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SUPPORTING INFORMATION

Electrophilic Phosphonium Cations Catalyzed Hydroarylation and Hydrosulfuration of Olefins

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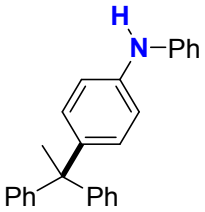
General Procedures:

All preparations and manipulations were carried out under an anhydrous N_2 atmosphere using standard Schlenk and glovebox techniques. All glassware was oven-dried and cooled under vacuum before use. Commercial reagents were purchased from Sigma Aldrich, Strem or Apollo Scientific and used without further purification unless indicated otherwise. Compounds $[(C_6F_5)_3PF][B(C_6F_5)_4]$ (**1a**) and $[(C_6H_5)_2(C_6F_5)P][CF_3SO_3]$ (**1b**) were prepared follow the procedure described in literature.[1] Solvents CH_2Cl_2, Et_2O, *n*-pentane, and toluene were dried using an Innovative Technologies solvent purification system. CD_2Cl_2 (Aldrich) was deoxygenated, distilled over CaH_2, then stored over 4 Å molecular sieves before use. The solvent C_6D_5Br (Aldrich) was deoxygenated and stored over 4 Å molecular sieves before use. Reactions were monitored using NMR spectroscopy or thin-layer chromatography (TLC) on EMD Silica Gel 60 F254 plates. TLC visualization of the developed plates was performed under UV light (254 nm), $KMnO_4$ or anisaldehyde stains. Neutral silica (Silica-P, 40-63 μm, Silicycle, Québec, Canada) for flash column chromatography was used as received. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. NMR spectra were obtained on a Bruker AvanceIII-400 MHz spectrometer and Agilent DD2-500 MHz spectrometer. Data for ^1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, dm = doublet of multiplets, br = broad), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ / ppm). High-resolution mass spectra (HRMS) were obtained on a micro mass 70S-250 spectrometer (EI), an ABI/Sciex QStar Mass Spectrometer (DART), or on a JOEL AccuTOF-DART (DART). GC-MS spectra were obtained on an Agilent Technologies 5975C VL MSD with Triple-Axis Detector and 7890A GC System. Column Agilent 19091S-433 (30m × 250μm × 0.25μm), Oven: 40 °C for first 10 min, 10 °C/min to 300 °C for 10 min. Injection volume: 1 μL.

Friedel-Crafts Reaction with Anilines.

[1] Caputo, C.B.; Hounjet, L.J.; Dobrovetsky, R.; Stephan, D.W. *Science*, **2013**, *341*, 1374; Hounjet, L.J., Caputo, C,B., Stephan, D.W.,* *Dalton Trans.*, **2013**, *42*, 2629–2635.

Reactions were allowed to proceed for 16 h even in instances where the reaction was complete in a shorter time. Various mole% of the catalysts 1.5 - 5.5 mol% were used.



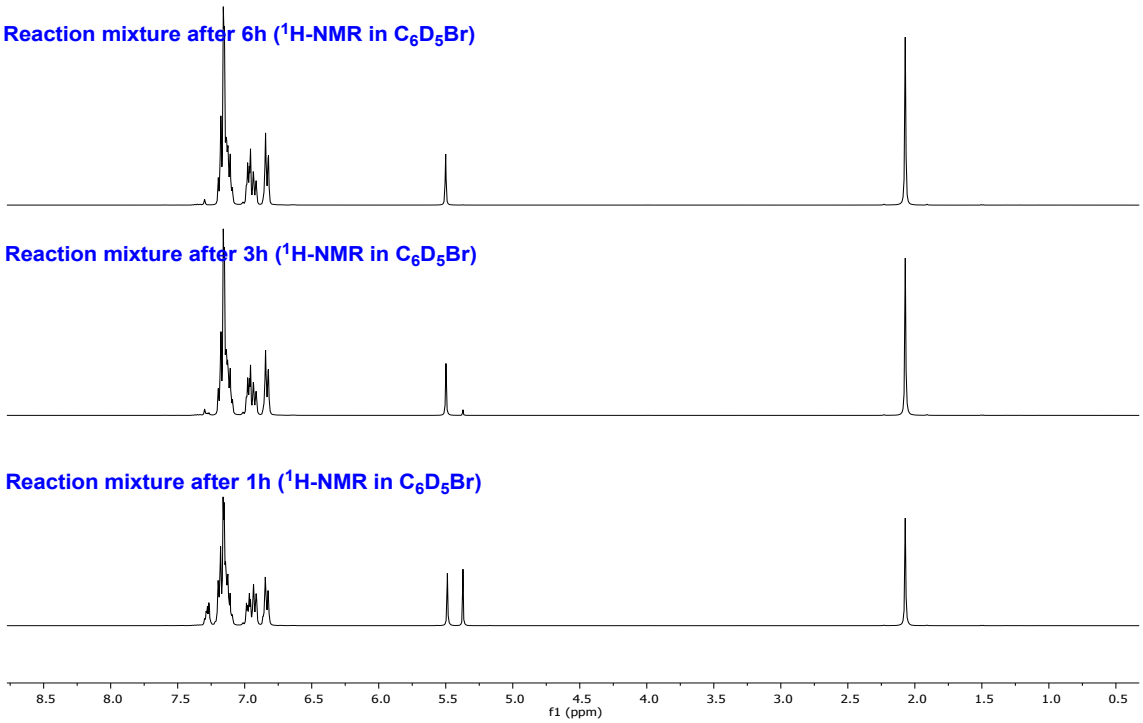
4-(1,1-diphenylethyl)-N-phenylaniline (2). To a solution of the catalyst **1a** (3 mg, 1.5 mol%) in C_6D_5Br (1.0 mL) were added diphenylamine (29 mg, 0.17 mmol) and then 1,1-diphenylethylene (30 mg, 0.17 mmol) at r.t. After 6 h the reaction was complete. This was followed by saturated $NaHCO_3$ (5 mL) extraction with dichloromethane (3 × 5 mL). The organic phase was dried over magnesium sulfate, filtered over silica-gel and the solvent was removed (59 mg, >99% yield).

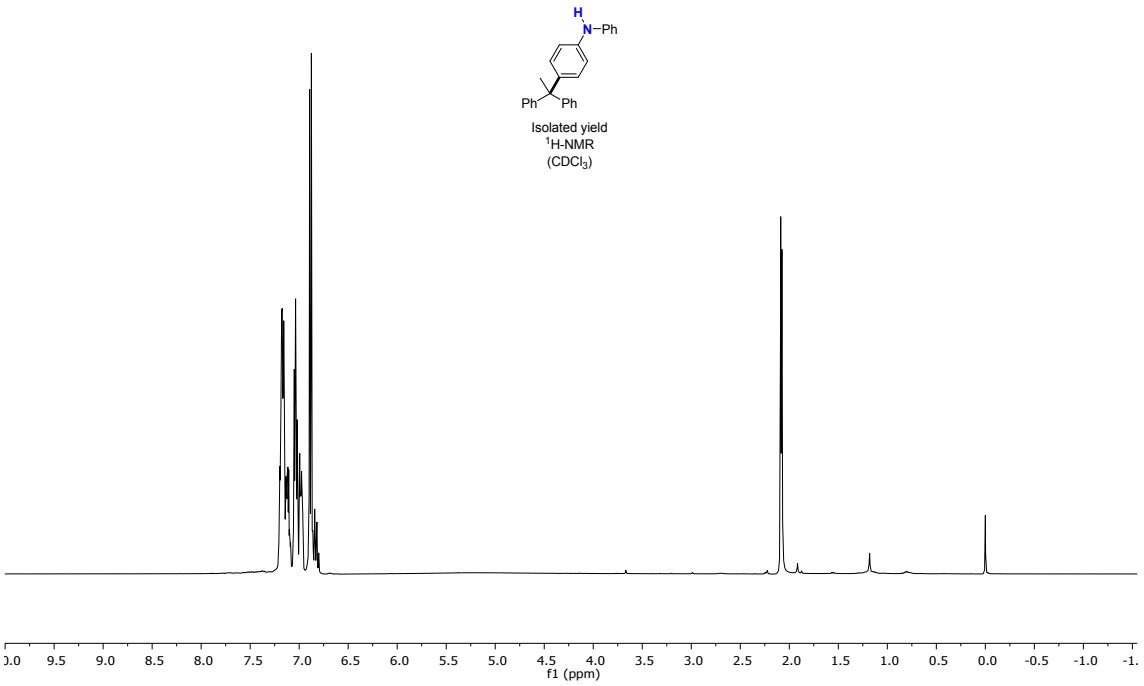
^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.21-7.09 (m, 8H), 7.06-7.01 (m, 4H), 7.01-6.96 (m, 2H), 6.88 (d, *J*= 7.8 Hz, 4H), 6.84 (m, 1H), 5.20 (br s, 1H), 2.09 and 2.08 (s, 3H).

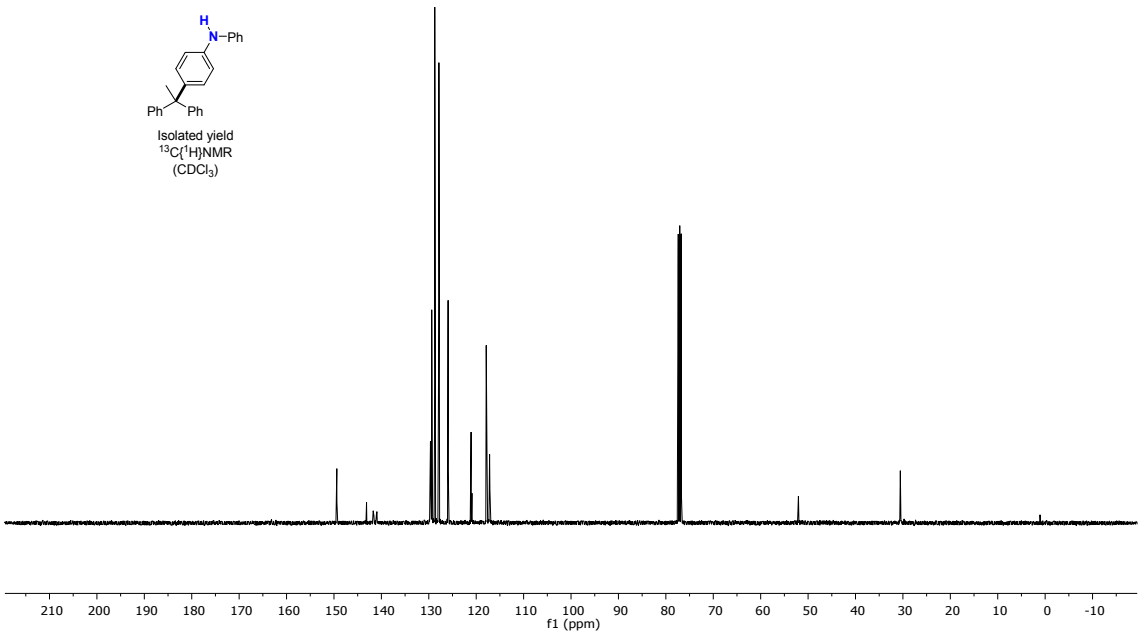
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$), δ: 149.3 (2C), 143.1 (1C), 141.6, 141.6, 140.9 and 140.9 (1C), 129.6 and 129.5 (1C), 129.3 and 129.2 (2C), 128.7 (4C), 127.8 and 127.8 (6C), 125.8 and 125.8 (2C), 121.0 and 120.8 (1C), 117.8 and 117.6 (2C), 117.1 and 117.0 (2C), 51.9 (1C), 30.5 (1C).

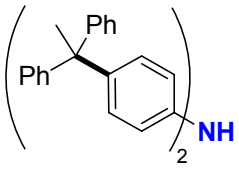
MS (DART Ionization), [*m/z*, (%)]: 350.2 ([M+H]$^+$, 50), 198.1 (30), 170.1 (100).

HRMS (DART Ionization, *m/z*): calcd. for $C_{18}H_{24}N$, [M+H]$^+$: 350.19087; found: 350.19151.




H
N–Ph
Ph
Ph
Isolated yield
1H-NMR
(CDCl3)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


H
N–Ph
Ph
Ph
Isolated yield
13C{1H}NMR
(CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



Bis(4-(1,1-diphenylethyl)phenyl)amine (3). To a solution of the catalyst **1a** (3 mg, 1.5 mol%) in C_6D_5Br (1.0 mL) were added diphenylamine (29 mg, 0.17 mmol) and then 1,1-diphenylethylene (69 mg, 0.38 mmol) at r.t. After 6 h the reaction was complete. This was followed by saturated $NaHCO_3$ (5 mL) extraction with dichloromethane (3 × 5 mL). The organic phase was dried over magnesium sulfate, filtered over silica-gel and the solvent was removed (90 mg, >99% yield).

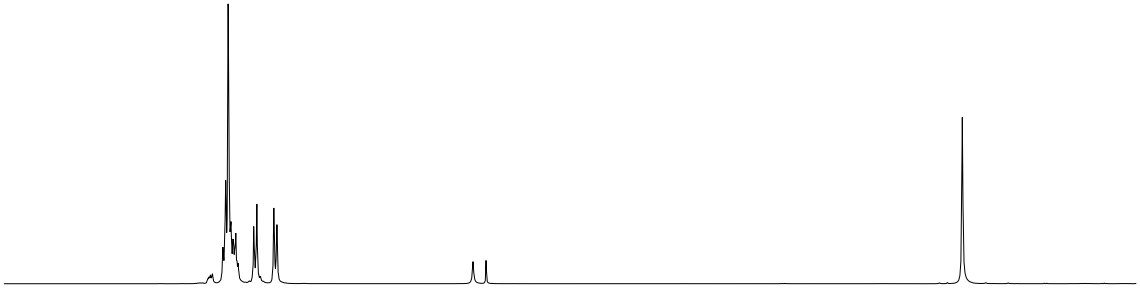
^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.25-7.17 (m, 2H), 7.18-7.10 (m, 8H), 7.10-7.04 (m, 4H), 7.04-6.98 (m, 7H), 6.84 (m, 7H), 5.47 (br s, 1H), 2.03 (s, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$), δ: 149.5 (2C), 141.7 (1C), 130.0 (1C), 129.2 (4C), 128.7 (2C), 128.5 (4C), 126.4 (2C), 115.8 (2C), 51.2 (1C), 30.0 (1C).

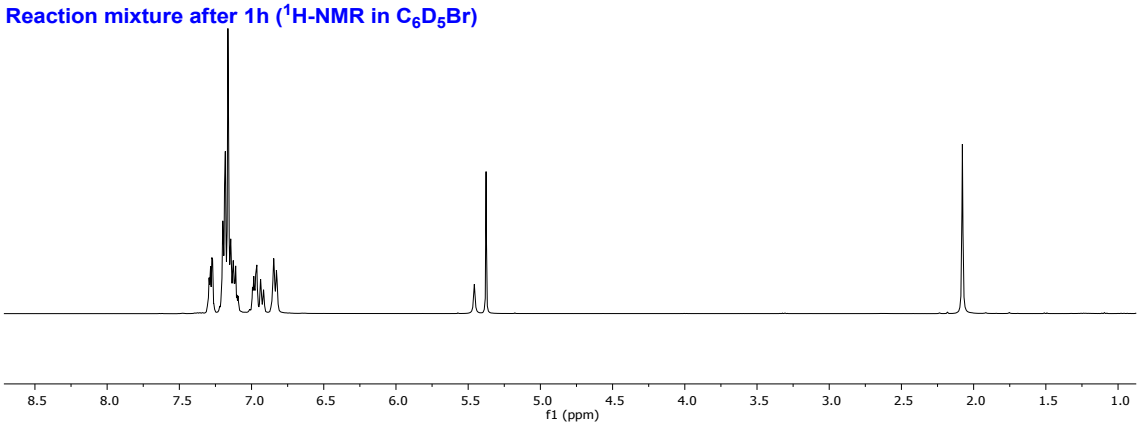
MS (DART Ionization), [*m/z*, (%)]: 530.3 ([M+H]$^+$, 25), 391.3 (100), 350.2 (60).

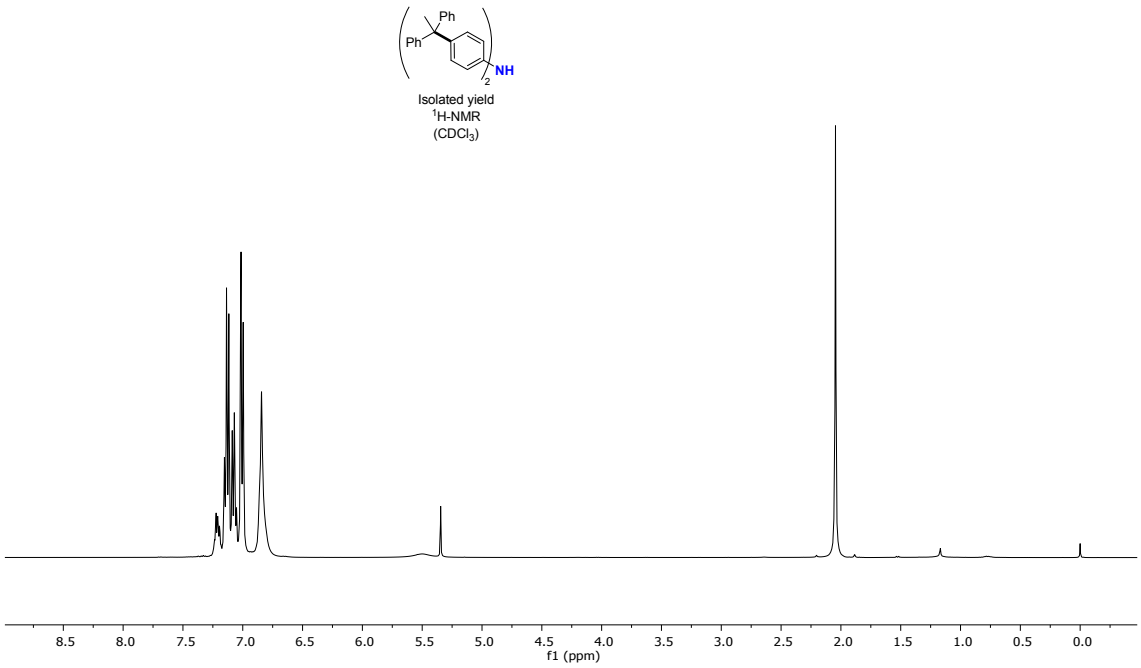
HRMS (DART Ionization, *m/z*): calcd. for $C_{40}H_{36}N$, [M+H]$^+$: 530.28477; found: 530.28414.

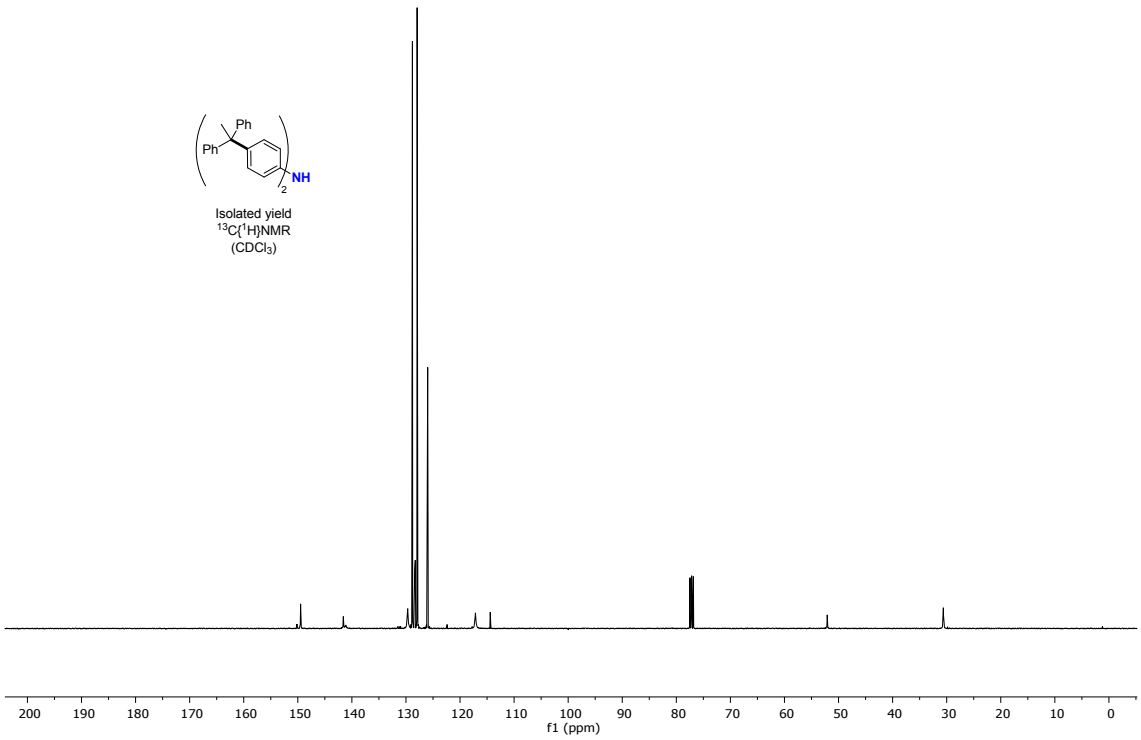
Reaction mixture after 6h (^{1}H-NMR in C_6D_5Br)

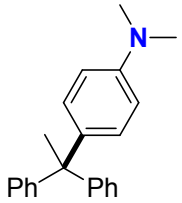


Reaction mixture after 1h (^{1}H-NMR in C_6D_5Br)




Ph
Ph
NH
2
Isolated yield
1H-NMR
(CDCl3)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Ph
Ph
NH
2
Isolated yield
13C{1H}NMR
(CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



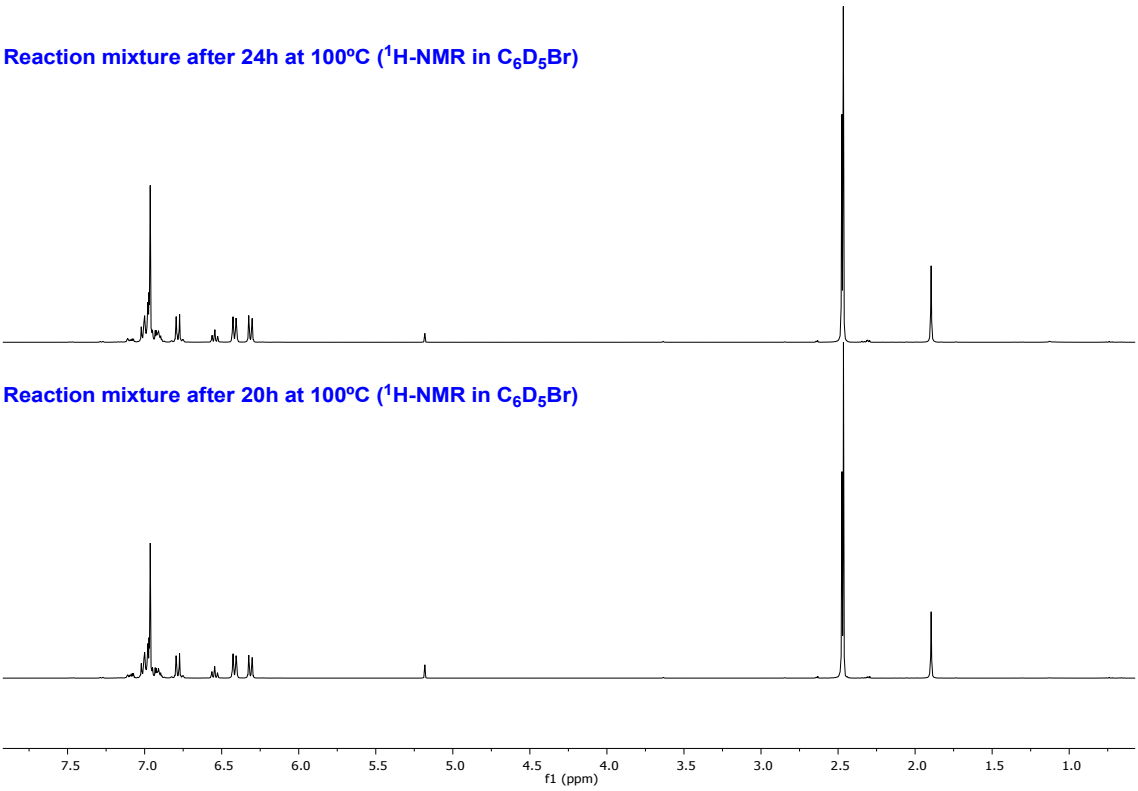
4-(1,1-Diphenylethyl)-N,N-dimethylaniline (4). To a solution of the catalyst **1a** (6 mg, 5.5 mol%) in C_6D_5Br (1.0 mL) were added *N,N*-dimethylaniline (21 mg, 0.17 mmol) and then 1,1-diphenylethylene (15 mg, 0.085 mmol) at r.t. After 24 h at 100ºC the reaction reached 94% conversion. This was followed by saturated $NaHCO_3$ (5 mL) extraction with dichloromethane (3 × 5 mL). The organic phase was dried over magnesium sulfate, filtered over silica-gel and the solvent was removed (23 mg, 90% yield).

