Supplementary Information for

A metal-free approach for the hydrogenolysis of C(aryl)–C(alkyl) bonds

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1. Materials and Methods

Commercially available chemicals were purchased from Alfa Aesar, Acros, Sigma Aldrich, J&K, Innochem, Sinopharm and TCI, and used as received unless otherwise noted. H_2 (purity 99.9999%) was purchased from Air Liquide (China). THF was purified by an MBraun solvent purification system (MB-SPS-800). Bromobenzene, chlorobenzene and fluorobenzene were dried by reflux under N_2 over CaH_2 and freshly distilled prior to use. Difluorobenzene was dried by reflux under N_2 over sodium and freshly distilled prior to use. tert-Butylbenzene (TCI), (1,1-dimethylpropyl)benzene (Ark Pharm.), cumene (TCI), diphenylmethane (Innochem), ethylbenzene (Innochem), 1,4-di-tert-butylbenzene (TCI), 1,1,4,4-tetramethyl-1,2,3,4-tetrahydronaphthalene (Ark Pharm.) were dried over 4Å molecular sieves prior to use. Laboratory-grade polystyrene was purchased from Acros (Code number: 178890250) and used as received. Single use polystyrene cups were produced by CHULV, China. Expanded polystyrene foam was from the package material for THF bottles purchased from Sinopharm, China. Borenium complexes **1a** and **1b** were synthesized according the literature. [1,2]

High pressure autoclaves were purchased from Shanghai LABE Instrument Co. Ltd (Model DCS-30N). NMR spectra were recorded on Bruker SPECT NMR (400 MHz for ^{1}H, 376 MHz for ^{19}F, 100 MHz for ^{13}C) spectrometer with $CDCl_3$ (from J&K) or CD_2Cl_2 (from Cambridge Isotope Laboratories) as solvent. Spectra were referenced to tetramethylsilane using the residual ^{1}H and $^{13}C\{1H\}$ chemical shifts of the deuterated solvents. GC-MS analyses were obtained on a Thermo Scientific Focus GC Gas Chromatograph system equipped with a TG-SQC-15 m × 0.25 mm × 0.25 μm capillary column (Thermo Scientific) and FID detector. Gel Permeation Chromatography (GPC) was used to obtain molecular weight (M_n and M_w) and polydispersity index (PDI) of polymers or long-chain phenylalkanes using an Agilent Technologies 1260 Infinity equipped with three columns (Agilent PLgel (5μm, 10^3Å), Agilent PLgel (5μm, 10^6Å) and Agilent PLgel (10μm, MIXED BLS)) in a column oven, one differential refractometer and one UV Detector (λ = 260 nm). THF (HPLC Grade) was used as the eluent with a flow rate of 1 mL/min. Polystyrene standards (from Agilent Technologies, M_n = 162 ~ 6.57 × 10^6 g mol^{-1}) were used for calibration.

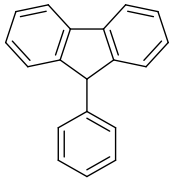
2. General procedure for the synthesis of alkylarenes [3]

A solution of *n*BuLi (2.5 M in hexane, 6.3 mL, 1.05 eq.) was added dropwise via a syringe into a solution of arylbromide (15 mmol, 1.0 equivalent) in THF (30 mL) under nitrogen atmosphere at -78 ℃ in a cooling bath. The reaction mixture was stirred at -78 ℃ for 1 h. Subsequently, to this reaction mixture, the solution of ketone (15 mmol, 1.0 equivalent) in THF (10 mL) was added dropwise at -78 ℃ via a syringe. Then the cooling bath was removed and the reaction mixture was stirred for 10h at room temperature. The resulting yellow solution was quenched by saturated aqueous ammonium chloride solution, and extracted by ethyl acetate (20 mL) three times. The organic phases were combined and washed by water (30 mL), dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude benzyl alcohol was directly used for reduction without any purification.

To a stirred mixture of benzyl alcohol (10 mmol), NH_4F (13 mmol, 0.48 g) and triethylsilane (13 mmol, 1.50 g) in CH_2Cl_2 (30 mL), CF_3COOH (50 mmol, 3.7 mL) was slowly added at 0 ℃ via a syringe. After stirring at room temperature for 10 hours, the reaction mixture was quenched with ice water (20 mL), then extracted with CH_2Cl_2 (20 mL) three times. The combined organic extract was washed by saturated aqueous $NaHCO_3$ solution (20 mL x 2) and water (20 mL),

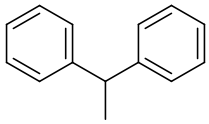
dried over $MgSO_4$ and concentrated in a rotary evaporator. Further purification by silica gel flash column chromatography yielded the target alkylarene derivative.

9-phenylfluorene



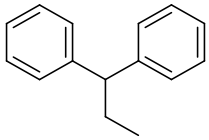
Prepared according to the general procedure from 9-phenyl-9-fluorenol (7.1 mmol, 1.83 g), NH_4F (17.9 mmol, 0.66 g), triethylsilane (12.8 mmol, 1.49 g) and CF_3COOH (27 mmol, 2.0 mL). 9-Phenylfluorene was obtained as white solid (1.60 g, 6.60 mmol) in 93% yield.
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.84 (d, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.37-7.26 (m, 7H), 7.13 (dd, *J* = 8.0, 1.7 Hz, 2H), 5.09 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 148.03, 141.73, 141.13, 128.82, 128.47, 127.44, 126.96, 125.47, 120.00, 54.57.
Data in accordance with the literature.[4]

1,1-diphenylethane



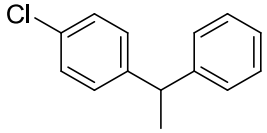
1,1-Diphenylethanol was prepared using benzophenone as the starting material. A solution of CH_3MgBr (3.0 M in hexane, 24 mmol, 8.0 mL) was added dropwise via a syringe into a solution of benzophenone (20.0 mmol, 3.64 g) in THF (60 mL) under nitrogen atmosphere at 0 ℃ in a cooling bath. Subsequently, the cooling bath was removed and the reaction mixture was stirred for 10h at room temperature. The resulting solution was quenched by saturated aqueous ammonium chloride solution, and extracted by ethyl acetate (20 mL) three times. The organic phases were combined and washed by water (20 mL), dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude benzyl alcohol was directly used for reduction without any purification. The reduction of 1,1-diphenylethanol was carried out according to the general procedure using NH_4F (18.9 mmol, 0.70 g), triethylsilane (19.8 mmol, 2.30 g) and CF_3COOH (50 mmol, 3.7 mL). 1,1-Diphenylethane was obtained as colorless liquid (2.35 g, 12.9 mmol) in 64% yield.
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.27 (t, *J* = 7.7 Hz, 4H), 7.21 (d, *J* = 7.0 Hz, 4H), 7.16 (t, *J* = 7.1 Hz, 2H), 4.14 (q, *J* = 7.2 Hz, 1H), 1.63 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 146.49, 128.49, 127.76, 126.15, 44.90, 22.00.
Data in accordance with the literature.[5]

1,1-diphenylpropane



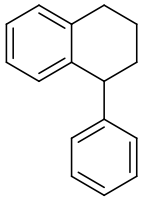
Prepared according to the general procedure using bromobenzene (15 mmol, 2.35 g), ^{n}BuLi (2.5 M in hexane, 15.0 mmol, 6.0 mL), propiophenone (13.9 mmol, 1.87 g), NH_4F (16.8 mmol, 0.62 g), triethylsilane (16.3 mmol, 1.89 g) and CF_3COOH (74.3 mmol, 5.5 mL). 1,1-Diphenylpropane was obtained as a colorless liquid (2.36 g, 12.0 mmol) in 80% yield.
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.37-7.27 (m, 8H), 7.23 (t, *J* = 7.4 Hz, 2H), 3.86 (t, *J* = 7.8 Hz, 1H), 2.14 (m, 2H), 0.97 (t, *J* = 7.8 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 145.30, 128.49, 128.05, 126.14, 53.39, 28.73, 12.93.
Data in accordance with the literature.[6]

1-(4-chlorophenyl)-1-phenylethane



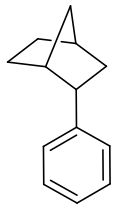
1-(4-Chlorophenyl)-1-phenylethanol was prepared using benzophenone as the starting material. A solution of CH_3MgBr (3.0 M in hexane, 12 mmol, 4.0 mL) was added dropwise via a syringe into a solution of benzophenone (10.0 mmol, 2.20 g) in THF (60 mL) under nitrogen atmosphere at 0 ℃ in a cooling bath. Subsequently, the cooling bath was removed and the reaction mixture was stirred for 10h at room temperature. The resulting solution was quenched by saturated aqueous ammonium chloride solution, and extracted by ethyl acetate (20 mL) three times. The organic phases were combined and washed by water (20 mL), dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude benzyl alcohol was directly used for reduction without any purification. The reduction of 1-(4-chlorophenyl)-1-phenylethanol was carried out according to the general procedure using NH_4F (12.3 mmol, 0.46 g), triethylsilane (11.2 mmol, 1.30 g) and CF_3COOH (51.3 mmol, 3.8 mL). 1-(4-Chlorophenyl)-1-phenylethane was obtained as a colorless liquid (1.73 g, 7.98 mmol) in 80% yield.
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.37 (t, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.31-7.25 (m, 3H), 7.23 (d, *J* = 8.6 Hz,, 2H), 4.20 (q, *J* = 7.2 Hz, 1H), 1.70 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 145.92, 144.99, 131.87, 129.11, 128.60, 128.58, 127.65, 126.37, 44.29, 21.91.
Data in accordance with the literature.[7]

1-phenyl-1,2,3,4-tetrahydronaphthalene



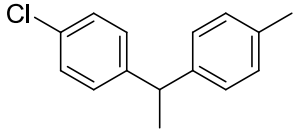
Prepared according to the general procedure using bromobenzene (10.0 mmol, 1.57 g), ^{n}BuLi (2.5 M in hexane, 10.5 mmol, 4.2 mL), 1-tetralone (10 mmol, 1.46 g, 1.0 equivalent), NH_4F (13 mmol, 0.48 g), triethylsilane (13 mmol, 1.51 g) and CF_3COOH (50 mmol, 3.7 mL). 1-Phenyl-1,2,3,4-tetrahydronaphthalene was obtained as a colorless liquid (0.88 g, 4.22 mmol) in 42% yield.
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.32 (t, *J* = 7.0 Hz, 2H), 7.25-7.19 (tt, *J* = 7.3, 1.6 Hz, 1H), 7.20-7.10 (m, 4H), 7.07 (td, *J* = 6.5, 2.5 Hz, 1H), 6.88 (d, *J* = 7.6 Hz 1H), 4.17 (t, *J* = 6.8 Hz, 1H), 3.02-2.83 (m, 2H), 2.22 (m, 1H), 2.01-1.86 (m, 2H), 1.81 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 147.66, 139.52, 137.73, 130.32, 129.10, 128.99, 128.36, 126.07, 126.03, 125.77, 45.76, 33.40, 29.92, 21.10.
Data in accordance with the literature.[8]

2-phenylbicyclo[2.2.1]heptane



The corresponding benzyl alcohol was prepared according to the general procedure using bromobenzene (10.0 mmol, 1.57 g), ^{n}BuLi (2.5 M in hexane, 10.5 mmol, 4.2 mL), 2-norbornanone (10.0 mmol, 1.10 g). The reduction of benzyl alcohol was achieved by treatment of the benzyl alcohol with 10% Pd/C (555 mg) under H_2 (20 bar) in methanol (6.0 mL) for 72 hours. After purification by chromatography, 2-phenylbicyclo[2.2.1]heptane was obtained as a mixture of endo-isomer (major) and exo-isomer (minor) in a 10:1 ratio (1.12 g, 6.50 mmol) in 65% yield.
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): endo-isomer: 7.30 (t, *J* = 7.7 Hz, 2H), 7.22 (d, *J* = 7.3 Hz, 2H), 7.18 (t, *J* = 7.1 Hz, 2H), 3.23 (m, 1H), 2.42 (bs, 1H), 2.33 (t, *J* = 4.5 Hz, 1H), 1.98 (m, 1H), 1.62-1.50 (m, 2H), 1.48-1.41(m, 2H), 1.33-1.17(m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): endo-isomer: 143.81, 128.36, 128.11, 125.63, 46.18, 42.74, 40.75, 37.71, 34.40, 30.31, 23.04.
Data in accordance with the literature.[9]

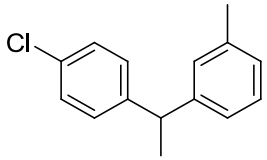
1-(4-chlorophenyl)-1-(4-methylphenyl)ethane



Prepared according to the general procedure using 4-bromotoluene (8.0 mmol, 1.37 g), ^{n}BuLi (2.5 M in hexane, 8.5 mmol, 3.4 mL), 4-chloroacetophenone (8.0 mmol, 1.24 g), NH_4F (10.5 mmol, 0.39 g), triethylsilane (10.3 mmol, 1.20 g) and CF_3COOH (40.5 mmol, 3.0 mL). 1-(4-Chlorophenyl)-1-(4-methylphenyl)ethane was obtained as a colorless liquid (1.10 g, 4.77 mmol) in 60% yield.
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.27 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 7.15-7.09 (m, 4H), 4.12 (q, *J* = 7.2 Hz, 1H), 2.34 (s, 3H), 1.62 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 145.26, 142.99, 135.90, 131.79, 129.30, 129.08, 128.57, 127.53, 43.93, 22.00, 21.12.

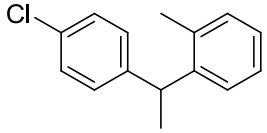
Data in accordance with the literature.[10]

1-(4-chlorophenyl)-1-(3-methylphenyl)ethane



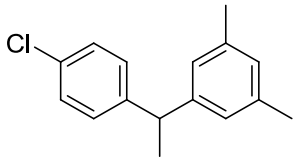
Prepared according to the general procedure using 3-bromotoluene (10 mmol, 1.71 g), ^{n}BuLi (2.5 M in hexane, 10.5 mmol, 4.2 mL), 4-chloroacetophenone (10 mmol, 1.55 g), NH_4F (13 mmol, 0.48 g), triethylsilane (13 mmol, 1.51 g) and CF_3COOH (50 mmol, 3.7 mL). 1-(4-Chlorophenyl)-1-(3-methylphenyl)ethane was obtained as a colorless liquid (1.30 g, 5.64 mmol) in 56% yield.
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.30 (d, *J* = 8.5 Hz, 2H), 7.25-7.18 (m, 3H), 7.09-7.04 (m, 3H), 4.14 (q, *J* = 7.2 Hz, 1H), 2.38 (s, 3H), 1.66 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 145.91, 145.13, 138.18, 131.82, 129.12, 128.67, 128.50, 128.48, 127.15, 124.67, 44.28, 21.95, 21.63.
Data in accordance with the literature.[10]

1-(4-chlorophenyl)-1-(2-methylphenyl)ethane



Prepared according to the general procedure using 2-bromotoluene (15.1 mmol, 2.57 g), ^{n}BuLi (2.5 M in hexane, 15.8 mmol, 6.3 mL), 4-chloroacetophenone (15.0 mmol, 2.32 g), NH_4F (19.5 mmol, 0.72 g), triethylsilane (19.5 mmol, 2.27 g) and CF_3COOH (75.6 mmol, 5.6 mL). 1-(4-Chlorophenyl)-1-(2-methylphenyl)ethane as a colorless liquid (1.70 g, 7.37 mmol) in 49% yield.
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.33-7.27 (m, 4H), 7.23-7.20 (m, 2H), 7.15 (d, *J* = 8.6 Hz, 2H), 4.36 (q, *J* = 7.2 Hz, 1H), 2.29 (s, 3H), 1.66 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 144.91, 143.47, 136.16, 131.67, 130.66, 129.16, 128.56, 126.69, 126.46, 126.28, 40.60, 22.16, 19.84.
Data in accordance with the literature.[10]

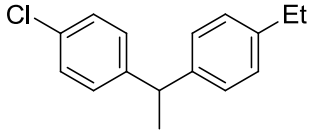
1-(4-chlorophenyl)-1-(3,5-dimethylphenyl)ethane



Prepared according to the general procedure using 3,5-dimethylbromobenzene (15.1 mmol, 2.79 g), ^{n}BuLi (2.5 M in hexane, 6.3 mL), 4-chloroacetophenone (15.1 mmol, 2.33 g), NH_4F (24.1 mmol, 0.89 g), triethylsilane (23.7 mmol, 2.76 g) and CF_3COOH (78.4 mmol, 5.8 mL). 1-(4-Chlorophenyl)-1-(3,5-dimethyl- phenyl)ethane was obtained as a colorless liquid (2.70 g, 11.0 mmol) in 73% yield.
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.28 (d, *J* = 8.6 Hz, 2H), 7.19 (d, *J* = 8.6 Hz, 2H), 6.87 (s, 1H), 6.84 (s, 2H), 4.08 (q, *J* = 7.2 Hz, 1H), 2.31 (s, 6H), 1.62 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 145.90, 145.22, 138.06, 131.76, 129.10, 128.55, 128.07, 125.50, 44.23, 21.96, 21.50.

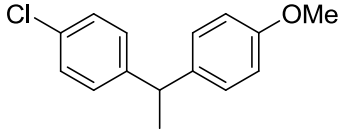
HRMS (m/z): calcd. for $C_{16}H_{17}Cl$, 244.1013; found 244.1014.

1-(4-chlorophenyl)-1-(4-ethylphenyl)ethane



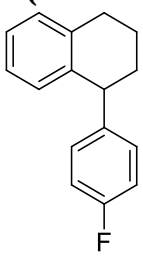
Prepared according to the general procedure using 4-bromoethylbenzene (12.2 mmol, 2.26 g), ^{n}BuLi (2.5 M in hexane, 12.8 mmol, 5.1 mL), 4-chloroacetophenone (12.2 mmol, 1.89 g), NH_4F (17.3 mmol, 0.64 g), triethylsilane (17.2 mmol, 2.00 g) and CF_3COOH (67.5 mmol, 5.0 mL). 1-(4-Chlorophenyl)-1-(4-ethylphenyl)ethane was obtained as a colorless liquid (2.00 g, 8.17 mmol) in 67% yield.
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.29 (d, *J* = 8.6 Hz, 2H), 7.21-7.13 (m, 6H), 4.14 (q, *J* = 7.2 Hz, 1H), 2.66 (q, *J* = 7.6 Hz, 2H), 1.65 (d, *J* = 7.2 Hz, 3H), 1.27 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 145.26, 143.17, 142.24, 131.78, 129.09, 128.55, 128.06, 127.55, 43.95, 28.52, 21.99, 15.65.
HRMS (m/z): calcd. for $C_{16}H_{17}Cl$, 244.1013; found 244.1016.

1-(4-chlorophenyl)-1-(4-methoxyphenyl)ethane



Prepared according to the general procedure using 4-bromoanisole (12.1 mmol, 2.27 g), ^{n}BuLi (2.5 M in hexane, 5.0 mL), 4-chloroacetophenone (12.1 mmol, 1.87 g), NH_4F (16.2 mmol, 0.60 g), triethylsilane (16.0 mmol, 1.85 g) and CF_3COOH (60.8 mmol, 4.5 mL). 1-(4-Chlorophenyl)-1-(4-methoxyphenyl)ethane was obtained as a colorless liquid (1.10 g, 4.46 mmol) in 37% yield.
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.28 (d, *J* = 8.6 Hz, 2H), 7.19-7.12 (m, 4H), 6.87 (d, *J* = 8.6 Hz, 2H), 4.11 (q, *J* = 7.3 Hz, 1H), 3.82 (s, 3H), 1.63 (d, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 158.13, 145.43, 138.10, 131.77, 129.04, 128.58, 128.56, 113.97, 55.38, 43.49, 22.13.
Data in accordance with the literature.[11]

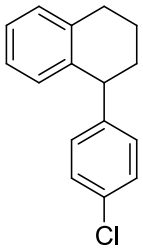
1-(4-fluorophenyl)-1,2,3,4-tetrahydronaphthalene



Prepared according to the general procedure using 4-bromofluorobenzene (10.1 mmol, 1.75 g), ^{n}BuLi (2.5 M in hexane, 10.5 mmol, 4.2 mL), 1-tetralone (10 mmol, 1.46 g), NH_4F (13 mmol, 0.48 g), triethylsilane (13 mmol, 1.50 g) and CF_3COOH (50.0 mmol, 3.7 mL). 1-(4-

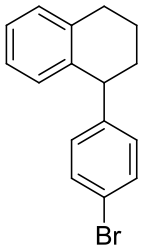
Fluorophenyl)-1,2,3,4-tetrahydronaphthalene was obtained as a colorless liquid (1.48 g, 6.50 mmol) in 65% yield.
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.18-7.14 (m, 2H), 7.10-7.04 (m, 3H), 6.99 (pseudo-t, *J* = 8.7 Hz, 2H) 6.85 (d, *J* = 7.7 Hz, 1H), 4.13 (t, *J* = 6.3 Hz, 1H), 2.99-2.82 (m, 2H), 2.18 (m, 1H), 1.95-1.74 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 152.96 (d, *J* = 1930.45 Hz), 139.30, 137.68, 130.30, 130.21 (d, *J* = 2.27 Hz), 129.18, 128.48, 126.17,125.84, 115.10 (d, *J* = 21.33 Hz), 44.97, 33.48, 29.84, 20.96.
Data in accordance with the literature.[7]

1-(4-chlorophenyl)-1,2,3,4-tetrahydronaphthalene



Prepared according to the general procedure using 4-bromochlorobenzene (10.1 mmol, 1.91 g), ^{n}BuLi (2.5 M in hexane, 10.5 mmol, 4.2 mL), 1-tetralone (10 mmol, 1.46 g), NH_4F (13.0 mol, 0.48 g), triethylsilane (13.0 mmol, 1.50 g) and CF_3COOH (50.0 mmol, 3.7 mL). 1-(4-Chlorophenyl)-1,2,3,4-tetrahydronaphthalene was obtained as a colorless liquid (1.70 g, 7.00 mmol) in 70% yield.
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.23 (d, *J* = 8.4 Hz, 2H), 7.15-7.08 (m, 2H), 7.06-6.98 (m, 3H), 6.80 (d, *J* = 7.7 Hz 1H), 4.09 (t, *J* = 6.6 Hz, 1H), 2.96-2.78 (m, 2H), 2.14 (m, 1H), 1.91-1.67 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 146.16, 138.92, 137.70, 131.78, 130.28, 130.19, 129.22,128.48, 126.25,125.88, 45.12, 33.34, 29.81, 20.93.
Data in accordance with the literature.[12]

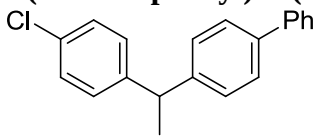
1-(4-bromophenyl)-1,2,3,4-tetrahydronaphthalene



Prepared according to the general procedure using 1,4-dibromobenzene (14.8 mmol, 3.50 g), ^{n}BuLi (2.5 M in hexane, 15.0 mmol, 6.0 mL), 1-tetralone (15.7 mmol, 2.30 g), NH_4F (18.9 mmol, 0.70 g), triethylsilane (17.2 mmol, 2.00 g) and CF_3COOH (59 mmol, 4.4 mL). 1-(4-Bromophenyl)-1,2,3,4-tetrahydronaphthalene was obtained as a colorless liquid (2.33 g, 8.10 mmol) in 55% yield.
^{1}H NMR (400 MHz, $CDCl_3$), δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.19-7.13 (m, 2H), 7.06 (m, 1H), 7.00 (d, *J* = 8.3Hz, 2H), 6.83 (d, *J* = 7.7 Hz 1H), 4.11 (t, *J* = 6.4 Hz, 1H), 2.99-2.78 (m, 2H), 2.17 (m, 1H), 1.94-1.72 (m, 3H).

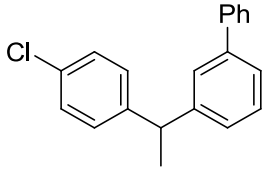
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 146.68, 138.82, 137.69, 131.43, 130.70, 130.18, 129.22,126.27, 125.89,119.87, 45.20, 33.30, 29.80, 20.93.
HRMS (m/z): calcd. for $C_{16}H_{15}Br$, 286.0352; found 286.0355.

1-(4-chlorophenyl)-1-(4-phenylphenyl)ethane



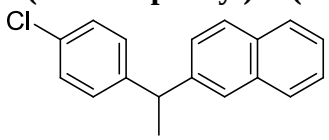
Prepared according to the general procedure using 4-bromobiphenyl (11.9 mmol, 2.78 g), ^{n}BuLi (2.5 M in hexane, 12.8 mmol, 5.1 mL), 4-chloroacetophenone (12.0 mmol, 1.86 g,), NH_4F (10.8 mmol, 0.40 g), triethylsilane (12.0 mmol, 1.40 g) and CF_3COOH (40.5 mmol, 3.0 mL). 1-(4-Chlorophenyl)-1-(4-phenylphenyl)ethane was obtained as a white solid (1.70 g, 5.81 mmol) in 49% yield.
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.60 (d, *J* = 7.6 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.46 (t, *J* = 7.3 Hz, 2H) 7.36 (tt, *J* = 7.3, 1.1 Hz, 1H), 7.33-7.26 (m, 4H), 7.22 (d, *J* = 8.5 Hz, 2H), 4.20 (q, *J* = 7.2 Hz, 1H), 1.68 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 145.04, 144.89, 140.99, 139.32, 131.96, 129.13, 128.87, 128.65, 128.06, 127.33, 127.28, 127.14, 44.01, 21.94.
HRMS (m/z): calcd. for $C_{20}H_{17}Cl$, 292.1013; found 292.1018.

1-(4-chlorophenyl)-1-(3-phenylphenyl) ethane



Prepared according to the general procedure using 3-bromobiphenyl (10 mmol, 2.33 g), ^{n}BuLi (2.5 M in hexane, 10.5 mmol, 4.2 mL), 4-chloroacetophenone (10 mmol, 1.55 g), NH_4F (13 mmol, 0.48 g), triethylsilane (13 mmol, 1.51 g) and CF_3COOH (50 mmol, 3.7 mL). 1-(4-Chlorophenyl)-1-(3-phenylphenyl) ethane was obtained as a white solid (1.20 g, 4.10 mmol) in 41% yield.
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.59 (d, *J* = 8.2 Hz, 2H), 7.49-7.43 (m, 4H), 7.42-7.34 (m, 2H), 7.29 (d, *J* = 8.2 Hz, 2H, 2H), 7.24-7.19 (m, 3H), 4.22 (q, *J* = 7.2 Hz, 1H), 1.70 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 146.45, 144.87, 141.60, 141.39, 131.96, 129.14, 129.03, 128.87, 128.65, 127.42, 127.35, 126.62, 125.32, 44.43, 21.99.
HRMS (m/z): calcd. for $C_{20}H_{17}Cl$, 292.1013; found 292.1019.

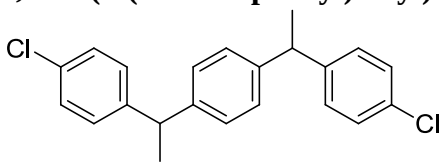
1-(4-chlorophenyl)-1-(2-naphthyl)ethane



Prepared according to the general procedure using 2-bromonaphthalene (11.9 mmol, 2.48 g), ^{n}BuLi (2.5 M in hexane, 12.5 mmol, 5.0 mL), 4-chloroacetophenone (12.0 mmol, 1.86 g), NH_4F (9.7 mmol, 0.36 g), triethylsilane (9.9 mmol, 1.15 g) and CF_3COOH (40 mmol, 3.0 mL). 1-(4-

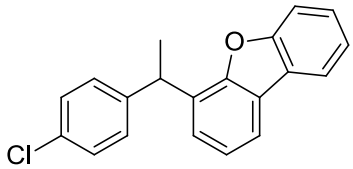
Chlorophenyl)-1-(2-naphthyl)ethane was obtained as a colorless liquid (1.40 g, 5.25 mmol) in 44% yield.
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.86-7.81 (m, 2H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.71 (s, 1H), 7.53-7.44 (m, 2H), 7.33-7.27 (m, 3H), 7.22 (d, *J* = 8.3 Hz, 2H), 4.32 (q, *J* = 7.2 Hz, 1H), 1.75 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 144.84, 143.31, 133.63, 132.28, 131.96, 129.25, 128.63, 128.24, 127.85, 127.72, 126.73, 126.20, 125.66, 125.49, 44.37, 21.83.
Data in accordance with the literature.[13]

1,4-bis(1-(4-chlorophenyl)ethyl)benzene



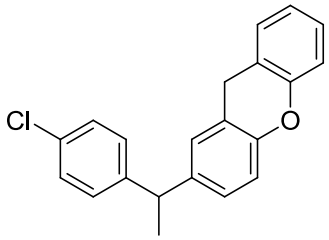
Prepared according to the general procedure using 1-(4-chlorophenyl)-1-(4-bromophenyl)ethane (11.3 mmol, 3.34 g), ^{n}BuLi (2.5 M in hexane, 11.5 mmol, 4.6 mL), 4-chloroacetophenone (11.5 mmol, 1.78 g), NH_4F (13.0 mmol, 0.48 g), triethylsilane (12.9 mmol, 1.50 g) and CF_3COOH (47 mmol, 3.5 mL). 1,4-Bis(1-(4-chlorophenyl)ethyl)benzene was obtained as a white solid (2.40 g, 6.75 mmol) in 60% yield.
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.27 (d, *J* = 8.2 Hz, 4H), 7.19-7.11 (m 8H), 4.09 (q, *J* = 7.2 Hz, 2H), 1.62 (d, *J* = 7.2 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 145.04, 143.81, 131.86, 129.09, 128.59, 127.68, 43.94, 21.93.
HRMS (m/z): calcd. for $C_{22}H_{20}Cl_2$, 354.0937; found 354.0943.

1-(4-chlorophenyl)-1-(4-dibenzofuryl)ethane



Prepared according to the general procedure using dibenzofuran (15.1 mmol, 2.54 g), ^{n}BuLi (2.5 M in hexane, 15.8 mmol, 6.3 mL), 4-chloroacetophenone (15.1 mmol, 2.33 g), NH_4F (15.7 mmol, 0.58 g), triethylsilane (14.1 mmol, 1.64 g) and CF_3COOH (54 mmol, 4.0 mL). 1-(4-Chlorophenyl)-1-(4-dibenzofuryl)ethane was obtained as a white solid (2.30 g, 7.50 mmol) in 50% yield.
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): δ (ppm): 7.97 (dd, *J* = 7.7, 0.7 Hz, 1H), 7.85 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.48 (td, *J* = 7.8, 1.3 Hz, 1H), 7.39-7.25 (m, 7H), 4.83 (q, *J* = 7.2 Hz, 1H), 1.82 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 156.13, 154.13, 143.80, 132.00, 130.07, 129.15, 128.57, 127.16, 125.27, 124.57, 124.27, 123.07, 122.79, 120.79, 118.83, 111.85, 38.59, 20.78.
HRMS (m/z): calcd. for $C_{20}H_{15}OCl$, 306.0806; found 306.0803.

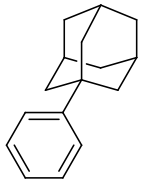
1-(4-chlorophenyl)-1-(3-xanthyl)ethane



Prepared according to modified procedure using 3-bromoxanthene (8.73 mmol, 2.28 g), ^{n}BuLi (2.5 M in hexane, 9.3 mmol, 3.7 mL), 4-chloroacetophenone (14.0 mmol, 2.16 g), NH_4F (10.8 mmol, 0.40 g), triethylsilane (6.3 mmol, 0.73 g) and CF_3COOH (27 mmol, 2.0 mL). 1-(4-Chlorophenyl)-1-(3-xanthyl)ethane was obtained as a white solid (1.00 g, 3.12 mmol) in 36% yield.

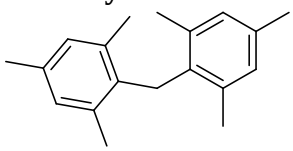
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.28 (d, *J* = 8.2 Hz, 2H), 7.23-7.14 (m, 4H), 7.07-6.97 (m, 5H), 4.11 (q, *J* = 7.2 Hz, 1H), 4.02 (s, 2H), 1.63 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 152.20, 150.59, 145.15, 140.59, 131.91, 129.06, 129.03, 128.63, 127.92, 127.75, 126.88, 123.04, 120.65, 116.56, 43.65, 28.18, 22.11.
HRMS (m/z): calcd. for $C_{21}H_{17}OCl$, 320.0962; found 320.0964.

1-phenyladamantane [14]



A mixture of 1-bromoadamantane (14.9 mmol, 3.20 g), benzene (150 mmol, 11.7 g) and $In(OTf)_3$ (0.45 mmol, 0.250 g) in CH_2Cl_2 (20 mL) was stirred at 55 ℃ under nitrogen atmosphere for 10 hours. Afterwards the reaction mixture was quenched with water (20 mL). The organic layer was washed with aqueous $NaHCO_3$ solution (20 mL x 2) and water (20 mL), dried over $MgSO_4$ and condensed under vacuum. Further purification by silica gel flash column chromatography (eluent: petroleum ether) gave 1-phenyladamantane as a white solid (1.20 g, 5.65 mmol) in 38% yield.
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.40 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 2.13 (s 3H), 1.96 (s, 6H), 1.86-1.75 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.47, 128.23, 125.64, 124.99, 43.31, 36.97, 36.32, 29.12.
Data in accordance with the literature.[14]

Dimesitylmethane [15]



A mixture of paraformaldehyde (0.31 g) and formic acid (98%, 48 mmol, 2.30 g,) was stirred at 80 ℃ until paraformaldehyde was completely dissolved. Subsequently, mesitylene (30.0 mmol, 3.60 g) was added dropwise to the mixture and the reaction mixture was stirred under reflux for 6

hours. Afterwards, the reaction mixture was cooled to room temperature, resulting in formation of a large amount of white crystalline powder. The solid was collected by filtration, washed with toluene (5 mL) and dried under vacuum, yielding dimesitylmethane as white crystals (1.50 g, 5.94 mmol) in 40% yield.
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): δ 6.81 (s, 4H), 4.02 (s, 2H), 2.27 (s, 6H), 2.11 (s, 12H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 136.84, 135.06, 134.96, 129.45, 31.15, 20.94, 20.86.
Data in accordance with the literature.[15]

3. General procedure for borenium-catalyzed hydrodealkylation of alkylarenes

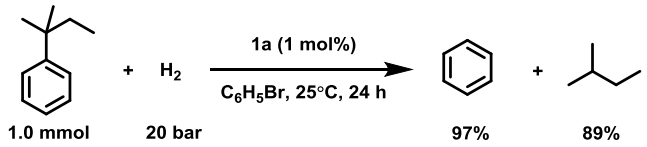
Inside of a N_2-filled glovebox, **1a** and alkylarene were dissolved in C_6H_5Br (0.5 mL) and transferred into the well of an autoclave. After the head of the autoclave was assembled, the autoclave was taken out of the glovebox and connected to a H_2 gas cylinder. The connection line was flushed with H_2 three times. Then the autoclave was pressurized to 20 bar of H_2 and allowed to stand at room temperature for 24 hours. The autoclave was then cooled to -40 ℃ in a cold ethanol bath for 15 mins, followed by releasing the H_2 pressure. After removing the head of autoclave, octane and diphenylmethane were added into the well of an autoclave as internal standards. The resulting reaction mixture was then subjected to GC/MS analysis. The identities of products were confirmed by comparison of the mass spectra and retention times of the products with those of authentic compounds.

