

Supplementary Information

Stereoselective Iron-Catalyzed Alkyne Hydrogenations in Ionic Liquids

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General

Analytical Thin-Layer Chromatography

TLC was performed using aluminium plates with silica gel and fluorescent indicator (Merck, 60, F254). Thin layer chromatography plates were visualized by exposure to ultraviolet light (366 or 254 nm) or by immersion in a staining solution of molybdato-phosphoric acid in ethanol or a solution of potassium permanganate in water.

Column Chromatography

Flash column chromatography with silica gel 60 from *KMF* (0.040-0.063 mm). Mixtures of hexanes / ethyl acetate or *n*-pentane / ethyl acetate were used as eluents.

Chemicals and Solvents

Commercially available chemicals were used with no further purification, unless otherwise mentioned. Catalytic reactions were held in dry solvents. THF was distilled over sodium and benzophenone under an argon atmosphere. Heptane (*SigmaAldrich*, puriss. Absolute >99.5%) EtMgCl in THF (2 M, *SigmaAldrich*) and iron(III) chloride (98%, anhydrous) were stored and handled in a glovebox under argon (99.996%). Solvents used for column chromatography were distilled under reduced pressure before use.

High Pressure Reactor

Hydrogenation reactions were carried out in 4 mL glass vials which were placed inside 150 or 300 mL high pressure reactors (*Parr*). The reactors were loaded under argon, purged with H₂ (1 min), sealed, and the internal pressure was adjusted. Hydrogen (99.9992%) was purchased from *Linde*.

¹H- und ¹³C-NMR-Spectroscopy

Nuclear magnetic resonance spectras were recorded on a *Bruker Advance 300* (300 MHz) und *Bruker Advance 400* (400 MHz). ¹H-NMR: The following abbreviations are used to indicate multiplicities: s = singlet; d = doublet; t = triplet, q = quartet; m = multiplet, dd = doublet of doublet, dt = doublet of triplet, dq = doublet of quartet, ddt = doublet of doublet of quartett. Chemical shifts δ are given in ppm relative to SiMe₄. Quantifications were referenced vs. hexamethyldisiloxane.

Fourier-Transformations-Infrared-Spectroscopy (FT-IR)

Spectras were recorded on a *Varian Scimitar 1000 FT-IR* with ATR-device. All spectras were recorded at room temperate. Wave number is given in cm^{-1} . Bands are marked as s = strong, m = medium, w = weak and b = broad.

Gas chromatography with FID (GC-FID)

HP6890 GC-System with injector 7683B and Agilent 7820A System, carrier gas: H_2 . GC-FID was used for reaction control and catalyst screening (Calibration with internal standard *n*-pentadecane and analytically pure samples).

Gas chromatography with mass-selective detector (GC-MS)

Agilent 6890N Network GC-System, mass detector 5975 MS. Column: HP-5MS (30m x 0.25 mm x 0.25, 5% phenylmethylsiloxane, carrier gas: H_2 . Standard heating procedure: 50 °C (2 min), 25 °C/min -> 300 °C (5 min)

High resolution mass spectrometry (HRMS)

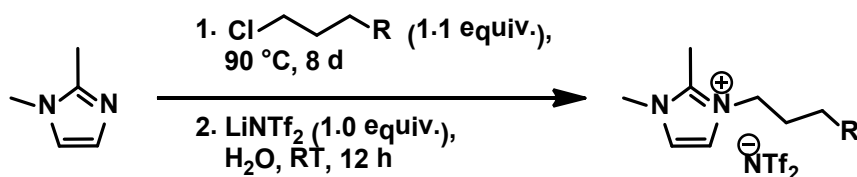
Mass spectra were taken on a *Finnigan MAT SSQ 710 A* (EI).

Inductively coupled plasma optical emission spectrometry (ICP-OES)

ICP-OES measurements were taken on a *Spectro Analytical Instruments ICP Modula EOP*.

Synthesis of Starting Materials

Synthesis of Ionic Liquids ILs 1-3



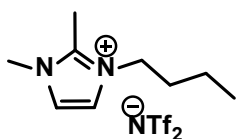
Synthesis according to literature references with slight modifications:

Z. Fei, D. Zhao, D. Pieraccini, W. H. Ang, T. J. Geldbach, R. Scopelliti, C. Chiappe, P. J. Dyson, *Organometallics* **2007**, *26*, 1588–1598.

D. Zhao, Z. Fei, R. Scopelliti, P. J. Dyson, *Inorg. Chem.* **2004**, *43*, 2197–2205.

A 25 mL flask was charged with freshly distilled 1,2-dimethylimidazole (20.0 mmol, 1.92 g) and heated to 90 °C. 1-Chlorobutane (20.0 mmol, 2.09 mL) was added slowly and the reaction mixture was stirred at 90 °C for 5 days. For completion of the reaction 1-chlorobutane (1.00 mmol, 105 μ L) was added and the mixture was stirred for another 3 days. Then, LiNTf₂ (14.5 mmol, 4.16 g) and dist. H₂O (7.25 mL) was added and the mixture was stirred at room temperature for 12 h. The aqueous phase was removed and the organic phase washed with dist. H₂O (2 \times 4 mL) and dried at 130 °C for 3 days (oil pump).

3-*n*-Butyl-1,2-dimethylimidazolium bis(trifluoromethane)sulfonimide (IL-1):



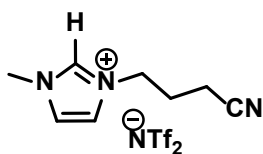
C₁₁H₁₇F₆N₃O₄S₂, **433.39 g/mol**

¹H-NMR (400 MHz, MeOD) δ 7.49 (d, J = 2.0 Hz, 1H), 7.44 (d, J = 2 Hz, 1H), 4.13 (t, J = 7.4 Hz, 2H), 3.80 (s, 3H), 2.61 (s, 3H), 1.87–1.70 (m, 2H), 1.39 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H).

¹³C{¹H}-NMR (101 MHz, MeOD) δ 145.8, 126.0, 123.6, 122.9, 122.2, 119.7, 116.5, 35.5, 32.8, 20.5, 13.9, 9.6.

F. F. Bazito, Y. Kawano, R. M. Torresi, *Electrochim. Acta* **2007**, *52*, 6427–6437.

3-(3-Cyanopropyl)-1-methylimidazolium bis(trifluoromethane)sulfonimide (IL-2):



$C_{10}H_{12}F_6N_4O_4S_2$, **430.34 g/mol**

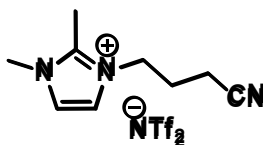
MS (EI, 70 eV): 150

1H -NMR: (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.56 (s, 1H), 7.54 (s, 1H), 4.46 (t, 6.7 Hz, 2H), 4.0 (s, 3H), 2.69 (t, 6.8 Hz, 2H), 2.36 (m, 2H)

$^{13}C\{^1H\}$ -NMR: (101 MHz, $CDCl_3$) δ 135.8, 130.4, 120.0, 116.0, 44.5, 35.1, 22.5, 10.0

D. Zhao, Z. Fei, R. Scopelliti, P. J. Dyson, *Inorg. Chem.* **2004**, *43*, 2197–2205.

3-(3-Cyanopropyl)-1,2-dimethylimidazolium bis(trifluoromethane)sulfonimide (IL-3):



$C_{11}H_{14}F_6N_4O_4S_2$, **444.37 g/mol**

1H -NMR (400 MHz, MeOD) δ 7.56–7.42 (m, 2H), 4.26 (t, $J = 7.2$ Hz, 2H), 3.81 (s, 3H), 2.64 (s, 3H), 2.57 (t, $J = 7.2$ Hz, 2H), 2.18 (dt, $J = 7.2$ Hz, 2H).