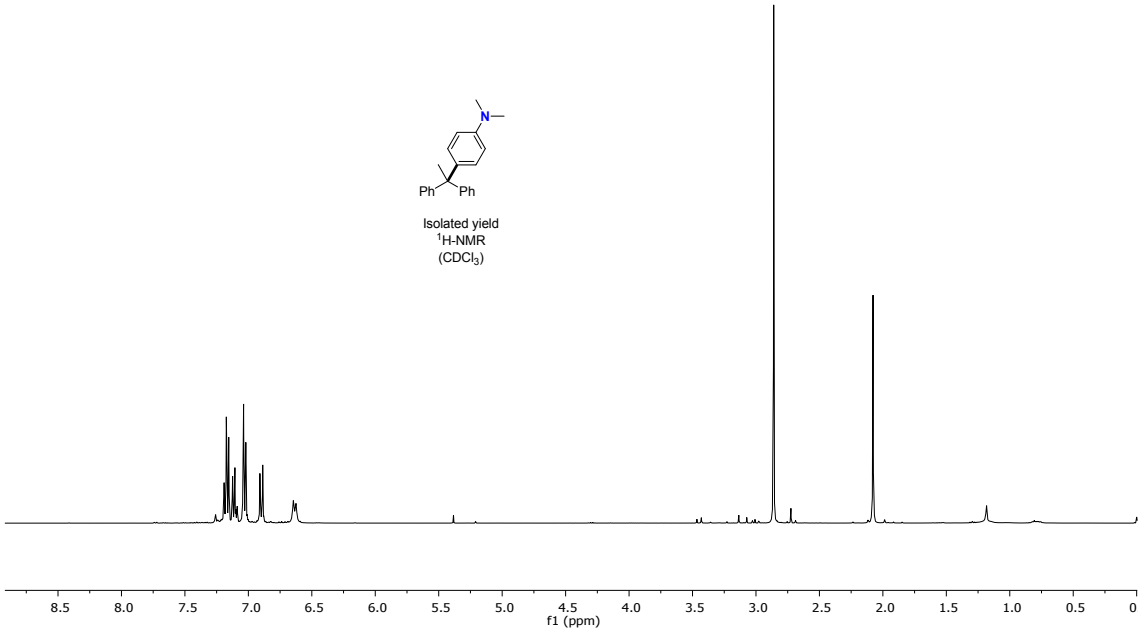
^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.17 (m, 4H), 7.11 (m, 2H), 7.03 (m, 4H), 6.96 (d, *J*= 9.0 Hz, 2H), 6.63 (m, 2H), 2.86 (s, 6H), 2.08 (s, 3H).

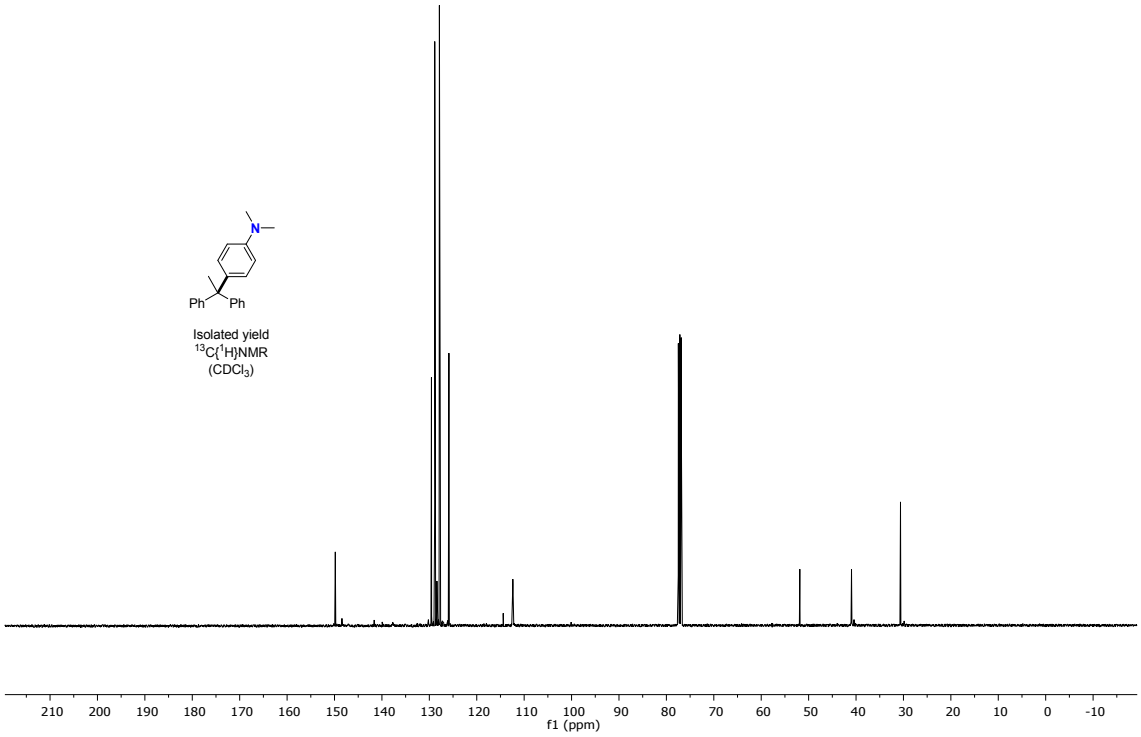
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$), δ: 149.8 (2C), 148.4 (1C), 137.7 (1C), 129.6 (2C), 128.9 (4C), 127.9 (4C), 125.9 (2C), 112.4 (2C), 51.9 (1C), 41.0 (2C), 30.6 (1C).

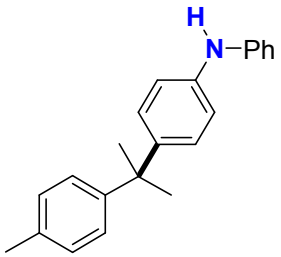
MS (DART Ionization), [*m/z*, (%)]: 302.2 ([M+H]$^+$, 40), 122.1 (100).

HRMS (DART Ionization, *m/z*): calcd. for $C_{22}H_{24}N$, [M+H]$^+$: 302.19087; found: 302.19186.




N
Ph
Ph
Isolated yield
1H-NMR
(CDCl3)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


N
Ph
Ph
Isolated yield
13C{1H}NMR
(CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

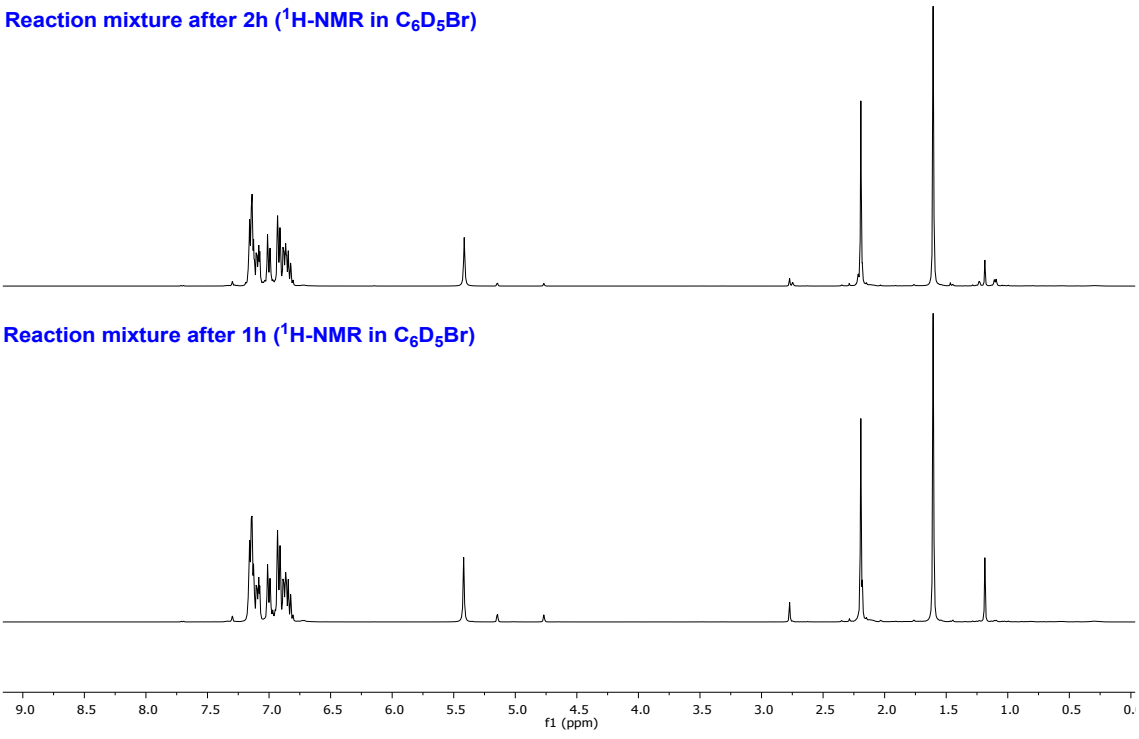


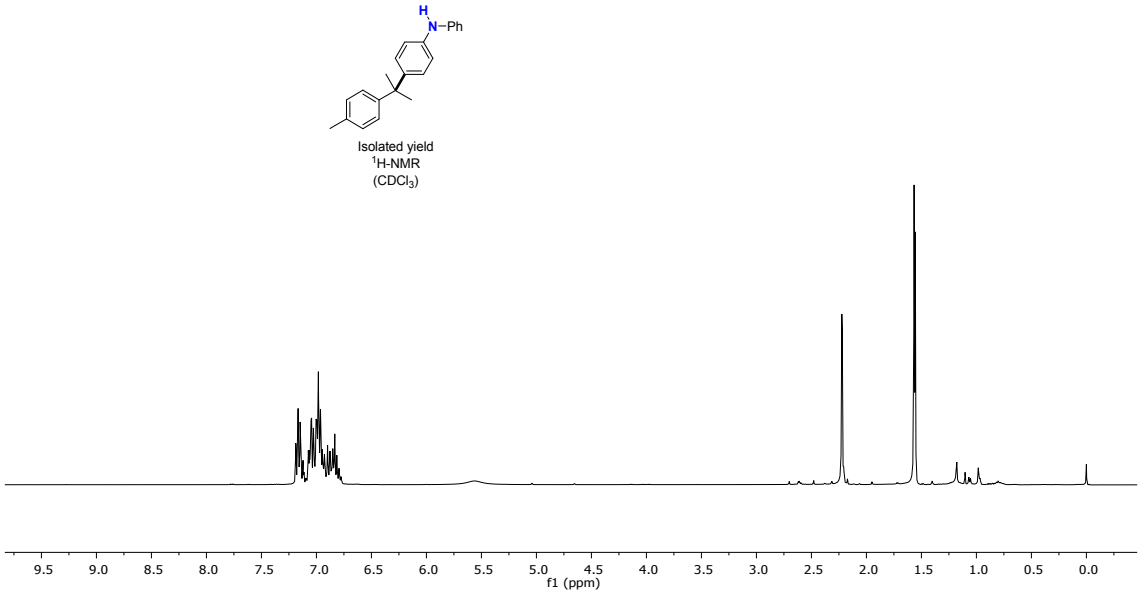
Bis(4-(1,1-diphenylethyl)phenyl)amine (5). To a solution of the catalyst **1a** (3 mg, 1.5 mol%) in C_6D_5Br (1.0 mL) were added diphenylamine (29 mg, 0.17 mmol) and then 1-isopropenyl-4-methyl-benzene (23 mg, 0.17 mmol) at r.t. After 2 h the reaction was complete. This was followed by saturated $NaHCO_3$ (5 mL) extraction with dichloromethane (3 × 5 mL). The organic phase was dried over magnesium sulfate, filtered over silica-gel and the solvent was removed (45 mg, 89% yield).

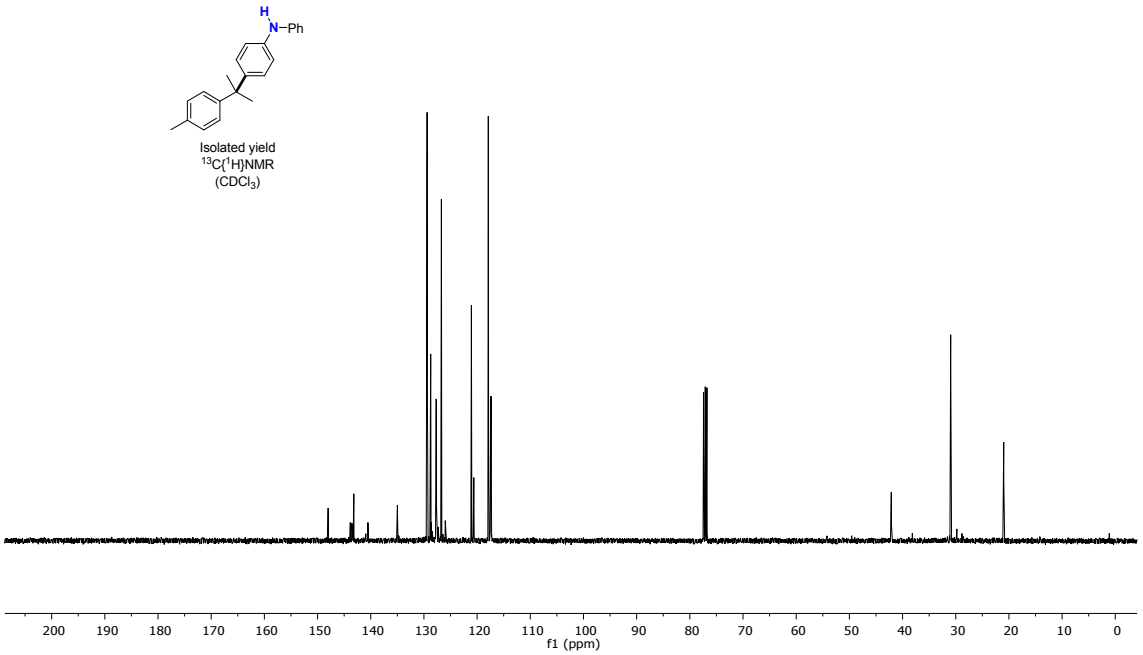
^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.21-6.75 (m, 13H), 5.53 (br s, 1H), 2.18 (s, 3H), 1.52 (s, 3H), 1.51 (s, 3H).

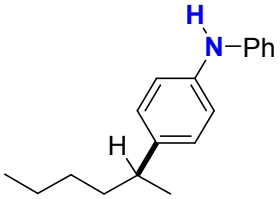
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$), δ: 148.6 (1C), 144.7 (2C), 144.4 (1C),133.1 (1C), 129.6 (2C), 129.3 (2C),128.5 (2C),127.7 (2C),121.9 (1C), 118.4 (2C),118.0 (2C), 42.5 (1C), 30.4 (1C), 21.1 (1C).

MS (DART Ionization), [*m/z*, (%)]: 302.2 ([M+NH_4]$^+$, 100), 170.1 (30).




H
N–Ph
Isolated yield
1H-NMR
(CDCl3)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


H
N–Ph
Isolated yield
13C{1H}NMR
(CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



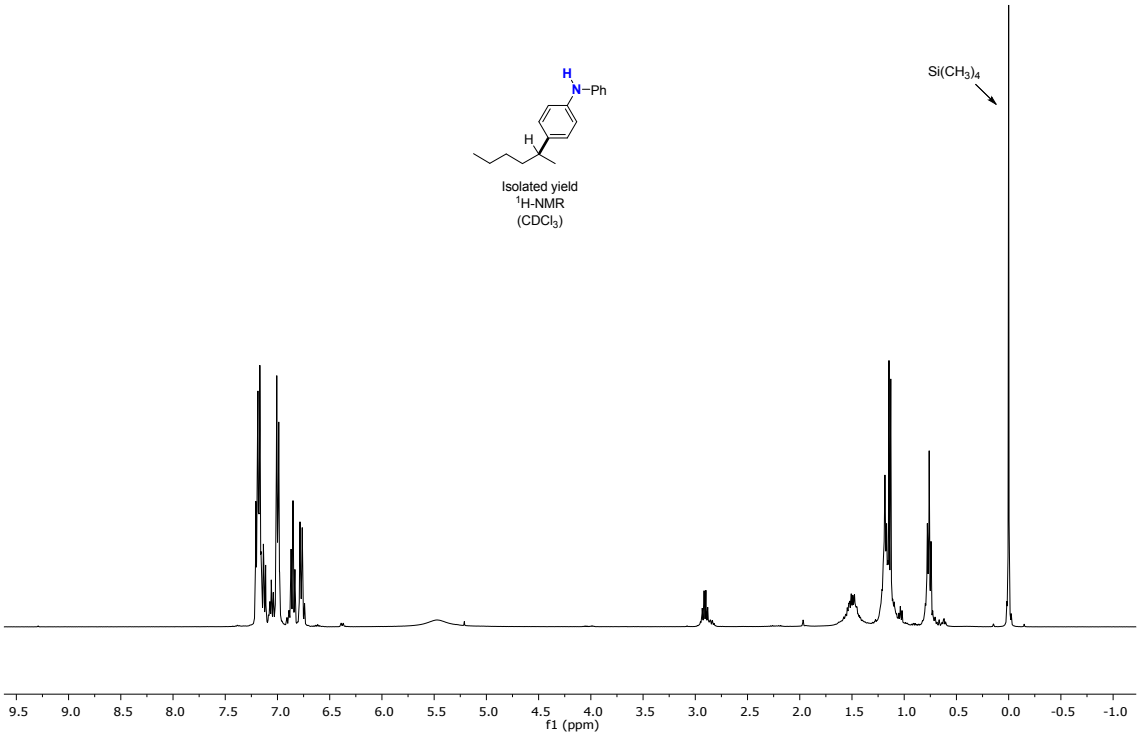
4-(Hexan-2-yl)-N-phenylaniline (6). To a solution of the catalyst **1a** (12 mg, 6 mol%) in C_6D_5Br (1.0 mL) were added diphenylamine (29 mg, 0.17 mmol) and then 1-hexene (15 mg, 0.17 mmol) at r.t. After 24 h at 100ºC the reaction was complete. This was followed by saturated $NaHCO_3$ (5 mL) extraction with dichloromethane (3 × 5 mL). The organic phase was dried over magnesium sulfate, filtered over silica-gel and the solvent was removed (30 mg, 70% yield).

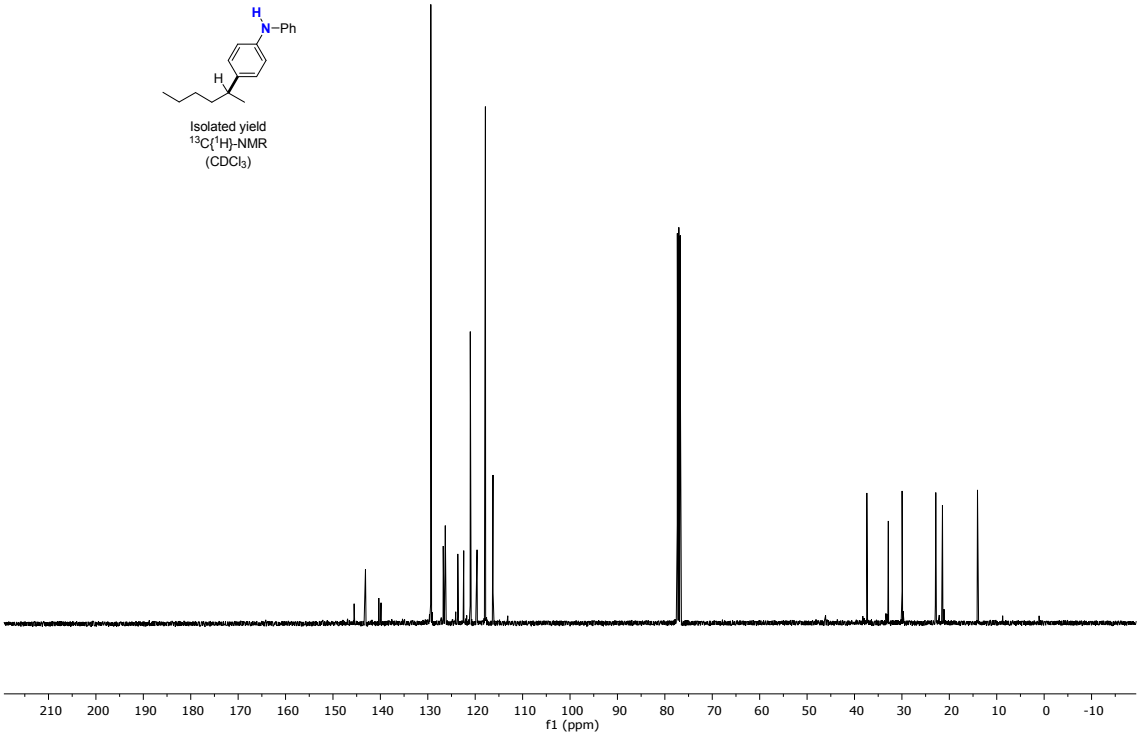
^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.22-7.11 (m, 4H), 7.09-6.97 (m, 3H), 6.86 (m, 1H), 6.77 (m, 1H), 5.48 (b.s., 1H), 2.91 (sextet, *J* = 7.0 Hz, 1H), 1.50 (m, 2H), 1.18 (m, 4H), 1.14 (d, *J*= 6.7 Hz, 3H), 0.76 (t, *J*= 6.8 Hz, 3H).