Table S1. Results of condition screening for the hydrodealkylation of 2[a]

Entry	Catalyst	H_2 pressure (bar)	solvent	Yield of C_6H_6 (%)	Yield of isopentane (%)
1	**1a** (10 mol%)	1	C_6H_5Br	97	91
2	**1a** (1 mol%)	20	C_6H_5Br	97	89
3	**1a** (1 mol%)	20	C_6H_5Cl	96	91
4	**1a** (1 mol%)	20	C_6H_5F	96	89
5	**1a** (1 mol%)	20	*o*-$C_6H_4F_2$	98	88
6	**1b** (1 mol%)[b]	20	C_6H_5Br	23	5
7	$B(C_6F_5)_3$ (1 mol%)	20	C_6H_5Br	0	0
8	CF_3SO_3H (1 mol%)	20	C_6H_5Br	0	0

[a] Reactions were run on a 0.20 mmol scale at room temperature; yields were determined by GC analysis. [b] The reaction was carried out at 50 ℃.

Hydrodealkylation of tert-pentylbenzene



The reaction was conducted according to the general procedure with tert-pentylbenzene (143.4 mg, 0.967 mmol) and **1a** (12.4 mg, 0.010 mmol) in bromobenzene (0.5 mL) under H_2 atmosphere (20 bar) at 25 ℃ for 24 h. GC/MS analysis of the reaction mixture showed complete conversion of tert-pentylbenzene and formation of benzene (78 m/z) in 97% yield and isopentane (72 m/z) in 89% yield with octane (114.9 mg, 1.006 mmol) as internal standard.

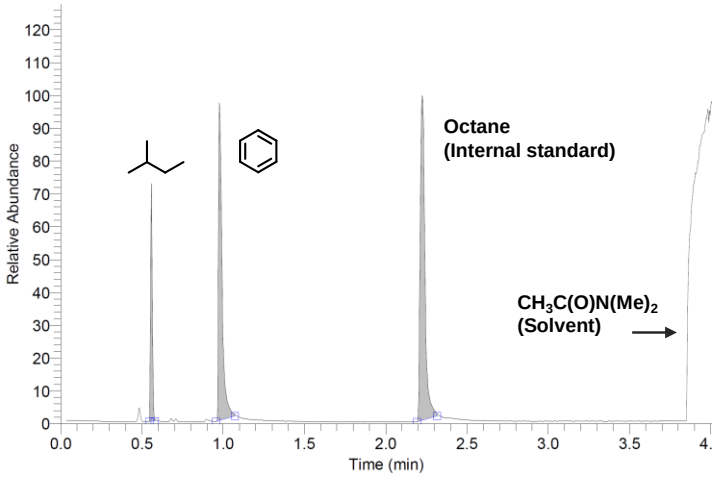


Fig. S1. GC data for hydrodealkylation of tert-pentylbenzene

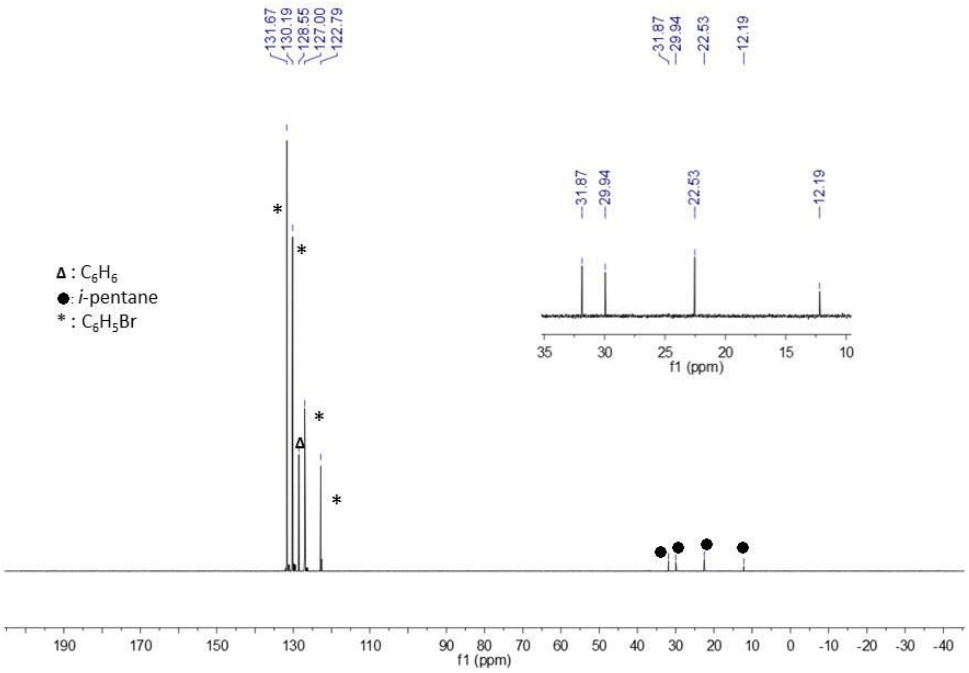
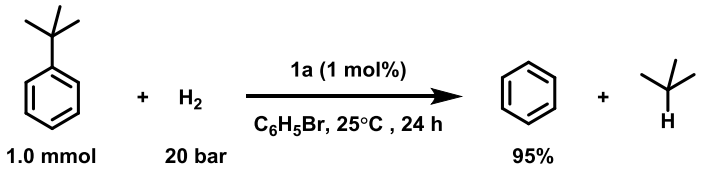


Fig. S2. $^{13}C\{^{1}H\}$ NMR of the reaction mixture after hydrodealkylation of tert-pentylbenzene

Hydrodealkylation of tert-butylbenzene



The reaction was conducted according to the general procedure with tert-butylbenzene (134.4 mg, 1.00 mmol) and **1a** (13.0 mg, 0.010 mmol) in bromobenzene (0.5 mL) under H_2 atmosphere (20 bar) at 25 ℃ for 24 h. GC/MS analysis of the reaction mixture showed complete conversion of tert-butylbenzene and formation of benzene (78 m/z) in 95% yield with octane (111.8 mg, 0.979 mmol) as internal standard. iso-Butane (58 m/z) was detected in the overhead gas by GC-MS.

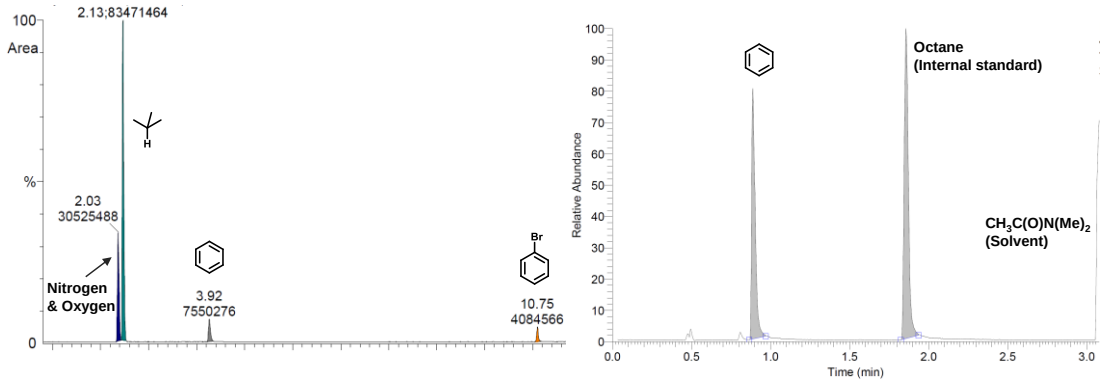
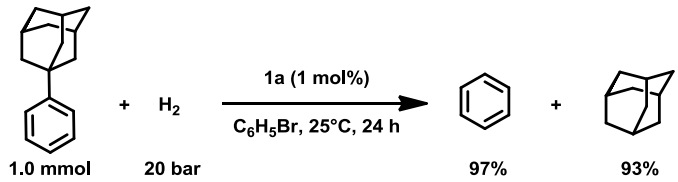


Fig. S3. GC data for hydrodealkylation of tert-butylbenzene

Hydrodealkylation of 1-phenyladamantane



The reaction was conducted according to the general procedure with 1-phenyladamantane (213.0 mg, 1.003 mmol) and **1a** (12.8 mg, 0.010 mmol) in bromobenzene (0.5 mL) under H_2 atmosphere (20 bar) at 25 ℃ for 24 h. GC/MS analysis of the reaction mixture showed complete conversion of 1-phenyladamantane and formation of benzene (78 m/z) in 97% yield and adamantane (136 m/z) in 93% yield with octane (114.9 mg, 1.006 mmol) and diphenylmethane (151.1 mg, 0.898 mmol) as internal standards.

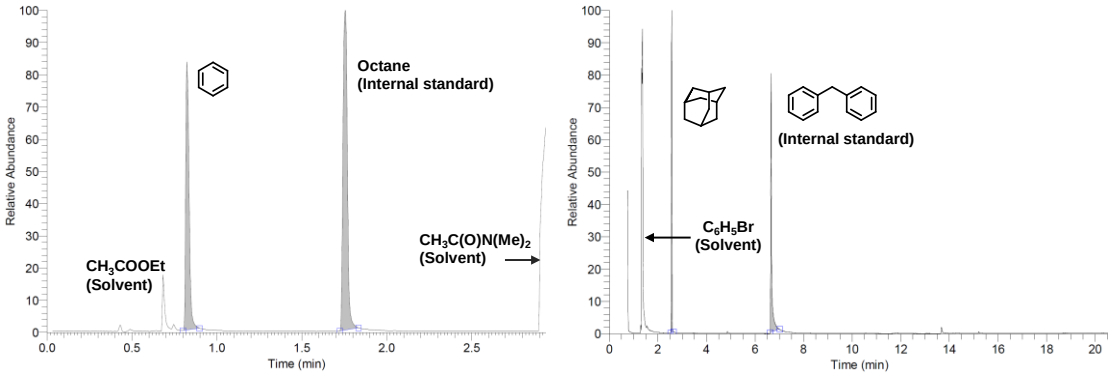


Fig. S4. GC data for hydrodealkylation of 1-phenyladamantane

Hydrodealkylation of 9-phenylfluorene

The reaction was conducted according to the general procedure with 9-phenylfluorene (123.0 mg, 0.508 mmol) and **1a** (32.8 mg, 0.026 mmol) in bromobenzene (1.0 mL) under H_2 atmosphere (20 bar) at 25 ℃ for 24 h. GC/MS analysis of the reaction mixture showed complete conversion of 9-phenylfluorene and formation of benzene (78 m/z) in 97% yield and fluorene (166 m/z) in 95% yield with octane (52.4 mg, 0.459 mmol) and 4,4'-dimethylbenzophenone (110.6 mg, 0.526 mmol) as internal standards. The mixture was then dried under reduced pressure and fluorene was purified by chromatography with petroleum ether as eluent (white solid, 77.0 mg, 91% yield).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): δ 7.81 (d, *J* = 7.5 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.32 (td, *J* = 7.5, 1.0 Hz, 2H), 3.92 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 143.34, 141.82, 126.85, 126.83, 125.16, 120.01, 37.05.

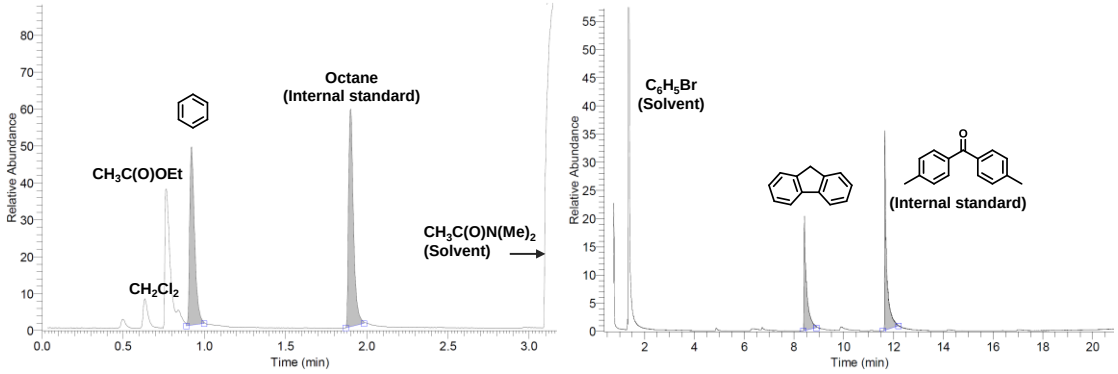
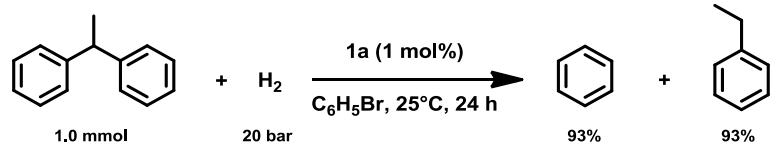


Fig. S5. GC data for hydrodealkylation of 9-phenylfluorene

Hydrodealkylation of 1,1-diphenylethane



The reaction was conducted according to the general procedure with 1,1-diphenylethane (182.0 mg, 0.999 mmol) and **1a** (13.6 mg, 0.011 mmol) in bromobenzene (0.5 mL) under H_2 atmosphere (20 bar) at 25 ℃ for 24 h. GC/MS analysis of the reaction mixture showed complete conversion of 1,1-diphenylethane and formation of benzene (78 m/z) in 93% yield and ethylbenzene (106 m/z) in 93% yield with octane (107.3 mg, 0.939 mmol) as internal standard.

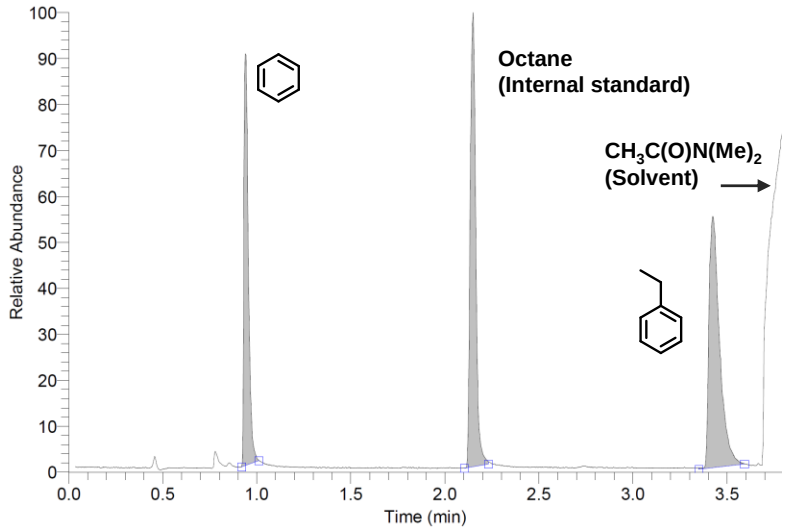
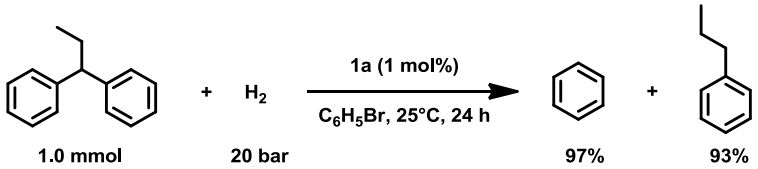


Fig. S6. GC data for hydrodealkylation of 1,1-diphenylethane

Hydrodealkylation of 1,1-diphenylpropane



The reaction was conducted according to the general procedure with 1,1-diphenylpropane (195.3 mg, 0.995 mmol) and **1a** (12.4 mg, 0.010 mmol) in bromobenzene (0.5 mL) under H_2 atmosphere (20 bar) at 25 ℃ for 24 h. GC/MS analysis of the reaction mixture showed complete conversion of 1,1-diphenylpropane and formation of benzene (78 m/z) in 97% yield and phenylpropane (120 m/z) in 93% yield with octane (114.1 mg, 0.999 mmol) and diphenylmethane (162.3 mg, 0.965 mmol) as internal standards.

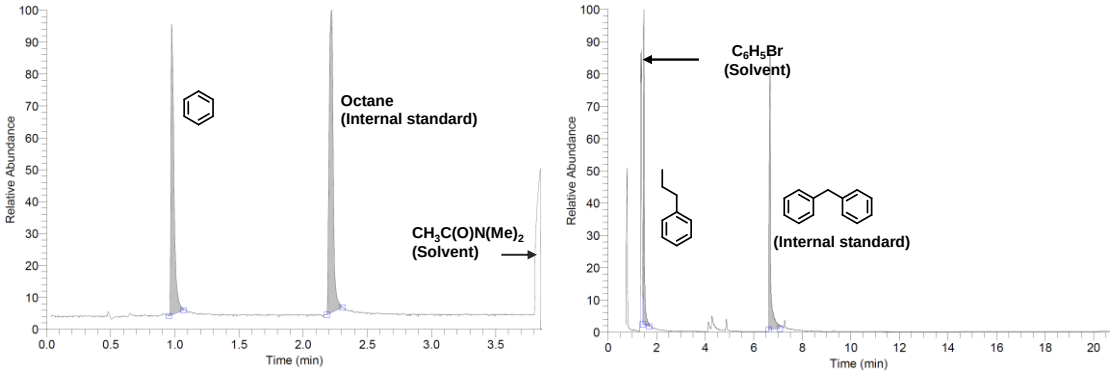
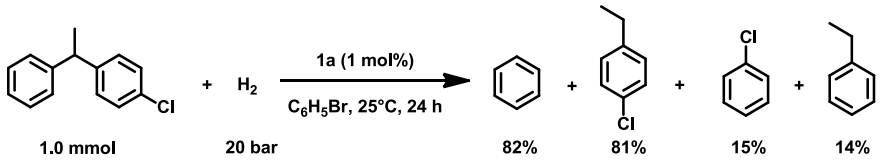


Fig. S7. GC data for hydrodealkylation of 1,1-diphenylpropane

Hydrodealkylation of 1-(4-chlorophenyl)-1-phenylethane



The reaction was conducted according to the general procedure with 1-(4-chlorophenyl)-1-phenylethane (216.4 mg, 0.999 mmol) and **1a** (13.1 mg, 0.010 mmol) in bromobenzene (0.5 mL) under H_2 atmosphere (20 bar) at 25 ℃ for 24 h. GC/MS analysis of the reaction mixture showed complete conversion of 1-(4-chlorophenyl)-1-phenylethane and formation of benzene (78 m/z) in 82% yield, chlorobenzene (m/z 112) in 15% yield, ethylbenzene (m/z 106) in 14% and 4-chloro(ethylbenzene) (m/z 140) in 81% yield with octane (52.4 mg, 0.459 mmol) and diphenylmethane (145.3 mg, 0.864 mmol) as internal standards.

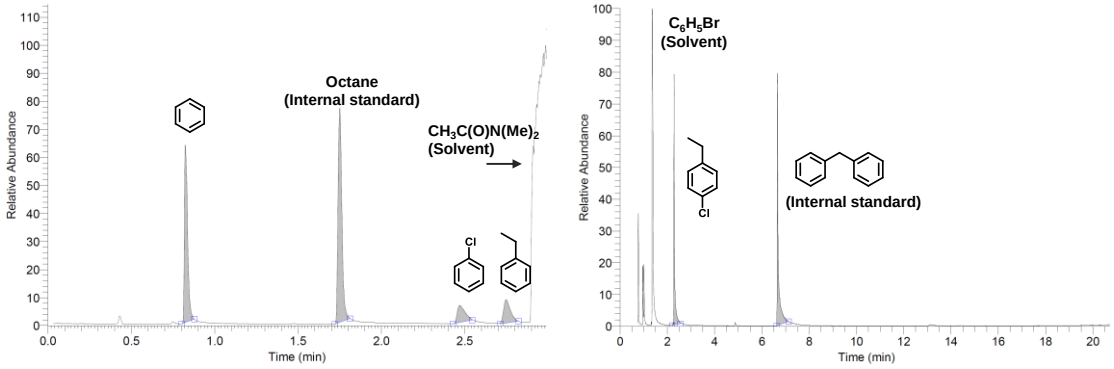
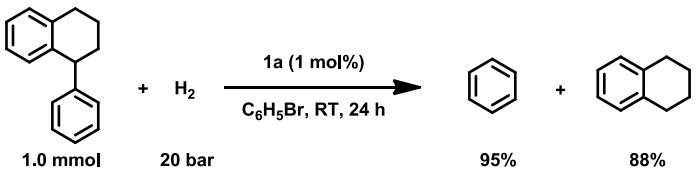


Fig. S8. GC data for hydrodealkylation of 1-(4-chlorophenyl)-1-phenylethane

Hydrodealkylation of 1-phenyl-1,2,3,4-tetrahydronaphthalene



The reaction was conducted according to the general procedure with 1-phenyl-1,2,3,4-tetrahydronaphthalene (204.4 mg, 0.981 mmol) and **1a** (13.4 mg, 0.010 mmol) in bromobenzene (0.5 mL) under H_2 atmosphere (20 bar) at 25 ℃ for 24 h. GC/MS analysis of the reaction mixture showed complete conversion of 1-phenyl-1,2,3,4-tetrahydronaphthalene and formation of benzene (78 m/z) in 95% yield and tetrahydronaphthalene (132 m/z) in 88% yield with octane (105.6 mg, 0.924 mmol) and diphenylmethane (155.8 mg, 0.926 mmol) as internal standards.

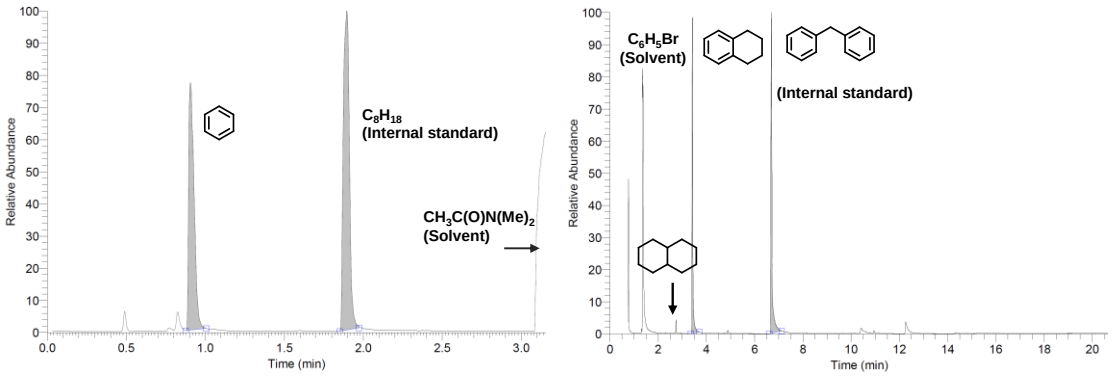
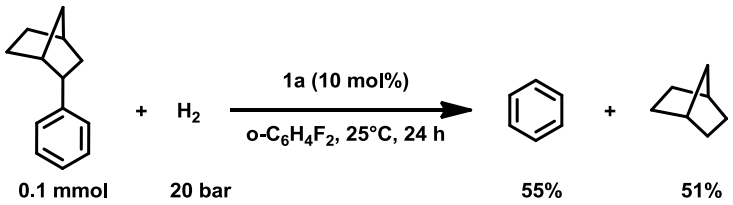


Fig. S9. GC data for hydrodealkylation of 1-phenyl-1,2,3,4-tetrahydronaphthalene

Hydrodealkylation of 2-phenylbicyclo[2.2.1]heptane



The reaction was conducted according to the general procedure with 2-phenylbicyclo[2.2.1]heptane (17.3 mg, 0.100 mmol) and **1a** (12.6 mg, 0.010 mmol) in *o*-difluorobenzene (0.25 mL) under H_2 atmosphere (20 bar) at 25 ℃ for 24 h. GC/MS analysis of the reaction mixture showed formation of benzene (78 m/z) in 55% yield and norbornane (96 m/z) in 51% yield with octane (12.9 mg, 0.113 mmol) as internal standard.

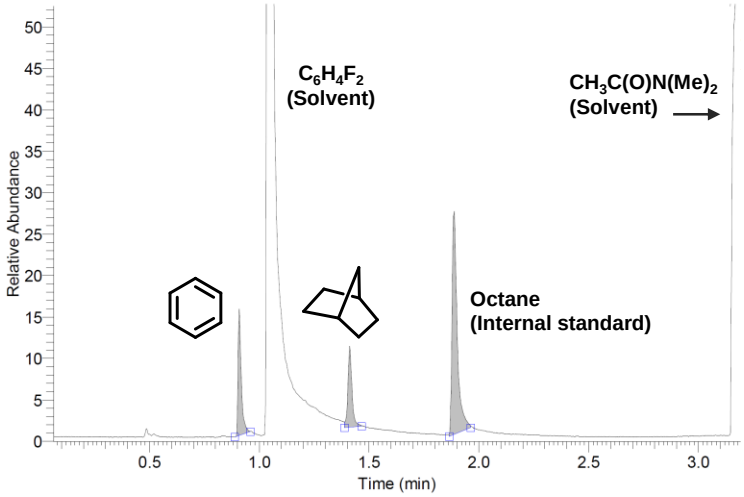
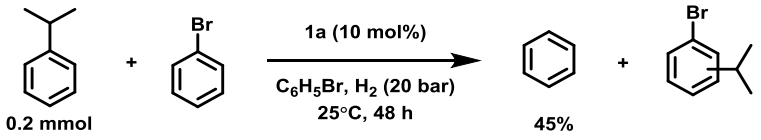


Fig. S10. GC data for hydrodealkylation of 2-phenylbicyclo[2.2.1]heptane

Attempted hydrodealkylation of cumene



The reaction was conducted according to the general procedure with cumene (24.9 mg, 0.207 mmol) and **1a** (26.4 mg, 0.021 mmol) in bromobenzene (0.25 mL) under H_2 atmosphere (20 bar) at 25 ℃ for 48 h. GC/MS analysis of the reaction mixture showed formation of benzene (78 m/z) in 45% yield with octane (18.0 mg, 0.158 mmol) as internal standard.

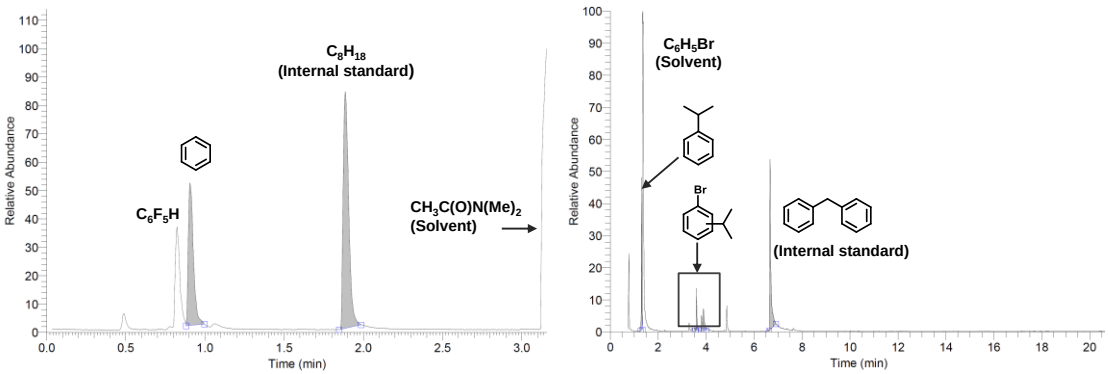
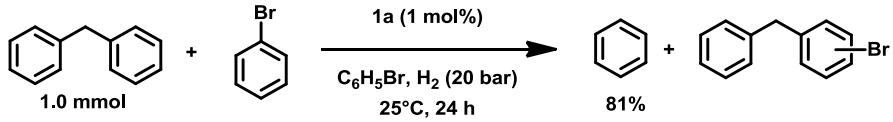


Fig. S11. GC data for hydrodealkylation of cumene

Attempted hydrodealkylation of diphenylmethane



The reaction was conducted according to the general procedure with diphenylmethane (170.3 mg, 1.012 mmol) and **1a** (13.0 mg, 0.010 mmol) in bromobenzene (0.5 mL) under H_2 atmosphere (20 bar) at 25 ℃ for 24 h. GC/MS analysis of the reaction mixture showed formation of benzene (78 m/z) in 81% yield with octane (85.9 mg, 0.752 mmol) as internal standard.

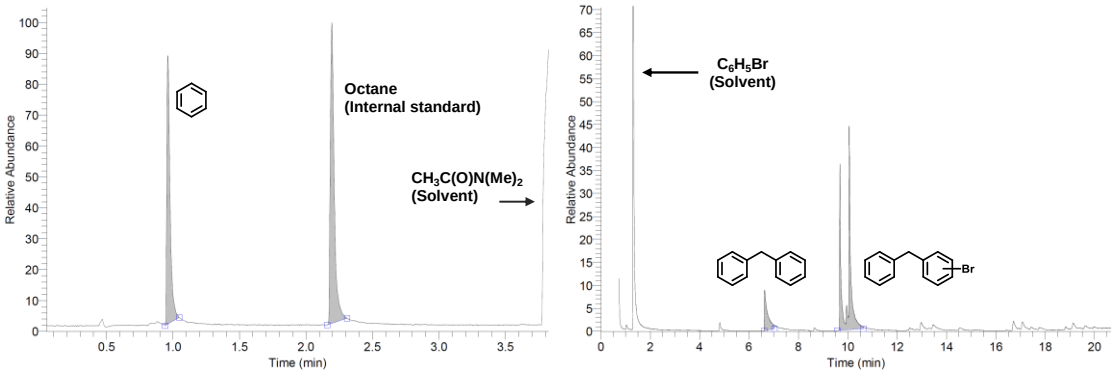
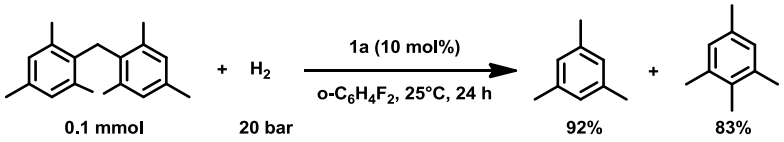


Fig. S12. GC data for hydrodealkylation of diphenylmethane

Hydrodealkylation of dimesitylmethane



The reaction was conducted according to the general procedure with dimesitylmethane (26.0 mg, 0.103 mmol) and **1a** (13.5 mg, 0.011 mmol) in *o*-difluorobenzene (0.25 mL) under H_2 atmosphere (20 bar) at 25 ℃ for 24 h. GC/MS analysis of the reaction mixture showed complete conversion of dimesitylmethane and formation of trimethylbenzene (120 m/z) in 92% yield and 1,2,3,5- tetramethylbenzene (134 m/z) in 83% yield with diphenylmethane (20.1 mg, 0.119 mmol) as internal standard.

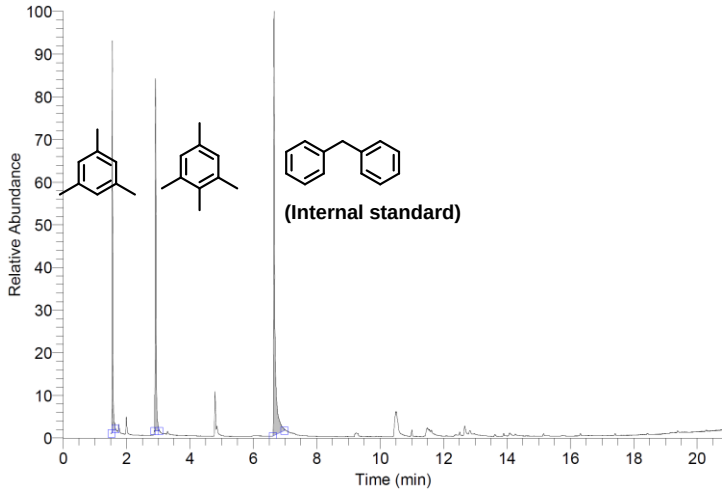
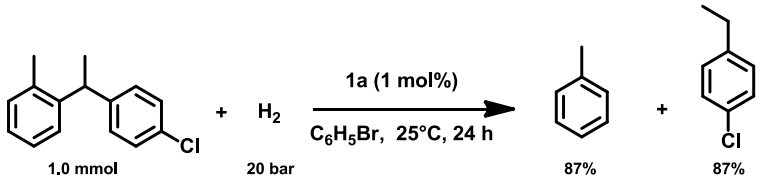


Fig. S13. GC data for hydrodealkylation of dimesitylmethane

Hydrodealkylation of 1-(4-chlorophenyl)-1-(2-methylphenyl)ethane



The reaction was conducted according to the general procedure with 1-(4-chlorophenyl)-1-(2-methylphenyl)ethane (231.2 mg, 1.002 mmol) and **1a** (13.5 mg, 0.011 mmol) in bromobenzene (0.5 mL) under H_2 atmosphere (20 bar) at 25 ℃ for 24 h. GC/MS analysis of the reaction mixture showed complete conversion of 1-(4-chlorophenyl)-1-(2-methylphenyl)ethane and formation of toluene (92 m/z) in 87% yield and 4-chloro(ethylbenzene) (m/z 140) in 87% yield with octane (101.7 mg, 0.890 mmol) and diphenylmethane (149.3 mg, 0.887 mmol) as internal standards.

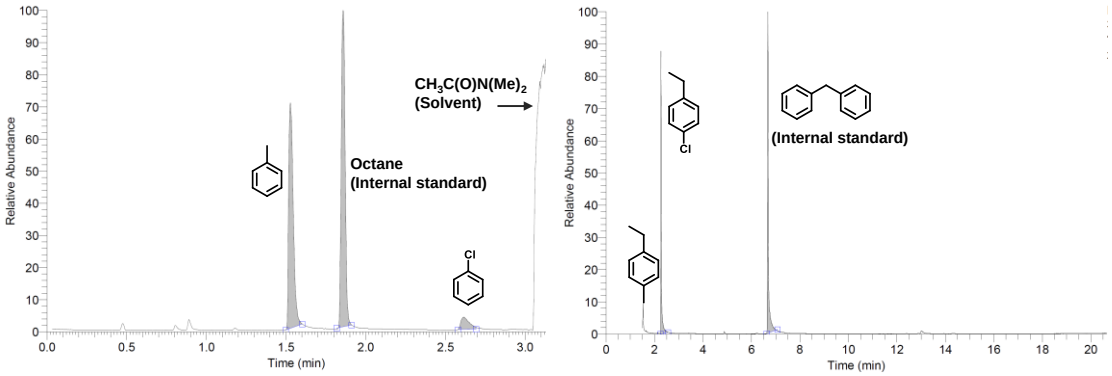
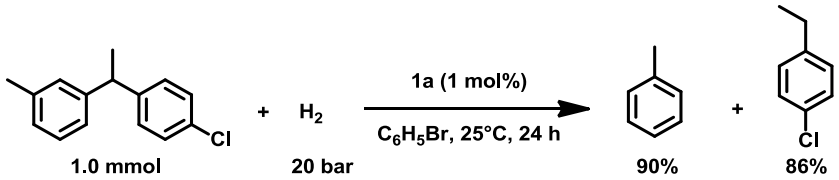


Fig. S14. GC data for hydrodealkylation of 1-(4-chlorophenyl)-1-(2-methylphenyl)ethane

Hydrodealkylation of 1-(4-chlorophenyl)-1-(3-methylphenyl)ethane



The reaction was conducted according to the general procedure with 1-(4-chlorophenyl)-1-(3-methylphenyl)ethane (231.8 mg, 1.005 mmol) and **1a** (13.4 mg, 0.010 mmol) in bromobenzene (0.5 mL) under H_2 atmosphere (20 bar) at 25 ℃ for 24 h. GC/MS analysis of the reaction mixture showed complete conversion of 1-(4-chlorophenyl)-1-(3-methylphenyl)ethane and formation of toluene (92 m/z) in 90% yield and 4-chloro(ethylbenzene) (m/z 140) in 86% yield with octane (95.1 mg, 0.833 mmol) and diphenylmethane (140.7 mg, 0.836 mmol) as internal standards.

