

# SUPPORTING INFORMATION

## **Preparation, Structure and Reactivity of Non-Stabilized Organoiron Compounds. Implications for Iron-Catalyzed Cross Coupling Reactions**

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**General.** All reactions were carried out under Ar. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et<sub>2</sub>O, DME (Mg-anthracene), CH<sub>2</sub>Cl<sub>2</sub> (P<sub>4</sub>O<sub>10</sub>), MeCN, Et<sub>3</sub>N, TMEDA, pyridine, DMF (CaH<sub>2</sub>), MeOH (Mg), hexane, cyclohexane, toluene, benzene (Na/K); Flash chromatography: Merck silica gel 60 (230-400 mesh); NMR: Spectra were recorded on a DPX 300 or AV 400 in the solvents indicated; chemical shifts ( $\delta$ ) are given in ppm relative to residual solvent peaks, coupling constants ( $J$ ) in Hz. IR: Nicolet FT-7199 spectrometer, wavenumbers in cm<sup>-1</sup>. MS (EI): Finnigan MAT 8200 (70 eV), HRMS: Finnigan MAT 95, Bruker APEX III FT-ICR-MS (7 T magnet); Melting points: Büchi melting point apparatus (uncorrected); Elemental analyses: H. Kolbe, Mülheim/Ruhr. All commercially available compounds (Lancaster, Fluka, Aldrich) were used as received unless stated otherwise.

### Preparation of the Iron Complexes

For a large scale syntheses of [CpFe(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>][Li(tmeda)] (**7**) and [CpFe(cod)][Li(dme)] (**11**) and a discussion of the structure of these complexes in the solid state, see ref. <sup>1</sup>. For large scale syntheses of [Cp\*(tmeda)FeCl] (**13**), [Cp\*Fe(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>][Li(tmeda)] (**14**), and [Cp\*Fe(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>] (**15**), see ref. <sup>2</sup>.

**Large Scale Preparation of [Fe(C<sub>2</sub>H<sub>4</sub>)<sub>4</sub>][Li(tmeda)]<sub>2</sub> (**8**).** A carefully dried autoclave was charged with THF (75 mL), which was saturated with ethylene at -40°C. Ferrocene (12.6 g, 68 mmol) and lithium granules (2.80 g, 406 mmol) were then successively added while keeping the temperature at -40°C. The autoclave was closed and the mixture allowed to reach ambient temperature before pressurizing the autoclave with ethylene such that a constant pressure of 5-8 bars was maintained over a period of 22 h, during which time the mixture was vigorously stirred. After venting the autoclave, all insoluble materials were carefully filtered off under Ar at 0°C. Freshly distilled TMEDA (75 mL) was added to the greenish-brown filtrate and the resulting mixture kept at -10°C for 1h and at -25°C for 22 h. The precipitate formed was filtered off at -30°C, rinsed with cold Et<sub>2</sub>O (2 x 20 mL) and dried to give crude **8** as an olive-green solid (12.1 g, 43%).

Analytically pure samples were obtained by recrystallization as follows: An aliquot of the crude material (5.0 g) was suspended at 0°C in THF (25 mL) and insoluble residues were filtered off under Ar. A mixture of freshly distilled TMEDA (5 mL) and Et<sub>2</sub>O (20 mL) was then added and the resulting solution kept for 24 h at -30°C, leading to the precipitation of pure **8** in form of olive-green crystals (3.84 g, 77%). The material can be stored at -20°C under Ar for extended periods of time (>> 1 year) without noticeable loss of activity. <sup>13</sup>C NMR (100 MHz, THF-d<sub>8</sub>, -30°C):  $\delta$  = 57.0 (t), 50.9 (t), 46.2 (q), 27.9 (t); elemental analysis, calcd for C<sub>20</sub>H<sub>48</sub>FeLi<sub>2</sub>N<sub>4</sub> (414.36): C 57.97, H 11.68, N 13.52; found: C 57.70, H 11.83, N 13.31.

<sup>1</sup> Fürstner, A.; Majima, K.; Martín, R.; Krause, H.; Kattinig, E.; Goddard, R.; Lehmann, C. W. *J. Am. Chem. Soc.* **2008**, *130*, 1992.

<sup>2</sup> Jonas, K.; Klusmann, P.; Goddard, R. *Z. Naturforsch., B: Chem. Sci.* **1995**, *50*, 394.

**Large Scale Preparation of [Fe(cod)<sub>2</sub>][Li(dme)]<sub>2</sub> (9).**<sup>3</sup> A carefully dried autoclave was charged at  $-80^{\circ}\text{C}$  with ferrocene (50.0 g, 269 mmol), Li granules (9.20 g, 1.33 mol) and 1,2-dimethoxyethane (DME, 250 mL, saturated with ethylene at  $-30^{\circ}\text{C}$  immediately prior to use). The autoclave was closed and pressurized with ethylene such that a pressure of 4-6 bar was maintained constant while the vigorously stirred mixture was allowed to reach ambient temperature. After stirring for 22 h under constant ethylene pressure, the autoclave was vented, and all insoluble materials were carefully filtered off under Ar at  $0^{\circ}\text{C}$ . Freshly distilled 1,5-cyclooctadiene (COD, 100 mL) was introduced and the resulting mixture stirred under a constant vacuum of ca. 0.5 bar at  $70^{\circ}\text{C}$  for 9 h before it was slowly cooled to  $-30^{\circ}\text{C}$  over a period of 20 h with the aid of a cryostat. The precipitate was filtered off at  $-30^{\circ}\text{C}$  and washed with cold Et<sub>2</sub>O (2 x 100 mL). The crude product thus formed was suspended in DME (400 mL) and COD (8 mL) at  $80^{\circ}\text{C}$ , all insoluble residues were filtered off, and the filtrate was again slowly cooled to  $-30^{\circ}\text{C}$  with the aid of a cryostat over a period of 20h. The resulting product was filtered off at this temperature, rinsed with cold Et<sub>2</sub>O (2 x 80 mL) and dried in vacuo to give complex **9** in form of orange crystals (27.4 g, 22%). <sup>13</sup>C NMR (100 MHz, THF-d<sub>8</sub>,  $-20^{\circ}\text{C}$ ):  $\delta = 65.0, 58.6, 47.7$  (br), 46.1, 39.0, 31.1; elemental analysis, calcd for C<sub>20</sub>H<sub>32</sub>FeLi<sub>2</sub>O<sub>4</sub> (406.20): C 59.14, H 7.94; found C 59.42, H 8.11. The material can be stored at  $-20^{\circ}\text{C}$  under Ar for extended periods of time ( $>> 1$  year) without noticeable loss of activity.

**Preparation of [(Me<sub>4</sub>Fe)(MeLi)][Li(OEt<sub>2</sub>)<sub>2</sub>] (3).** A solution of FeCl<sub>3</sub> (3.80 g, 23.4 mmol) in Et<sub>2</sub>O (50 mL) was slowly added to a solution of MeLi (1.6 M in Et<sub>2</sub>O, 73 mL, 117 mmol) in Et<sub>2</sub>O (20 mL) at  $-78^{\circ}\text{C}$ . The resulting dark brown mixture was stirred at that temperature for 17 h and then for another 24 h at  $-30^{\circ}\text{C}$ , whereby a color change to red-brown was observed. The precipitated salts were filtered off under Ar through a jacketed frit at  $-30^{\circ}\text{C}$ , the resulting filtrate was concentrated to ca. 1/2 of its original volume and then kept at  $-78^{\circ}\text{C}$  for 3 d. The precipitated complex was filtered off at  $-78^{\circ}\text{C}$  and dried in vacuo to give the title product as red-brownish, exceptionally sensitive crystals which can be stored at that temperature for months (4.98 g, 71%). However, the product is thermally labile even under inert atmosphere at temperatures  $\geq 0^{\circ}\text{C}$  and vigorously ignites in air.

**Preparation of [(Ph<sub>4</sub>Fe)][Li(OEt<sub>2</sub>)<sub>2</sub>][Li(1,4-dioxane)] (5).** A solution of PhLi (1.8 M in Et<sub>2</sub>O, 5.8 mL, 10.5 mmol) was slowly added to a suspension of FeCl<sub>2</sub>(THF)<sub>1.44</sub> (606 mg, 2.62 mmol) in Et<sub>2</sub>O (40 mL) at  $-40^{\circ}\text{C}$  and the resulting suspension was stirred for 18 h at  $-20^{\circ}\text{C}$ . The precipitated salts were filtered off through a jacketed frit at  $-20^{\circ}\text{C}$  and the resulting filtrate was concentrated to ca. 1/3 of its original volume before 1,4-dioxane (20 mL) was introduced, causing the precipitation of a mustard colored solid. This highly pyrophoric material was filtered off and dried in vacuo (735 mg, 46%). Repeated recrystallization from Et<sub>2</sub>O gave crystals suitable for X-ray structure analysis.

**Preparation of [Cp\*Fe(allyl)(C<sub>2</sub>H<sub>4</sub>)] (38).** Freshly distilled allyl chloride (500 mg, 6.56 mmol) was slowly added to a stirred orange colored suspension of [Cp\*Fe(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>][Li(tmeda)] (**14**) (2.43 g, 6.56 mmol) in pentane (50 mL) at  $-20^{\circ}\text{C}$ , causing an almost instantaneous color change to dark red and the slow precipitation of LiCl. After stirring for 16 h at  $-20^{\circ}\text{C}$ , the

<sup>3</sup> Schieferstein, L.; Dissertation, Ruhr-Universität Bochum, 1978.

mixture was allowed to reach 0°C, the solvent was distilled off under reduced pressure and the residue suspended in cold (-10°C) pentane (15 mL). Insoluble materials were filtered off under Ar at 0°C and the resulting filtrate was kept at -30°C, causing the precipitation of the title complex in form of dark red crystals (736 mg, 43%, collected in three fractions). The material is highly air sensitive but can be stored at -30°C under Ar for prolonged periods of time without noticeable decomposition. <sup>1</sup>H NMR (300 MHz, THF-d<sub>8</sub>): δ = 2.83 (d, *J* = 7.3 Hz, 2H), 1.50 (s, 15H), 0.94 (m, 2H), 0.79 (d, *J* = 11.3 Hz, 2H), 0.41 (m, 1H), 0.20 (m, 2H); <sup>13</sup>C NMR (75 MHz, THF-d<sub>8</sub>): δ = 99.9, 90.4, 49.4, 44.4, 9.5; MS (EI): *m/z* (%): 260 (4) [M<sup>+</sup>], 232 (68), 190 (100), 188 (48), 174 (29), 133 (24), 119 (14); elemental analysis calcd (%) for C<sub>15</sub>H<sub>24</sub>Fe: C 69.23, H 9.30; found: C 69.11, H 9.19.

