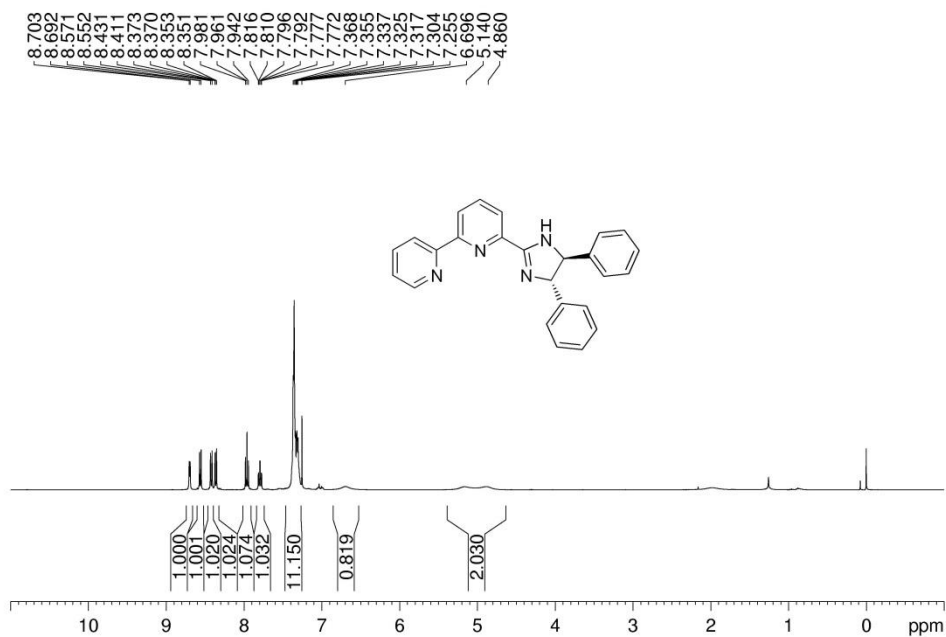
**Figure S15.** <sup>13</sup>C NMR of compound **1b** in CDCl<sub>3</sub>.



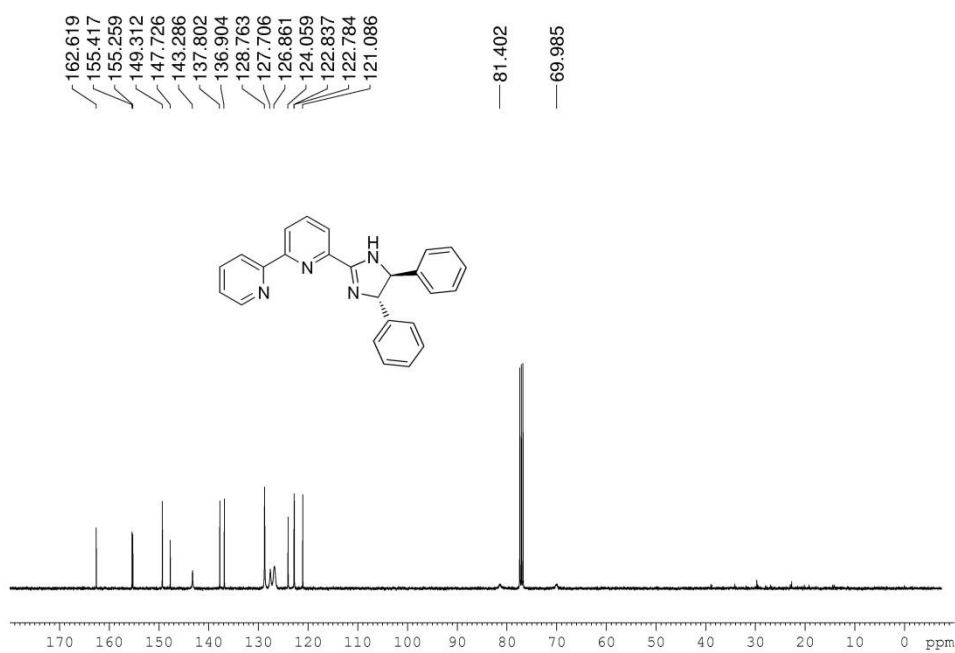
**Figure S16.** <sup>1</sup>H NMR of compound **1c** in CDCl<sub>3</sub>.



**Figure S17.** <sup>13</sup>C NMR of compound **1c** in CDCl<sub>3</sub>.

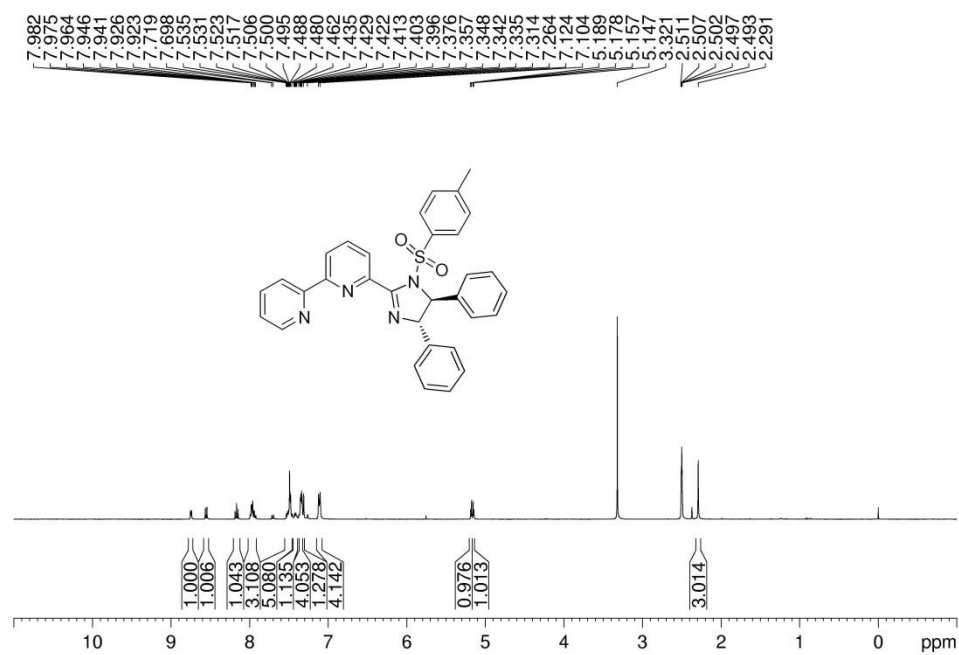


**Figure S18.** <sup>1</sup>H NMR of compound **1d** in CDCl<sub>3</sub>.

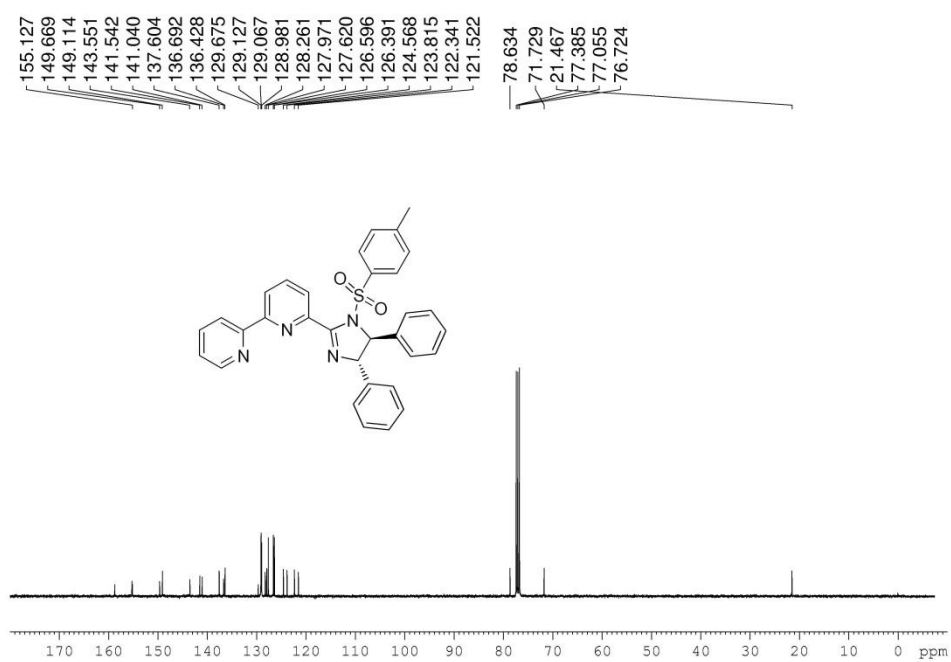


**Figure S19.** <sup>13</sup>C NMR of compound **1d** in CDCl<sub>3</sub>.

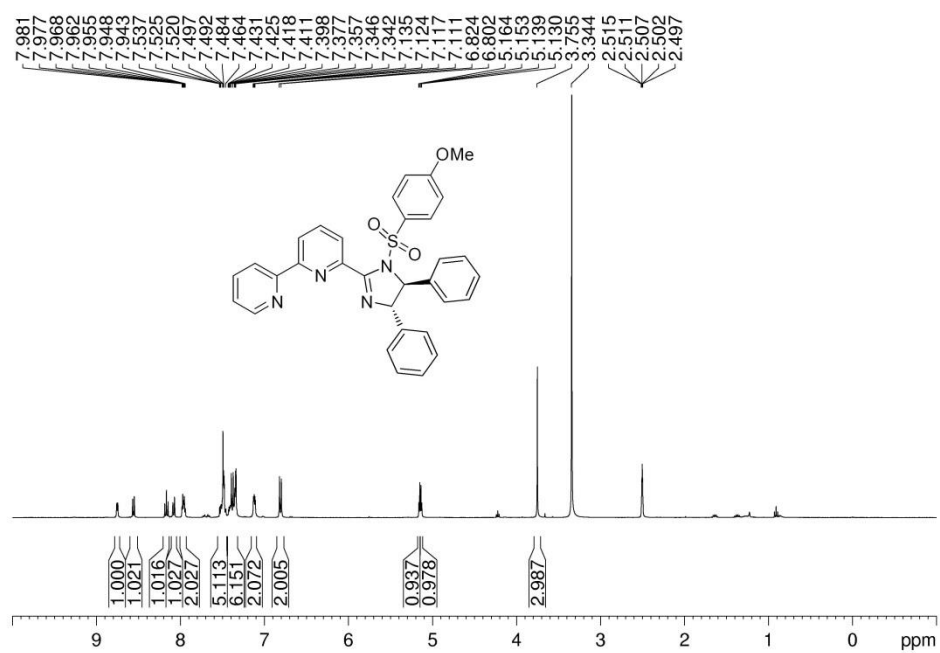




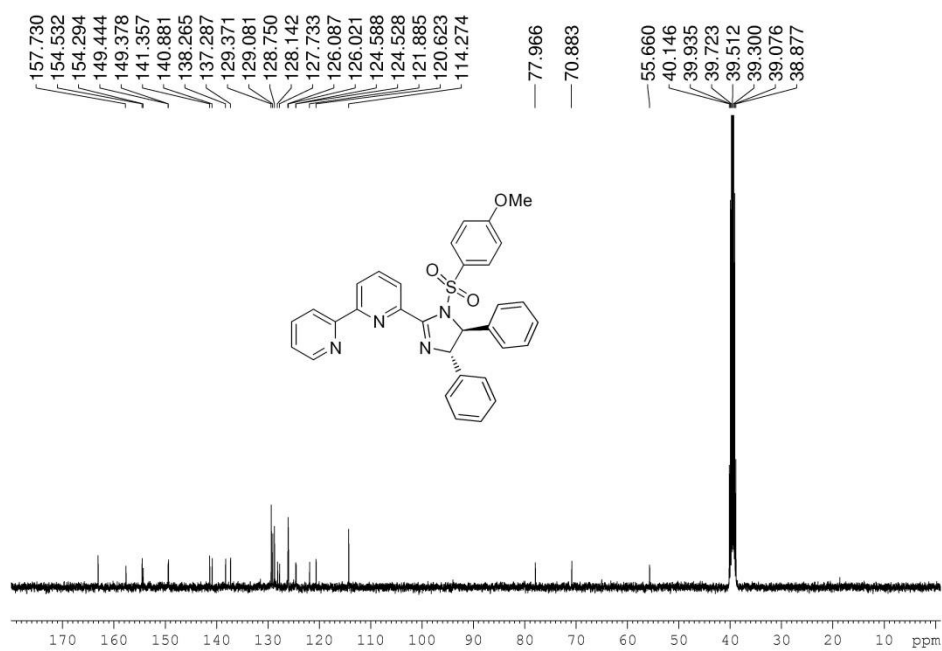
**Figure S22.** <sup>1</sup>H NMR of compound **1f** in d<sub>6</sub>-DMSO.



**Figure S23.** <sup>13</sup>C NMR of compound **1f** in CDCl<sub>3</sub>.

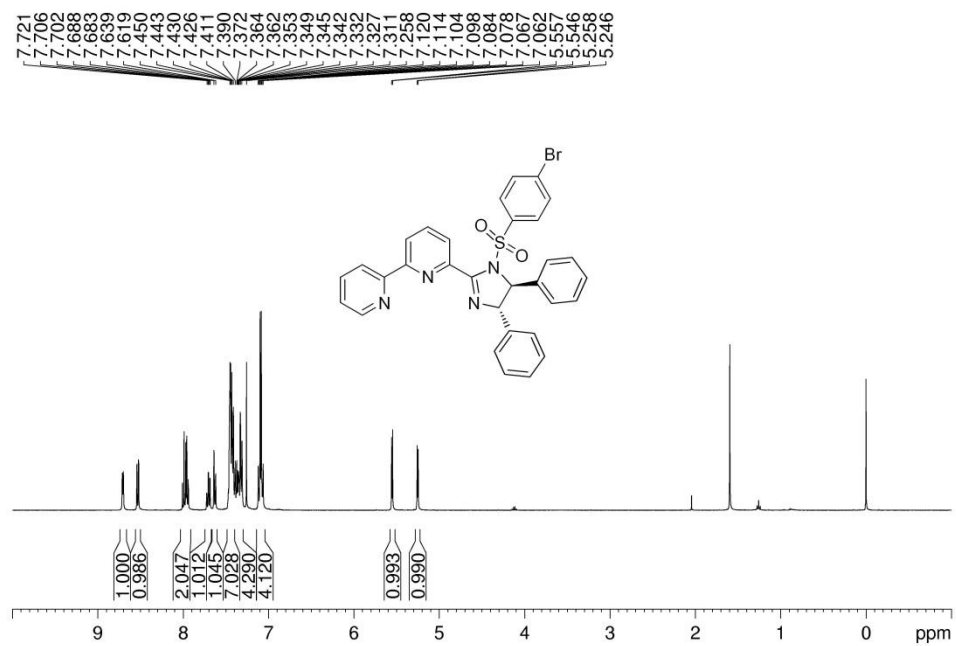


**Figure S24.** <sup>1</sup>H NMR of compound **1g** in *d*<sub>6</sub>-DMSO.

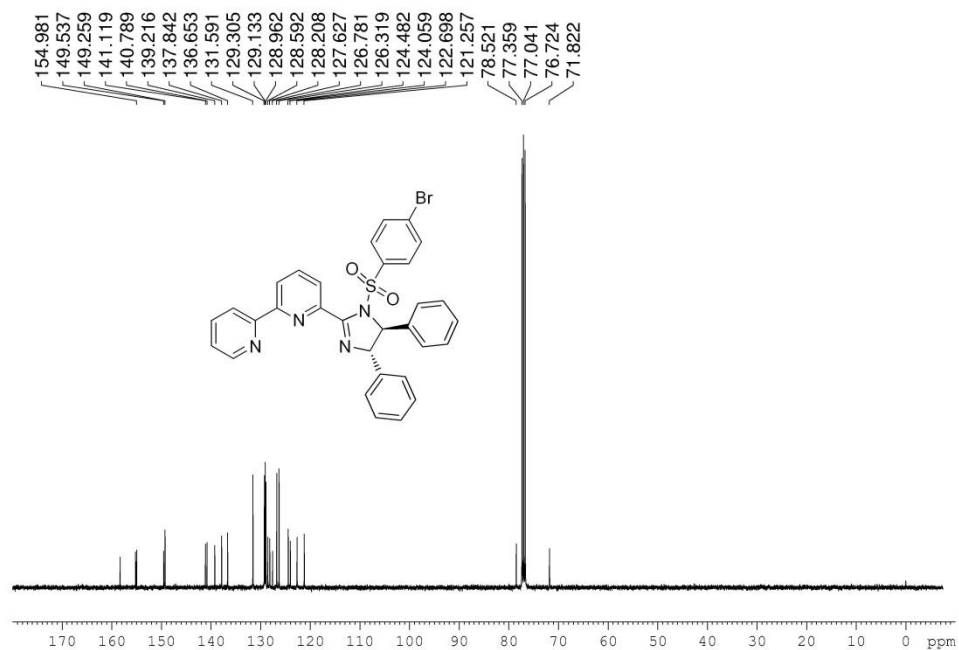


**Figure S25.** <sup>13</sup>C NMR of compound **1g** in *d*<sub>6</sub>-DMSO.

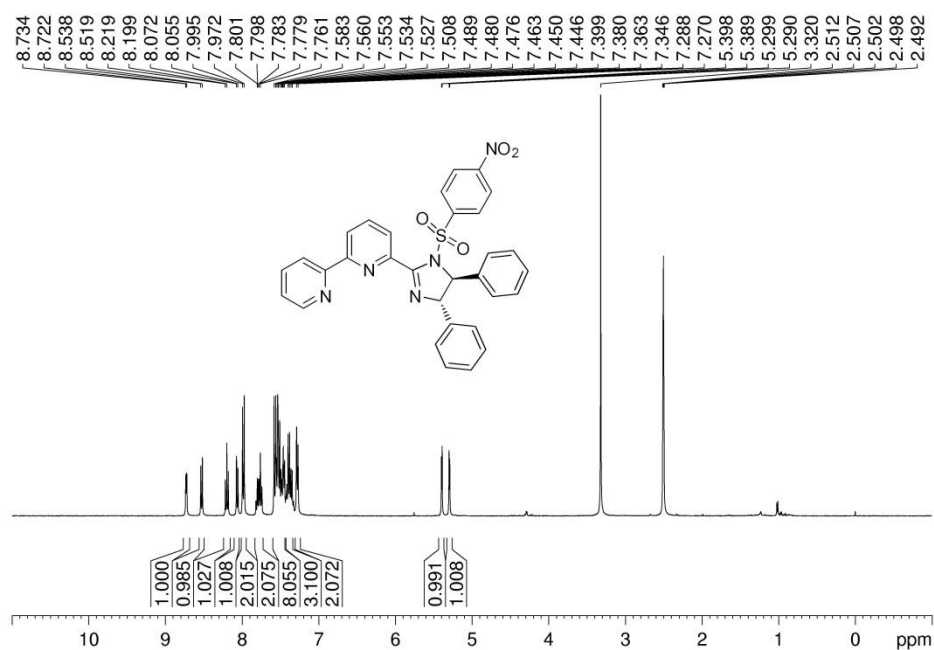




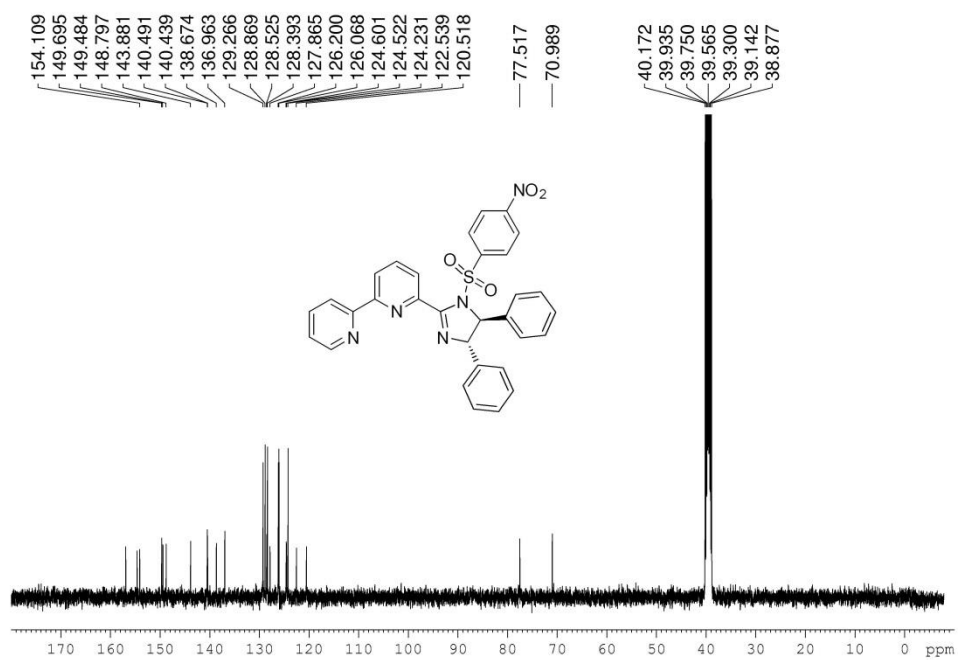
**Figure S26.** <sup>1</sup>H NMR of compound **1h** in CDCl<sub>3</sub>.