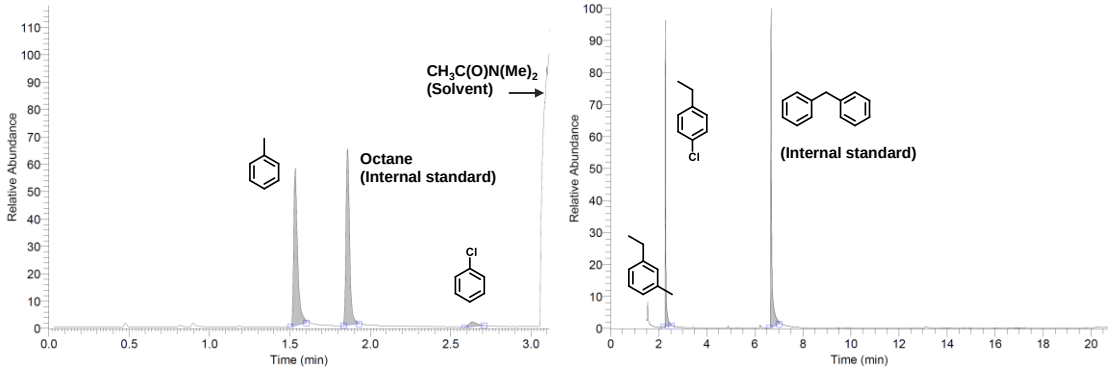
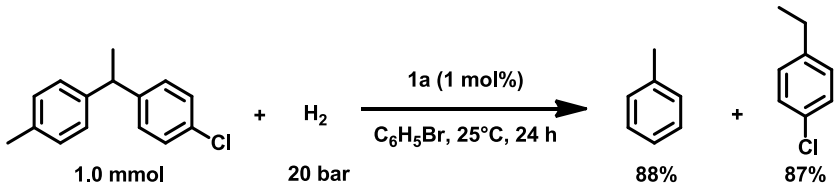


Fig. S15. GC data for hydrodealkylation of 1-(4-chlorophenyl)-1-(3-methylphenyl)ethane

Hydrodealkylation of 1-(4-chlorophenyl)-1-(4-methylphenyl)ethane



The reaction was conducted according to the general procedure with 1-(4-chlorophenyl)-1-(4-methylphenyl)ethane (232.0 mg, 1.005 mmol) and **1a** (12.8 mg, 0.010 mmol) in bromobenzene (0.5 mL) under H_2 atmosphere (20 bar) at 25 ℃ for 24 h. GC/MS analysis of the reaction mixture showed complete conversion of 1-(4-chlorophenyl)-1-(4-methylphenyl)ethane and formation of toluene (92 m/z) in 88% yield and 4-chloro(ethylbenzene) (m/z 140) in 87% yield with octane (101.3 mg, 0.887 mmol) and diphenylmethane (152.8 mg, 0.908 mmol) as internal standards.

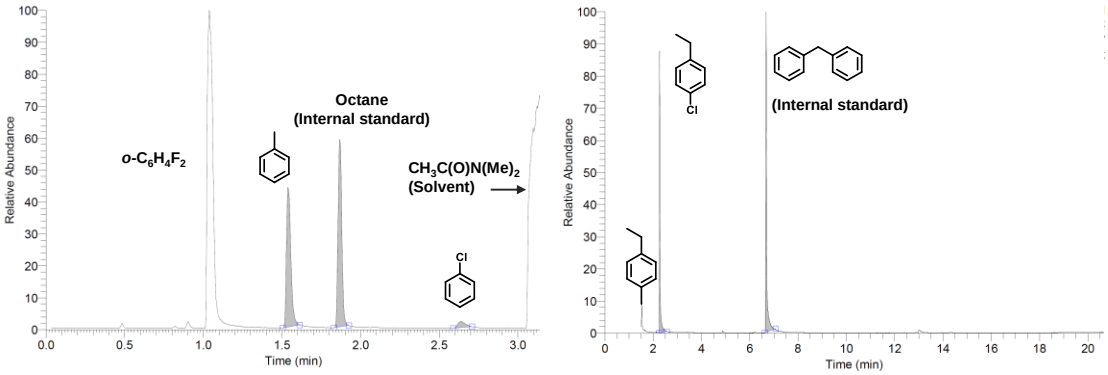
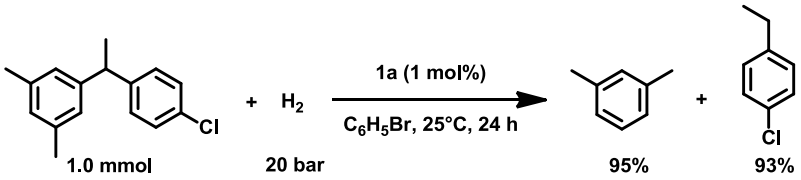


Fig. S16. GC data for hydrodealkylation of 1-(4-chlorophenyl)-1-(4-methylphenyl)ethane

Hydrodealkylation of 1-(4-chlorophenyl)-1-(3,5-dimethylphenyl)ethane



The reaction was conducted according to the general procedure with 1-(4-chlorophenyl)-1-(3,5-dimethylphenyl)ethane (244.3 mg, 0.998 mmol) and **1a** (13.0 mg, 0.010 mmol) in bromobenzene (0.5 mL) under H_2 atmosphere (20 bar) at 25 ℃ for 24 h. GC/MS analysis of the reaction mixture showed complete conversion of 1-(4-chlorophenyl)-1-(3,5-dimethylphenyl)ethane and formation of *m*-xylene (106 m/z) in 95% yield and 4-chloro(ethylbenzene) (m/z 140) in 93% yield with diphenylmethane (142.8 mg, 0.849 mmol) as internal standards.

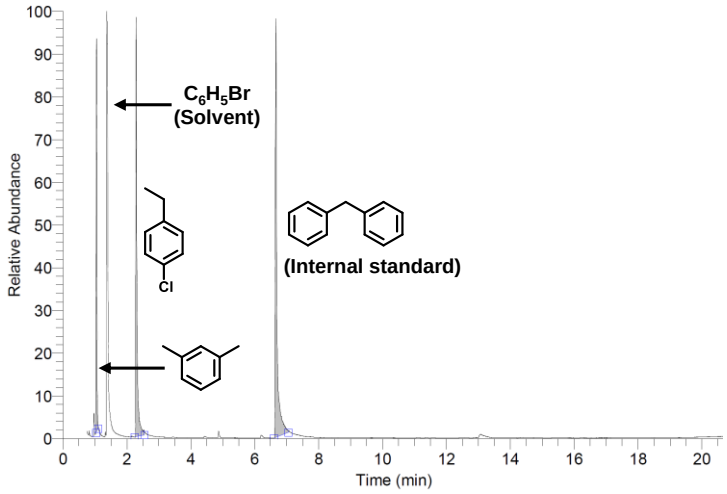
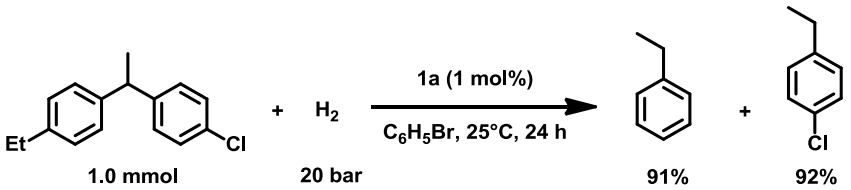


Fig. S17. GC data for hydrodealkylation of 1-(4-chlorophenyl)-1-(3,5-dimethylphenyl)ethane

Hydrodealkylation of 1-(4-chlorophenyl)-1-(4-ethylphenyl)ethane



The reaction was conducted according to the general procedure with 1-(4-chlorophenyl)-1-(4-ethylphenyl)ethane (244.6 mg, 0.999 mmol) and **1a** (13.4 mg, 0.010 mmol) in bromobenzene (0.5 mL) under H_2 atmosphere (20 bar) at 25 ℃ for 24 h. GC/MS analysis of the reaction mixture showed complete conversion of 1-(4-chlorophenyl)-1-(4-ethylphenyl)ethane and formation of ethylbenzene (106 m/z) in 91% yield and 4-chloro(ethylbenzene) (m/z 140) in 92% yield with octane (100.9 mg, 0.883 mmol) and diphenylmethane (137.3 mg, 0.816 mmol) as internal standards.

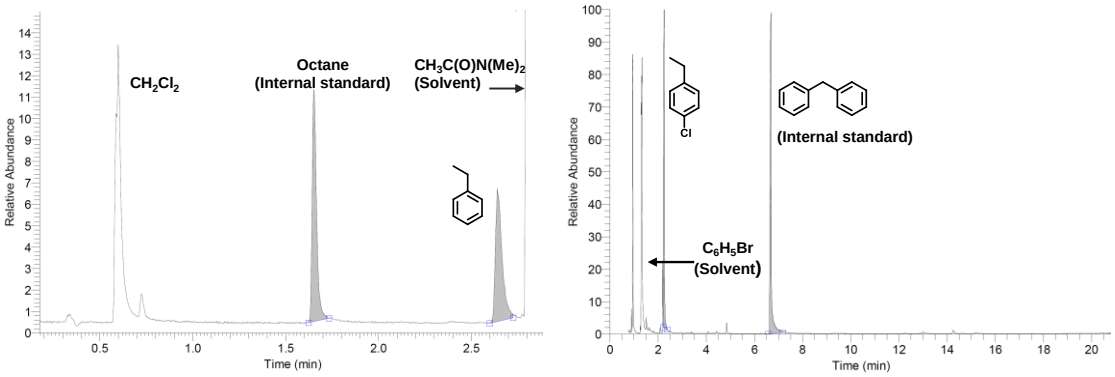
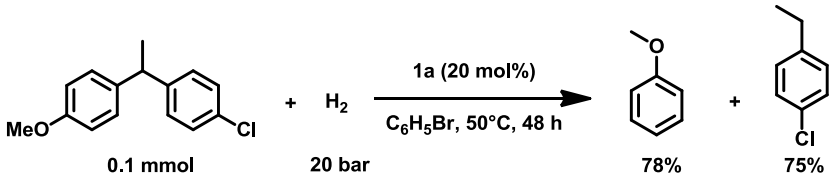


Fig. S18. GC data for hydrodealkylation of 1-(4-chlorophenyl)-1-(4-ethylphenyl)ethane

Hydrodealkylation of 1-(4-chlorophenyl)-1-(4-methoxyphenyl)ethane



The reaction was conducted according to the general procedure with 1-(4-chlorophenyl)-1-(4-methoxyphenyl)ethane (23.9 mg, 0.097 mmol) and **1a** (26.4 mg, 0.021 mmol) in bromobenzene (0.25 mL) under H_2 atmosphere (20 bar) at 50 ℃ for 48 h. GC/MS analysis of the reaction mixture showed formation of anisole (108 m/z) in 78% yield and 4-chloro(ethylbenzene) (m/z 140) in 75% yield with diphenylmethane (17.4 mg, 0.103 mmol) as internal standard.

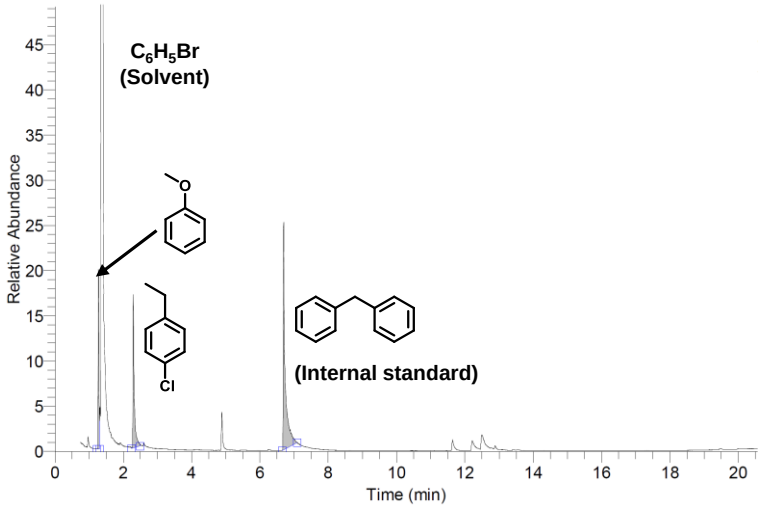
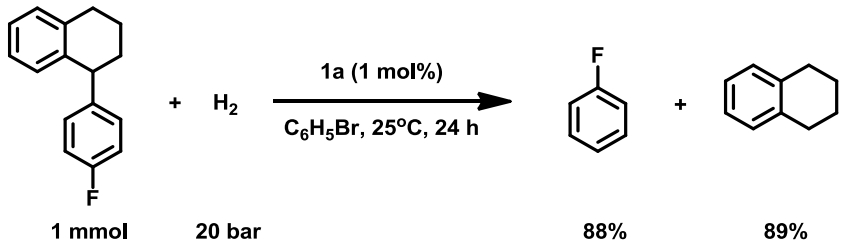


Fig. S19. GC data for hydrodealkylation of 1-(4-chlorophenyl)-1-(4-methoxyphenyl)ethane

Hydrodealkylation of 1-(4-fluorophenyl)-1,2,3,4-tetrahydronaphthalene



The reaction was conducted according to the general procedure with 1-(4-fluorophenyl)-1,2,3,4-tetrahydronaphthalene (226.8 mg, 1.002 mmol) and **1a** (12.7 mg, 0.010 mmol) in bromobenzene (0.5 mL) under H_2 atmosphere (20 bar) at 25 ℃ for 24 h. GC/MS analysis of the reaction mixture showed formation of fluorobenzene (96 m/z) in 88% yield and tetrahydronaphthalene (132 m/z) in 89% yield with octane (113.3 mg, 0.992 mmol) and diphenylmethane (144.0 mg, 0.856 mmol) as internal standards.

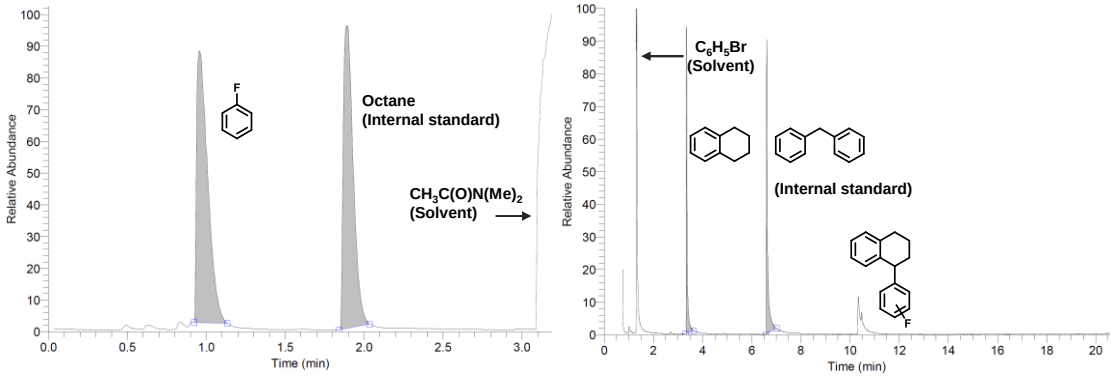
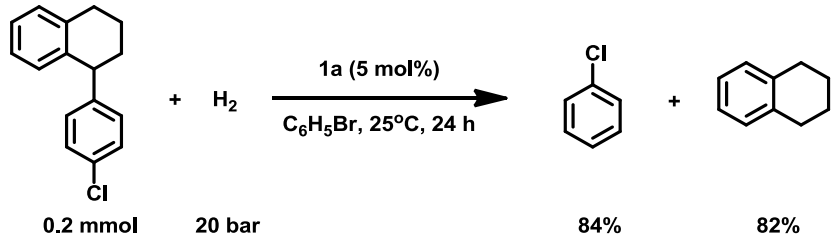


Fig. S20. GC data for hydrodealkylation of 1-(4-fluorophenyl)-1,2,3,4-tetrahydronaphthalene

Hydrodealkylation of 1-(4-chlorophenyl)-1,2,3,4-tetrahydronaphthalene



The reaction was conducted according to the general procedure with 1-(4-chlorophenyl)tetrahydronaphthalene (49.5 mg, 0.204 mmol) and **1a** (12.3 mg, 0.010 mmol) in bromobenzene (0.25 mL) under H_2 atmosphere (20 bar) at 25 ℃ for 24 h. GC/MS analysis of the reaction mixture showed formation of chlorobenzene (112 m/z) in 84% yield and tetrahydronaphthalene (132 m/z) in 82% yield with octane (19.7 mg, 0.172 mmol) and diphenylmethane (36.6 mg, 0.218 mmol) as internal standards.

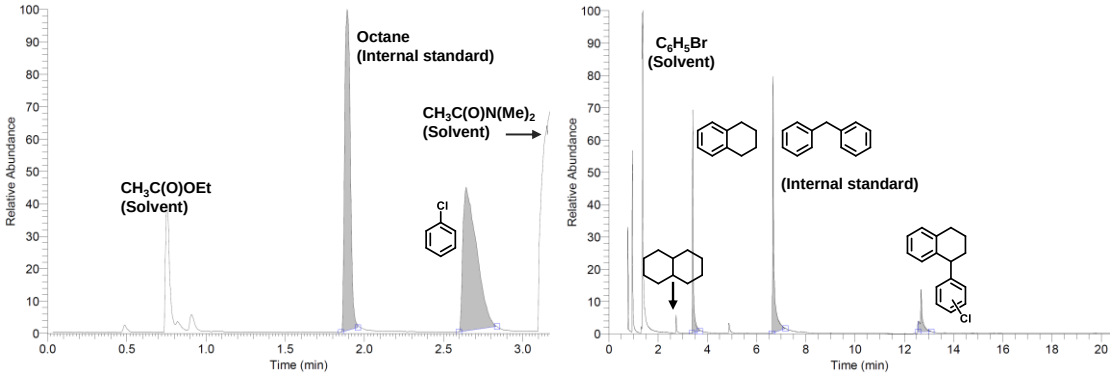


Fig. S21. GC data for hydrodealkylation of 1-(4-chlorophenyl)-1,2,3,4-tetrahydronaphthalene

Hydrodealkylation of 1-(4-bromophenyl)-1,2,3,4-tetrahydronaphthalene

The reaction was conducted according to the general procedure with 1-(4-bromophenyl)-1,2,3,4-tetrahydronaphthalene (60.6 mg, 0.211 mmol) and **1a** (13.8 mg, 0.011 mmol) in bromobenzene (0.25 mL) under H_2 atmosphere (20 bar) at 25 ℃ for 24 h. GC/MS analysis of the reaction mixture showed formation of bromobenzene (157 m/z) in 72% yield and tetrahydronaphthalene (132 m/z) in 68% yield with diphenylmethane (31.1 mg, 0.185 mmol) as internal standard.

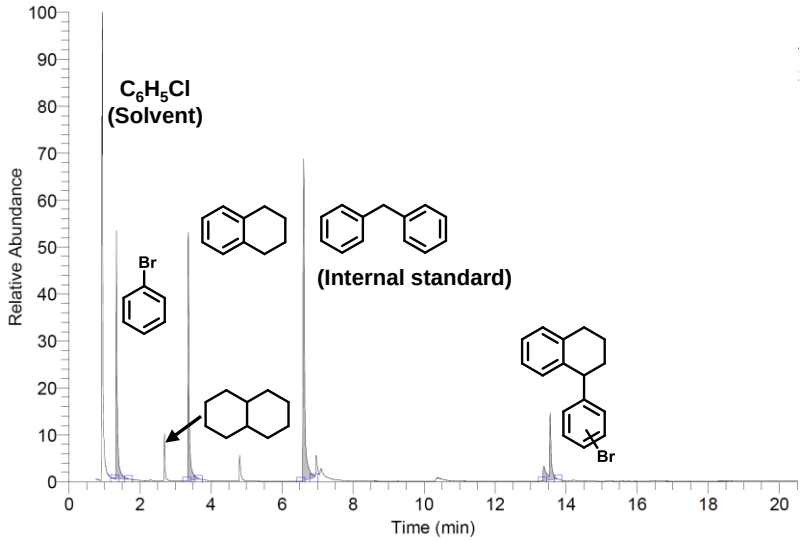
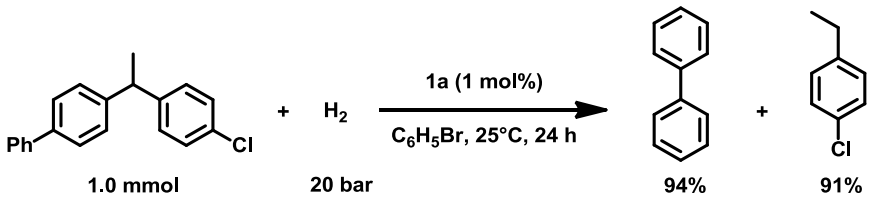


Fig. S22. GC data for hydrodealkylation of 1-(4-bromophenyl)-1,2,3,4-tetrahydronaphthalene

Hydrodealkylation of 1-(4-chlorophenyl)-1-(4-phenylphenyl)ethane



The reaction was conducted according to the general procedure with 1-(4-chlorophenyl)-1-(4-phenylphenyl)ethane (294.4 mg, 1.005 mmol) and **1a** (13.4 mg, 0.010 mmol) in bromobenzene (0.5 mL) under H_2 atmosphere (20 bar) at 25 ℃ for 24 h. GC/MS analysis of the reaction mixture showed complete conversion of 1-(4-chlorophenyl)-1-(4-phenylphenyl)ethane and formation of biphenyl (154 m/z) in 94% yield and 4-chloro(ethylbenzene) (m/z 140) in 91% yield with diphenylmethane (131.8 mg, 0.783 mmol) as internal standard. The mixture was then dried under reduced pressure and biphenyl was purified by chromatography with petroleum ether as eluent (white solid, 142.2 mg, 92% yield).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.61 (d, *J* = 7.7 Hz, 4H), 7.46 (t, *J* = 7.1 Hz, 4H), 7.36 (t, *J* = 7.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 141.37, 128.89, 127.38, 127.29.

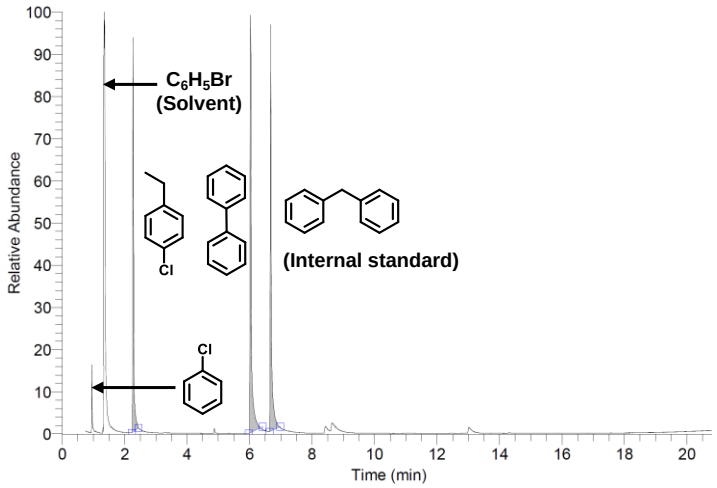
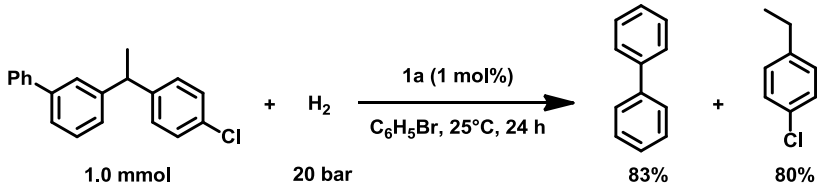


Fig. S23. GC data for hydrodealkylation of 1-(4-chlorophenyl)-1-(4-phenylphenyl)ethane

Hydrodealkylation of 1-(4-chlorophenyl)-1-(3-phenylphenyl)ethane



The reaction was conducted according to the general procedure with 1-(4-chlorophenyl)-1-(3-phenylphenyl)ethane (293.1 mg, 1.001 mmol) and **1a** (12.8 mg, 0.010 mmol) in bromobenzene (0.5 mL) under H_2 atmosphere (20 bar) at 25 ℃ for 24 h. GC/MS analysis of the reaction mixture showed complete conversion of 1-(4-chlorophenyl)-1-(3-phenylphenyl)ethane and formation of biphenyl (154 m/z) in 83% yield and 4-chloro(ethylbenzene) (m/z 140) in 80% yield with diphenylmethane (154.9 mg, 0.921 mmol) as internal standard. The mixture was then dried under reduced pressure and biphenyl was purified by chromatography with petroleum ether as eluent (white solid, 120.0 mg, 78% yield).

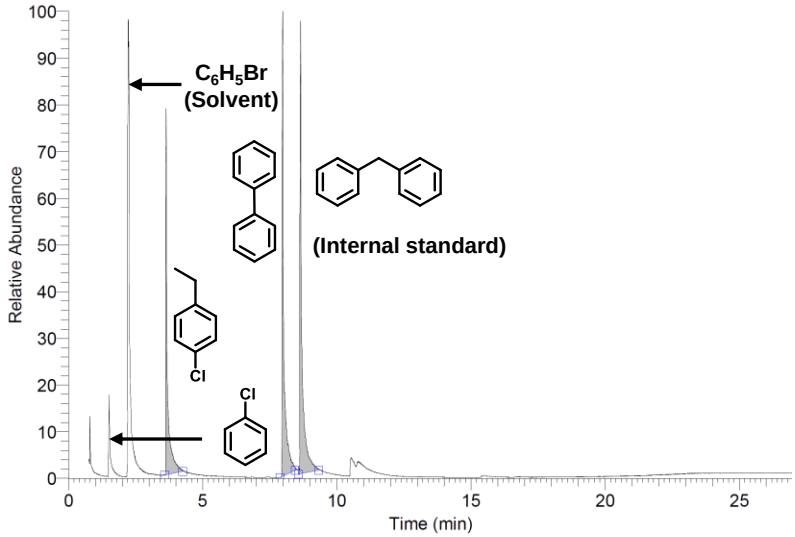
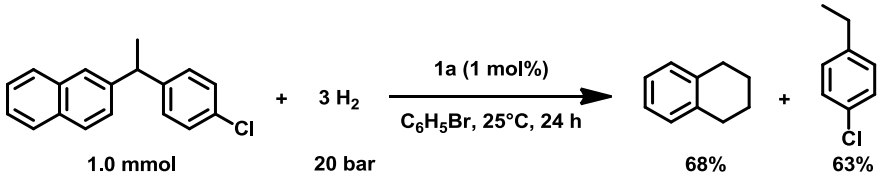


Fig. S24. GC data for hydrodealkylation of 1-(4-chlorophenyl)-1-(3-phenylphenyl)ethane

Hydrodealkylation of 1-(4-chlorophenyl)-1-(2-naphthyl)ethane



The reaction was conducted according to the general procedure with 1-(4-chlorophenyl)-1-(2-naphthyl)ethane (267.1 mg, 1.001 mmol) and **1a** (13.5 mg, 0.011 mmol) in bromobenzene (0.5 mL) under H_2 atmosphere (20 bar) at 25 ℃ for 24 h. GC/MS analysis of the reaction mixture showed formation of tetrahydronaphthalene (132 m/z) in 68% yield and 4-chloro(ethylbenzene) (m/z 140) in 63% yield with diphenylmethane (129.1 mg, 0.767 mmol) as internal standard.

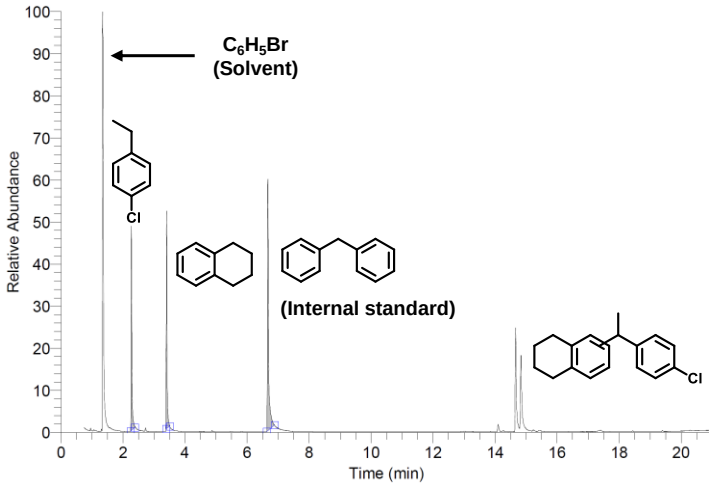
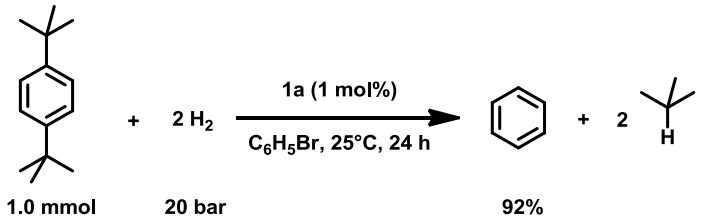


Fig. S25. GC data for hydrodealkylation of 1-(4-chlorophenyl)-1-(2-naphthyl)ethane

Hydrodealkylation of 1,4-di-tert-butylbenzene



The reaction was conducted according to the general procedure with 1,4-di-tert-butylbenzene (190.2 mg, 0.999 mmol) and **1a** (13.2 mg, 0.010 mmol) in bromobenzene (0.5 mL) under H_2 atmosphere (20 bar) at 25 ℃ for 24 h. GC/MS analysis of the reaction mixture showed complete conversion of 1,4-di-tert-butylbenzene and formation of benzene (78 m/z) in 92% yield with octane (109.1 mg, 0.955 mmol) as internal standard. iso-Butane (58 m/z) was detected in the overhead gas by GC-MS.

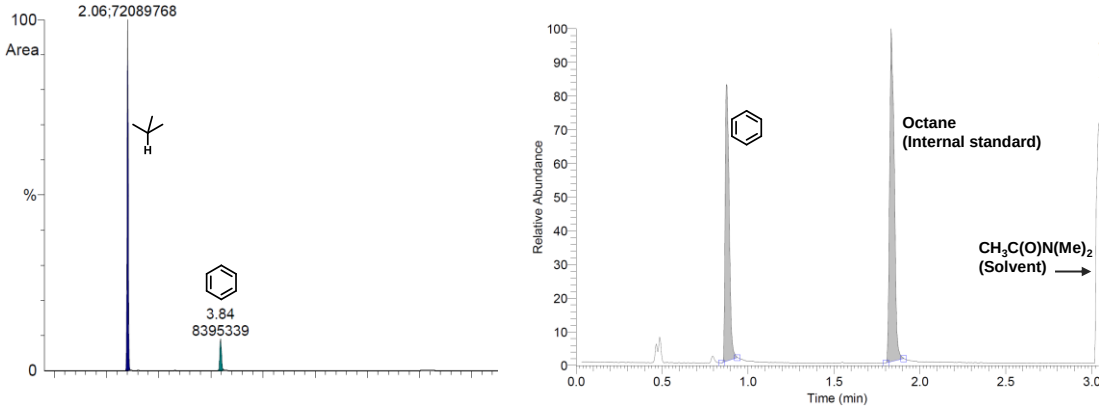
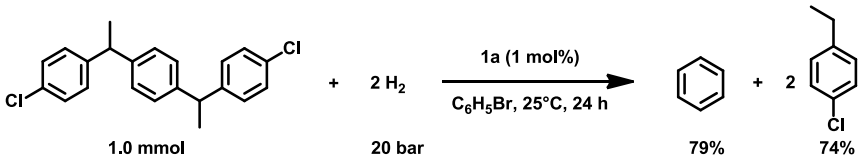


Fig. S26. GC data for hydrodealkylation of 1,4-di-tert-butylbenzene

Hydrodealkylation of 1,4-bis(1-(4-chlorophenyl)ethyl)benzene



The reaction was conducted according to the general procedure with 1,4-bis(1-(4-chlorophenyl)ethyl)benzene (357.8 mg, 1.007 mmol) and **1a** (13.6 mg, 0.011 mmol) in bromobenzene (0.5 mL) under H_2 atmosphere (20 bar) at 25 ℃ for 24 h. GC/MS analysis of the reaction mixture showed complete conversion of 1,4-bis(1-(4-chlorophenyl)ethyl)benzene and formation of benzene (78 m/z) in 79% yield and 4-chloro(ethylbenzene) (m/z 140) in 74% yield with octane (113.9 mg, 0.997 mmol) and diphenylmethane (246.8 mg, 1.467 mmol) as internal standards.

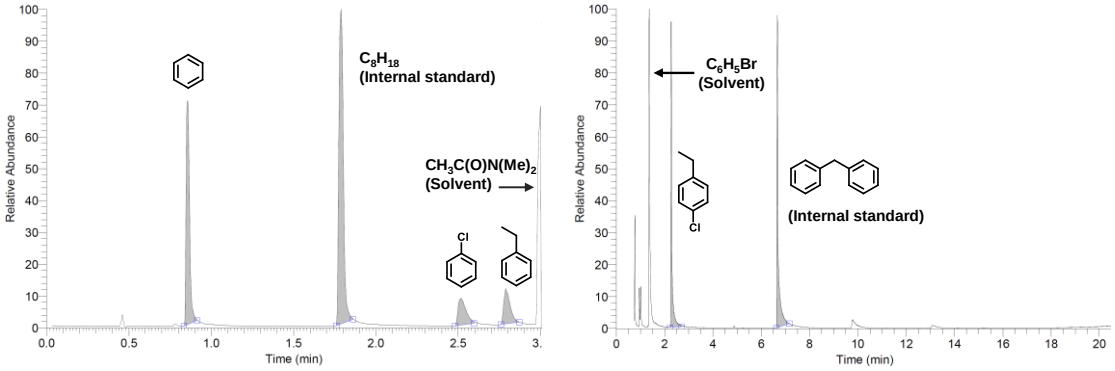
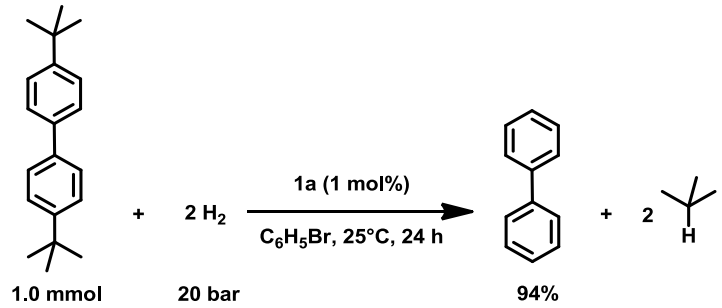


Fig. S27. GC data for hydrodealkylation of 1,4-bis(1-(4-chlorophenyl)ethyl)benzene

Hydrodealkylation of 4,4'-di-tert-butylbiphenyl



The reaction was conducted according to the general procedure with 4,4'-di-tert-butylbiphenyl (266.9 mg, 1.002 mmol) and **1a** (12.4 mg, 0.010 mmol) in bromobenzene (0.5 mL) under H_2 atmosphere (20 bar) at 25 ℃ for 24 h. GC/MS analysis of the reaction mixture showed complete conversion of 4,4'-di-tert-butylbiphenyl and formation of biphenyl (154 m/z) in 94% yield with benzophenone (153.5 mg, 0.842 mmol) as internal standard. iso-Butane (58 m/z) was detected in the overhead gas by GC-MS.