**Preparation of [CpFe(cyclooctenyl)(C<sub>2</sub>H<sub>4</sub>)] (36).** Prepared analogously from [CpFe(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>][Li(tmeda)] (7) and cyclooctenyl bromide in form of dark red crystals (2.50 g, 50%). The material is highly air sensitive but can be stored at -30°C under Ar for prolonged periods of time without noticeable decomposition. <sup>1</sup>H NMR (300 MHz, THF-d<sub>8</sub>, 243 K): δ = 4.21 (s, 5H), 3.99 (q, *J* = 8.4 Hz, 2H), 2.33 (m, 2H), 1.84 (d, *J* = 11.1 Hz, 2H), 1.72 (s, 1H), 1.32 (br s, 4H), 1.09 (m, 3H), -0.04 (d, *J* = 11.1 Hz, 2H), -0.20 (t, *J* = 8.0 Hz, 1H); <sup>13</sup>C NMR (75 MHz, THF-d<sub>8</sub>, 193 K): δ = 123.4 (trace of free ethene), 99.3, 85.2, 59.4 (br), 40.6, 34.0, 28.6 (br), 22.8 (br); elemental analysis calcd (%) for C<sub>15</sub>H<sub>22</sub>Fe (258.19): C 69.78, H 8.59; found: C 69.40, H 8.38.

**Preparation of [Cp\*Fe(allyl)Cl] (46).** Freshly distilled allyl chloride (199 mg, 2.60 mmol) was added to a solution of [Cp\*Fe(allyl)(C<sub>2</sub>H<sub>4</sub>)] (38) (674 mg, 2.59 mmol) in Et<sub>2</sub>O (10 mL) at 0°C and the resulting mixture was stirred at that temperature for 24 h. After evaporation of the solvent, the residue was suspended in Et<sub>2</sub>O (5 mL), insoluble materials were filtered off under Ar at 0°C, and the filtrate was kept at -30°C overnight, causing the precipitation of the title complex in form of red-black crystals (304 mg, 44%). The material is highly air sensitive but can be stored at -30°C under Ar for prolonged periods of time without noticeable decomposition. MS (EI): *m/z* (%): 269 (13), 267 (40) [M<sup>+</sup>], 226 (100), 211 (24), 190 (71), 188 (22), 174 (14), 135 (22), 133 (20), 119 (35), 105 (17), 91 (18), 41 (12); elemental analysis calcd (%) for C<sub>13</sub>H<sub>20</sub>FeCl (267.60): C 58.35, H 7.53; found: C 58.08, H 7.56.

**Preparation of [Cp\*Fe(allyl)Me] (48).** A solution of MeLi (1.6 M in Et<sub>2</sub>O, 1.65 mL, 2.65 mmol) was added to a suspension of [Cp\*Fe(allyl)Cl] (46) (710 mg, 2.65 mmol) in Et<sub>2</sub>O (25 mL) at -78°C, leading to the formation of a dark-red solution from which LiCl started to precipitate when the mixture was allowed to reach 0°C. After stirring for 30 min at that temperature, all volatile materials were distilled off in vacuo, the residue was suspended in cold (0°C) pentane (5 mL), insoluble materials were filtered off, and the filtrate was kept at -30°C, causing the precipitation of the title complex in form of red needles (459 mg, 70%). The material is highly air sensitive but can be stored at -30°C under Ar for prolonged periods of time without noticeable decomposition. MS (EI): *m/z* (%): 247 (4) [M<sup>+</sup>], 246 (17), 245 (91), 232 (22), 191 (50), 190 (100), 189 (49), 188 (51), 186 (13), 174 (32), 135 (34), 134 (22), 133 (65), 132 (12), 119 (40), 117 (11), 105 (15), 91 (18), 56 (16); elemental analysis calcd (%) for C<sub>14</sub>H<sub>23</sub>Fe (247.18): C 68.03, H 9.38; found: C 67.84, H 9.09.

**Preparation of [CpFePh(PMe<sub>3</sub>)<sub>2</sub>] (40).** A solution of complex 7 (1.67 g, 5.5 mmol), chlorobenzene (624 mg, 5.5 mmol) and PMe<sub>3</sub> (845 mg, 11.1 mmol) in THF (120 mL) was

stirred for 20 h at ambient temperature. For work up, the solvent was distilled off under reduced pressure ( $10^{-3}$  Torr), the residue was suspended in pentane (100 mL), all insoluble materials were filtered off and the dark red filtrate was concentrated to a volume of ca. 20 mL. This concentrated solution was slowly cooled to  $-20^{\circ}\text{C}$  and kept at that temperature for 3 d, causing the precipitation of dark red crystals (345 mg, 18%). The material must not be dried under high vacuum as this may cause spontaneous decomposition.  $^1\text{H}$  NMR (400 MHz, THF- $d_8$ ):  $\delta$  = 7.47 (d,  $J$  = 6.8 Hz, 2H), 6.56 (dd,  $J$  = 6.8, 6.7 Hz, 2H), 6.49 (t,  $J$  = 6.7 Hz, 1H), 3.91 (t,  $J$  = 1.7 Hz, 5H), 1.32 [ $J(\text{P}_{\text{A}}\text{H} + \text{P}_{\text{B}}\text{H})$  = 7.8 Hz, 18H];  $^{13}\text{C}$  NMR (100 MHz, THF- $d_8$ ):  $\delta$  = 172.6 (t,  $J_{\text{CP}}$  = 27 Hz), 147.3 (t,  $J_{\text{CP}}$  = 5 Hz), 124.8, 119.4, 78.7, 22.4 [ $J(\text{P}_{\text{A}}\text{C} + \text{P}_{\text{B}}\text{C})$  = 21.4 Hz];  $^{31}\text{P}$  NMR (162 MHz, THF- $d_8$ ):  $\delta$  = 36.8 ppm; MS (EI):  $m/z$  (%): 350 (34), 275 (11), 274 (61), 273 (26), 272 (100), 259 (31), 209 (10), 198 (31), 197 (32), 196 (14), 186 (21), 153 (18), 142 (20), 141 (18), 132 (14), 121 (25), 78 (28), 76 (43), 75 (14), 61 (55), 59 (35); elemental analysis calcd (%) for  $\text{C}_{17}\text{H}_{28}\text{P}_2\text{Fe}$  (350.20): C 58.31, H 8.06; found: C 58.45, H 8.19.

## Iron Catalyzed Cross Coupling Experiments

### Representative Procedure for the Iron Catalyzed Cross Coupling of Alkyl Halides with Arylmagnesium Halides. Preparation of 1,4-Diphenyl-butan-1-one (Table 4, entry 19).<sup>4</sup>


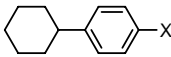
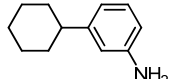
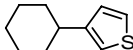

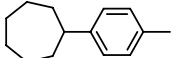
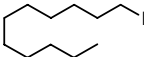
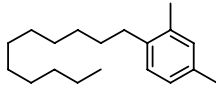
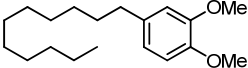
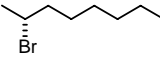
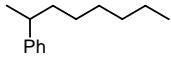
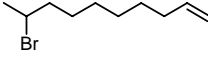
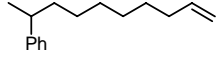
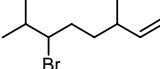
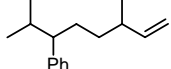




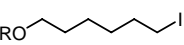
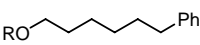
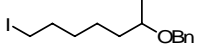
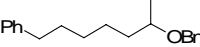
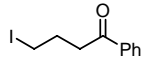
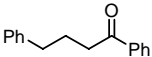
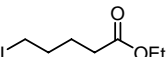
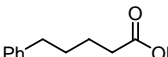
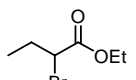
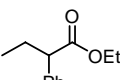
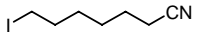
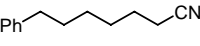
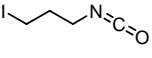
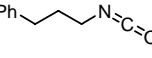
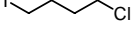
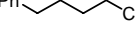
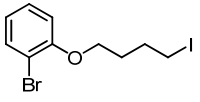
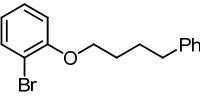
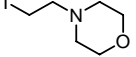
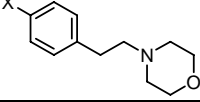
A solution of 4-iodo-1-phenylbutan-1-one<sup>5</sup> (137 mg, 0.5 mmol) in THF (1 mL) was added to a solution of complex **8** (10 mg, 5 mol%) in THF (2 mL) at  $-20^{\circ}\text{C}$ , causing an immediate color change from green to dark red. A solution of PhMgBr (1.2 M in  $\text{Et}_2\text{O}$ ; 0.50 mL, 0.6 mmol) was then introduced and the resulting mixture stirred at that temperature for 5 min. For work up, the reaction was carefully quenched with HCl (1 M, 3 mL), the aqueous layer was extracted with  $\text{Et}_2\text{O}$  (3 x 5 mL), the combined organic phases were dried over  $\text{Na}_2\text{SO}_4$  and evaporated, and the residue purified by flash chromatography, affording the title compound as a yellow solid (102 mg, 91%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  = 7.47 (m, 10H), 3.24 (t,  $J$  = 6.6 Hz, 2H), 3.04 (t,  $J$  = 6.9 Hz, 2H), 2.18 (2H, m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  = 199.7, 141.5, 137.2, 132.5, 129.4, 128.9, 128.5, 127.7, 125.6, 39.8, 36.2, 24.1; IR (film):  $\tilde{\nu}$  = 3055, 2946, 1766, 1616, 1491, 1344, 1220, 1008, 892, 706; elemental analysis calcd (%) for  $\text{C}_{16}\text{H}_{16}\text{O}$ : C, 85.68; H, 7.19; found: C, 85.59; H, 7.33.

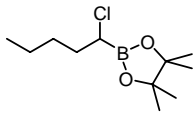
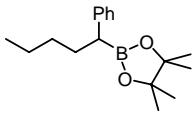
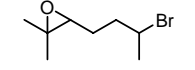
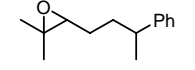
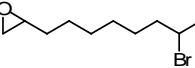
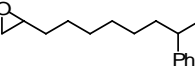
All compounds compiled in Tables 4 and 5 were prepared analogously; their analytical and spectroscopic data are compiled below.

<sup>4</sup> Matsuda, T.; Makino, M.; Murakami, M. *Org. Lett.* **2004**, *6*, 1257.

<sup>5</sup> Zhou, J. (S.); Fu, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 14726.

