

**Supplementary Information for**

**Iron Complexes of a Bidentate Picolyl–NHC Ligand: Synthesis,  
Structure and Reactivity**

Qiuming Liang, Trevor Janes, Xhoana Gjergji and Datong Song\*

*Davenport Chemical Research Laboratories, Department of Chemistry, University of Toronto*

*80 St. George Street, Toronto, Ontario, Canada, M5S 3H6*

E-mail: [dsong@chem.utoronto.ca](mailto:dsong@chem.utoronto.ca); Tel: +1 416 978 7014; Fax: +1 416 978 7013

1. <b>X-ray crystallography</b> .....	S2
2. <b>NMR spectra</b> .....	S4
3. <b>IR spectra</b> .....	S9
4. <b>C-C coupling reaction</b> .....	S11
5. <b>References</b> .....	S14

## 1. X-ray Crystallography

The X-ray diffraction data were collected on a Bruker Kappa Apex II diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 150 K controlled by an Oxford Cryostream 700 series low-temperature system and processed with the Bruker Apex 2 software package.<sup>1</sup> The structures were solved by direct methods and refined using SHELX-2013 and SHELX-2014 software packages.<sup>2,3</sup> All non-hydrogen atoms were refined anisotropically, except for those involved in the disordered THF molecules in the lattice of **1**. All hydrogen atoms were calculated using the riding model. The disordered THF molecules in the lattice of **1** were successfully modeled using two sets of coordinates with the occupancies constrained to a 1:1 ratio. The diffuse residual electron density from solvent molecules in the lattice of **4** was removed with the SQUEEZE function of PLATON<sup>4</sup> and was not included in the formula or the refinement. Selected crystallographic data are summarized in Tables S1–S2.

**Table S1.** Selected crystallographic data for compounds **1–4**.

	<b>1·(2THF)</b>	<b>2</b>	<b>3</b>	<b>4</b>
Empirical formula	C <sub>44</sub> H <sub>54</sub> N <sub>6</sub> O <sub>2</sub> Br <sub>2</sub> Fe	C <sub>24</sub> H <sub>37</sub> N <sub>4</sub> BrSi <sub>2</sub> Fe	C <sub>18</sub> H <sub>19</sub> N <sub>3</sub> Br <sub>2</sub> Fe	C <sub>36</sub> H <sub>36</sub> FeN <sub>6</sub>
FW (g·mol <sup>-1</sup> )	914.60	573.51	493.03	608.56
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space Group	P 2 <sub>1</sub> /n	P -1	P 2 <sub>1</sub> /n	I 2/a
Z	4	4	4	8
a (Å)	17.771(1)	9.9454(9)	11.9641(7)	22.229(2)
b (Å)	10.0076(8)	16.077(1)	10.4299(6)	9.3929(6)
c (Å)	25.439(2)	19.406(2)	16.3971(9)	32.344(3)
$\alpha$ (deg)	90	65.934(4)	90	90
$\beta$ (deg)	108.204(3)	84.261(6)	110.354(3)	108.287(6)
$\gamma$ (deg)	90	89.170(4)	90	90
V (Å <sup>3</sup> )	4297.7(5)	2817.8(4)	1918.4(2)	6701(1)
D <sub>calcd</sub> (g·cm <sup>-3</sup> )	1.414	1.352	1.707	1.206
$\mu$ (mm <sup>-1</sup> )	2.253	2.057	4.956	0.483
F(000)	1888	1192	976	2560
no. of obsd rflns	5883	6521	2728	4336
no. of params refnd	493	595	220	394
goodness of fit	1.053	1.098	1.020	1.069
R <sub>1</sub> (I > 2 $\sigma$ )	0.0545	0.0855	0.0305	0.0490
wR <sub>2</sub> (I > 2 $\sigma$ )	0.1657	0.2007	0.0705	0.1232

**Table S2.** Selected crystallographic data for compounds **5–8**.

	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>
Empirical formula	C <sub>25</sub> H <sub>26</sub> BrFeN <sub>3</sub>	C <sub>32</sub> H <sub>33</sub> Fe N <sub>3</sub>	C <sub>21</sub> H <sub>19</sub> FeN <sub>3</sub> O <sub>3</sub>	C <sub>22</sub> H <sub>19</sub> FeN <sub>3</sub> O <sub>4</sub>
FW (g·mol <sup>-1</sup> )	504.25	515.46	417.24	445.25
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space Group	P-1	P-1	P2 <sub>1</sub> /n	P2 <sub>1</sub> /c
<i>Z</i>	2	2	4	4
<i>a</i> (Å)	8.041(2)	9.2244(9)	15.764(2)	12.795(1)
<i>b</i> (Å)	10.612(2)	9.846(1)	8.828(1)	13.232(1)
<i>c</i> (Å)	14.202(3)	15.696(1)	16.118(2)	12.3477(9)
$\alpha$ (deg)	103.803(7)	94.162(4)	90	90
$\beta$ (deg)	96.614(8)	104.009(4)	118.981(6)	94.594(4)
$\gamma$ (deg)	91.387(8)	96.291(4)	90	90
<i>V</i> (Å <sup>3</sup> )	1167.4(4)	1367.5(2)	1962.3(5)	2083.8(3)
<i>D</i> <sub>calcd</sub> , (g·cm <sup>-3</sup> )	1.434	1.252	1.412	1.419
$\mu$ (mm <sup>-1</sup> )	2.373	0.576	0.795	0.757
<i>F</i> (000)	516	544	864	920
no. of obsd reflns	2326	4338	3381	3689
no. of params refnd	274	328	256	274
goodness of fit	0.986	1.012	1.067	1.016
R <sub>1</sub> (I>2 $\sigma$ )	0.0495	0.0445	0.0378	0.0329
wR <sub>2</sub> (I>2 $\sigma$ )	0.1011	0.0838	0.0961	0.0747