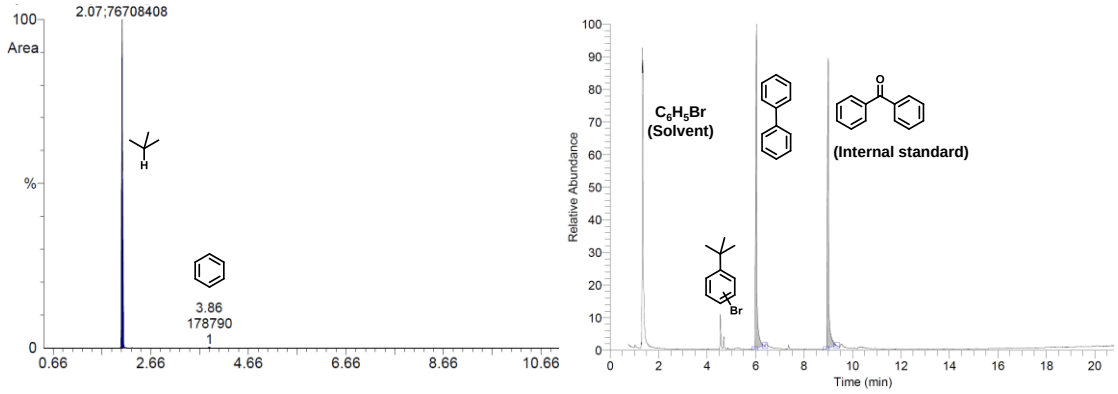
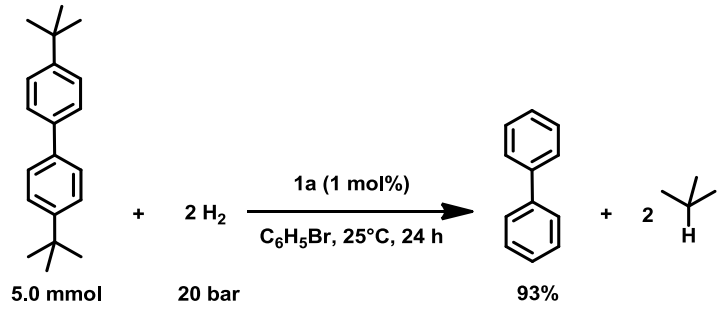


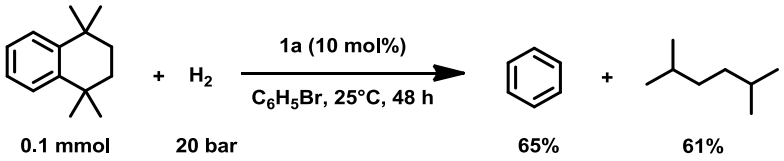
Fig. S28. GC data for hydrodealkylation of 4,4'-di-tert-butylbiphenyl

Gram-scale reaction:



The reaction was conducted according to the general procedure with 4,4′-di-tert-butylbiphenyl (1.333 g, 5.004 mmol) and **1a** (64.8 mg, 0.051 mmol) in bromobenzene (2.5 mL) under H_2 atmosphere (20 bar) at 25 ℃ for 24 h. After purification by silica gel flash column chromatography, biphenyl was obtained as a white solid (718.0 mg, 4.662 mmol) in 93% yield.

Hydrodealkylation of 1,2,3,4-tetrahydro-1,1,4,4-tetramethylnaphthalene



The reaction was conducted according to the general procedure with 1,2,3,4-tetrahydro-1,1,4,4-tetramethylnaphthalene (37.0 mg, 0.196 mmol) and **1a** (25.7 mg, 0.020 mmol) in bromobenzene (0.25 mL) under H_2 atmosphere (20 bar) at 25 ℃ for 48 h. GC/MS analysis of the reaction mixture showed formation of benzene (78 m/z) in 65% yield and 2,5-dimethyhexane (114 m/z) in 61% yield with octane (109.1 mg, 0.955 mmol) as internal standard.

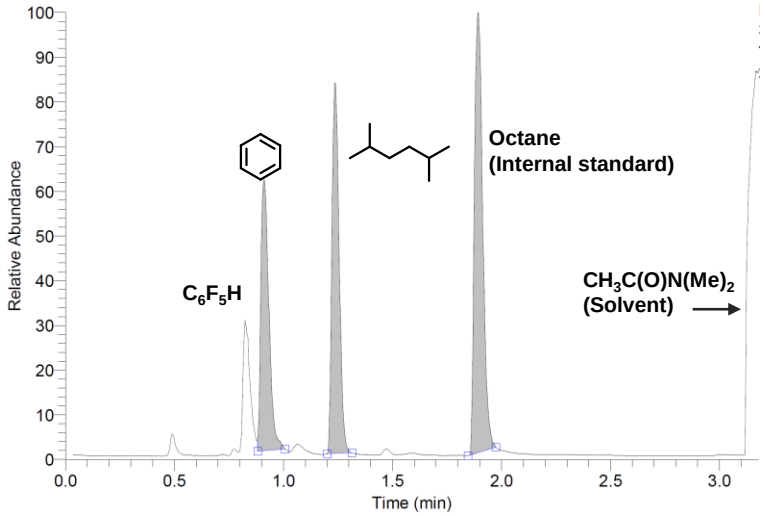
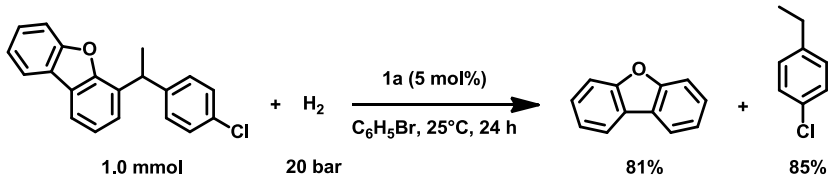


Fig. S29. GC data for hydrodealkylation of 1,2,3,4-tetrahydro-1,1,4,4-tetramethylnaphthalene

Hydrodealkylation of 1-(4-chlorophenyl)-1-(4-dibenzofuryl)ethane



The reaction was conducted according to the general procedure with 1-(4-chlorophenyl)-1-(4-dibenzofuryl)ethane (309.1 mg, 1.008 mmol) and **1a** (66.0 mg, 0.052 mmol) in bromobenzene (1 mL) under H_2 atmosphere (20 bar) at 25 ℃ for 24 h. GC/MS analysis of the reaction mixture showed formation of dibenzofuran (168 m/z) in 81% yield and 4-chloro(ethylbenzene) (m/z 140) in 85% yield with diphenylmethane (141.3 mg, 0.840 mmol) as internal standard. The mixture was then dried under reduced pressure and dibenzofuran was purified by chromatography with petroleum ether as eluent (white solid, 122.0 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.00 (d, *J* = 7.7 Hz, 2H), 7.65 (d, *J* = 8.1 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.9 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 156.30, 127.25, 124.34, 122.81, 120.78, 111.79.

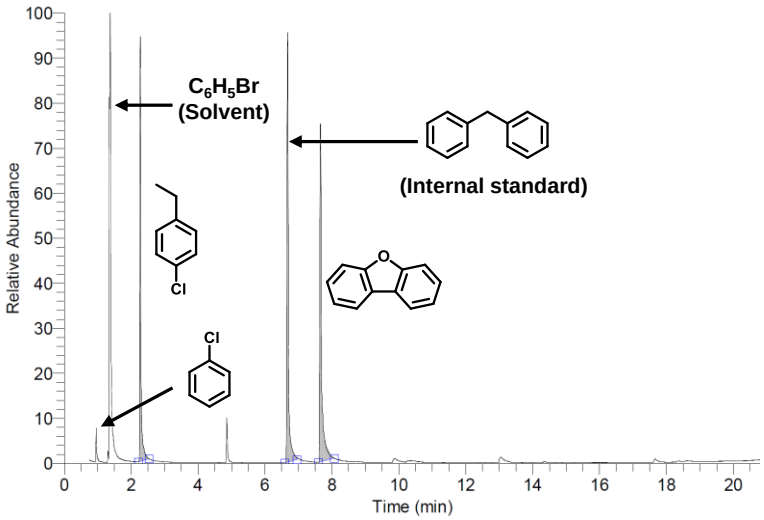
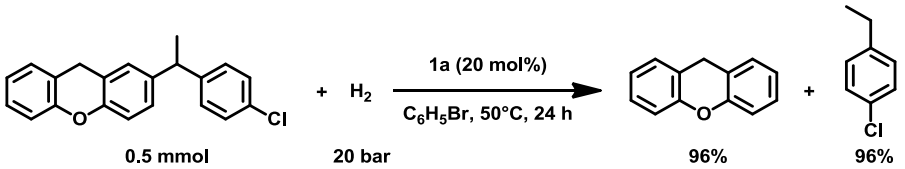


Fig. S30. GC data for hydrodealkylation of 1-(4-chlorophenyl)-1-(4-dibenzofuryl)ethane

Hydrodealkylation of 1-(4-chlorophenyl)-1-(3-xanthyl)ethane



The reaction was conducted according to the general procedure with 1-(4-chlorophenyl)-1-(3-xanthryl)ethane (160.9 mg, 0.502 mmol) and **1a** (124.0 mg, 0.097 mmol) in bromobenzene (0.5 mL) under H_2 atmosphere (20 bar) at 25 ℃ for 24 h. GC/MS analysis of the reaction mixture showed complete conversion of 1-(4-chlorophenyl)-1-(3-xanthryl)ethane and formation of xanthene (182 m/z) in 96% yield and 4-chloroethylbenzene (m/z 140) in 96% yield with diphenylmethane (70.5 mg, 0.419 mmol) as internal standard. The mixture was then dried under reduced pressure and xanthene was purified by chromatography with petroleum ether as eluent (white solid, 84.0 mg, 92% yield).

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.23-7.15 (m, 4H), 7.07-7.00 (m, 4H), 4.06 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 152.10, 129.06, 127.78, 123.09, 120.71, 116.61, 28.01.

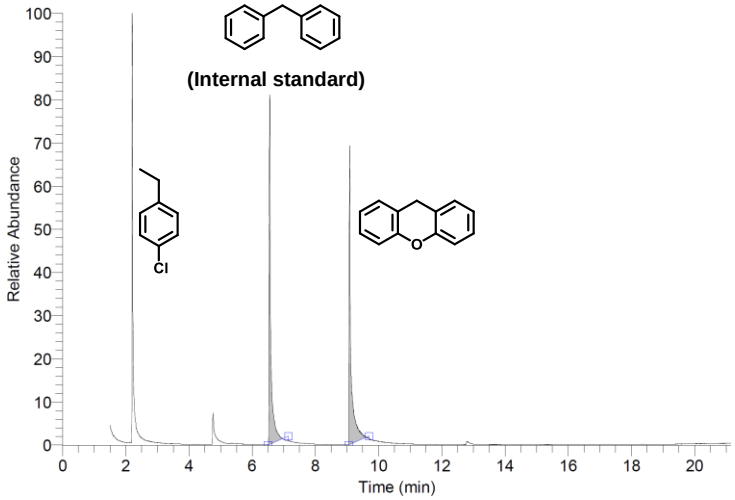


Fig. S31. GC data for hydrodealkylation of 1-(4-chlorophenyl)-1-(3-xanthyl)ethane

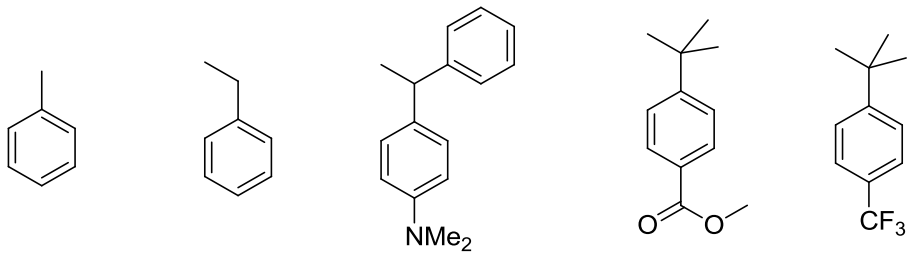


Fig. S32. Substrates with less than 1% conversion under the standard catalytic conditions

4. Experimental procedure for kinetic study of the hydrodealkylation of 6

Inside of a N_2-filled glovebox, **1a** and **6** (0.075 mmol) were dissolved in C_6D_5Br (0.25 mL) and transferred into a NMR tube with a J-Young valve. This NMR tube was taken outside of the glovebox and cooled to -196 ℃ by immersion into a liquid nitrogen bath. Then the NMR tube was connected to a vacuum line for about 1 min. After disconnection with the vacuum line, the NMR tube was removed from the liquid nitrogen bath and warmed to room temperature. This "free-pump-thaw" process was repeated three times. Afterwards, the NMR tube was again cooled to -196 ℃ and connected to a H_2 or D_2 gas cylinder for about 1 min. Subsequently, the NMR tube was warmed to room temperature and inserted into the NMR machine in which the console temperature reached the target temperature. The concentration of **6** was determined by the integration ratio of **6** and ethylbenzene.

Determination of the order of 6

Table S2. Data from monitoring of hydrodealkylation of **6** (0.3 M) in C_6D_5Br with **1a** (0.060 M) under H_2 (6 bar) at 25 ℃

t (s)	3600	12300	20100	26160	31680	38100	43800	57300
[**6**] (M)	0.281	0.232	0.212	0.178	0.166	0.156	0.134	0.104
ln[**6**]	-1.271	-1.461	-1.549	-1.727	-1.796	-1.858	-2.009	-2.266

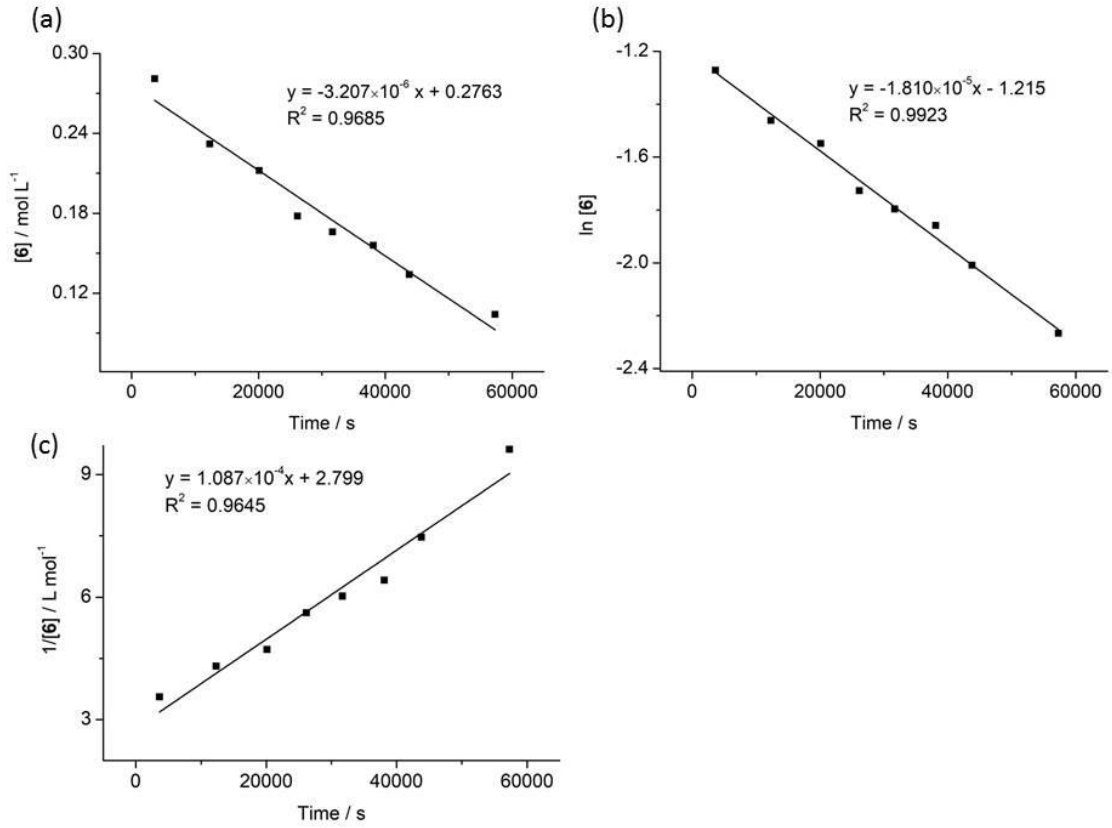


Fig. S33. a) Plot according to zero order of **6**. b) Plot according to first order of **6**. C) b) Plot according to second order of **6**.

Determination of the order of 1a

Table S3. Data from monitoring of hydrodealkylation of **6** (0.3 M) in C_6D_5Br with **1a** (0.045 M) under H_2 (6 bar) at 25 ℃

t (s)	4500	14100	20400	29880	41880
[**6**] (M)	0.271	0.239	0.225	0.182	0.161
ln[**6**]	-1.306	-1.431	-1.492	-1.704	-1.826

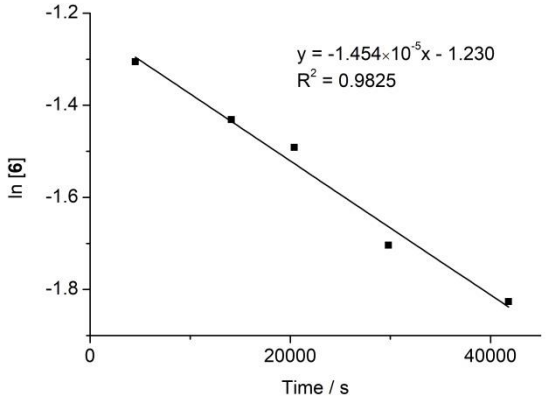


Fig. S34. Pseudo-first-order plot of hydrodealkylation of **6** with 15 mol% of **1a** under H_2 (6 bar) at 25 ℃

Table S4. Data from monitoring of hydrodealkylation of **6** (0.3 M) in C_6D_5Br with **1a** (0.030 M) under H_2 (6 bar) at 25 ℃

t (s)	4620	13380	21420	27180	29100	36900
[**6**] (M)	0.288	0.267	0.243	0.236	0.229	0.210
ln[**6**]	-1.245	-1.321	-1.415	-1.444	-1.474	-1.561

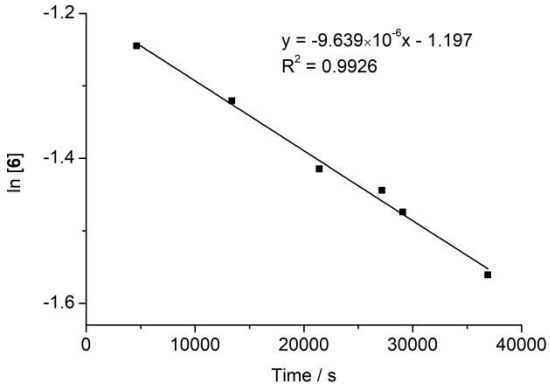


Fig. S35. Pseudo-first-order plot of hydrodealkylation of **6** with 10 mol% of **1a** under H_2 (6 bar) at 25 ℃

Table S5. Rate constants of hydrodealkylation of **6** (0.3 M) in C_6D_5Br with varying concentration of **1a** under H_2 (6 bar) at 25 ℃

[**1a**] (M)	ln[**1a**]	k_{obs} ($\times 10^{-5}$ s^{-1})	ln k_{obs}
0.030	-3.507	0.964	-11.55
0.045	-3.101	1.454	-11.14
0.060	-2.813	1.810	-10.92

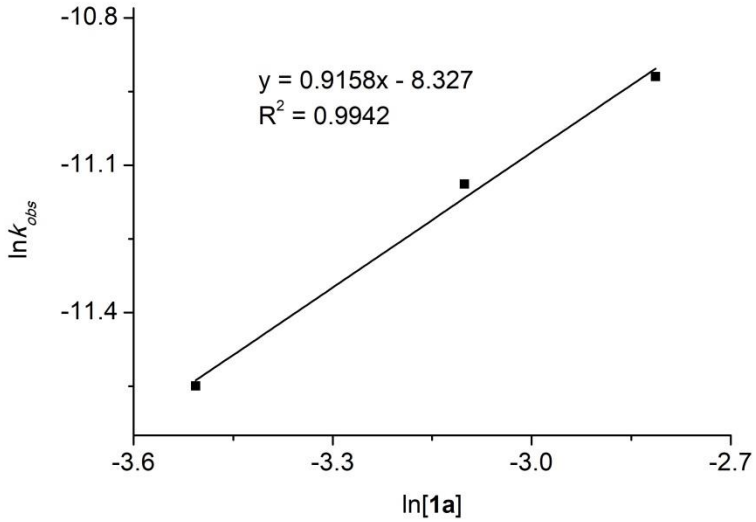


Fig. S36. Plot of lnk_{obs} vs ln[**1a**] for hydrodealkylation of **6** under H_2 (6 bar) at 25 ℃

Determination of the order of H_2

Table S6. Data from monitoring of hydrodealkylation of **6** (0.30 M) in C_6D_5Br with **1a** (0.060 M) under H_2 (1.5 bar) at 80 ℃

t (s)	240	480	720	960	1200	1440
[**6**] (M)	0.267	0.264	0.261	0.258	0.255	0.253
ln[**6**]	-1.321	-1.332	-1.343	-1.355	-1.366	-1.374

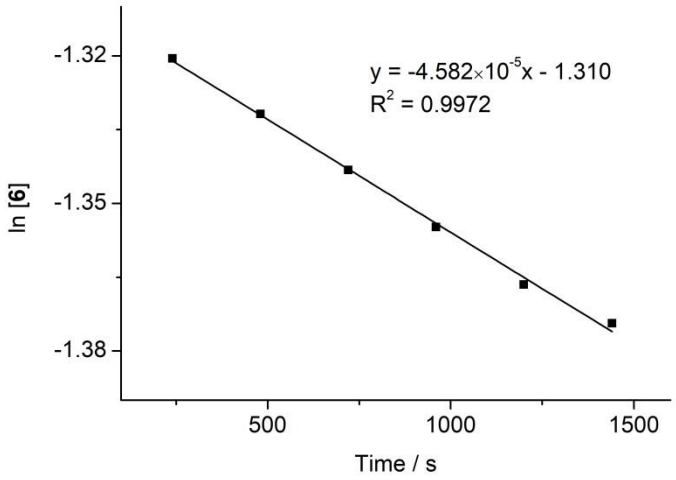


Fig. S37. Pseudo-first-order plot of hydrodealkylation of **6** with 20 mol% of **1a** at 80 ℃ under 1.5 bar of H_2

Table S7. Data from monitoring of hydrodealkylation of **6** (0.30 M) in C_6D_5Br with **1a** (0.060 M) under H_2 (1.8 bar) at 80 ℃

t (s)	240	480	720	960	1200	1440
[**6**] (M)	0.269	0.265	0.261	0.258	0.255	0.251
ln[**6**]	-1.313	-1.328	-1.343	-1.355	-1.366	-1.382

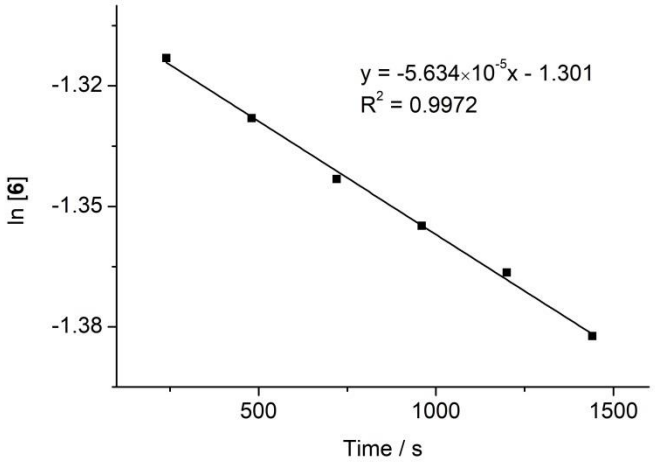


Fig. S38. Pseudo-first-order plot of hydrodealkylation of **6** with 20 mol% of **1a** at 80 ℃ under 1.8 bar of H_2

Table S8. Data from monitoring of hydrodealkylation of **6** (0.30 M) in C_6D_5Br with **1a** (0.060 M) under H_2 (2.3 bar) at 80 ℃

t (s)	240	480	720	960	1200	1440
[**6**] (M)	0.264	0.260	0.255	0.251	0.247	0.242
ln[**6**]	-1.332	-1.347	-1.366	-1.382	-1.398	-1.419

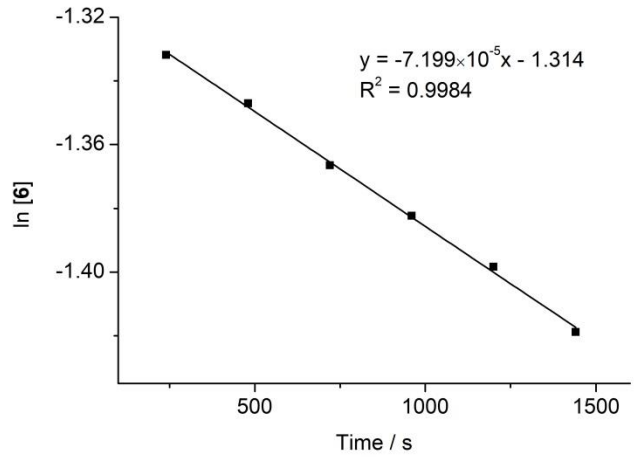


Fig. S39. Pseudo-first-order plot of hydrodealkylation of **6** with 20 mol% of **1a** at 80 ℃ under 2.3 bar of H_2

Table S9. Data from monitoring of hydrodealkylation of **6** (0.30 M) in C_6D_5Br with **1a** (0.060 M) under H_2 (5.9 bar) at 80 ℃

t (s)	300	600	900	1200	1500	1800
[**6**] (M)	0.234	0.223	0.211	0.199	0.187	0.175
ln[**6**]	-1.452	-1.501	-1.556	-1.614	-1.677	-1.743

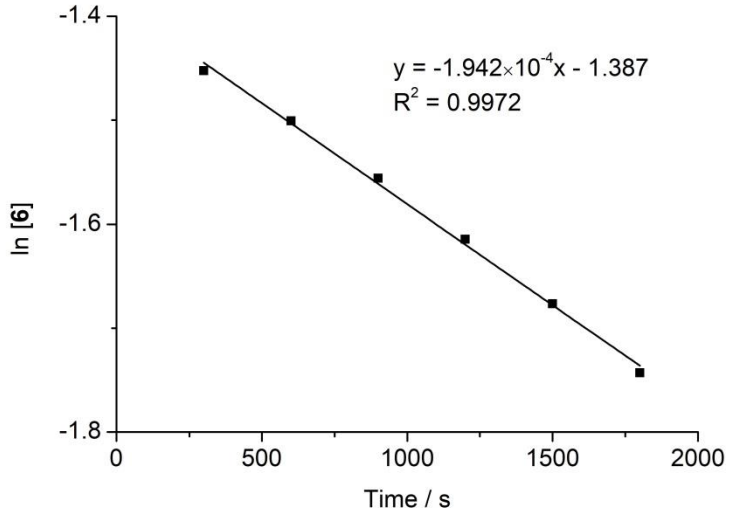


Fig. S40. Pseudo-first-order plot of hydrodealkylation of **6** with 20 mol% of **1a** at 80 ℃ under 5.9 bar of H_2

Table S10. Rate constants of hydrodealkylation of **6** (0.30 M) in C_6D_5Br with **1a** (0.060 M) under varying pressue of H_2 at 80 ℃

P_{H2} ($\times10^5$ Pa)	$\ln P_{H2}$	$k_{obs}/(\times10^{-5}\ s^{-1})$	$\ln k_{obs}$
1.5	11.92	4.582	-9.991
1.8	12.10	5.634	-9.784
2.3	12.35	7.199	-9.539
5.9	13.28	19.42	-8.547

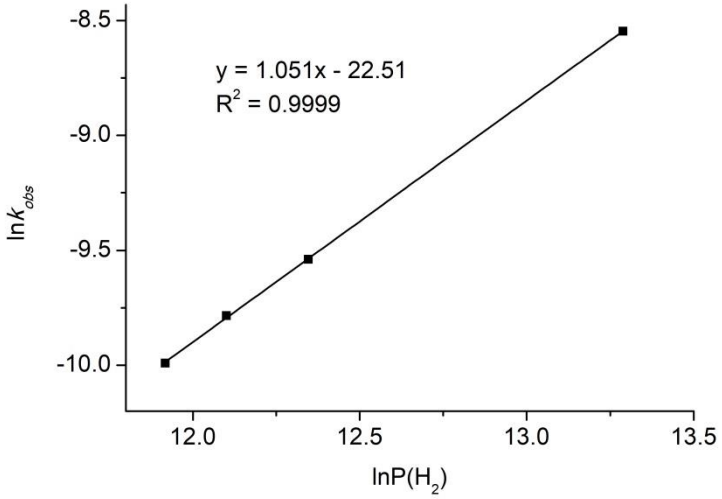


Fig. S41. Plot of $\ln k_{obs}$ vs $\ln P_{H2}$ for hydrodealkylation of **6** with 20 mol% of **1a** at 80 ℃

Determination of the activation parameters

Table S11. Data from monitoring of hydrodealkylation of **6** (0.30 M) in C_6D_5Br with **1a** (0.060 M) under H_2 (6 bar) at 50 ℃

t (s)	420	840	1260	1680	2100
[**6**] (M)	0.275	0.273	0.271	0.269	0.267
ln[**6**]	-1.291	-1.298	-1.306	-1.313	-1.321

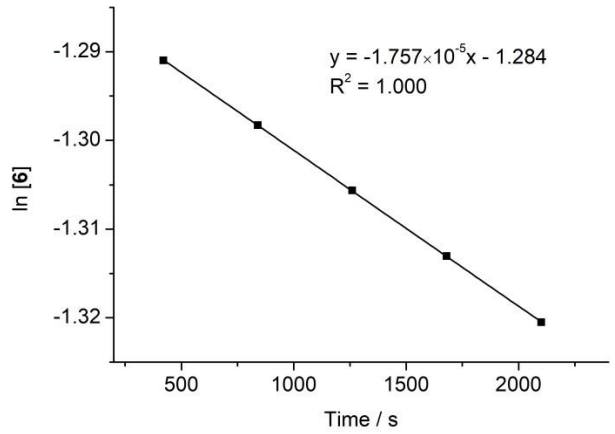


Fig. S42. Pseudo-first-order plot of hydrodealkylation of **6** with 20 mol% of **1a** at 50 ℃ under 6 bar of H_2

Table S12. Data from monitoring of hydrodealkylation of **6** (0.30 M) in C_6D_5Br with **1a** (0.060 M) under H_2 (6 bar) at 60 ℃

t (s)	300	600	900	1200	1500	1800
[**6**] (M)	0.266	0.264	0.263	0.260	0.258	0.256
ln[**6**]	-1.324	-1.332	-1.336	-1.347	-1.355	-1.363

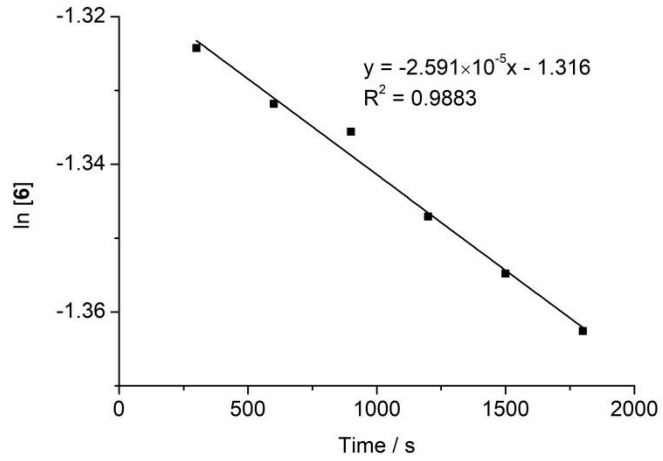


Fig. S43. Pseudo-first-order plot of hydrodealkylation of **6** with 20 mol% of **1a** at 60 ℃ under 6 bar of H_2

Table S13. Data from monitoring of hydrodealkylation of **6** (0.30 M) in C_6D_5Br with **1a** (0.060 M) under H_2 (6 bar) at 70 ℃

t (s)	300	600	900	1200	1500	1800
[**6**] (M)	0.239	0.233	0.228	0.222	0.217	0.211
ln[**6**]	-1.431	-1.457	-1.478	-1.505	-1.528	-1.556

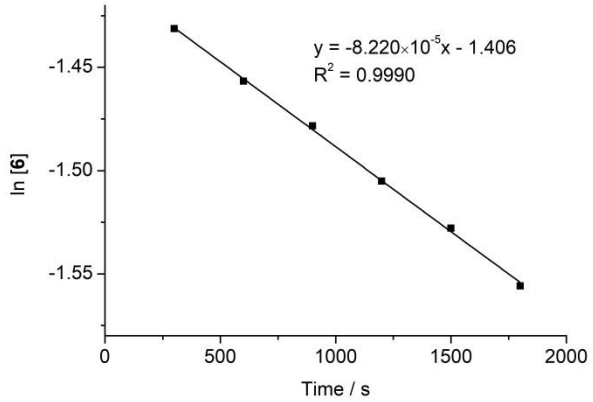


Fig. S44. Pseudo-first-order plot of hydrodealkylation of **6** with 20 mol% of **1a** at 70 ℃ under 6 bar of H_2

Table S14. Data from monitoring of hydrodealkylation of **6** (0.30 M) in C_6D_5Br with **1a** (0.060 M) under H_2 (6 bar) at 80 ℃

t (s)	300	600	900	1200	1500	1800
[**6**] (M)	0.223	0.211	0.199	0.187	0.175	0.163
ln[**6**]	-1.501	-1.556	-1.614	-1.677	-1.743	-1.814

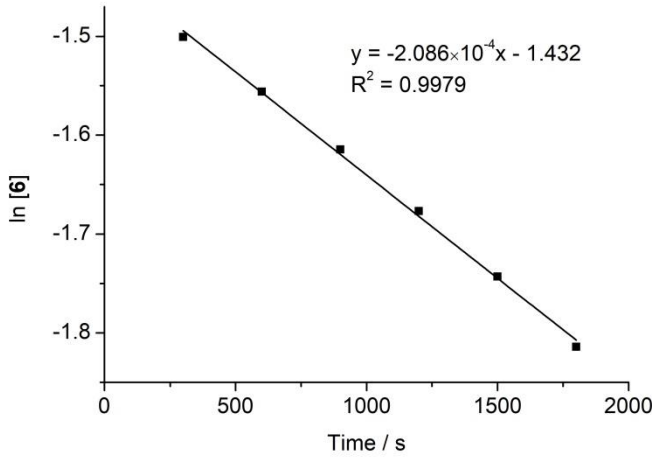


Fig. S45. Pseudo-first-order plot of hydrodealkylation of **6** with 20 mol% of **1a** at 80 ℃ under 6 bar of H_2