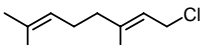
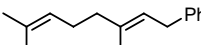
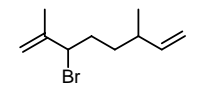
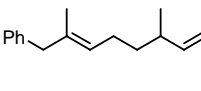




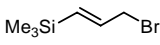
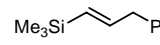
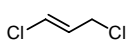
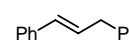
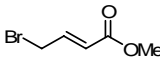
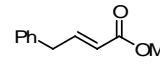
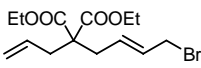
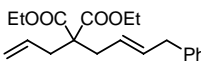
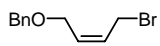
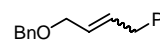
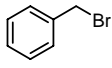
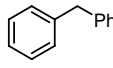
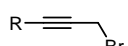
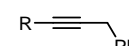
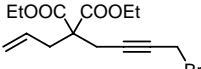
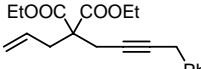
**Table 4 (full list).** Cross coupling of alkyl halides with aromatic Grignard reagents catalyzed by the lithium ferrate complex **8**.<sup>a</sup>

Nr	Substrate	Product	Yield <sup>b</sup>
1			94% (X = H)
2			95% (X = OMe)
3			67% (X = Cl) <sup>c</sup>
4			93% (X = Ph) <sup>c</sup>
5			86% (X = NMe <sub>2</sub> )
6			88% (X = NH <sub>2</sub> ) <sup>c,d</sup>
7			77%
8			95%
9			94%
10			94%
11			93% <sup>e</sup>
12			96%
13			89%
14			58% <sup>f</sup>
15			74%
16			82% (R = Ac)
17			84% (R = TBS)
18			95%
19			91%
20			88%
21			87%
22			83%
23			90%
24			86%
25			68%
26			87% (X = H) <sup>c</sup>
27			85% (X = Ph) <sup>c</sup>

28			92%
29			66%
30			56%

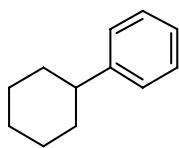
<sup>a</sup> complex **8** (5 mol%), THF,  $-20^{\circ}\text{C}$ , unless stated otherwise; <sup>b</sup> isolated yield of pure product; variable amounts of Ar–Ar derived from the homocoupling of the ArMgX reagent were removed by flash chromatography; <sup>c</sup> at  $0^{\circ}\text{C}$ ; <sup>d</sup> the product is racemic; <sup>e</sup> *exo:endo* = 94:6

**Table 5 (full list).** Cross coupling of allylic, benzylic and propargylic halides with aromatic Grignard reagents catalyzed by the lithium ferrate complex **8**.<sup>a</sup>

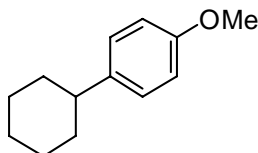
Nr	Substrate	Product	Yield <sup>b</sup>
1			87%
2			84%
3			95%
4			81%
5			97%
6			96% <sup>c</sup>
7			94%
8			93%
9			80% <sup>d</sup>
10			62%
11			93% (R = Ph) <sup>e</sup>
12			96% (R = TMS) <sup>e</sup>
13			87%

<sup>a</sup> complex **8** (5 mol%), THF,  $-20^{\circ}\text{C}$ ; <sup>b</sup> isolated yield of pure product; variable amounts of biphenyl were removed by flash chromatography; <sup>c</sup> using 2.2 equivalents of PhMgBr; <sup>d</sup> *E:Z* = 4.4:1; <sup>e</sup> traces of allenic by-products were removed by flash chromatography

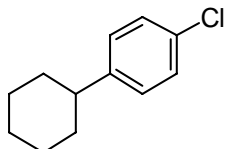
**Cyclohexylbenzene.** Colorless oil (0.075 g, 94%); the spectroscopic data correspond to those previously reported in the literature.<sup>6</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.26 (5H, m), 2.56 (1H, m), 1.86 (5H, m), 1.42 (5H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 147.8, 128.4, 127.3, 126.1, 45.2, 35.1, 27.3; IR:  $\tilde{\nu}$  = 3045, 3015, 2910, 1606, 1455, 1044, 997, 515; elemental analysis calcd (%) for C<sub>12</sub>H<sub>16</sub>: C, 89.94; H, 10.06; found: C, 90.18; H, 9.82.



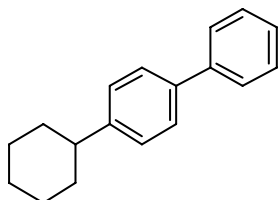
**1-Cyclohexyl-4-methoxybenzene.** Yellow solid (0.090 g, 95%); the spectroscopic data correspond to those previously reported in the literature.<sup>7</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.16 (2H, d,  $J$  = 8.2 Hz), 6.81 (2H, d,  $J$  = 8.2 Hz), 3.73 (3H, s), 2.42 (1H, m), 1.82 (5H, m), 1.34 (5H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 158.1, 140.8, 127.3, 113.8, 55.0, 44.1, 34.9, 26.6, 25.9; IR:  $\tilde{\nu}$  = 3022, 2931, 1577, 1478, 1235, 1066, 799; HRMS (CI): calcd for C<sub>13</sub>H<sub>18</sub>O: 190.1358; found: 190.1355.



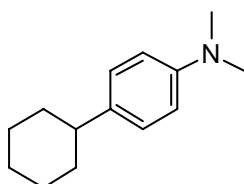
**1-Chloro-4-cyclohexylbenzene.** The compound was prepared according to the representative procedure, except that the reaction was performed at 0°C (1 h). Colorless oil (0.065 g, 67%); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.47 (2H, d,  $J$  = 8.2 Hz), 7.12 (2H, d,  $J$  = 8.2 Hz), 2.55 (1H, m), 1.89 (5H, m), 1.41 (5H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 146.7, 131.4, 128.4, 119.03, 43.7, 34.2, 26.4, 25.3; IR:  $\tilde{\nu}$  = 3015, 2977, 1610, 1550, 1422, 1337, 1105, 956, 707; HRMS (CI): calcd for C<sub>12</sub>H<sub>15</sub>Cl: 194.08623; found: 194.08609.



**4-Cyclohexyl-biphenyl.** The compound was prepared according to the representative procedure, except that the reaction was performed at 0°C (1 h). White solid (0.11 g, 93%); Mp 75-77 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  = 7.38 (9H, m), 2.48 (1H, m), 1.74 (5H, m), 1.29 (5H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  = 146.3, 141.2, 138.7, 128.7, 127.2, 127.0, 126.9, 126.8, 44.2, 34.5, 26.9, 26.2; IR:  $\tilde{\nu}$  = 3028, 2923, 2849, 2667, 1598, 1581, 1484, 1447, 1409, 1335, 1177, 1075, 909, 830, 762, 733, 697; MS (EI):  $m/z$  (%): 167 (34), 180 (29), 193 (51), 236 (100); HRMS (CI): calcd for C<sub>18</sub>H<sub>20</sub>: 236.15650; found: 236.15678.



**4-Cyclohexyl-N,N-dimethylbenzenamine.** Yellow oil (0.114 g, 86%); the spectroscopic data were identical to those previously reported in the literature.<sup>8</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.16 (2H, d,  $J$  = 8.6 Hz), 6.77 (2H, d,  $J$  = 8.6 Hz), 2.97 (6H, s), 2.48 (1H, m), 1.93 (4H, m), 1.79 (1H, m), 1.45 (4H, m), 1.30 (1H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 149.0, 136.5, 127.2, 112.9, 43.5, 40.8, 34.7, 27.0, 26.2; IR:  $\tilde{\nu}$  = 2923, 2850, 2796, 1614, 1521, 1479, 1344, 1210, 1163, 1135, 1060, 948, 813, 780; MS (EI):  $m/z$  (%): 134 (32), 146 (15), 160 (82), 203 (100); HRMS (CI): calcd for C<sub>14</sub>H<sub>21</sub>N: 203.16740; found: 203.16728.



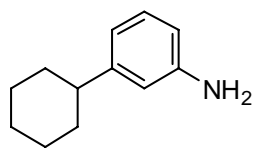
<sup>6</sup> Powell, D. A.; Fu, G. C. *J. Am. Chem. Soc.* **2004**, *126*, 7788.

<sup>7</sup> Nakamura, M.; Matsuo, K.; Ito, S.; Nakamura, E. *J. Am. Chem. Soc.* **2004**, *126*, 3686.

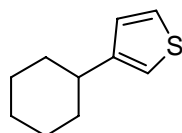
<sup>8</sup> Oosterbaan, W. D.; van Gerven, P. C. M.; van Walree, C. A.; Koeberg, M.; Piet, J. J.; Havenith, R. W. A.; Zwicker, J. W.; Jennekens, L. d. W.; Gleiter, R. *Eur. J. Org. Chem.* **2003**, 3117.



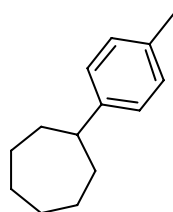
**3-Cyclohexyl-phenylamine.** The compound was prepared according to the representative procedure using *m*-bistrimethylsilylaminophenylmagnesium bromide, but performing the reaction at 0°C (1.5 h); Hydrolytic workup gave the title compound as a yellow oil (0.077 g, 88%); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 6.89 (4H, m), 3.49 (2H, brs), 2.41 (1H, m), 1.73 (5H, m), 1.41 (5H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 149.6, 146.4, 129.5, 117.3, 114.1, 112.8, 44.6, 34.4, 27.0, 26.2; IR: ν̄ = 3345, 2966, 1617, 1409, 1210, 997, 841, 787, 602; elemental analysis calcd (%) for C<sub>12</sub>H<sub>17</sub>N: C, 82.23; H, 9.78; found: C, 82.06; H, 9.66.



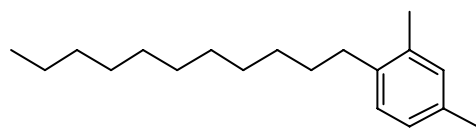
**3-Cyclohexylthiophene.** Yellow oil (0.064 g, 77%); the spectroscopic data correspond to those previously reported in the literature.<sup>9</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 7.22 (1H, dd, *J* = 5.0, 2.9 Hz), 6.97 (1H, dd, *J* = 5.0, 1.2 Hz), 6.91 (1H, m), 2.60 (1H, m), 2.13 (1H, m), 1.96 (2H, m), 1.81-1.35 (7H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 149.2, 127.0, 124.9, 118.3, 39.6, 34.2, 26.7, 26.2; IR: ν̄ = 2925, 2851, 2656, 1532, 1448, 1411, 1081, 938, 891, 834, 772, 710; MS (EI): *m/z* (%): 45 (19), 91 (17), 98 (94), 110 (42), 123 (89), 137 (17), 166 (100); HRMS (CI): calcd for C<sub>10</sub>H<sub>14</sub>S: 166.08162; found: 166.08143; elemental analysis calcd (%) for C<sub>10</sub>H<sub>14</sub>S: C, 72.23; H, 8.49; found: C, 72.39; H, 8.42.



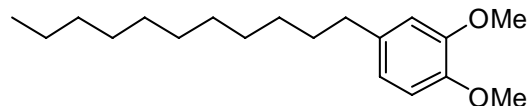
***p*-Tolyl-cycloheptane.** Colorless oil (0.089 g, 95%); the spectroscopic data correspond to those previously reported in the literature.<sup>10</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 7.14 (4H, m), 2.63 (1H, m), 2.31 (3H, s), 1.73 (12H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 147.8, 134.2, 128.7, 126.6, 46.5, 37.4, 28.5, 27.4, 21.2; IR: ν̄ = 3046, 2981, 1605, 1455, 1041, 934, 701; elemental analysis calcd (%) for C<sub>14</sub>H<sub>20</sub>: C, 89.29; H, 10.71; found: C, 89.44; H, 10.56.



**2,4-Dimethyl-1-undecylbenzene.** Colorless oil (0.171 g, 94%); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 6.93 (1H, d, *J* = 7.6 Hz), 6.85 (2H, m), 2.46 (2H, t, *J* = 7.7 Hz), 2.20 (3H, s), 2.18 (3H, s), 1.45 (2H, m), 1.25-1.10 (16H, m), 0.78 (3H, t, *J* = 6.8 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 140.0, 135.5, 135.0, 130.8, 128.7, 126.4, 33.7, 32.9, 31.6, 30.5, 29.7 (2C), 29.6 (2C), 29.4, 22.7, 20.4, 19.1, 14.1; IR: ν̄ = 3004, 29225, 2854, 1617, 1503, 1303, 1465, 1377, 1158, 1033, 873, 816, 721; MS (EI): *m/z* (%): 91 (4), 119 (100), 260 (37); HRMS (CI): calcd for C<sub>19</sub>H<sub>32</sub>: 260.25040; found: 260.25071.