## 2. NMR spectra

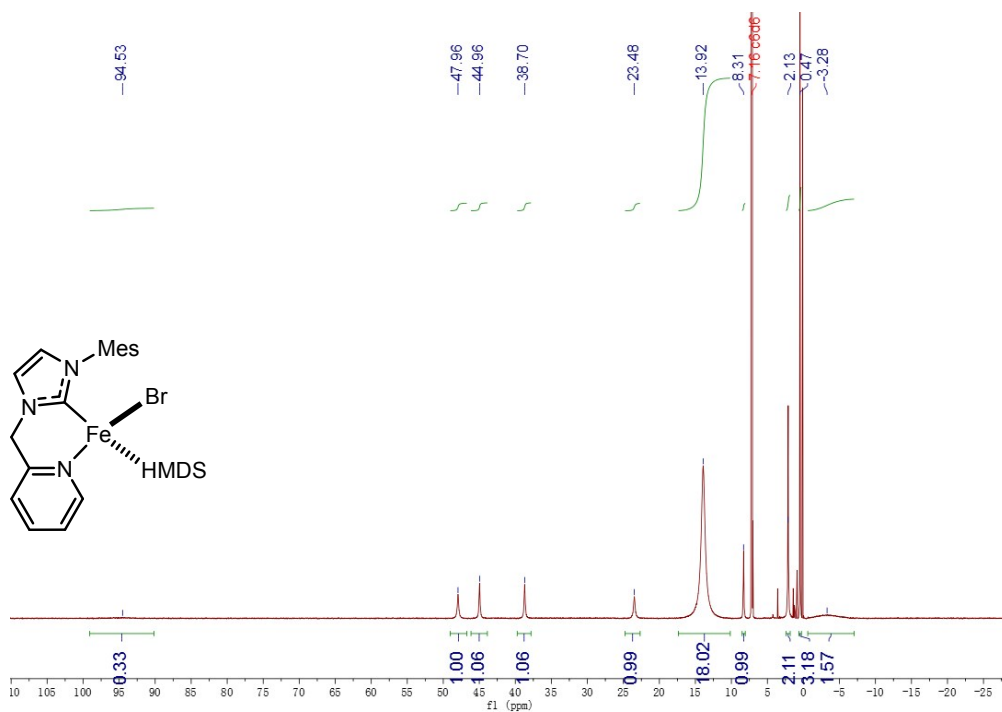


Figure S1. <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>) spectrum of [FeBr(HL)(HMDS)] (2).

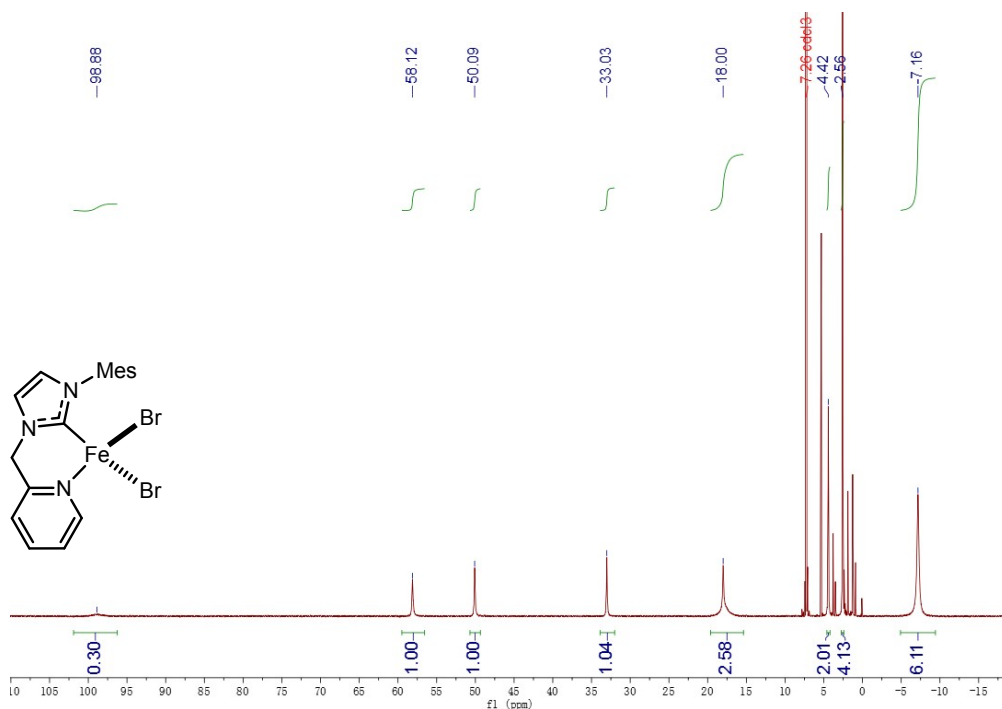
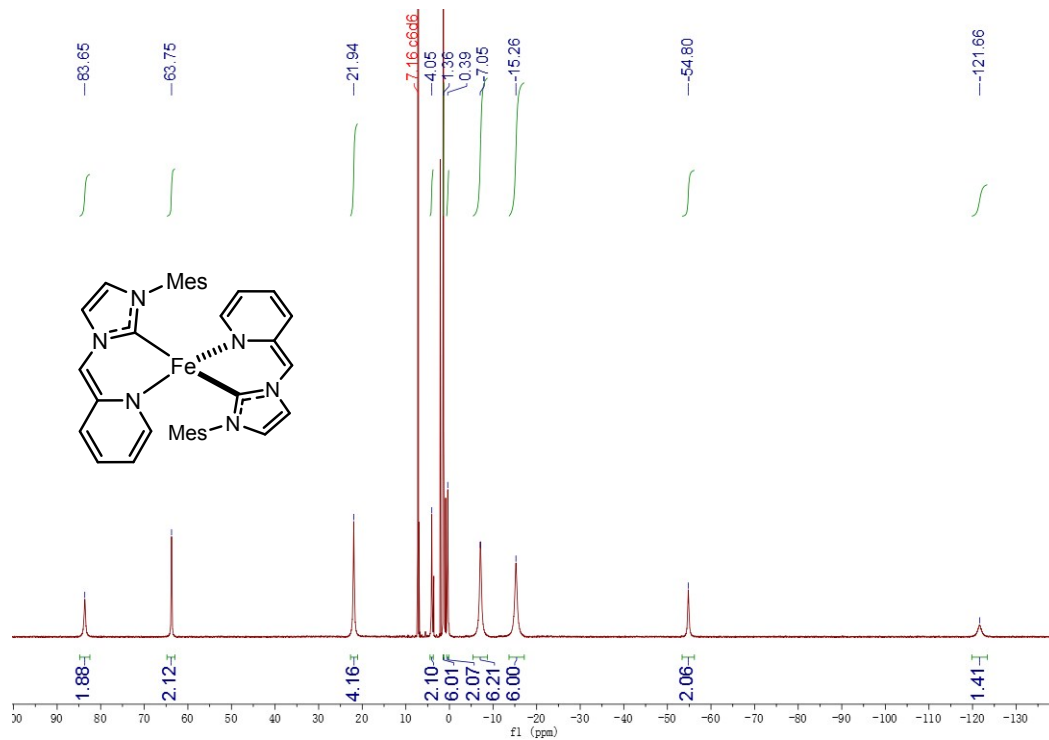
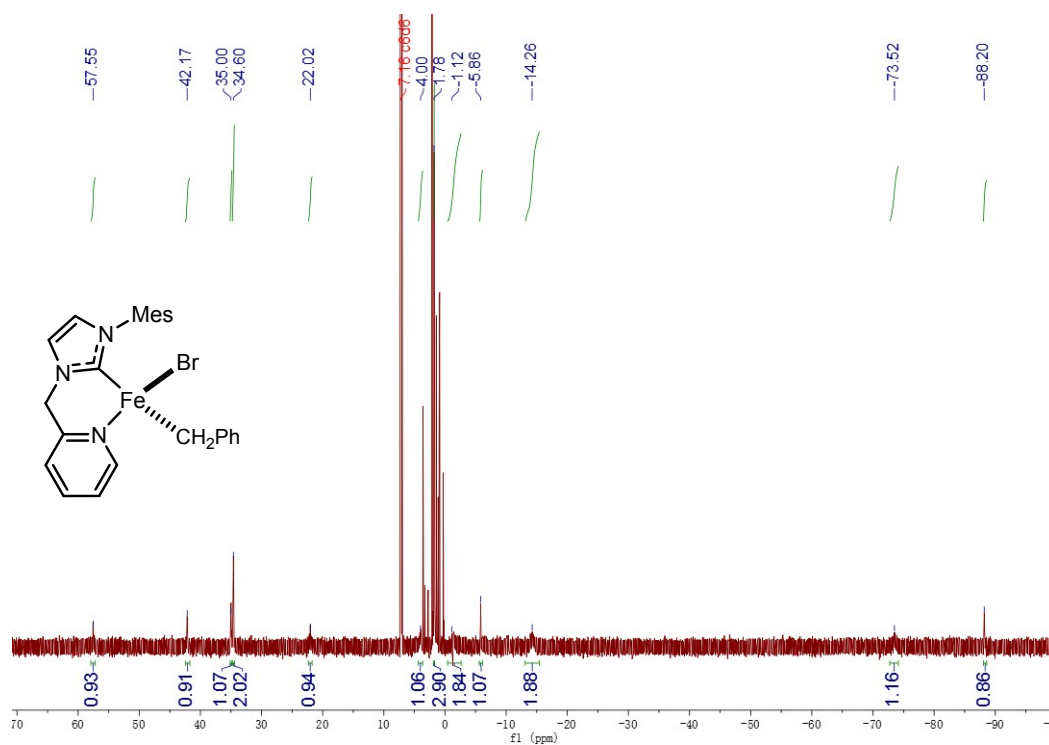