Table S15. Data from monitoring of hydrodealkylation of **6** (0.30 M) in C_6D_5Br with **1a** (0.060 M) under H_2 (6 bar) at 90 ℃

t (s)	240	480	720	960	1200	1440	1680
[**6**] (M)	0.220	0.205	0.188	0.172	0.158	0.142	0.129
ln[**6**]	-1.514	-1.585	-1.671	-1.760	-1.845	-1.952	-2.048

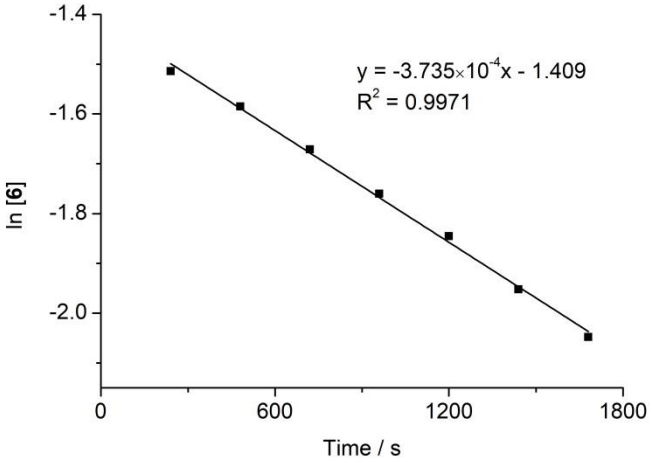


Fig. S46. Pseudo-first-order plot of hydrodealkylation of **6** with 20 mol% of **1a** at 90 ℃ under 6 bar of H_2

Table S16. Rate constants of hydrodealkylation of **6** (0.30 M) in C_6D_5Br with **1a** (0.060 M) under H_2 (6 bar) at varying temperatures

T/ K	k_{obs} ($\times 10^{-5}$ s^{-1})	ln(k_{obs}/T)
323	1.757	-16.73
333	2.591	-16.37
343	8.220	-15.24
353	20.86	-14.34
363	37.35	-13.79

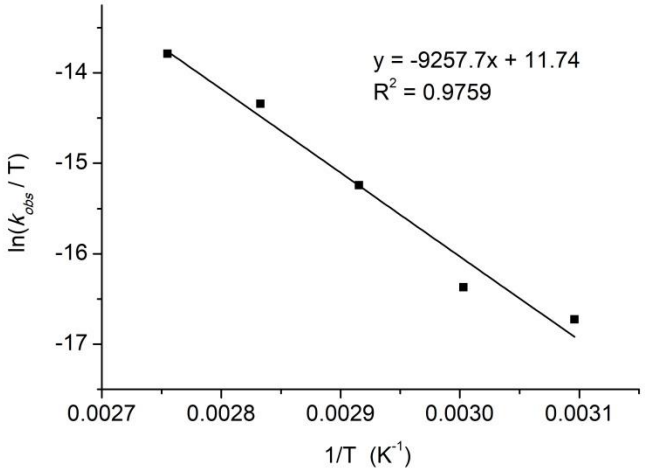


Fig. S47. Eyring plot of hydrodealkylation of **6** in C_6D_5Br with **1a** (0.060 M) under H_2 (6 bar)

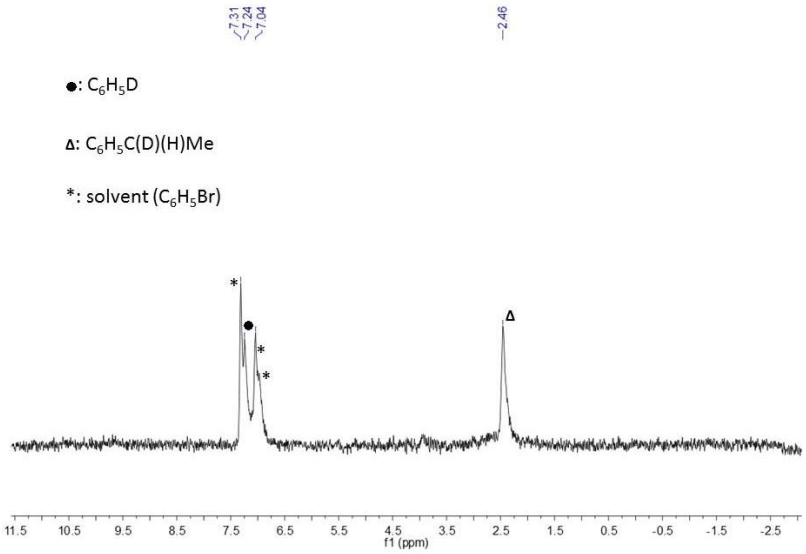


Fig. S48. ^2H NMR spectrum of the mixture of **6** (0.30 M) and **1a** (0.060 M) in C_6H_5Br under D_2 (6 bar) after 24 h

Determination of KIE

Table S17. Data from monitoring of hydrodealkylation of **6** (0.40 M) in C_6D_5Br with **1a** (0.080 M) under H_2 (6 bar) at 25 ℃

t (s)	5400	10200	15000	24480	32160
[**6**] (M)	0.377	0.341	0.295	0.239	0.187
ln[**6**]	-0.975	-1.075	-1.222	-1.433	-1.678

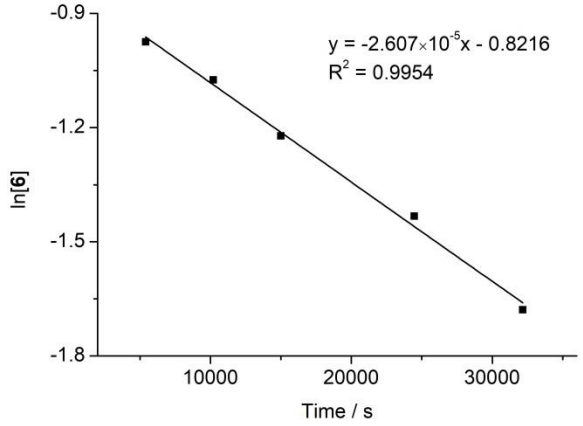


Fig. S49. Pseudo-first-order plot of hydrodealkylation of **6** (0.40 M) in C_6D_5Br with **1a** (0.080 M) under H_2 (6 bar) at 25 ℃

Table S18. Data from monitoring of hydrodealkylation of **6** (0.40 M) in C_6D_5Br with **1a** (0.080 M) under D_2 (6 bar) at 25 ℃

t (s)	3960	8760	13560	23160	30840
[**6**] (M)	0.369	0.339	0.295	0.241	0.204
ln[**6**]	-0.996	-1.083	-1.222	-1.422	-1.590

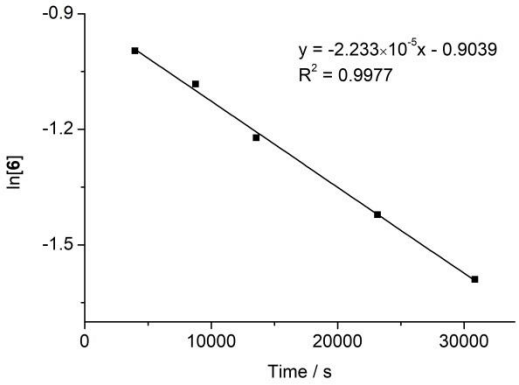


Fig. S50. Pseudo-first-order plot of hydrodealkylation of **6** (0.40 M) in C_6D_5Br with **1a** (0.080 M) under D_2 (6 bar) at 25 ℃

The value of KIE = k_{H2} / k_{D2} = (2.607 $\times 10^{-5}$) / (2.223 $\times 10^{-5}$) = 1.17

5. Determination of Hammett parameter ρ

Inside of a N_2-filled glovebox, **1a** (0.008 mmol) and *para*-substituted (1,2,3,4-tetrahydronaphthalen-1-yl)benzene (0.80 mmol) were dissolved in C_6H_5Br (0.5 mL) and transferred into the well of an autoclave. After the head of the autoclave was assembled, the autoclave was taken out of the glovebox and connected to a H_2 gas cylinder. The connection line was flushed with H_2 three times. Then the autoclave was pressurized to 20 bar of H_2 and allowed to stand at room temperature for certain time (see Tables S19). The autoclave was then cooled to -40 ℃ in a cold ethanol bath for 15 mins, followed by releasing the H_2 pressure. After removing the head of autoclave, diphenylomethane was added into the well of an autoclave as internal standard. The resulting reaction mixture was then subjected to GC/MS analysis. The initial rate was calculated by dividing the concentration of 1,2,3,4-tetrahydronaphthalene with the reaction time.

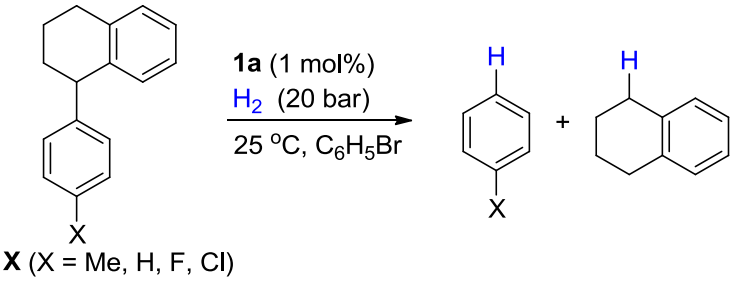


Table S19. Experimental results for Hammett parameter measurement

Entry	X	t (s)	$[C_{10}H_{12}]$ (M)	Initial Rate (M s^{-1})	k_X/k_H	$\log(k_X/k_H)$	σ_p
1	Me	300	0.114	3.80×10^{-4}	2.35	0.371	-0.17
2	H	1800	0.291	1.62×10^{-4}	1	0	0
3	F	3060	0.301	9.84×10^{-5}	0.61	-0.215	0.062
4	Cl	1920	0.078	4.06×10^{-5}	0.25	-0.602	0.227

6. Procedure for borenium-catalyzed hydrogenolysis of polystyrene

6.1 Laboratory-grade polystyrene

Inside of a N_2-filled glovebox, **1a** (64.9 mg, 0.051 mmol), laboratory-grade polystyrene sample (106.2 mg) and 10 mL of *o*-$C_6H_4F_2$ were transferred into the well of an autoclave. After the head of the autoclave was assembled, the autoclave was taken out of the glovebox and connected to a H_2 gas cylinder. The connection line was flushed with H_2 three times. Then the autoclave was pressurized to 5 bars of H_2 and stirred (800 rpm) in a 60 ℃ oil bath for 16 hours. The autoclave was then cooled in a liquid nitrogen bath for 5 min, followed by releasing the H_2 pressure. Afterwards, the autoclave was moved out of the liquid nitrogen bath and warmed to room temperature in about 30 min. The head of autoclave was removed, and octane (103.4 mg) was added into the well of an autoclave as an internal standard. A few drop of the resulting reaction mixture was taken out and subjected to GC/MS analysis. 200 mg of silica gel was added to the reaction mixture and the volatile was removed under vacuum. The resulting mixture was transferred to a column prefilled with 700 mg of silica gel. About 90 mL of petroleum ether / CH_2Cl_2 mixture (20:1) was used to rinse the phenylalkane product out of the column. After removal of solvent under vacuum, the phenylalkane product was obtained as 47.0 mg of colorless oil. The percentage of the remaining phenyl rings in this polymer residue was calculated by following equation: $x = 4I_{Ar}/(5I_{al} + I_{Ar})$, where x is the percentage of the remaining phenyl rings, I_{Ar} is the integration of the aromatic protons, and I_{al} is the integration of the aliphatic protons.

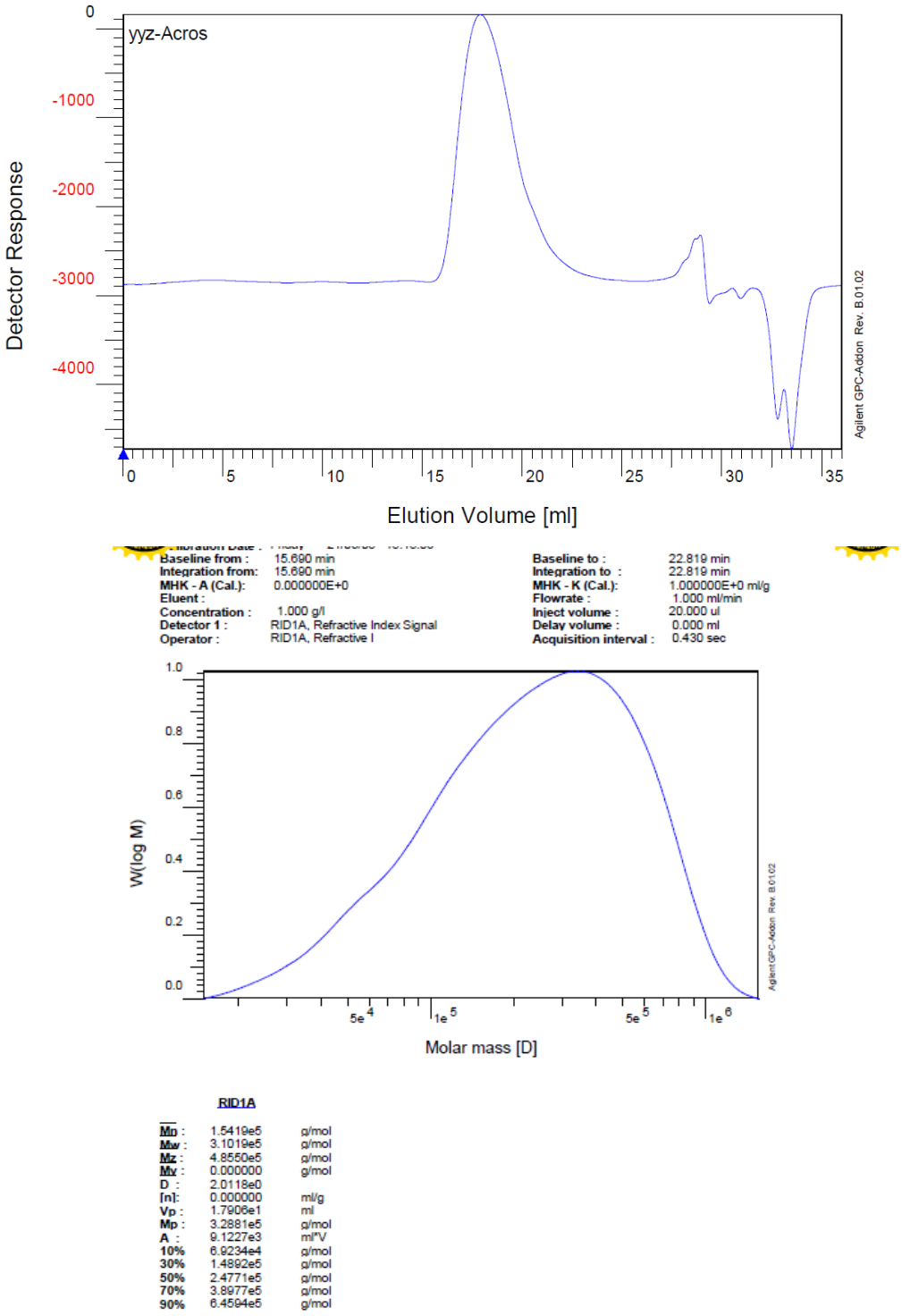


Fig. S51. GPC trace of laboratory-grade polystyrene

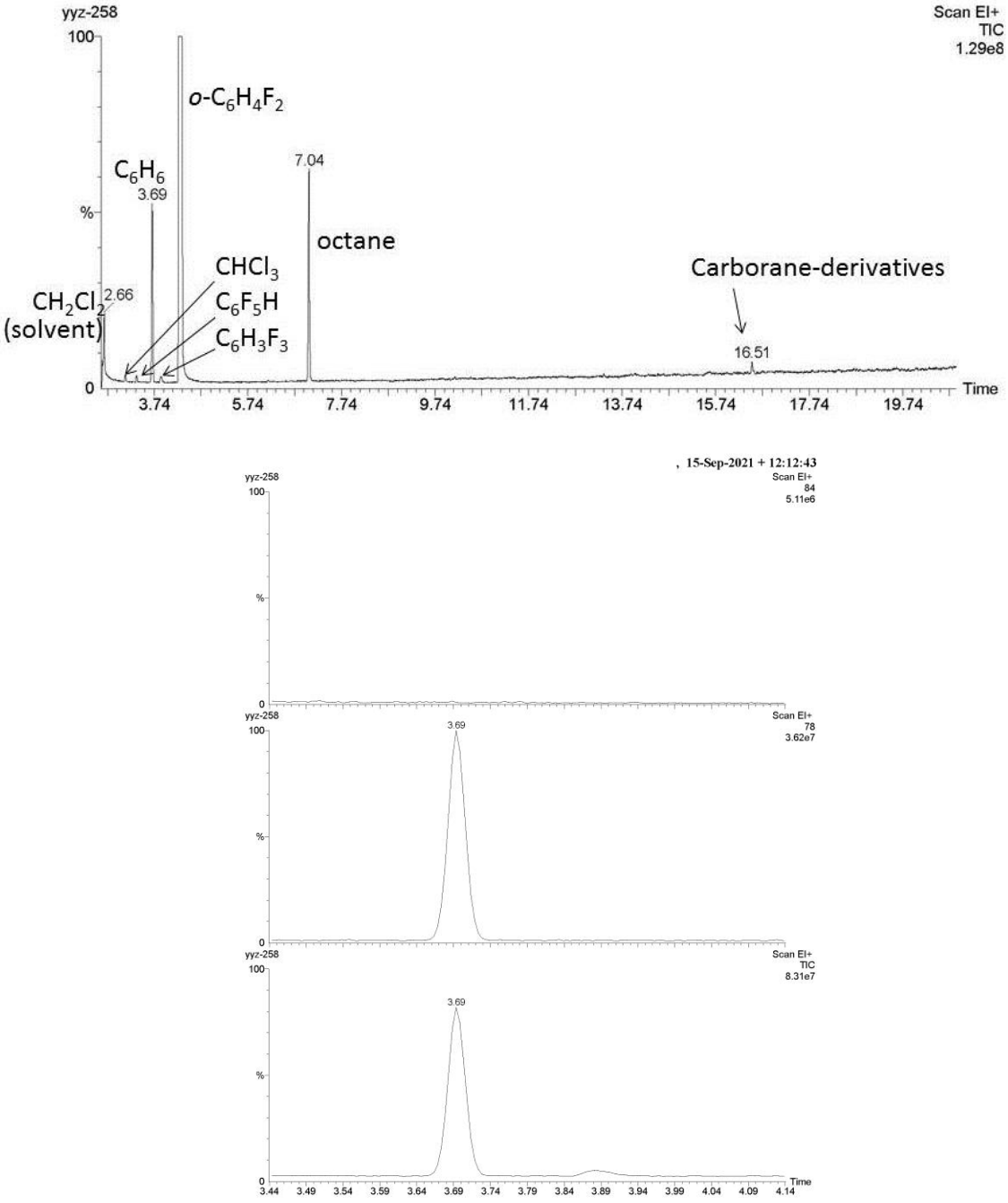


Fig. S52. GC-MS data for the reaction mixture of the hydrogenolysis of laboratory-grade polystyrene. The scanning of the m/z value of 84 ruled out the formation of cyclohexane during the hydrogenolysis process.

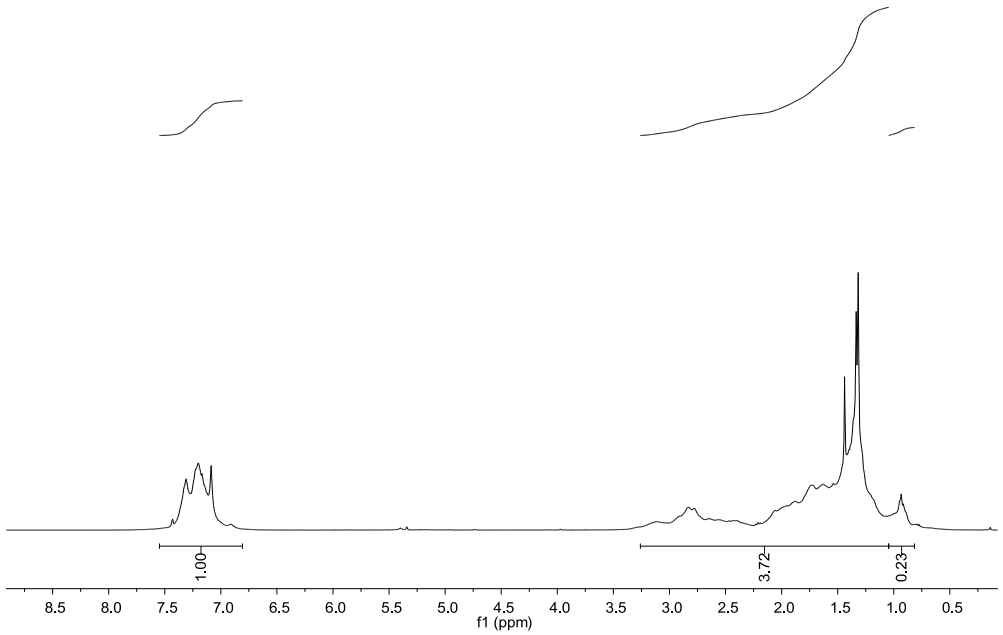


Fig. S53. ^{1}H NMR spectrum of the phenylalkane product from the hydrogenolysis of laboratory-grade polystyrene in CD_2Cl_2

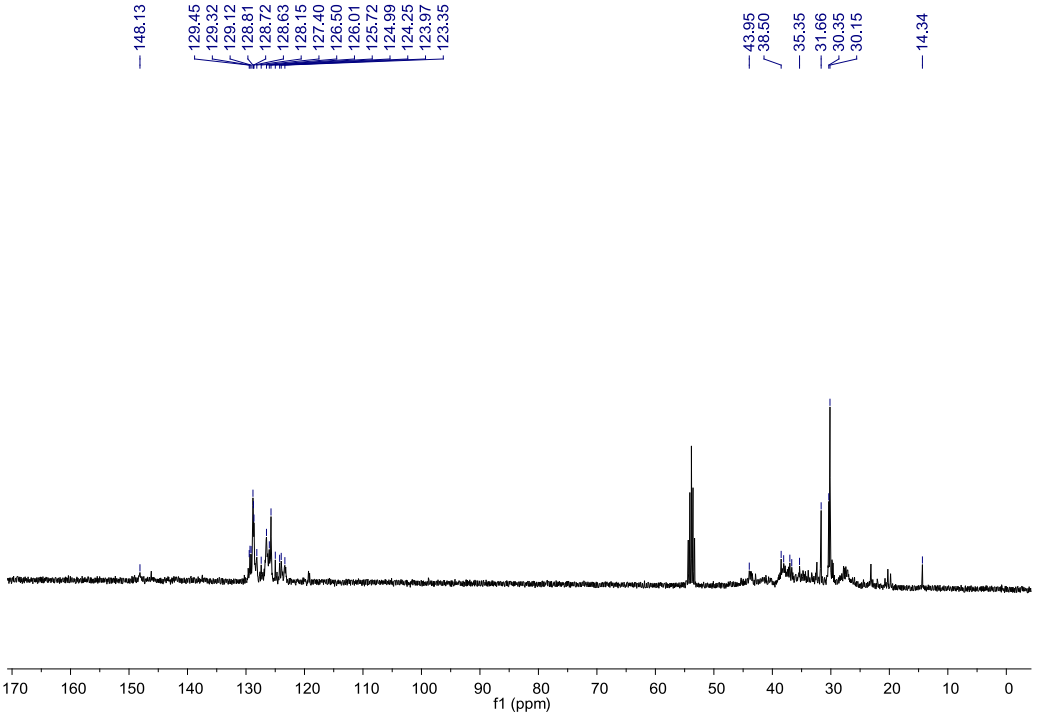


Fig. S54. $^{13}C\{^{1}H\}$ NMR spectrum of the phenylalkane product from the hydrogenolysis of laboratory-grade polystyrene in CD_2Cl_2

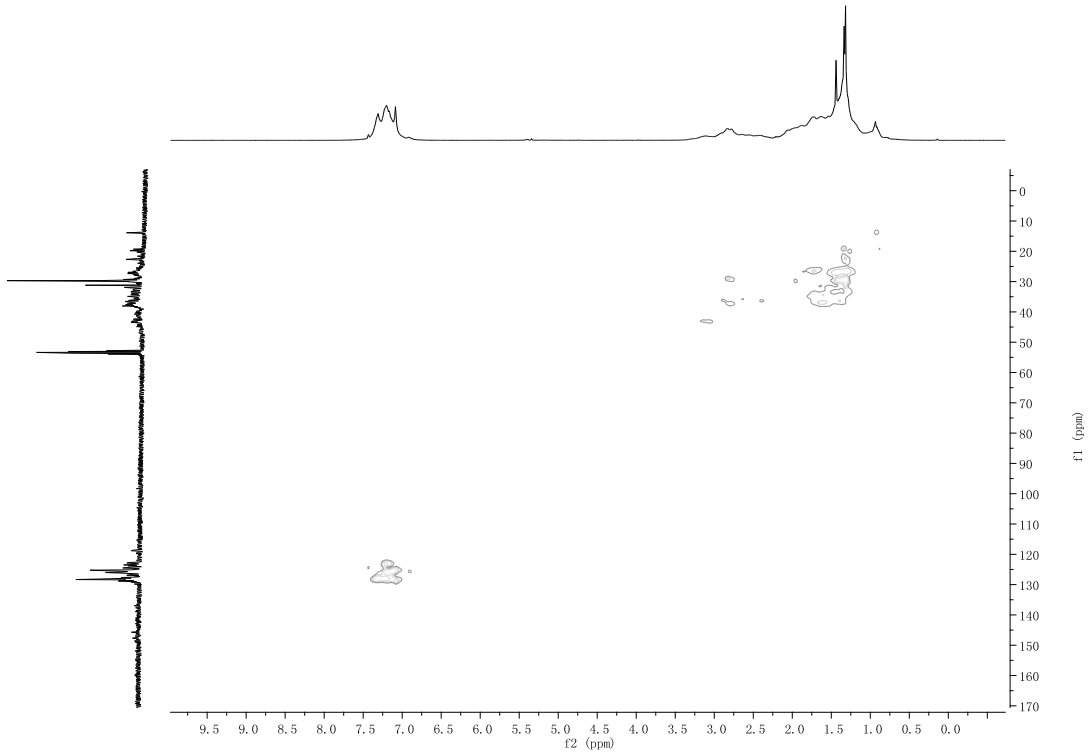


Fig. S55. $^{1}H,^{13}C$ HSQC NMR spectrum of the phenylalkane product from the hydrogenolysis of laboratory-grade polystyrene in CD_2Cl_2

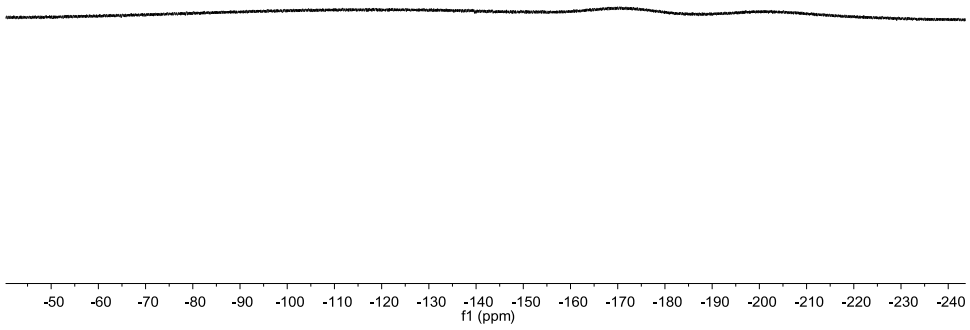
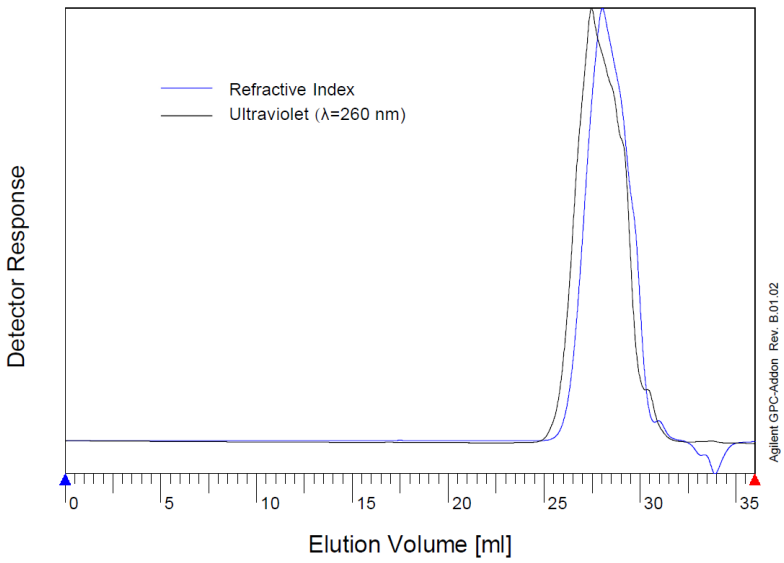
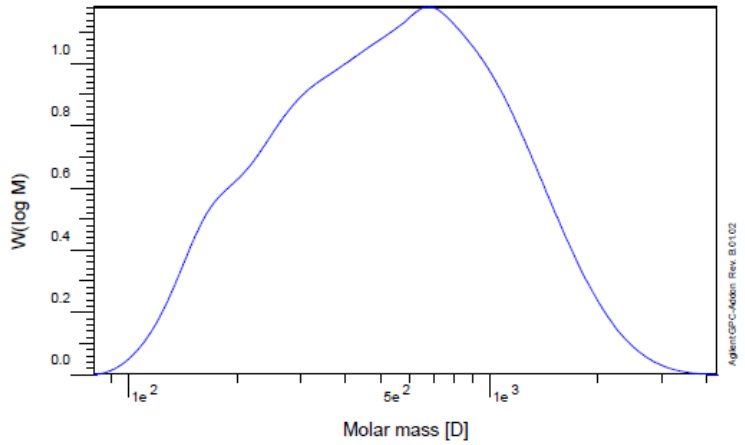


Fig. S56. ^{19}F NMR spectrum of the polymer residue from the hydrogenolysis of laboratory-grade polystyrene in CD_2Cl_2



Sample :	yyz-258		
Injection Date :	14-Sep-21, 13:25:14		
Calibration File :	E:\1METHOD\PS-GPC-LS-VS-20210603.CAL		
Calibration Date :	Thursday 21/06/03 15:00:16		
Baseline from :	25.284 min	**Baseline to :**	30.706 min
Integration from:	25.284 min	**Integration to :**	30.706 min
MHK - A (Cal.):	0.000000E+0	**MHK - K (Cal.):**	1.000000E+0 ml/g
Eluent :	THF	**Flowrate :**	1.000 ml/min
Concentration :	1.000 g/l	**Inject volume :**	20.000 µl
Detector 1 :	RID1A, Refractive Index Signal	**Delay volume :**	0.000 ml
Operator :	RID1A, Refractive I	**Acquisition interval :**	0.430 sec



RID1A

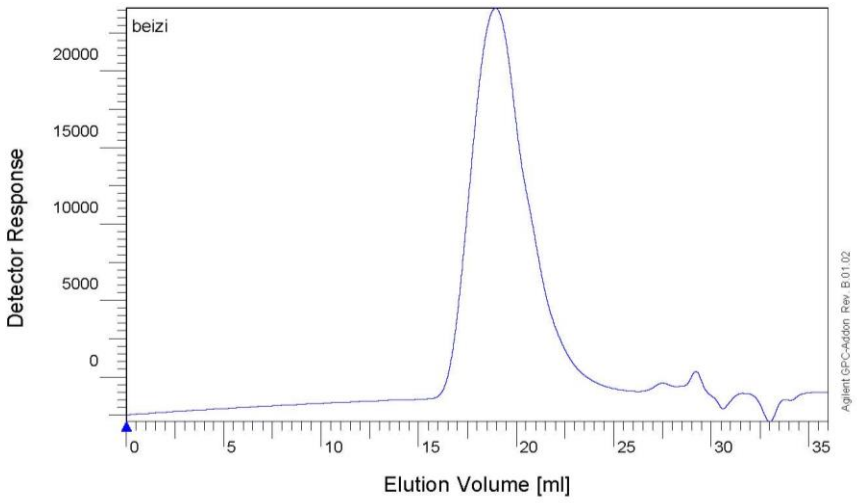
$\overline{Mn}$:	4.1047e2	g/mol
Mw :	6.7364e2	g/mol
Mz :	1.0218e3	g/mol
Mv :	0.000000	g/mol
D :	1.6411e0	
[η]:	0.000000	ml/g
Vp :	2.8037e1	ml
Mp :	6.5874e2	g/mol
A :	5.8771e4	ml*V
10%	1.9585e2	g/mol
30%	3.4879e2	g/mol
50%	5.4491e2	g/mol
70%	8.1165e2	g/mol
90%	1.3318e3	g/mol

Fig. S57. GPC trace of the phenylalkane product from the hydrogenolysis of laboratory-grade polystyrene

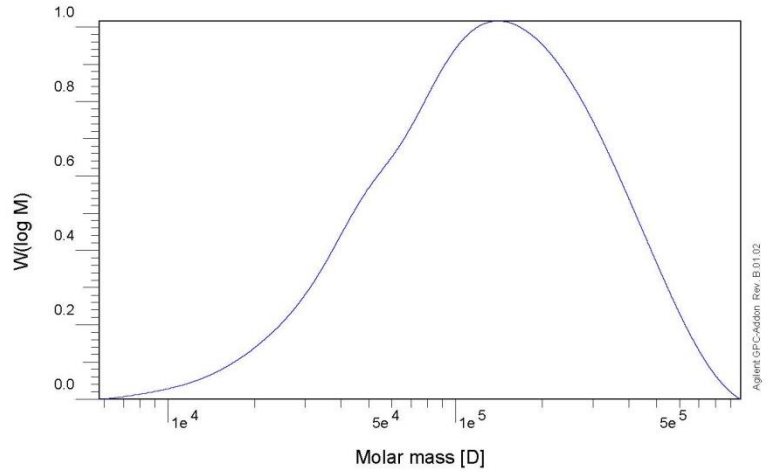
6.2 Polystyrene from single-use cups

Inside of a N_2-filled glovebox, **1a** (61.8 mg, 0.048 mmol), a sample from a polystyrene single-use cup (105.6 mg, Figure S58), and 10 mL of *o*-$C_6H_4F_2$ were transferred into the well of an autoclave. After the head of the autoclave was assembled, the autoclave was taken out of the glovebox and connected to a H_2 gas cylinder. The connection line was flushed with H_2 three times. Then the autoclave was pressurized to 5 bars of H_2 and stirred (800 rpm) in a 60 ℃ oil bath for 16 hours. The autoclave was then cooled in a liquid nitrogen bath for 5 min, followed by releasing the H_2 pressure. Afterwards, the autoclave was moved out of the liquid nitrogen bath and warmed to room temperature in about 30 min. The head of autoclave was removed, and octane (108.0 mg) was added into the well of an autoclave as an internal standard. A few drop of the resulting reaction mixture was taken out and subjected to GC/MS analysis. 200 mg of silica gel was added to the reaction mixture and the volatile was removed under vacuum. The resulting mixture was transferred to a column prefilled with 800 mg of silica gel. About 70 mL of petroleum ether / CH_2Cl_2 mixture (20:1) was used to rinse the phenylalkane product out of the column. After removal of solvent under vacuum, the phenylalkane product was obtained as 44.3 mg of colorless oil.