**1,2-Dimethoxy-4-undecylbenzene.** Yellow solid (0.137 g, 94%); Mp 77-79°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 6.85-6.63 (3H, m), 3.90 (3H, s), 3.86 (3H, s), 2.57 (2H, t, *J* = 7.5 Hz), 1.61 (2H, t, *J* = 7.4 Hz), 1.28 (16H, m), 0.90 (3H, t, *J* = 6.5 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 148.8, 147.0, 135.7, 120.1, 111.9, 111.3, 56.0, 55.8, 35.6, 31.9, 31.7, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 22.7, 14.1; IR: ν̄ = 2926, 2853, 1608, 1591, 1516, 1465, 1417, 1332, 1262, 1237, 1156,

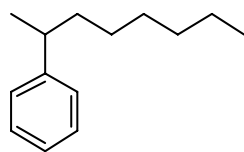


<sup>9</sup> Bongini, A.; Barbarella, G.; Favaretto, L.; Sotgiu, G.; Zambianchi, M.; Casarini, D. *Tetrahedron*, **2002**, *58*, 10151.

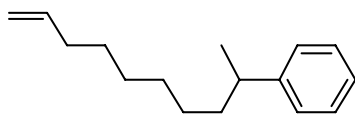
<sup>10</sup> Mahindaratne, M.P.D.; Wimalasena, K.W. *J. Org. Chem.* **1998**, *63*, 2858.

1141, 1032, 849, 803, 764; MS (EI):  $m/z$  (%): 137 (6), 151 (100), 164 (3), 292 (88); HRMS (ESI+): calcd for  $C_{19}H_{32}O_2+Na$ : 315.23000; found: 315.23005 (M+Na).

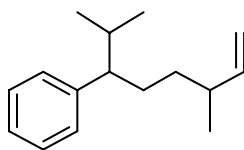
**1-(Octan-2-yl)benzene.** Colorless oil (0.078 g, 93%);  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  = 7.38 (2H, m), 7.28 (3H, m), 2.76 (1H, m), 1.67 (2H, m), 1.36 (11H, m), 0.83 (3H, d,  $J$  = 7.1 Hz);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  = 148.0, 128.3, 127.0, 125.7, 40.0, 38.5, 31.9, 29.4, 27.7, 22.7, 22.6, 14.1; IR:  $\tilde{\nu}$  = 3018, 2956, 2924, 1609, 1494, 1452, 1376, 1158, 1119, 760, 721, 698; elemental analysis calcd (%) for  $C_{14}H_{22}$ : C, 88.35; H, 11.65; found: C, 88.43; H, 11.57.



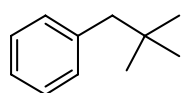
**(1-Methyl-non-8-enyl)benzene.** Colorless oil (0.104 g, 96%);  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  = 7.13 (5H, m), 5.71 (1H, m), 4.87 (2H, m), 2.59 (1H, m), 1.94 (2H, m), 1.48 (2H, m), 1.25 (11H, m);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  = 148.3, 139.6, 128.6, 127.4, 126.1, 114.6, 40.3, 38.8, 34.2, 29.9, 29.2, 28.2, 28.0, 22.7; IR:  $\tilde{\nu}$  = 3057, 2956, 1644, 1603, 1507, 1425, 1106, 1089, 909, 706; elemental analysis calcd (%) for  $C_{16}H_{24}$ : C, 88.82; H, 11.18; found: C, 88.96; H, 11.04.



**(1-Isopropyl-4-methyl-hex-5-enyl)benzene.** Yellow oil (0.096 g, 89%);  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  = 7.21 (5H, m), 5.61 (1H, m), 4.97 (2H, m), 2.61 (2H, m), 2.08-1.1 (5H, m), 0.93 (3H, d,  $J$  = 6.4 Hz), 0.87 (3H, d,  $J$  = 6.8 Hz), 0.68 (3H, d,  $J$  = 6.6 Hz);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  = 147.9, 144.6, 128.7, 127.5, 125.9, 112.8, 48.5, 39.7, 35.8, 31.9, 30.6, 21.5, 20.3, 20.1. IR:  $\tilde{\nu}$  = 3092, 2899, 1637, 1612, 1465, 1099, 910, 827; MS (EI):  $m/z$  (%): 55 (22), 69 (100), 91 (45), 125 (47), 216 (20); HRMS (CI): calcd for  $C_{16}H_{24}$ : 216.18780; found: 216.18797; elemental analysis calcd (%) for  $C_{16}H_{24}$ : C, 88.82; H, 11.18; found: C, 88.98; H, 11.02.



**1-Neopentylbenzene.** The compound was prepared according to the representative procedure, except that the reaction was performed at 0°C (4 h). Colorless oil (0.077 g, 74%); the spectroscopic data was identical to those previously reported in the literature.<sup>11</sup>  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  = 7.24 (5H, m), 2.53 (2H, s), 0.88 (9H, s);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  = 141.5, 128.5, 128.1, 126.1, 47.6, 29.1, 28.0; IR:  $\tilde{\nu}$  = 3011, 2933, 1614, 1499, 1288, 1477, 1360, 1201, 1018, 880, 773; elemental analysis calcd (%) for  $C_{11}H_{16}$ : C, 89.12; H, 10.88; found: C, 89.35; H, 10.65.



**6-Phenylhexyl acetate.** Colorless oil (0.114 g, 82%);  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  = 7.21 (2H, m), 7.13 (3H, m), 4.01 (2H, t,  $J$  = 6.4 Hz), 2.56 (2H, t,  $J$  = 6.0 Hz), 1.98 (3H, s), 1.58 (4H, m), 1.32 (4H, m);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  = 171.1, 142.6, 128.3, 128.2, 125.6, 64.5, 35.8, 31.3, 28.8, 28.5, 25.8, 20.9; IR:  $\tilde{\nu}$  = 3062, 3026, 2933, 2857, 1740, 1604, 1496, 1365, 1241, 1048, 1032, 970, 748, 699; MS (EI):  $m/z$  (%): 43 (46), 91 (93), 104 (100), 117 (43), 160 (44), 220 (9); HRMS (ESI+): calcd for  $C_{14}H_{20}O_2+Na$ : 243.13610; found: 243.13626 (M+Na).

<sup>11</sup> Hiegel, G. A.; Carney, J. R. *Synth. Commun.*, **1996**, *24*, 2625.

**(6-Phenylhexyloxy)(tert-butyl)dimethylsilane.** Colorless oil (0.172 g, 84%); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 7.48-7.11$  (5H, m), 3.55 (2H, t,  $J = 6.5$  Hz), 2.55 (2H, t,  $J = 7.6$  Hz), 1.58 (2H, t,  $J = 7.5$  Hz), 1.46-1.21 (6H), 0.86 (9H, s), 0.1 (6H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 142.7, 128.4, 128.2, 125.5, 65.8, 35.9, 32.8, 31.5, 29.1, 25.9, 25.7, 18.3, -5.3$ ; IR:  $\tilde{\nu} = 3063, 3028, 2930, 2857, 1599, 1496, 1483, 1471, 1463, 1388, 1360, 1255, 1100, 1032, 836, 776, 733, 699$ ; MS (EI):  $m/z$  (%): 75 (44), 91 (44), 117 (14), 235 (100), 277 (2); HRMS (ESI+): calcd for C<sub>18</sub>H<sub>32</sub>OSi+Na: 315.21201; found: 315.21196 (M+Na).

**(6-Benzyloxy-heptyl)benzene.** Colorless oil (0.134 g, 95%); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 7.26$  (10H, m), 4.41 (1H, d,  $J = 9.9, 6.2$  Hz), 4.31 (1H, dd,  $J = 9.9, 2.73$  Hz), 3.33 (1H, m), 2.5 (2H, t,  $J = 7.6$  Hz), 1.63-1.17 (8H, m), 1.1 (3H, d,  $J = 6.6$  Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 141.5, 140.4, 128.9, 128.7, 128.4, 127.8, 126.4, 125.7, 56.7, 36.7, 34.2, 31.3, 30.6, 26.8, 20.9$ ; IR:  $\tilde{\nu} = 3067, 2957, 1611, 1456, 1355, 1248, 1165, 1105, 1095, 1030, 926, 790$ ; MS (EI):  $m/z$  (%): 91 (100), 191 (16), 282 (4); HRMS (CI): calcd for C<sub>20</sub>H<sub>26</sub>O: 282.19837; found: 282.19866; elemental analysis calcd (%) for C<sub>20</sub>H<sub>26</sub>O: C, 85.06; H, 9.28; found: C, 85.11; H, 9.20.

**Ethyl 5-phenylpentanoate.** Colorless oil (0.118 g, 88%); the spectroscopic data correspond to those previously reported in the literature.<sup>12</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 7.20$  (5H, m), 4.17 (2H, q,  $J = 7.0$  Hz), 2.65 (2H, t,  $J = 7.5$  Hz), 2.31 (2H, t,  $J = 7.1$  Hz), 1.67 (4H, m), 1.21 (3H, t,  $J = 7.0$  Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 170.7, 137.1, 128.4, 126.9, 125.9, 61.5, 37.8, 37.3, 34.1, 23.1, 14.1$ ; IR:  $\tilde{\nu} = 3026, 2957, 2815, 1738, 1615, 1533, 1490, 1402, 1319, 1277, 1222, 1183, 1165, 1098, 977, 865, 763$ ; MS (EI):  $m/z$  (%): 77 (9), 91 (100), 105 (9), 161 (10), 206 (21); elemental analysis calcd (%) for C<sub>13</sub>H<sub>18</sub>O<sub>2</sub>: C, 75.69; H, 8.80; found: C, 75.77; H, 8.66.

**2-Phenyl-butyric acid ethyl ester.** Colorless oil (0.083 g, 87%); the spectroscopic data correspond to those previously reported in the literature.<sup>13</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 7.21$  (5H, m), 4.02 (2H, m), 3.35 (1H, t,  $J = 7.7$  Hz), 2.05 (1H, m), 1.74 (1H, m), 1.10 (3H, t,  $J = 7.1$  Hz), 0.8 (3H, t,  $J = 7.4$  Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 174.4, 139.7, 128.8, 128.3, 127.5, 60.9, 53.9, 27.2, 14.5, 2.5$ ; IR:  $\tilde{\nu} = 3066, 1733, 1610, 1414, 1202, 1031, 924, 702$ ; elemental analysis calcd (%) for C<sub>12</sub>H<sub>16</sub>O<sub>2</sub>: C, 74.97; H, 8.39; found: C, 74.91; H, 8.47.

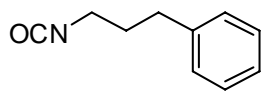
**7-Phenyl-heptanenitrile.** Yellow oil (0.078 g, 83%); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 7.27$  (5H, m), 2.55 (2H, t,  $J = 7.6$  Hz), 2.24 (2H, t,  $J = 7.1$  Hz), 1.47 (4H, m), 1.37 (2H, m), 1.30 (2H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 142.0, 128.0, 127.9, 125.4, 119.4, 35.4, 30.7, 28.1, 27.9, 24.9, 16.7$ ; IR:  $\tilde{\nu} = 3062, 2932, 2857, 2245, 1603, 1496$ ,

<sup>12</sup> Joung, M. J.; Ahn, J. H.; Lee, D. W.; Yoon, N. M. *J. Org. Chem.* **1998**, *63*, 2755.