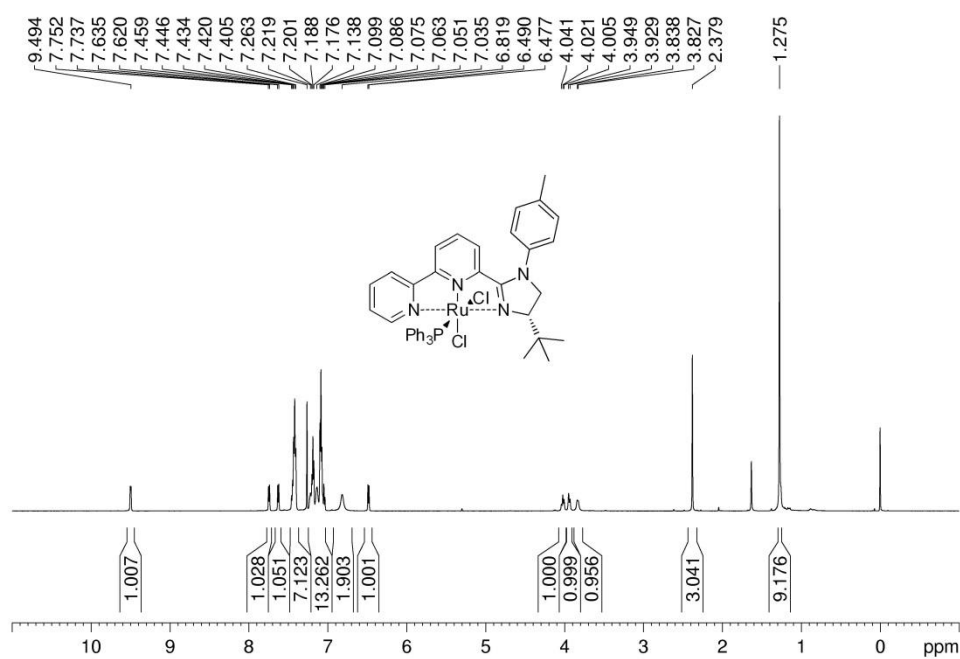
**Figure S27.** <sup>13</sup>C NMR of compound **1h** in CDCl<sub>3</sub>.



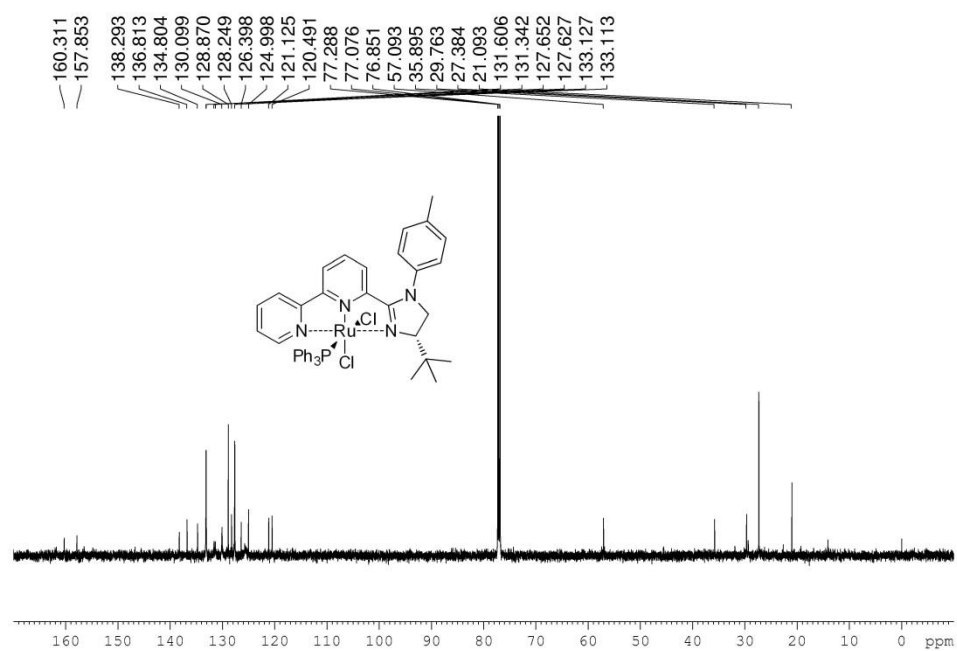
**Figure S28.** <sup>1</sup>H NMR of compound **1i** in *d*<sub>6</sub>-DMSO.



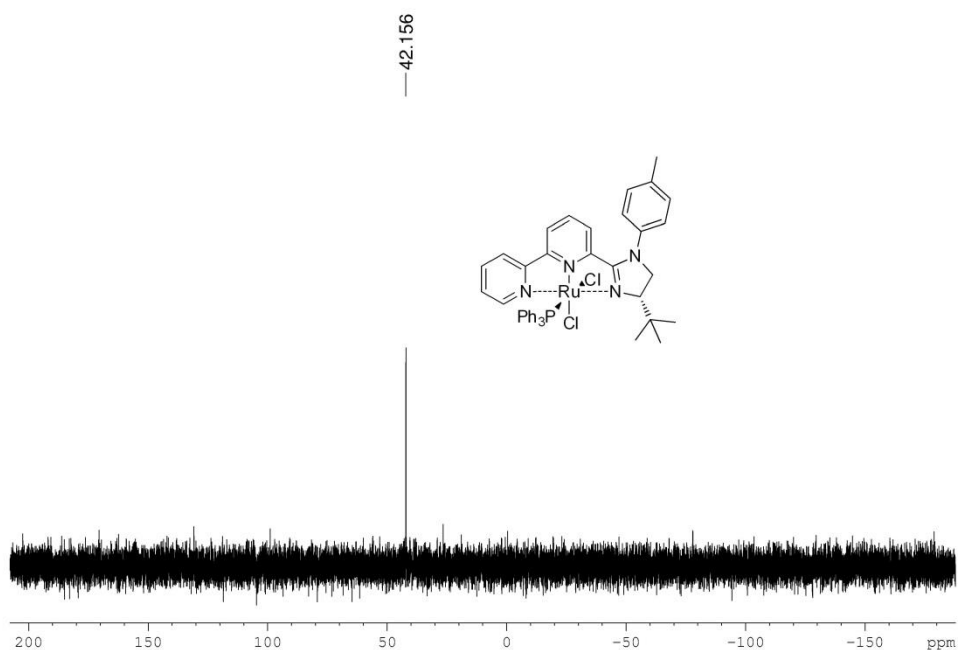
**Figure S29.** <sup>13</sup>C NMR of compound **1i** in *d*<sub>6</sub>-DMSO.



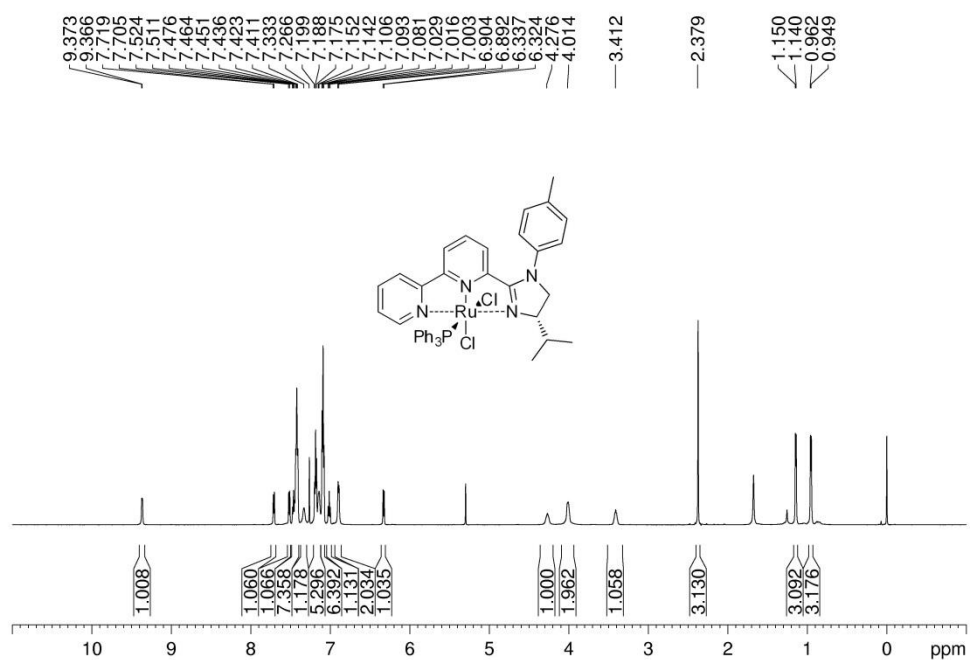
**Figure S30.** <sup>1</sup>H NMR of compound **2a** in CDCl<sub>3</sub>.



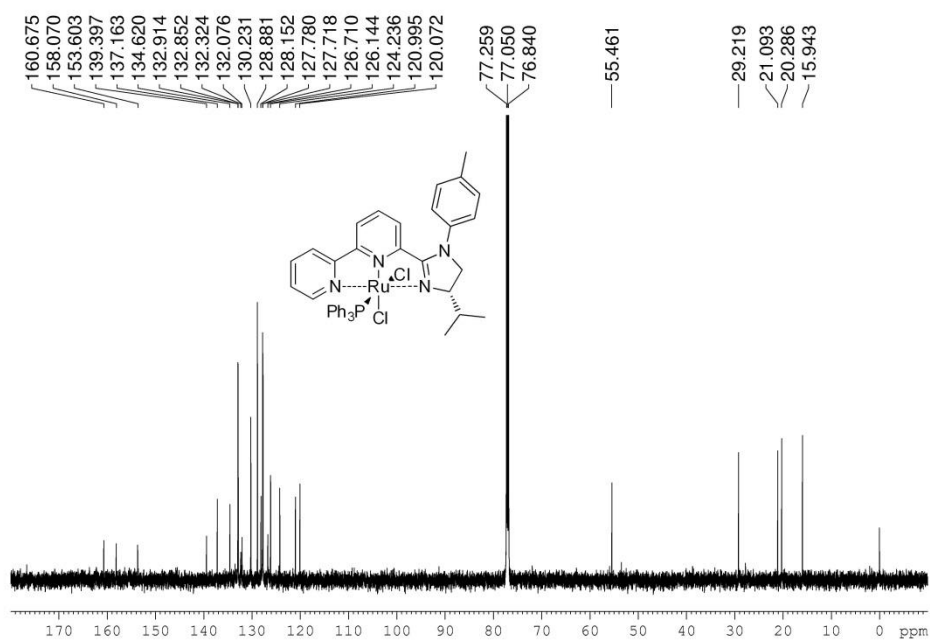
**Figure S31.** <sup>13</sup>C NMR of compound **2a** in CDCl<sub>3</sub>.



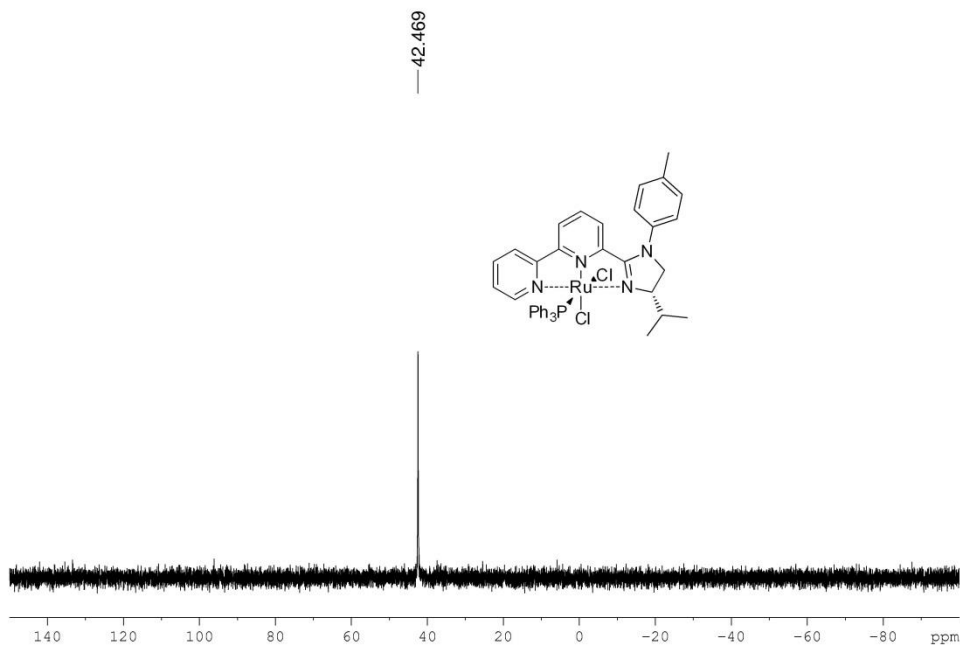
**Figure S32.**  $^{31}\text{P}$  NMR of compound **2a** in  $\text{CDCl}_3$ .



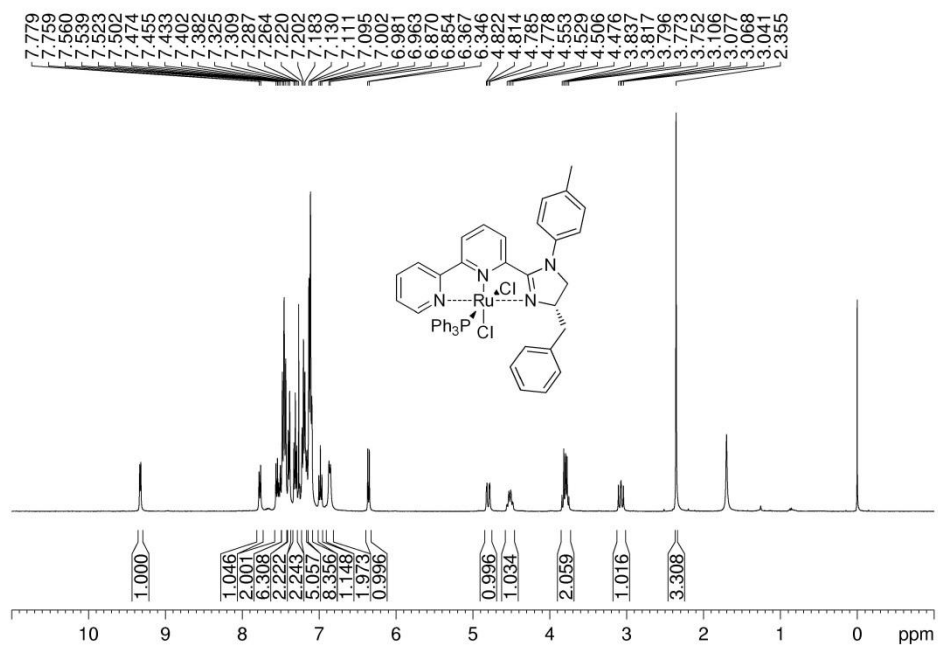
**Figure S33.**  $^1\text{H}$  NMR of compound **2b** in  $\text{CDCl}_3$ .



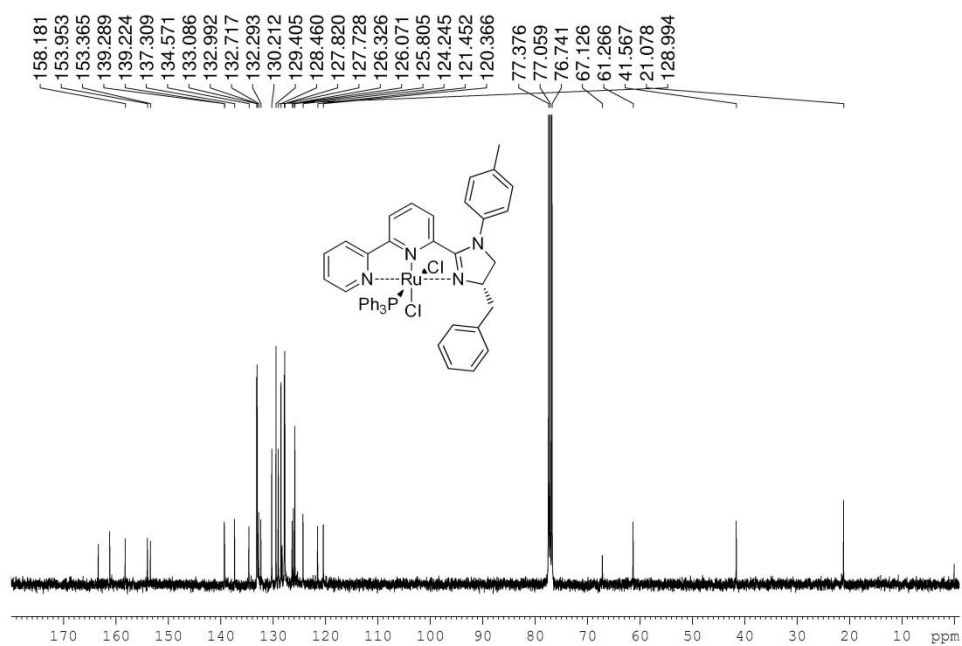
**Figure S34.** <sup>13</sup>C NMR of compound **2b** in CDCl<sub>3</sub>.



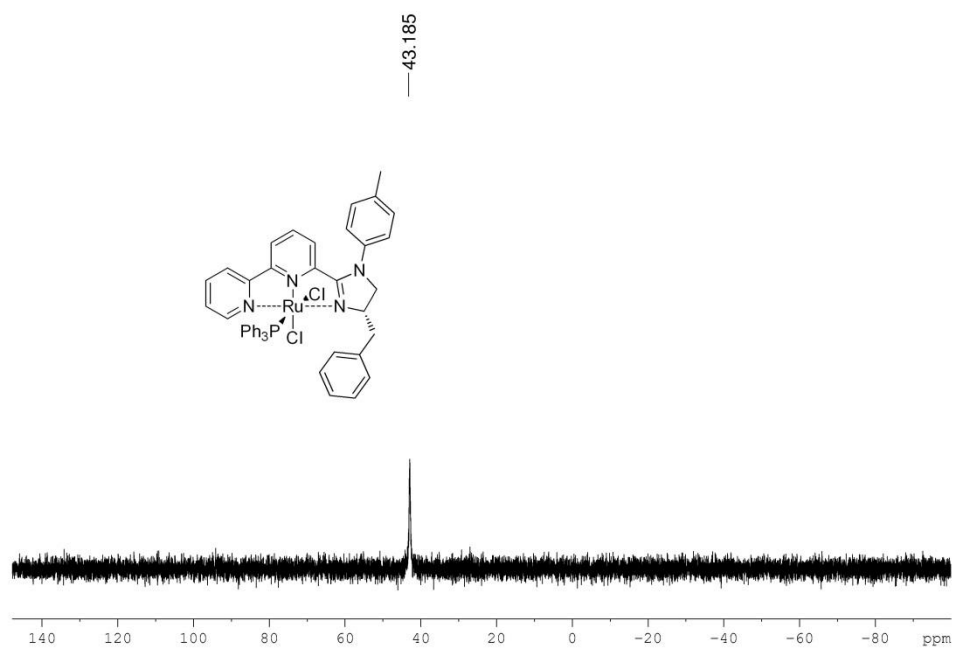
**Figure S35.** <sup>31</sup>P NMR of compound **2b** in CDCl<sub>3</sub>.



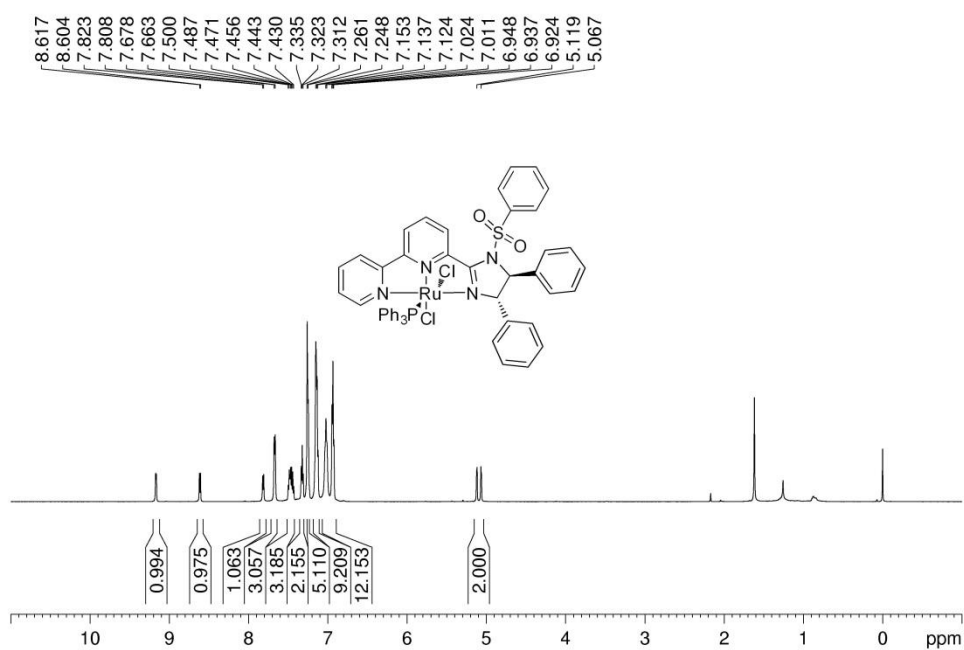
**Figure S36.** <sup>1</sup>H NMR of compound **2c** in CDCl<sub>3</sub>.



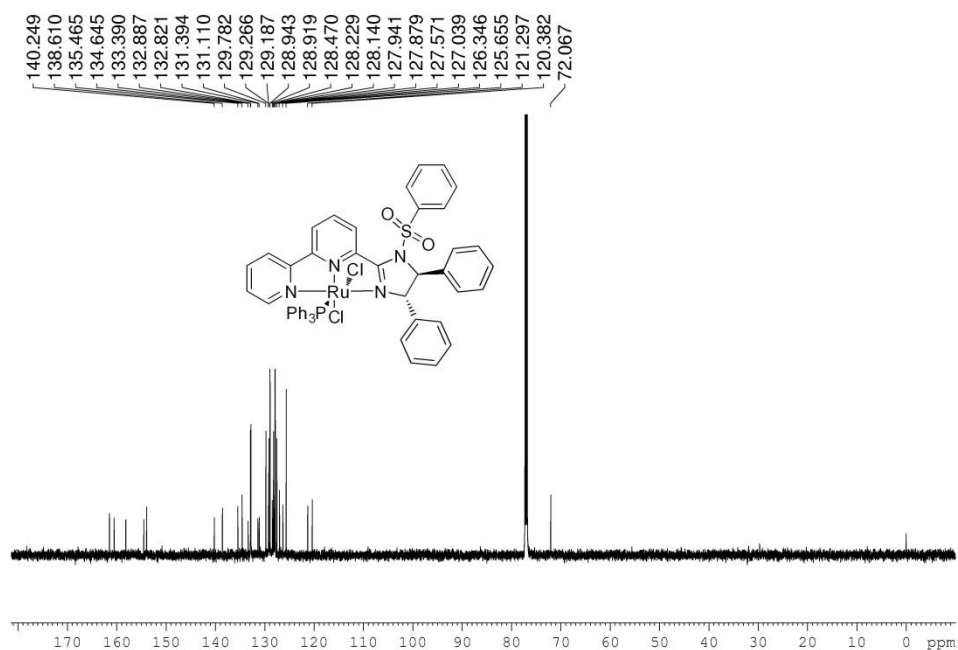
**Figure S37.** <sup>13</sup>C NMR of compound **2c** in CDCl<sub>3</sub>.