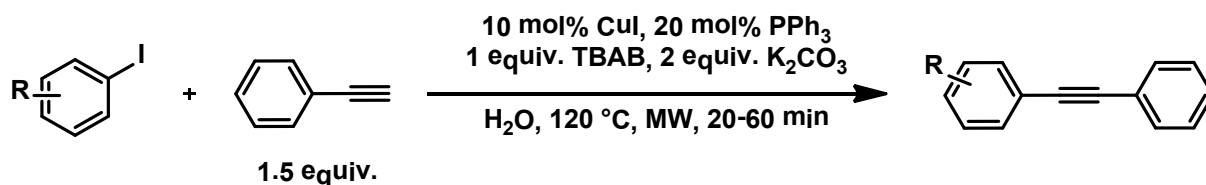
$^{13}C\{^1H\}$ -NMR (101 MHz, MeOD) δ 146.4, 124.1, 122.9, 122.2, 120.0, 119.7, 48.0, 35.6, 26.6, 14.6, 9.7.

Z. Fei, D. Zhao, D. Pieraccini, W. H. Ang, T. J. Geldbach, R. Scopelliti, C. Chiappe, P. J. Dyson, *Organometallics* **2007**, *26*, 1588–1598.

Synthesis of Alkynes

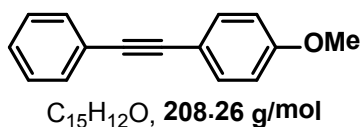
Alkynes were purchased from *SigmaAldrich* and *AcrosOrganics* or were synthesized by the following methods.

Synthesis of diphenylacetylenes



A 10 mL glass tube equipped with a stirring bar was charged with 0.2 mmol CuI (38 mg), 0.4 mmol PPh₃ (104 mg), 2 mmol Bu₄NBr (644 mg), 4 mmol K₂CO₃ (525 mg), 2 mmol aryl iodide and 3 mL deionized water. The suspension was then stirred at r.t. for 1 min. Then, 3 mmol phenylacetylene (330 μL) were added by syringe. The reaction vessel was purged with argon, sealed and placed into the microwave. The temperature was ramped to 120 °C within 1 min and then held at this temperature for 20 to 60 min. The reaction mixture was extracted with ethyl acetate (3x 10 mL), the combined organic layers were dried (MgSO₄) and the solvent removed by vacuum evaporation. The residue was then purified by silica gel column chromatography (cyclohexane/dichloromethane).

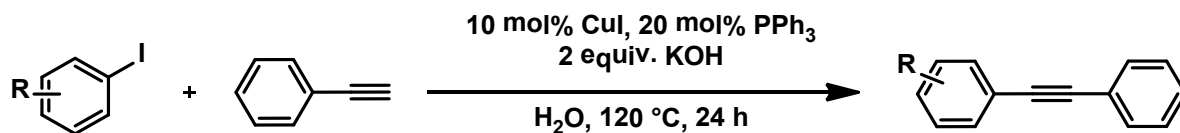
1-Methoxy-4-(phenylethynyl)benzene



¹H-NMR (300 MHz, CDCl₃) δ 7.49 (m, 4H), 7.33 (d, *J* = 6.1 Hz, 3H), 6.88 (d, *J* = 8.6 Hz, 2H), 3.83 (s, 3H).

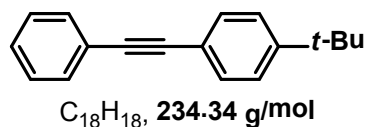
¹³C{¹H}-NMR (75 MHz, CDCl₃) δ 159.60, 133.05, 131.44, 128.30, 127.92, 123.59, 115.37, 113.99, 89.36, 88.06, 55.31.

GC-MS *t*_R = 9.80 min, (EI, 70 eV): *m/z* = 208 [M⁺].



A 50 mL *Schlenk* tube with a screw cap was equipped with a stirring bar, charged with 0.190 g (1 mmol) CuI, 0.525 g (2 mmol) PPh₃ and 1.122 g (20 mmol) KOH, evacuated three times and purged with nitrogen. Then, 20 mL deionized water were added. The suspension was stirred at r.t. for 10 min, 10 mmol aryl iodide and 1.328 g (13 mmol) phenylacetylene were added *via* syringe. The reaction was shortly purged with N₂ and sealed. After 24 h at 120 °C, the mixture was extracted with Et₂O (4 x 20 mL), the combined organic layers were dried (MgSO₄) and the solvent removed in vacuum. The residue was purified by silica gel column chromatography (pentane or pentane/dichloromethane).

1-*tert*-Butyl-4-(phenylethynyl)benzene



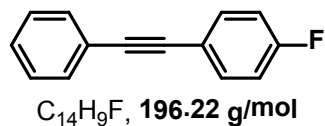
¹H-NMR (300 MHz, CDCl₃) δ 7.56-7.44 (m, 4H), 7.40-7.30 (m, 5H), 1.33 (s, 9H).

¹³C{¹H}-NMR (75 MHz, CDCl₃) δ 151.55, 131.59, 131.34, 128.32, 128.08, 125.37, 123.52, 120.24, 89.53, 88.73, 34.81, 31.20.

GC-MS $t_R = 10.27$ min, (EI, 70 eV): $m/z = 234$ [M⁺].

J. Moon, M. Jeong, H. Nam, J. Ju, J. H. Moon, H. M. Jung, S. Lee, *Org. Lett.* **2008**, *10*, 945-948.

1-Fluoro-4-(phenylethynyl)benzene



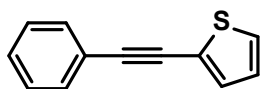
¹H-NMR (300 MHz, CDCl₃) δ 7.49- 7.38 (m, 4H), 7.31- 7.22 (m, 3H), 7.03-6.91 (m, 2H).

¹³C{¹H}-NMR (75 MHz, CDCl₃) δ 164.16, 160.86, 133.55, 133.44, 131.57, 128.39, 128.35, 123.09, 119.40, 119.35, 115.80, 115.51, 89.05, 88.29.

GC-MS $t_R = 8.63$ min, (EI, 70 eV): $m/z = 196$ [M⁺].

H. Huang, H. Jiang, K. Chen, H. Liu, *J. Org. Chem.* **2008**, *73*, 9061-9064.

2-(Phenylethynyl)thiophene



$C_{12}H_8S$, **184.26 g/mol**

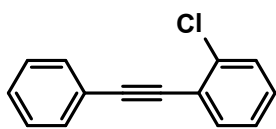
1H -NMR (300 MHz, $CDCl_3$) δ 7.56-7.47 (m, 2H), 7.38- 7.31 (m, 3H), 7.31- 7.26 (m, 2H), 7.01 (dd, $J = 5.0, 3.8$ Hz, 1H).

$^{13}C\{^1H\}$ -NMR (75 MHz, $CDCl_3$) δ 131.91, 131.43, 128.44, 128.39, 127.27, 127.12, 123.34, 122.94, 93.03, 82.61.

GC-MS $t_R = 8.84$ min, (EI, 70 eV): $m/z = 184 [M^+]$.

H. Huang, H. Jiang, K. Chen, H. Liu, *J. Org. Chem.* **2008**, *73*, 9061-9064.

1-Chloro-2-(phenylethynyl)benzene



$C_{14}H_9Cl$, **212.67 g/mol**

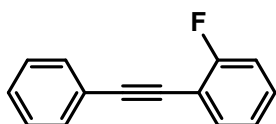
1H -NMR (400 MHz, $CDCl_3$) δ 7.58 (m, 3H), 7.44 (m, 1H), 7.37 (m, 3H), 7.30 – 7.22 (m, 2H).