Fig. S58. Pieces of the plastic cup (105.6 mg) in a vial prior to hydrogenolysis



Baseline from :	16.332 min	**Baseline to :**	24.335 min
Integration from:	16.332 min	**Integration to :**	24.335 min
MHK - A (Cal.):	0.000000E+0	**MHK - K (Cal.):**	1.000000E+0 ml/g
Eluent :		**Flowrate :**	1.000 ml/min
Concentration :	1.000 g/l	**Inject volume :**	20.000 ul
Detector 1 :	RID1A, Refractive Index Signal	**Delay volume :**	0.000 ml
Operator :	SYSTEM	**Acquisition interval :**	0.430 sec



RID1A

Mn :	8.3296e4	g/mol
Mw :	1.7645e5	g/mol
Mz :	2.9782e5	g/mol
Mv :	0.000000	g/mol
D :	2.1184e0	
[n]:	0.000000	ml/g
Vp :	1.8936e1	ml
Mp :	1.5615e5	g/mol
A :	7.9607e4	ml*V
10%	3.8749e4	g/mol
30%	8.1137e4	g/mol
50%	1.3208e5	g/mol
70%	2.1004e5	g/mol
90%	3.8029e5	g/mol

Fig. S59. GPC curve of the plastic cup

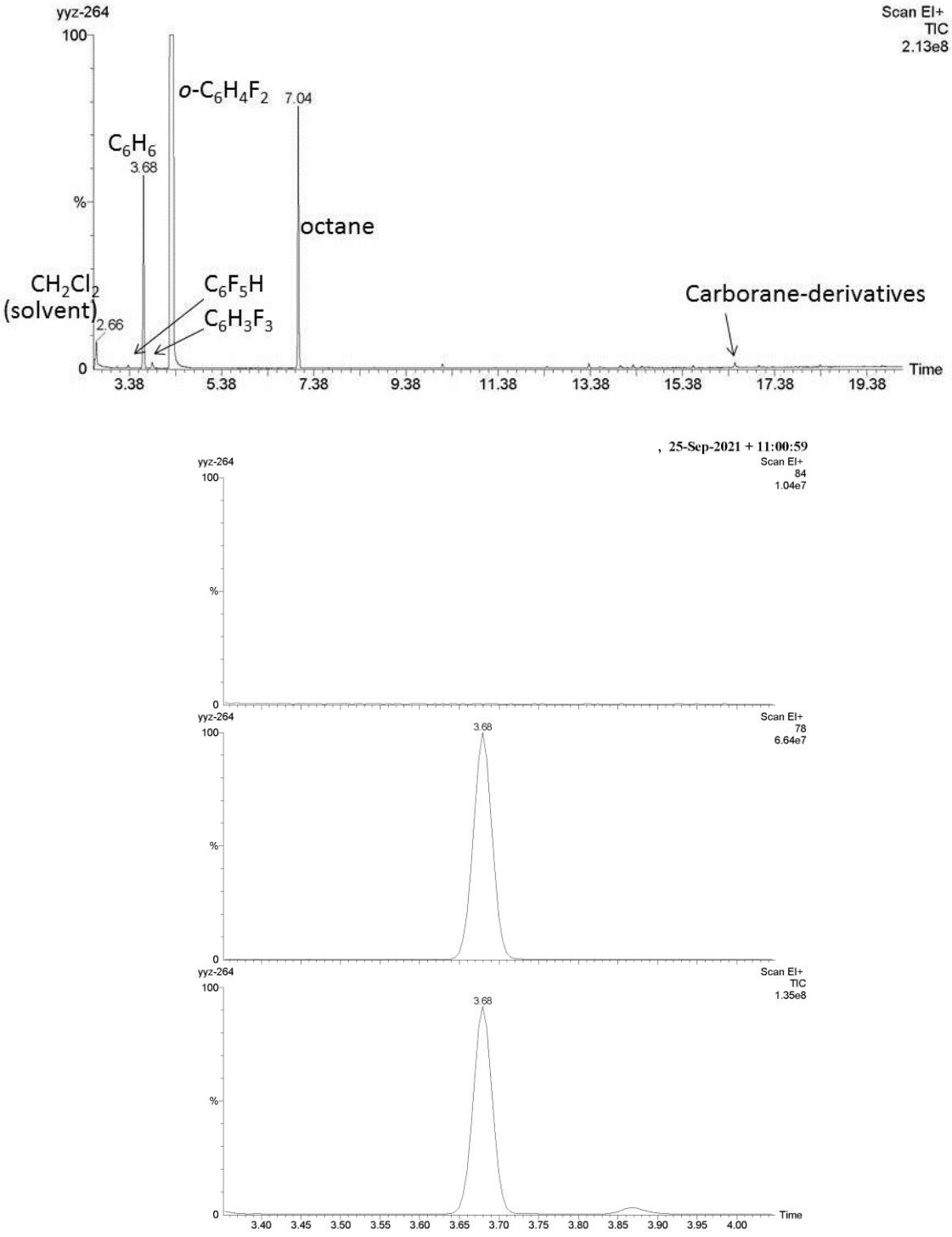


Fig. S60. GC-MS data for the reaction mixture of the hydrogenolysis of polystyrene from plastic cups. The scanning of the m/z value of 84 ruled out the formation of cyclohexane during the hydrogenolysis process.

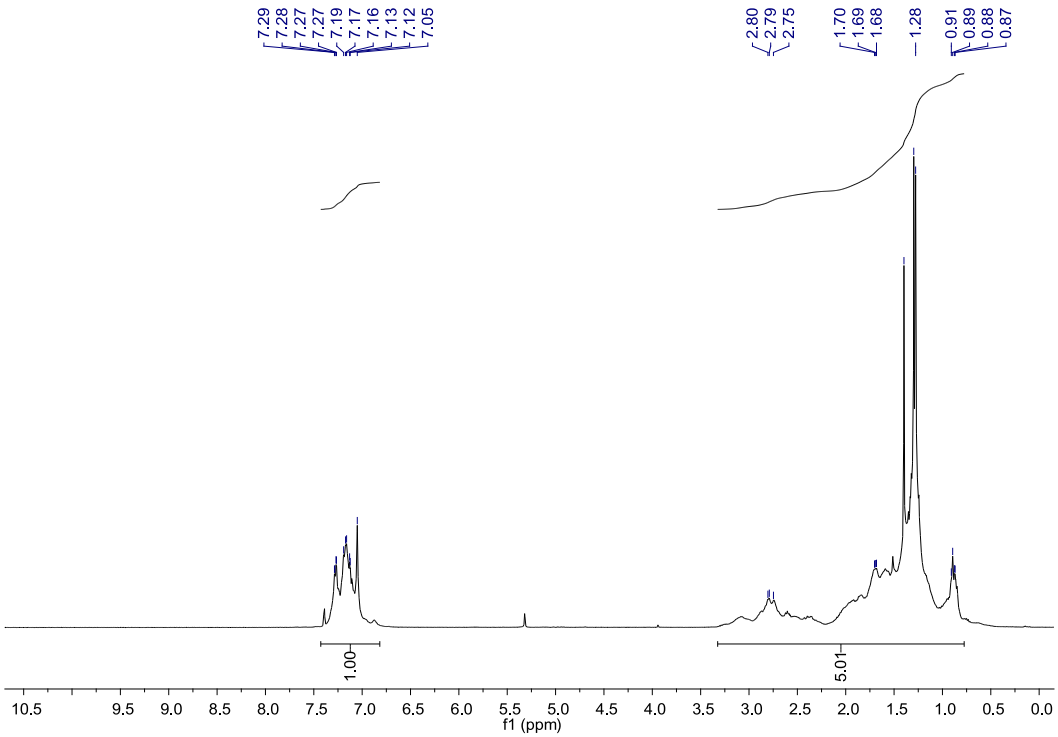


Fig. S61. ^{1}H NMR spectrum of the polymer residue from the hydrogenolysis of polystyrene from plastic cups in CD_2Cl_2

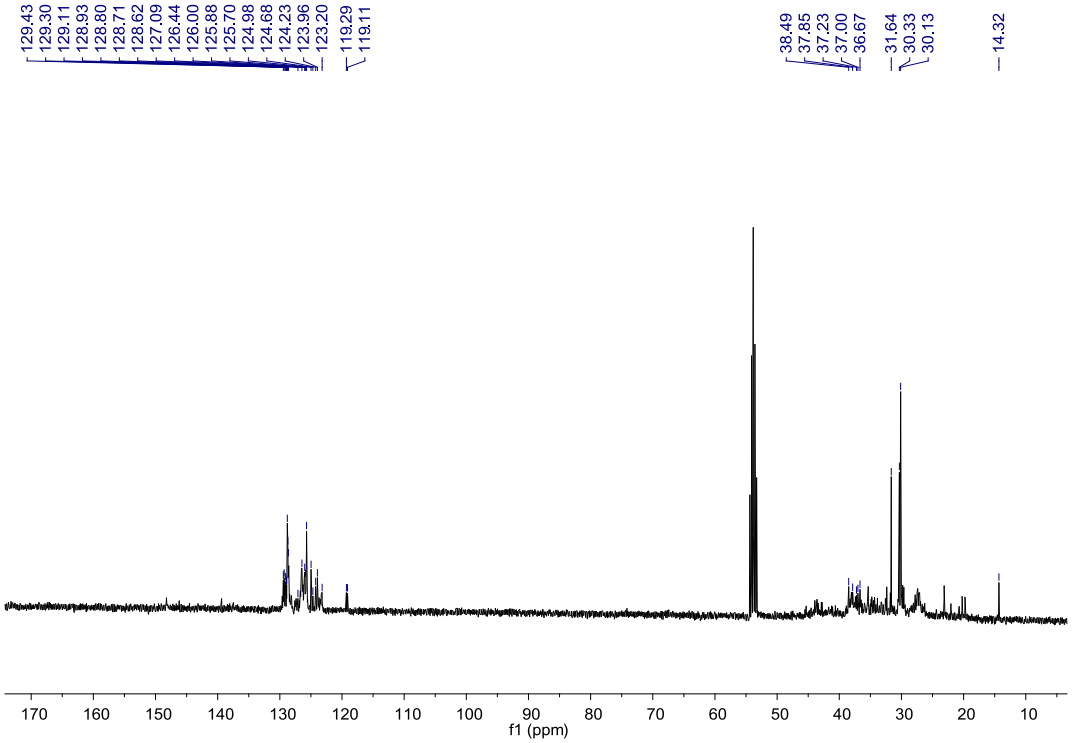


Fig. S62. $^{13}C\{^{1}H\}$ NMR spectrum of the polymer residue from the hydrogenolysis of polystyrene from plastic cups in CD_2Cl_2

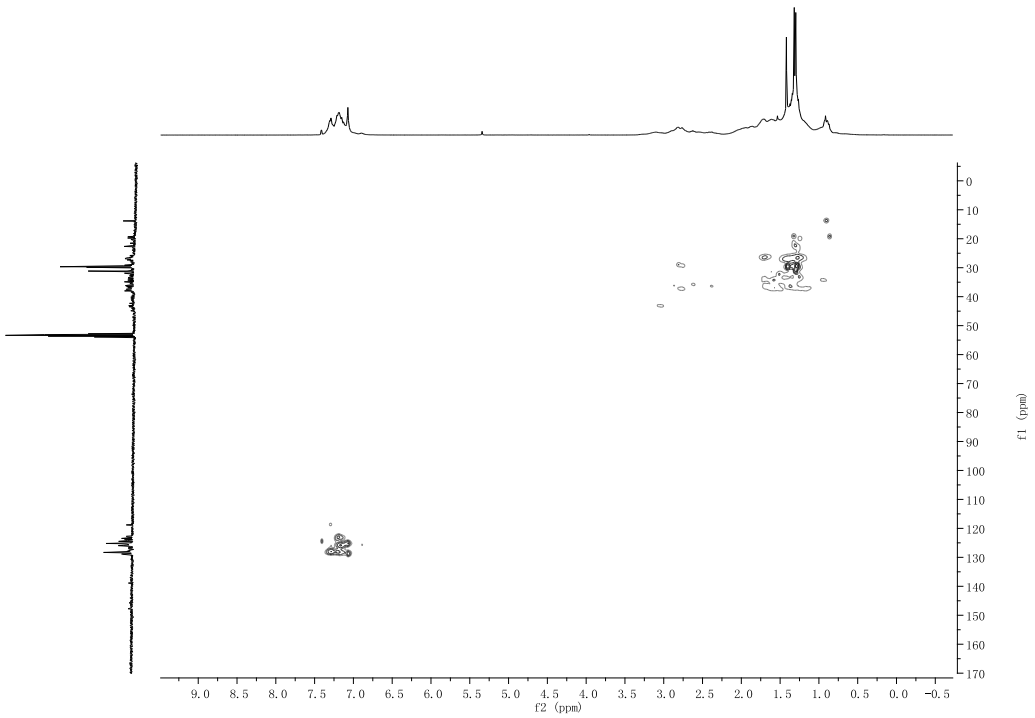


Fig. S63. $^{1}H,^{13}C$ HSQC NMR spectrum of the phenylalkane product from the hydrogenolysis of polystyrene from plastic cups in CD_2Cl_2

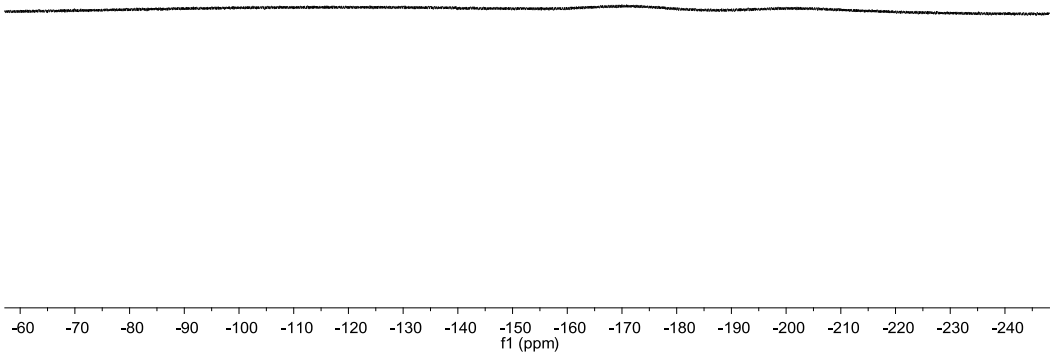


Fig. S64. ^{19}F NMR spectrum of the polymer residue from the hydrogenolysis of polystyrene from plastic cups in CD_2Cl_2

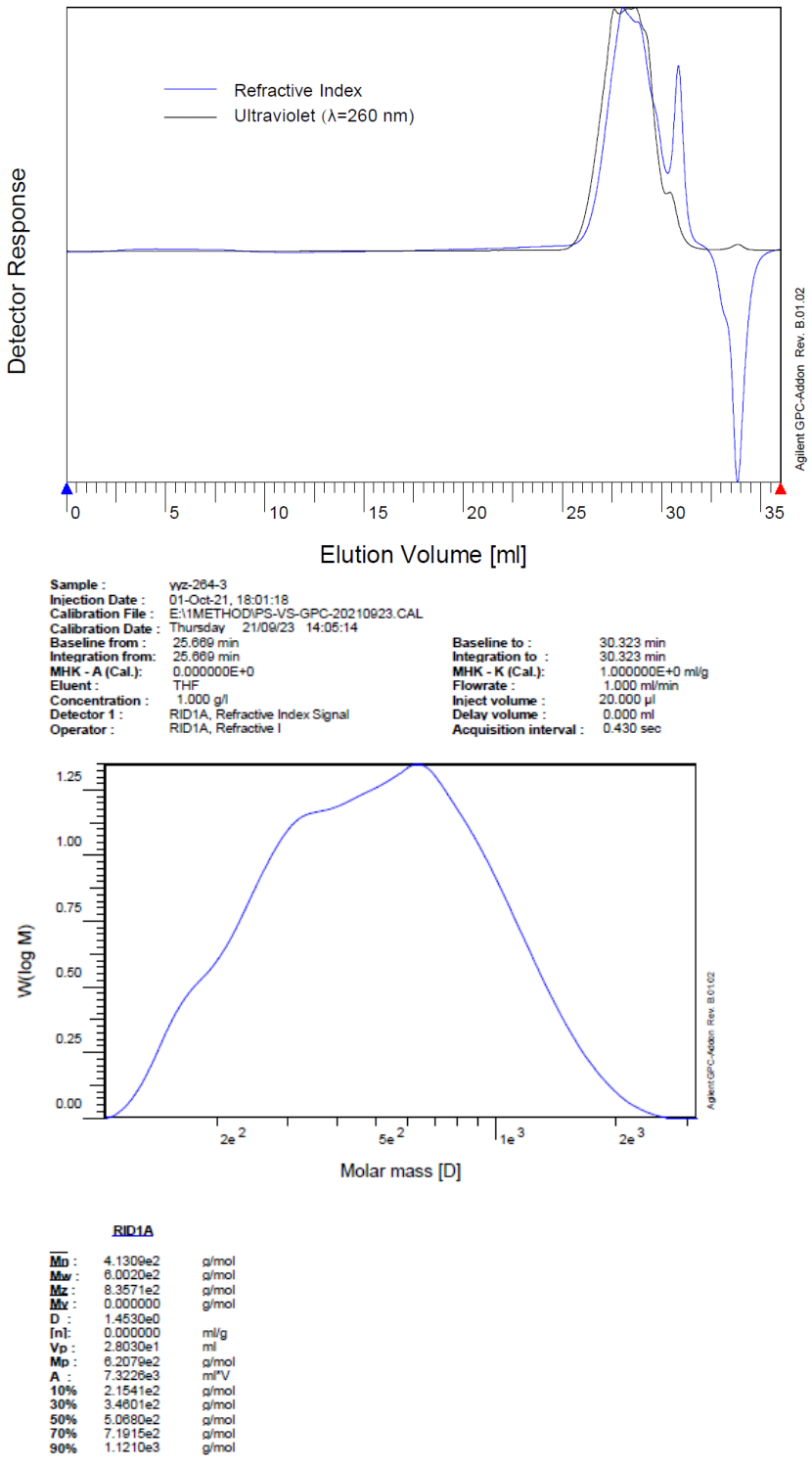
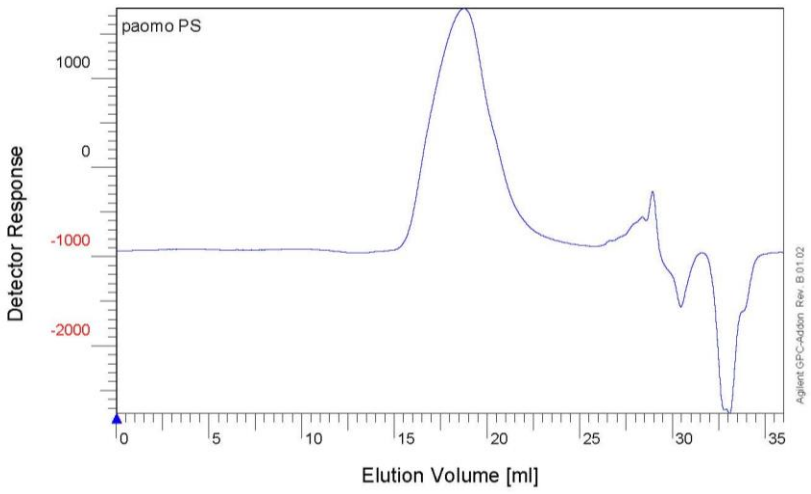


Fig. S65. GPC trace of the phenylalkane product from the hydrogenolysis of polystyrene from plastic cups

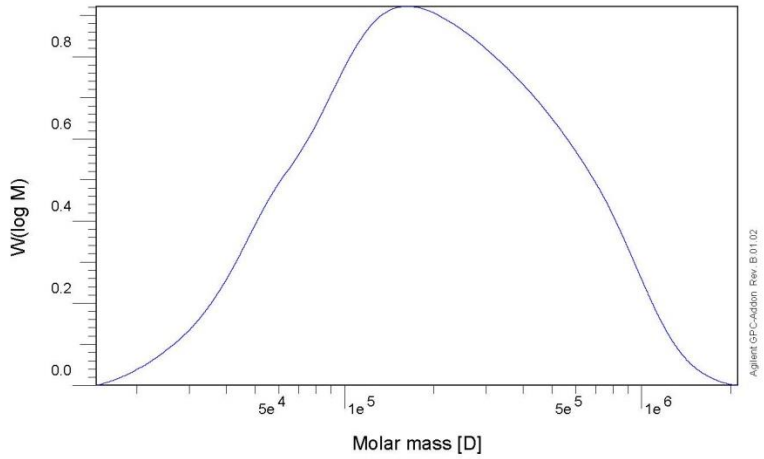
6.3 Expanded polystyrene foam

Inside of a N_2-filled glovebox, **1a** (61.5 mg, 0.048 mmol), a sample from expanded polystyrene foam packing material (109.3 mg, Figure S66), and 10 mL of *o*-$C_6H_4F_2$ were transferred into the well of an autoclave. After the head of the autoclave was assembled, the autoclave was taken out of the glovebox and connected to a H_2 gas cylinder. The connection line was flushed with H_2 three times. Then the autoclave was pressurized to 5 bars of H_2 and stirred (800 rpm) in a 60 ℃ oil bath for 16 hours. The autoclave was then cooled in a liquid nitrogen bath for 5 min, followed by releasing the H_2 pressure. Afterwards, the autoclave was moved out of the liquid nitrogen bath and warmed to room temperature in about 30 min. The head of autoclave was removed, and octane (109.6 mg) was added into the well of an autoclave as an internal standard. A few drop of the resulting reaction mixture was taken out and subjected to GC/MS analysis. 200 mg of silica gel was added to the reaction mixture and the volatile was removed under vacuum. The resulting mixture was transferred to a column prefilled with 700 mg of silica gel. About 90 mL of petroleum ether / CH_2Cl_2 mixture (20:1) was used to rinse the phenylalkane product out of the column. After removal of solvent under vacuum, the phenylalkane product was obtained as 48.5 mg of colorless oil.

Fig. S66. Pieces of expanded polystyrene foam (109.3 mg) in a vial prior to hydrogenolysis



Baseline from :	15.332 min	**Baseline to :**	22.876 min
Integration from:	15.332 min	**Integration to :**	22.876 min
MHK - A (Cal.):	0.000000E+0	**MHK - K (Cal.):**	1.000000E+0 ml/g
Eluent :		**Flowrate :**	1.000 ml/min
Concentration :	1.000 g/l	**Inject volume :**	20.000 ul
Detector 1 :	RID1A, Refractive Index Signal	**Delay volume :**	0.000 ml
Operator :	SYSTEM	**Acquisition interval :**	0.430 sec



RID1A

Mn :	1.2953e5	g/mol
Mw :	2.8637e5	g/mol
Mz :	5.3043e5	g/mol
Mv :	0.000000	g/mol
D :	2.2108e0	
[n]:	0.000000	ml/g
Vp :	1.8749e1	ml
Mp :	1.7841e5	g/mol
A :	9.1229e3	ml*V
10%	5.7831e4	g/mol
30%	1.1643e5	g/mol
50%	1.9335e5	g/mol
70%	3.3056e5	g/mol
90%	6.5631e5	g/mol

Fig. S67. GPC trace of expanded polystyrene foam

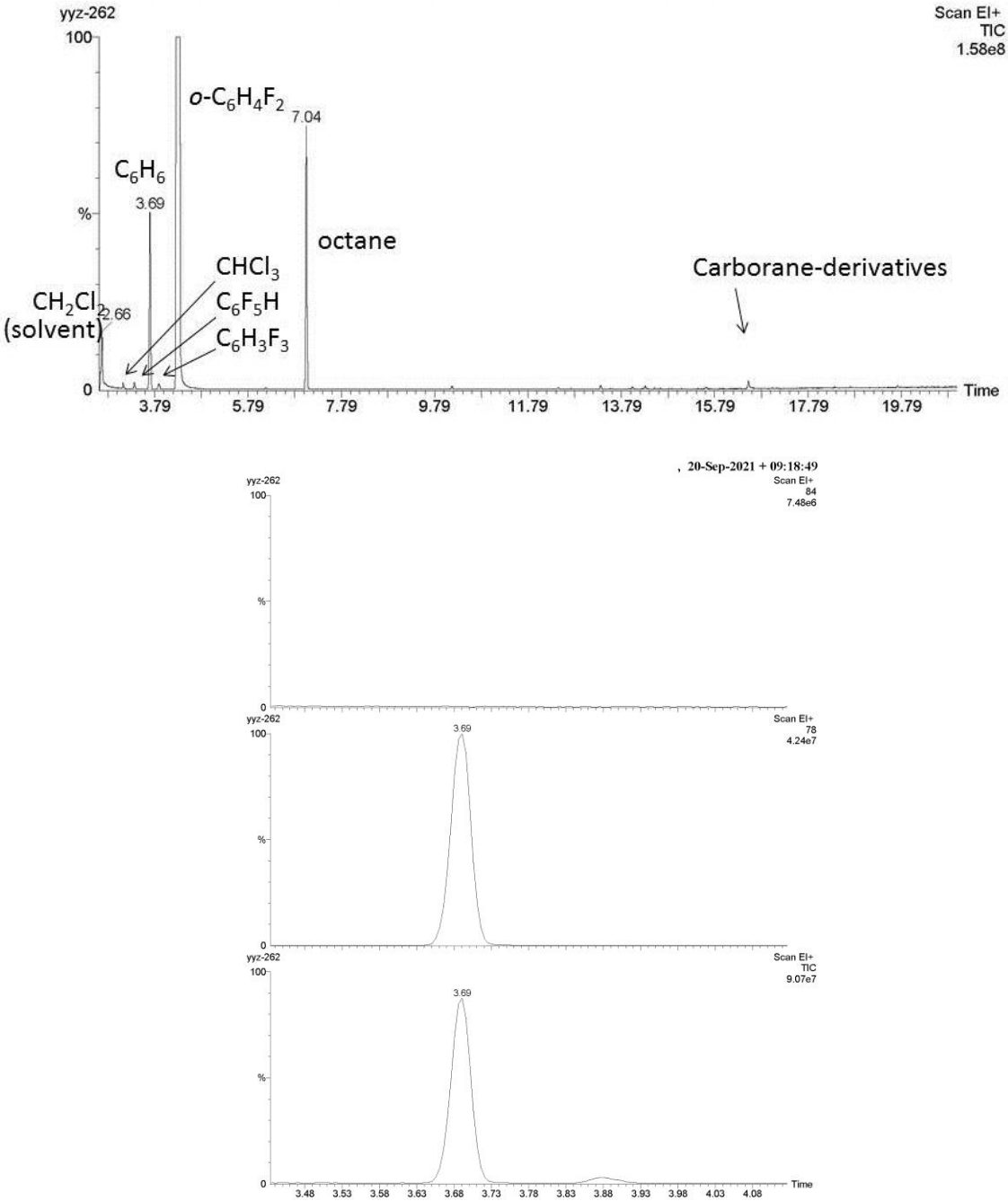


Fig. S68. GC-MS data for the reaction mixture of the hydrogenolysis of expanded polystyrene foam. The scanning of the m/z value of 84 ruled out the formation of cyclohexane during the hydrogenolysis process.

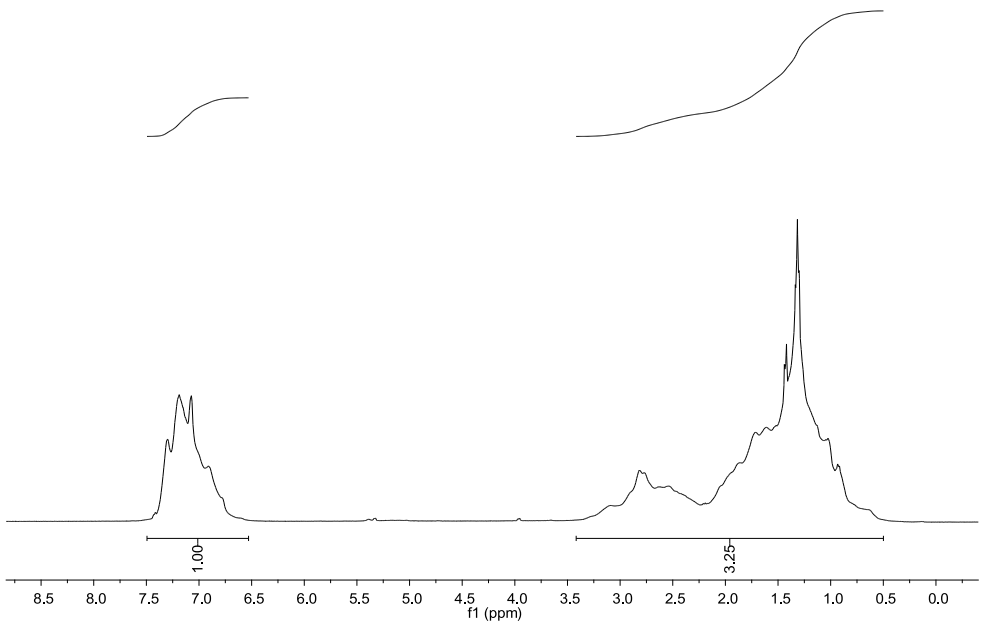


Fig. S69. ^{1}H NMR spectrum of the polymer residue from the hydrogenolysis of expanded polystyrene foam in CD_2Cl_2

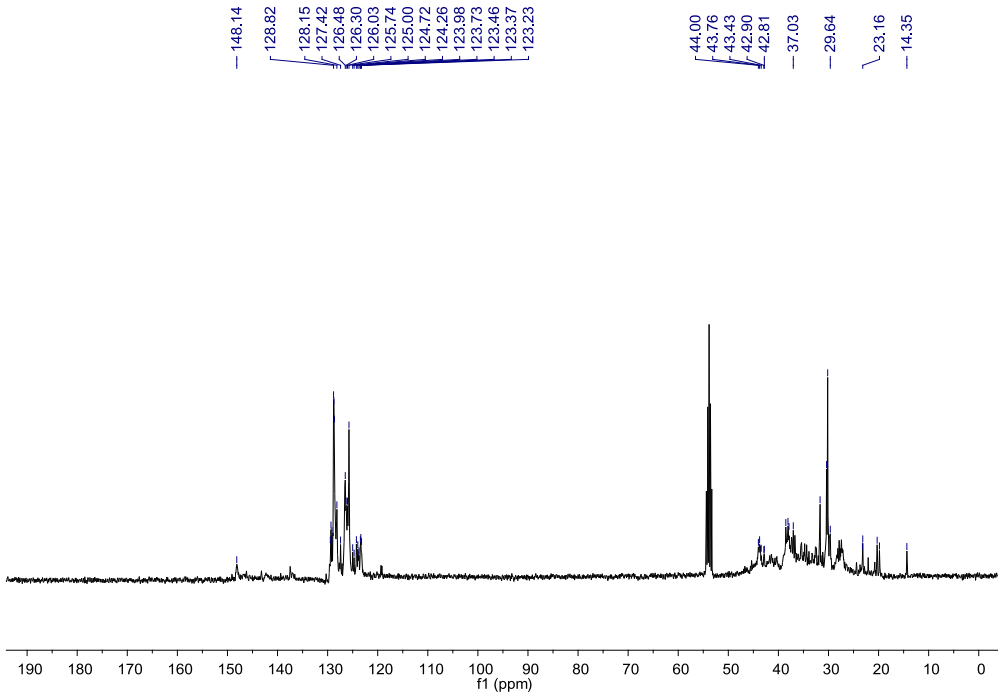


Fig. S70. $^{13}C\{^{1}H\}$ NMR spectrum of the polymer residue from the hydrogenolysis of expanded polystyrene foam in CD_2Cl_2

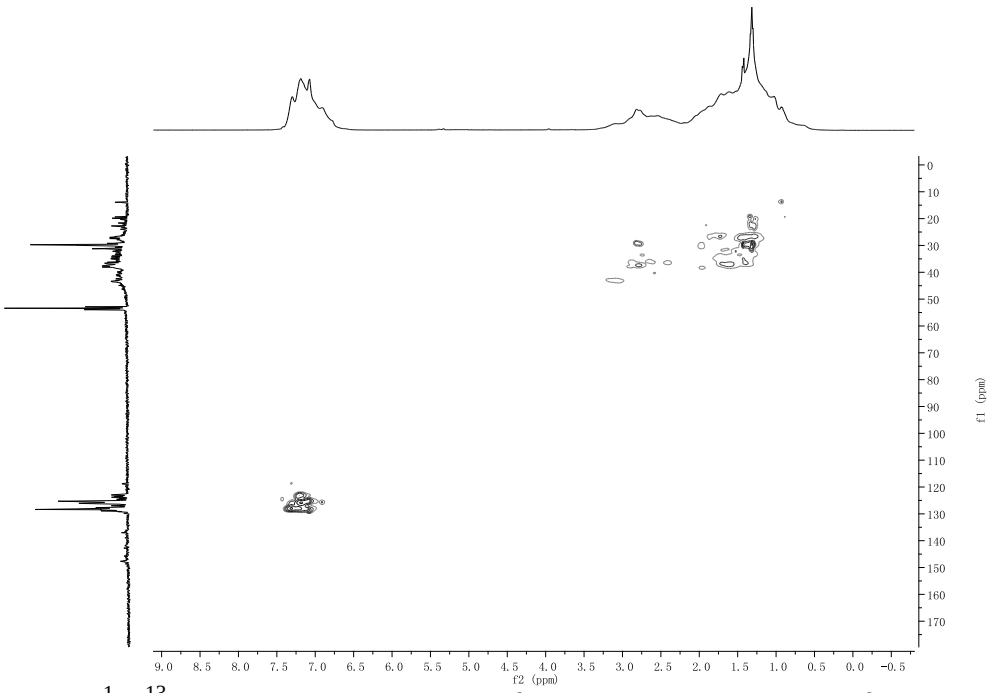


Fig. S71. $^{1}H,^{13}C$ HSQC NMR spectrum of the phenylalkane product from the hydrogenolysis of expanded polystyrene foam in CD_2Cl_2