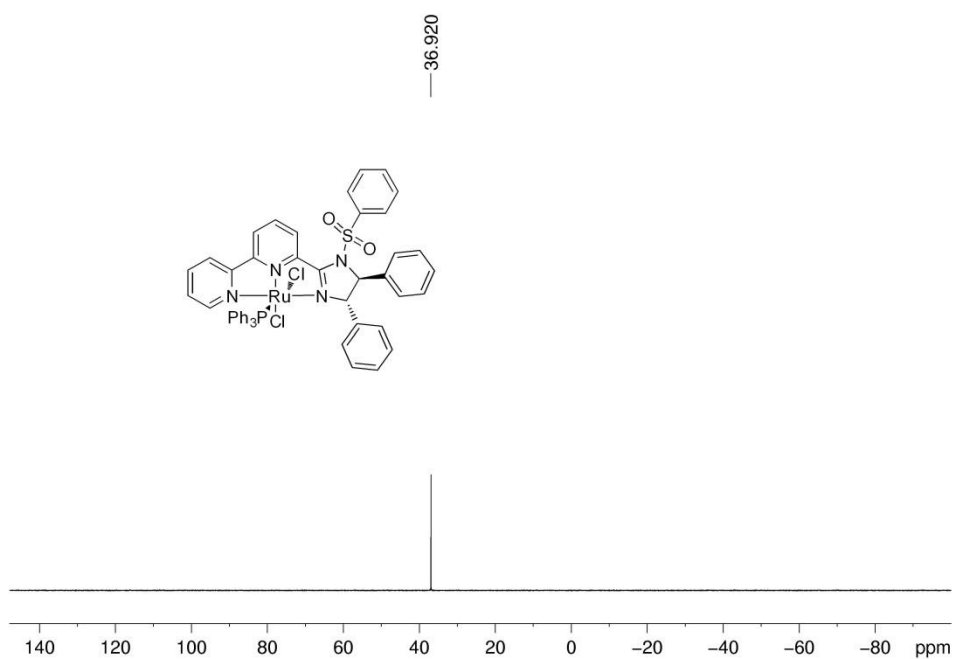
**Figure S38.**  $^{31}\text{P}$  NMR of compound **2c** in  $\text{CDCl}_3$ .



**Figure S39.**  $^1\text{H}$  NMR of compound **2d** in  $\text{CDCl}_3$ .

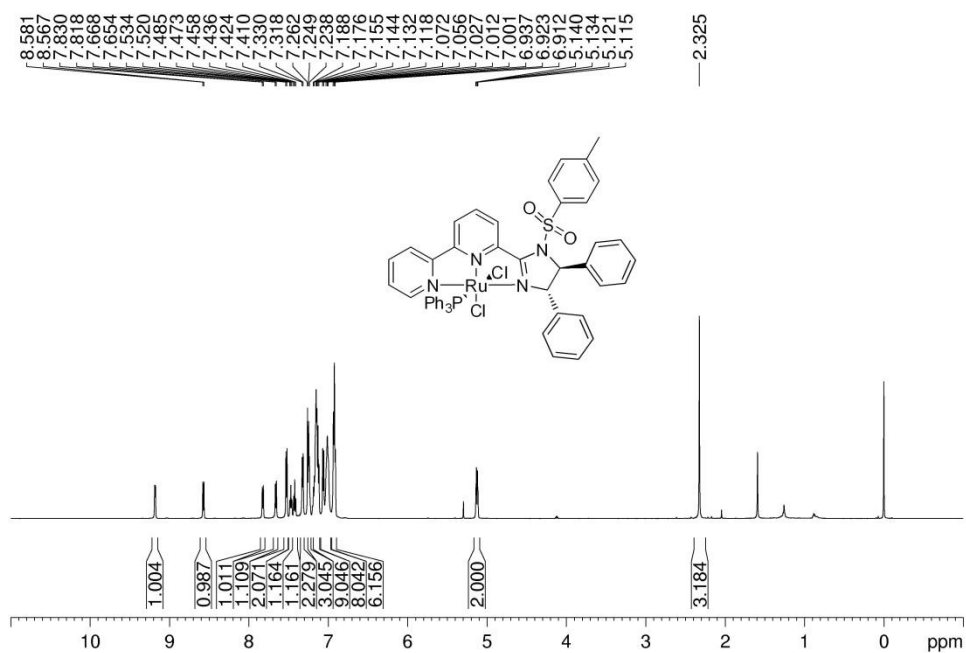


**Figure S40.** <sup>13</sup>C NMR of compound **2d** in CDCl<sub>3</sub>.

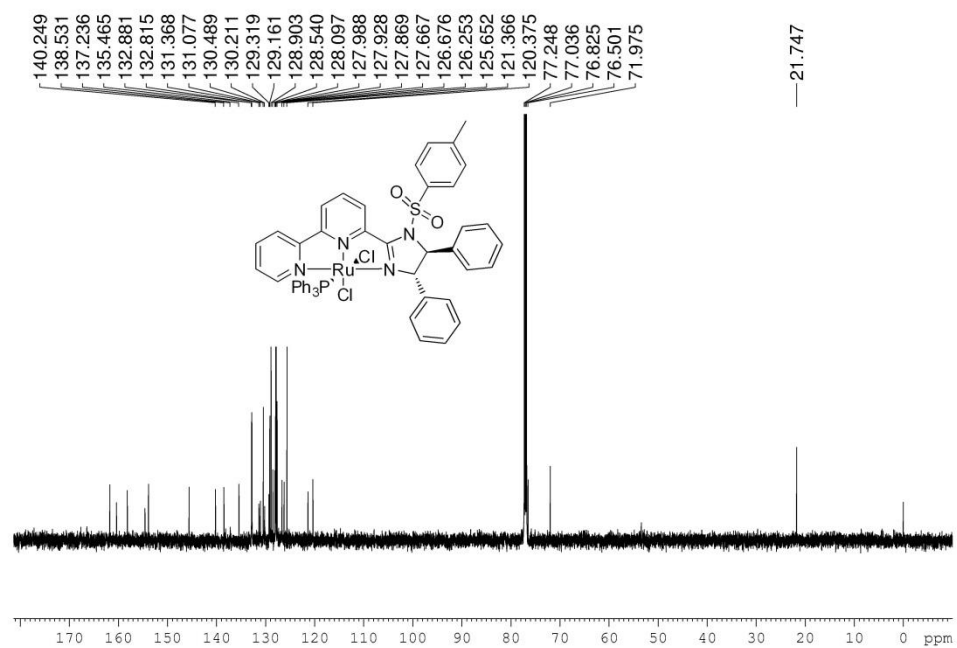


**Figure S41.** <sup>31</sup>P NMR of compound **2d** in CDCl<sub>3</sub>.

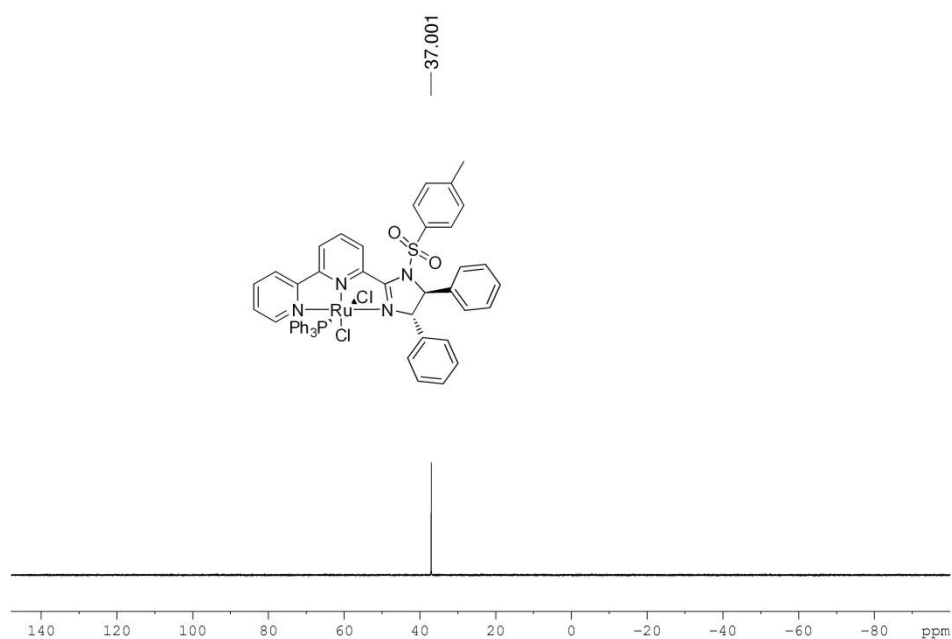




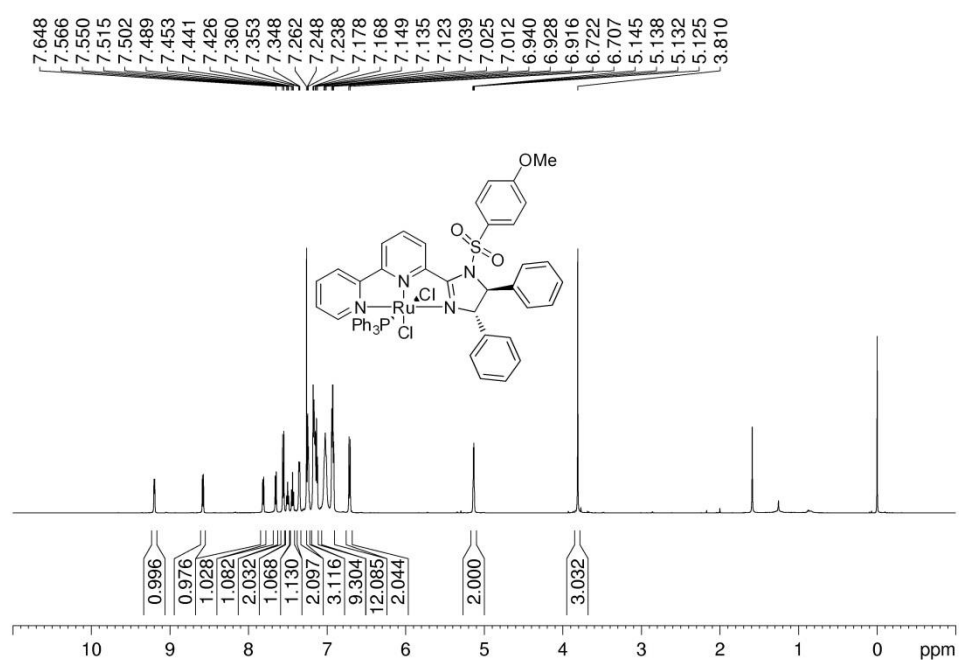
**Figure S42.** <sup>1</sup>H NMR of compound **2e** in CDCl<sub>3</sub>.



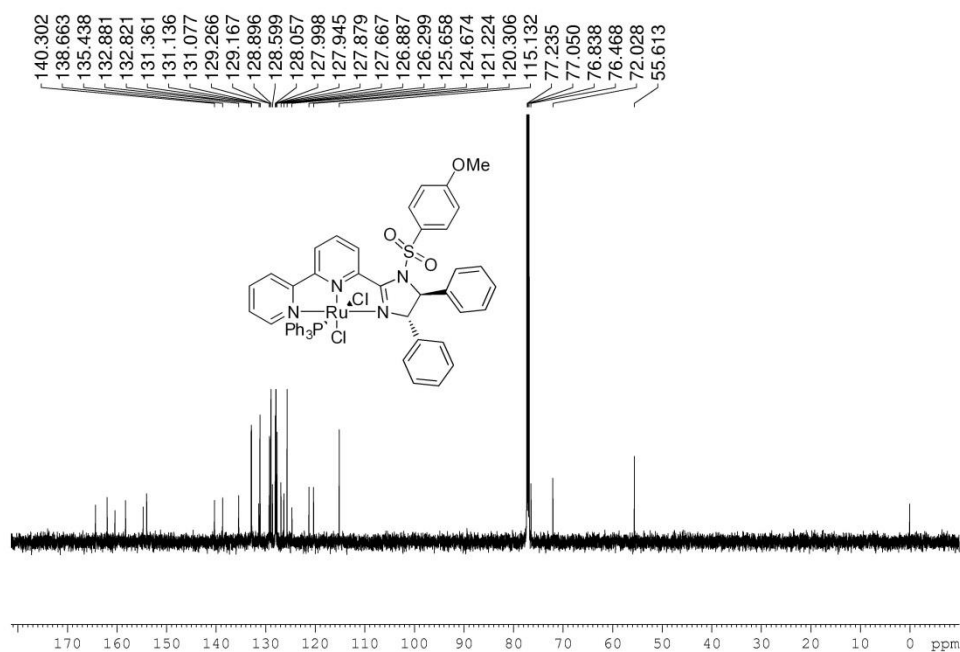
**Figure S43.** <sup>13</sup>C NMR of compound **2e** in CDCl<sub>3</sub>.



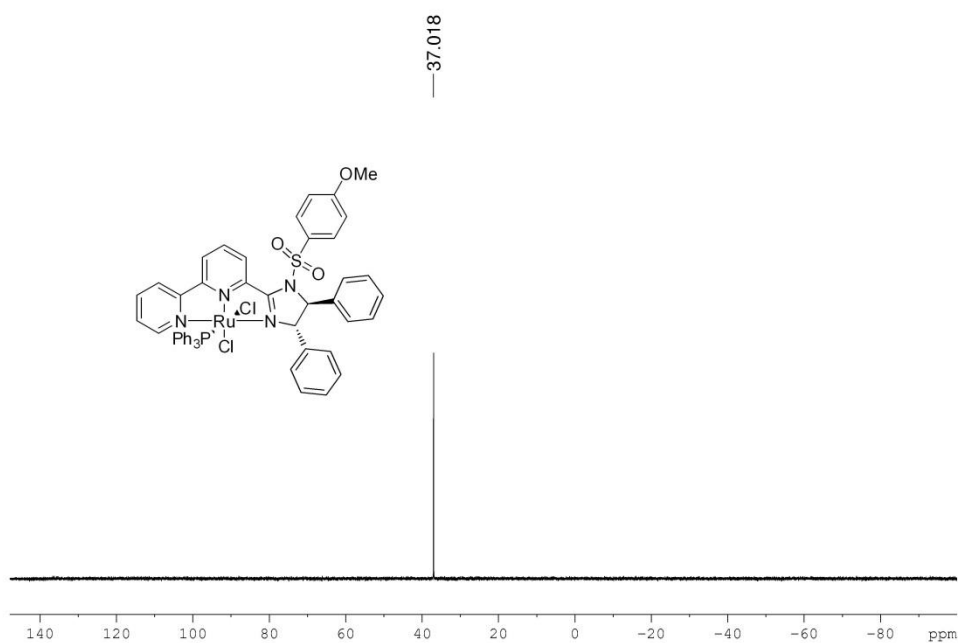
**Figure S44.**  $^{31}\text{P}$  NMR of compound **2e** in  $\text{CDCl}_3$ .



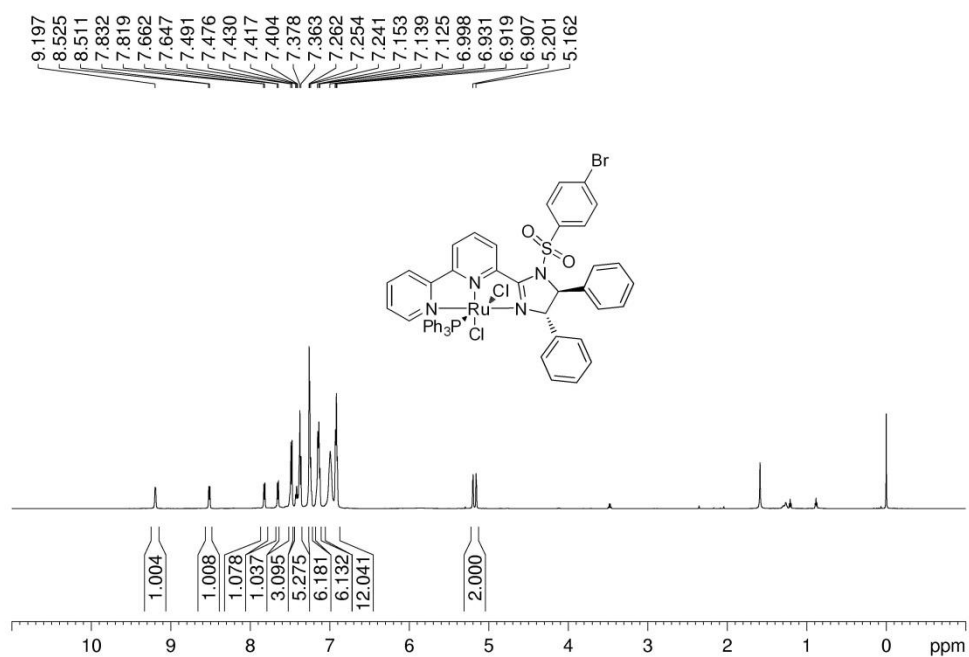
**Figure S45.**  $^1\text{H}$  NMR of compound **2f** in  $\text{CDCl}_3$ .



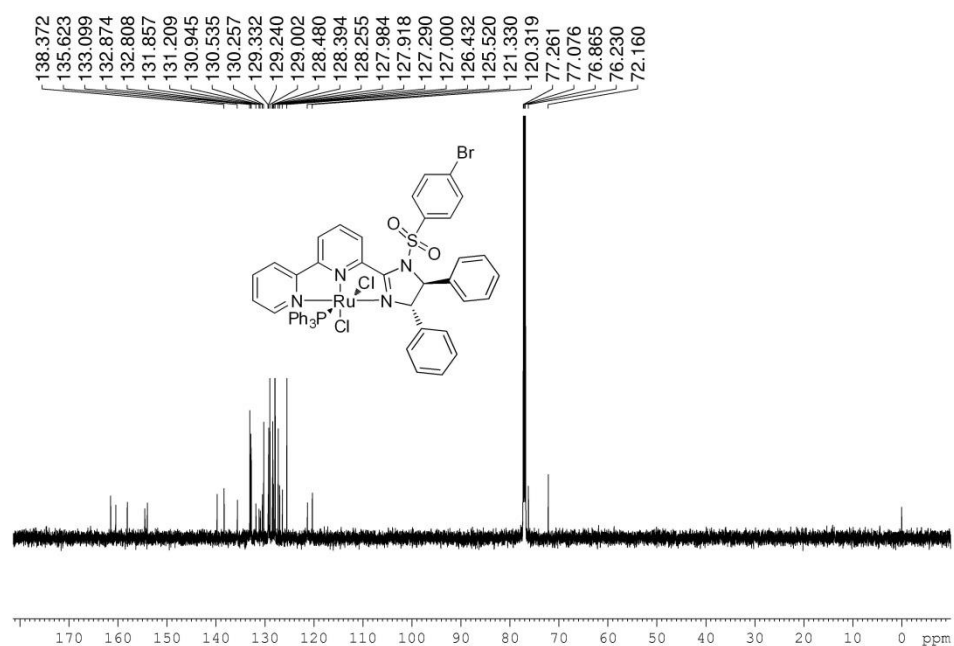
**Figure S46.**  $^{13}\text{C}$  NMR of compound **2f** in  $\text{CDCl}_3$ .



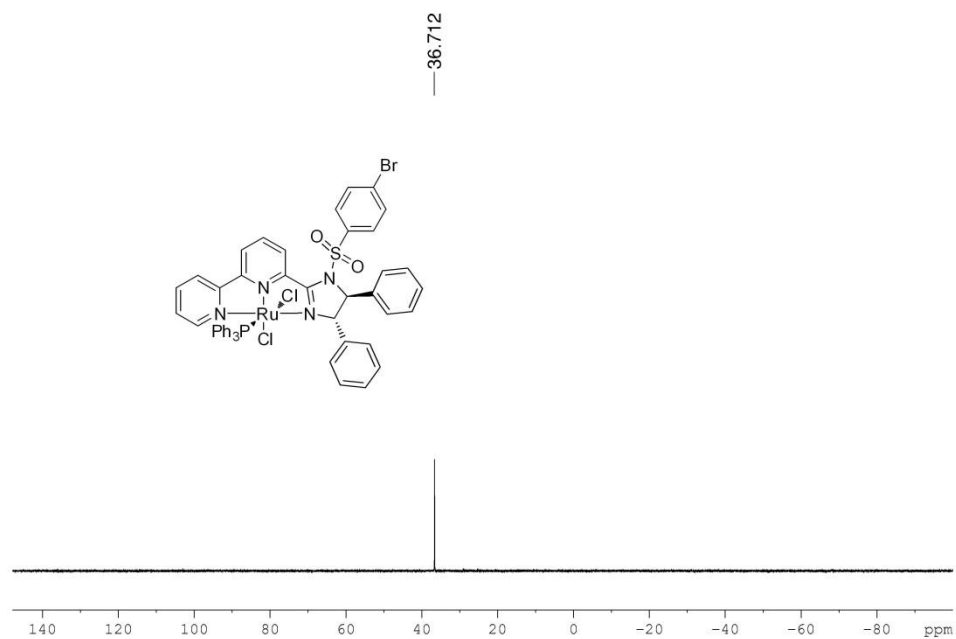
**Figure S47.**  $^{31}\text{P}$  NMR of compound **2f** in  $\text{CDCl}_3$ .