$^{13}C\{^1H\}$ -NMR (101 MHz, $CDCl_3$) δ . 135.96, 133.24, 131.77, 129.33, 129.27, 128.67, 128.40, 126.48, 123.25, 122.94, 94.56, 86.20.

GC-MS $t_R = 9.55$ min, (EI, 70 eV): $m/z = 212 [M^+]$.

T. Suzuka, Y. Okada, K. Ooshiro, Y. Uozumi, *Tetrahedron* **2010**, *66*, 1064-1069.

1-Fluoro-2-(phenylethynyl)benzene



$C_{14}H_9F$, **196.22 g/mol**

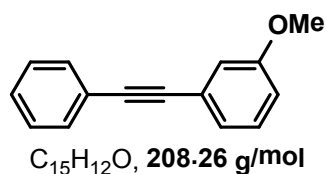
1H -NMR (300 MHz, $CDCl_3$) δ 7.62 – 7.48 (m, 3H), 7.40 – 7.26 (m, 4H), 7.17 – 7.06 (m, 2H).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, CDCl_3) δ . 133.45, 131.72, 130.02, 129.92, 128.60, 128.37, 123.99, 123.94, 122.91, 115.69, 115.41, 77.23.

GC-MS $t_R = 8.70$ min, (EI, 70 eV): $m/z = 196$ [M^+].

S. Enthaler, M. Haberberger, E. Irran, *Chem. Asian J.* **2011**, *6*, 1613-1623.

1-Methoxy-3-(phenylethynyl)benzene

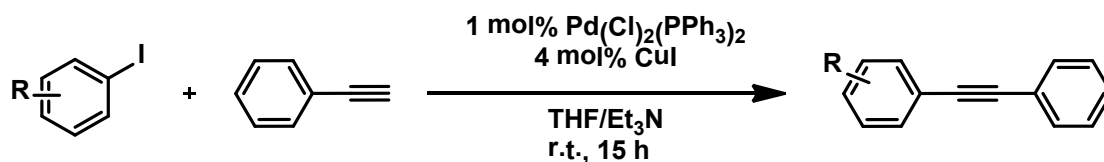


^1H -NMR (300 MHz, CDCl_3) δ 7.58 – 7.51 (m, 2H), 7.40 – 7.32 (m, 3H), 7.26 (m, 1H), 7.14 (m, 2H), 7.07 (m, 1H), 6.90 (m, 2H), 3.83 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, CDCl_3) δ 159.35, 131.65, 129.43, 128.37, 128.33, 124.20, 123.19, 116.32, 114.98, 89.30, 89.20, 55.32.

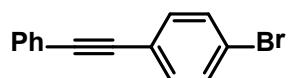
GC-MS $t_R = 9.90$ min, (EI, 70 eV): $m/z = 208$ [M^+].

K. G. Thakur, G. Sekar, *Synthesis* **2009**, *16*, 2785-2789.



A 50 mL *Schlenk* tube with a screw cap was equipped with a stirring bar, charged with 27.0 mg (0.14 mmol) CuI , 25.2 mg (0.04 mmol) $\text{PdCl}_2(\text{PPh}_3)_2$ and 3.59 mmol of the substituted iodobenzene, evacuated three times and purged with nitrogen. Then 4 mL THF and 4 mL Et_3N was added. 395 μL (3.59 mmol) phenylacetylene were added slowly via syringe and the reaction mixture was stirred at room temperature for 15 h. Then, CH_2Cl_2 (25 mL) and aqueous HCl (25 mL, 1 M) were added and the reaction mixture was extracted with CH_2Cl_2 (2×25 mL). The combined organic layers were dried (Na_2SO_4) and the solvent removed in vacuum. The residue was then purified by silica gel column chromatography (petroleum ether/ethyl acetate)

1-Bromo-4-(phenylethynyl)benzene

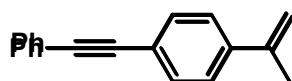


C₁₄H₉Br, 257.13 g/mol

Appearance	white solid
Yield	1.19 g, 4.64 mmol (83%)
TLC	$R_f = 0.59$ (SiO ₂ , petroleum ether)
¹H-NMR	¹ H NMR (300 MHz, CDCl ₃) δ 7.57 – 7.45 (m, 4H), 7.43 – 7.31 (m, 5H).
¹³C-NMR	¹³ C NMR (75 MHz, CDCl ₃) δ 133.04, 131.64, 131.61, 128.54, 128.42, 122.91, 122.49, 122.25, 90.53, 88.33.
GC-MS	$t_R = 10.00$ min, (EI, 70 eV): $m/z = 257$ [M ⁺], 176, 151, 110, 98, 88, 75, 63, 51.

Che-Hung Lin, Yu-Jen Wang, Chin-Fa Lee, *Eur. J. Org. Chem.*, **2010**, 23, 4368–4371.

1-(Phenylethynyl)-4-(prop-1-en-2-yl)benzene



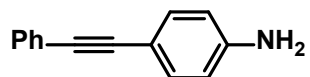
C₁₇H₁₄, 218.29 g/mol

Appearance	yellow solid
Yield	735 mg, 12.18 mmol (94%)
TLC	$R_f = 0.51$ (SiO ₂ , petroleum ether)
¹H-NMR	¹ H NMR (300 MHz, CDCl ₃) δ 7.59 – 7.42 (m, 6H), 7.40 – 7.31 (m, 3H), 5.43 (m, 1H), 5.14 (m, 1H), 2.16 (dd, $J = 1.4, 0.7$ Hz, 3H).
¹³C-NMR	¹³ C NMR (75 MHz, CDCl ₃) δ 142.54, 140.94, 131.61, 131.50, 128.37, 128.26, 125.44, 123.32, 122.18, 113.25, 89.89, 89.42, 21.66.
GC-MS	$t_R = 10.20$ min, (EI, 70 eV): $m/z = 218$ [M ⁺], 202, 189, 178, 165, 152, 126, 115, 91, 77, 63, 51.
GC-HRMS	(CI, m/z): found 218.1099 [M ⁺] (calculated 218.1096).

FT-IR (ATR-film) in $[\text{cm}^{-1}]$ 3077 (w), 2943 (w), 2363 (w), 2338 (w), 1961 (w), 1792 (w), 1620 (m), 1593 (m), 1503 (m), 1485(m), 1441 (m), 1403 (m), 1373 (m), 1119 (m), 1070 (m), 892 (s), 839 (s), 753 (s), 689 (s), 631 (m), 492 (s).

Melting Point 77 °C

1-Amino-4-(phenylethynyl)benzene



C₁₄H₁₁N, 193.24 g/mol

Appearance brown solid

Yield 2.35 g, 12.2 mmol (87%)

TLC $R_f = 0.21$ (SiO₂, petroleum ether/ethyl acetate = 4/1 + 1% triethylamine)

¹H-NMR ¹H NMR (300 MHz, CDCl₃) δ 7.54 – 7.46 (m, 2H), 7.39 – 7.28 (m, 5H), 6.65 (m, 2H), 3.86 (s, 2H).

¹³C-NMR ¹³C NMR (75 MHz, CDCl₃) δ 146.56, 132.99, 131.37, 128.29, 127.69, 123.89, 114.81, 112.71, 90.09, 87.35.

GC-MS $t_R = 10.54$ min, (EI, 70 eV): $m/z = 193$ [M^+], 177, 165, 152, 139, 126, 115, 89, 74, 63, 52.