Figure S2. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of [FeBr<sub>2</sub>(HL)] (3).



**Figure S3.**  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ ) spectrum of  $\text{FeL}_2$  (**4**).



**Figure S4.**  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ ) spectrum of  $[\text{FeBnBr}(\text{HL})]$  (**5**). Note: the poor quality of the spectrum is due to low solubility.

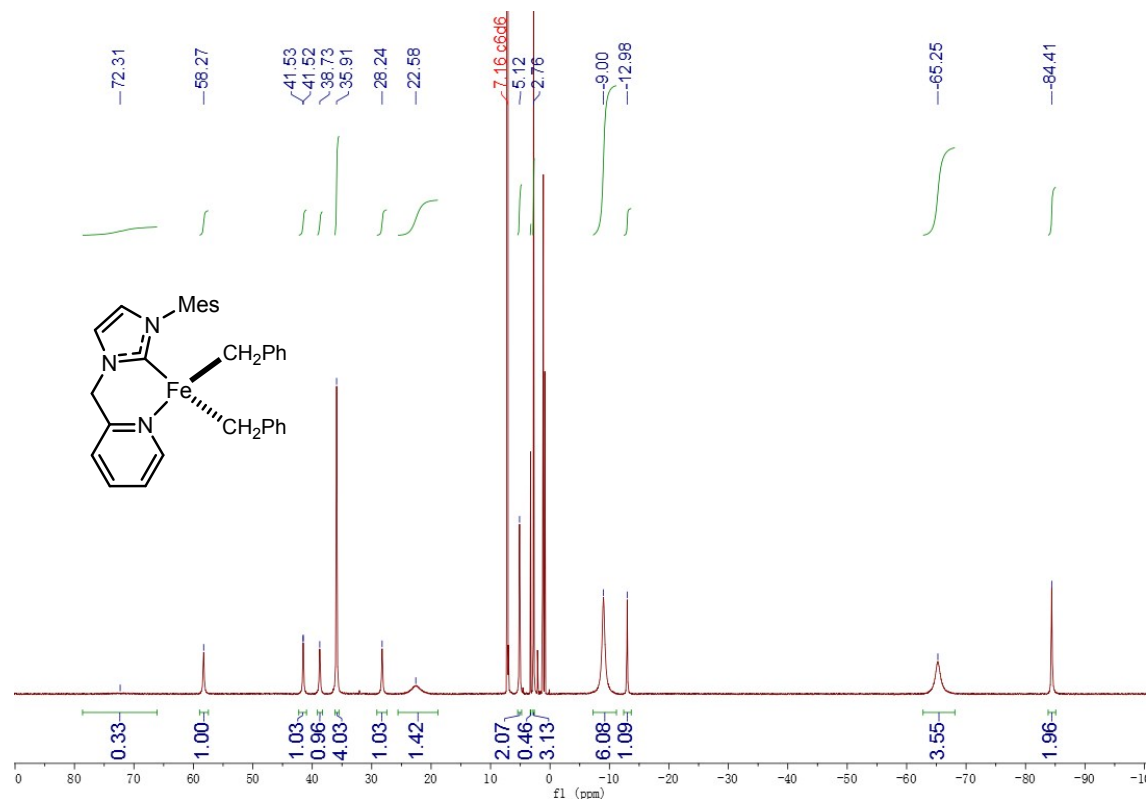


Figure S5.  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ ) spectrum of  $[\text{Fe}(\text{Bn})_2(\text{HL})]$  (6).