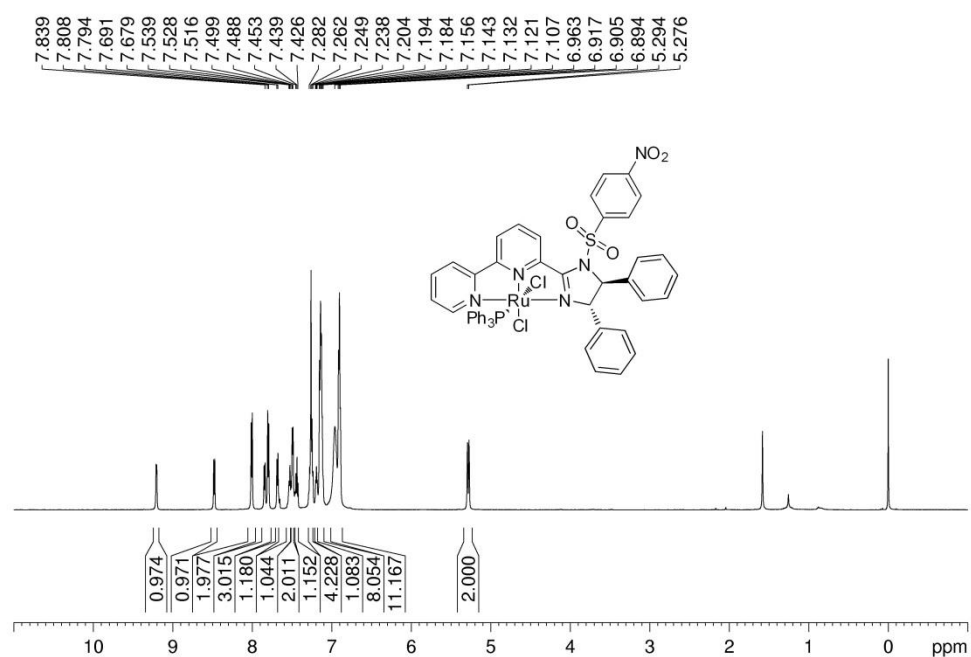
**Figure S48.** <sup>1</sup>H NMR of compound **2g** in CDCl<sub>3</sub>.



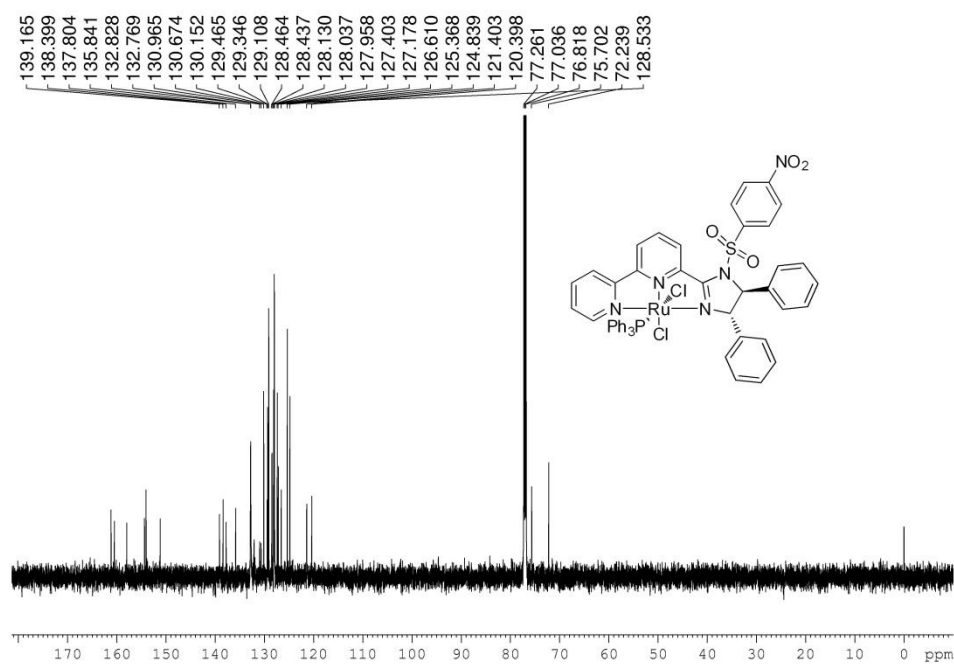
**Figure S49.** <sup>13</sup>C NMR of compound **2g** in CDCl<sub>3</sub>.



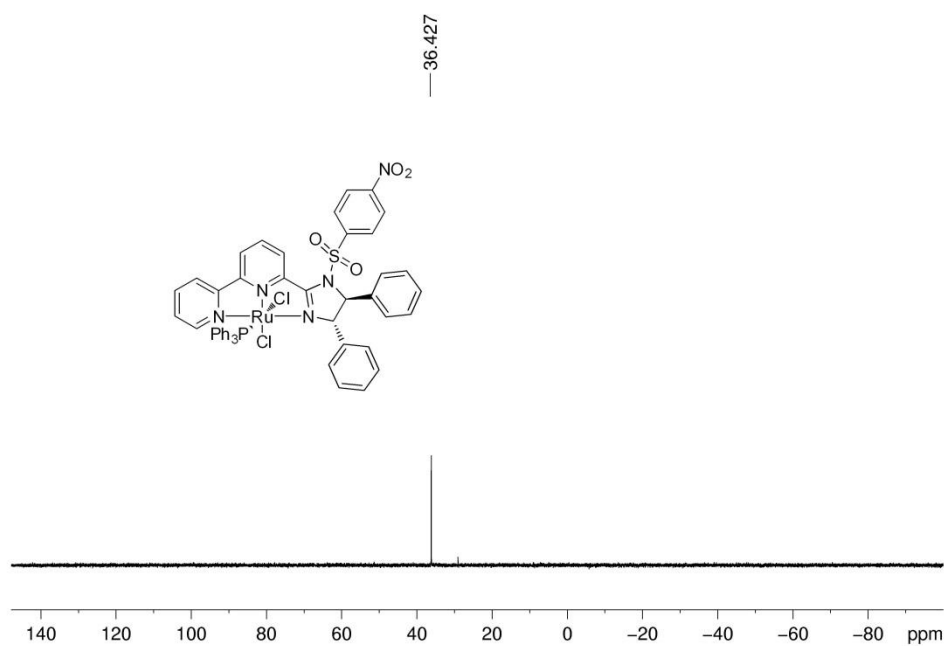
**Figure S50.**  $^{31}\text{P}$  NMR of compound **2g** in  $\text{CDCl}_3$ .



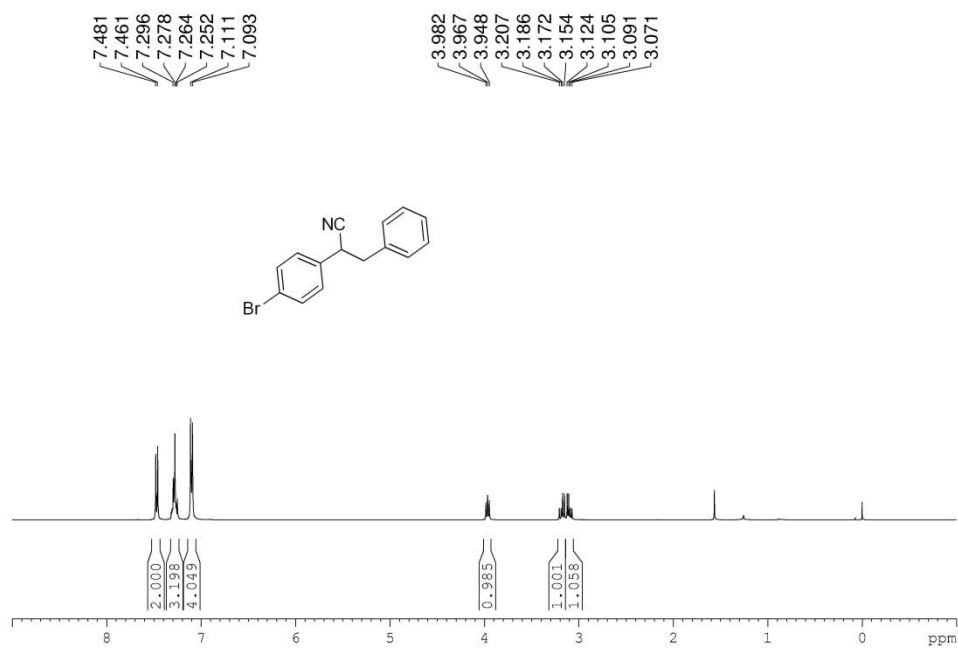
**Figure S51.**  $^1\text{H}$  NMR of compound **2h** in  $\text{CDCl}_3$ .



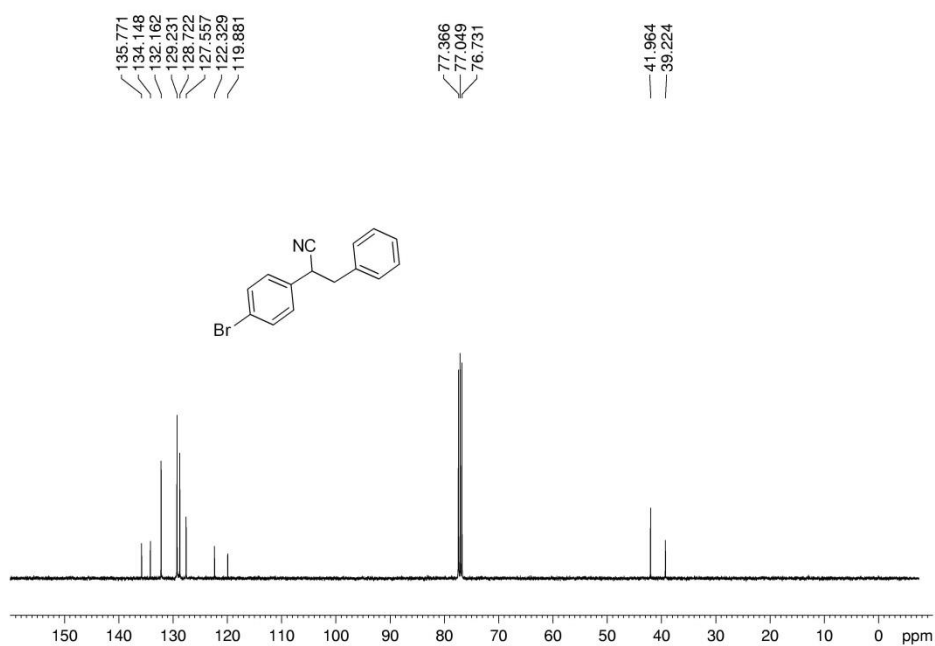
**Figure S52.** <sup>13</sup>C NMR of compound **2h** in CDCl<sub>3</sub>.



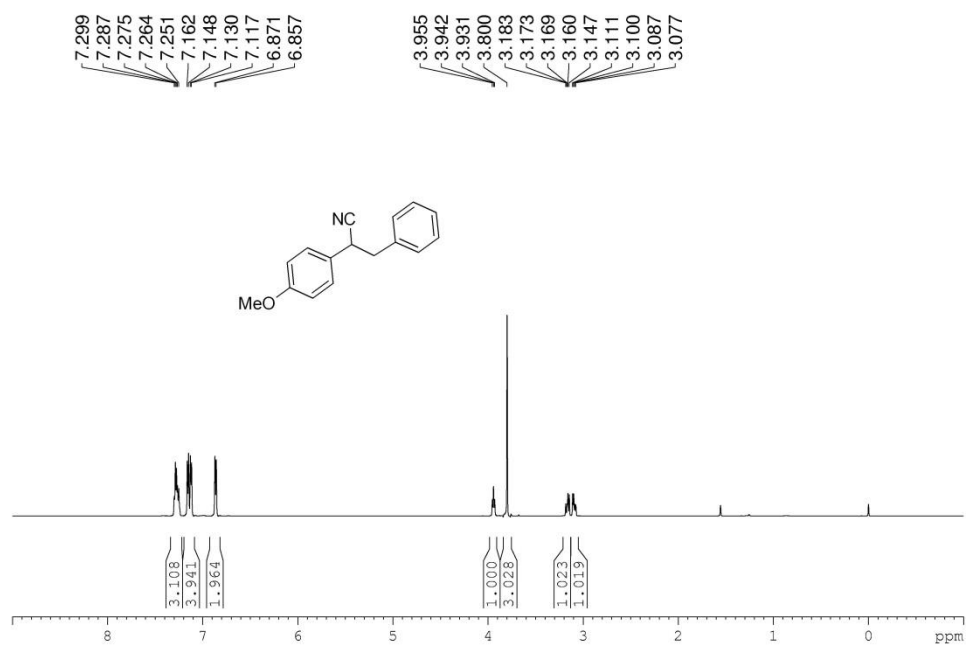
**Figure S53.** <sup>31</sup>P NMR of compound **2h** in CDCl<sub>3</sub>.



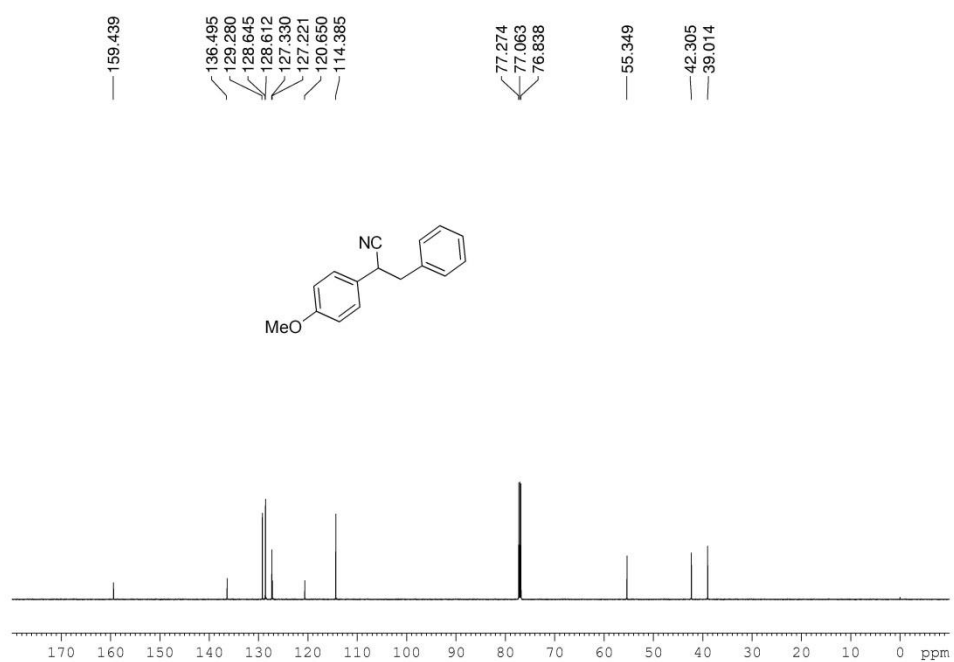
**Figure S54.** <sup>1</sup>H NMR of compound **5a** in CDCl<sub>3</sub>.



**Figure S55.** <sup>13</sup>C NMR of compound **5a** in CDCl<sub>3</sub>.

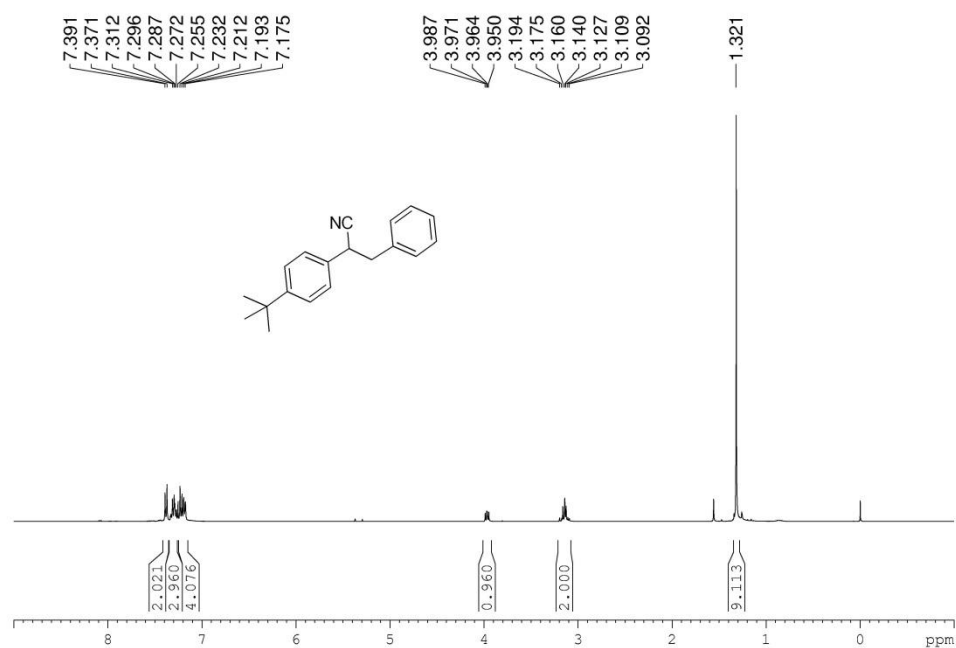


**Figure S56.** <sup>1</sup>H NMR of compound **5b** in CDCl<sub>3</sub>.

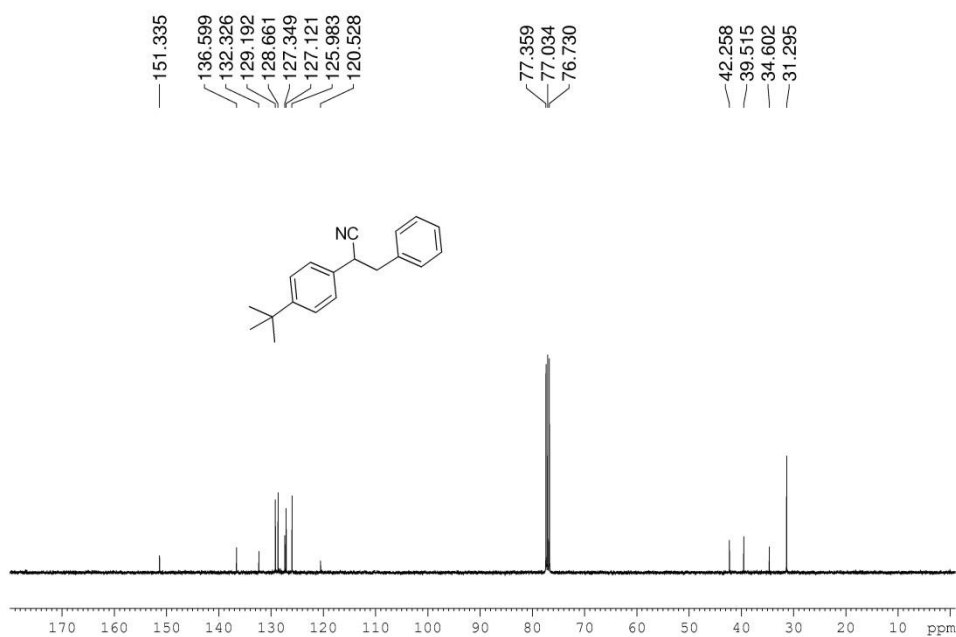


**Figure S57.** <sup>13</sup>C NMR of compound **5b** in CDCl<sub>3</sub>.





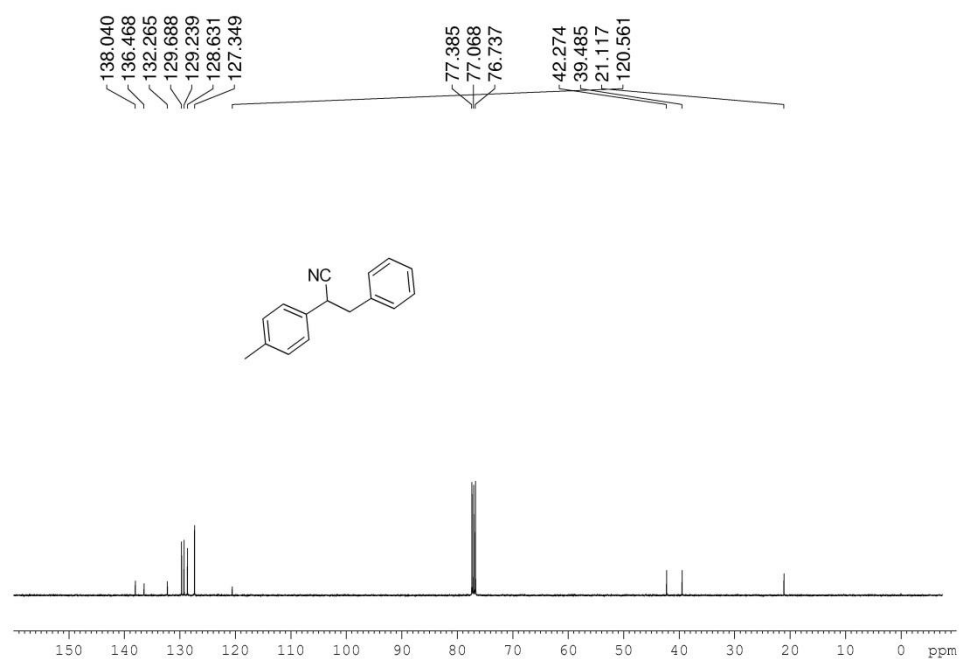
**Figure S58.** <sup>1</sup>H NMR of compound **5c** in CDCl<sub>3</sub>.