General Procedure for Hydrogenation Reactions

Preparation of Catalyst Solution:

A 10 mL flask was charged with FeCl₃ (0.20 mmol, 33.1 mg) and THF (3.6 mL) in a glovebox. Under vigorous stirring EtMgCl in THF (2 M, 0.80 mmol, 0.40 mL) was added dropwisely. The resulting dark mixture was stirred at room temperature for 30 min before use.

Hydrogenation of Alkynes with [Fe]/IL-1/MeCN (Table 4):

A 4 mL vial with screw cap and PTFE septum was charged with [BMIM][NTf₂] (IL-1) (150 μL) and 0.50 mL of the freshly prepared catalyst solution in a glove box and the mixture was stirred for 2 min, before THF was evaporated under reduced pressure (oil pump). The vial was transferred back into the glove box, charged with alkyne (0.50 mmol), dry acetonitrile (0.50 mmol) and dry *n*-heptane (0.50 mL), placed into a high pressure reactor and punctured with a short needle, and the reactor was sealed. The reactor was purged three times with hydrogen and pressurized with 53 bar of H₂, heated to 80 °C by a heating jacket (resulting pressure 60 bar) and stirred with an external magnetic stirrer for 18 h. The reactor was then depressurized, the vial removed, the heptane phase separated by decantation and the catalyst phase washed with 2 × 1 mL *n*-heptane. The product mixture was analyzed by GC and ¹H-NMR. Quantifications by ¹H-NMR are vs. hexamethyldisiloxane as internal reference. For identification of *E/Z* stereochemistry of the alkenes, the characteristic vinyl signals were analyzed and compared with literature data.

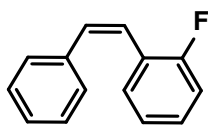
Hydrogenation of Alkynes with [Fe]/IL-1/Additive (Table 3):

Following the protocol of hydrogenation of alkynes with [Fe]/IL-1/MeCN, instead of acetonitrile, various additives had been tested (50 or 100 mol%).

Hydrogenation of Alkynes with [Fe]/IL-3 (Table 2):

A 4 mL vial with screw cap and PTFE septum was charged with [BMIM-CN][NTf₂] (IL-3) (150 μL) and 0.50 mL of the freshly prepared black catalyst solution in a glove box and the mixture was stirred for 2 min, before THF was evaporated under reduced pressure (oil pump). The vial was transferred back into the glovebox, charged with alkyne (0.50 mmol) and dry *n*-heptane (0.50 mL), put into a high pressure reactor and punctured with a short needle, and the reactor was sealed. The reactor was purged three times with hydrogen and pressurized with 52-55 bar of H₂, heated to 80 °C by a heating jacket (giving a pressure of 60 bar) and stirred with an external magnetic stirrer for 2 d. The reactor was then depressurized, the vial removed, the heptane phase separated by decantation and the catalyst phase washed two more times with 1 mL *n*-heptane. The product mixture was analyzed by GC and ¹H-NMR.

(Z)-2-Fluoro stilbene



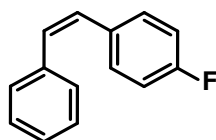
$C_{14}H_{11}F$, **198.24 g/mol**

1H -NMR (400 MHz, $CDCl_3$) δ 7.33–7.21 (m, 7H), 7.13–7.05 (m, 1H), 6.99 (m, 1H), 6.79 (d, $J = 12.3$ Hz, 1H), 6.69 (d, $J = 12.3$ Hz, 1H).

GC-MS $t_R = 7.96$ min, (EI, 70 eV): m/z 198 [M^+], 183, 177, 170, 152, 144, 133, 120, 107, 98, 89, 75, 63.

J. Li, R. Hua, T. Liu, *J. Org. Chem.* **2010**, *75*, 2966–2970.

(Z)-4-Fluoro-stilbene



$C_{14}H_{11}F$, **198.24 g/mol**

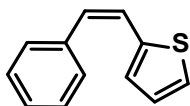
1H -NMR (300 MHz, $CDCl_3$) δ 7.23–7.17 (m, 7H), 6.92–6.85 (m, 2H), 6.58 (d, $J = 12.25$ Hz), 6.52 (d, $J = 12.25$ Hz).

$^{13}C\{^1H\}$ -NMR (75 MHz, $CDCl_3$) δ 161.74 (d, $J = 246$ Hz), 136.98, 133.13 (d, $J = 3.2$ Hz), 130.48 (d, $J = 8.0$ Hz), 130.21 (d, $J = 1.3$ Hz), 129.02, 128.78, 128.27, 127.15, 1145.10 (d, $J = 21.3$ Hz)

GC-MS $t_R = 7.98$ min, (EI, 70 eV): m/z 198 [M^+].

F. Luo, C. Pan, W. Wang, Z. Yea, J. Cheng, *Tetrahedron* **2010**, *66*, 1399–1403.

(Z)-2-(β -Styryl) thiophene



$C_{12}H_{10}S$, **186.27 g/mol**

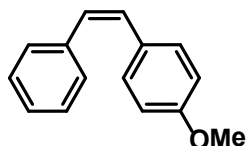
$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 7.35-7.28 (m, 5H), 7.07 (d, $J = 5$ Hz, 1H), 6.96 (d, $J = 3.3$ Hz, 1H), 6.87 (dd, $J = 5$ Hz, 3.7 Hz, 1H), 6.69 (d, $J = 12$ Hz, 1H), 6.56 (d, $J = 12$ Hz, 1H).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, CDCl_3) δ 139.72, 137.30, 128.82, 128.77, 128.49, 128.13, 127.48, 26.38, 125.48, 123.32.

GC-MS $t_R = 8.21$ min, (EI, 70 eV): m/z 186 [M^+].

M. K. Deliomeroglu, C. Dengiz, R. Çalışkan, M. Balci, *Tetrahedron* **2012**, *68*, 5838-5844.

(Z)-1-Methoxy-4-styrylbenzene



$\text{C}_{15}\text{H}_{14}\text{O}$, 210.27 g/mol

TLC $R_f = 0.31$ (SiO_2 , petroleum ether)

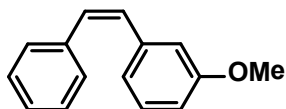
$^1\text{H-NMR}$ ^1H NMR (300 MHz, CDCl_3) δ 7.28 (m, 7H), 6.82 – 6.74 (m, 2H), 6.55 (m, 2H), 3.80 (s, 3H).

$^{13}\text{C-NMR}$ ^{13}C NMR (75 MHz, CDCl_3) δ 158.70, 137.65, 130.20, 129.81, 128.86, 128.79, 128.37, 128.28, 126.95, 113.62, 55.22.

GC-MS $t_R = 9.27$ min, (EI, 70 eV): $m/z = 210$ [M^+], 195, 179, 165, 152, 139, 128, 115, 102, 89, 77, 63, 51.