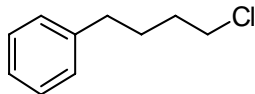
<sup>13</sup> Yang, H.; Henke, E.; Bornscheuer, U. T.; *J. Org. Chem.* **1999**, *64*, 1709.

1453, 1030, 749, 700; MS (EI):  $m/z$  (%): 91 (100), 159 (8), 187 (19); HRMS (CI): calcd for  $C_{13}H_{17}N$ , 187.13610; found: 187.13659.

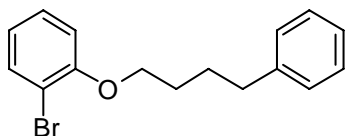
**1-(3-Isocyanatopropyl)benzene.** Colorless oil (0.217 g, 90%); the spectroscopic data correspond to those previously reported in the literature.<sup>14</sup>  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  = 7.28 (5H, m), 3.67 (2H, t,  $J$  = 6.4 Hz), 2.81 (2H, t,  $J$  = 6.9 Hz), 2.04 (2H, quint.,  $J$  = 6.5 Hz);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  = 140.9, 128.8, 128.6, 126.7, 122.1, 42.0, 32.9, 32.4; IR:  $\tilde{\nu}$  = 2966, 2252, 1695, 1608, 1447, 1427, 1356, 1298, 1209, 1164, 990, 879, 833, 761; elemental analysis calcd (%) for  $C_{10}H_{11}NO$ : C, 74.51; H, 6.88; N, 8.69; found: C, 74.60; H, 6.81; N, 8.74.



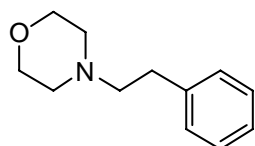
**1-(4-Chlorobutyl)benzene.** Yellow oil (0.087 g, 86%);  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  = 7.29 (5H, m), 3.58 (2H, t,  $J$  = 6.4 Hz), 2.69 (2H, d,  $J$  = 7.1 Hz), 1.83 (4H, m);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  = 141.8, 128.6, 128.4, 125.9, 44.9, 35.1, 32.1, 28.6; IR:  $\tilde{\nu}$  = 3085, 3062, 2940, 2860, 1603, 1496, 1453, 1309, 1277, 1180, 1082, 1030, 749, 699; MS (EI):  $m/z$  (%): 65 (9), 78 (6), 91 (100), 168 (17); HRMS (CI): calcd for  $C_{10}H_{13}Cl$ : 168.07058; found: 168.07078.



**1-(4-(2-Bromophenoxy)butyl)benzene.** Colorless oil (0.134 g, 68%);  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  = 7.56 (1H, dd,  $J$  = 7.9, 1.6 Hz), 7.28 (6H, m), 6.90 (1H, dd,  $J$  = 8.2, 1.3 Hz), 6.85 (1H, td,  $J$  = 7.6, 1.4 Hz), 4.06 (2H, t,  $J$  = 5.9 Hz), 2.75 (2H, t,  $J$  = 7.1 Hz), 1.91 (4H, m);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  = 155.4, 142.2, 133.3, 128.4, 128.3, 128.2, 125.8, 121.7, 113.2, 112.3, 68.9, 35.5, 28.6, 27.7; IR:  $\tilde{\nu}$  = 3062, 2940, 2860, 1587, 1572, 1482, 1468, 1453, 1278, 1248, 1161, 1126, 1052, 1030, 747, 699; MS (EI):  $m/z$  (%): 91 (100), 104 (17), 132 (31), 172 (6), 304 (5); HRMS (CI): calcd for  $C_{16}H_{17}BrO$ : 304.04629; found: 304.04662.



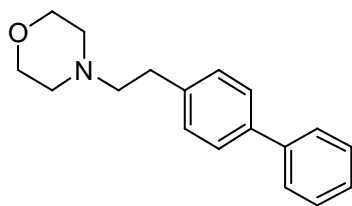
**4-(Phenethyl)morpholine.** The compound was prepared according to the representative procedure, but performing the reaction at 0°C (1 h); the reaction was diluted with  $Et_2O$  (4 mL) and quenched by addition of HCl (2 M, 3 mL); the organic phase was washed with HCl (2 M, 2 x 3 mL) and the combined aqueous phases were successively washed with  $Et_2O$  (4 mL); next, aq. sat.  $NaHCO_3$  was added until a pH of ca. 10 was reached and the aqueous layer was repeatedly extracted with  $Et_2O$ . The combined organic phases were dried over  $Na_2SO_4$ , filtered and evaporated, yielding the title compound as an analytically pure colorless oil (0.083 g, 87%); the spectroscopic data correspond to those previously reported in the literature.<sup>15</sup>  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  = 7.23 (5H, m), 3.66 (4H, t,  $J$  = 4.6 Hz), 2.73 (2H, m), 2.54 (2H, m), 2.45 (4H, t,  $J$  = 4.6 Hz);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  = 140.1, 128.7, 128.4, 126.1, 66.9, 60.8, 53.6, 33.4; IR:  $\tilde{\nu}$  = 3026, 2953, 2853, 2806, 1602, 1496, 1453, 1356, 1255, 1134, 1115, 1070, 1006, 868, 747, 698; MS (EI):  $m/z$  (%): 77 (100), 91 (46), 100 (34), 130 (22), 160 (52); elemental analysis calcd (%) for  $C_{12}H_{17}NO$ : C, 75.35; H, 8.96; N, 7.32; found: C, 75.41; H, 8.89; N, 7.28.



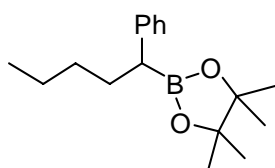
<sup>14</sup> Van Esch, J.; Schoonbeek, F.; De Loos, M.; Kooijman, H.; Spek, A. L.; Kellogg, R. M.; Feringa, B. L. *Chem. Eur. J.* **1999**, *5*, 937.

<sup>15</sup> Utsunomiya, M.; Kuwano, R.; Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 5608.

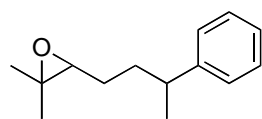
**4-(2-[1,1'-Biphenyl]-4-ylethyl)morpholine.** Prepared analogously as a white solid (0.113 g, 85%); the spectroscopic data correspond to those previously reported in the literature.<sup>16</sup> Mp 154-156 (decomp.); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.46 (9H, m), 3.68 (4H, t,  $J$  = 4.4 Hz), 2.77 (2H, m), 2.57 (2H, m), 2.47 (4H, t,  $J$  = 4.4 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 140.7, 138.9, 138.7, 128.8, 128.5, 127.1, 126.9, 126.8, 66.7, 60.5, 53.4, 32.7; IR:  $\tilde{\nu}$  = 3028, 2943, 2853, 2807, 2687, 1677, 1580, 1486, 1447, 1401, 1357, 1259, 1115, 1068, 1006, 915, 870, 826, 762, 700; MS (EI):  $m/z$  (%): 100 (100), 181 (9), 206 (7), 267 (3); elemental analysis calcd (%) for C<sub>18</sub>H<sub>21</sub>NO: C, 80.86; H, 7.92; N, 5.24; found: C, 80.91; H, 7.84; N, 5.19.



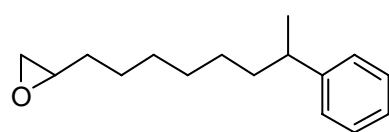
**4,4,5,5-Tetramethyl-2-(1-phenylpentyl)-1,3,2-dioxaborolane.** Colorless oil (0.151 g, 92%); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.04-7.23 (5H, m), 2.33 (1H, t,  $J$  = 7.9 Hz), 1.78 (1H, m), 1.60 (1H, m), 1.27-1.16 (4H, m), 1.14 (6H, s), 1.12 (6H, s), 0.81 (3H, t,  $J$  = 7.0 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 143.5, 128.3, 128.1, 125.0, 83.1, 32.2, 31.5, 24.6, 24.5, 22.7, 14.0 (CH-B not observed);<sup>17</sup> <sup>11</sup>B NMR (CDCl<sub>3</sub>, 96.3 MHz):  $\delta$  = 31.1; IR:  $\tilde{\nu}$  = 3025, 2978, 2858, 1601, 1482, 1467, 1360, 1323, 1271, 1165, 1144, 967, 849, 738, 700; MS (EI):  $m/z$  (%): 91 (36), 118 (33), 174 (27), 217 (64), 274 (100); HRMS (CI): calcd for C<sub>17</sub>H<sub>27</sub>BO<sub>2</sub>: 274.21041; found: 274.21069.



**2,2-Dimethyl-3-(3-phenylbutyl)oxirane.** Colorless oil (0.081 g, 66%, dr = 1:1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.22 (4H, m), 7.13 (6H, m), 2.65 (2H, m), 2.60 (1H, t,  $J$  = 6.1 Hz), 2.57 (1H, t,  $J$  = 5.6 Hz), 1.71 (2H, m), 1.59 (2H, m), 1.38-1.17 (10H, m), 1.15-1.08 (12H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 147.1, 128.3, 127.0, 126.9, 126.0, 64.5, 64.2, 58.1, 58.0, 40.0, 39.6, 35.1, 34.8, 27.2, 26.9, 24.8, 22.5, 22.3, 18.6, 18.5, 14.0; IR:  $\tilde{\nu}$  = 3027, 2960, 2925, 2870, 1603, 1494, 1453, 1377, 1326, 1249, 1121, 871, 762, 701; MS (EI):  $m/z$  (%): 41 (19), 77 (17), 91 (28), 104 (100), 118 (73), 131 (87), 143 (11), 186 (22), 204 (2); HRMS (ESI+): calcd for C<sub>14</sub>H<sub>20</sub>O+Na: 227.14118; found: 227.14124 (M+Na); elemental analysis calcd (%) for C<sub>14</sub>H<sub>20</sub>O: C, 82.30; H, 9.87; found: C, 82.39; H, 9.82.



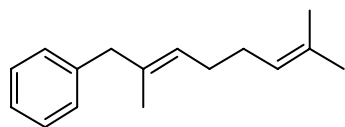
**2-(7-Phenylheptyl)oxirane.** Colorless oil (0.078 g, 56%); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.24 (2H, m), 7.13 (3H, m), 2.83 (1H, m), 2.67 (1H, dd,  $J$  = 5.1, 4.0 Hz), 2.59 (1H, sext.,  $J$  = 7.1 Hz), 2.36 (1H, dd,  $J$  = 5.1, 2.7 Hz), 1.52-1.21 (12H), 1.15 (3H, d,  $J$  = 7.1 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 147.8, 128.2, 126.9, 125.7, 52.3, 47.1, 39.9, 38.4, 32.4, 29.6, 29.3, 27.6, 25.9, 22.3; IR:  $\tilde{\nu}$  = 3027, 2927, 2855, 1603, 1493, 1452, 1410, 1376, 1260, 1130, 1090, 907, 834, 762, 700; MS (EI):  $m/z$  (%): 79 (7), 91 (14), 105 (100), 118 (33), 131 (11), 232 (5); HRMS (ESI+): calcd for C<sub>16</sub>H<sub>24</sub>O+Na: 255.17248; found: 255.17231 (M+Na).