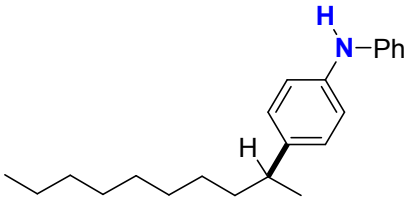
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$), δ: 146.2 (1C), 144.5 (1C), 141.8 (1C), 140.9 (1C), 130.7 (1C), 127.1 (1C), 124.1 (1C), 123.0 (1C), 121.5 (1C), 120.2 (1C), 118.8 (1C), 115.4 (1C), 37.5 (1C), 33.0 (1C), 30.1 (1C), 23.0 (1C), 21.6 (1C), 14.2 (1C).

MS (DART Ionization), [*m/z*, (%)]: 254.2 ([M+H]$^+$, 100), 170.1 (25).

HRMS (DART Ionization, *m/z*): calcd. for $C_{18}H_{24}N$, [M+H]$^+$: 254.19087; found: 254.19062.







4-(Decan-2-yl)-N-phenylaniline (7). To a solution of the catalyst **1a** (12 mg, 6 mol%) in C_6D_5Br (1.0 mL) were added diphenylamine (29 mg, 0.17 mmol) and then 1-decene (24 mg, 0.17 mmol) at r.t. After 16 h at 100ºC the reaction was complete. This was followed by saturated $NaHCO_3$ (5 mL) extraction with dichloromethane (3 × 5 mL). The organic phase was dried over magnesium sulfate, filtered over silica-gel and the solvent was removed (40 mg, 75% yield).

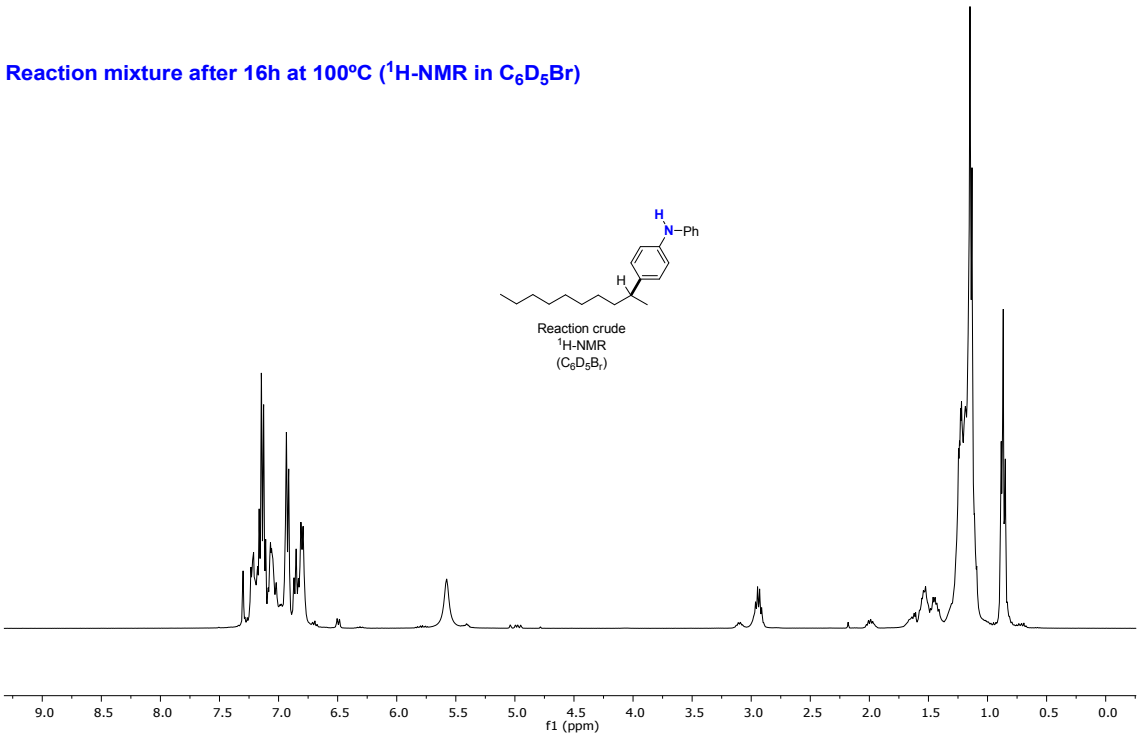
^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.21-7.10 (m, 4H), 7.06-6.98 (m, 3H), 6.85 (m, 1H), 6.77 (m, 1H), 5.15 (br s, 1H), 2.90 (sextet, *J* = 6.8 Hz, 1H), 1.47 (m, 2H), 1.22-1.09 (m, 15H), 0.79 (t, *J*= 6.9 Hz, 3H).

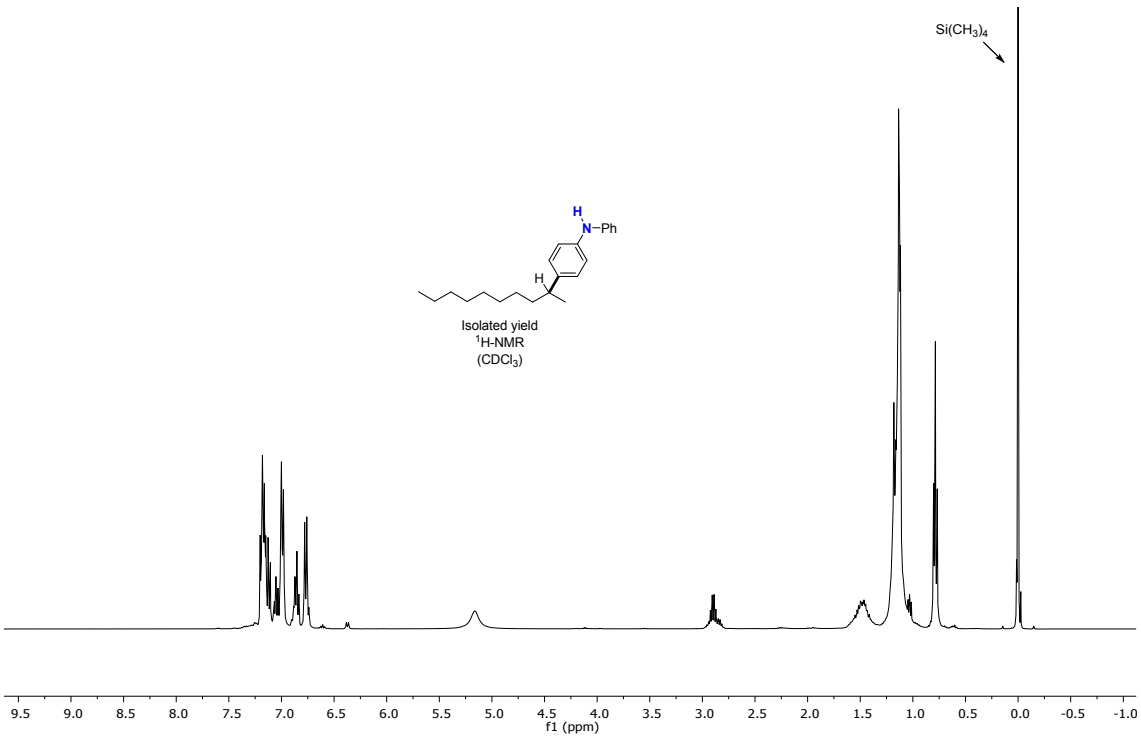
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$), δ: 144.3 (1C), 142.1 (1C), 140.3 (1C), 128.7 (2C), 123.8 (1C), 122.6 (1C), 121.0 (1C), 119.5 (1C), 117.9 (1C), 116.4 (1C), 115.7 (1C), 36.6 (1C), 31.8 (1C), 30.8 (1C), 28.7 (1C), 28.5 (1C), 28,3 (1C), 26.7 (1C), 21.6 (1C), 20.4 (1C), 13.1 (1C).

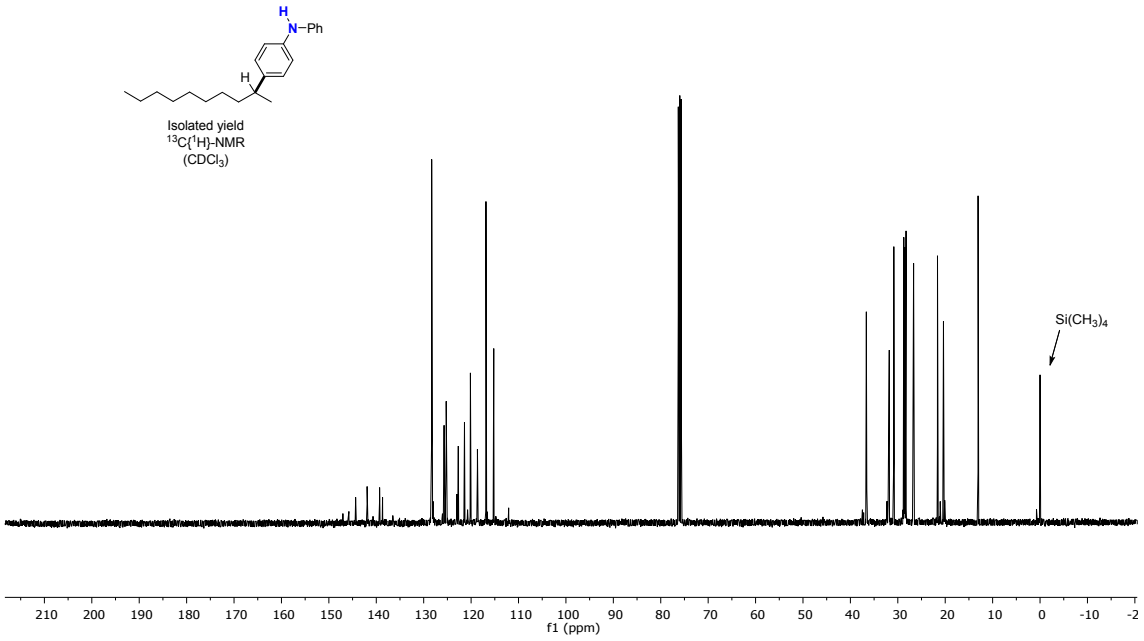
MS (DART Ionization), [*m/z*, (%)]: 310.2 ([M+H]$^+$, 100).

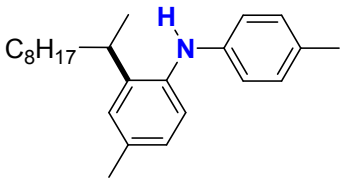
HRMS (DART Ionization, *m/z*): calcd. for $C_{22}H_{32}N$, [M+H]$^+$: 310.25347; found: 310.25261.

Reaction mixture after 16h at 100ºC (^{1}H-NMR in C_6D_5Br)









2-(Decan-2-yl)-4-methyl-N-*p*-tolylaniline (8). To a solution of the catalyst **1a** (6 mg, 5.5 mol%) in C_6D_5Br (1.0 mL) were added *p*-Tol_2NH (33 mg, 0.17 mmol) and then 1-decene (12 mg, 0.085 mmol) at r.t. After 12 days at 100ºC the reaction was complete. This was followed by saturated $NaHCO_3$ (5 mL) extraction with dichloromethane (3 × 5 mL). The organic phase was dried over magnesium sulfate, filtered over silica-gel and the solvent was removed (24 mg, 85% yield).

Isomers of the product were observed, all peaks in the NMR have been reported.

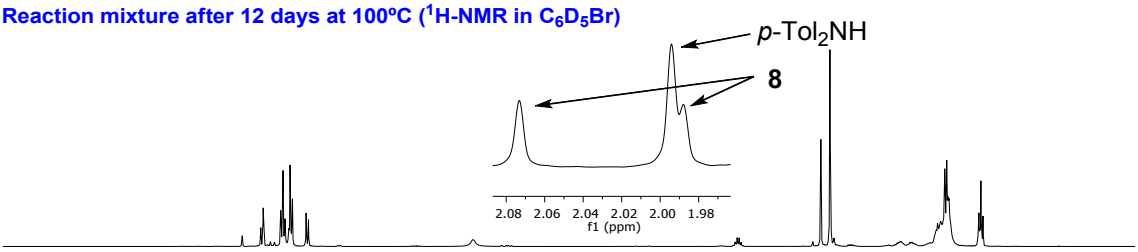
^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.1-6.9 (m, 6H), 6.75 (m, 1H), 5.15 (bs, 1H), 2.98 (m, 1H), 2.33 (m, 6H), 1.58 (m, 2H), 1.32-1.20 (m, 15H), 0.90 (t, *J*= 7.0 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$), δ: 143.6, 141.1, 140.6, 137.6, 133.1, 130.3, 128.6, 129.95, 129.8, 127.41, 127.1, 123.0, 118.1, 116.3, 37.9, 32.9, 32.0, 29.3, 29.7, 29.5, 22.9, 22.8, 21.6, 21.1, 20.8, 20.6, 14.2.

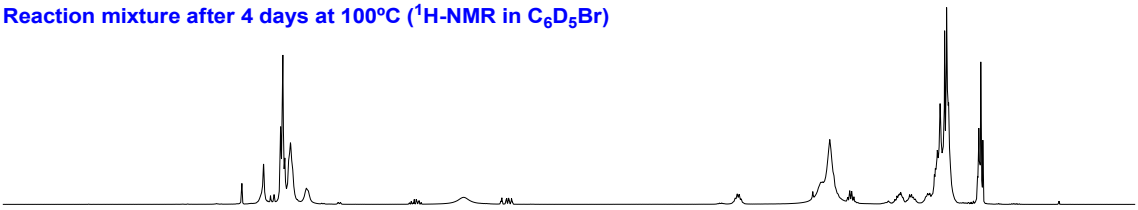
MS (DART Ionization), [*m/z*, (%)]: 338.3 ([M+H]$^+$, 100), 198.1 (50).

HRMS (DART Ionization, *m/z*): calcd. for $C_{22}H_{36}N$, $[M+H]^+$: 338.28477; found: 338.28415.

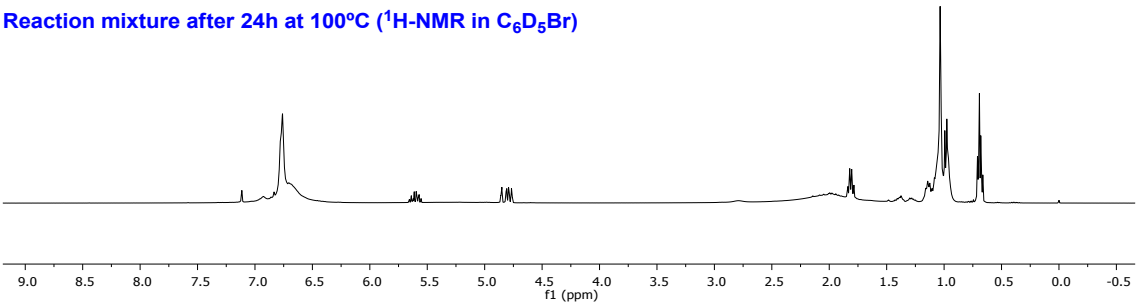
Reaction mixture after 12 days at 100ºC (^{1}H-NMR in C_6D_5Br)

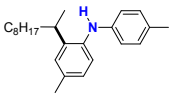


Reaction mixture after 4 days at 100ºC (^{1}H-NMR in C_6D_5Br)

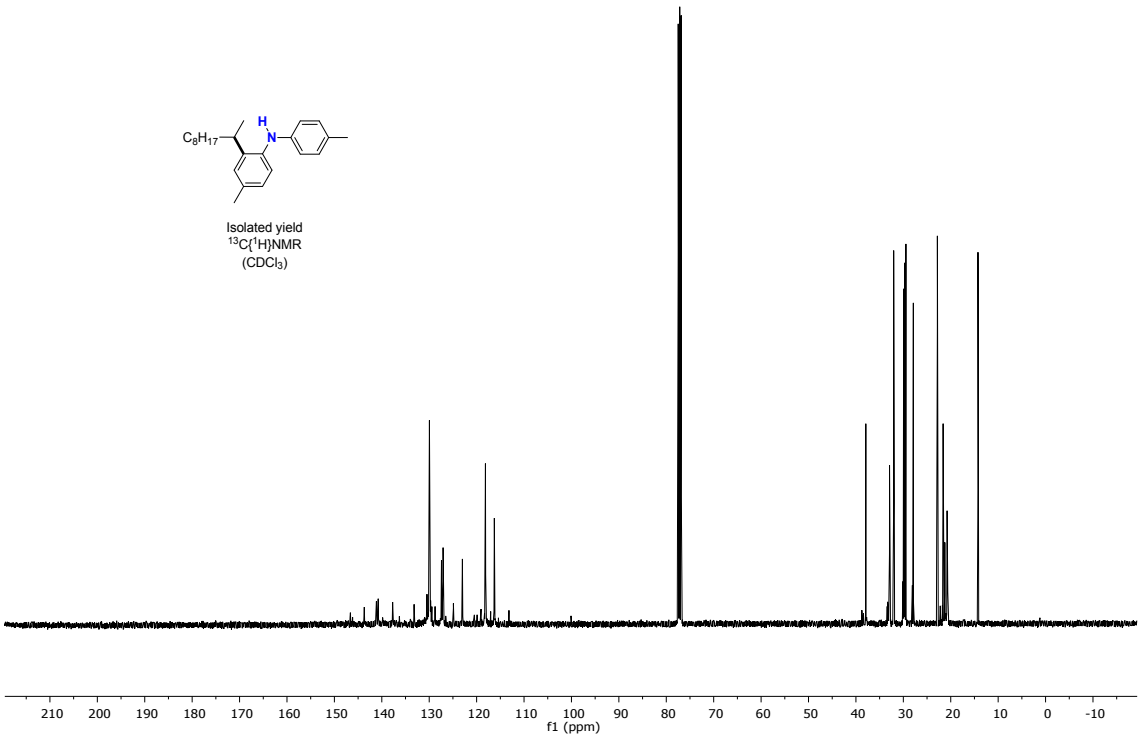


Reaction mixture after 24h at 100ºC (^{1}H-NMR in C_6D_5Br)

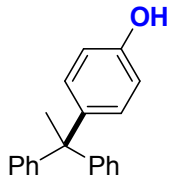




Isolated yield
^{1}H-NMR
($CDCl_3$)



Friedel-Crafts reaction with Phenols.



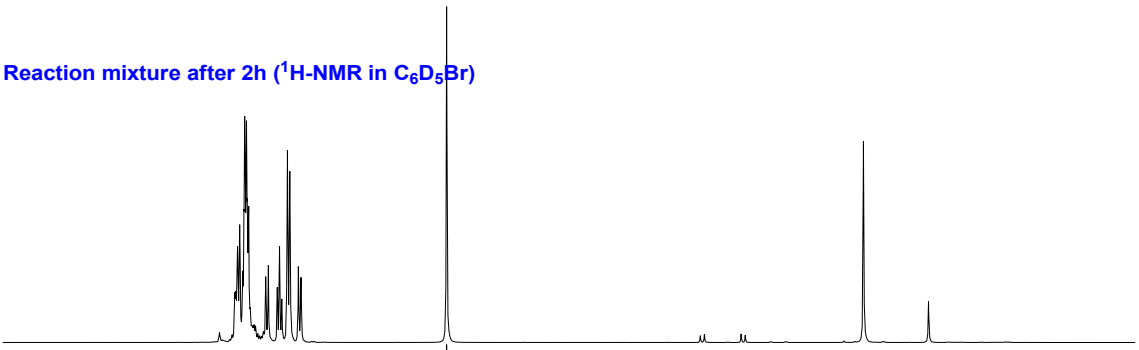
4-(1,1-Diphenylethyl)phenol (9). To a solution of the catalyst **1a** (3 mg, 1.5 mol%) in C_6D_5Br (1.0 mL) were added phenol (80 mg, 0.85 mmol) and then 1,1-diphenylethylene (30 mg, 0.17 mmol) at r.t. After 2 h the reaction was complete (mixture 4-(1,1-diphenylethyl)phenol and 1-methyl-1,3,3-triphenyl-2,3-dihydro-1H-indene 85:15). This was followed by saturated $NaHCO_3$ (5 mL) extraction with dichloromethane (3 × 5 mL). The organic phase was dried over magnesium sulfate, filtered and the solvent was removed. The crude was purified by silica-gel chromatography (5% AcOEt/Hexanes) (35 mg, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.20 (t, $^3J_{HH}$ = 7.2 Hz, 4H), 7.18 (t, $^3J_{HH}$ = 7.2 Hz, 2H), 7.05 (d, $^3J_{HH}$ = 7.2 Hz, 4H), 6.82 (d, $^3J_{HH}$ = 6.8 Hz, 2H), 6.62 (d, $^3J_{HH}$ = 6.8 Hz, 2H), 4.60 (br s, 1H), 2.09 (s, 3H).