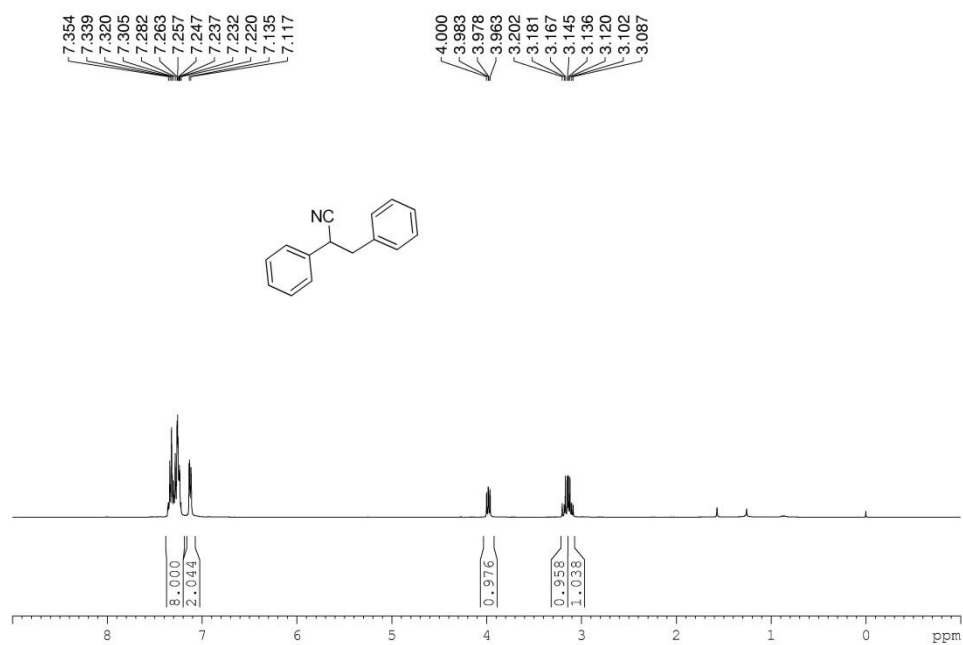
**Figure S59.** <sup>13</sup>C NMR of compound **5c** in CDCl<sub>3</sub>.



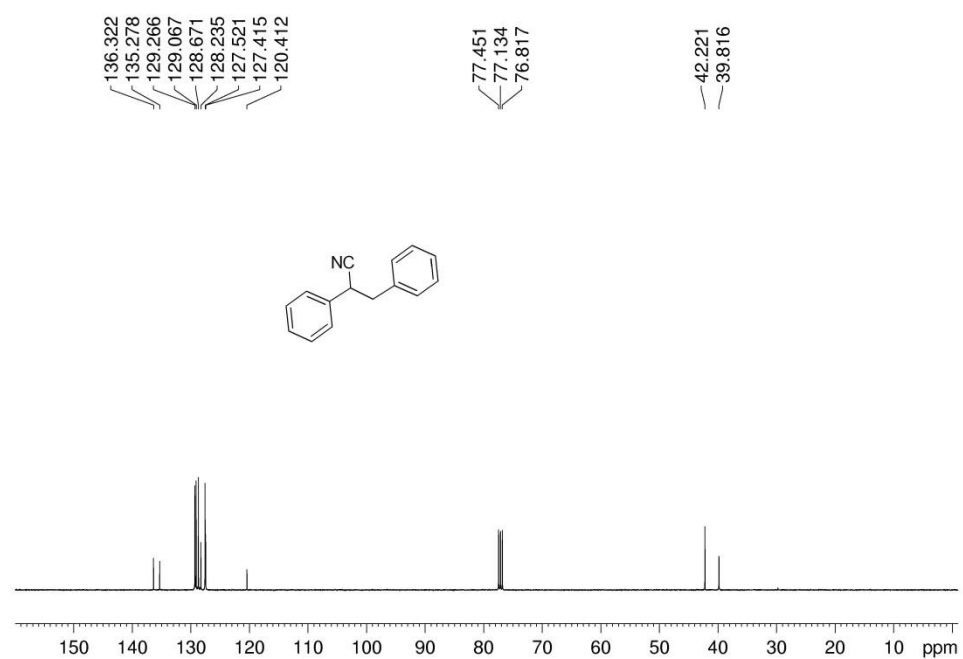
**Figure S60.** <sup>1</sup>H NMR of compound **5d** in CDCl<sub>3</sub>.



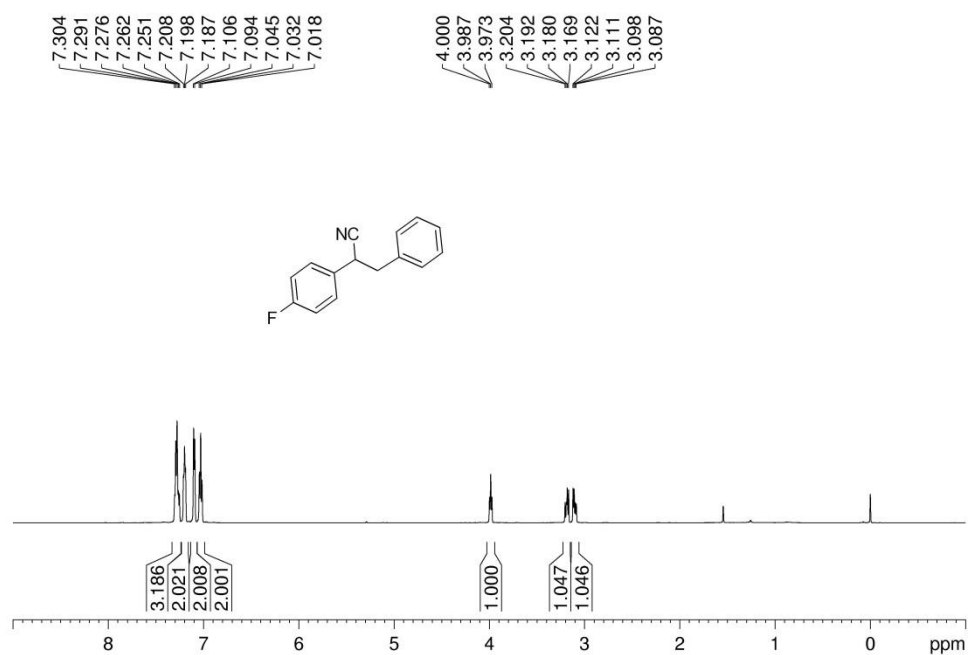
**Figure S61.** <sup>13</sup>C NMR of compound **5d** in CDCl<sub>3</sub>.



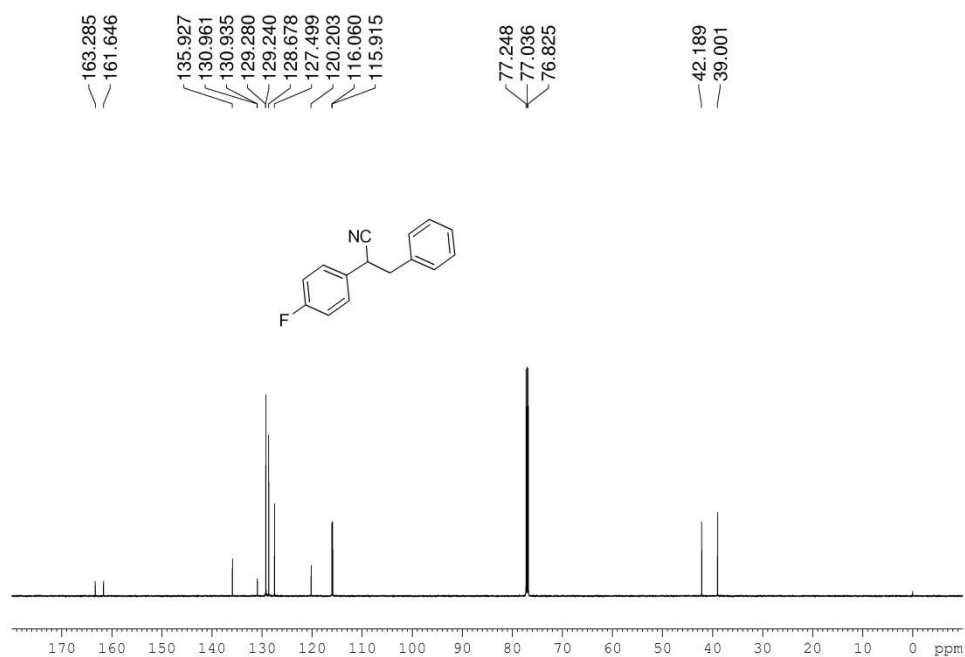
**Figure S62.** <sup>1</sup>H NMR of compound **5e** in CDCl<sub>3</sub>.



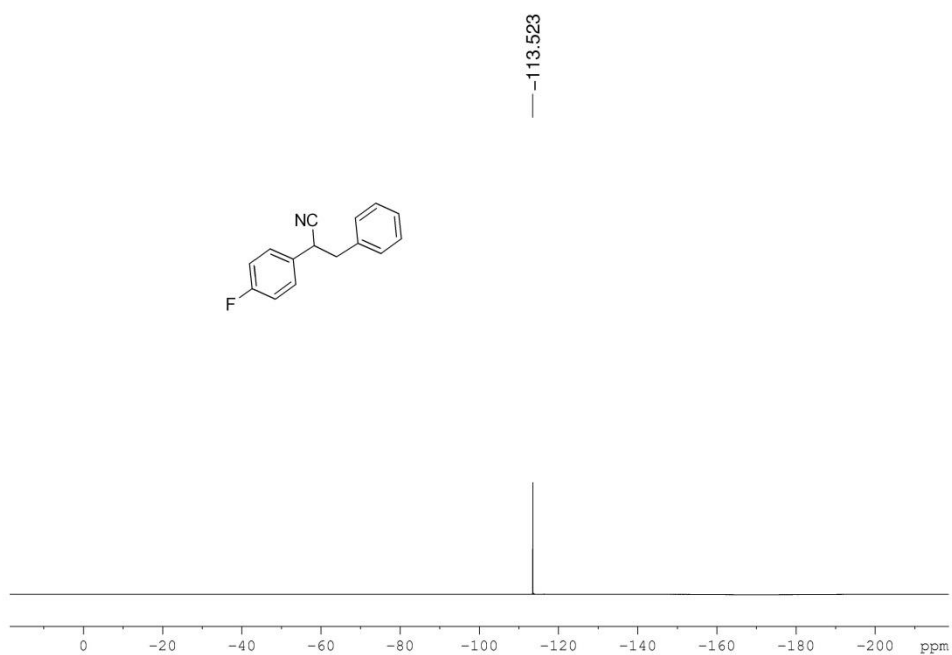
**Figure S63.** <sup>13</sup>C NMR of compound **5e** in CDCl<sub>3</sub>.



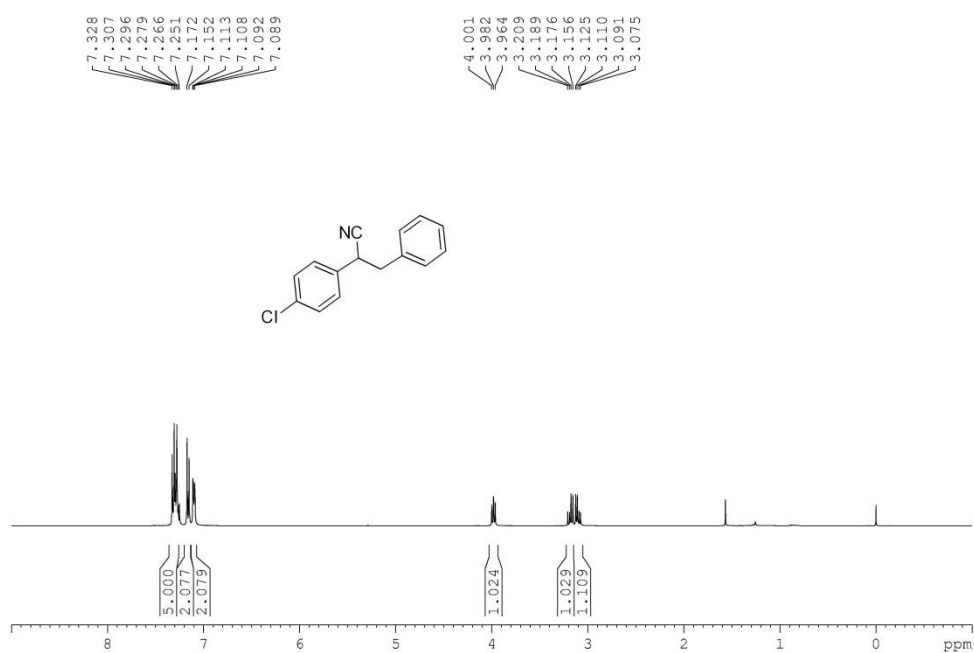
**Figure S64.** <sup>1</sup>H NMR of compound **5f** in CDCl<sub>3</sub>.



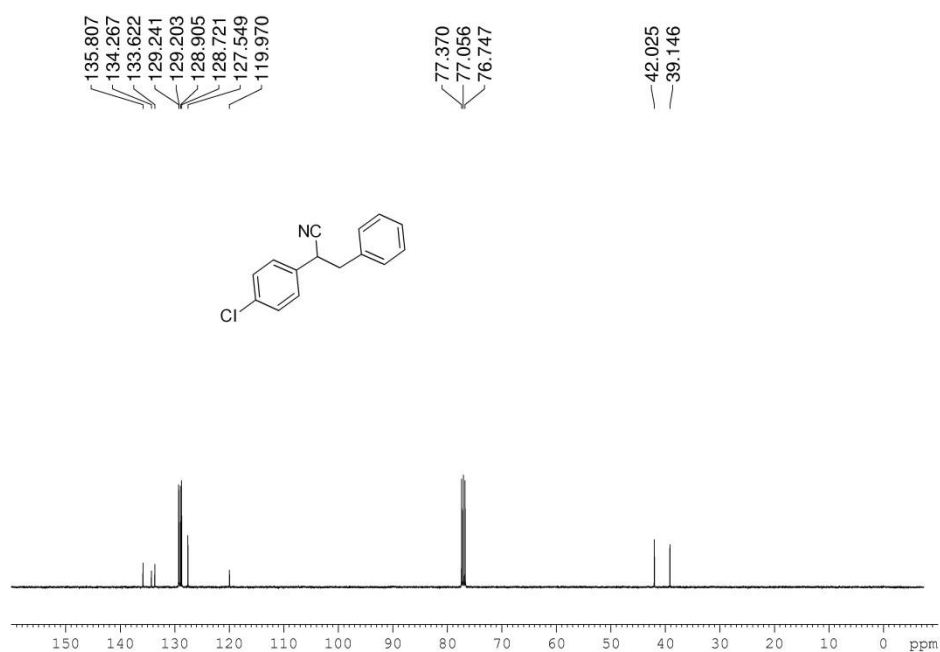
**Figure S65.** <sup>13</sup>C NMR of compound **5f** in CDCl<sub>3</sub>.



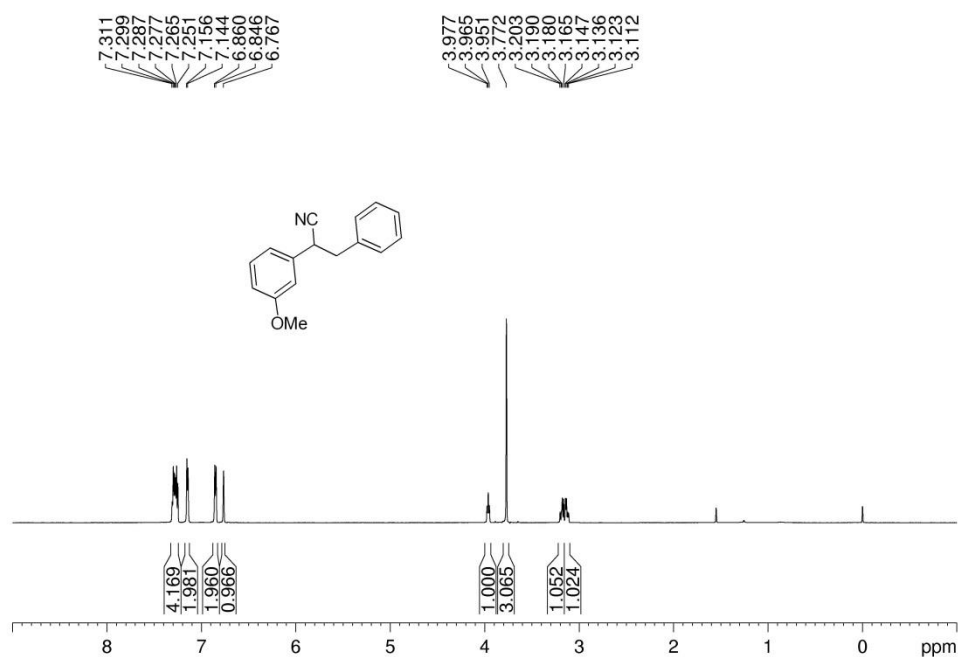
**Figure S66.**  $^{19}\text{F}$  NMR of compound **5f** in CDCl<sub>3</sub>.



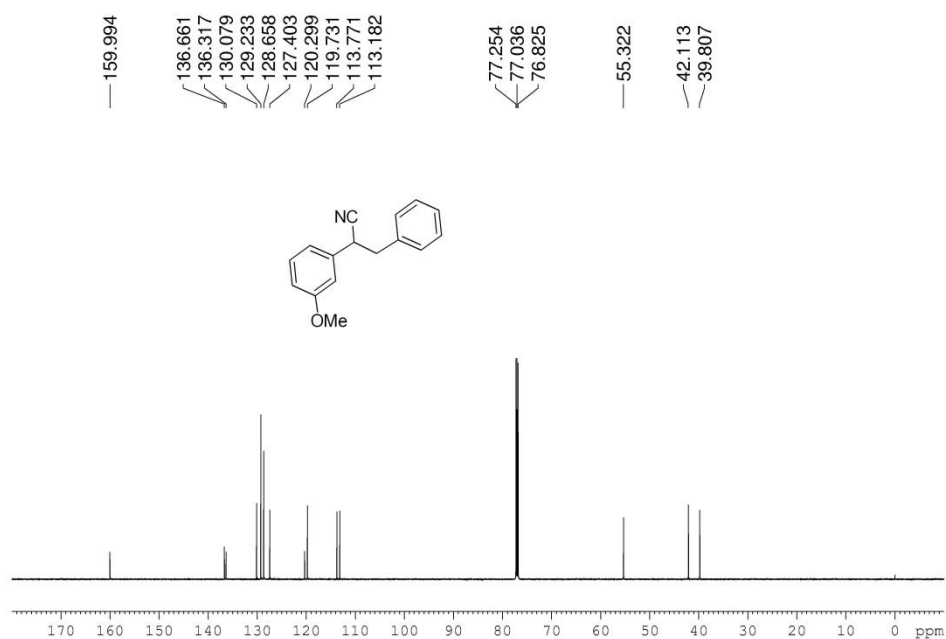
**Figure S67.**  $^1\text{H}$  NMR of compound **5g** in CDCl<sub>3</sub>.



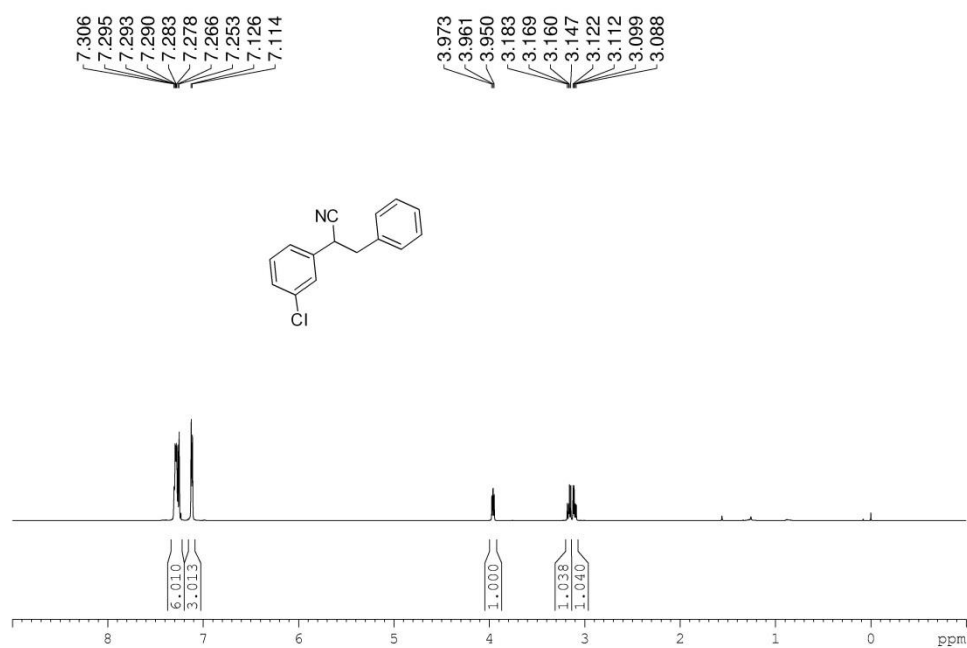
**Figure S68.** <sup>13</sup>C NMR of compound **5g** in CDCl<sub>3</sub>.



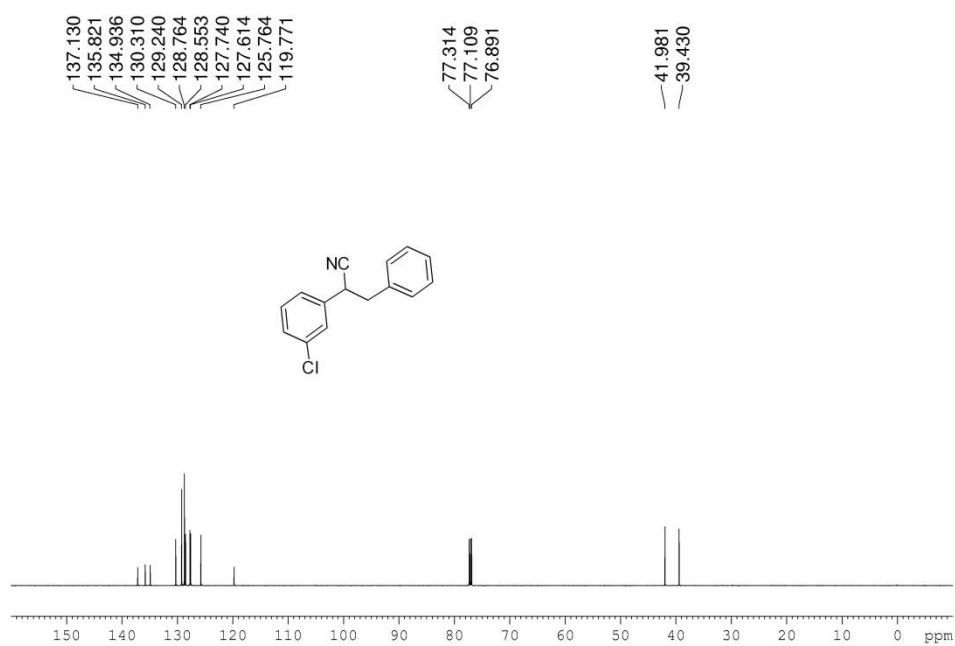
**Figure S69.** <sup>1</sup>H NMR of compound **5h** in CDCl<sub>3</sub>.