T. Schabel, C. Belge, B. Plietker, *Org. Lett.*, **2013**, *15* (11), 2858–2861.

(Z)-1-Methoxy-3-styrylbenzene



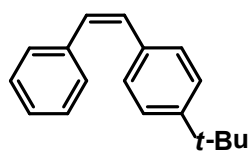
$\text{C}_{15}\text{H}_{14}\text{O}$, 210.27 g/mol

TLC $R_f = 0.31$ (SiO_2 , petroleum ether)

¹H-NMR	¹ H NMR (300 MHz, CDCl ₃) δ 7.34 – 7.24 (m, 5H), 7.11 (dd, <i>J</i> = 2.4, 1.3 Hz, 1H), 6.88 (d, <i>J</i> = 7.6 Hz, 1H), 6.83 (s, 1H), 6.81 – 6.74 (m, 1H), 6.65 (d, <i>J</i> = 12.3 Hz, 1H), 6.60 (d, <i>J</i> = 12.3 Hz, 1H), 3.67 (s, 3H).
¹³C-NMR	¹³ C NMR (75 MHz, CDCl ₃) δ 159.40, 138.58, 137.30, 130.53, 130.19, 129.28, 128.96, 128.27, 127.20, 121.56, 113.76, 113.35, 55.04.
GC-MS	<i>t</i> _R = 9.07 min, (EI, 70 eV): <i>m/z</i> = 210 [M ⁺], 194, 179, 165, 152, 139, 128, 115, 102, 89, 77, 63, 51.

J. C. Roberts, J. A. Pincock, *J. Org. Chem.*, **2004**, *69* (12), 4279–4282.

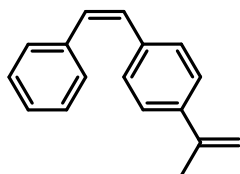
(Z)-1-tert-Butyl-4-styrylbenzene



C₁₈H₂₀, 236.35 g/mol

TLC	<i>R</i> _f = 0.33 (SiO ₂ , petroleum ether)
¹H-NMR	¹ H NMR (300 MHz, CDCl ₃) δ 7.29 (ddd, <i>J</i> = 6.3, 5.4, 4.5 Hz, 4H), 7.25 – 7.19 (m, 5H), 6.58 (s, 2H), 1.32 (s, 9H).
¹³C-NMR	¹³ C NMR (75 MHz, CDCl ₃) δ 150.19, 137.63, 134.21, 130.12, 129.61, 128.85, 128.62, 128.25, 127.00, 125.12, 34.59, 31.32.
GC-MS	<i>t</i> _R = 9.43 min, (EI, 70 eV): <i>m/z</i> = 236 [M ⁺], 221, 202, 193, 178, 165, 152, 143, 128, 115, 91, 77, 63, 51.
GC-HRMS	(CI, <i>m/z</i>): found 234.1408 [M ⁺] (calculated 234.1409).
FT-IR	(ATR-film) in [cm ⁻¹] 3014 (w), 2961 (m), 2868 (w), 1599 (w), 1509 (m), 1447 (m), 1363 (m), 1269 (m), 1200 (w), 1106 (w), 1073 (w), 1027 (w), 908 (s), 874 (m), 830 (m), 781 (s), 732 (s), 699 (s), 575 (s), 530 (m).

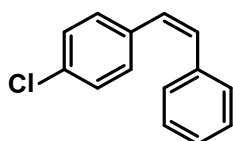
(Z)-1-(Prop-1-en-2-yl)-4-styrylbenzene



C₁₇H₁₆, 220.31 g/mol

TLC	$R_f = 0.31$ (SiO ₂ , petroleum ether)
¹H-NMR	¹ H NMR (300 MHz, CDCl ₃) δ 7.43 – 7.20 (m, 9H), 6.66 (d, $J = 12.3$ Hz, 1H), 6.61 (d, $J = 12.4$ Hz, 1H), 5.43 (s, 1H), 5.15 – 5.06 (m, 1H), 2.17 (s, 3H).
¹³C-NMR	¹³ C NMR (75 MHz, CDCl ₃) δ 142.76, 139.75, 137.42, 136.39, 130.30, 129.92, 128.92, 128.86, 128.33, 127.18, 125.30, 112.35, 21.74.
GC-MS	$t_R = 9.52$ min, (EI, 70 eV): $m/z = 220$ [M ⁺], 205, 191, 179, 165, 152, 127, 115, 91, 77, 95, 50.
GC-HRMS	(CI, m/z): found 220.1254 [M ⁺] (calculated 220.1252).
FT-IR	(ATR-film) in [cm ⁻¹] 3083 (w), 3011 (w), 2924 (w), 1626 (m), 1508 (m), 1446 (m), 1374 (m), 1310 (w), 1120 (w), 1073 (w), 890 (s), 874 (s), 836 (s), 797 (m), 733 (s), 694 (s), 647 (w), 567 (w).

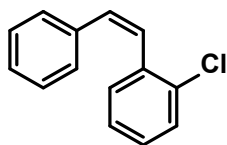
(Z)-4-Chloro-stilbene



C₁₄H₁₁Cl, 214.69 g/mol

¹H-NMR	(300 MHz, CDCl ₃) δ 7.29–7.12 (m, 9H), 6.65 (d, $J = 12.2$ Hz, 1H), 6.54 (d, $J = 12.2$ Hz, 1H).
GC-MS	$t_R = 8.95$ min, (EI, 70 eV): m/z 214 [M ⁺], 179, 152, 139, 126, 113, 102, 89, 76, 63, 51.

(Z)-2-Chloro-stilbene



$C_{14}H_{11}Cl$, **214.69 g/mol**

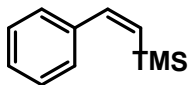
1H -NMR (400 MHz, $CDCl_3$) δ 7.41 (d, $J = 8.0$ Hz, 1H), 7.23–7.12 (m, 7H), 7.04 (td, $J = 7.6, 1.0$ Hz, 1H), 6.73 (d, $J = 12.2$ Hz, 1H), 6.68 (d, $J = 12.2$ Hz, 1H).

GC-MS $t_R = 8.78$ min, (EI, 70 eV): m/z 214 [M^+], 179, 152, 139, 126, 113, 101, 89, 76, 63, 51.

D.-J. Dong, H.-H. Li, S.-K. Tian, *J. Am. Chem. Soc.* **2010**, *132*, 5018–5020.

(Z)- β -Trimethylsilyl styrene

Because of signal overlay in the 1H -NMR spectrum only characteristic vinyl signals are noted.



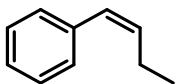
$C_{11}H_{16}Si$, **176.33 g/mol**

1H -NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, $J = 15.1, 1.4$ Hz, 1H), 5.91 (dd, $J = 15.1, 1.8$ Hz, 1H).

GC-MS $t_R = 5.92$ min, (EI, 70 eV): m/z 176 [M^+], 161, 145, 135, 115, 77, 59, 51.

Y. Nishihara, D. Saito, K. Tanemura, S. Noyori, K. Takagi, *Org. Lett.* **2009**, *11*, 3546–3549.

(Z)-But-1-ene-1-yl-benzene



$C_{10}H_{12}$, **132.20 g/mol**

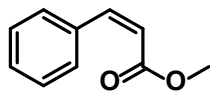
1H -NMR (400 MHz, $CDCl_3$) δ 7.40–7.31 (m, 4H), 7.26 (t, $J = 7.0$ Hz, 1H), 6.46 (d, $J = 11.6$ Hz, 1H), 5.71 (dt, $J = 11.6, 7.4$ Hz, 1H), 2.48–2.36 (m, 2H), 1.13 (t, $J = 7.4$ Hz, 3H).

GC-MS $t_R = 5.28$ min, (EI, 70 eV): m/z 132 [M^+], 115, 104, 91, 77, 65, 51.

E. H. P. Tan, G. C. Lloyd-Jones, J. N. Harvey, A. J. J. Lennox, B. M. Mills, *Angew. Chem. Int. Ed.* **2011**, *50*, 9602–9606.

(Z)-Methyl cinnamate

Because of signal overlay in the $^1\text{H-NMR}$ spectrum only vinyl signals are noted.