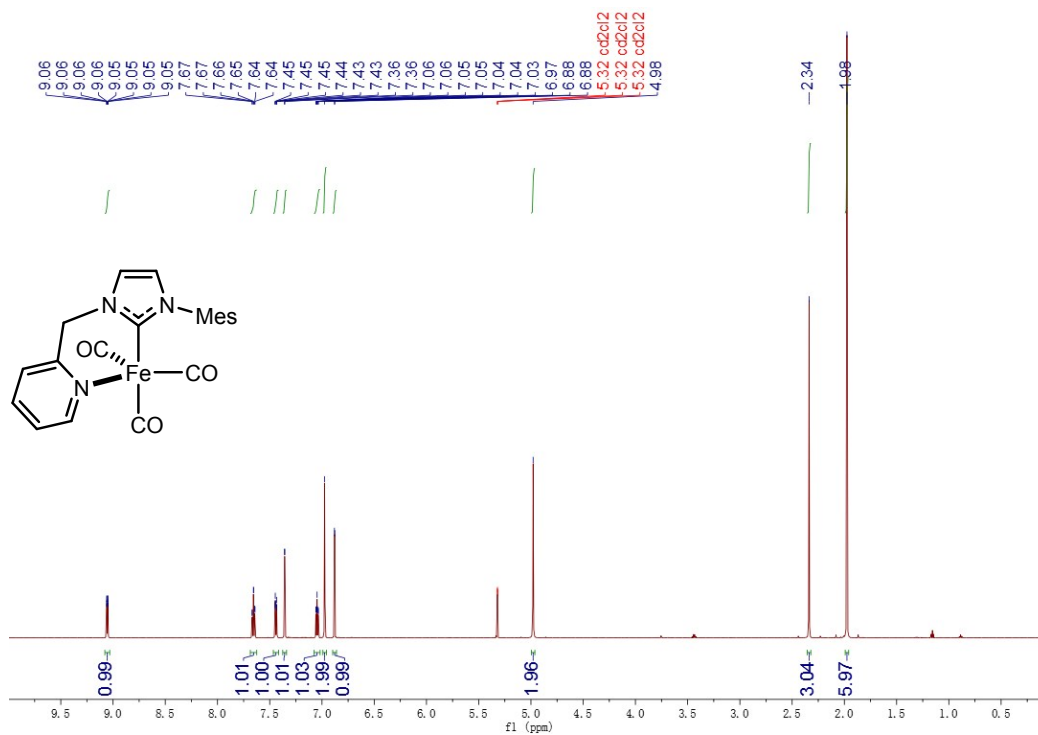


Figure S6.  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_2\text{Cl}_2$ ) spectrum of  $[\text{Fe}(\text{CO})_3(\text{HL})]$  (7).

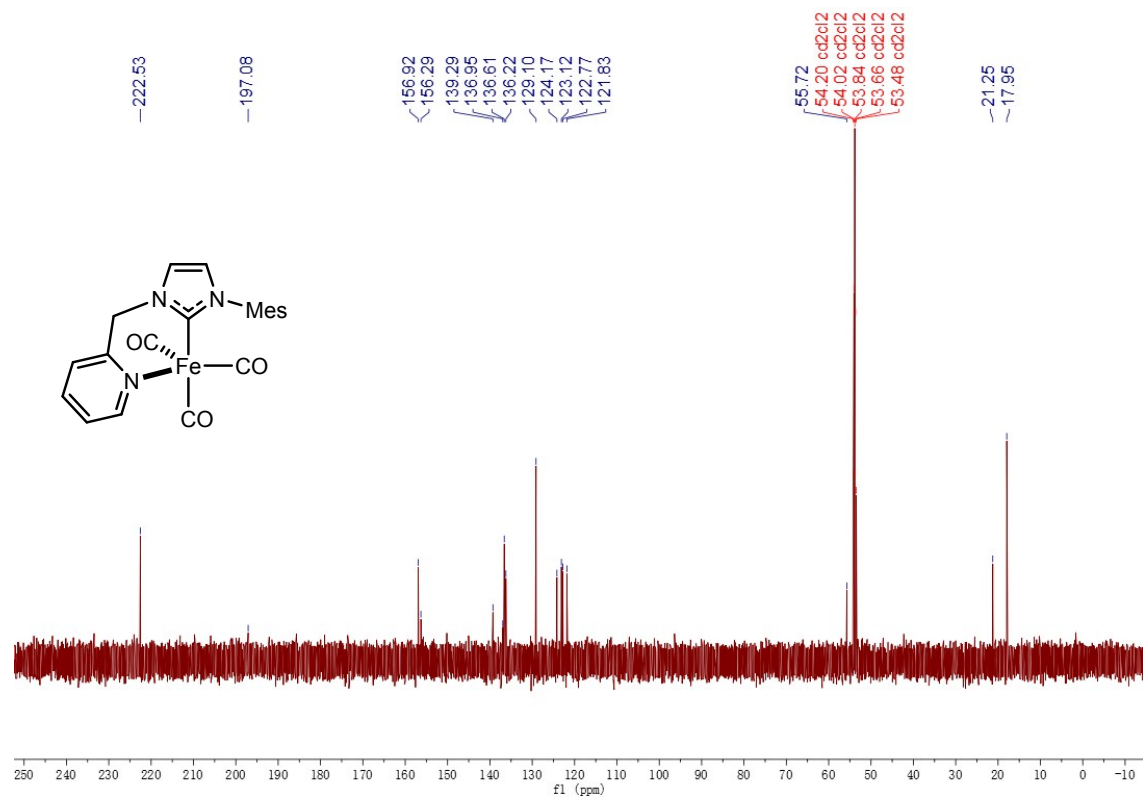


Figure S7.  $^{13}\text{C}$  NMR (151 MHz,  $\text{CD}_2\text{Cl}_2$ ) spectrum of  $[\text{Fe}(\text{CO})_3(\text{HL})]$  (7).