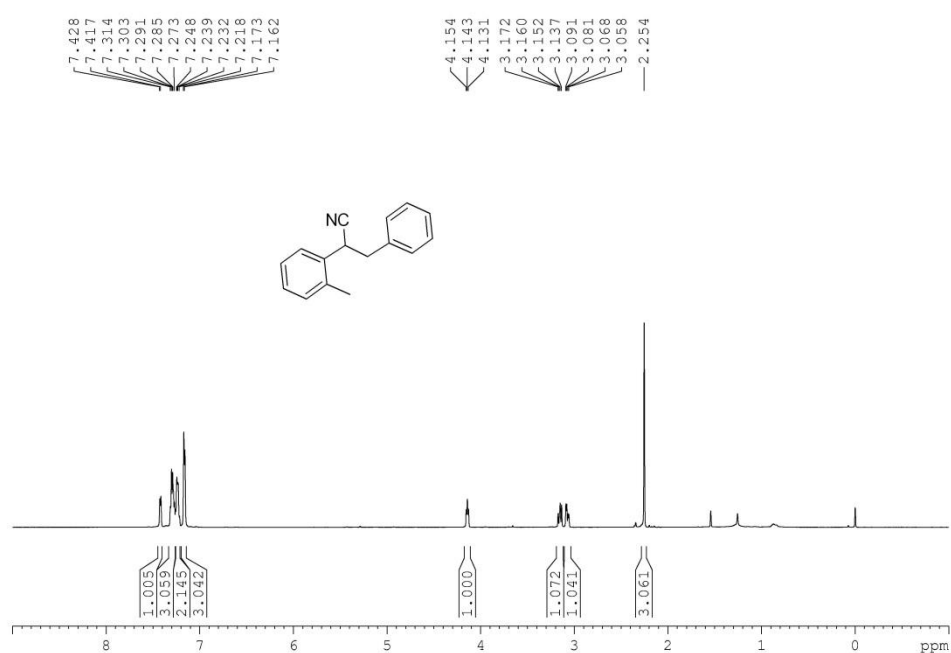
**Figure S70.** <sup>13</sup>C NMR of compound **5h** in CDCl<sub>3</sub>.



**Figure S71.** <sup>1</sup>H NMR of compound **5i** in CDCl<sub>3</sub>.

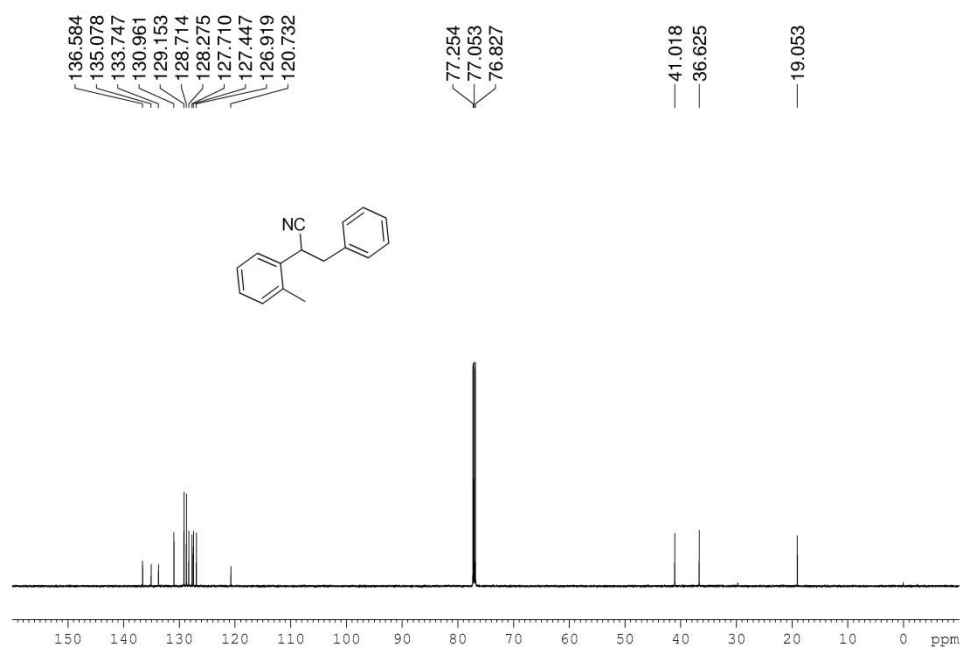


**Figure S72.** <sup>13</sup>C NMR of compound **5i** in CDCl<sub>3</sub>.

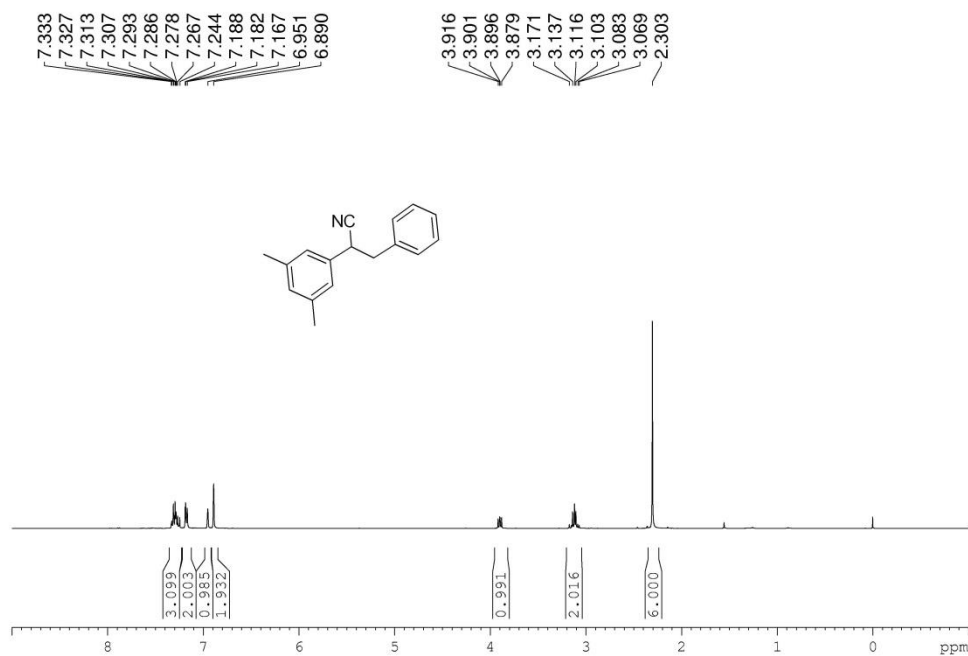


**Figure S73.** <sup>1</sup>H NMR of compound **5j** in CDCl<sub>3</sub>.

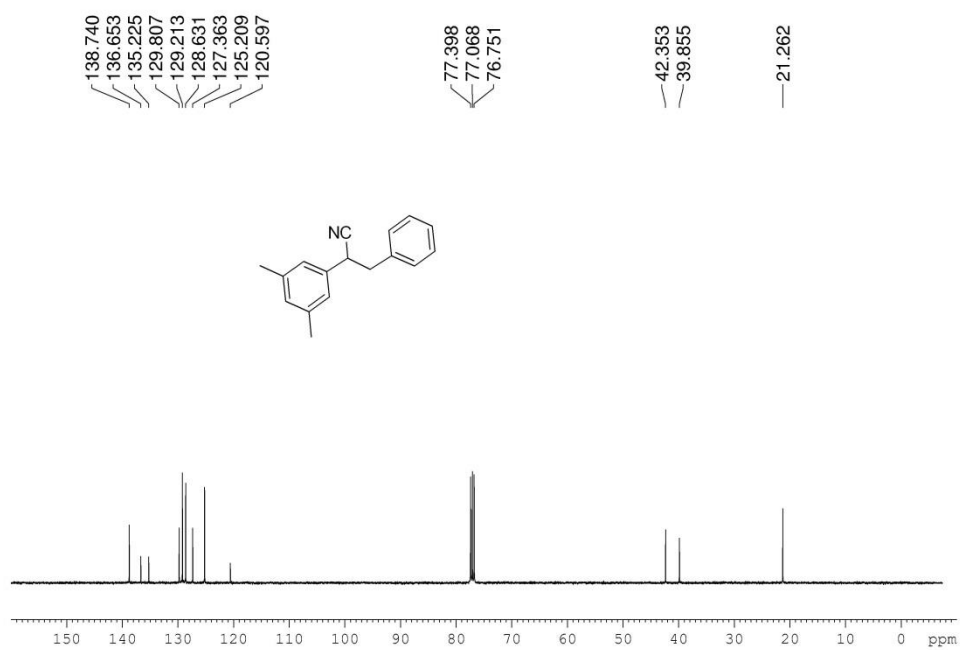




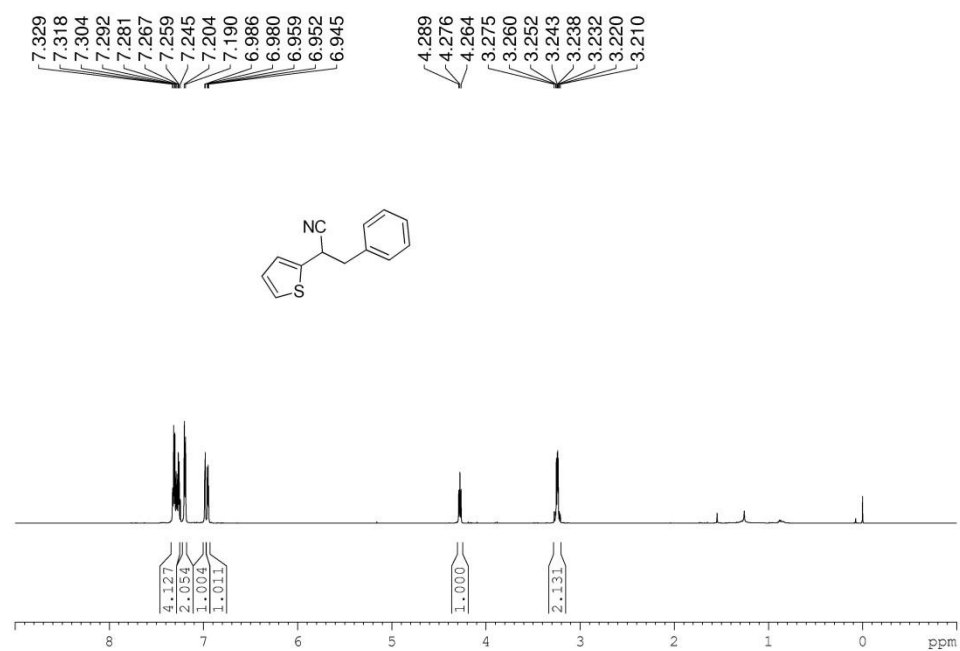
**Figure S74.**  $^{13}\text{C}$  NMR of compound **5j** in  $\text{CDCl}_3$ .



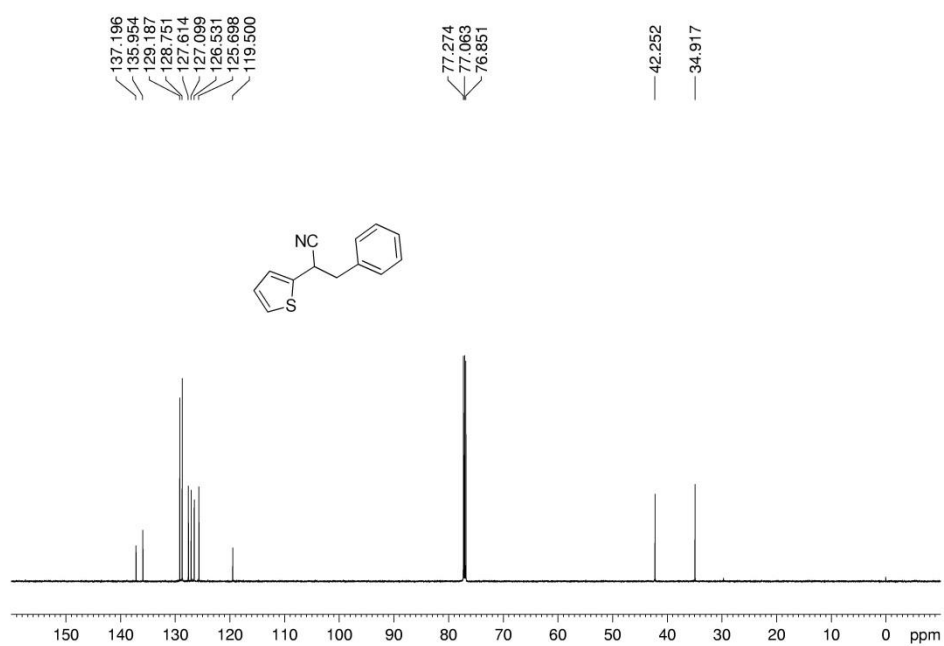
**Figure S75.**  $^1\text{H}$  NMR of compound **5k** in  $\text{CDCl}_3$ .



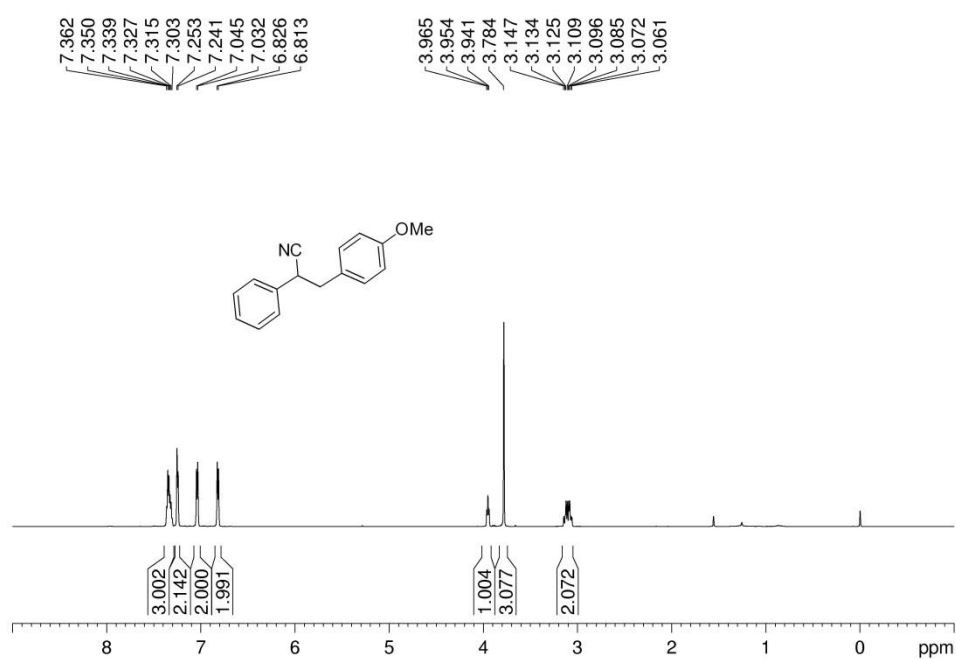
**Figure S76.** <sup>13</sup>C NMR of compound **5k** in CDCl<sub>3</sub>.



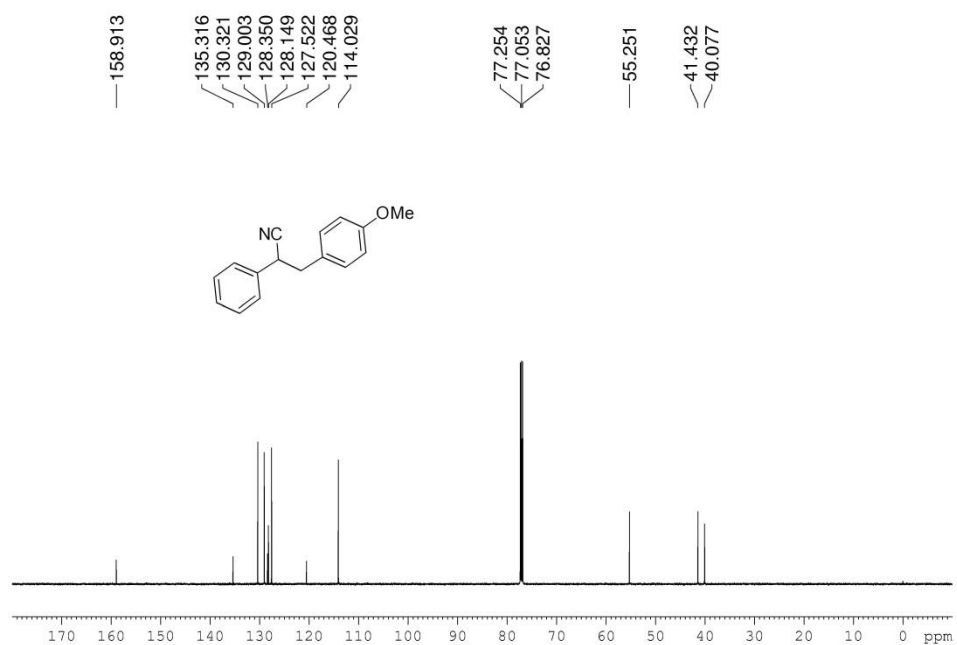
**Figure S77.** <sup>1</sup>H NMR of compound **5l** in CDCl<sub>3</sub>.



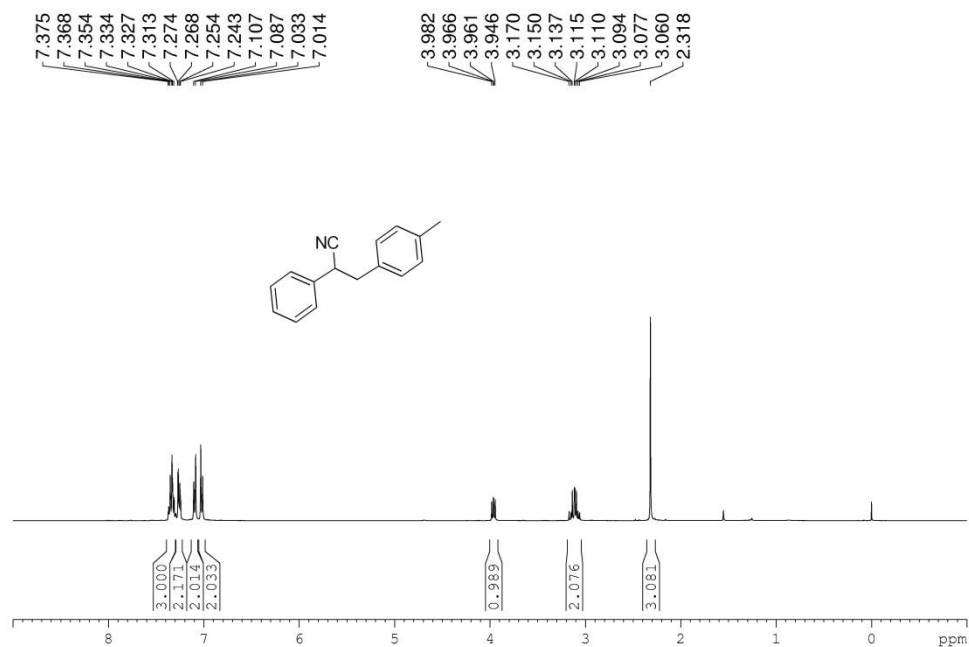
**Figure S78.** <sup>13</sup>C NMR of compound **5l** in CDCl<sub>3</sub>.



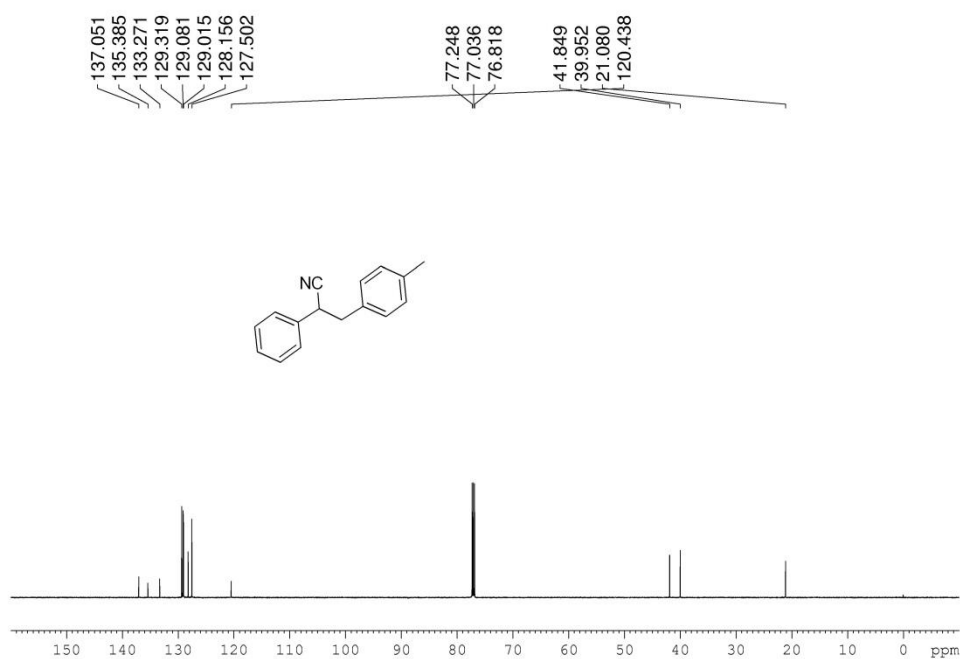
**Figure S79.** <sup>1</sup>H NMR of compound **5m** in CDCl<sub>3</sub>.