<sup>16</sup> Beller, M.; Trauthwein, H.; Eichberger, M.; Breindl, C.; Herwig, J.; Müller, T. E.; Thiel, O. R. *Chem. Eur. J.* **1999**, *5*, 1306.

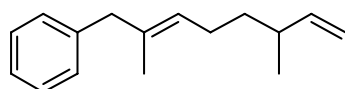
<sup>17</sup> Sometimes the carbon atom attached to a boron atom can be "invisible": Lawson, Y. G.; Gerard Lesley, M. J.; Marder, T. B.; Norman, N. C.; Rice, C. R. *Chem. Commun.*, **1997**, *21*, 2051.

**1-((E)-2,7-Dimethylocta-2,6-dienyl)benzene.** Yellow oil (0.093 g, 87%); the spectroscopic data correspond to those previously reported in the literature.<sup>18</sup>



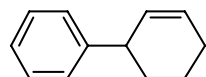
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.26 (5H, m), 5.32 (1H, qt,  $J$  = 7.7, 1.3 Hz), 5.11 (1H, m), 3.34 (2H, d,  $J$  = 7.7 Hz), 2.11 (2H, m), 2.01 (2H, m), 1.70 (3H, s), 1.66 (3H, s), 1.57 (3H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 142.1, 136.7, 131.9, 128.6, 128.5, 126.1, 124.9, 123.4, 40.1, 34.6, 26.9, 26.1, 18.0, 16.2; IR:  $\tilde{\nu}$  = 3061, 2918, 1620, 1606, 1494, 1451, 1266, 991, 823; elemental analysis calcd (%) for C<sub>16</sub>H<sub>22</sub>: C, 89.65; H, 10.35; found: C, 89.70; H, 10.30.

**(2,6-Dimethyl-octa-2,7-dienyl)benzene.** Yellow oil (0.090 g, 84%); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.23 (5H, m), 5.60 (1H, m), 5.16 (1H, m), 4.86 (2H, m), 3.32 (2H, m), 2.06 (2H, m), 1.93 (3H, m), 1.48 (3H, s), 0.93 (3H, d,  $J$  = 6.6 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 147.8,



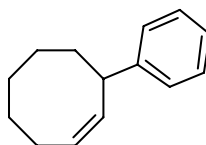
144.2, 133.9, 128.2, 127.5, 126.3, 125.4, 112.3, 45.9, 37.6, 36.4, 25.5, 19.8, 15.4; IR:  $\tilde{\nu}$  = 3082, 2962, 1640, 1602, 1494, 1373, 1030, 910, 698; elemental analysis calcd (%) for C<sub>16</sub>H<sub>22</sub>: C, 89.65; H, 10.35; found: C, 89.80; H, 10.20.

**Cyclohex-2-enylbenzene.** Yellow oil (0.075 g, 95%); the spectroscopic data correspond to those previously reported in the literature.<sup>19</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):



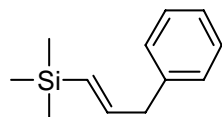
$\delta$  = 7.25 (5H, m), 5.88 (m, 1H), 5.73 (1H, dd,  $J$  = 10.2, 2.4 Hz), 3.42 (1H, m), 2.14-0.82 (6H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 146.3, 130.5, 128.9, 128.1, 127.4, 125.7, 41.6, 32.3, 23.5, 21.1; IR:  $\tilde{\nu}$  = 3066, 2918, 1649, 1618, 1490, 1033, 928, 881, 774; MS (EI):  $m/z$  (%): 77 (56), 91 (100), 105 (63), 115 (85), 144 (68), 158 (41); elemental analysis calcd (%) for C<sub>12</sub>H<sub>14</sub>: C, 91.08; H, 8.92; found: C, 91.19; H, 8.81.

**(Z)-3-Phenylcyclooct-1-ene.** Colorless oil (0.151 g, 81%); the spectroscopic data correspond to those previously reported in the literature.<sup>20</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):



$\delta$  = 7.31-7.15 (5H, m), 5.65 (2H, m), 3.75 (1H, m), 2.36 (1H, m), 2.13 (1H, m), 1.86-1.17 (8H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 146.5, 134.2, 129.0, 128.4, 127.3, 125.8, 42.3, 37.5, 29.6, 26.7, 26.5, 26.1; IR:  $\tilde{\nu}$  = 3025, 2922, 2851, 1601, 1491, 1449, 962, 840; MS (EI):  $m/z$  (%): 67 (13), 91 (41), 104 (100), 115 (33), 129 (55), 143 (23), 158 (15), 186 (37); HRMS (CI): calcd for C<sub>14</sub>H<sub>18</sub>: 186.14085; found: 186.14107.

**Trimethyl-(3-phenyl-propenyl)silane.** Colorless oil (0.092 g, 97%); the spectroscopic data correspond to those previously reported in the literature.<sup>21</sup> <sup>1</sup>H NMR



(CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.27 (5H, m), 6.14 (1H, dt,  $J$  = 18.2, 6.7 Hz), 5.68 (1H, dd,  $J$  = 18.2, 1.8 Hz), 3.51 (2H, dd,  $J$  = 6.7, 1.8 Hz, 2H), 0.41 (9H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 146.4, 140.2, 131.5, 128.8, 127.5, 126.2, 43.3, -1.0. MS(EI)  $m/z$  (rel. intensity): 73 (100), 91 (21), 99 (10), 122 (9), 145 (10), 159 (11), 175 (78), 190 (20); IR:  $\tilde{\nu}$  = 2987, 2778, 1635, 1609, 1415, 1129, 1031, 894; HRMS (CI): calcd for C<sub>12</sub>H<sub>18</sub>Si: 190.1178; found: 190.1171.

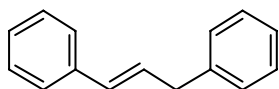
<sup>18</sup> Bäckvall, J-E.; Persson, E. S. M.; Bombrun, A. *J. Org. Chem.* **1994**, *59*, 4126.

<sup>19</sup> Mowery, M. E.; DeShong, P. *J. Org. Chem.* **1999**, *64*, 1684.

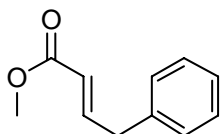
<sup>20</sup> Fristad, W. E.; Han, Y-K.; Paquette, L. A. *J. Organomet. Chem.* **1979**, *174*, 27.

<sup>21</sup> Fujiwara, N.; Yamamoto, Y. *J. Org. Chem.* **1999**, *64*, 4095.

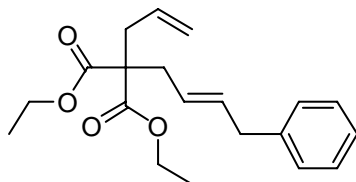
**1,3-Diphenylpropene.** The compound was prepared according to the representative procedure, but using 2.2 equivalents of phenylmagnesium bromide. Colorless oil (0.093 g, 96%); the spectroscopic data correspond to those previously reported in the literature.<sup>22</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.42 (10H, m), 6.51 (1H, d,  $J$  = 15.6 Hz), 6.38 (1H, dt,  $J$  = 15.6, 6.2 Hz), 3.56 (2H, d,  $J$  = 6.2 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 140.1, 137.5, 131.1, 129.2, 128.6, 128.5, 127.2, 126.1, 39.3; IR:  $\tilde{\nu}$  = 3053, 2978, 1647, 1611, 1432, 1008, 916, 793; HRMS (CI): calcd for C<sub>15</sub>H<sub>14</sub>: 194.1096; found: 194.1101.



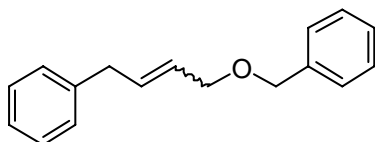
**4-Phenyl-but-2-enoic acid methyl ester.** Colorless oil (0.083 g, 94%); the spectroscopic data correspond to those previously reported in the literature.<sup>23</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.15 (5H, m), 5.74 (2H, m), 3.64 (3H, s), 3.44 (2H, dd,  $J$  = 6.6, 1.3 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 166.5, 147.2, 137.3, 128.7, 128.1, 126.2, 121.6, 51.07, 38.1; IR:  $\tilde{\nu}$  = 3035, 2899, 1721, 1692, 1625, 1411, 1110, 928, 886; MS (EI):  $m/z$  (%): 91 (48), 117 (100), 144 (37), 176 (81); HRMS (CI): calcd for C<sub>11</sub>H<sub>12</sub>O<sub>2</sub>: 176.0837; found: 176.0844.



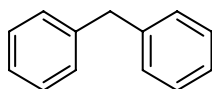
**2-Allyl-2-(4-phenyl-but-2-enyl)-malonic acid diethyl ester.** Colorless oil (0.153 g, 93%); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.15 (5H, m), 5.51 (2H, m), 5.32 (1H, m), 4.98 (2H, m), 4.05 (4H, q,  $J$  = 6.8 Hz), 3.23 (2H, d,  $J$  = 9.1 Hz), 2.58 (4H, m), 1.16 (6H, t,  $J$  = 6.8 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 170.8, 170.7, 142.4, 134.2, 132.3, 128.7, 128.3, 125.4, 124.1, 119.4, 61.5, 57.9, 37.2, 35.8, 34.5, 14.2, 14.1; IR:  $\tilde{\nu}$  = 3035, 2899, 1748, 1651, 1604, 1423, 1078, 902, 797; elemental analysis calcd (%) for C<sub>20</sub>H<sub>26</sub>O<sub>4</sub>: C, 72.70; H, 7.93; found: C, 72.53; H, 8.09.



**1-((4-Phenylbut-2-enyloxy)methyl)benzene.** Colorless oil (0.131 g, 80%, dr = 4.4:1); the spectroscopic data of the major isomer were identical to those previously reported in the literature (*E* isomer);<sup>24</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.47-7.20 (10H, m), 5.95 (1H, dt,  $J$  = 15.8, 6.7 Hz), 5.81 (2H, m), 5.75 (1H, dt,  $J$  = 15.8, 6.1 Hz), 4.61 (2H, s), 4.57 (2H, s), 4.23 (2H, d,  $J$  = 5.7 Hz), 4.07 (2H, d,  $J$  = 6.1 Hz), 3.46 (2H, d,  $J$  = 6.4 Hz), 3.43 (2H, d,  $J$  = 6.7 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 139.8, 139.7, 139.1, 138.7, 133.7, 132.9, 129.5, 129.4, 129.3, 129.2, 128.8, 128.5, 128.3, 127.7, 127.5, 126.9, 72.2, 72.0, 71.2, 66.8, 39.4, 35.4; IR:  $\tilde{\nu}$  = 3033, 2921, 1689, 1611, 1452, 1366, 1272, 1113, 1089, 935, 813, 713; elemental analysis calcd (%) for C<sub>17</sub>H<sub>18</sub>O: C, 85.67; H, 7.61; found: C, 85.80; H, 7.52.



**Diphenylmethane.** White waxy solid (0.048 g, 62%); the spectroscopic data correspond to those previously reported in the literature.<sup>25</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.28 (10H, m), 4.05 (2H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 141.1,



<sup>22</sup> Zhang, Q.; Lu, X.; Han, X. *J. Org. Chem.* **2001**, *66*, 7676.

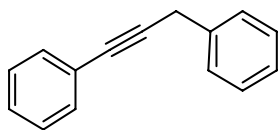
<sup>23</sup> Heck, R. F. *J. Organomet. Chem.* **1972**, *37*, 389.