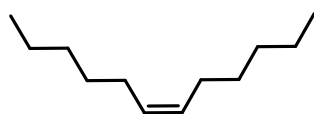
$\text{C}_{10}\text{H}_{10}\text{O}_2$, **162.19 g/mol**

$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 6.95 (d, $J = 12.6$ Hz, 1H), 5.94 (d, $J = 12.6$ Hz, 1H).

GC-MS $t_R = 6.76$ min, (EI, 70 eV): m/z 162 [M^+], 131, 109, 91, 77, 63, 51.

C. Belger, N. M. Neisius, B. Plietker, *Chem. Eur. J.* **2010**, *16*, 12214–12220.

(Z)-6-Dodecene



$\text{C}_{12}\text{H}_{24}$, **168.32 g/mol**

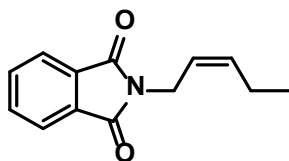
$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 5.36–5.20 (m, 2H), 1.94 (m, 4H), 1.27 (m, 12H), 0.82 (m, 6H).

GC-MS $t_R = 5.90$ min, (EI, 70 eV): m/z 168 [M^+], 140, 125, 111, 97, 83, 69, 55.

T. Hamatani, S. Matsubara, H. Matsuda, M. Schlosser, *Tetrahedron* **1988**, *44*, 2875–2881.

(Z)-N-(Pent-2-ene-1-yl)phthalimide

Because of signal overlay in the $^1\text{H-NMR}$ spectrum only vinyl signals are noted.



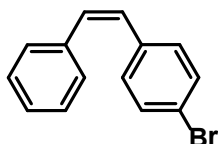
$\text{C}_{13}\text{H}_{13}\text{NO}_2$, **215.25 g/mol**

$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 5.58 (dt, $J = 10.7, 7.3$ Hz, 1H), 5.42 (dt, $J = 10.7, 7.0$ Hz, 1H).

GC-MS $t_R = 9.21$ min, (EI, 70 eV): m/z 215 [M^+], 186, 160, 148, 130, 104, 76, 67, 50.

C. Germon, A. Alexakis, J. F. Normant, *Synthesis* **1984**, 40, 40–43.

(Z)-1-Bromo-4-styrylbenzene



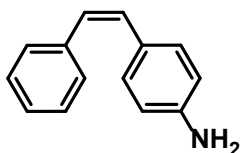
$C_{14}H_{11}Br$,
259.14 g/mol

1H -NMR 1H NMR (300 MHz, $CDCl_3$) δ 7.33 (d, $J = 8.4$ Hz, 2H), 7.25 – 7.20 (m, 5H), 7.10 (d, $J = 8.5$ Hz, 2H), 6.63 (d, $J = 12.2$ Hz, 1H), 6.49 (d, $J = 12.2$ Hz, 1H).

GC-MS $t_R = 9.44$ min, (EI, 70 eV): $m/z = 258$ [M^+], 179, 152, 126, 102, 89, 76, 63, 51.

T. Schabel, C. Belge, B. Plietker, *Org. Lett.*, **2013**, 15 (11), 2858–2861.

(Z)-1-Amino-4-styrylbenzene



$C_{14}H_{13}N$, 195.26 g/mol

1H -NMR 1H NMR (300 MHz, $CDCl_3$) δ 7.32 (dd, $J = 8.1, 1.3$ Hz, 2H), 7.29 – 7.16 (m, 3H), 7.12 – 7.04 (m, 2H), 6.56 – 6.50 (m, 2H), 6.50 (d, $J = 12.2$ Hz, 1H), 6.44 (d, $J = 12.2$ Hz, 1H), 3.61 (s, 2H).

GC-MS $t_R = 9.76$ min, (EI, 70 eV): $m/z = 195$ [M^+], 180, 165, 152, 139, 117, 106, 89, 77, 65, 51.

T. Schabel, C. Belge, B. Plietker, *Org. Lett.*, **2013**, 15 (11), 2858–2861.

Recycling Experiments

Recycling experiments were tested of the hydrogenation of diphenylacetylene with [Fe]/IL-1/MeCN. Therefore the general protocol hydrogenation of alkynes with [Fe]/IL-1/MeCN was used. Instead of 20 h the reaction mixture was stirred for 24 h at 60 bar H₂ and 80 °C. Then, the catalyst phase was extracted with *n*-heptane (3 × 0.5 mL) in a glove box. The combined organic layers were analyzed by GC-FID und GC-MS. The catalyst phase was charged again with acetonitrile (0.50 mmol, 26 μL), diphenylacetylene (0.5 mmol, 89.1 mg) and 0.5 mL *n*-heptane and transferred to the high pressure reactor for the next hydrogenation run.

Reaction of IL-1 and IL-3 with EtMgCl

The ionic liquids IL-1 and IL-3 were tested in the reaction with EtMgCl for determination of side products. Therefore, a 4 mL flask has been charged with IL-1 or IL-3 (0.5 mmol, 150 μL) and EtMgCl in THF (2 M in THF, 0.5 mmol, 0.25 mL) under argon atmosphere. The reaction mixture was stirred for 30 min, quenched with D₂O and dried (oil pump). The reaction mixture was analyzed by ESI-MS, ¹H-NMR and ²H-NMR.

Analysis of IL-1 after Hydrogenation

To check if missing product after decantation and extraction of the catalyst phase (IL) is due to trapped residues of product in the IL, a ¹H-NMR of the IL after hydrogenation of 1-methoxy-4-(phenylethynyl) benzene with [Fe]/IL-1 was measured. To that end, a small amount of the catalyst phase was diluted in MeOH-d₄ and filtered through a layer of celite (in a pipette) directly into the NMR tube.

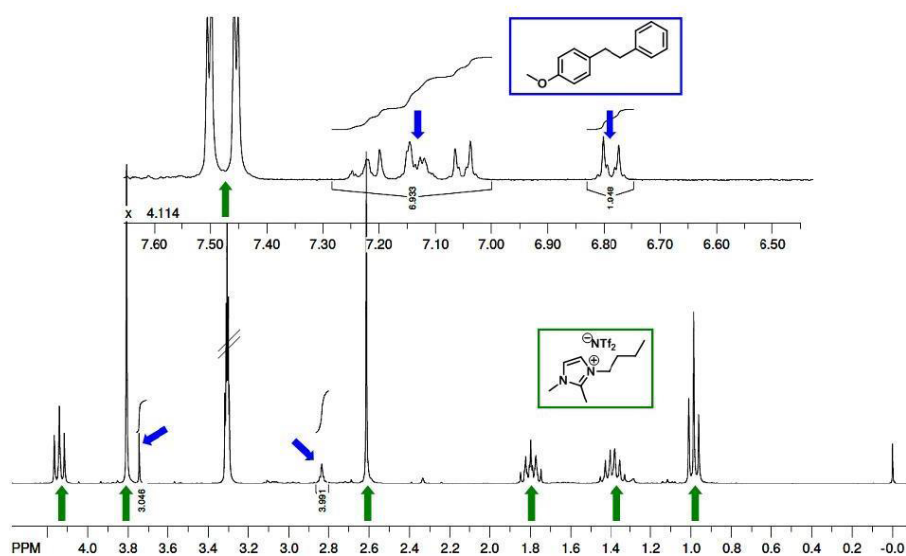


Figure 1: ¹H-NMR of IL-1 after hydrogenation of 1-methoxy-4-(phenylethynyl) benzene.