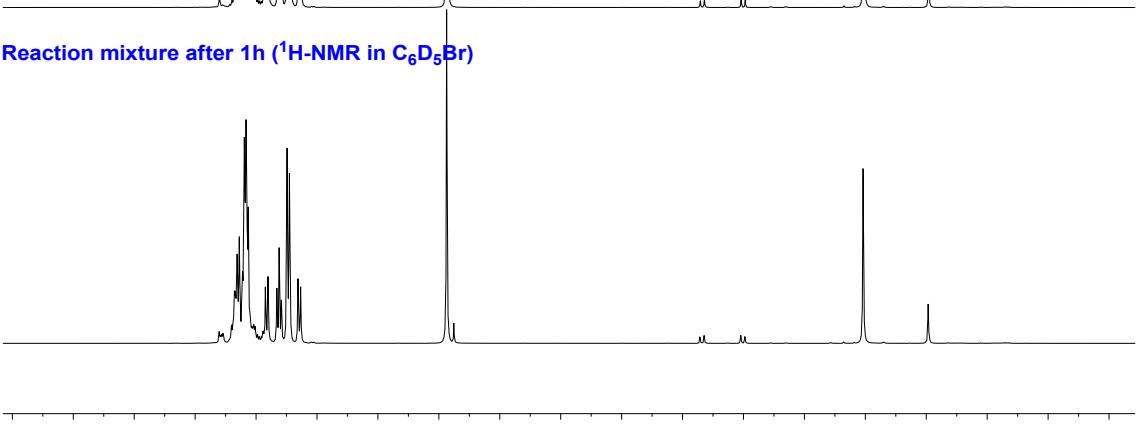
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$), δ: 154.3 (1C), 149.8 (2C), 141.2 (1C), 130.0 (2C), 129.5 (4C), 128.7 (4C), 125.6 (2C), 114.2 (2C), 51.7 (1C), 30.3 (1C).

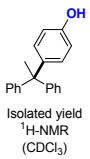
MS (DART Ionization), [*m/z*, (%)]: 283.1 ([M+NH_4]$^+$, 20), 181.1 (100).

Reaction mixture after 2h (^{1}H-NMR in C_6D_5Br)

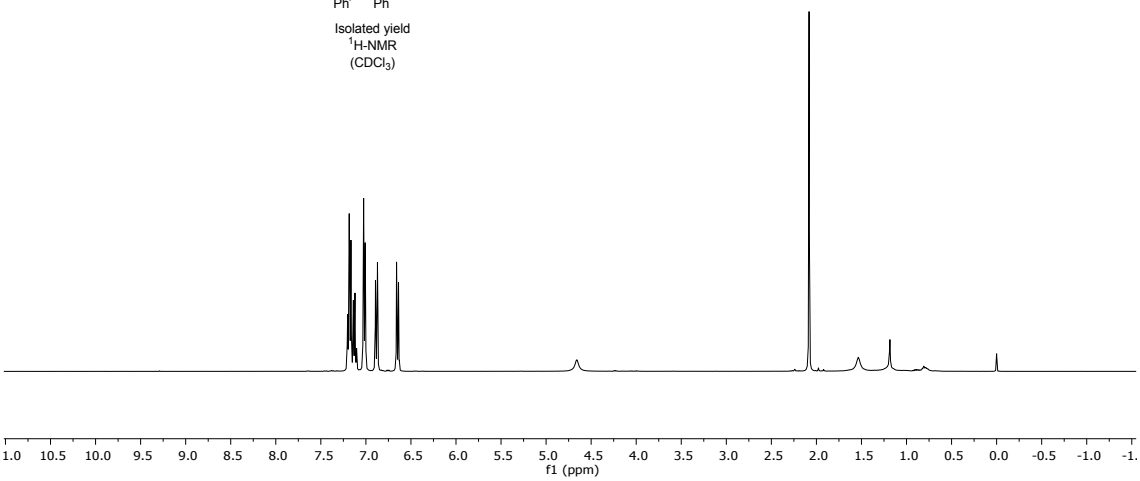


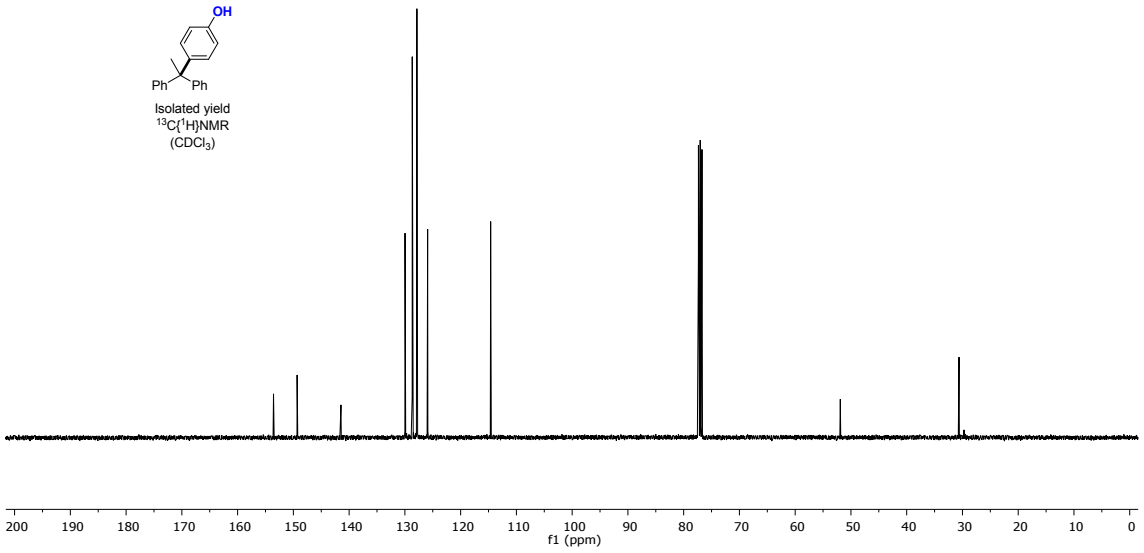
Reaction mixture after 1h (^{1}H-NMR in C_6D_5Br)

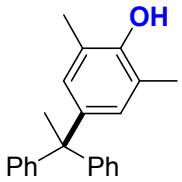




Isolated yield
^{1}H-NMR
($CDCl_3$)







4-(1,1-Diphenylethyl)-2,6-dimethylphenol (10). To a solution of the catalyst **1a** (3 mg, 1.5 mol%) in C_6D_5Br (1.0 mL) were added 2,6-dimethylphenol (42 mg, 0.34 mmol) and then 1,1-diphenylethylene (30 mg, 0.17 mmol) at r.t. After 1 h the reaction was complete (mixture 4-(1,1-diphenylethyl)-2,6-dimethylphenol and 1-methyl-1,3,3-triphenyl-2,3-dihydro-1H-indene 90:10). This was followed by saturated $NaHCO_3$ (5 mL) extraction with dichloromethane (3 × 5 mL). The organic phase was dried over magnesium sulfate, filtered and the solvent was removed. The crude was purified by silica-gel chromatography (5% AcOEt/Hexanes) (65 mg of a mixture of 4-(1,1-diphenylethyl)-2,6-dimethylphenol and 2,6-dimethylphenol 60:40).

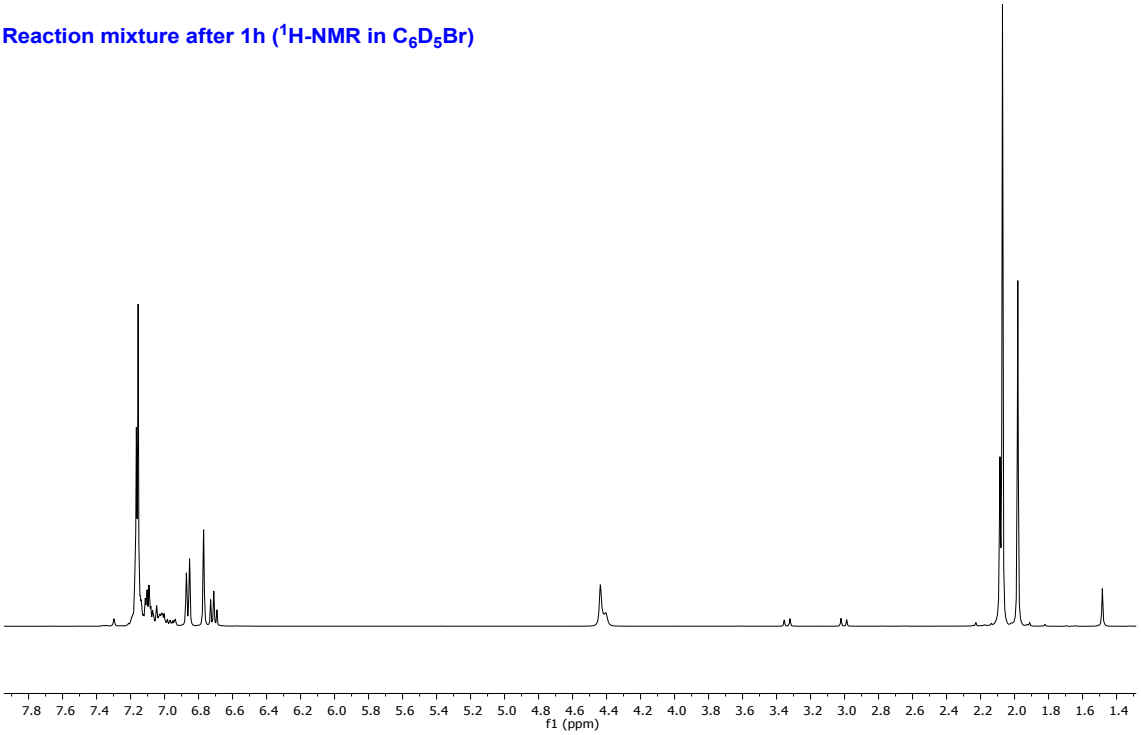
^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.30 (t, $^3J_{HH}$ = 7.0 Hz, 4H), 7.28 (t, $^3J_{HH}$ = 7.0 Hz, 2H), 7.14 (d, $^3J_{HH}$ = 7.0 Hz, 4H), 6.64 (s, 2H), 4.48 (br s, 1H), 2.21 (s, 3H), 2.14 (s, 6H).

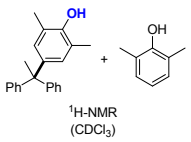
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$), δ: 149.9 (1C), 148.6 (2C), 142.0 (1C), 129.7 (2C), 129.6 (4C), 127.3 (4C), 126.2 (2C), 123.3 (2C), 51.5 (1C), 30.8 (1C), 15.7 (2C).

MS (DART Ionization), [*m/z*, (%)]: 320.1 ([M+NH_4]$^+$, 60), 181.1 (100), 122.1 (50).

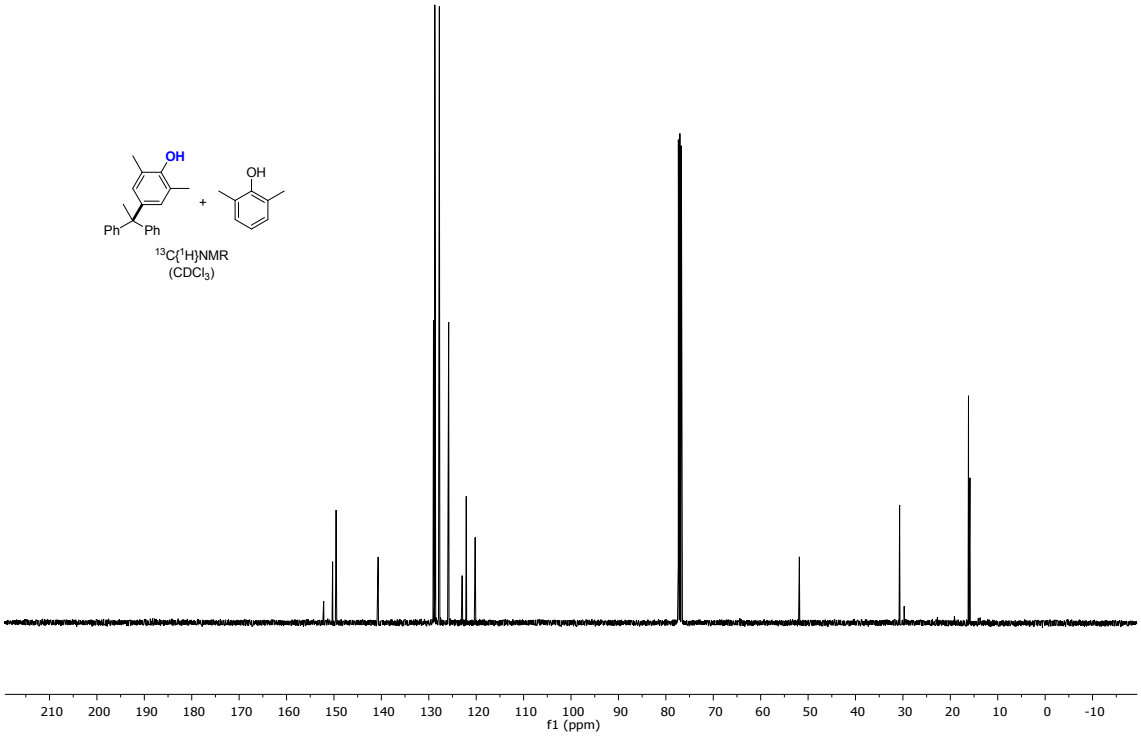
HRMS (DART Ionization, *m/z*): calcd. for $C_{22}H_{26}NO$, $[M+NH_4]^+$: 320.20144; found: 320.20208.

Reaction mixture after 1h (^{1}H-NMR in C_6D_5Br)

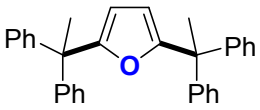




^{1}H-NMR
($CDCl_3$)



Friedel-Crafts reaction with Furan.



2,5-Bis(1,1-diphenylethyl)furan (11). To a solution of the catalyst **1a** (3 mg, 1.5 mol%) in C_6D_5Br (1.0 mL) were added furan (12 mg, 0.17 mmol) and then 1,1-diphenylethylene (60 mg, 0.34 mmol) at r.t. After 1 day at 60ºC the reaction was complete. This was followed by saturated $NaHCO_3$ (5 mL) extraction with dichloromethane (3 × 5 mL). The organic phase was dried over magnesium sulfate, filtered over silica-gel and the solvent was removed (57 mg, 80% yield).

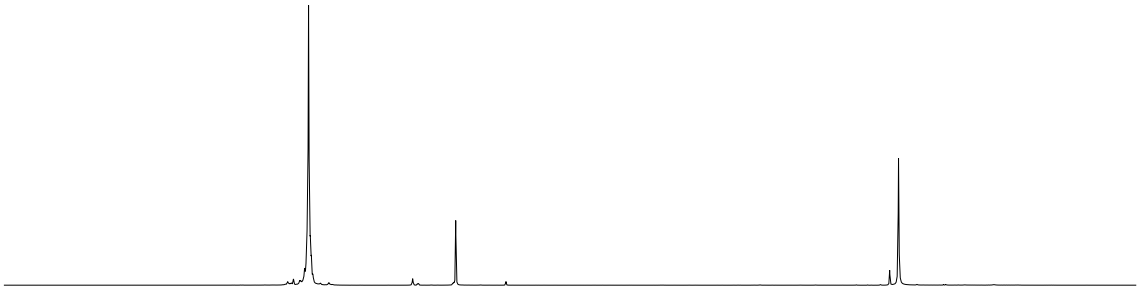
^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.22 – 7.18 (m, 6H), 7.10 (d, $^{3}J_{HH}$ = 7.4 Hz, 4H), 5.71 (s, 1H), 1.78 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$), δ: 160.0 (1C), 148.2 (2C), 128.7 (8C), 127.1 (2C), 108.4 (1C), 50.1 (1C), 26.5 (1C).

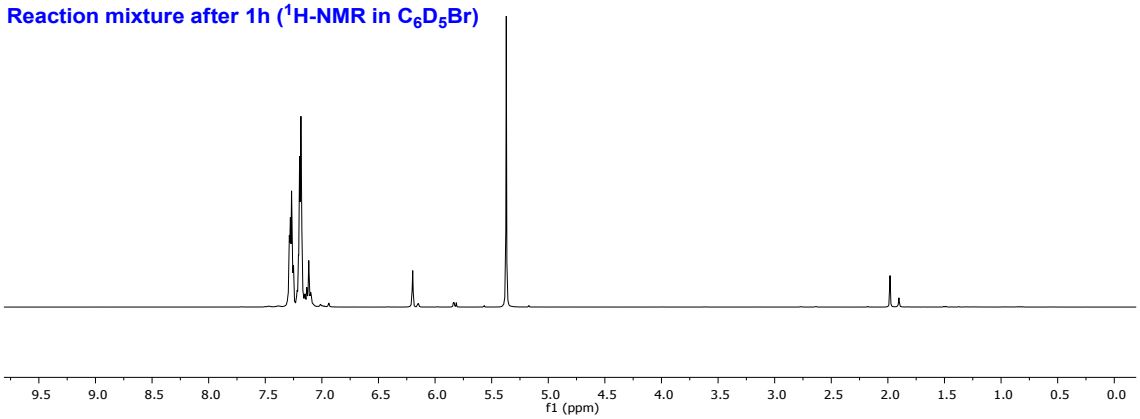
MS (DART Ionization), [*m/z*, (%)]: 446.2 ($[M+NH_4]^+$, 20), 181.1 (100).

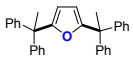
HRMS (DART Ionization, *m/z*): calcd. for $C_{32}H_{32}NO$, $[M+H]^+$: 446.24839; found: 446.24866.

Reaction mixture after 1 day at 60ºC (^{1}H-NMR in C_6D_5Br)

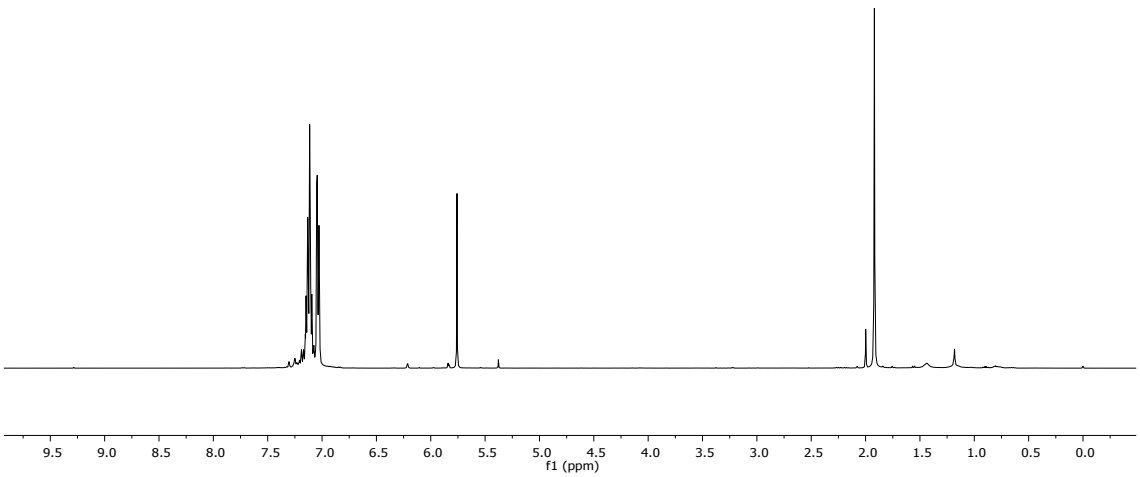


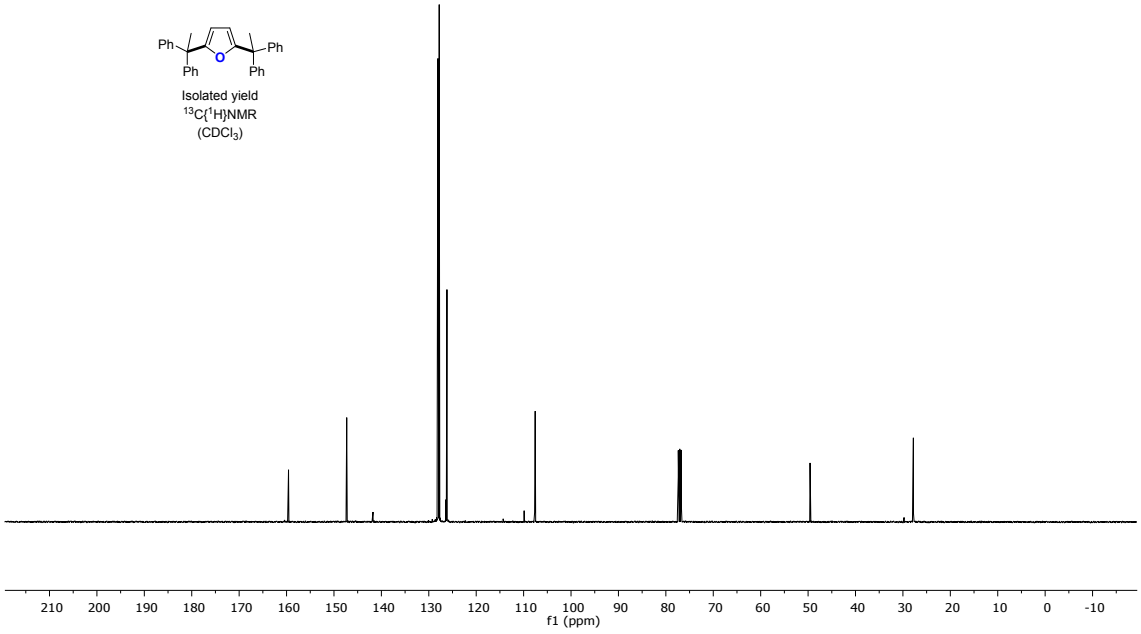
Reaction mixture after 1h (^{1}H-NMR in C_6D_5Br)



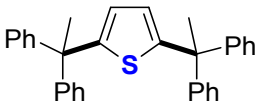


Isolated yield
^{1}H-NMR
($CDCl_3$)





Friedel-Crafts reaction with Thiophene.



2,5-Bis(1,1-diphenylethyl)thiophene (12). In the glovebox, a 4 dram vial equipped with a stirbar was charged with the substrate (1.18 mmol) and the catalyst **1a** (29.2 mg, 0.023 mmol) in bromobenzene (1 mL). To the vial, the olefin 1,1-diphenylethylene (425.4 mg, 2.36 mmol) was added dropwise. The reaction was allowed to stir overnight at 60 ºC outside of the glovebox. This was followed by saturated $NaHCO_3$ (20 mL) extraction with dichloromethane (3 × 10 mL). The organic phase was dried over magnesium sulfate and the solvent was removed to yield the product.