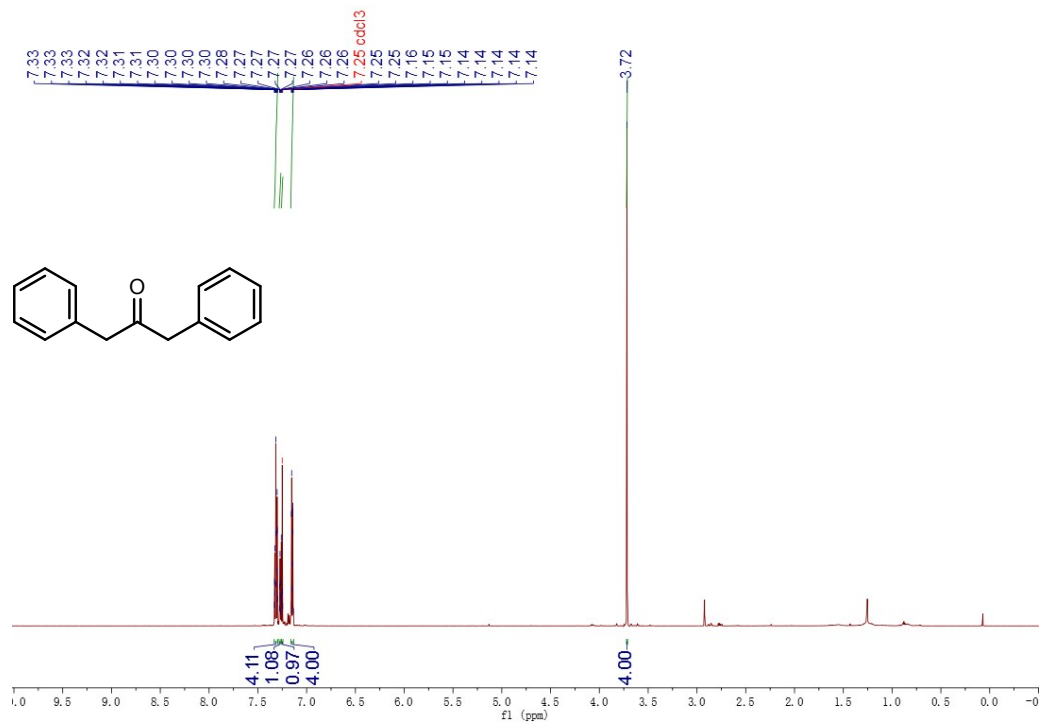


Figure S8.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) spectrum of dibenzyl ketone.

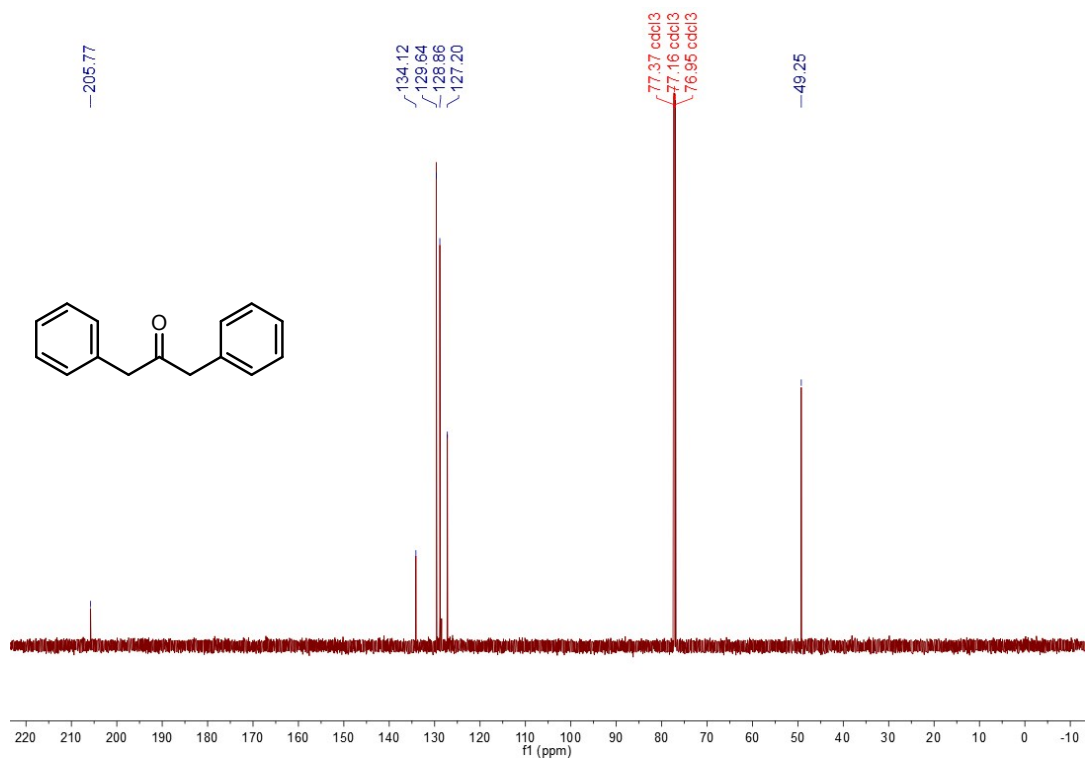


Figure S9. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) spectrum of dibenzyl ketone.

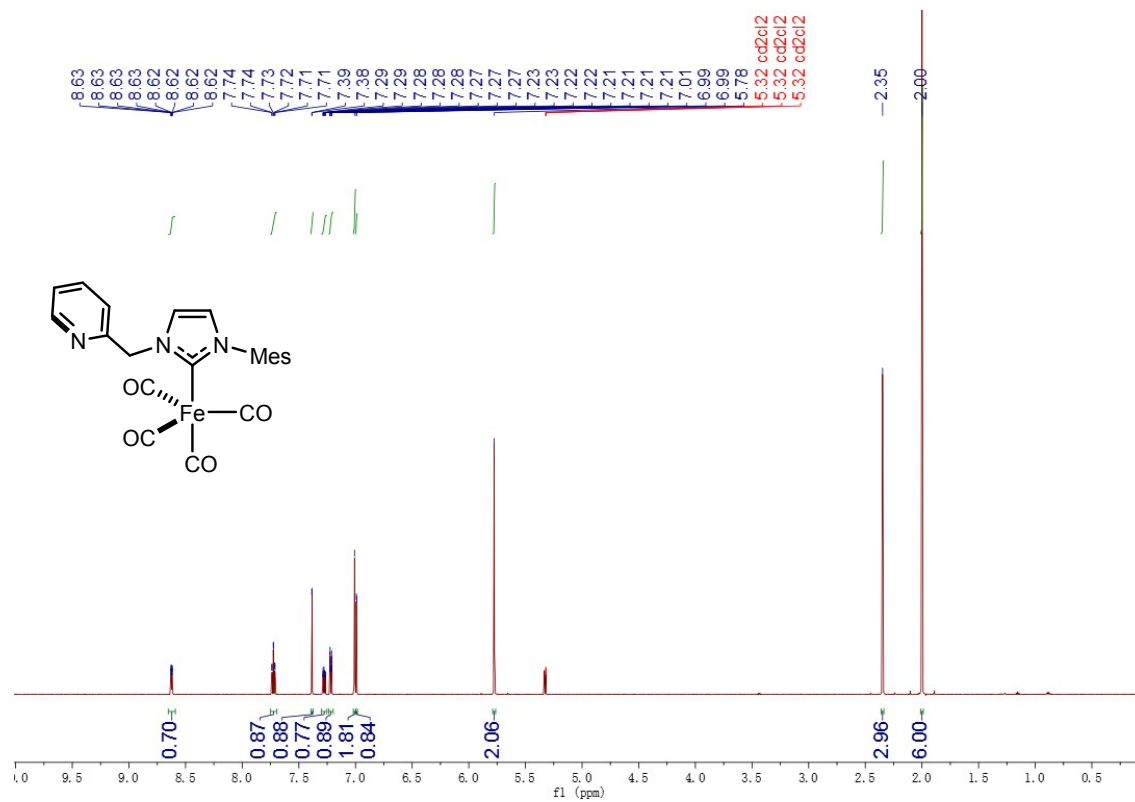


Figure S10. <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) spectrum of [Fe(CO)<sub>4</sub>(HL)] (**8**).