TEM-Analysis

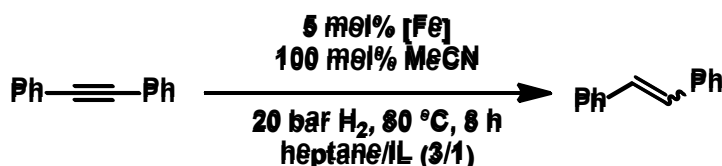
A sample of the corresponding catalyst embedded in IL was dispersed in abs. THF. The highly diluted suspension was placed in an ultrasound bath for approx. 5 minutes. In a glove box, a small amount of the dispersion was placed on a carbon-coated copper grid and the solvent evaporated at ambient temperature. The particle size distribution was determined using *Lince24e*, by measuring 200-300 particles on the enlarged digital images. TEM measurements have been carried out three weeks after preparation of the samples. During this time, the samples fixed on the copper grid were stored in a glove box under an argon atmosphere at room temperature.

Selective scavenging with dct

The heterogeneity of the catalyst species was further indicated by experiments in the presence of dibenzo[*a,e*]cyclooctatetraene (dct). Dct selectively binds homogeneous metal species due to its rigid tub-like structure and π -acceptor ability, and it is resistant to hydrogenation. No inhibition of catalytic activity was observed in the hydrogenation of diphenylacetylene when dct was added at ~50% conversion.

Standard procedure with 5 mol% Fe catalyst solution in 150 μ L IL-1, 0.5 mmol diphenylacetylene, 100 mol% MeCN, 0.5 mL heptane, 0.5 mmol pentadecane (GC reference). Reaction in a 4 mL vial at 80°C, 20 bar H₂.

After 5 h, the autoclave reactor was cooled and depressurized, transferred into a glovebox (argon) and a sample was taken for quantitative GC-FID analysis (entry 2). Then, 10 mol% (2 equiv. per Fe) dibenzo[*a,e*]cyclooctatetraene (dct) were added, and the reactor again pressurized and heated (20 bar, 80°C). After another 3h, the sampling procedure was repeated (entry 4). A parallel reaction was run in a separate vial under identical conditions inside the same autoclave reactor but without addition of dct (entries 1 and 3).

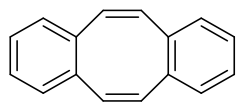


Entry	Conditions	Yield (Conversion) in % ^[a]	Z/E
1	after 5 h	49 (72)	96/4
2	after 5 h	50 (71)	96/4
3	w/out dct, after 8 h	60 (81)	97/3
4	w/ diene after 8 h	59 (79)	97/3

[a] Yields determined by quantitative GC-FID vs. *n*-pentadecane

Preparation of Dibenzo[*a,e*]cyclooctatetraene (dct):

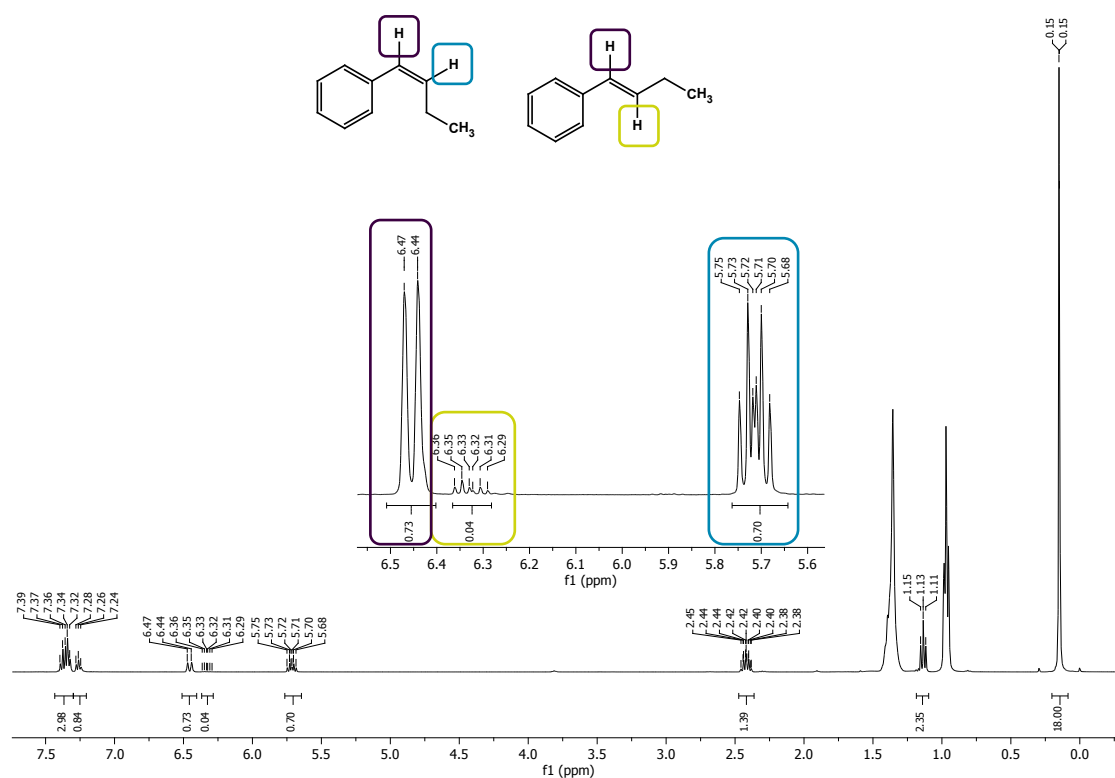
dct was synthesized in a 3-step synthesis according to a recent literature report: G. Franck, M. Brill, G. Helmchen, *J. Org. Chem.* **2012**, *89*, 55-65.