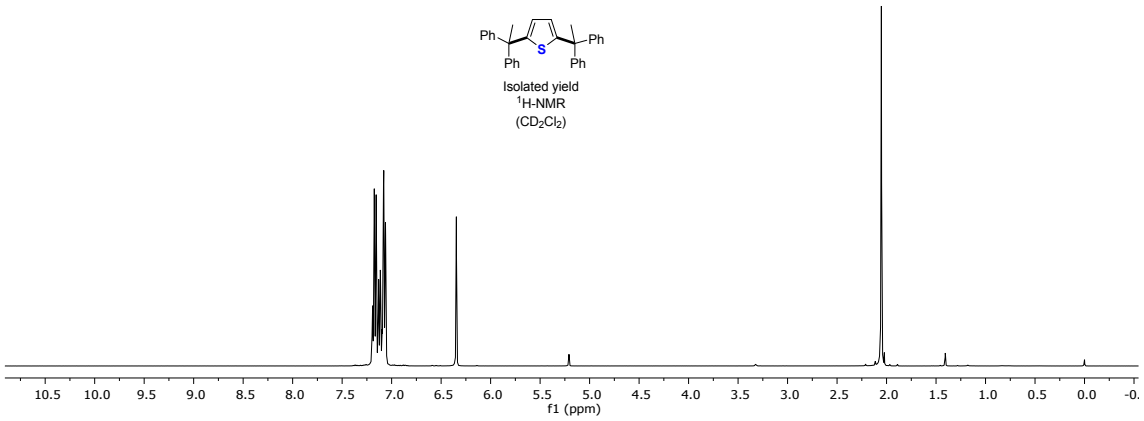
Substrate - Thiophene (100 mg); pale-yellow solid isolated in 91 % yield.

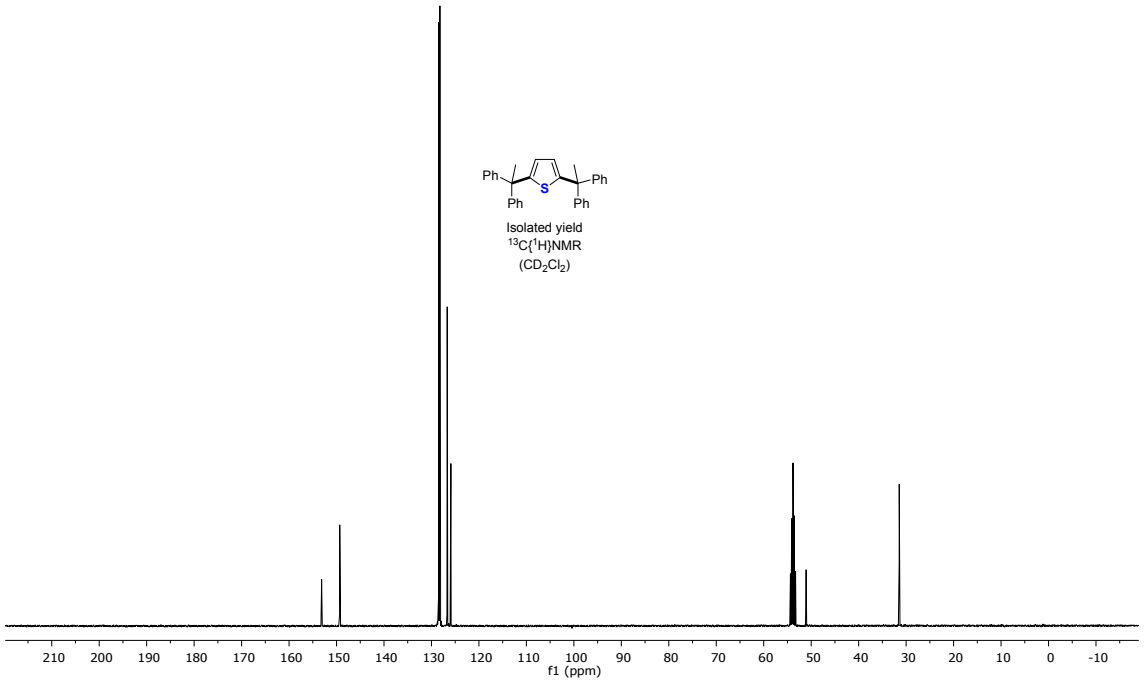
^{1}H NMR (400 MHz, CD_2Cl_2), δ 7.18 (m, 4H), 7.11 (m, 2H), 7.06 (m, 4H), 6.35 (s, 1H), 2.06 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2), δ 153.1 (1C), 149.3 (2C), 128.3 (8C), 126.7 (2C), 125.9 (1C), 51.1 (1C), 31.5 (1C).

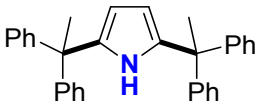
MS (DART Ionization), [*m/z*, (%)]: 462.2 ([M+NH_4]$^+$, 15), 181.1 (100).

HRMS (DART Ionization, *m/z*): calcd. for $C_{32}H_{32}NS$, $[M++NH_4]^+$: 462.22554; found: 462.22683.





Friedel-Crafts reaction with 1*H*-Pyrrole.



2,5-Bis(1,1-diphenylethyl)-1H-pyrrole (13). In the glovebox, a 4 dram vial equipped with a stirbar was charged with the substrate (1.18 mmol) and the catalyst **1a** (29.2 mg, 0.023 mmol) in bromobenzene (1 mL). To the vial, the olefin 1,1-diphenylethylene (425.4 mg, 2.36 mmol) was added dropwise. The reaction was allowed to stir overnight 16 h at 60 ºC outside of the glovebox. This was followed by saturated $NaHCO_3$ (20 mL) extraction with dichloromethane (3 × 10 mL). The organic phase was dried over magnesium sulfate and the solvent was removed to yield the product.

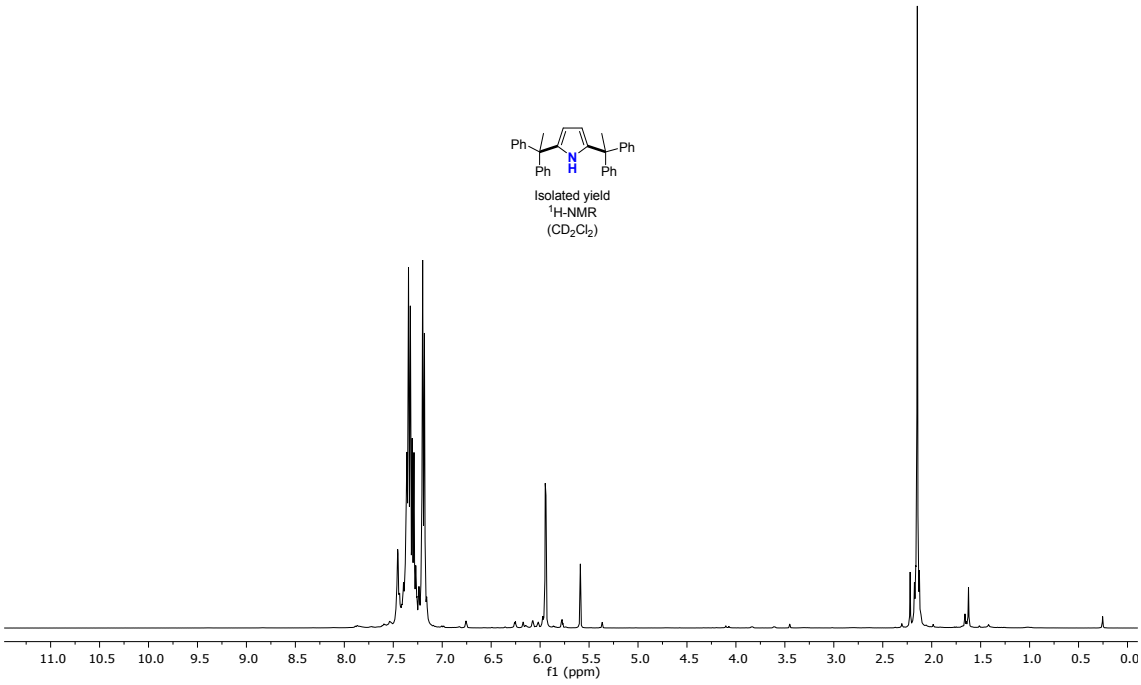
Substrate - 1*H*-pyrrole (79.2 mg); brown oil isolated in 89 % yield.

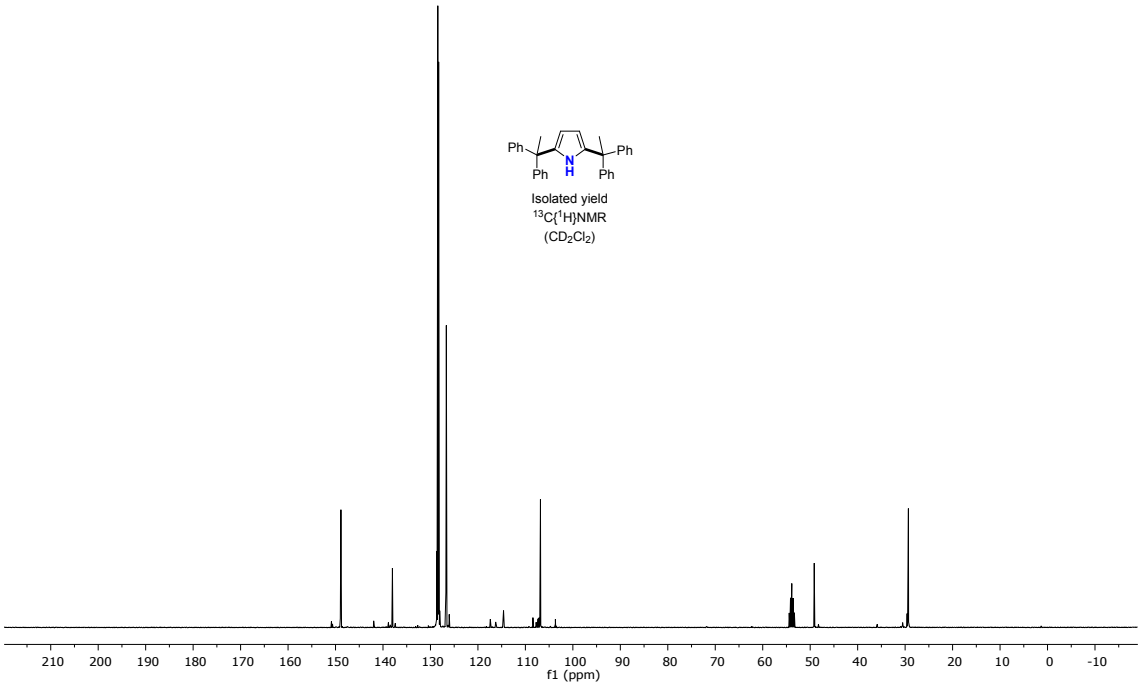
^{1}H NMR (400 MHz, CD_2Cl_2), δ 7.45 (s, 1H), 7.35 (m, 4H), 7.31 (m, 2H), 7.21 (m, 4H), 5.95 (d, J_{HH} = 2.66 Hz, 1H), 2.16 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2), δ 148.9 (2C), 138.0 (1C), 128.4 (8C), 126.7 (2C), 106.8 (1C), 49.1 (1C), 29.3 (1C).

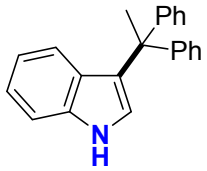
MS (DART Ionization), [*m/z*, (%)]: 428.2 ([M+H]$^+$, 20), 181.1 (100).

HRMS (DART Ionization, *m/z*): calcd. for $C_{32}H_{30}N$, [M+H]$^+$: 428.23782; found: 428.23871.




Ph
Ph
N
H
Ph
Ph
Isolated yield
13C{1H}NMR
(CD2Cl2)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Friedel-Crafts reaction with 1*H*-Indole.



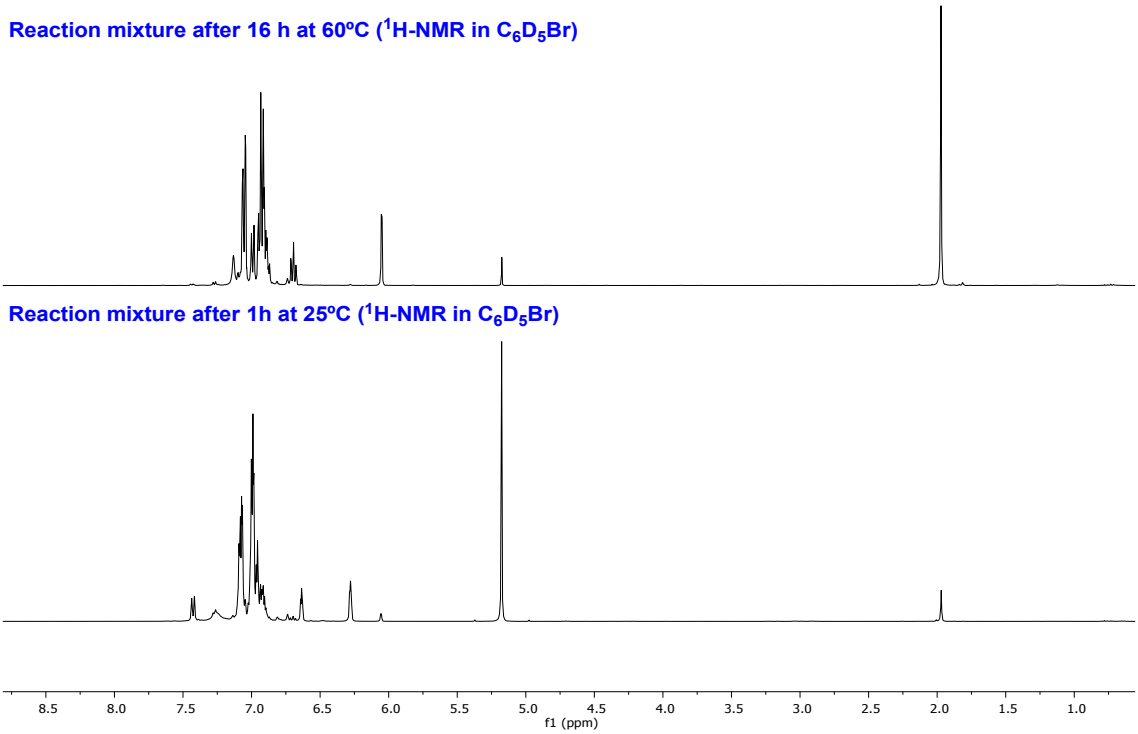
3-(1,1-Diphenylethyl)-1*H*-indole (14). To a solution of the catalyst **1a** (6.0 mg, 3.0 mol%) in C_6D_5Br (1.0 mL) were added 1*H*-indole (20 mg, 0.17 mmol) and then 1,1-diphenylethylene (32 mg, 0.18 mmol) at r.t. After 16 h at 60ºC the reaction was complete. This was followed by saturated $NaHCO_3$ (5 mL) extraction with dichloromethane (3 × 5 mL). The organic phase was dried over magnesium sulfate, filtered over silica-gel and the solvent was removed (50 mg, 98% yield).

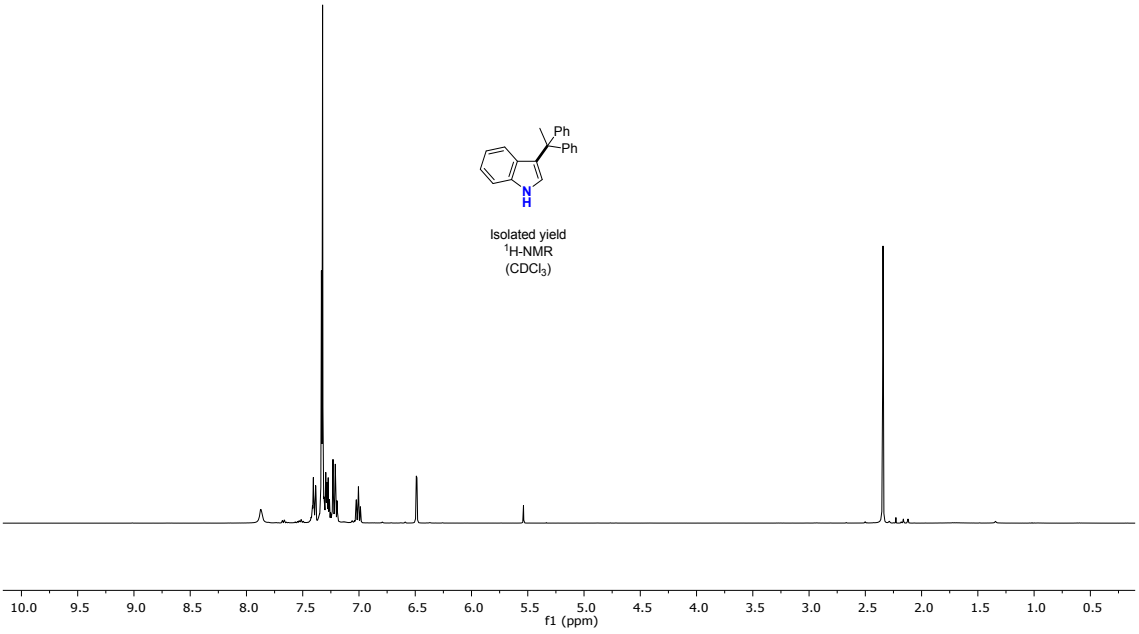
^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.87 (bs, 1H), 7.40 (m, 1H), 7.35-7.25 (m, 10H), 7.21 (m, 2H), 7.01 (t, *J*= 7.5 Hz, 1H), 6.49 (d, *J*= 2.2 Hz, 1H), 2.34 (s, 3H).

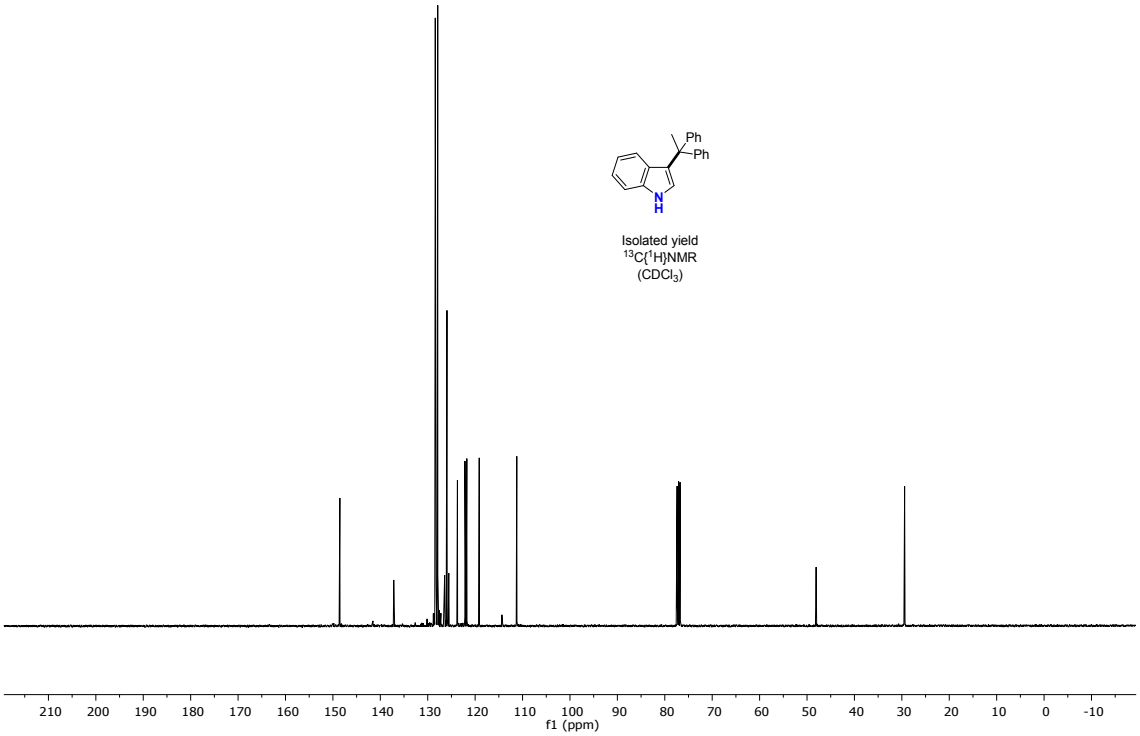
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$), δ: 148.3 (2C), 137.2 (1C), 128.4 (4C), 127.9 (4C), 126.4 (1C), 125.9 (2C), 125.6 (1C), 123.7 (1C), 122.2 (1C), 121.7 (1C), 119.1 (1C), 111.2 (1C), 48.1 (1C), 29.4 (1C).

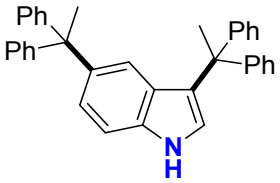
MS (DART Ionization), [*m/z*, (%)]: 298.2 ([M+H]$^+$, 20), 181.1 (100).

HRMS (DART Ionization, *m/z*): calcd. for $C_{22}H_{20}N$, [M+H]$^+$: 298.15957; found: 298.16016.




Ph
Ph
N
H
Isolated yield
1H-NMR
(CDCl3)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


Ph
Ph
N
H
Isolated yield
13C{1H}NMR
(CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3,5-Bis(1,1-diphenylethyl)-1H-indole (15). In the glovebox, a 4 dram vial equipped with a stirbar was charged with the substrate (1.18 mmol) and the catalyst **1a** (29.2 mg, 0.023 mmol) in bromobenzene (1 mL). To the vial, the olefin 1,1-diphenylethylene (425.4 mg, 2.36 mmol) was added dropwise. The reaction was allowed to stir overnight at 60 ºC outside of the glovebox. This was followed by saturated $NaHCO_3$ (20 mL) extraction with dichloromethane (3 × 10 mL). The organic phase was dried over magnesium sulfate and the solvent was removed to yield the product.

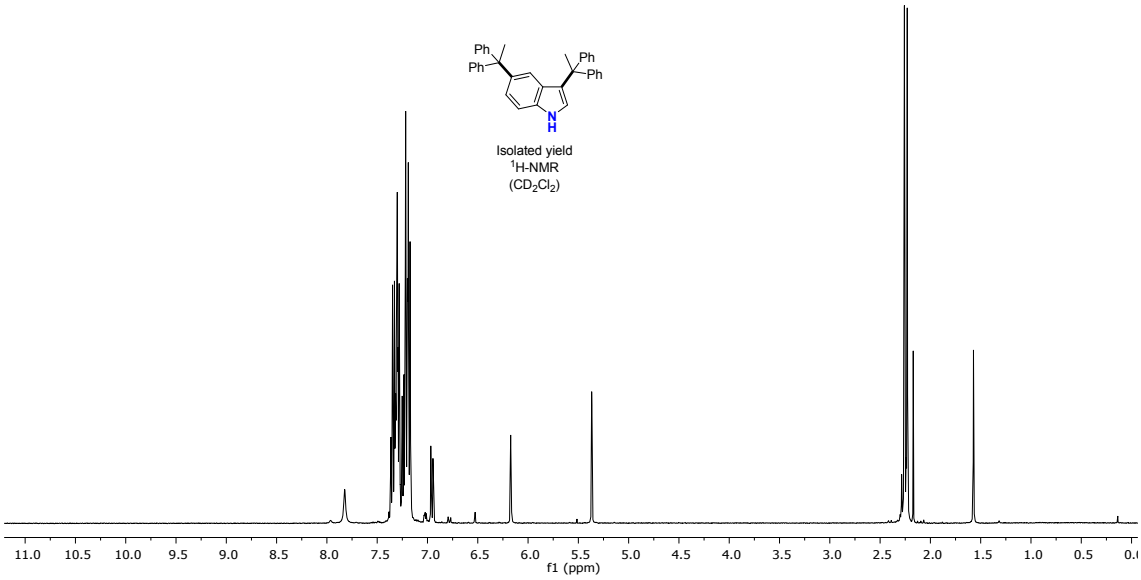
Substrate – 1*H*-Indole (138 mg); white solid isolated in 78 % yield.