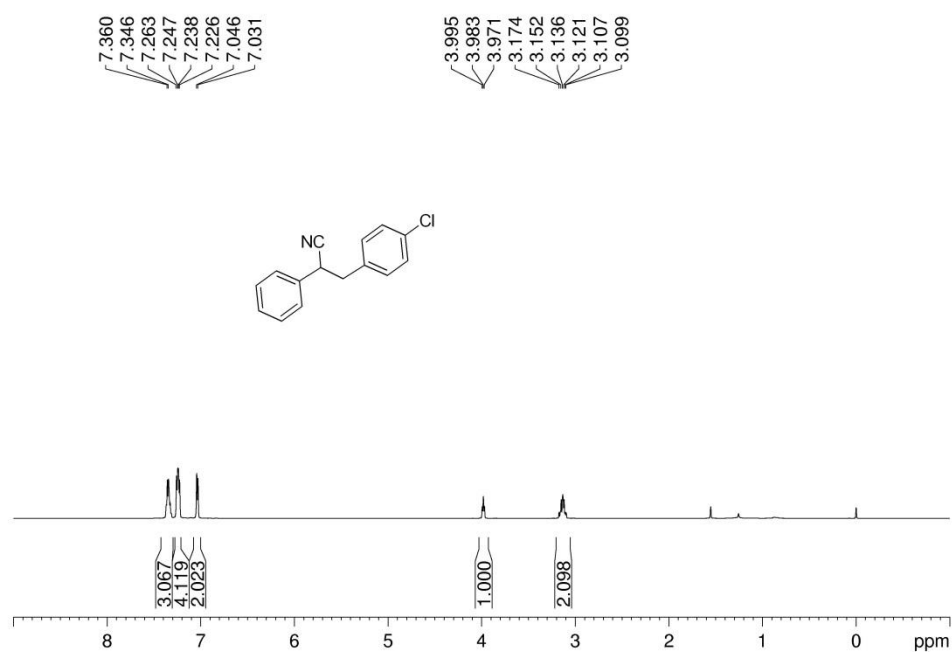
**Figure S80.** <sup>13</sup>C NMR of compound **5m** in CDCl<sub>3</sub>.



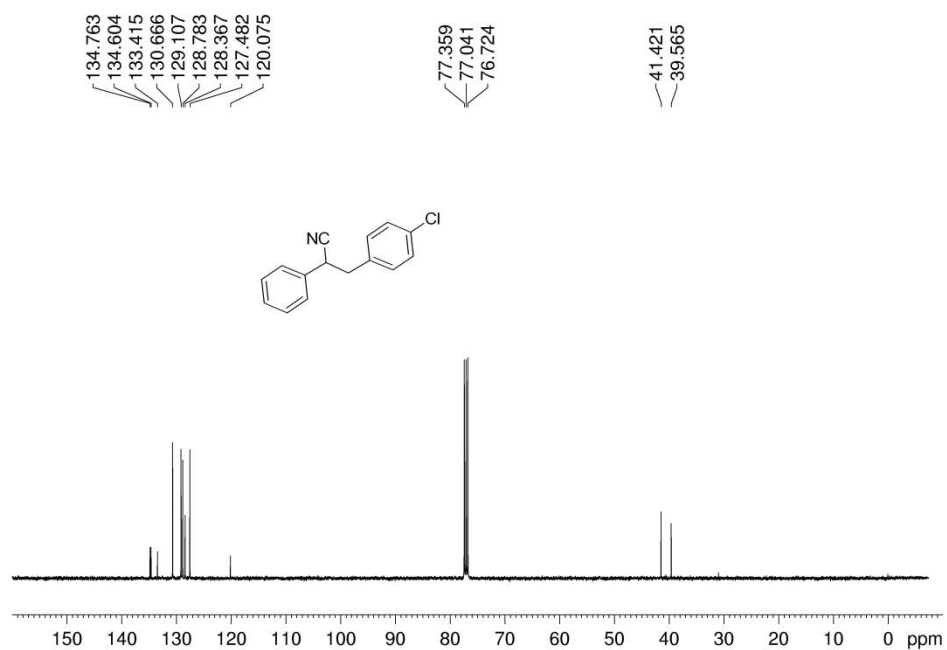
**Figure S81.** <sup>1</sup>H NMR of compound **5n** in CDCl<sub>3</sub>.



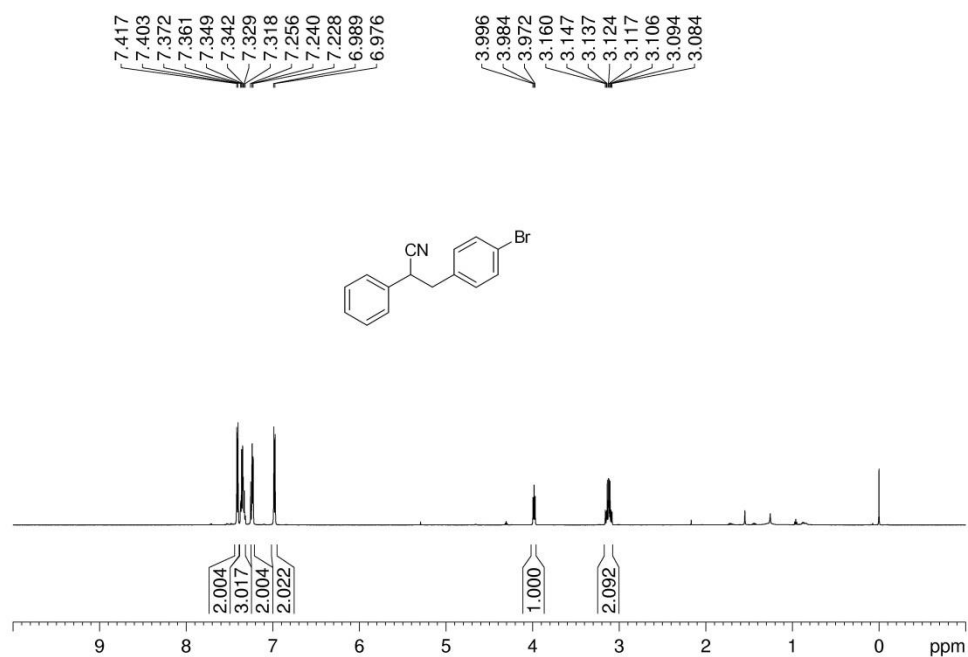
**Figure S82.** <sup>13</sup>C NMR of compound **5n** in CDCl<sub>3</sub>.



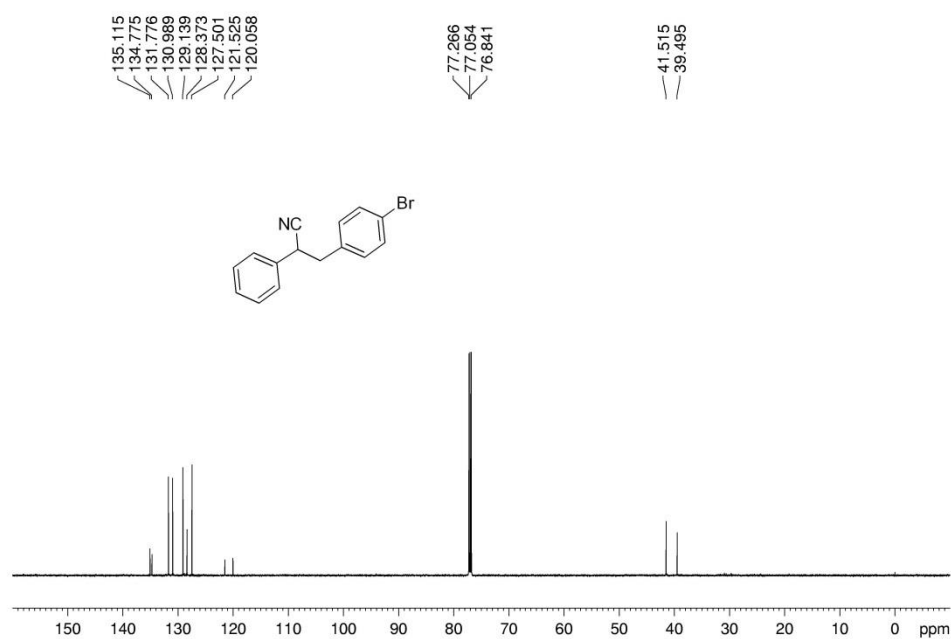
**Figure S83.** <sup>1</sup>H NMR of compound **5o** in CDCl<sub>3</sub>.



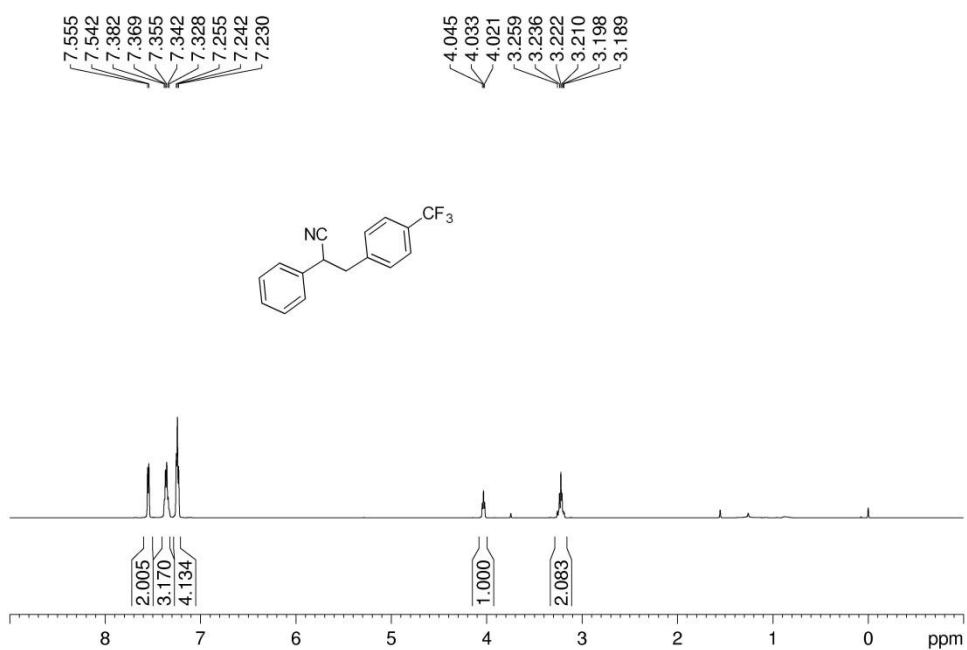
**Figure S84.** <sup>13</sup>C NMR of compound **5o** in CDCl<sub>3</sub>.



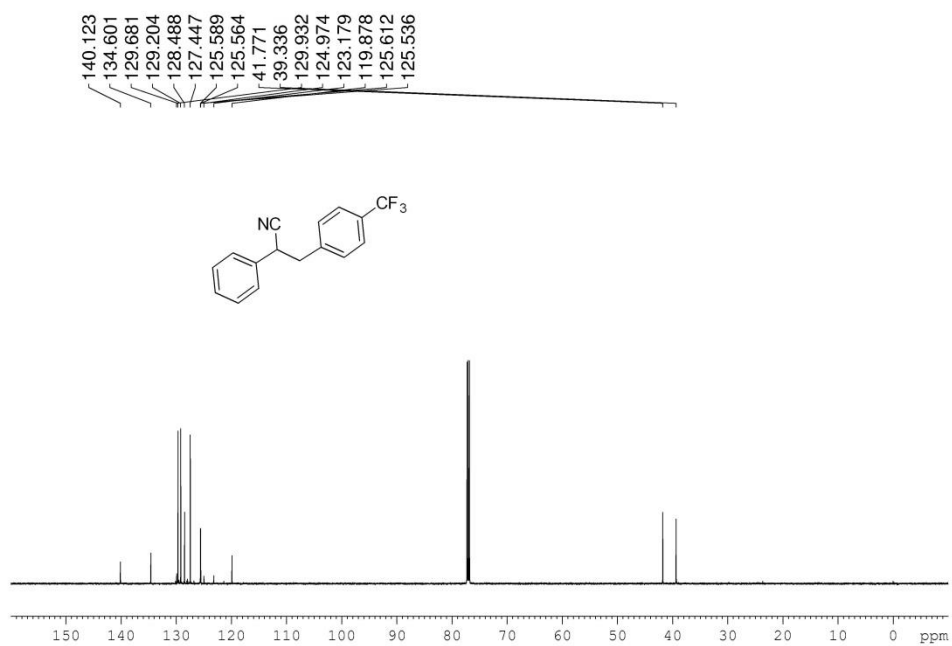
**Figure S85.** <sup>1</sup>H NMR of compound **5p** in CDCl<sub>3</sub>.



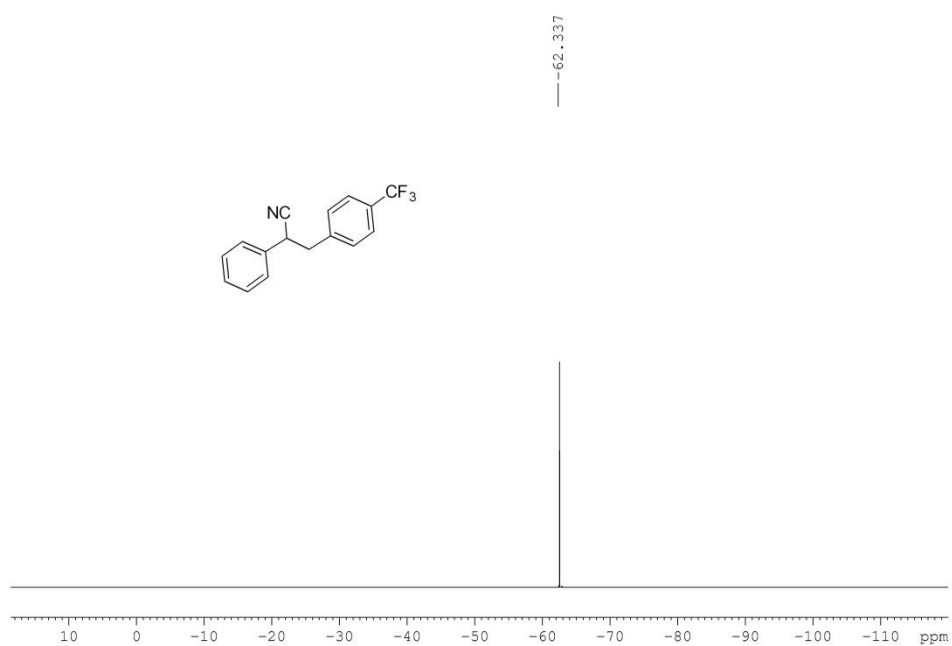
**Figure S86.** <sup>13</sup>C NMR of compound **5p** in CDCl<sub>3</sub>.



**Figure S87.** <sup>1</sup>H NMR of compound **5q** in CDCl<sub>3</sub>.

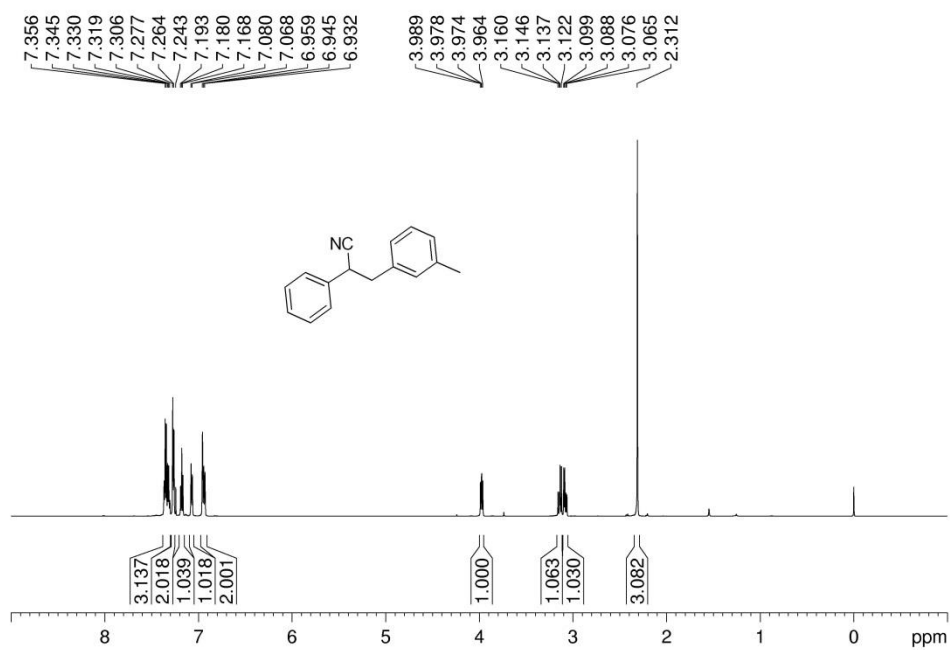


**Figure S88.** <sup>13</sup>C NMR of compound **5q** in CDCl<sub>3</sub>.

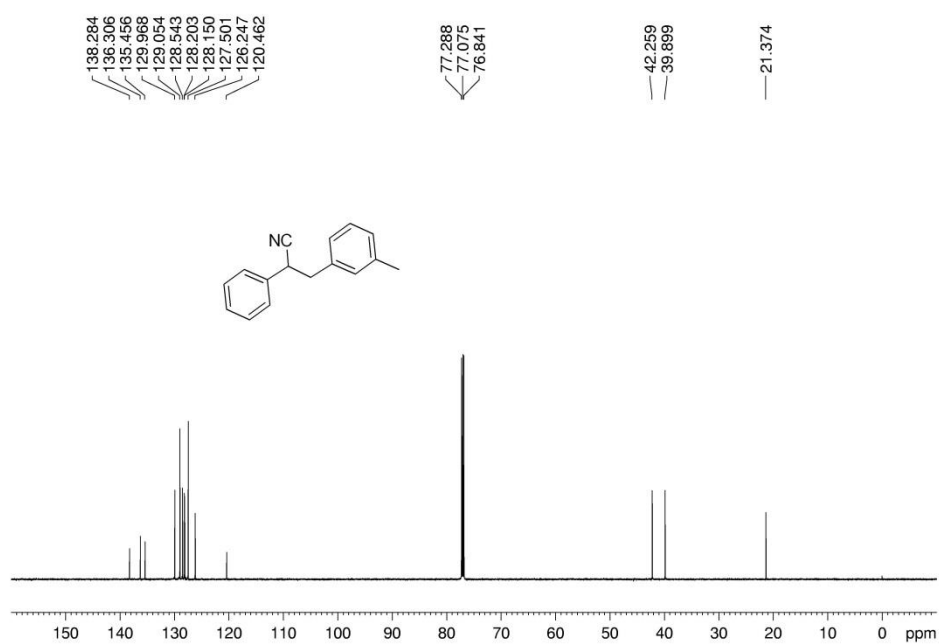


**Figure S89.** <sup>19</sup>F NMR of compound **5q** in CDCl<sub>3</sub>.

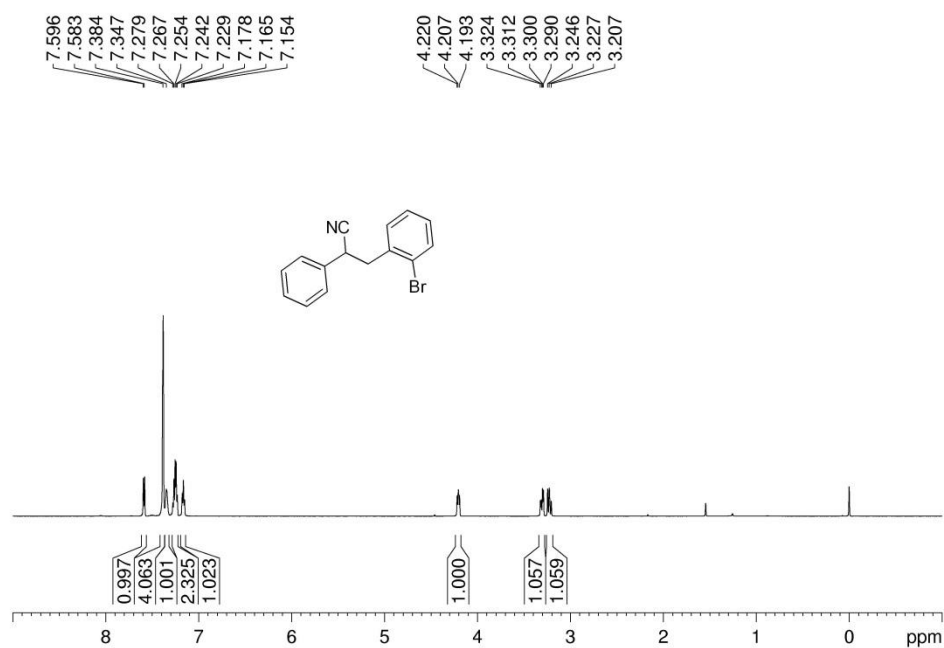




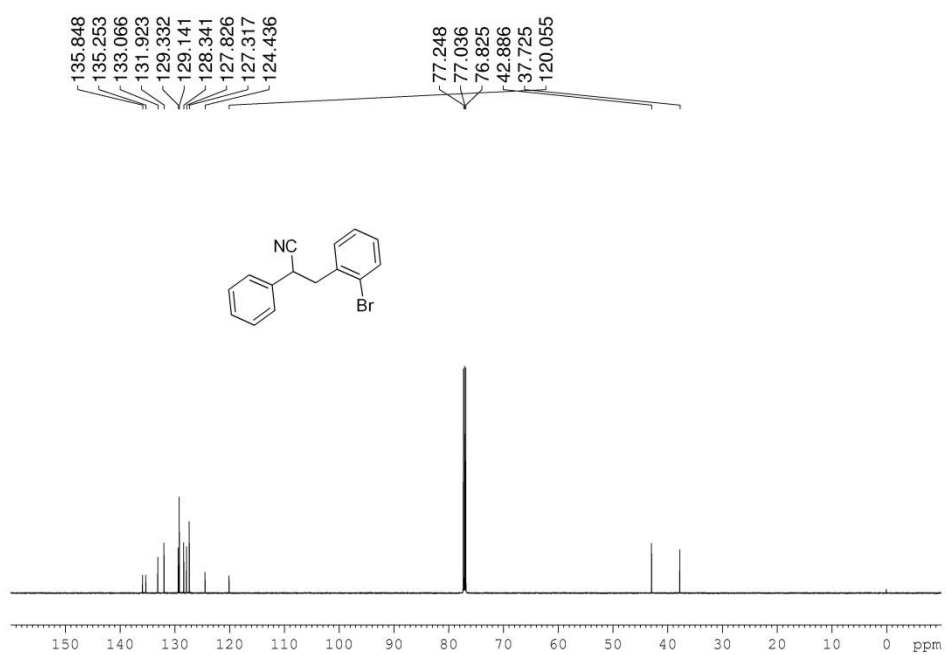
**Figure S90.** <sup>1</sup>H NMR of compound **5r** in CDCl<sub>3</sub>.