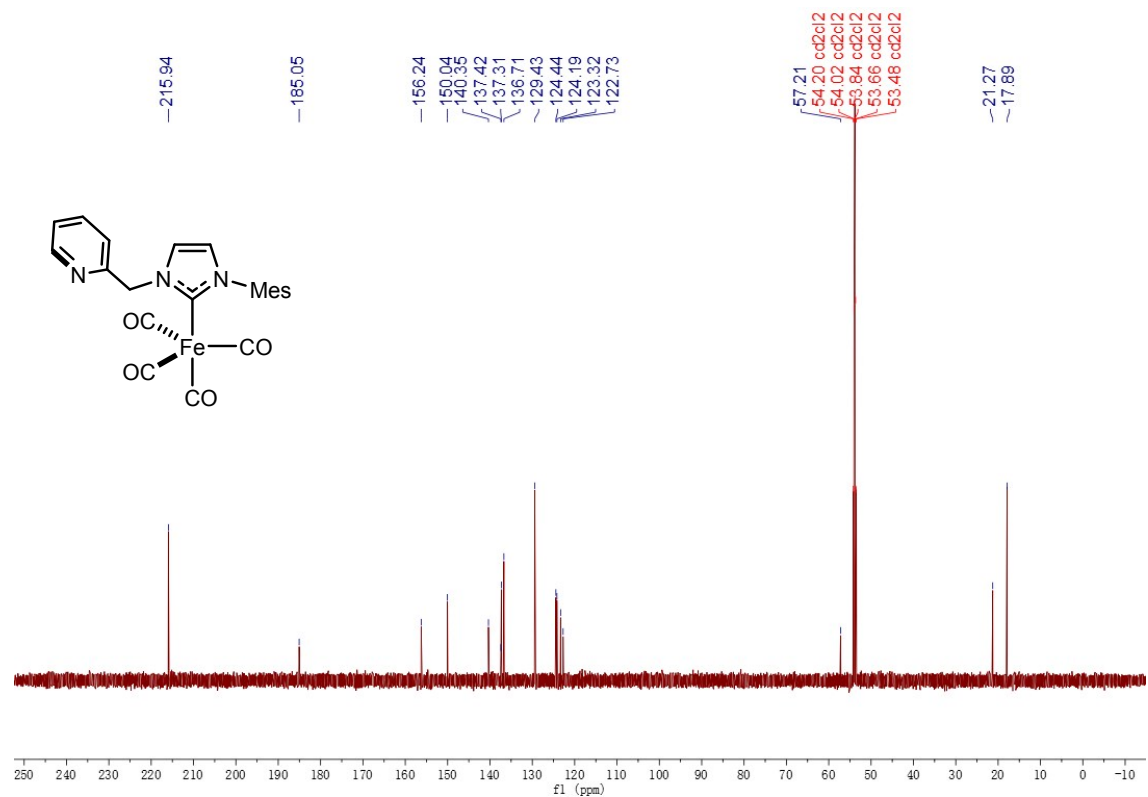


Figure S11.  $^{13}\text{C}$  NMR (151 MHz,  $\text{CD}_2\text{Cl}_2$ ) spectrum of  $[\text{Fe}(\text{CO})_4(\text{HL})]$  (8).

### 3. IR spectra

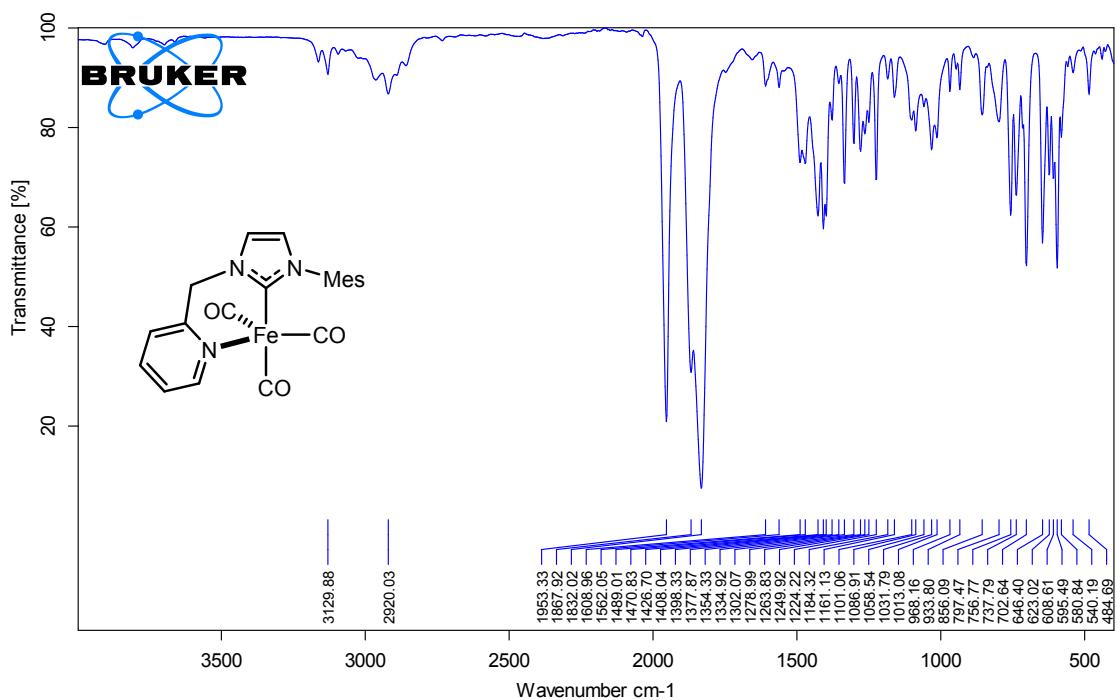


Figure S12. IR spectrum of  $[\text{Fe}(\text{CO})_3(\text{HL})]$  (7) as a neat solid.