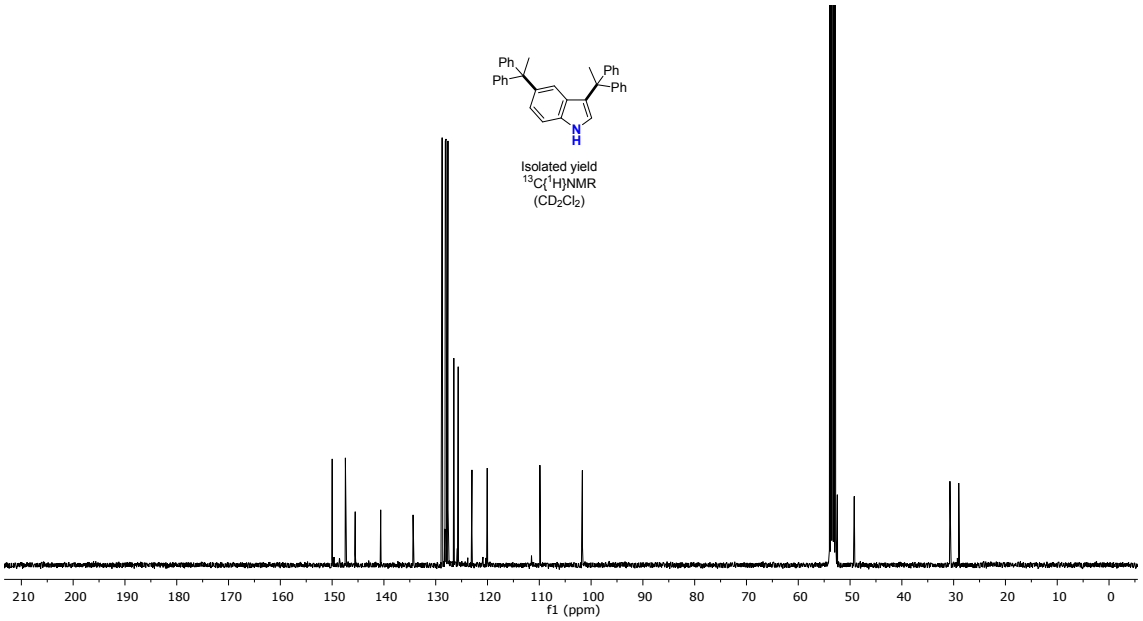
^{1}H NMR (400 MHz, CD_2Cl_2), δ 7.82 (s, 1H), 7.36 – 7.27 (m, 10H), 7.23 – 7.18 (m, 12H), 6.96 (dd, J_{HH} = 8.7 Hz, 2.08 Hz, 1H), 6.14 (dd, J_{HH} = 2.20 Hz, 0.79 Hz, 1H), 2.26 (s, 3H), 2.23 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2), δ 150.0 (2C), 147.4 (2C), 145.5 (1C), 140.6 (1C), 134.4 (1C), 128.8 (4C), 128.2 (4C), 128.0 (4C), 127.6 (5C), 126.5 (2C), 125.7 (2C), 123.0 (1C), 120.1 (1C), 109.9 (1C), 101.7 (1C), 52.6 (1C), 49.2 (1C), 30.7 (1C), 29.0 (1C).

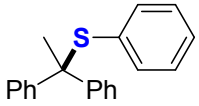
MS (DART Ionization), [*m/z*, (%)]: 478.3 ([M+H]$^{+}$, 100), 181.1 (40).

HRMS (DART Ionization, *m/z*): calcd. for $C_{36}H_{32}N$, [M+H]$^{+}$: 478.25347; found: 478.25355.




Ph
Ph
Ph
Ph
N
H
Isolated yield
13C{1H}NMR
(CD2Cl2)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Hydrosulfuration of Olefins with Thiophenols.

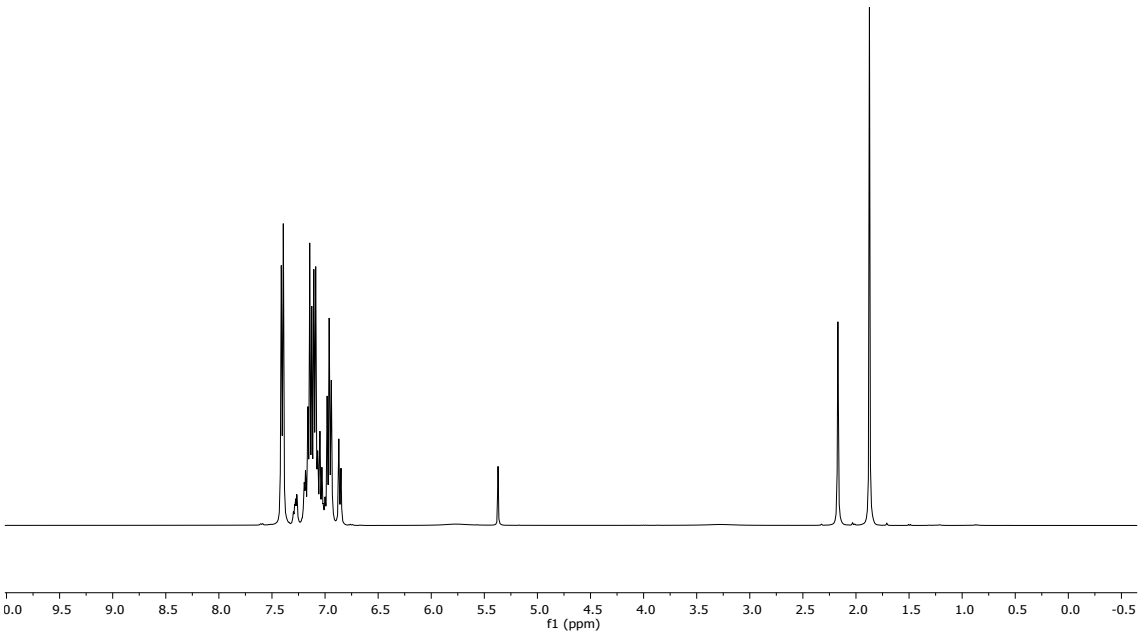


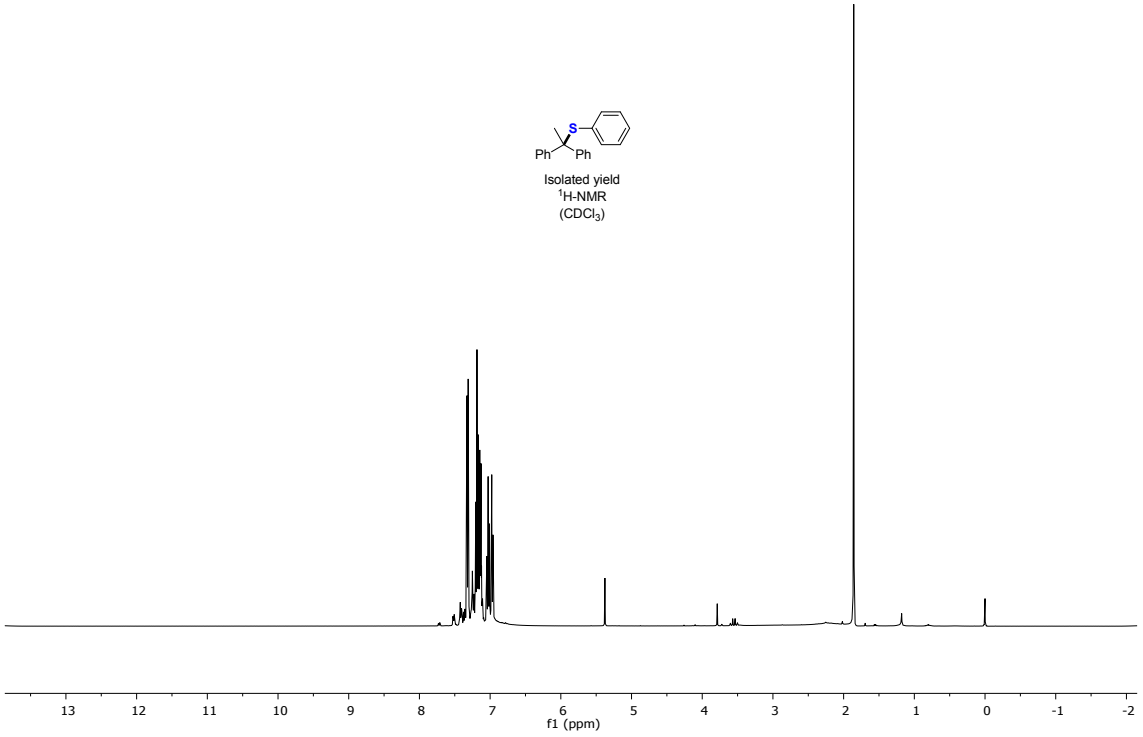
(1,1-Diphenylethyl)(phenyl)sulfane (16). To a solution of the catalyst **1a** (3 mg, 1.5 mol%) in C_6D_5Br (1.0 mL) were added benzenethiol (19 mg, 0.17 mmol), di*p*-tolylamine (5 mg, 0.025 mmol) and then 1,1-diphenylethylene (30 mg, 0.17 mmol) at r.t. After 1 h the reaction was complete. This was followed by saturated $NaHCO_3$ (5 mL) extraction with dichloromethane (3 × 5 mL). The organic phase was dried over magnesium sulfate, filtered over silica-gel and the solvent was removed (40 mg, 83 % yield).

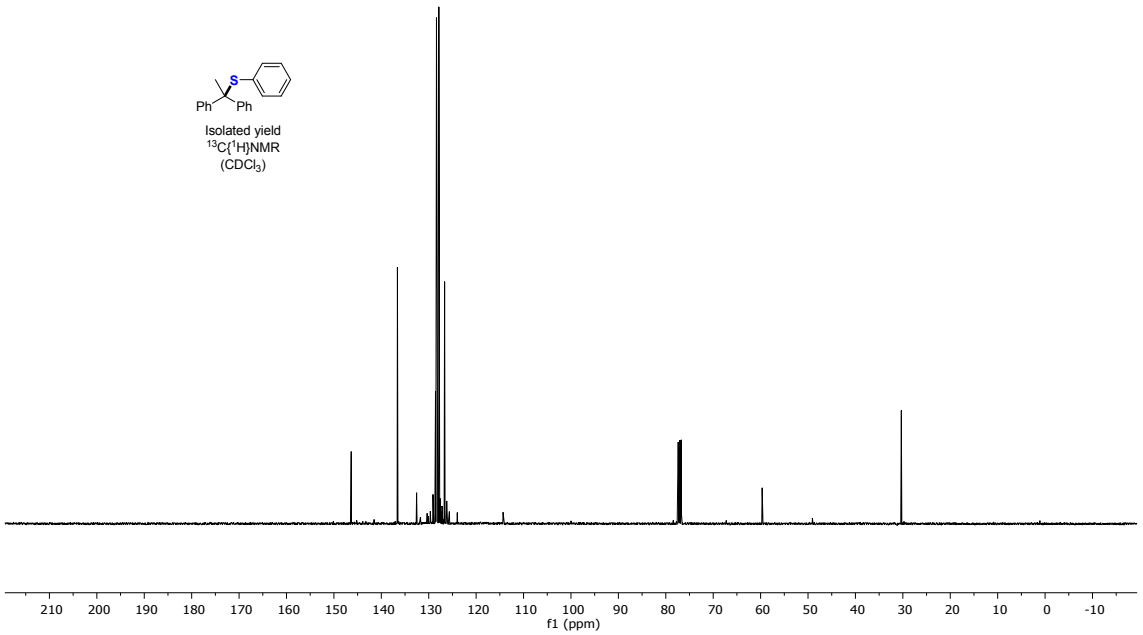
^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.32 (d, $^3J_{HH}$ = 6.8 Hz, 4H), 7.22 (t, $^3J_{HH}$ = 6.8 Hz, 4H), 7.14 (m, 3H), 7.03 (m, 2H), 6.97 (d, $^3J_{HH}$ = 7.2 Hz, 2H), 1.98 (s, 3H).

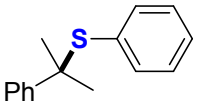
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$), δ: 146.6 (2C), 136.6 (2C), 132.3 (1C), 128.6 (1C), 128.3 (4C), 128.2 (2C), 127.8 (4C), 126.6 (2C), 60.0 (1C), 30.0 (1C).

Reaction mixture after 1h (^{1}H-NMR in C_6D_5Br)




Ph
S
Ph
Isolated yield
1H-NMR
(CDCl3)
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)


Ph
S
Ph
Isolated yield
13C{1H}NMR
(CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

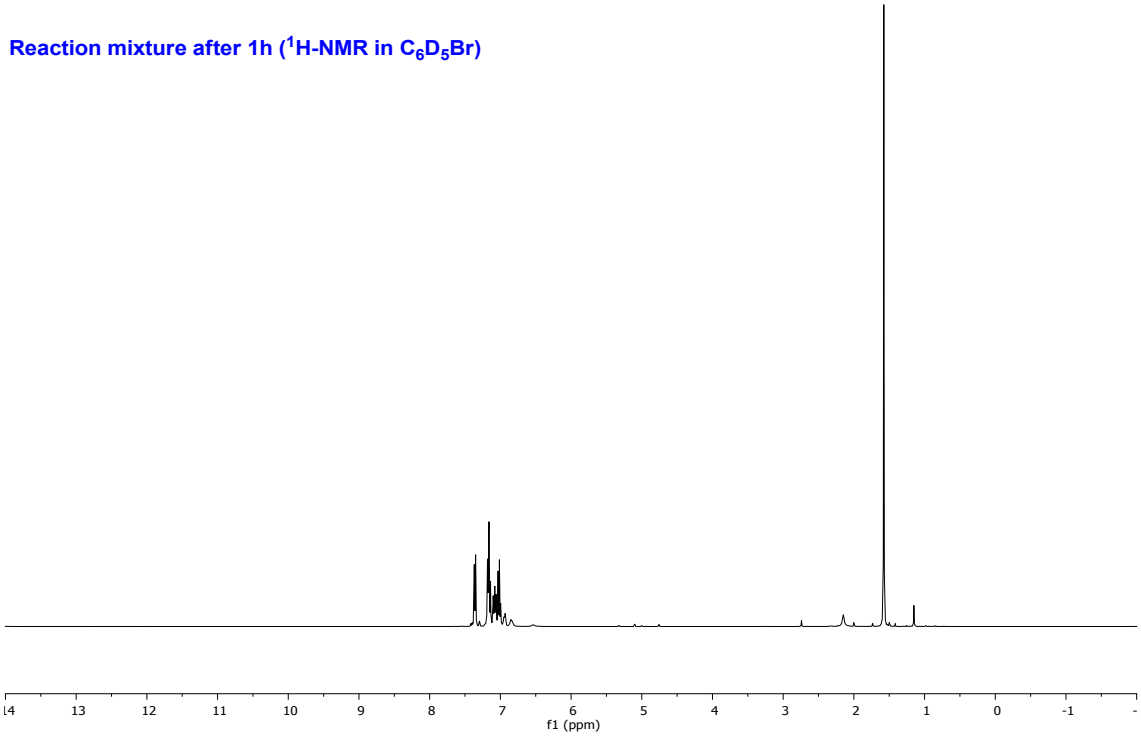


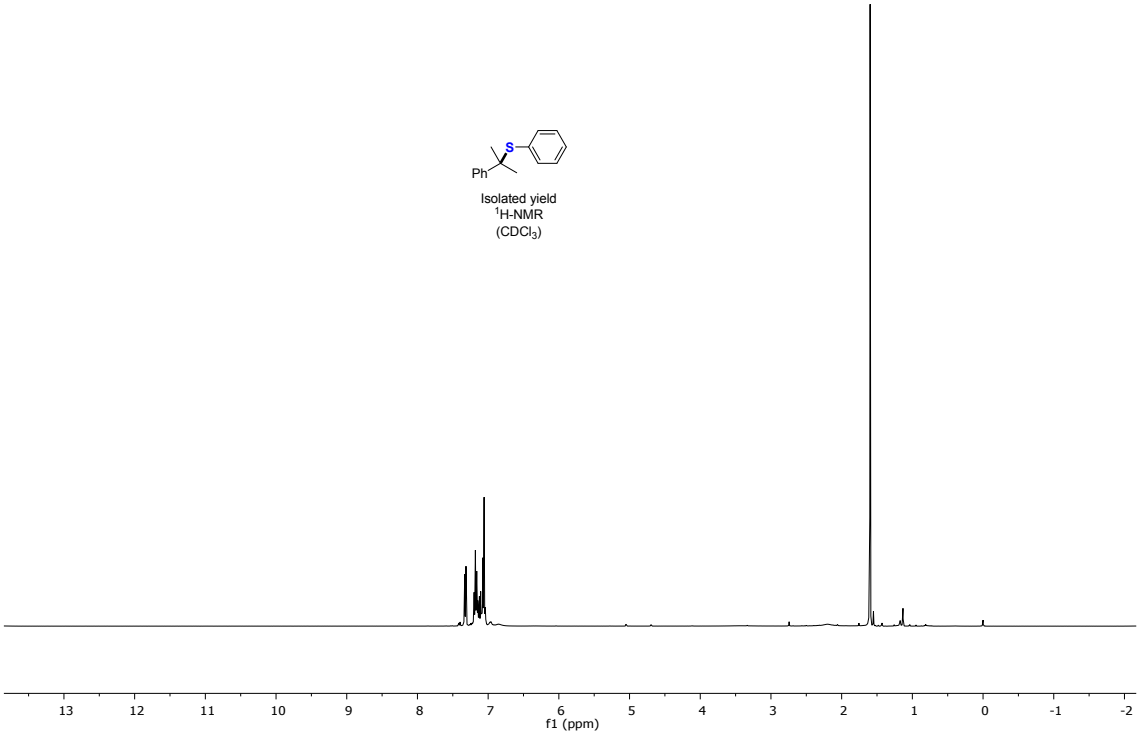
Phenyl(2-phenylpropan-2-yl)sulfane (17). To a solution of the catalyst **1a** (3 mg, 1.5 mol%) in C_6D_5Br (1.0 mL) were added benzenethiol (19 mg, 0.17 mmol), di*p*-tolylamine (5 mg, 0.025 mmol) and then prop-1-en-2-ylbenzene (22 mg, 0.19 mmol) at r.t. After 1 h the reaction was complete. This was followed by saturated $NaHCO_3$ (5 mL) extraction with dichloromethane (3 × 5 mL). The organic phase was dried over magnesium sulfate, filtered over silica-gel and the solvent was removed (34 mg, 92 % yield).

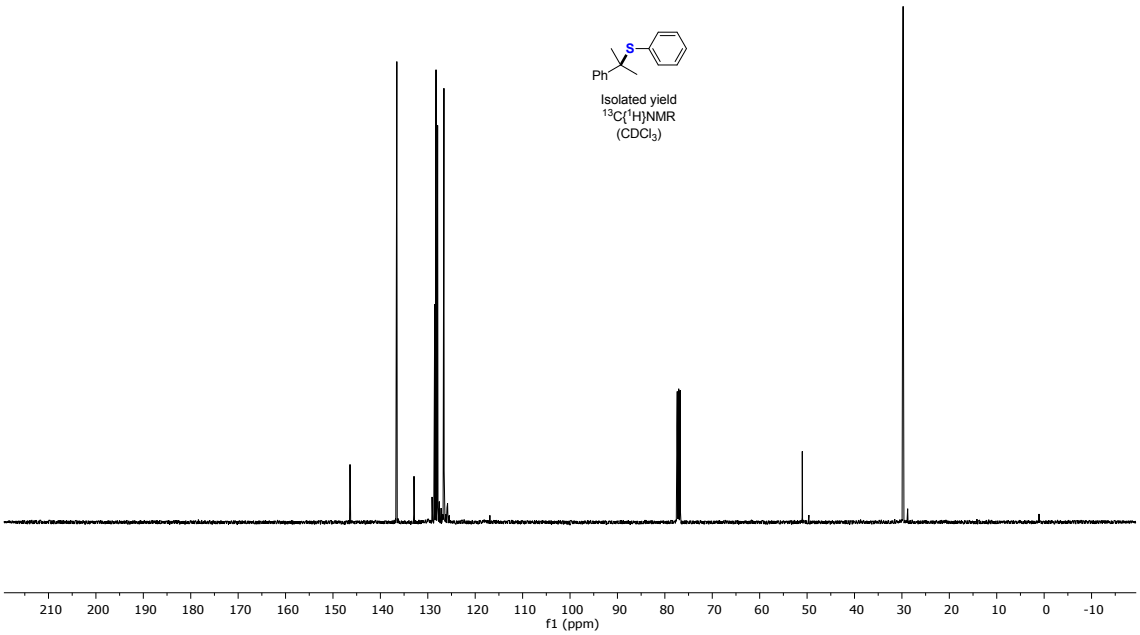
^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.33 (d, $^3J_{HH}$ = 7.3 Hz, 2H), 7.18 (m, 3H), 7.12 – 7.03 (m, 5H), 1.60 (s, 6H).

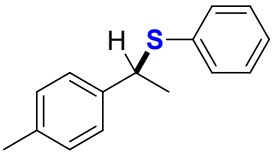
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$), δ: 146.5 (1C), 136.5 (2C), 132.9 (1C), 128.5 (1C), 128.3 (2C), 127.9 (2C), 126.6 (2C), 126.5 (1C), 51.0 (1C), 29.8 (2C).