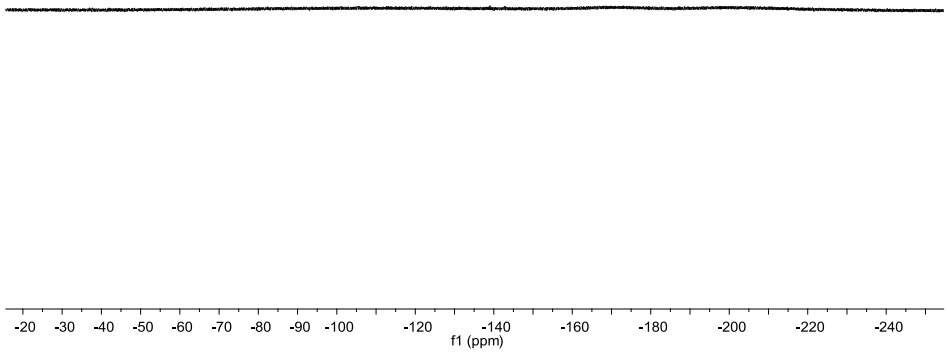
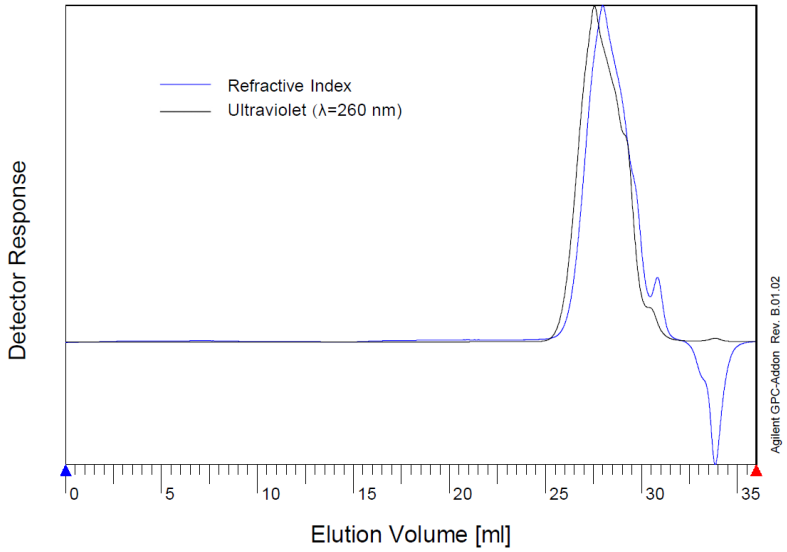
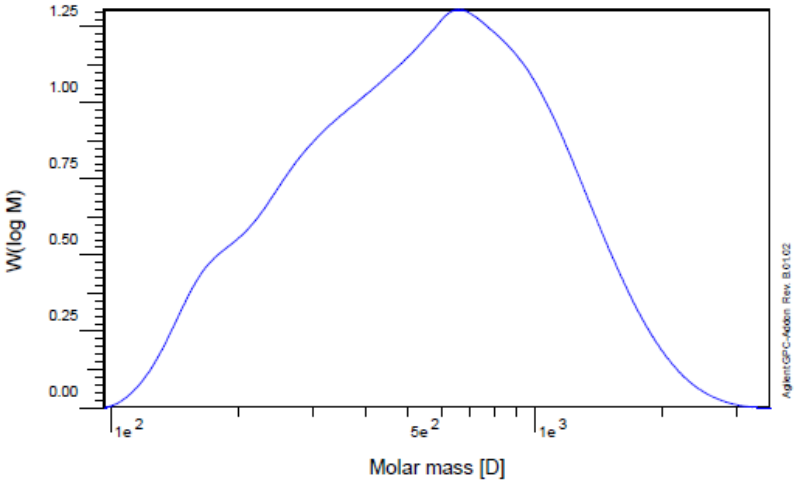


Fig. S72. ^{19}F NMR spectrum of the polymer residue from the hydrogenolysis of expanded polystyrene foam in CD_2Cl_2



Sample :	wz-262-4		
Injection Date :	01-Oct-21, 19:01:18		
Calibration File :	E:\1METHOD\PS-VS-GPC-20210923.CAL		
Calibration Date :	Thursday 21/09/23 14:05:14		
Baseline from :	25.472 min	**Baseline to :**	30.432 min
Integration from:	25.472 min	**Integration to :**	30.432 min
MHK - A (Cal.):	0.000000E+0	**MHK - K (Cal.):**	1.000000E+0 ml/g
Eluent :	THF	**Flowrate :**	1.000 ml/min
Concentration :	1.000 g/l	**Inject volume :**	20.000 µl
Detector 1 :	RID1A, Refractive Index Signal	**Delay volume :**	0.000 ml
Operator :	RID1A, Refractive I	**Acquisition interval :**	0.430 sec



RID1A

Mn :	4.3532e2	g/mol
Mw :	6.7078e2	g/mol
Mz :	9.5827e2	g/mol
Mv :	0.000000	g/mol
D :	1.5409e0	
[η]:	0.000000	ml/g
Vp :	2.7979e1	ml
Mp :	6.4522e2	g/mol
A :	2.0625e4	ml*V
10%	2.1336e2	g/mol
30%	3.7467e2	g/mol
50%	5.6771e2	g/mol
70%	8.1435e2	g/mol
90%	1.2743e3	g/mol

Fig. S73. GPC trace of the phenylalkane product from the hydrogenolysis of expanded polystyrene foam

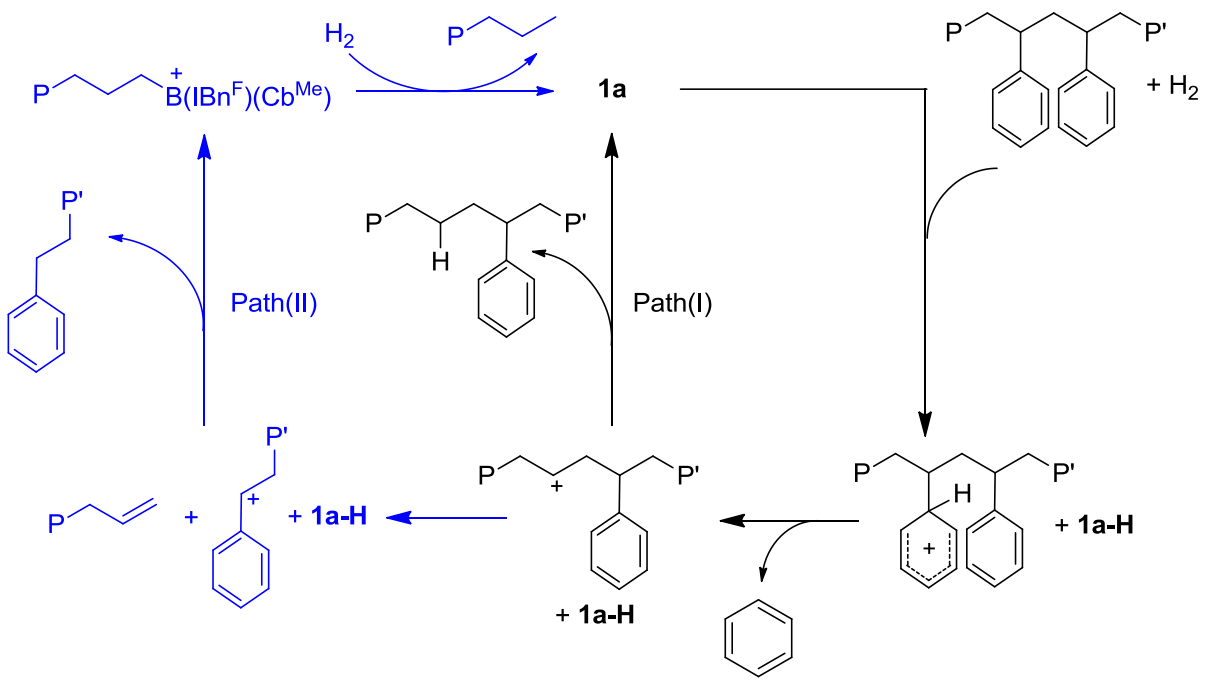


Fig. S74. Proposed mechanism for the hydrogenolysis of polystyrene. Path(I) (black) is responsible for the hydrogenolysis of $C(sp^2)$-$C(sp^3)$ bonds and Path (II) (blue) is responsible the hydrogenolysis of $C(sp^3)$-$C(sp^3)$ bonds.

7. NMR spectra

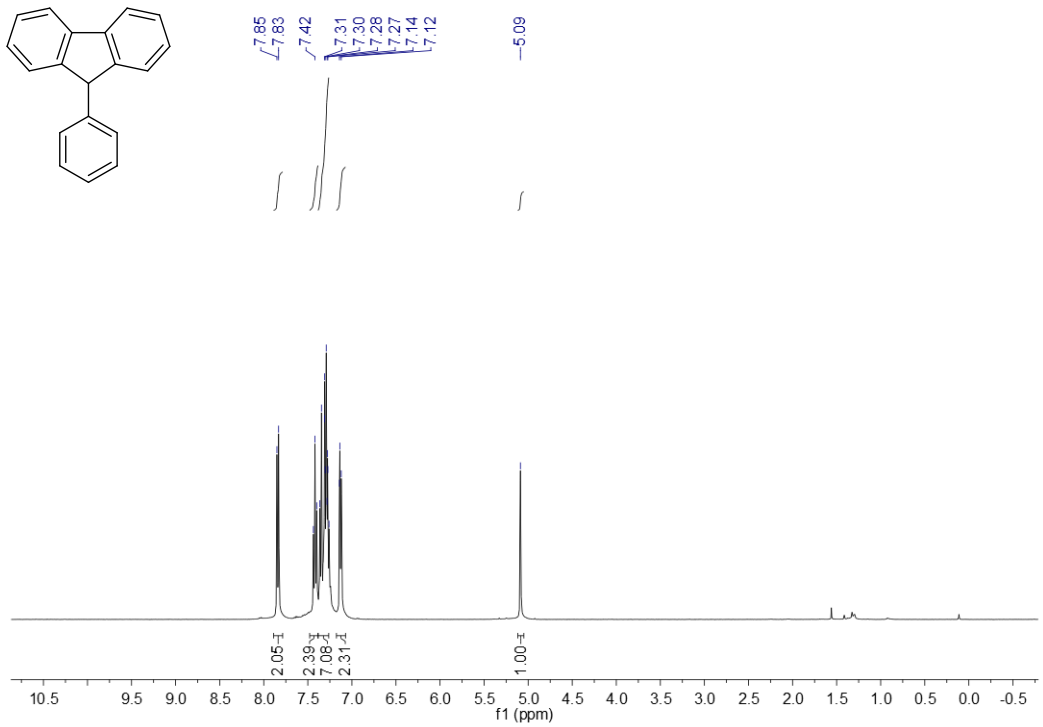


Fig. S75. ^{1}H NMR spectrum of 9-phenylfluorene in $CDCl_3$

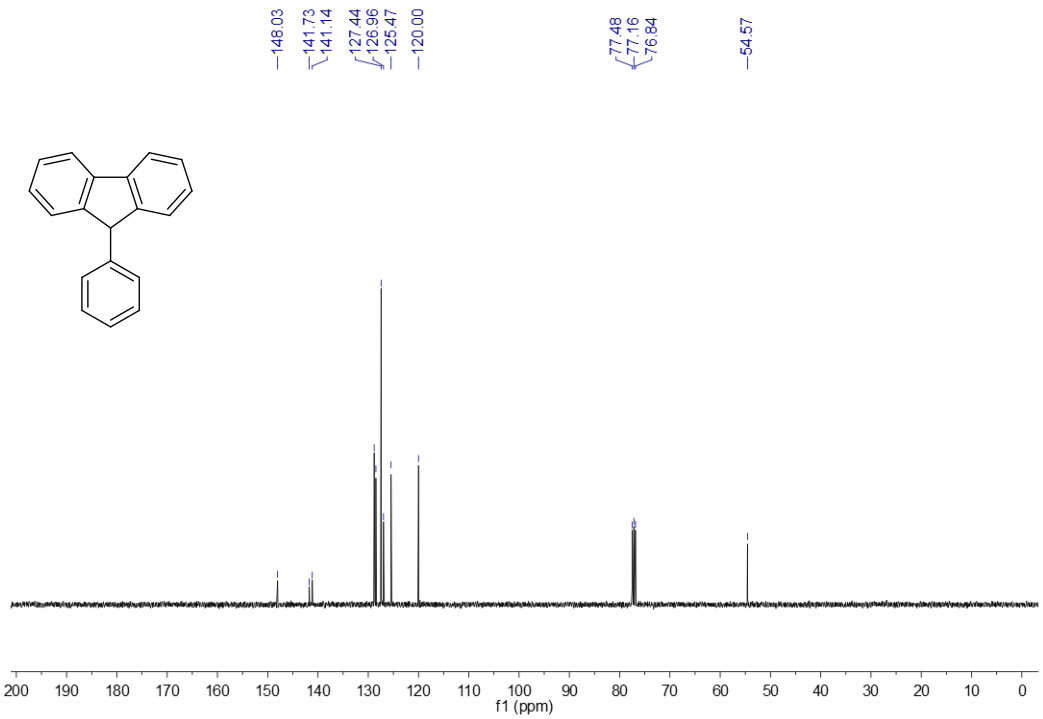


Fig. S76. $^{13}C\{^{1}H\}$ NMR spectrum of 9-phenylfluorene in $CDCl_3$

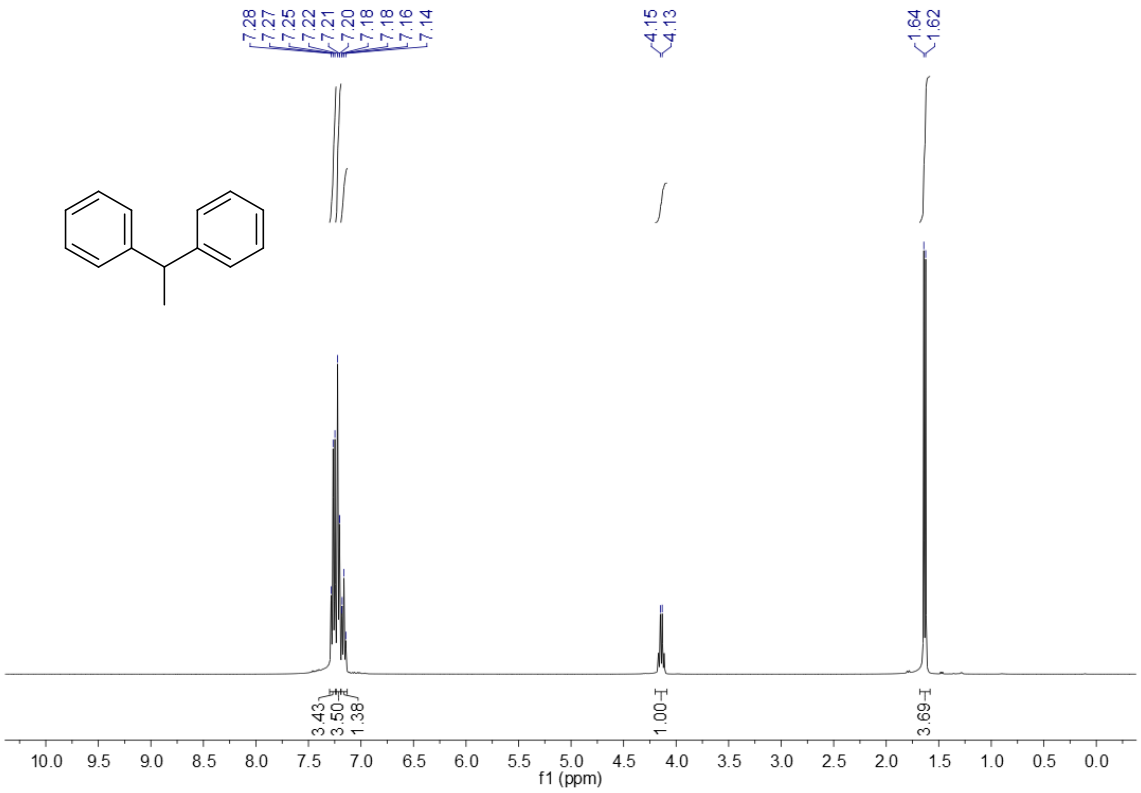


Fig. S77. ^{1}H NMR spectrum of 1,1-diphenylethane in $CDCl_3$

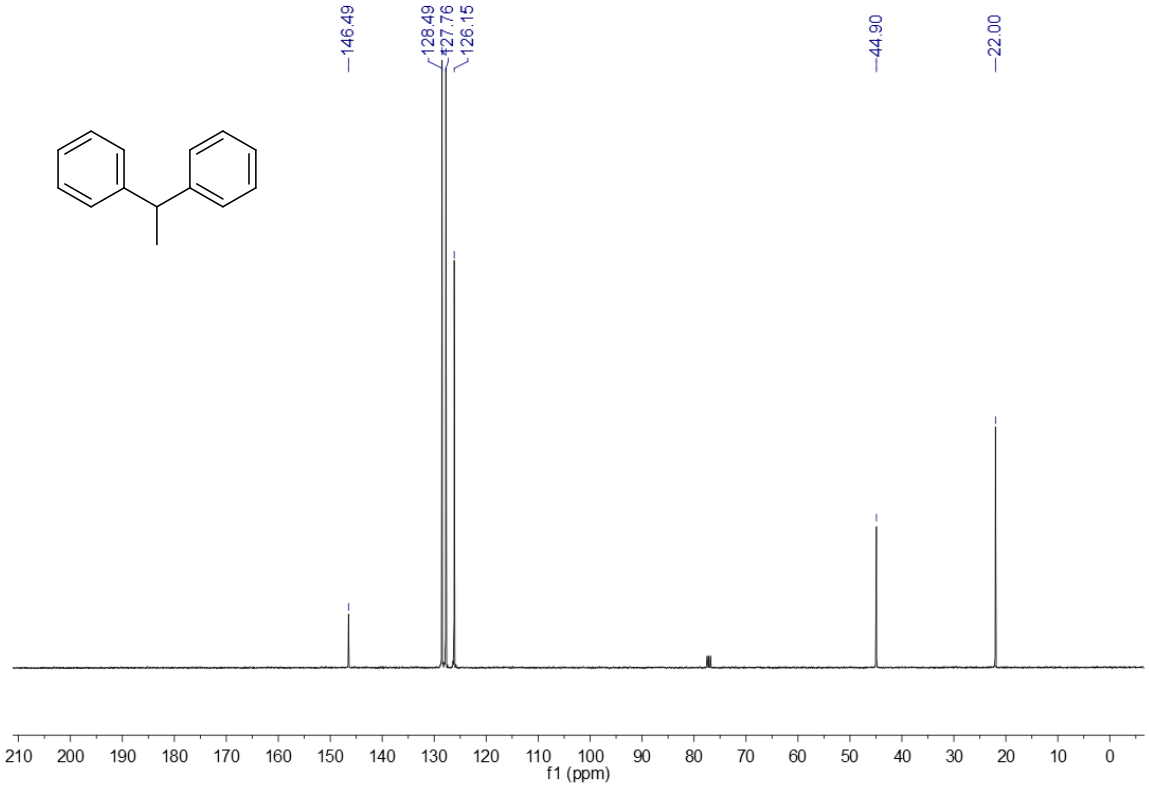


Fig. S78. $^{13}C\{^{1}H\}$ NMR spectrum of 1,1-diphenylethane in $CDCl_3$

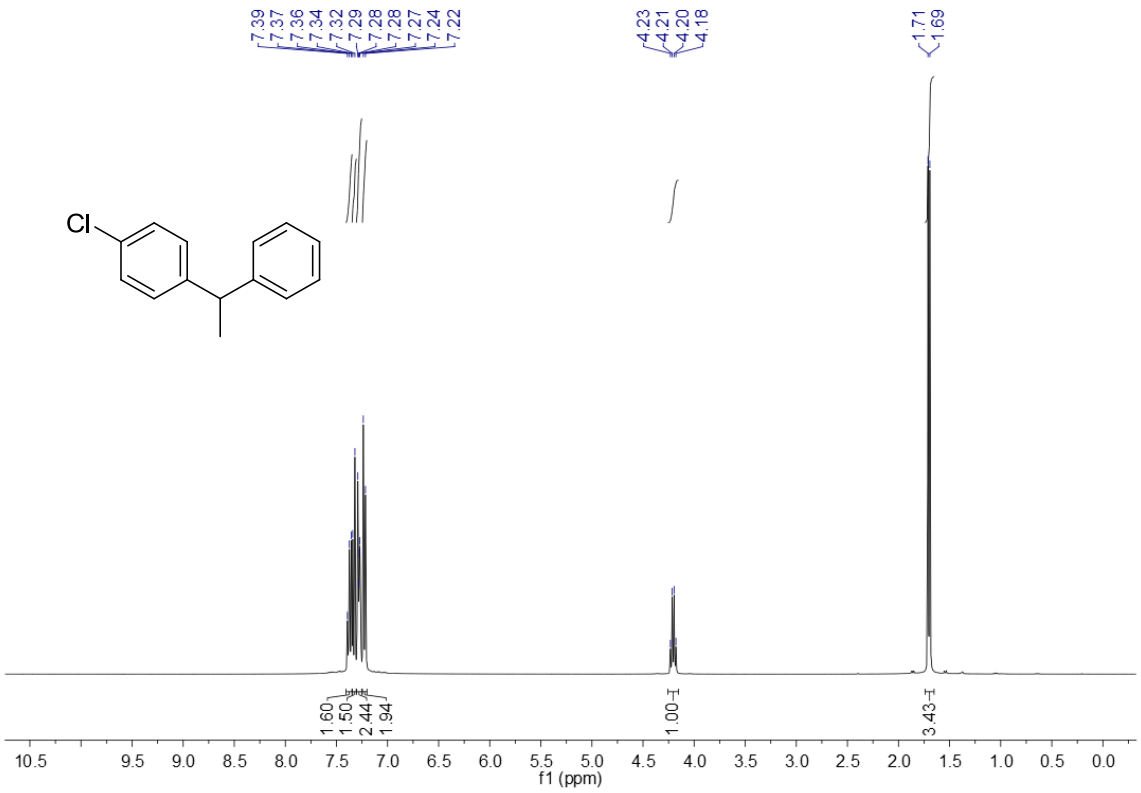


Fig. S79. ^{1}H NMR spectrum of 1-(4-chlorophenyl)-1-phenylethane in $CDCl_3$

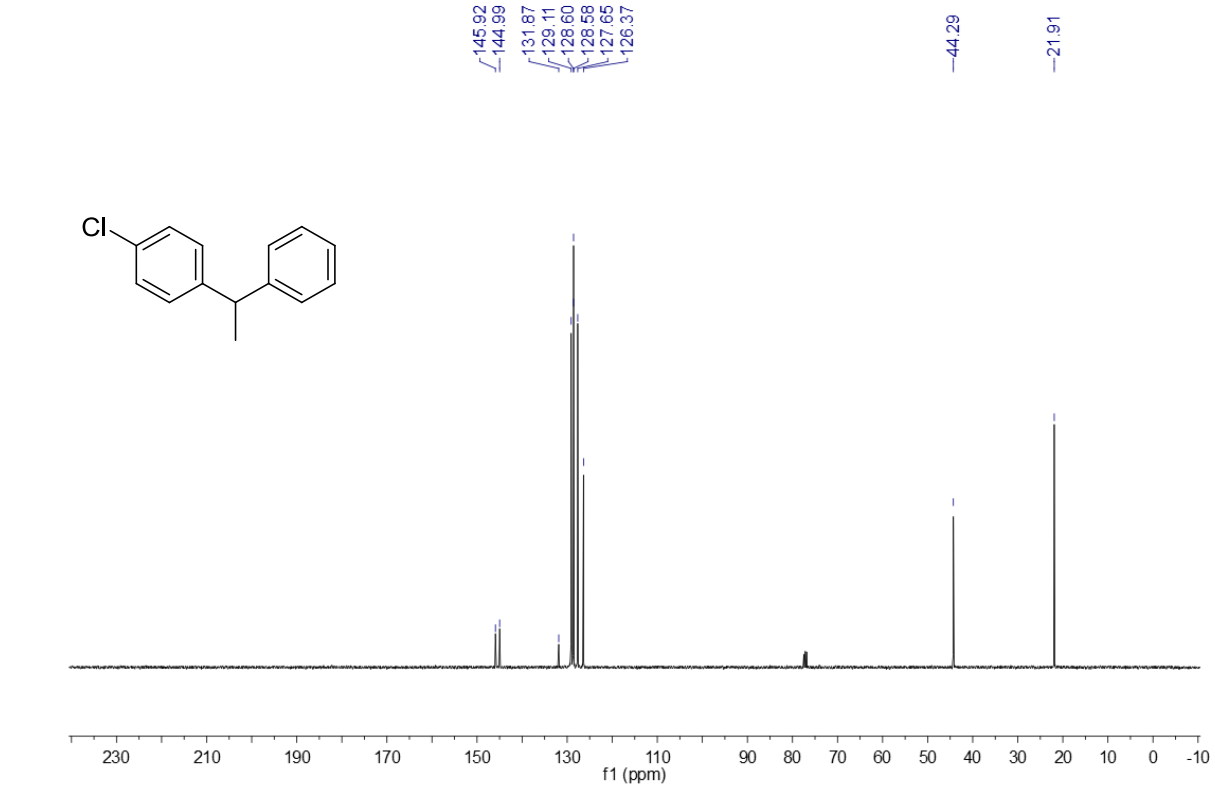


Fig. S80. $^{13}C\{^{1}H\}$ NMR spectrum of 1-(4-chlorophenyl)-1-phenylethane in $CDCl_3$

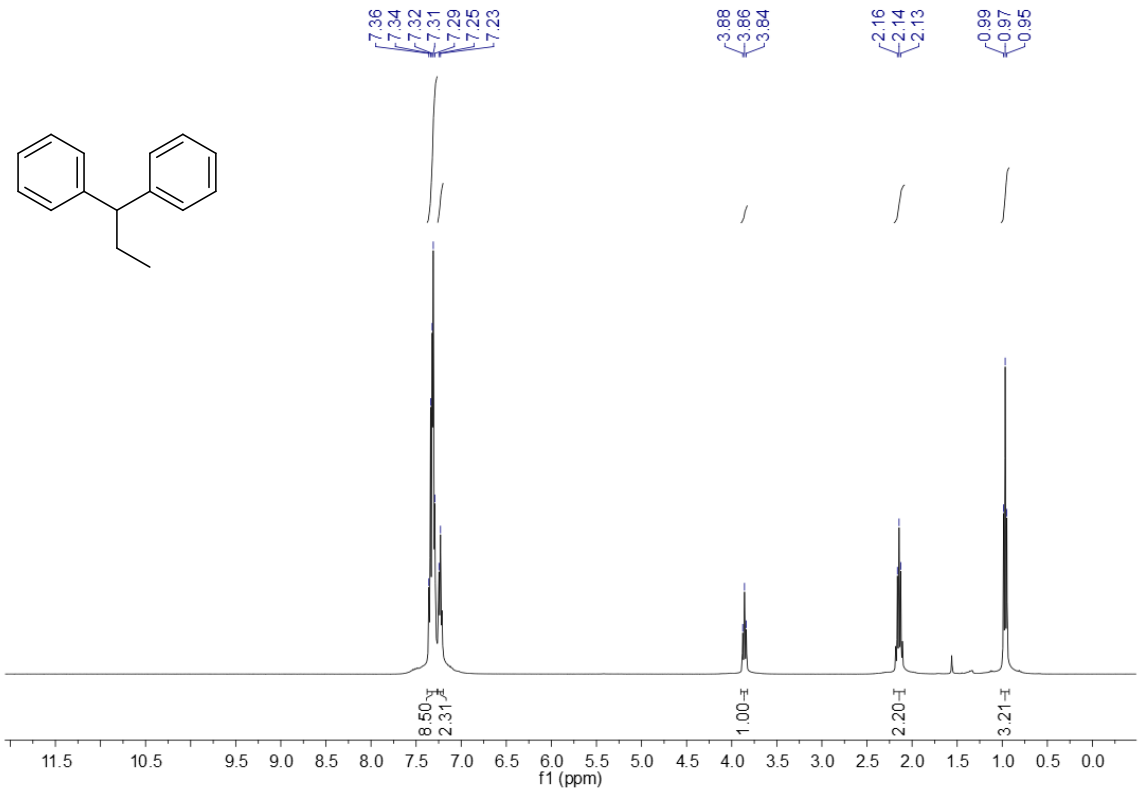


Fig. S81. ^{1}H NMR spectrum of 1,1-diphenylpropane in $CDCl_3$

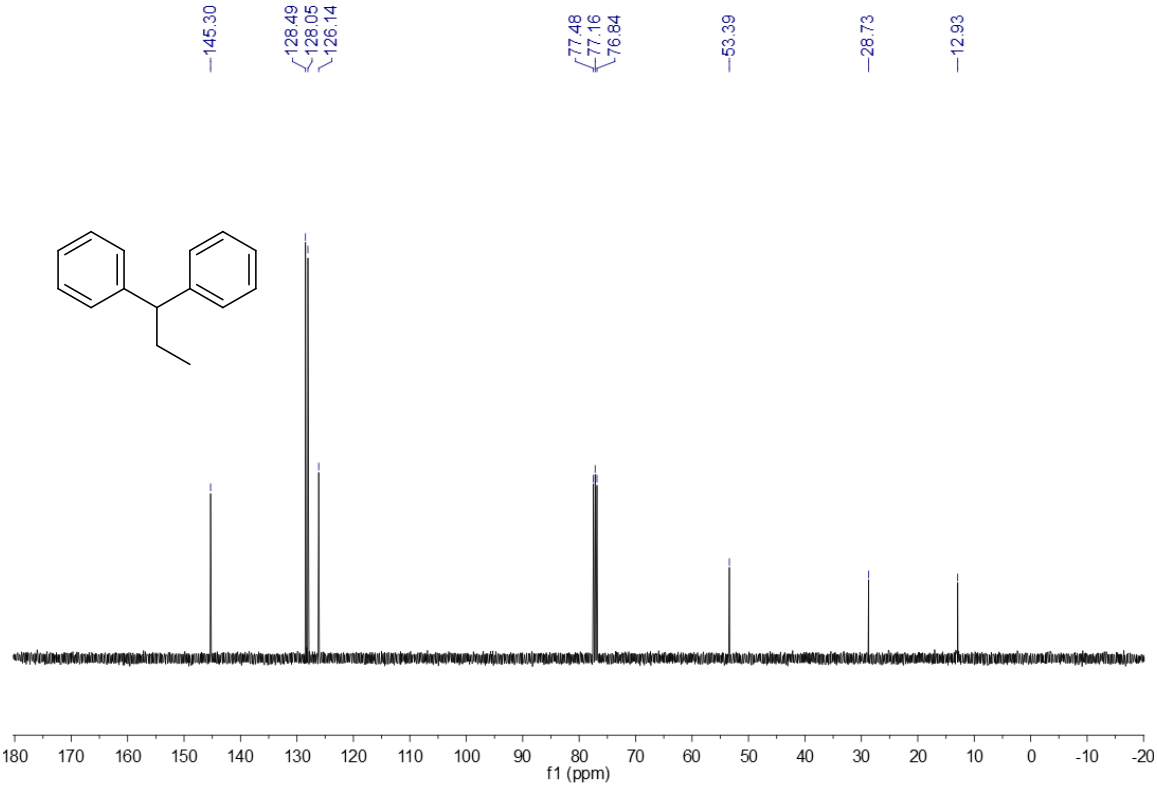


Fig. S82. $^{13}C\{^{1}H\}$ NMR spectrum of 1,1-diphenylpropane in $CDCl_3$

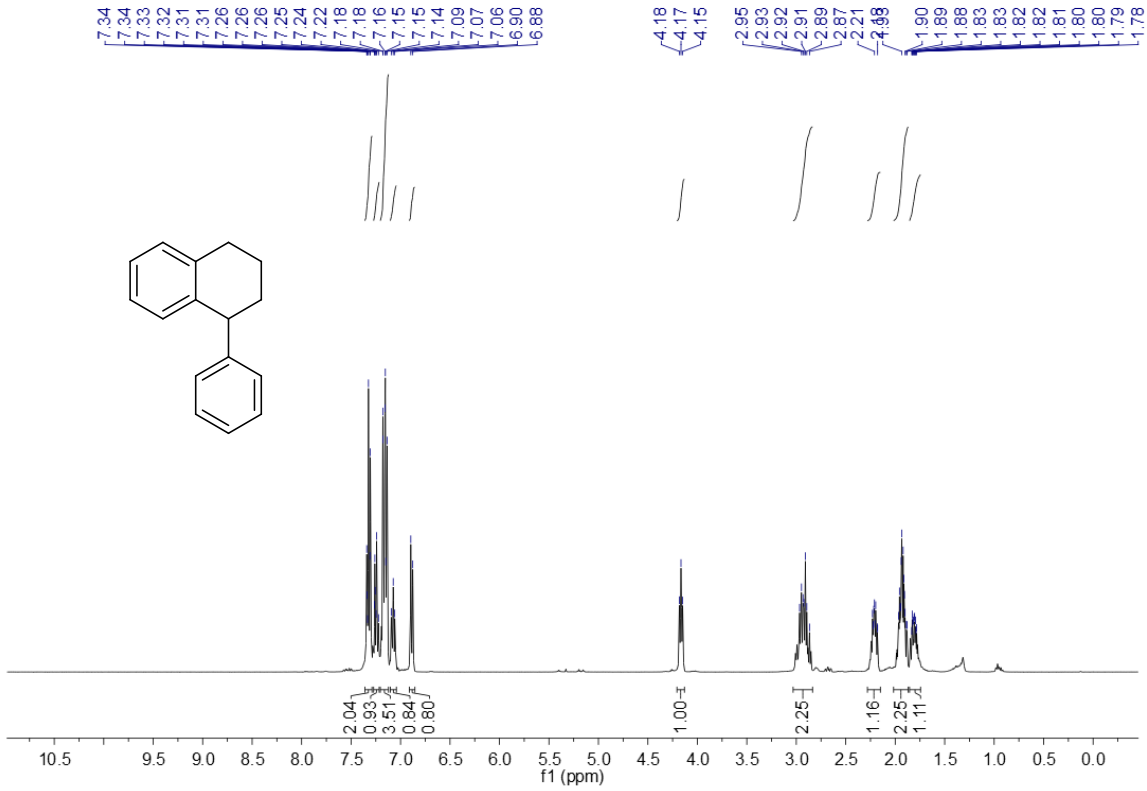


Fig. S83. ^{1}H NMR spectrum of 1-phenyl-1,2,3,4-tetrahydronaphthalene in $CDCl_3$