<sup>24</sup> Kim, J. D.; Lee, M. H.; Han, G.; Park, H.; Zee, O.P.; Jung, Y. H. *Tetrahedron* **2001**, *57*, 8257.

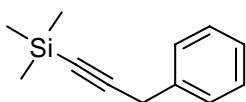
<sup>25</sup> de Lang, R. J., van Hooijdonk, M. J. C. M.; Brandsma, L. *Tetrahedron* **1998**, *54*, 2953.

128.9, 128.1, 126.0, 41.4; IR:  $\tilde{\nu}$  = 3039, 2905, 1606, 1580, 1477, 1448, 1425, 1311, 1270, 1235, 1203, 1152, 1030, 954; MS (EI):  $m/z$  (%): 91 (17), 152 (15), 168 (100).

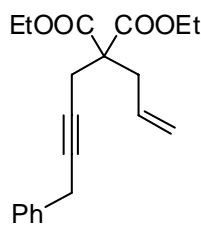
**1,3-Diphenylprop-1-yne** (Table 5, entry 11). Yellow oil (0.167 g, 87%)<sup>26</sup>; the spectroscopic data correspond to those previously reported in the literature.<sup>27</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.26 (10H, m), 3.74 (2H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 136.5, 131.4, 128.2, 127.9, 127.7, 127.5, 127.2, 126.3, 123.4, 87.2, 82.4, 25.4; IR:  $\tilde{\nu}$  = 3030, 2198, 1689, 1642, 1599, 1583, 1490, 1450, 1416, 1317, 1284, 1174, 1124, 1069, 1025, 995; MS (EI):  $m/z$  (%): 77 (55), 91 (100), 192 (44); elemental analysis calcd (%) for C<sub>15</sub>H<sub>12</sub>: C, 93.71; H, 6.29; found: C, 93.78; H, 6.22.



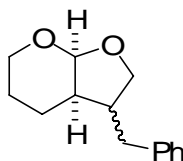
**Trimethyl-(3-phenyl-prop-1-ynyl)-silane**. Colorless oil (0.075 g, 80%)<sup>26</sup> The spectroscopic data correspond to those previously reported in the literature.<sup>28</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.28 (5H, m), 3.57 (2H, s), 0.20 (9H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 139.8, 128.9, 128.4, 126.9, 105.1, 86.2, 31.1, -0.1; MS (EI):  $m/z$  (%): 73 (23), 145 (26), 173 (100), 188 (35); IR:  $\tilde{\nu}$  = 3064, 3031, 2959, 2177, 1601, 1495, 1453, 1250, 1022, 844, 760, 697; HRMS (CI): calcd for C<sub>12</sub>H<sub>16</sub>Si: 188.10213; found: 188.10195.



**Diethyl 2-allyl-2-(4-phenylbut-2-ynyl)malonate**. Yellow oil (0.143 g, 87%); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.21 (5H, m), 5.58 (1H, m), 5.07 (1H, dd,  $J$  = 15.8, 2 Hz), 5.01 (1H, dd,  $J$  = 8.8, 2 Hz), 4.11 (4H, q,  $J$  = 7.1 Hz), 3.47 (2H, t,  $J$  = 2.2 Hz), 2.75 (4H, m), 1.14 (6H, t,  $J$  = 7.1 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 170.0, 137.1, 132.1, 129.0, 128.1, 126.6, 119.5, 80.9, 76.8, 61.5, 61.4, 57.0, 36.6, 25.1, 23.1, 14.1, 14.0; IR:  $\tilde{\nu}$  = 3064, 2982, 2939, 2237, 1734, 1645, 1600, 1582, 1465, 1449, 1391, 1368, 1252, 1201, 1097, 1071, 1029, 925, 860, 758; MS (EI):  $m/z$  (%): 77 (33), 91 (20), 105 (100), 167 (34), 195 (28), 212 (17), 269 (19), 329 (4); elemental analysis calcd (%) for C<sub>20</sub>H<sub>24</sub>O<sub>4</sub>: C, 73.15; H, 7.37; found: C, 73.28; H, 7.29.



**(±)-3-Benzyl-hexahydro-2H-furo[2,3-b]pyran**. The compound was prepared according to the representative procedure, except that the reaction was performed at 0°C (1 h). Colorless oil (0.130 g, 85%)<sup>29</sup> dr = 10:1; the spectroscopic data correspond to those previously reported in the literature.<sup>30</sup> Major isomer: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.23 (5H, m), 5.27 (1H, d,  $J$  = 3.7 Hz), 3.87 (1H, t,  $J$  = 7.7 Hz), 3.79 (2H, t,  $J$  = 8.8 Hz), 3.64 (1H, m), 2.77-2.56 (3H, m), 1.95 (1H, d,  $J$  = 5.6 Hz), 1.75 (1H, m), 1.62-1.53 (3H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 140.2, 128.5, 128.4, 126.2, 102.2, 69.9, 61.0, 42.6, 36.6, 33.4, 23.2, 19.6; IR:  $\tilde{\nu}$  = 3061, 3026, 2940, 2867, 1603, 1583, 1495, 1453, 1438, 1403, 1305, 1202, 1146, 1110, 1051, 1021, 991, 948, 903, 871, 754, 702; MS (EI):  $m/z$  (%): 41 (21), 69 (18), 81 (20), 91 (100), 97 (32), 117



<sup>26</sup> The allene byproduct was easily separated by flash chromatography.

<sup>27</sup> Cheng, J.; Sun, Y.; Wang, F.; Guo, M.; Xu, J.-H.; Pan, Y.; Zhang, Z. *J. Org. Chem.* **2004**, *69*, 5428.

<sup>28</sup> Ma, S.; Zhang, A. *J. Org. Chem.* **2002**, *67*, 2287.

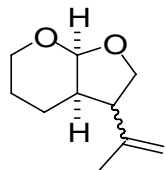
<sup>29</sup> The yield decreased to 54% when the corresponding bromide was used as starting material.

<sup>30</sup> Wakabayashi, K.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2001**, *123*, 5374.



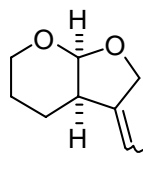
(91), 156 (9), 200 (22), 218 (22); HRMS (ESI+): calcd for  $C_{14}H_{18}O_2+Na$ : 241.12045; found: 241.12036 (M+Na).

**(3a*S*,7a*R*)-Hexahydro-3-(prop-1-en-2-yl)-2*H*-furo[2,3-*b*]pyran.** The compound was



prepared according to the representative procedure, except that the reaction was performed at 0°C (1 h). Colorless oil (0.129 g, 77%, d.r. = 1.8:1); the spectroscopic data correspond to those previously reported in the literature.<sup>31</sup>

Major isomer: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 5.33 (1H, d, *J* = 4.0 Hz), 4.86 (1H, s), 4.52 (1H, s), 4.04 (1H, dd, *J* = 10.3, 7.9 Hz), 3.92 (1H, dd, *J* = 7.9, 7.3 Hz), 3.67 (2H, m), 2.87 (1H, m), 2.04 (1H, dddd, *J* = 11.8, 5.8, 5.7, 4.2 Hz), 1.69 (3H, s), 1.61-1.09 (4H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 140.9, 110.9, 101.8, 66.9, 60.7, 47.5, 35.8, 23.3, 23.0, 19.1; IR:  $\tilde{\nu}$  = 2937, 1872, 1648, 1468, 1451, 1402, 1375, 1312, 1282, 1252, 1144, 1114, 1072, 1030, 1000, 990, 949, 889, 871, 836; MS (EI): *m/z* (%): 41 (23), 55 (27), 69 (14), 85 (100), 101 (16), 168 (37); elemental analysis calcd (%) for  $C_{10}H_{16}O_2$ : C, 71.39; H, 9.59; found: C, 71.27; H, 9.46.



**(±)-3-Benzylidene-hexahydro-2*H*-furo[2,3-*b*]pyran.** Yellow oil (0.11 g, 73%, dr = 4:1); the spectroscopic data correspond to those previously reported in the literature.<sup>32</sup> Spectroscopic data for the *E*-isomer: <sup>1</sup>H NMR

(CDCl<sub>3</sub>, 400 MHz): δ = 7.26 (5H, m), 6.21 (1H, s), 5.15 (1H, d, *J* = 3.9 Hz), 4.81 (2H, m), 3.83 (1H, d, *J* = 11.0 Hz), 3.46 (1H, t, *J* = 11.0 Hz), 2.80 (1H, d, *J* = 3.9 Hz), 2.07 (1H, d, *J* = 14.0 Hz), 1.94 (1H, m), 1.66 (1H, d, *J* = 11.7 Hz), 1.33 (1H, d, *J* = 13.8 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 140.1, 137.3, 128.6, 127.9, 126.8, 120.1, 100.7, 64.5, 60.1, 43.8, 23.1, 20.6; IR:  $\tilde{\nu}$  = 3033, 1703, 1655, 1613, 1217, 1188, 1120, 1078, 976, 810, 771, 745; elemental analysis calcd (%) for  $C_{14}H_{16}O_2$ : C, 77.75; H, 7.46; found: C, 77.61; H, 7.30.

## Crystallographic Summaries

**X-ray Crystal Structure Analysis of Complex 3:**  $C_{13}H_{35}FeLi_3O_2$ ,  $M_r = 300.08 \text{ g} \cdot \text{mol}^{-1}$ , yellow-orange plate, crystal 0.08 x 0.06 x 0.05 mm, orthorhombic, space group *Pnma*,  $a = 12.3527(5) \text{ \AA}$ ,  $b = 15.9319(8) \text{ \AA}$ ,  $c = 9.9546(5) \text{ \AA}$ ,  $V = 1959.08(16) \text{ \AA}^3$ ,  $T = 100 \text{ K}$ ,  $Z = 4$ ,  $D_{\text{calc}} = 1.017 \text{ g} \cdot \text{cm}^3$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu(\text{Mo-K}\alpha) = 0.762 \text{ mm}^{-1}$ , Nonius KappaCCD diffractometer,  $3.30 < \theta < 27.08^\circ$ , 17506 measured reflections, 2231 independent reflections, 1601 reflections with  $I > 2\sigma(I)$ , Structure solved by the direct method and refined by least-squares against  $F^2$  to  $R_1 = 0.050$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.114$ , 116 parameters, H atoms riding,  $S = 1.038$ , residual electron density +0.5 / -0.3 e  $\text{\AA}^{-3}$ .

**X-ray Crystal Structure Analysis of Complex 5:**  $C_{36}H_{48}FeLi_2O_4$ ,  $M_r = 614.47 \text{ g} \cdot \text{mol}^{-1}$ , yellow block, crystal size 0.26 x 0.12 x 0.10 mm, triclinic, space group  $P\bar{1}$ ,  $a = 9.7659(3) \text{ \AA}$ ,  $b = 9.9967(2) \text{ \AA}$ ,  $c = 18.5066(5) \text{ \AA}$ ,  $\alpha = 04.658(2)^\circ$ ,  $\beta = 94.970(1)^\circ$ ,  $\gamma = 98.647(1)^\circ$ ,  $V = 1713.32(8) \text{ \AA}^3$ ,  $T = 100 \text{ K}$ ,  $Z = 2$ ,  $D_{\text{calc}} = 1.191 \text{ g} \cdot \text{cm}^3$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu(\text{Mo-K}\alpha) = 0.475$

<sup>31</sup> Inoue, A.; Shinokubo, H.; Oshima, K. *Org. Lett.* **2000**, *2*, 651.