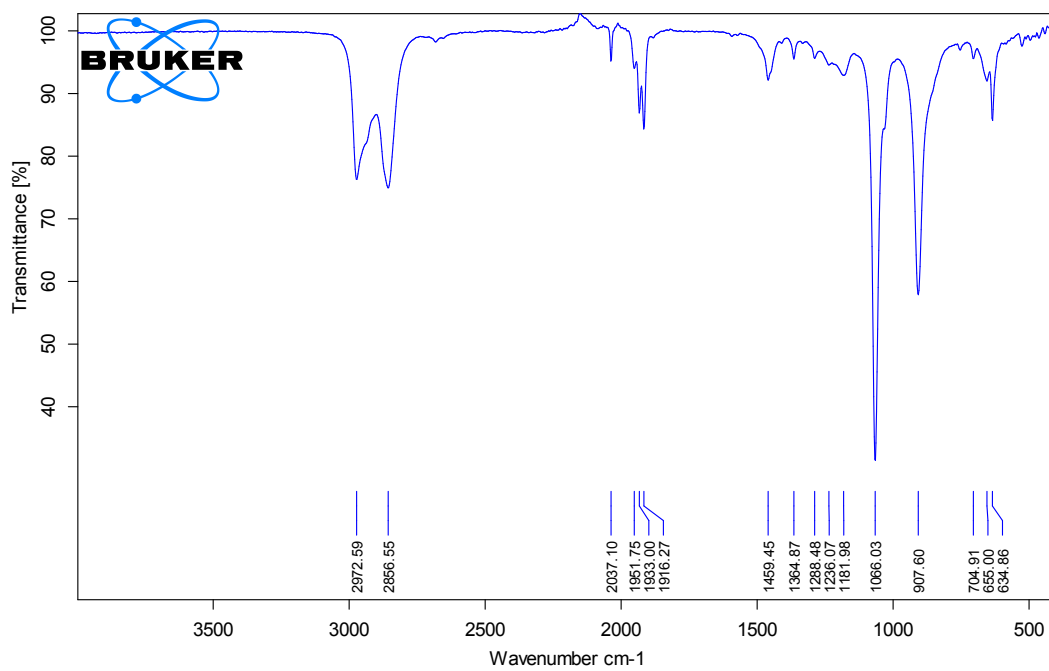
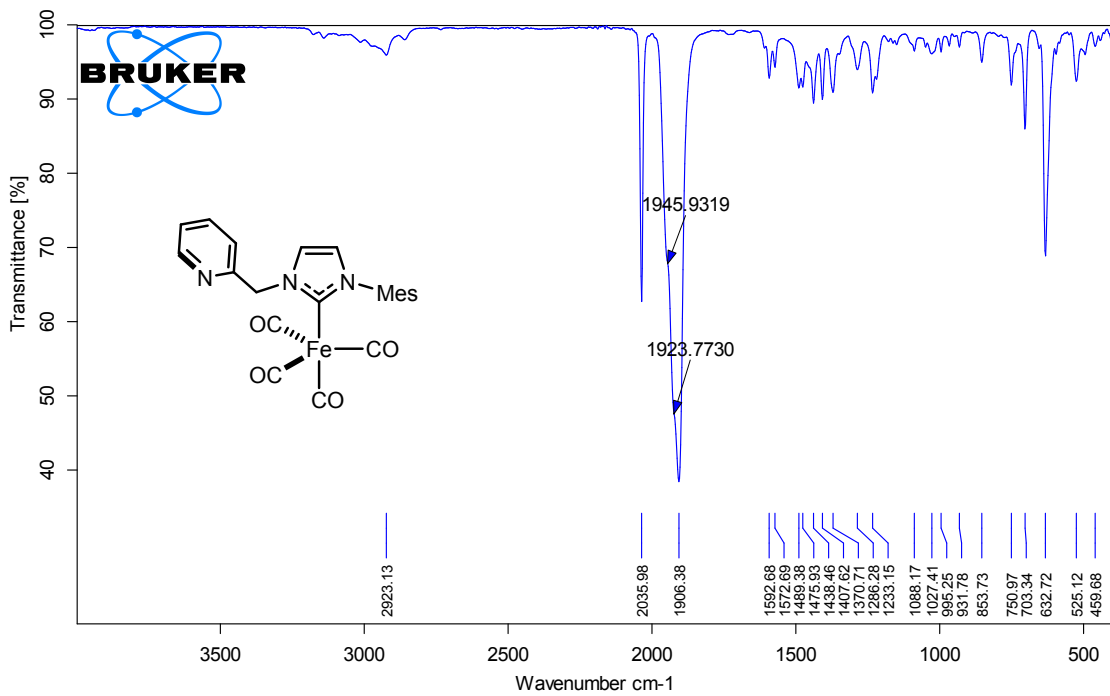
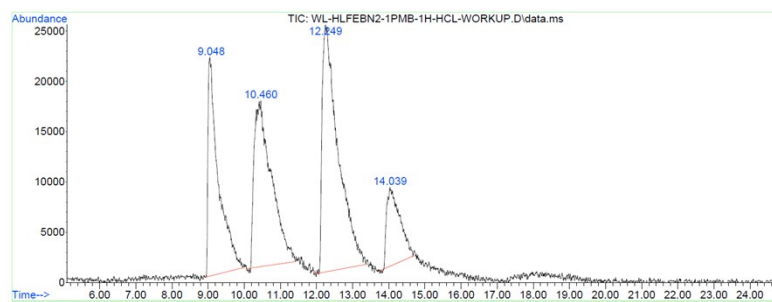
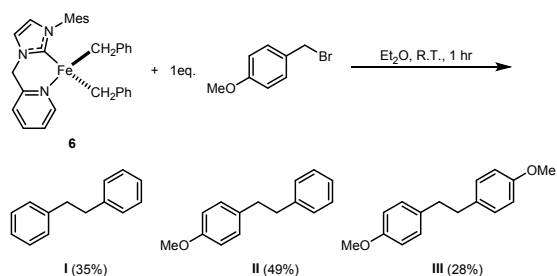


Figure S13. IR spectra of  $[\text{Fe}(\text{CO})_4(\text{HL})]$  (8): neat solid sample (top) and solution (bottom).