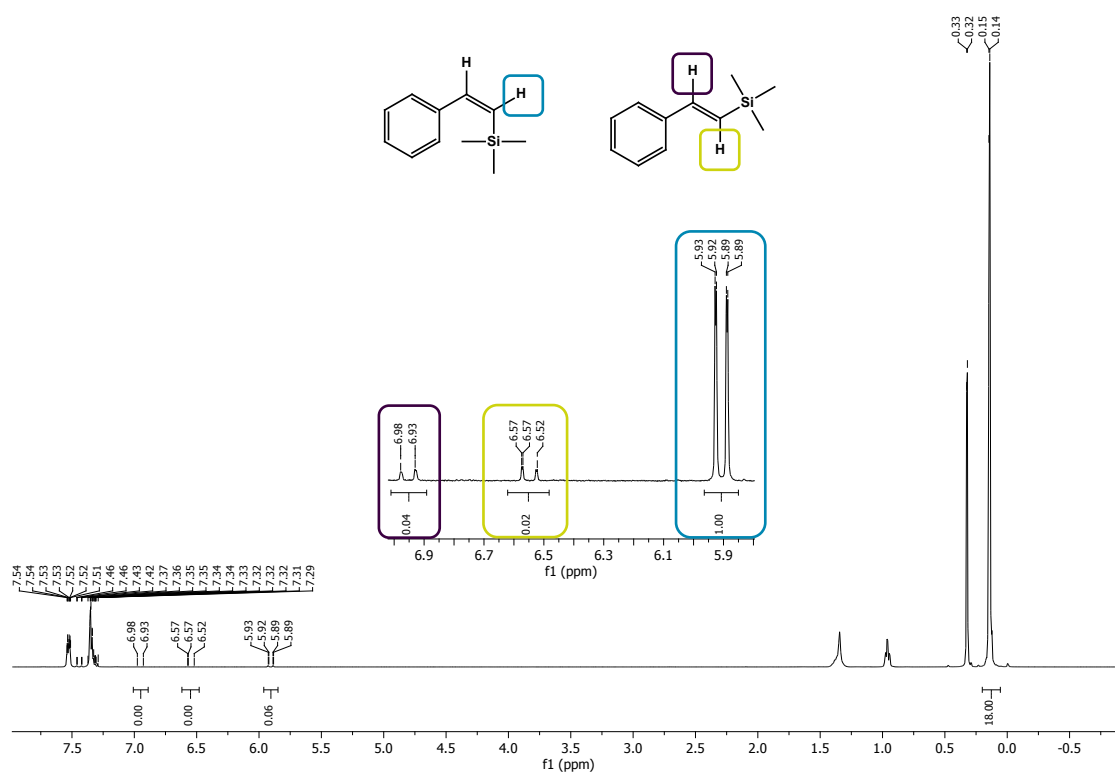
C₁₆H₁₂, 204.27 g/mol

Condition:	colourless solid
¹H-NMR (300 MHz, CDCl₃):	δ _H [ppm] = 7.19–7.13 (m, 4H), 7.10–7.02 (m, 4H), 6.76 (s, 4H).
¹³C{¹H} NMR (75 MHz, CDCl₃):	δ _C [ppm] = 137.1, 133.3, 129.1, 126.8.
Retention time GC-MS:	9.35 min
LR MS (EI, 70 eV, m/z):	204 [M ⁺]

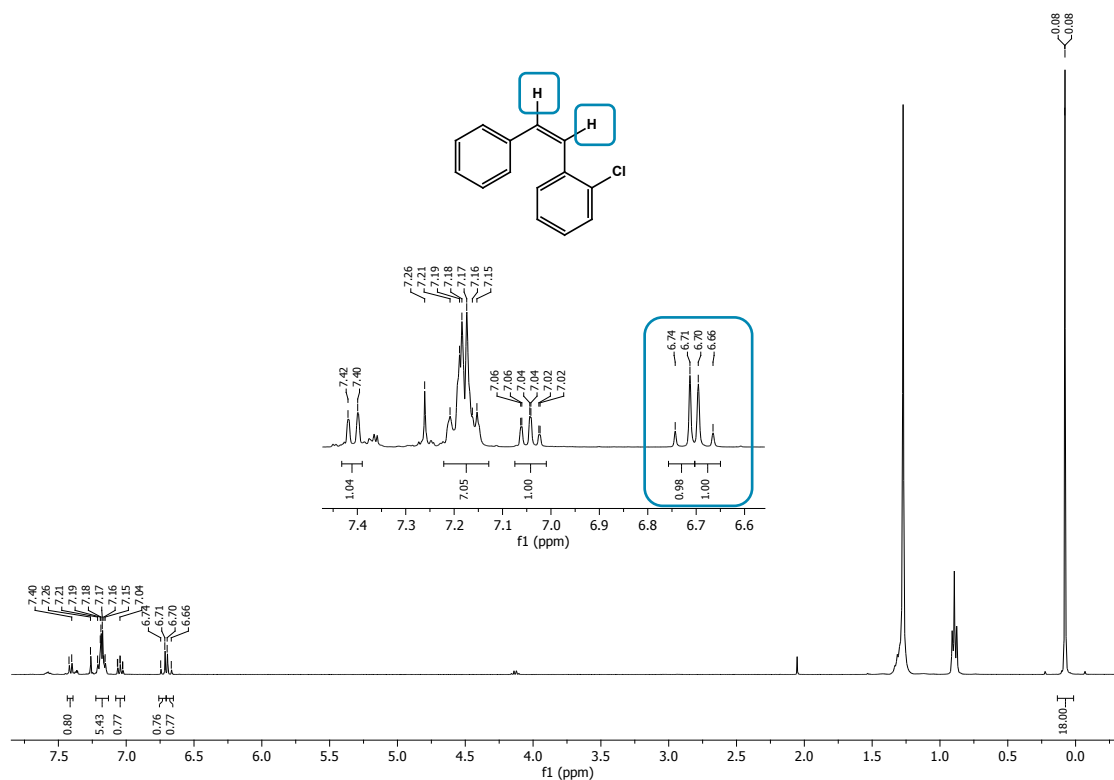
Selected Spectra



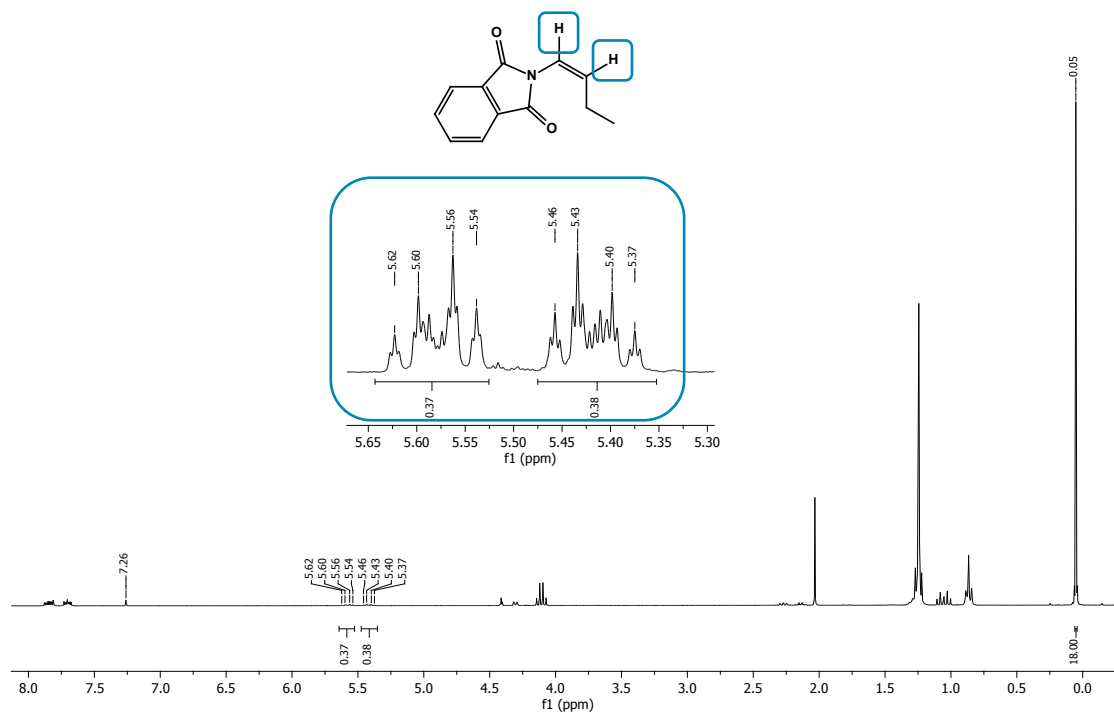
$^1\text{H-NMR}$ spectrum of product mixture after hydrogenation of but-1-yn-1-ylbenzene. Integrals vs. internal reference hexamethyldisiloxane (full spectrum).



$^1\text{H-NMR}$ spectrum of product mixture after hydrogenation of trimethyl(phenylethynyl)silane. Integrals vs. internal reference hexamethyldisiloxane (full spectrum).



$^1\text{H-NMR}$ spectrum of product mixture after hydrogenation of 2-chloro-stilbene. Integrals vs. internal reference hexamethyldisiloxane (full spectrum).



$^1\text{H-NMR}$ spectrum of product mixture after hydrogenation of *N*-(pent-2-yne-1-yl)phthalimide. Integrals vs. internal reference hexamethyldisiloxane (full spectrum).

GC-FID spectra after hydrogenation of diphenylacetylene in IL-1, IL-3 and IL-1/MeCN.