Reaction mixture after 1h (^{1}H-NMR in C_6D_5Br)




Ph
S
Isolated yield
1H-NMR
(CDCl3)
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)


Ph
S
Isolated yield
13C{1H}NMR
(CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

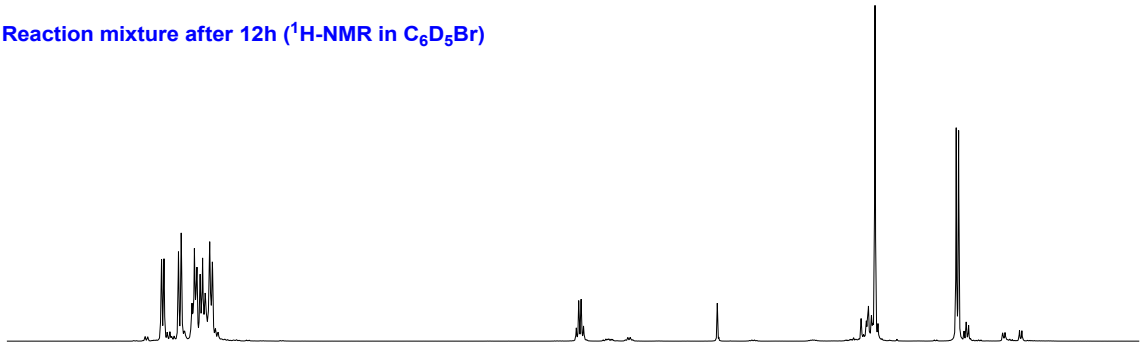


Phenyl(1-p-tolylethyl)sulfane (18). To a solution of the catalyst **1a** (3 mg, 1.5 mol%) in C_6D_5Br (1.0 mL) were added benzenethiol (21 mg, 0.19 mmol), and then *p,α*-dimethylstyrene (20 mg, 0.17 mmol) at r.t. After 3 h the reaction was complete. Attempts to try to purify the compound afford the reversible starting materials.

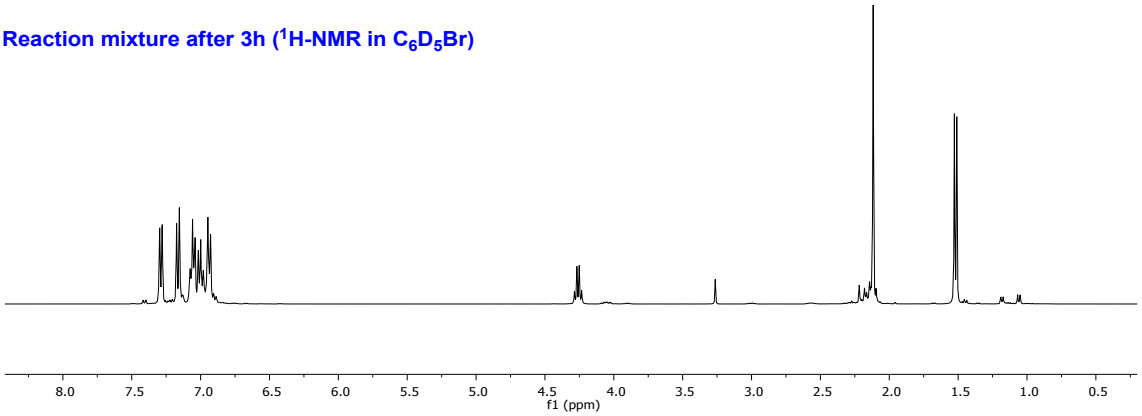
^{1}H NMR (400 MHz, C_6D_5Br), δ: 7.29 (d, $^3J_{HH}$ = 6.1 Hz, 2H), 7.16 (d, $^3J_{HH}$ = 7.7 Hz, 2H), 7.06 (t, $^3J_{HH}$ = 6.1 Hz, 2H), 7.00 (t, $^3J_{HH}$ = 6.1 Hz, 1H), 6.94 (d, $^3J_{HH}$ = 7.7 Hz, 2H), 4.26 (q, $^3J_{HH}$ = 7.4 Hz, 1H), 2.12 (s, 3H), 1.52 (d, $^3J_{HH}$ = 7.4 Hz, 3H).

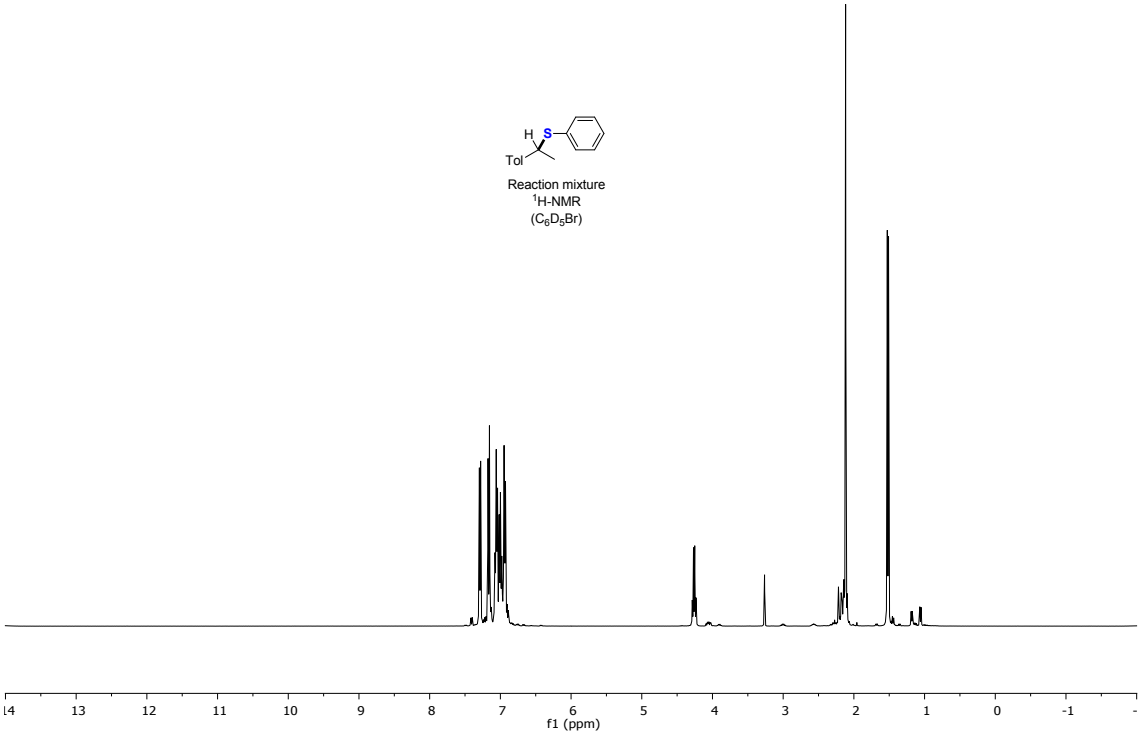
^{13}C{^{1}H} NMR (101 MHz, C_6D_5Br), δ: 140.2 (1C), 136.4 (1C), 132.0 (1C), 129.2 (2C), 128.7 (2C), 127.2 (2C), 126.8 (1C), 122.4 (2C), 47.5 (1C), 22.7 (1C), 21.2 (1C).

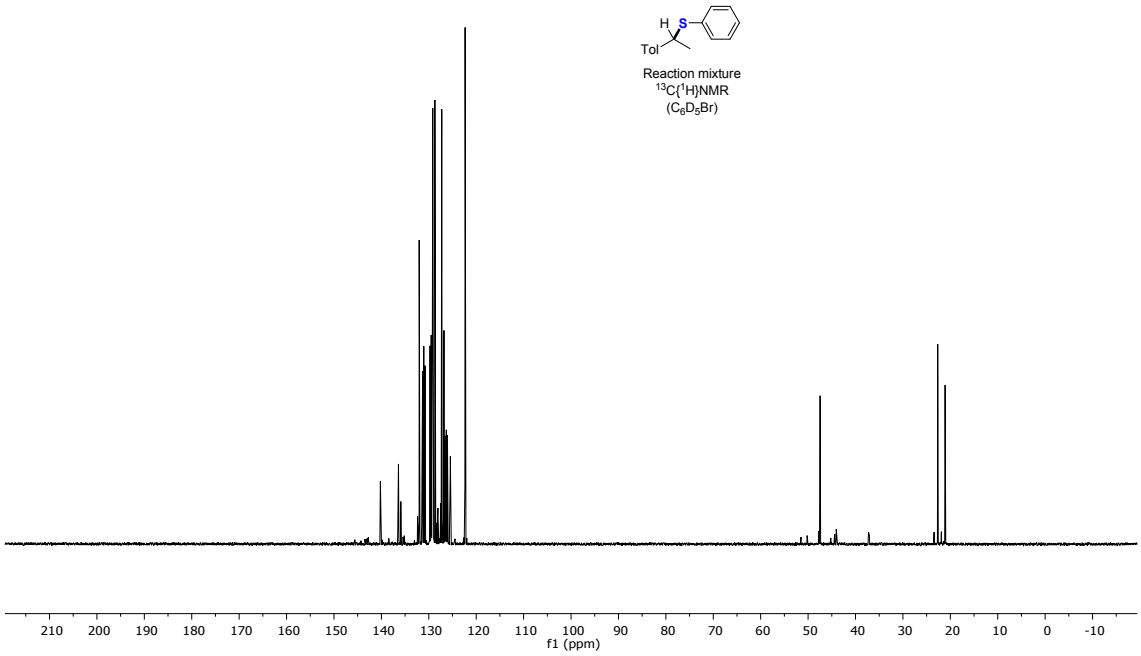
Reaction mixture after 12h (^{1}H-NMR in C_6D_5Br)

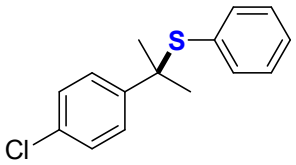


Reaction mixture after 3h (^{1}H-NMR in C_6D_5Br)




H
S
Tol
Reaction mixture
1H-NMR
(C6D5Br)
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)


H
S
Tol
Reaction mixture
13C{1H}NMR
(C6D5Br)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

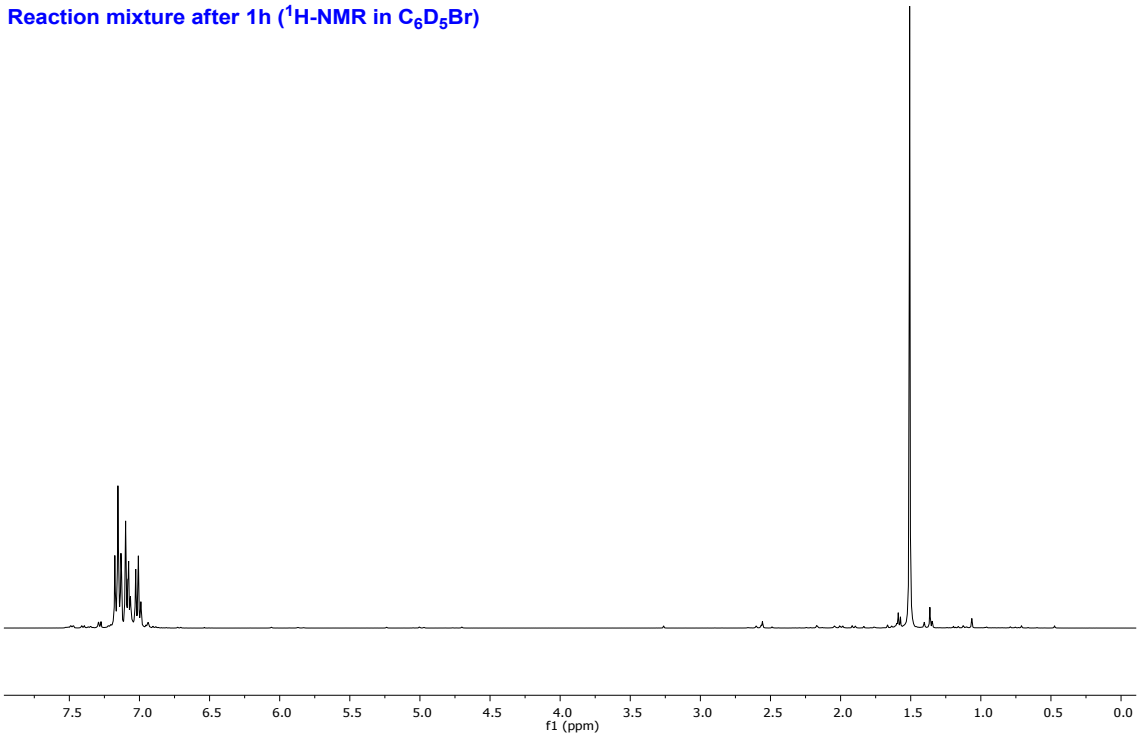


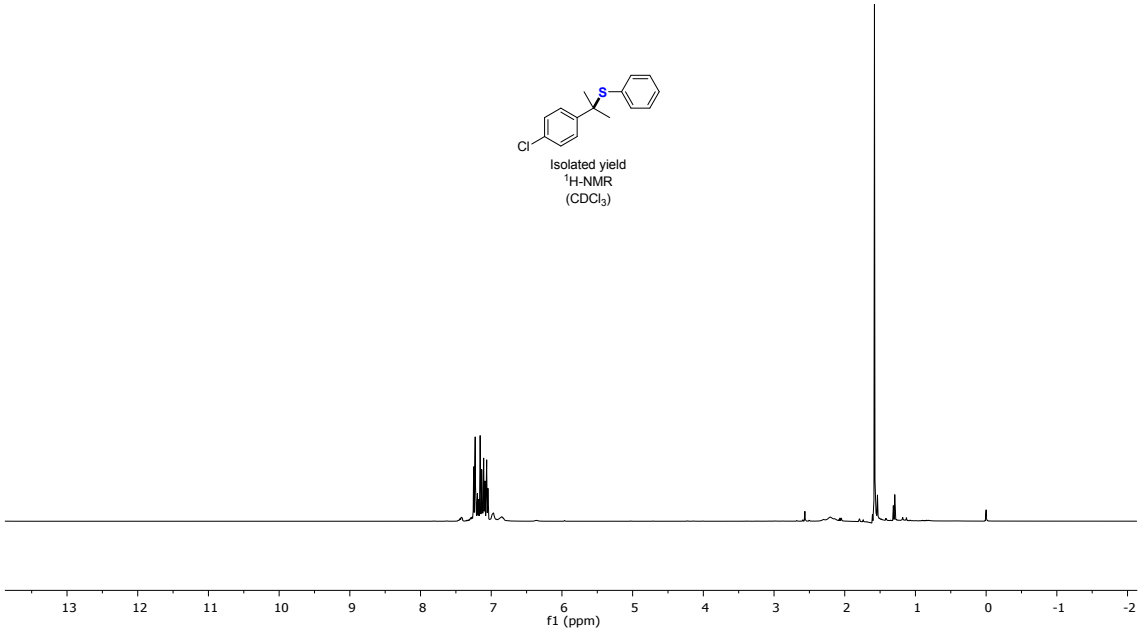
(2-(4-Chlorophenyl)propan-2-yl)(phenyl)sulfane (19). To a solution of the catalyst **1a** (3 mg, 1.5 mol%) in C_6D_5Br (1.0 mL) were added benzenethiol (19 mg, 0.17 mmol), and then 1-chloro-4-(prop-1-en-2-yl)benzene (26 mg, 0.17 mmol) at r.t. After 1 h the reaction was complete. This was followed by saturated $NaHCO_3$ (5 mL) extraction with dichloromethane (3 × 5 mL). The organic phase was dried over magnesium sulfate, filtered over silica-gel and the solvent was removed (40 mg, 91 % yield).

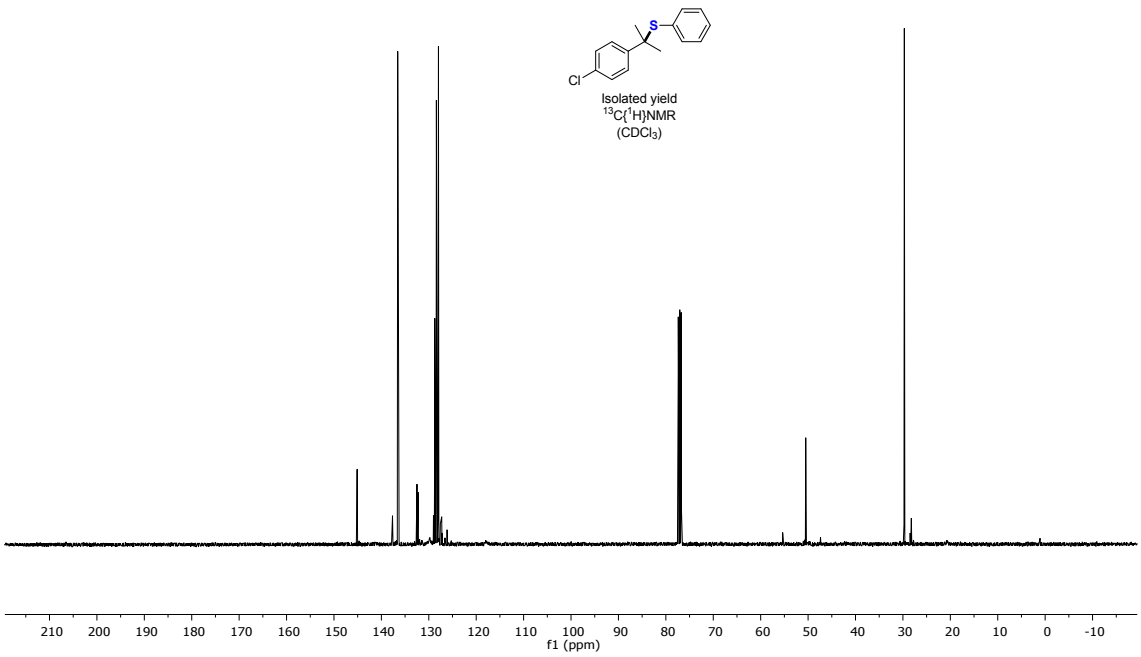
^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.24 (d, $^3J_{HH}$ = 8.6 Hz, 2H), 7.20 (m, 1H), 7.14 (d, $^3J_{HH}$ = 8.6 Hz, 2H), 7.11 (t, $^3J_{HH}$ = 8.3 Hz, 2H), 7.05 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 1.58 (s, 6H).

^{13}C{^{1}H} NMR (101 MHz, C_6D_5Br), δ: 145.1 (1C), 136.7 (2C), 132.5 (1C), 128.8 (1C), 128.4 (2C), 128.1 (2C), 128.0 (2C), 50.4 (1C), 29.7 (2C).

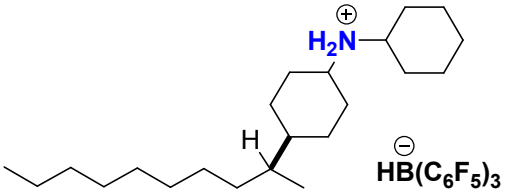
Reaction mixture after 1h (^{1}H-NMR in C_6D_5Br)




S
Cl
Isolated yield
^{1}H-NMR
($CDCl_3$)
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)


S
Cl
Isolated yield
$^{13}C\{^{1}H\}$NMR
($CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Aromatic hydrogenation of product 7.



In a 25 mL Schlenk bomb, compound **7** (105 mg, 0.34 mmol) and $B(C_6F_5)_3$ (173 mg, 0.34 mmol), were dissolved in toluene (2 mL) and pressurized with hydrogen gas (4 atm). The Schlenk was then sealed and placed in an oil bath 100 °C for 48 h. The solvent was removed under vacuum and the crude oil was washed with pentane (2 × 5 mL) to give a yellow solid isolated in approximately 40% yield. The remainder of the reaction mixture consisted of the starting materials amine and borane.

Product consists of a mixture of *trans* and *cis* isomers in a 1 : 2 ratio

NMR has been reported for the major *cis* isomer

^{1}H NMR (400 MHz, C_6D_5Br), δ: 4.61 (br s, 2H, NH), 3.42 (br q, 1H, $^1J_{HH}$ = 87 Hz, BH), 3.38 (m, 1H), 2.86 (m, 1H), 1.77-0.94 (m, 34 H), 0.91 (t, 3H, $^3J_{HH}$ = 7.4 Hz), 0.73 (d, 3H, $^3J_{HH}$ = 6.4 Hz).

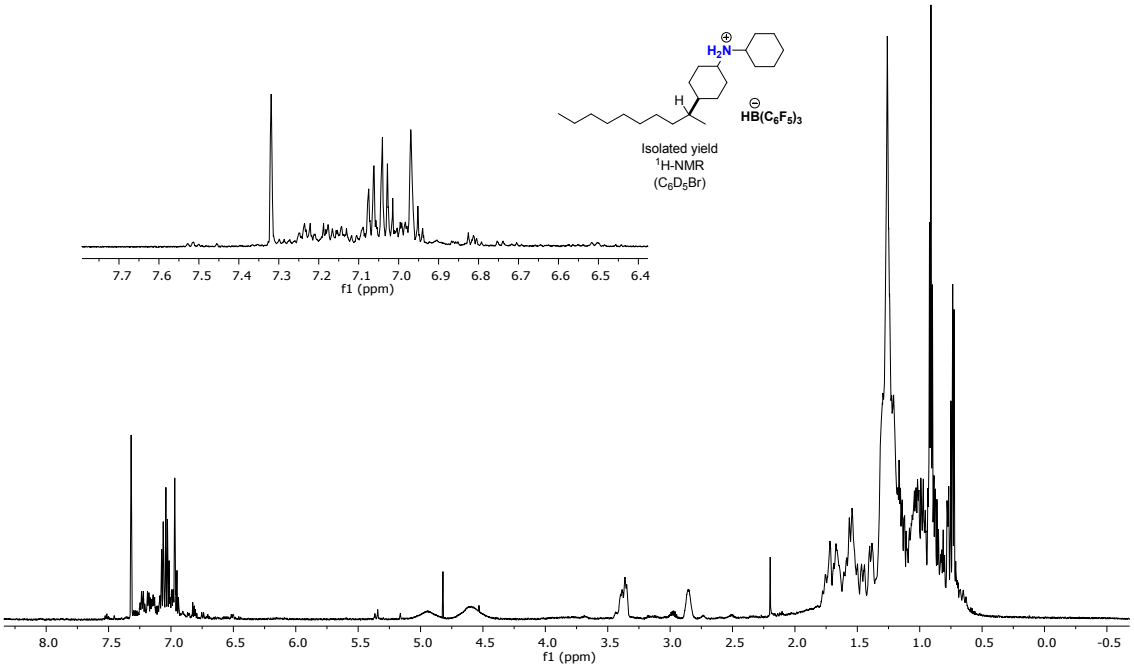
^{19}F NMR (377 MHz, C_6D_5Br), δ: -131.7 (m, 2F, *o*-C_6F_5), -161.8 (t, 1F, $^3J_{FF}$ = 24 Hz, *p*-C_6F_5), -165.8 (m, 2F, *m*-C_6F_5).