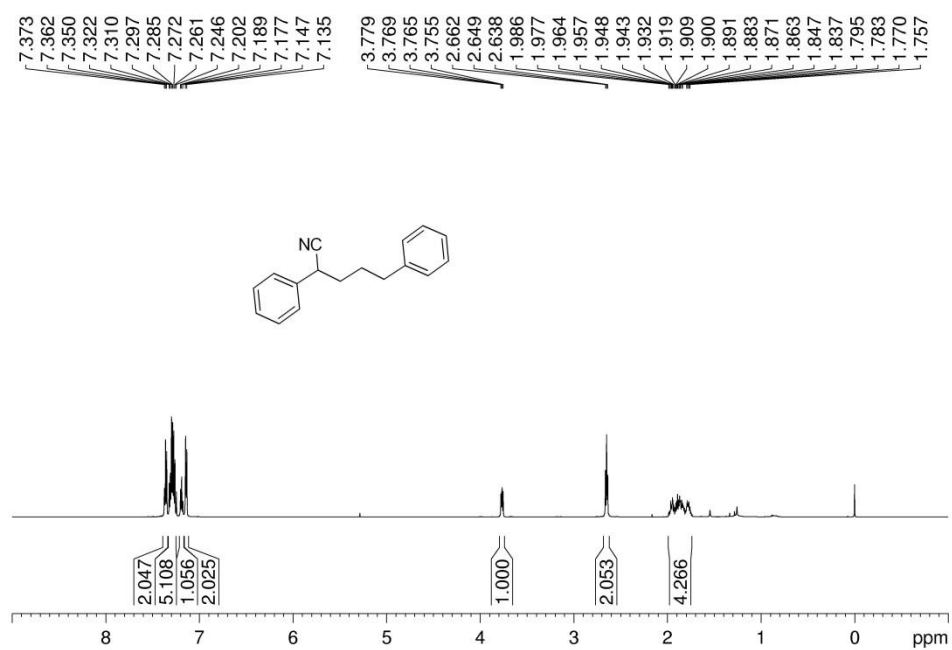
**Figure S91.** <sup>13</sup>C NMR of compound **5r** in CDCl<sub>3</sub>.



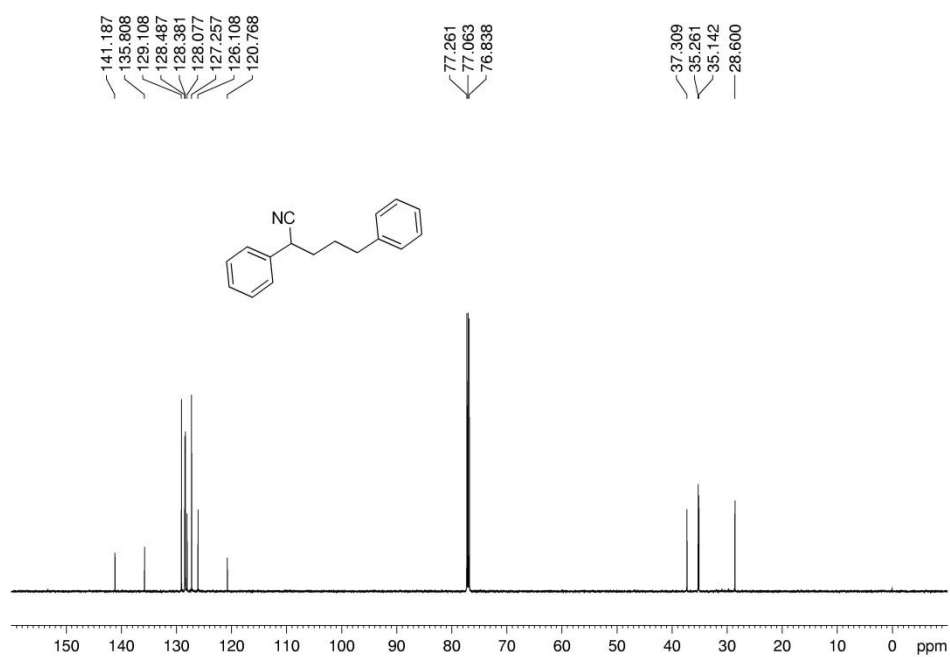
**Figure S92.** <sup>1</sup>H NMR of compound **5s** in CDCl<sub>3</sub>.



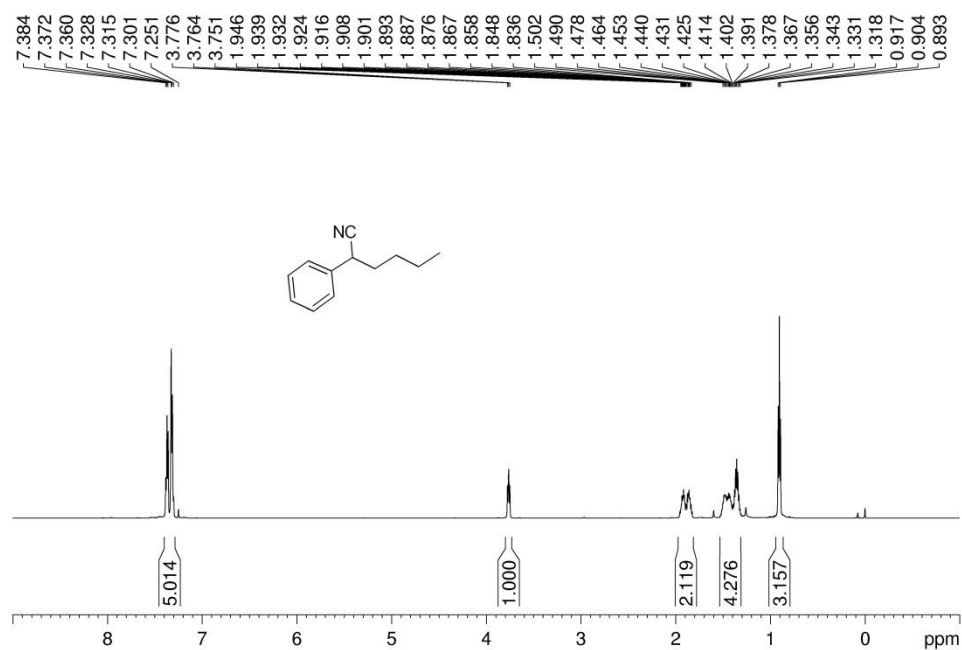
**Figure S93.** <sup>13</sup>C NMR of compound **5s** in CDCl<sub>3</sub>.



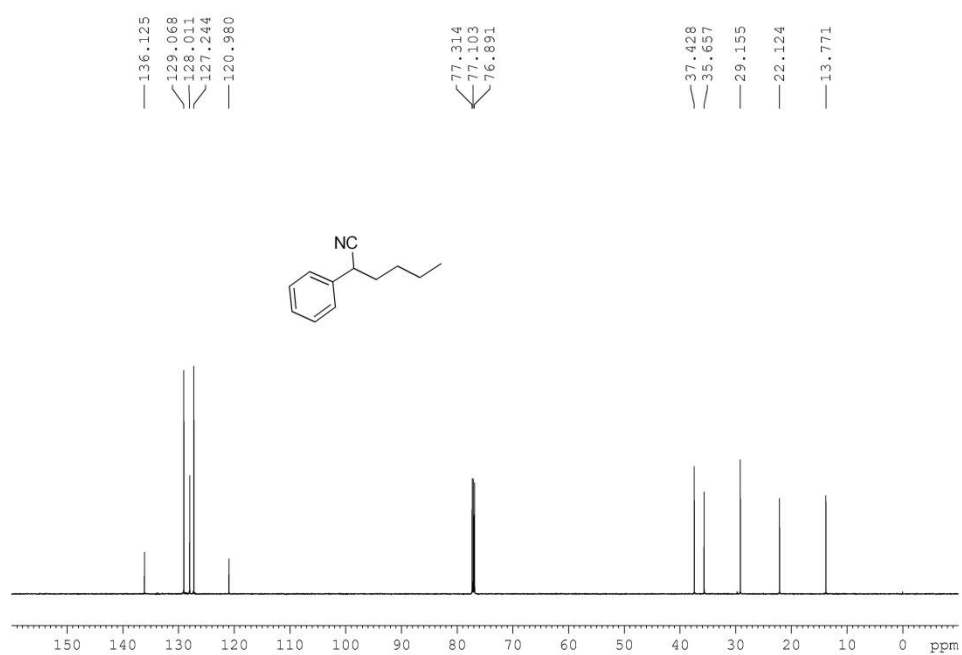
**Figure S94.** <sup>1</sup>H NMR of compound **5t** in CDCl<sub>3</sub>.



**Figure S95.** <sup>13</sup>C NMR of compound **5t** in CDCl<sub>3</sub>.



**Figure S96.** <sup>1</sup>H NMR of compound **5u** in CDCl<sub>3</sub>.



**Figure S97.** <sup>13</sup>C NMR of compound **5u** in CDCl<sub>3</sub>.

## IR of compound 2a-h

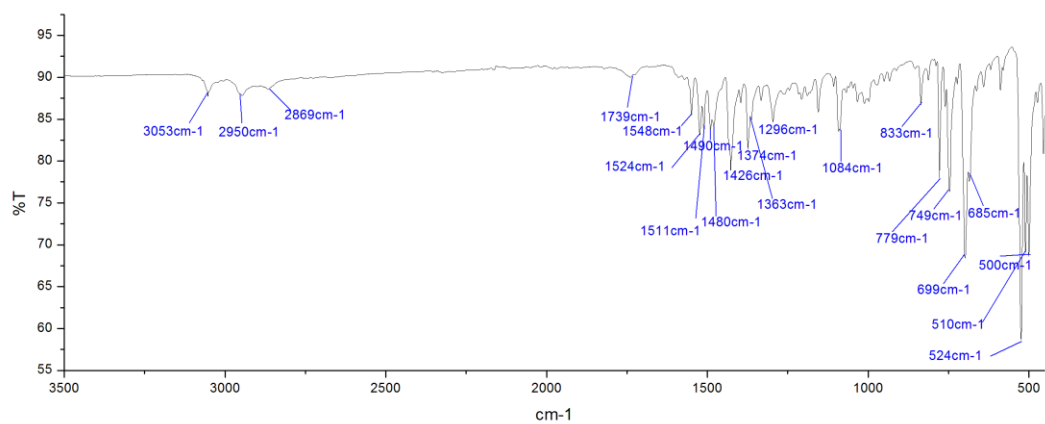


Figure S98. IR of compound 2a.

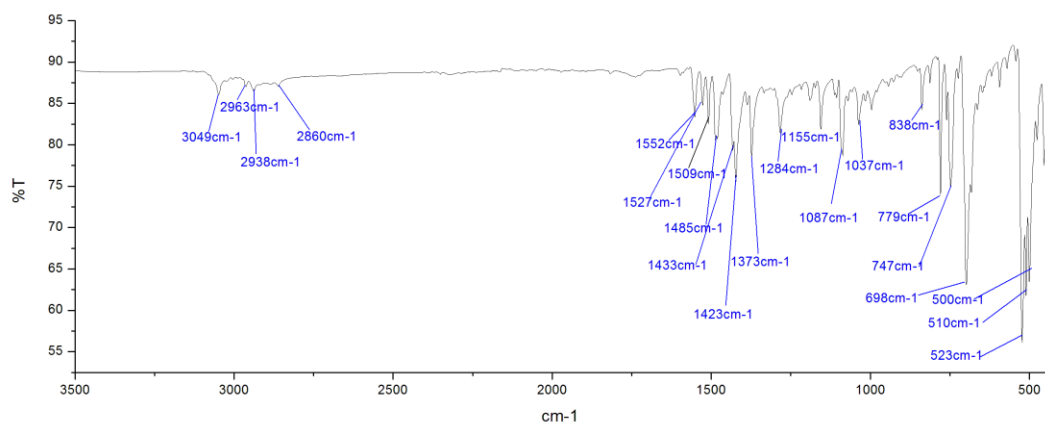


Figure S99. IR of compound 2b.

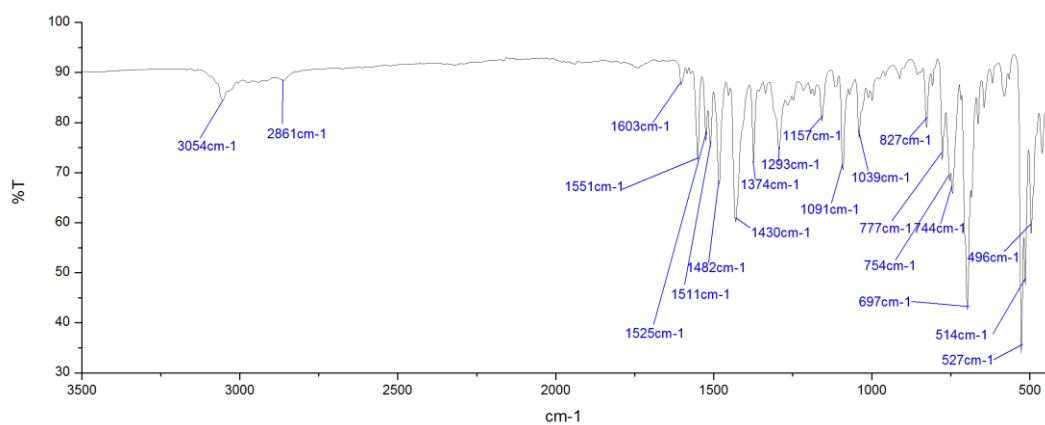
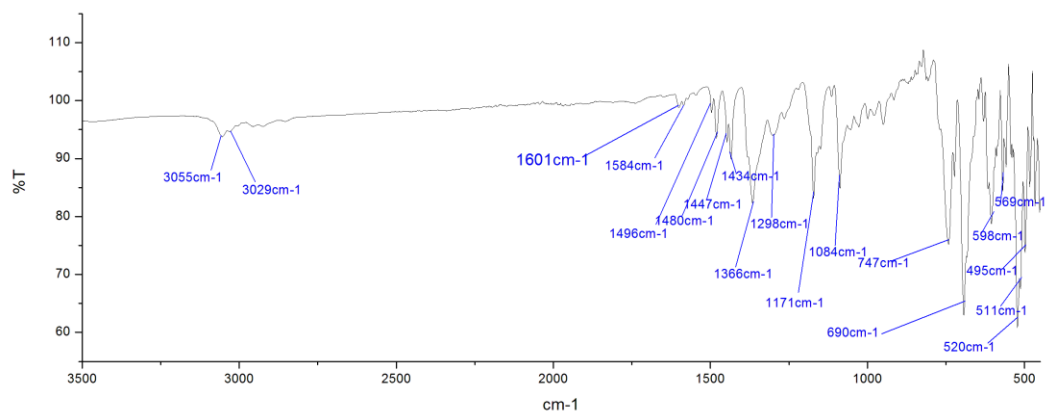
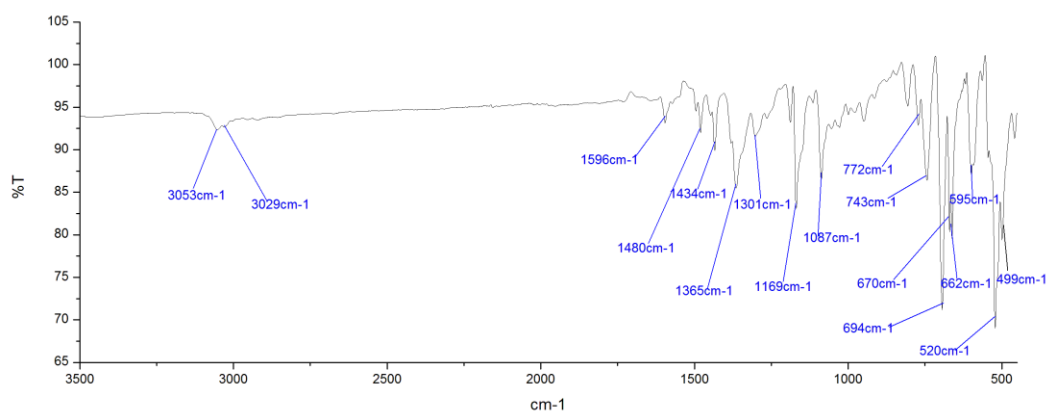


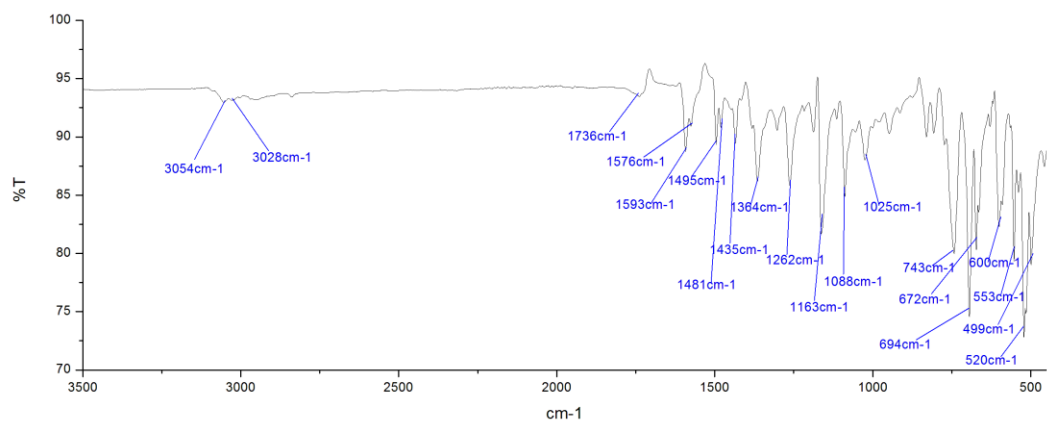
Figure S100. IR of compound 2c.



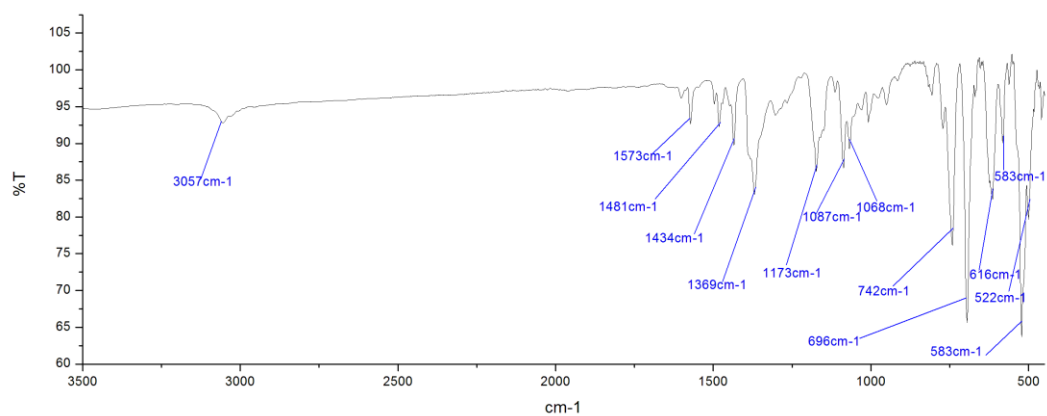
**Figure S101.** IR of compound **2d**.



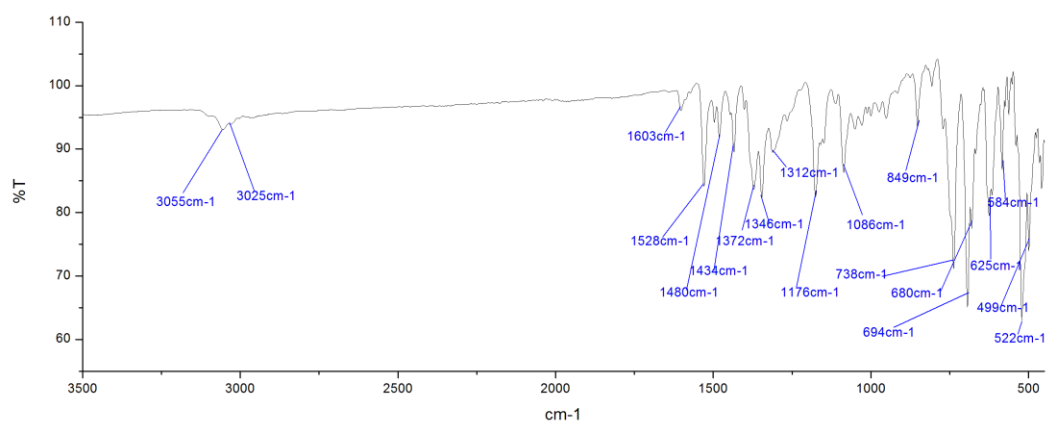
**Figure S102.** IR of compound **2e**.



**Figure S103.** IR of compound **2f**.



**Figure S104.** IR of compound **2g**.



**Figure S105.** IR of compound **2h**.