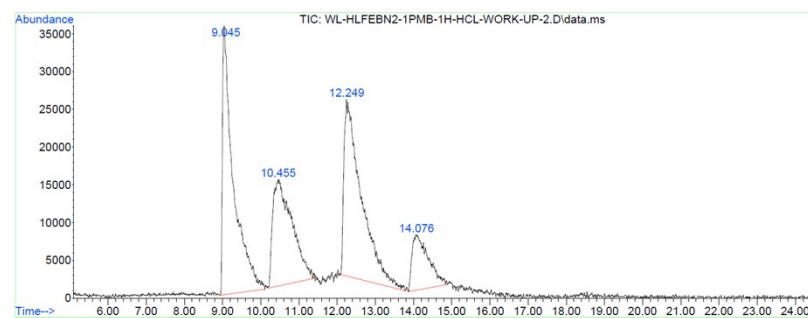
## 4. C-C coupling reaction

### Scheme S1. C-C bond formation reaction.



peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	9.048	565	582	719	BB 4	21670	4346752	57.91%	22.498
2	10.460	733	790	932	BB 3	16487	5493857	73.19%	28.435
3	12.249	1011	1054	1219	BV 5	24493	7506410	100.00%	38.851
4	14.039	1272	1318	1412	BV 3	7724	1973863	26.30%	10.216

Figure S14. GC trace of the CC bond formation reaction mixture run 1. Retention times: C<sub>6</sub>Me<sub>6</sub> 9.048 min, **I** 10.460 min, **II** 12.249 min, **III** 14.039 min. 1.6 mg of C<sub>6</sub>Me<sub>6</sub> was used as internal standard.

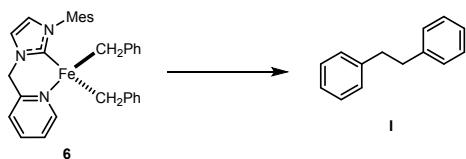


peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	9.045	566	582	739	EV 3	35589	6987122	94.24%	32.443
2	10.455	752	790	929	M3	14155	4964872	66.97%	23.053
3	12.249	1030	1054	1280	BV 4	23197	7414024	100.00%	34.426
4	14.076	1293	1323	1443	FV 6	7195	2170297	29.27%	10.077

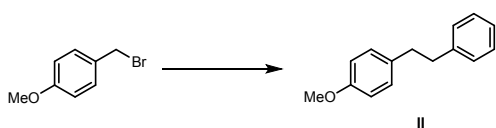
Figure S14. GC trace of the CC bond formation reaction mixture run 2. Retention times: C<sub>6</sub>Me<sub>6</sub> 9.045 min, **I** 10.455 min, **II** 12.249 min, **III** 14.076 min. 2.6 mg of C<sub>6</sub>Me<sub>6</sub> was used as internal standard.

### Yield Calculations for run 1:

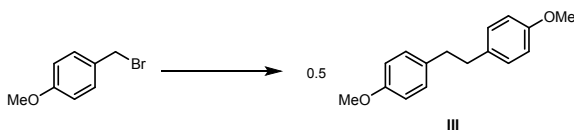
Compound **6** (17.7mg, 34.4  $\mu\text{mol}$ ), *p*-methoxybenzyl bromide (5  $\mu\text{L}$ , 34.3  $\mu\text{mol}$ ),  $\text{C}_6\text{Me}_6$  (1.6 mg, 9.9  $\mu\text{mol}$ )



$$n(\text{I}) = \frac{5493857}{4346752} \times 9.9 \mu\text{mol} = 12.5 \mu\text{mol} \quad \% \text{yield} = \frac{12.5 \mu\text{mol}}{34.4 \mu\text{mol}} = 36\%$$



$$n(\text{II}) = \frac{7506410}{4346752} \times 9.9 \mu\text{mol} = 17.0 \mu\text{mol} \quad \% \text{yield} = \frac{17.0 \mu\text{mol}}{34.3 \mu\text{mol}} = 49\%$$

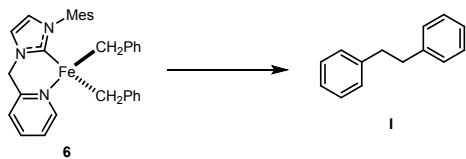


$$n(\text{III}) = \frac{1973863}{4346752} \times 9.9 \mu\text{mol} = 4.5 \mu\text{mol} \quad \% \text{yield} = \frac{4.5 \mu\text{mol} \times 2}{34.4 \mu\text{mol}} = 26\%$$

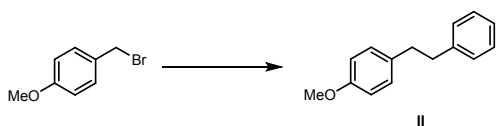
Conversion of *p*-methoxybenzyl bromide: 49% + 26% = 75%

## Yield Calculations for run 2:

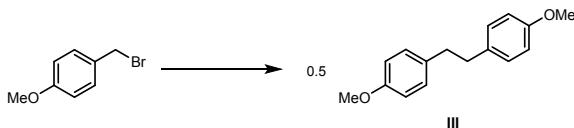
Compound **6** (17.7mg, 34.4  $\mu\text{mol}$ ), *p*-methoxybenzyl bromide (5  $\mu\text{L}$ , 34.3  $\mu\text{mol}$ ),  $\text{C}_6\text{Me}_6$  (2.6 mg, 16.0  $\mu\text{mol}$ )



$$n(\text{I}) = \frac{4964872}{6987122} \times 16.0 \mu\text{mol} = 11.4 \mu\text{mol} \quad \% \text{yield} = \frac{11.4 \mu\text{mol}}{34.4 \mu\text{mol}} = 33\%$$



$$n(\text{II}) = \frac{7414024}{6987122} \times 16.0 \mu\text{mol} = 17.0 \mu\text{mol} \quad \% \text{yield} = \frac{17.0 \mu\text{mol}}{34.3 \mu\text{mol}} = 49\%$$



$$n(\text{III}) = \frac{2170297}{6987122} \times 16.0 \mu\text{mol} = 5.0 \mu\text{mol} \quad \% \text{yield} = \frac{5.0 \mu\text{mol} \times 2}{34.3 \mu\text{mol}} = 29\%$$

Conversion of *p*-methoxybenzyl bromide:  $49\% + 29\% = 78\%$

Average yield of **I** =  $(36\% + 33\%) / 2 = 35\%$

Average yield of **II** =  $(49\% + 49\%) / 2 = 49\%$

Average yield of **III** =  $(26\% + 29\%) / 2 = 28\%$

Average conversion of *p*-methoxybenzyl bromide =  $(75\% + 78\%) / 2 = 77\%$

## 5. References:

1. Apex 2 Software Package; Bruker AXS Inc., Madison, WI, 2013. 6.
2. Sheldrick, G. M. *Acta Crystallogr.*, Sect. A: Found. Crystallogr. **2008**, *64*, 112.
3. <http://shelx.uni-ac.gwdg.de/SHELX/index.php> (accessed on July 4, 2013 and September 4, 2015).
4. Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.