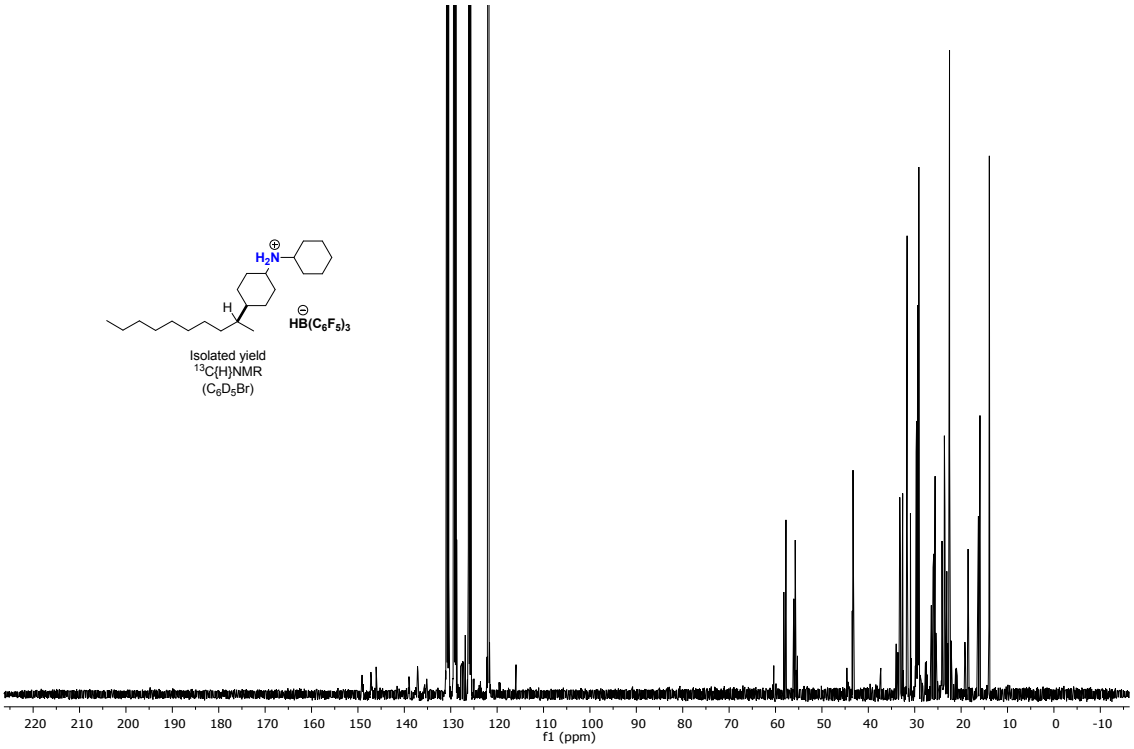
^{11}B{^{1}H} NMR (128 MHz, C_6D_5Br), δ: -24.4 (br s).

^{13}C{^{1}H} NMR (101 MHz, C_6D_5Br), δ: 148.1 (dm, 1C, $^1J_{CF}$ = 243 Hz, CF), 137.9 (dm, 1C, $^1J_{CF}$ = 249 Hz, CF), 135.9 (dm, 1C, $^1J_{CF}$ = 246 Hz, CF), 125.0 (br, 1C, *ipso*-C_6F_5), 58.7 (1C), 56.0 (1C), 43.4 (1C), 33.22 (1C), 32.6 (1C), 31.6 (1C), 29.4 (1C), 29.1 (1C), 29.0 (1C), 26.1 (1C), 25.6 (1C), 23.7 (1C), 23.6 (1C), 23.5 (1C), 22.5 (1C), 18.5 (1C), 15.9 (1C), 13.9 (1C).

GC-MS: 20.663 min, m/z = 321.4 [M], 306.3 [M-CH_3], 238.3 [M-C_6H_{11}], 208.2 [M-C_8H_{17}], 180.2 [M-$C_{10}H_{21}$].

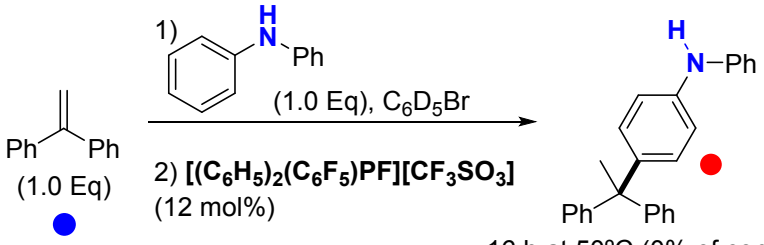
HRMS (DART Ionization, *m/z*): calcd. for $C_{22}H_{44}N$, $[M+H]^+$: 322.3468; found: 322.3468.


Isolated yield
1H-NMR
(C6D5Br)
HB(C6F5)3
f1 (ppm)


Isolated yield
13C{H}NMR
(C6D5Br)
HB(C6F5)3
f1 (ppm)

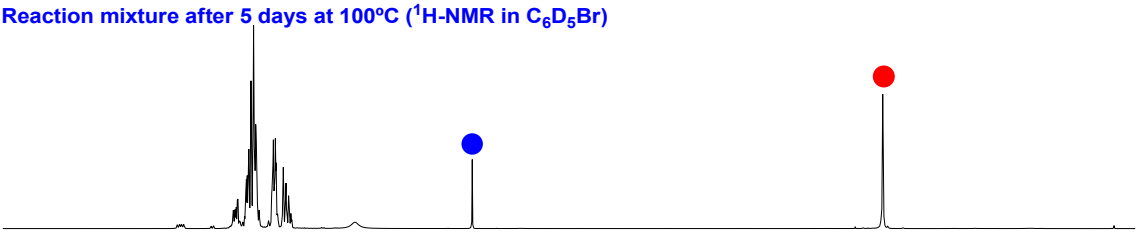
Mechanistic experiments.

- Reaction using $[(C_6H_5)_2(C_6F_5)PF][CF_3SO_3]$ as a catalyst:

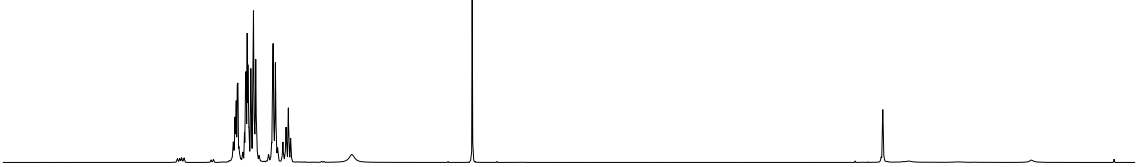


16 h at 50ºC (0% of conv.)
24 h at 100ºC (30% of conv.)
5 days at 100ºC (75% of conv.)

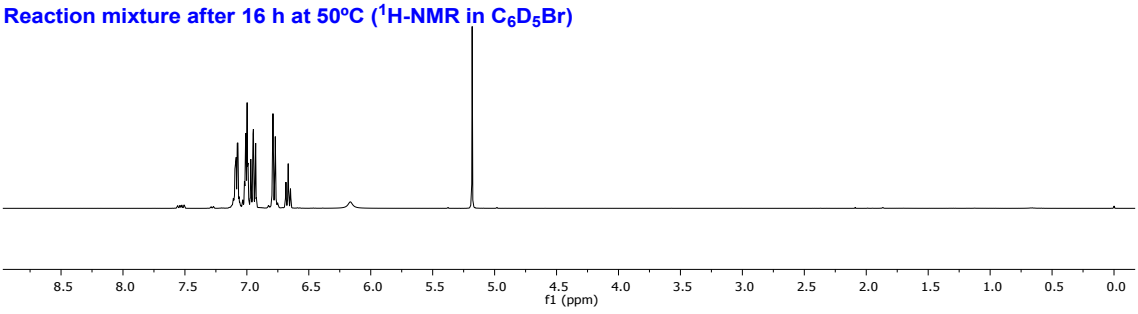
Reaction mixture after 5 days at 100ºC (^{1}H-NMR in C_6D_5Br)



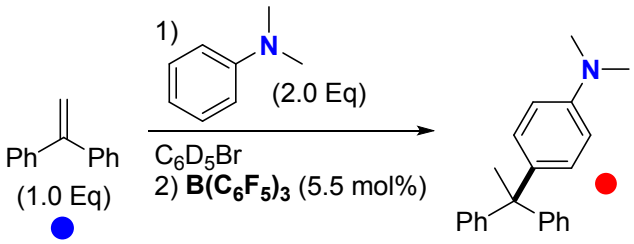
Reaction mixture after 1 day at 100ºC (^{1}H-NMR in C_6D_5Br)



Reaction mixture after 16 h at 50ºC (^{1}H-NMR in C_6D_5Br)

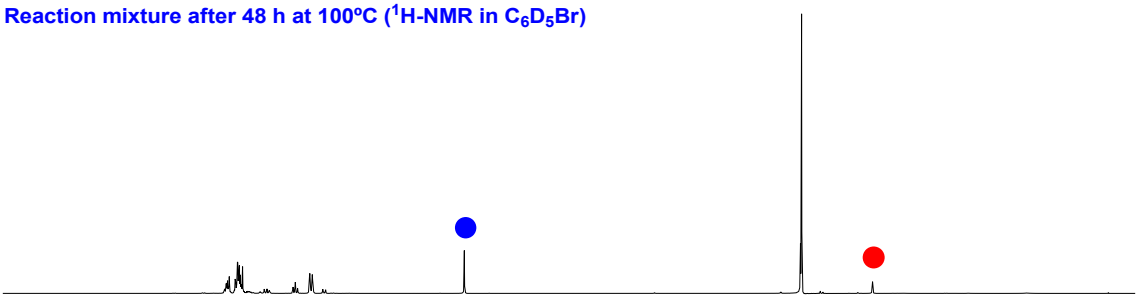


- Reactions using $B(C_6F_5)_3$ as a catalyst:

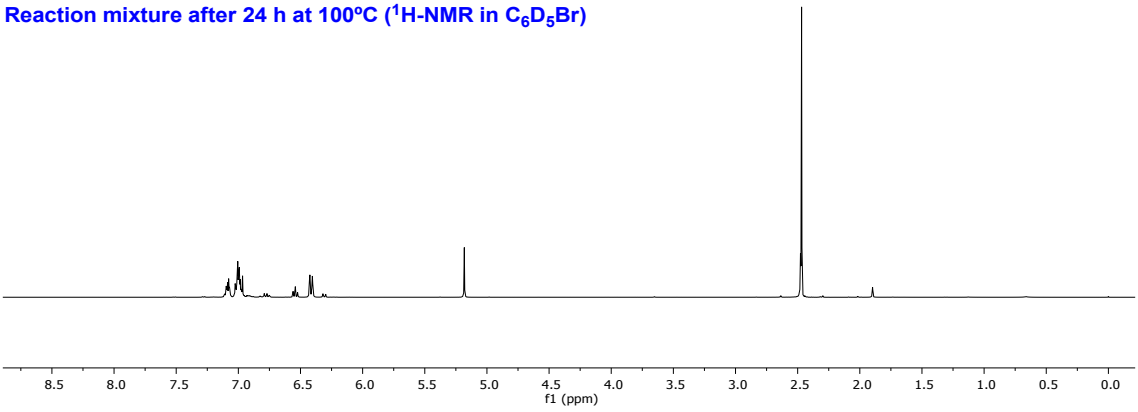


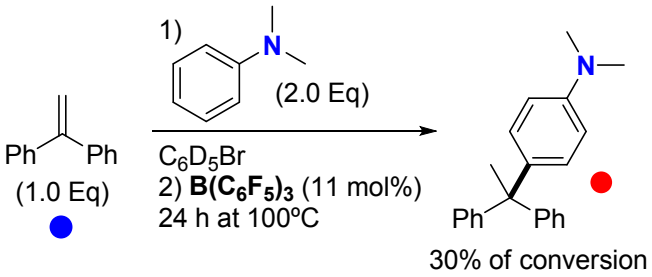
24 h at 100ºC (17% of conv.)
48 h at 100ºC (22% of conv.)

Reaction mixture after 48 h at 100ºC (^{1}H-NMR in C_6D_5Br)

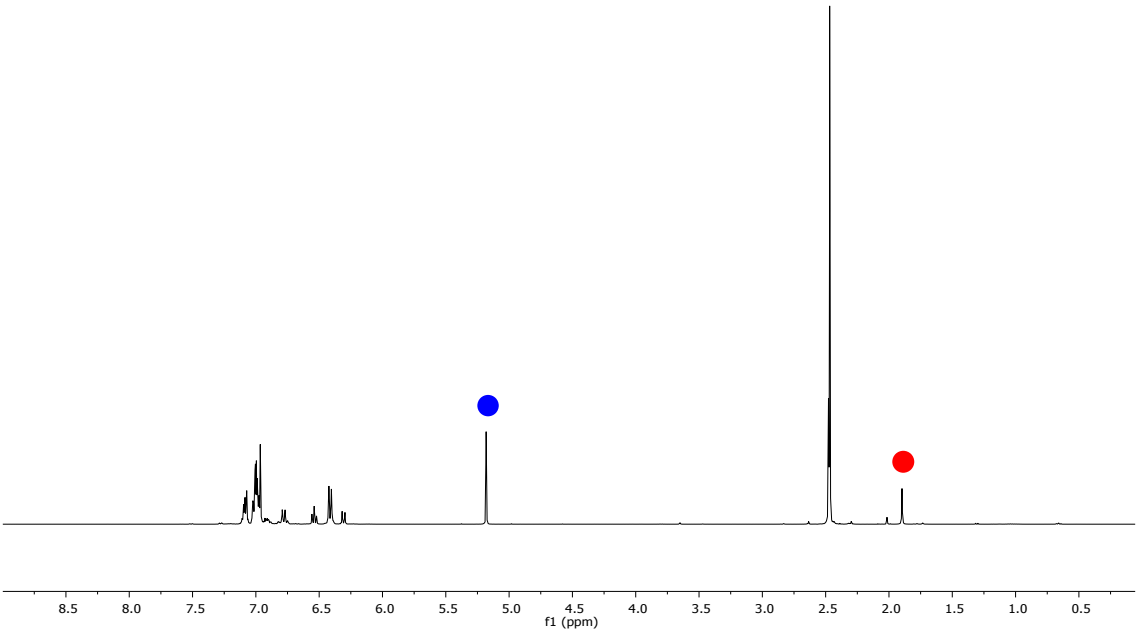


Reaction mixture after 24 h at 100ºC (^{1}H-NMR in C_6D_5Br)

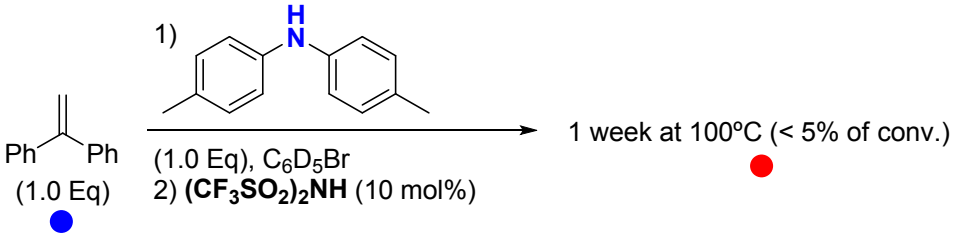




Reaction mixture after 24 h at 100ºC (^{1}H-NMR in C_6D_5Br)



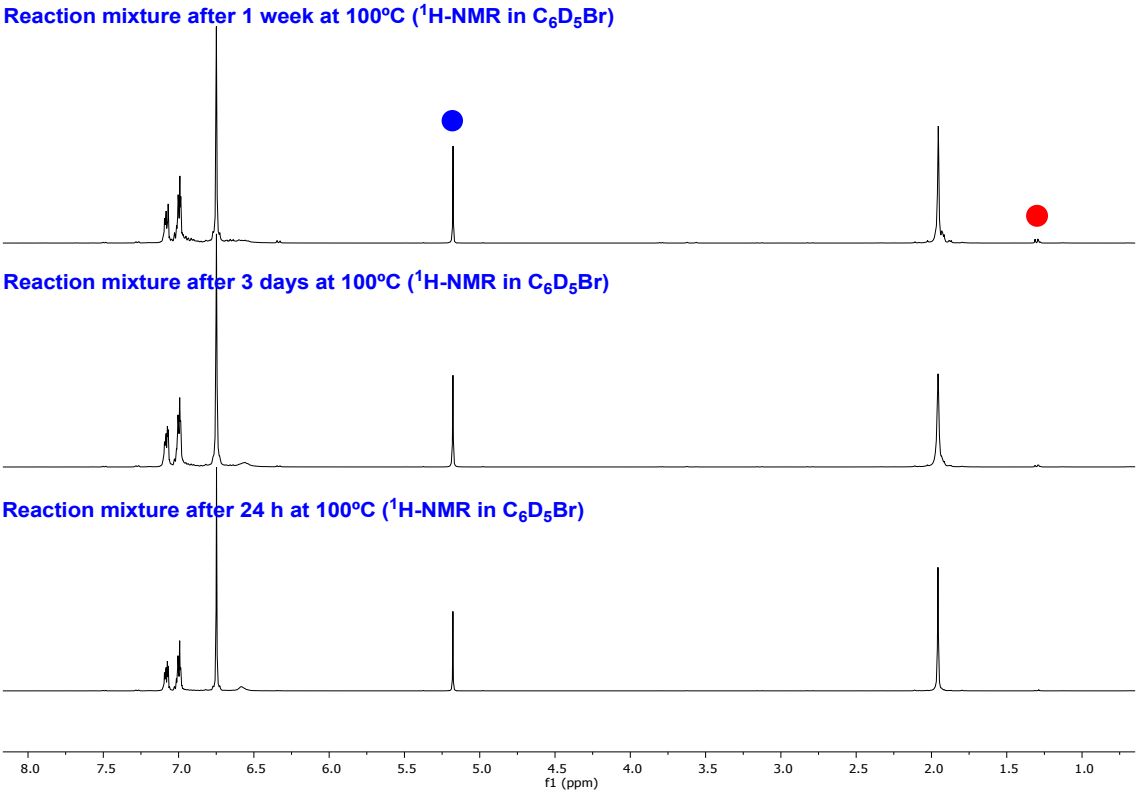
- Reactions using $(CF_3SO_2)_2NH$ as a catalyst:

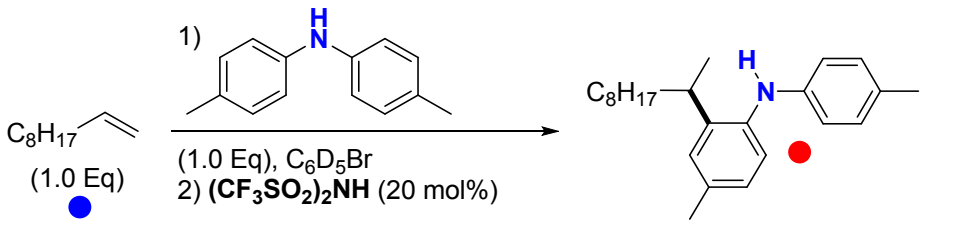


Reaction mixture after 1 week at 100ºC (^{1}H-NMR in C_6D_5Br)

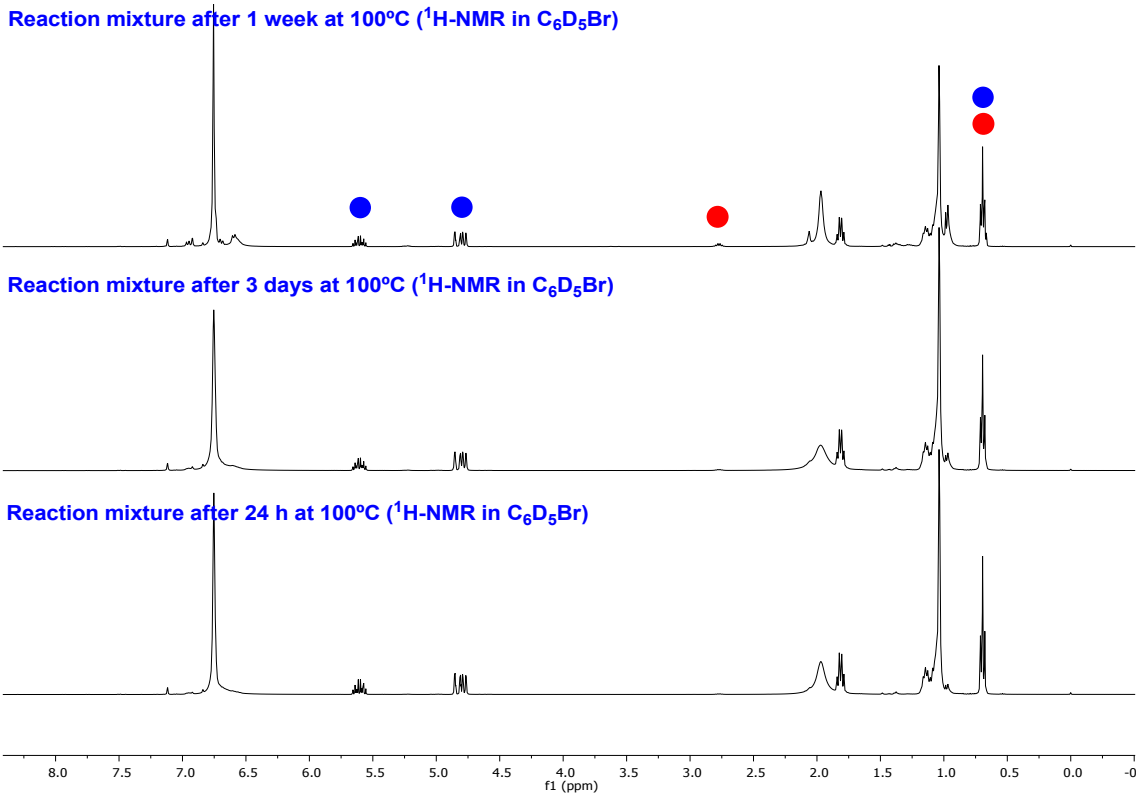
Reaction mixture after 3 days at 100ºC (^{1}H-NMR in C_6D_5Br)

Reaction mixture after 24 h at 100ºC (^{1}H-NMR in C_6D_5Br)

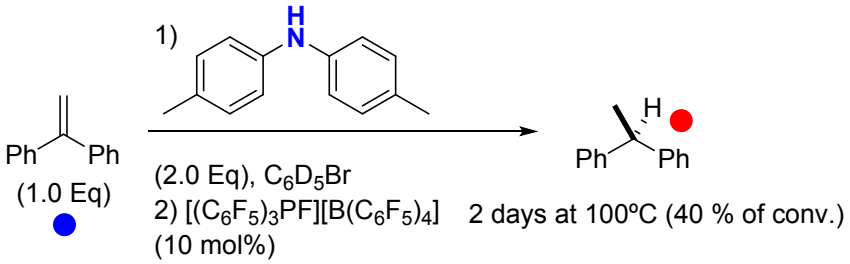




2 days at 100ºC (5% of conv.)
1 week at 100ºC (15% of conv.)



- Reaction using $[(C_6F_5)_3PF][B(C_6F_5)_4]$ as a catalyst:



Reaction mixture after 2 days at 100ºC (^{1}H-NMR in C_6D_5Br)

Reaction mixture after 24 h at 100ºC (^{1}H-NMR in C_6D_5Br)