<sup>32</sup> Yanada, R.; Koh, Y.; Nishimori, N.; Matsumura, A.; Obika, S.; Mitsuya, H.; Fujii, N.; Takemoto, Y. *J. Org. Chem.* **2004**, *69*, 2417.

$\text{mm}^{-1}$ , Semi-empirical absorption correction ( $T_{\min} = 0.90$ ,  $T_{\max} = 1.00$ ), Nonius KappaCCD diffractometer,  $2.92 < \theta < 33.18$ , 37326 measured reflections, 12994 independent reflections, 8637 reflections with  $I > 2\sigma(I)$ . Structure solved by direct methods and refined by full-matrix least-squares against  $F^2$  to  $R_1 = 0.079$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.179$ , 369 parameters, H atoms riding,  $S = 1.046$ , residual electron density  $+0.7 / -0.6 \text{ e } \text{\AA}^{-3}$ . One of the 1,4-dioxane ligands and both of the diethylether ligands, as well as one of the phenyl groups attached to iron in the asymmetric unit are disordered. The nature of the disorder (50:50) on an otherwise good data set indicated that the b axis may be doubled though the domination of the remaining atoms including the iron and lithium atoms meant that it was undetected. H atom positions were calculated and allowed to ride.

**X-ray Crystal Structure Analysis of Complex 8:**  $\text{C}_{20}\text{H}_{48}\text{FeLi}_2\text{N}_4$ ,  $M_r = 414.35 \text{ g} \cdot \text{mol}^{-1}$ , brown-green prism, crystal size  $0.16 \times 0.20 \times 0.22 \text{ mm}$ , orthorhombic, space group *Fdd2* [No. 43],  $a = 23.8208(6) \text{ \AA}$ ,  $b = 25.6482(6) \text{ \AA}$ ,  $c = 8.1007(2) \text{ \AA}$ ,  $V = 4949.2(2) \text{ \AA}^3$ ,  $T = 100 \text{ K}$ ,  $Z = 8$ ,  $D_{\text{calc}} = 1.112 \text{ g} \cdot \text{cm}^3$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu(\text{Mo-K}\alpha) = 0.620 \text{ mm}^{-1}$ , multiscan absorption correction ( $T_{\min/\max} = 0.88$ ), Nonius KappaCCD diffractometer,  $\theta_{\max} = 33.23$ , 112046 measured reflections, 4698 independent reflections ( $R_{\text{int}} = 0.094$ ), 4215 reflections with  $I > 2\sigma(I)$ , Structure solved by direct methods and refined by full-matrix least-squares against  $F^2$  to  $R_1 = 0.0513$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.1303$  [all data], 165 parameters. The ethylene bridges of the tetramethylethylenediamine ligands attached to Li are disordered over two positions (A:B 50:50). Since the iron atoms form a centrosymmetric arrangement in the unit cell (Wyckoff position *a*) it was not possible to determine the absolute configuration of the structure [Flack parameter 0.50(3)]. H atoms attached to C1-C4 restrained, otherwise riding,  $S = 1.164$ , residual electron density  $+0.803 / -0.633 \text{ e } \text{\AA}^{-3}$ .

This compound also crystallizes in the space group *Pbcn* [No. 60] in a unit cell with dimensions  $a = 12.279(1)$ ,  $b = 13.069(1)$ ,  $c = 16.336(1) \text{ \AA}$  (see, Jonas, K.; Schieferstein, L.; Krüger, C.; Tsay, Y.-H., *Angew. Chem.* **1979**, *91*, 590-591, *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 550).

**X-ray Crystal Structure Analysis of Complex 15:**  $\text{C}_{14}\text{H}_{23}\text{Fe}$ ,  $M_r = 247.17 \text{ g} \cdot \text{mol}^{-1}$ , orange block, crystal size  $0.08 \times 0.05 \times 0.02 \text{ mm}$ , monoclinic, space group *P2<sub>1</sub>/c*,  $a = 12.5561(5) \text{ \AA}$ ,  $b = 7.3323(3) \text{ \AA}$ ,  $c = 14.7157(6) \text{ \AA}$ ,  $\beta = 108.3520(10)^\circ$ ,  $V = 1285.90(9) \text{ \AA}^3$ ,  $T = 100 \text{ K}$ ,  $Z = 4$ ,  $D_{\text{calc}} = 1.277 \text{ g} \cdot \text{cm}^3$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu(\text{Mo-K}\alpha) = 1.140 \text{ mm}^{-1}$ , Semi-empirical absorption correction ( $T_{\min} = 0.94$ ,  $T_{\max} = 1.00$ ), Nonius KappaCCD diffractometer,  $2.91 < \theta < 31.53$ , 18912 measured reflections, 4284 independent reflections, 3559 reflections with  $I > 2\sigma(I)$ , Structure solved by direct methods and refined by full-matrix least-squares against  $F^2$  to  $R_1 = 0.030$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.073$ , 173 parameters, H atoms riding,  $S = 1.002$ , residual electron density  $+0.5 / -0.3 \text{ e } \text{\AA}^{-3}$ .

**X-ray Crystal Structure Analysis of Complex 37:**  $\text{C}_{15}\text{H}_{22}\text{Fe}$ ,  $M_r = 258.18 \text{ g} \cdot \text{mol}^{-1}$ , red block, crystal size  $0.07 \times 0.07 \times 0.04 \text{ mm}$ , monoclinic, space group *P2<sub>1</sub>/c*,  $a = 15.4528(2) \text{ \AA}$ ,  $b = 7.30770(10) \text{ \AA}$ ,  $c = 11.5264(2) \text{ \AA}$ ,  $\beta = 103.2770(10)^\circ$ ,  $V = 1266.82(3) \text{ \AA}^3$ ,  $T = 100 \text{ K}$ ,  $Z = 4$ ,  $D_{\text{calc}} = 1.354 \text{ g} \cdot \text{cm}^3$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu(\text{Mo-K}\alpha) = 1.161 \text{ mm}^{-1}$ , Multi-Scan absorption correction ( $T_{\min} = 0.92$ ,  $T_{\max} = 0.96$ ), Nonius KappaCCD diffractometer,  $3.33 < \theta < 31.52$ , 32990 measured reflections, 4224 independent reflections, 3771 reflections with  $I > 2\sigma(I)$ , Structure solved by direct methods and refined by full-matrix least-squares against  $F^2$  to  $R_1 =$

0.025 [ $I > 2\sigma(I)$ ],  $wR_2 = 0.068$ , 233 parameters, H atoms riding,  $S = 0.994$ , residual electron density  $+0.5 / -0.4 \text{ e } \text{Å}^{-3}$ .

**X-ray Crystal Structure Analysis of Complex 40:**  $\text{C}_{17} \text{H}_{28} \text{Fe P}_2$ ,  $M_r = 350.18 \text{ g} \cdot \text{mol}^{-1}$ , orange plate, crystal size  $0.14 \times 0.12 \times 0.06 \text{ mm}$ , orthorhombic, space group  $Pna2_1$ ,  $a = 27.265(6) \text{ Å}$ ,  $b = 8.1454(16) \text{ Å}$ ,  $c = 16.020(3) \text{ Å}$ ,  $V = 3557.8(12) \text{ Å}^3$ ,  $T = 100 \text{ K}$ ,  $Z = 8$ ,  $D_{\text{calc}} = 1.308 \text{ g} \cdot \text{cm}^3$ ,  $\lambda = 0.71073 \text{ Å}$ ,  $\mu(\text{Mo-K}\alpha) = 1.017 \text{ mm}^{-1}$ , Psi-scan absorption correction ( $T_{\text{min}} = 0.96$ ,  $T_{\text{max}} = 0.99$ ), Nonius KappaCCD diffractometer,  $4.56 < \theta < 27.50$ , 41460 measured reflections, 7935 independent reflections, 7134 reflections with  $I > 2\sigma(I)$ , Structure solved by direct methods and refined by full-matrix least-squares against  $F^2$  to  $R_1 = 0.053$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.159$ , 368 parameters, absolute structure parameter = 0.06(2), H atoms riding,  $S = 1.053$ , residual electron density  $+1.2 / -1.4 \text{ e } \text{Å}^{-3}$ .

**X-ray Crystal Structure Analysis of Complex 46:**  $\text{C}_{13} \text{H}_{20} \text{ClFe}$ ,  $M_r = 258.18 \text{ g} \cdot \text{mol}^{-1}$ , red-brown block, crystal size  $0.06 \times 0.02 \times 0.01 \text{ mm}$ , monoclinic, space group  $P2_1/m$ ,  $a = 6.7149(6) \text{ Å}$ ,  $b = 11.2061(8) \text{ Å}$ ,  $c = 8.4971(8) \text{ Å}$ ,  $\beta = 100.748(3)^\circ$ ,  $V = 628.17(9) \text{ Å}^3$ ,  $T = 100 \text{ K}$ ,  $Z = 2$ ,  $D_{\text{calc}} = 1.415 \text{ g} \cdot \text{cm}^3$ ,  $\lambda = 0.71073 \text{ Å}$ ,  $\mu(\text{Mo-K}\alpha) = 1.379 \text{ mm}^{-1}$ , Semi-empirical absorption correction ( $T_{\text{min}} = 0.91$ ,  $T_{\text{max}} = 1.00$ ), Nonius KappaCCD diffractometer,  $3.04 < \theta < 31.00$ , 9003 measured reflections, 2094 independent reflections, 1733 reflections with  $I > 2\sigma(I)$ , Structure solved by direct methods and refined by full-matrix least-squares against  $F^2$  to  $R_1 = 0.040$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.094$ , 84 parameters, H atoms riding,  $S = 1.043$ , residual electron density  $+0.6 / -0.7 \text{ e } \text{Å}^{-3}$ .

**X-ray Crystal Structure Analysis of Complex 48:**  $\text{C}_{14} \text{H}_{23} \text{Fe}$ ,  $M_r = 247.17 \text{ g} \cdot \text{mol}^{-1}$ , red-brown block, crystal size  $0.04 \times 0.03 \times 0.02 \text{ mm}$ , monoclinic, space group  $P2_1/c$ ,  $a = 13.6935(15) \text{ Å}$ ,  $b = 28.256(3) \text{ Å}$ ,  $c = 13.6923(11) \text{ Å}$ ,  $\beta = 90.412(7)^\circ$ ,  $V = 5297.8(9) \text{ Å}^3$ ,  $T = 100 \text{ K}$ ,  $Z = 16$ ,  $D_{\text{calc}} = 1.415 \text{ g} \cdot \text{cm}^3$ ,  $\lambda = 0.71073 \text{ Å}$ ,  $\mu(\text{Mo-K}\alpha) = 1.107 \text{ mm}^{-1}$ , Semi-empirical absorption correction ( $T_{\text{min}} = 0.96$ ,  $T_{\text{max}} = 1.00$ ), Nonius KappaCCD diffractometer,  $2.98 < \theta < 24.68$ , 37819 measured reflections, 8857 independent reflections, 4906 reflections with  $I > 2\sigma(I)$ , Structure solved by direct methods and refined by full-matrix least-squares against  $F^2$  to  $R_1 = 0.090$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.224$ , 538 parameters, H atoms riding,  $S = 1.021$ , residual electron density  $+0.6 / -0.9 \text{ e } \text{Å}^{-3}$ .