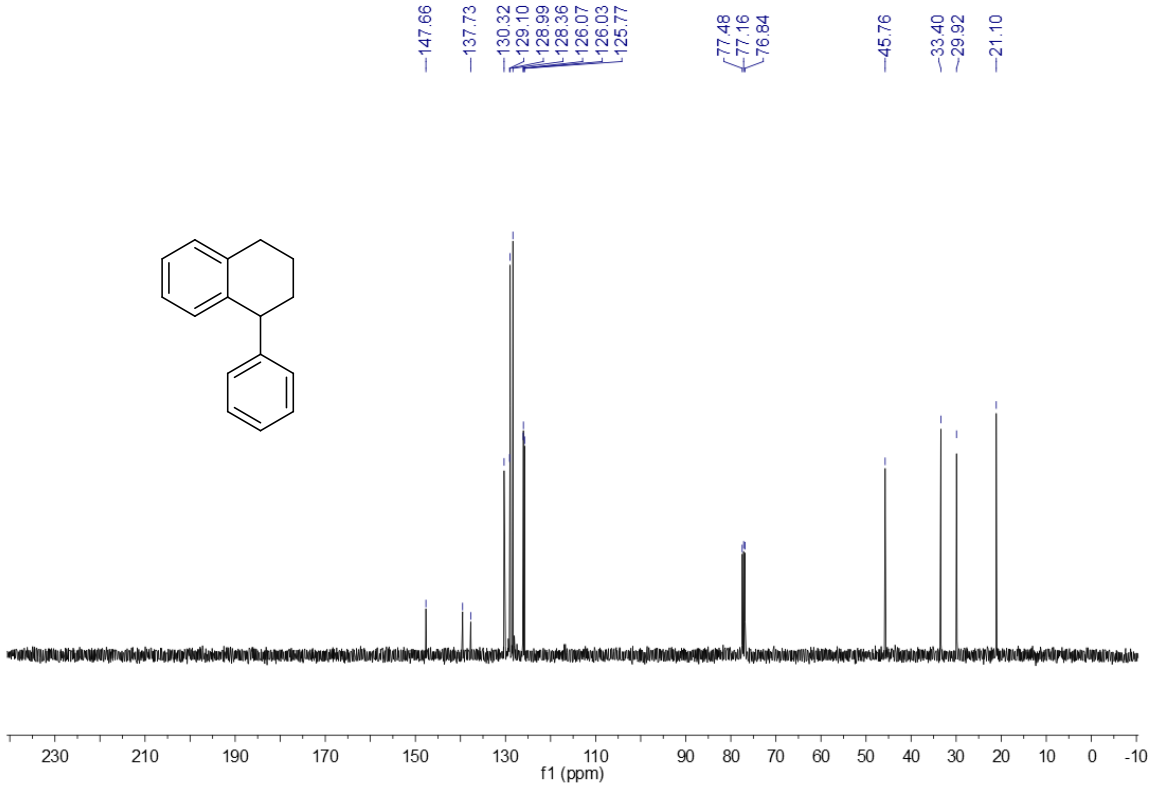


Fig. S84. $^{13}C\{^{1}H\}$ NMR spectrum of 1-phenyl-1,2,3,4-tetrahydronaphthalene in $CDCl_3$

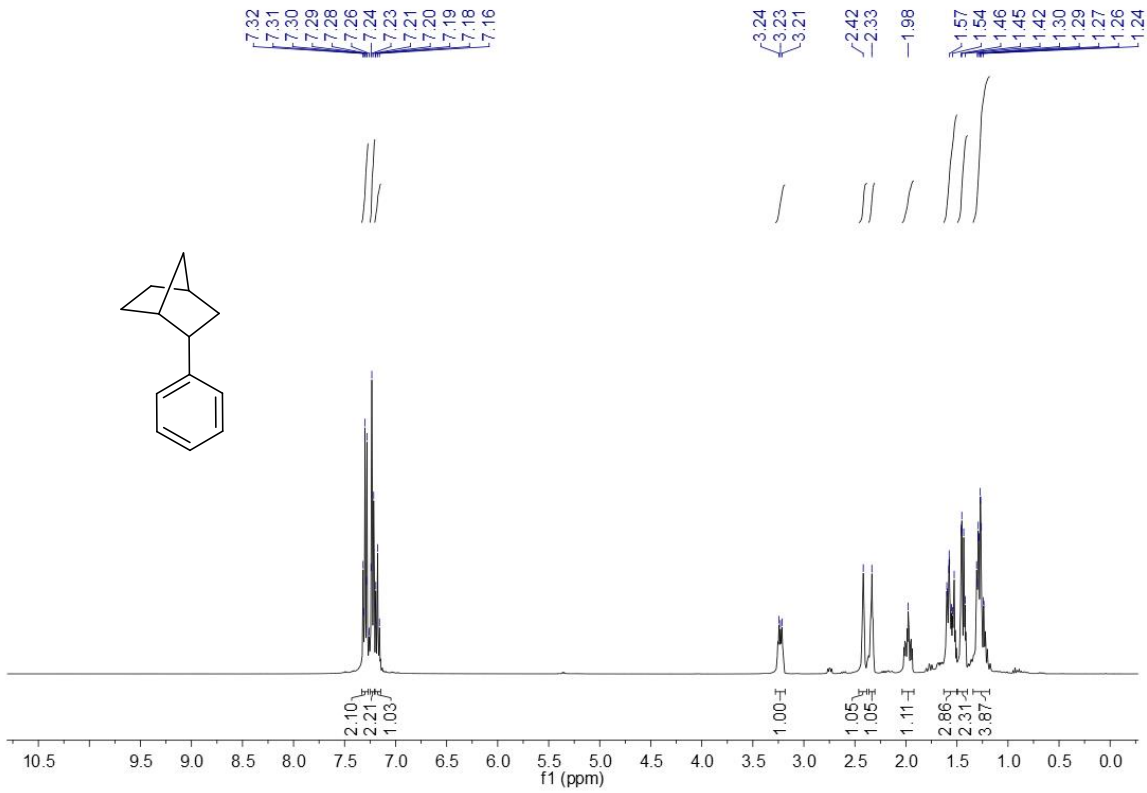


Fig. S85. ^{1}H NMR spectrum of 2-phenylbicyclo[2.2.1]heptane in $CDCl_3$

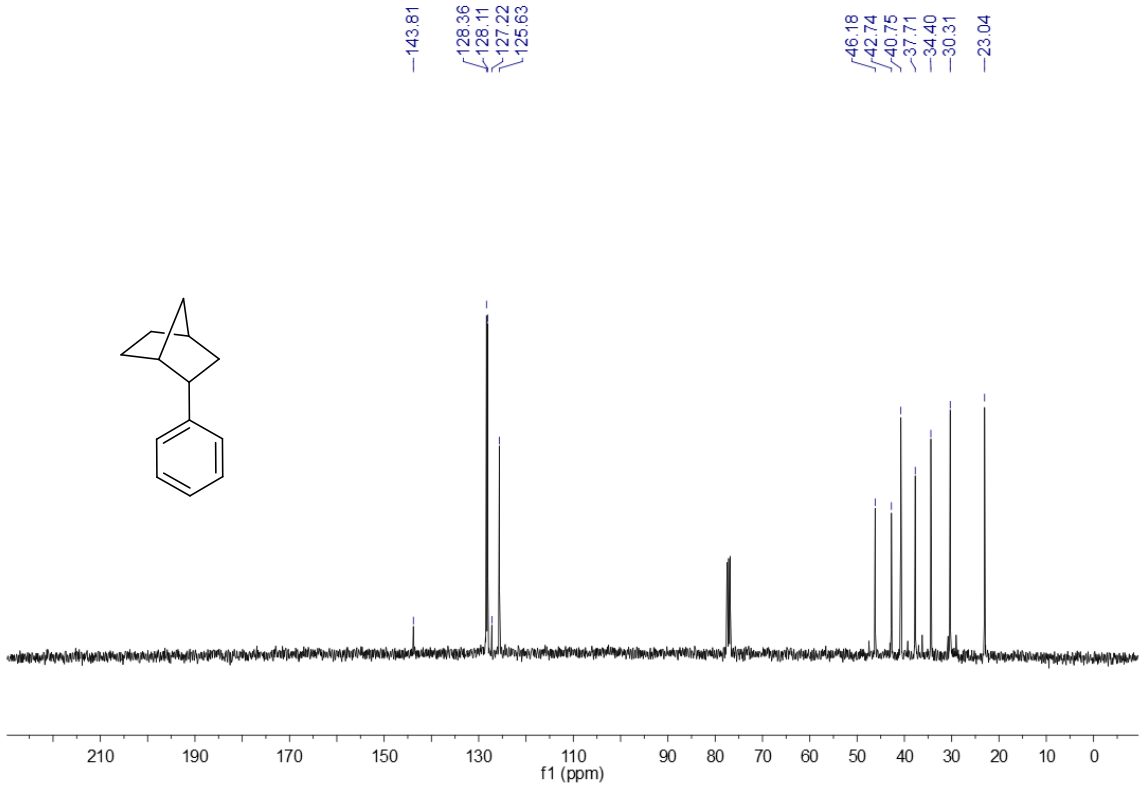


Fig. S86. $^{13}C\{^{1}H\}$ NMR spectrum of 2-phenylbicyclo[2.2.1]heptane in $CDCl_3$

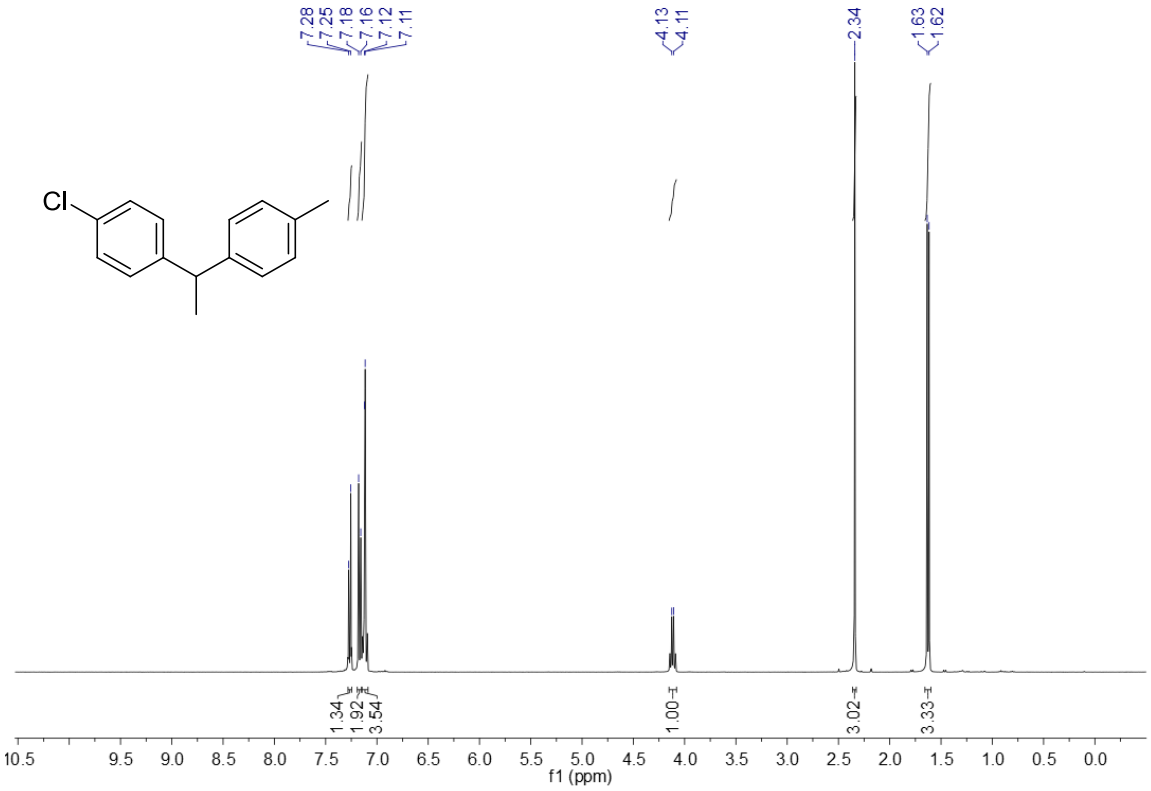


Fig. S87. ^{1}H NMR spectrum of 1-(4-chlorophenyl)-1-(4-methylphenyl)ethane in $CDCl_3$

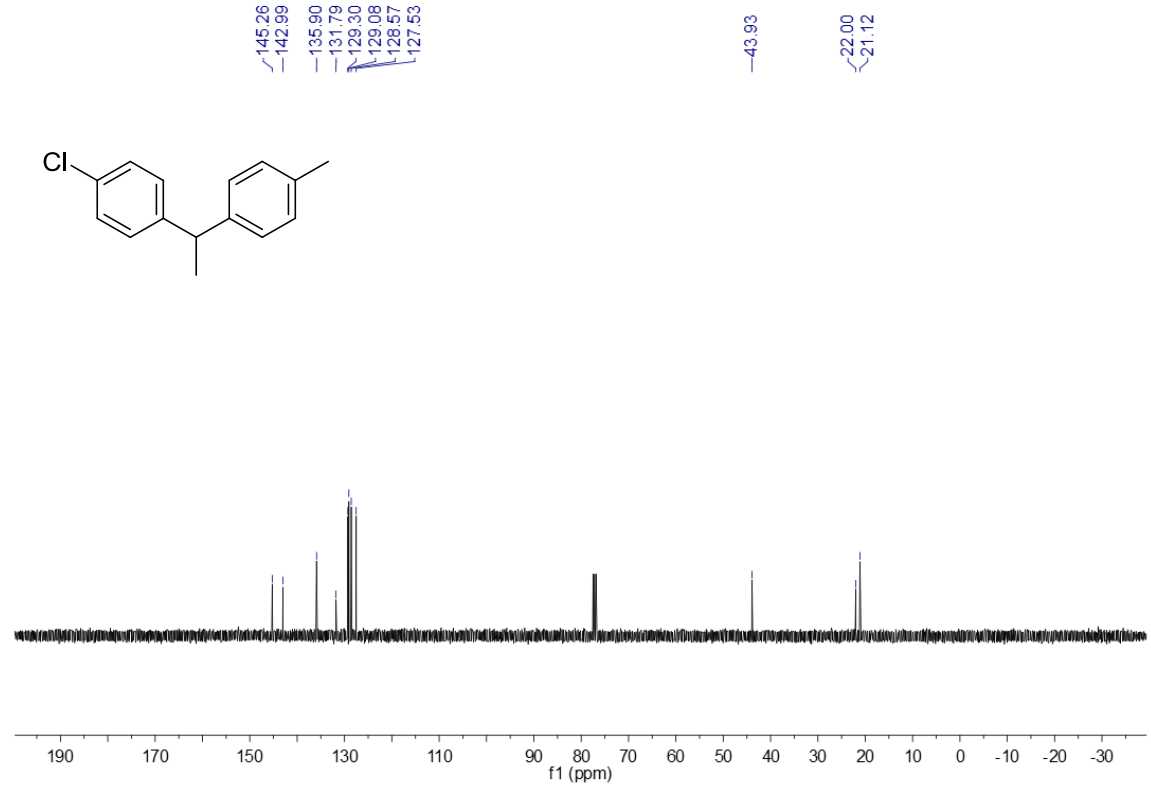


Fig. S88. $^{13}C\{^{1}H\}$ NMR spectrum of 1-(4-chlorophenyl)-1-(4-methylphenyl)ethane in $CDCl_3$

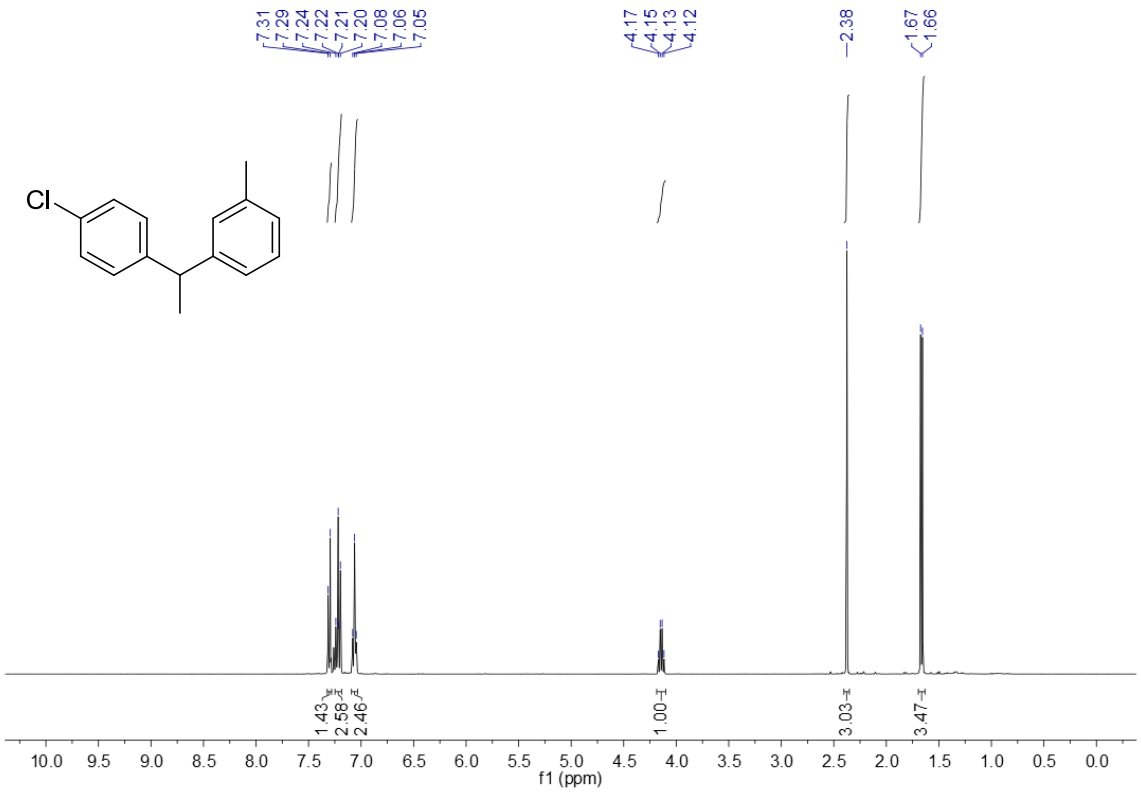


Fig. S89. ^{1}H NMR spectrum of 1-(4-chlorophenyl)-1-(3-methylphenyl)ethane in $CDCl_3$

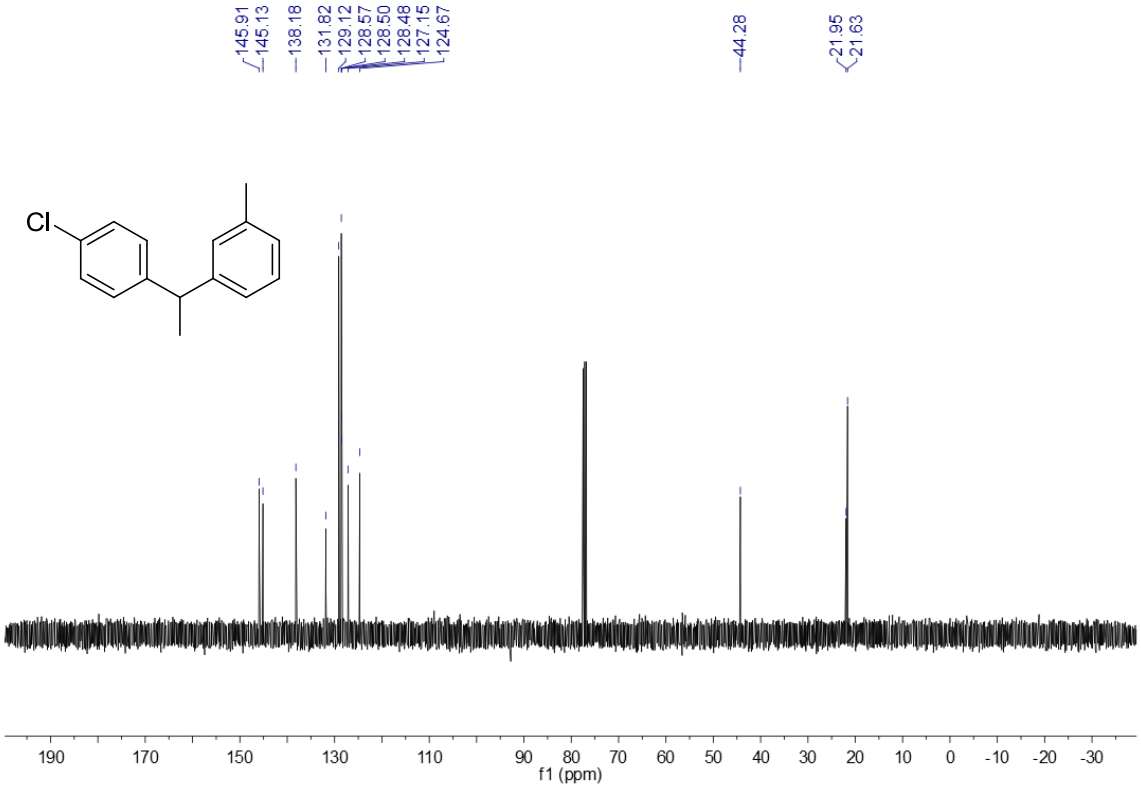


Fig. S90. $^{13}C\{^{1}H\}$ NMR spectrum of 1-(4-chlorophenyl)-1-(3-methylphenyl)ethane in $CDCl_3$

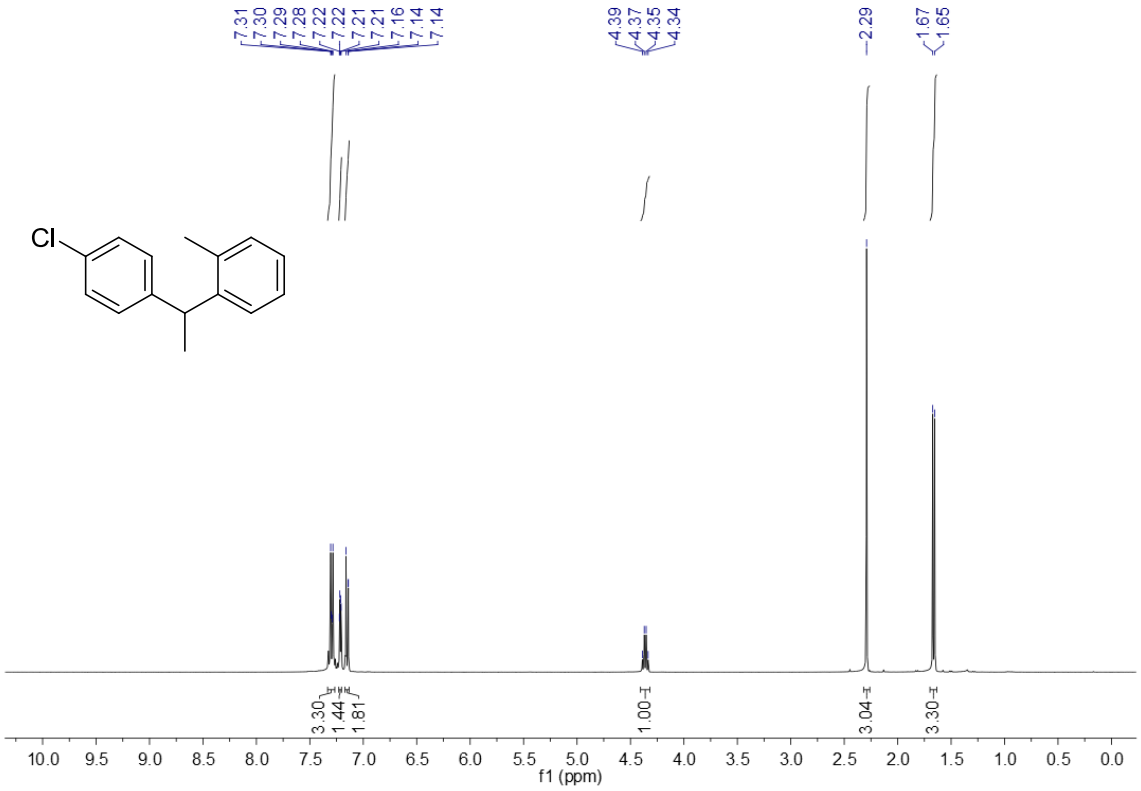


Fig. S91. ^{1}H NMR spectrum of 1-(4-chlorophenyl)-1-(2-methylphenyl)ethane in $CDCl_3$

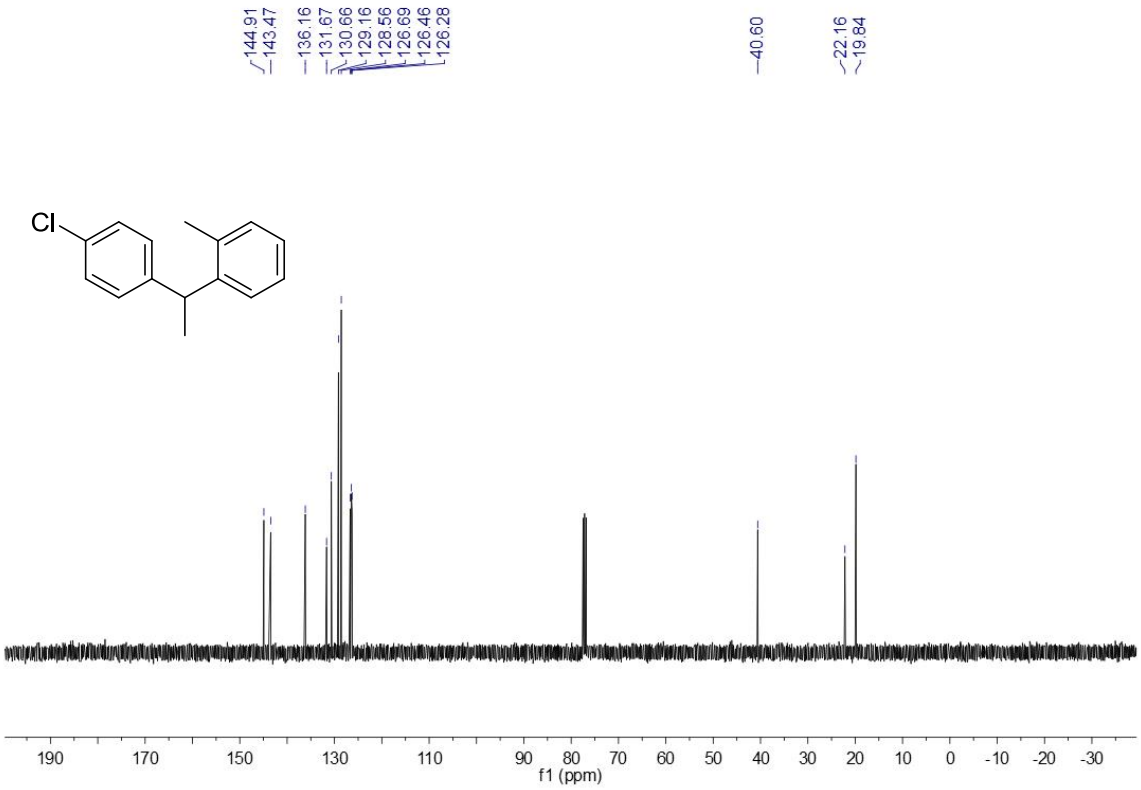


Fig. S92. $^{13}C\{^{1}H\}$ NMR spectrum of 1-(4-chlorophenyl)-1-(2-methylphenyl)ethane in $CDCl_3$

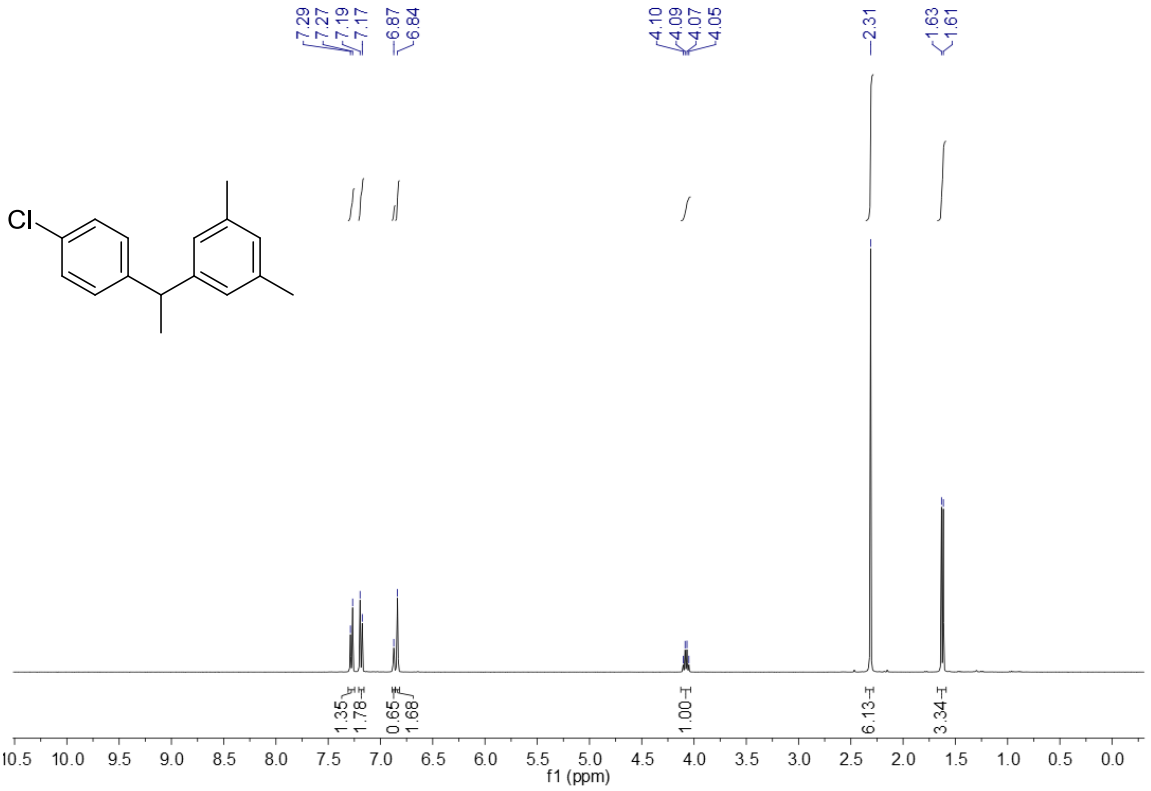


Fig. S93. ^{1}H NMR spectrum of 1-(4-chlorophenyl)-1-(3,5-dimethylphenyl)ethane in $CDCl_3$

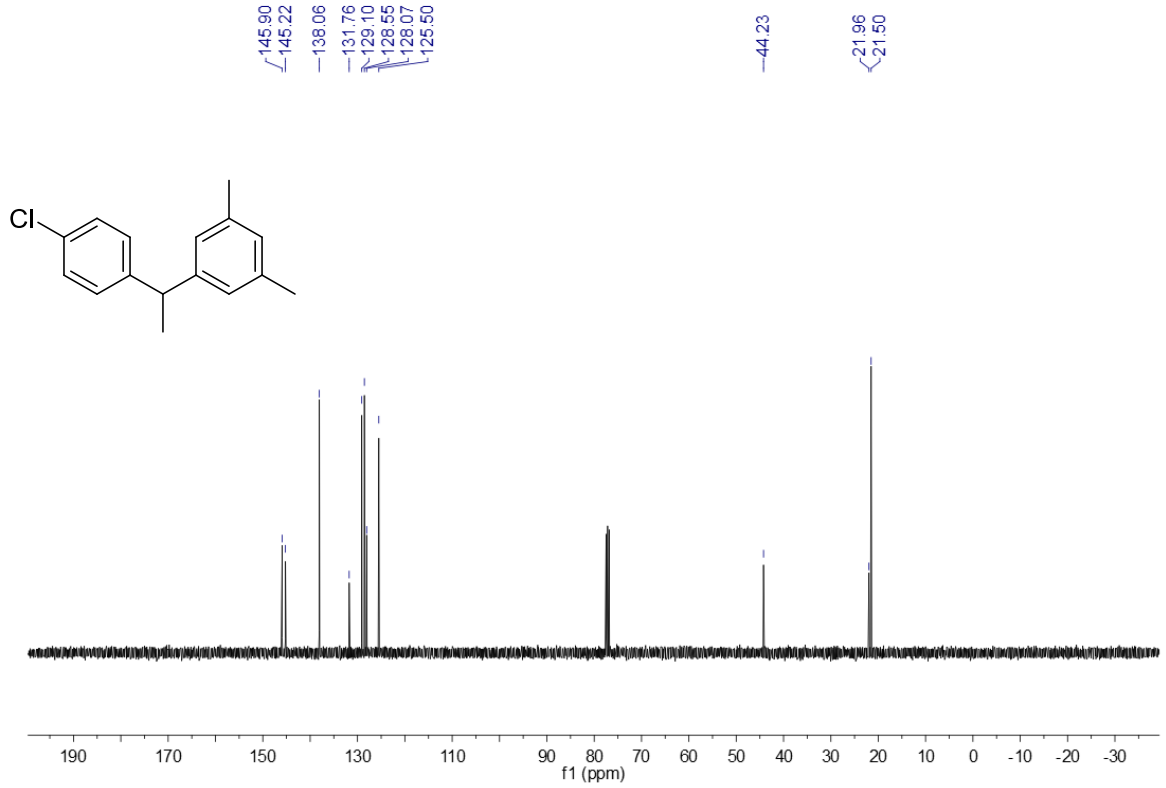


Fig. S94. $^{13}C\{^{1}H\}$ NMR spectrum of 1-(4-chlorophenyl)-1-(3,5-dimethylphenyl)ethane in $CDCl_3$

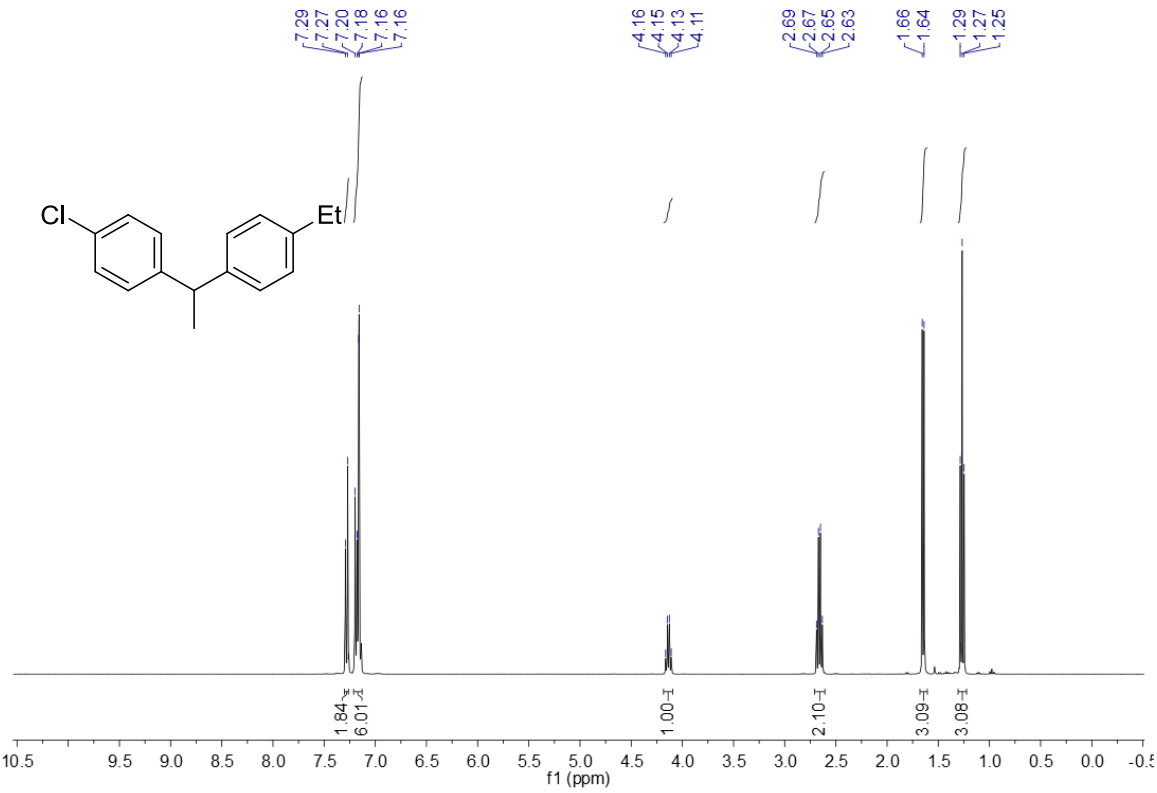


Fig. S95. ^{1}H NMR spectrum of 1-(4-chlorophenyl)-1-(4-ethylphenyl)ethane in $CDCl_3$

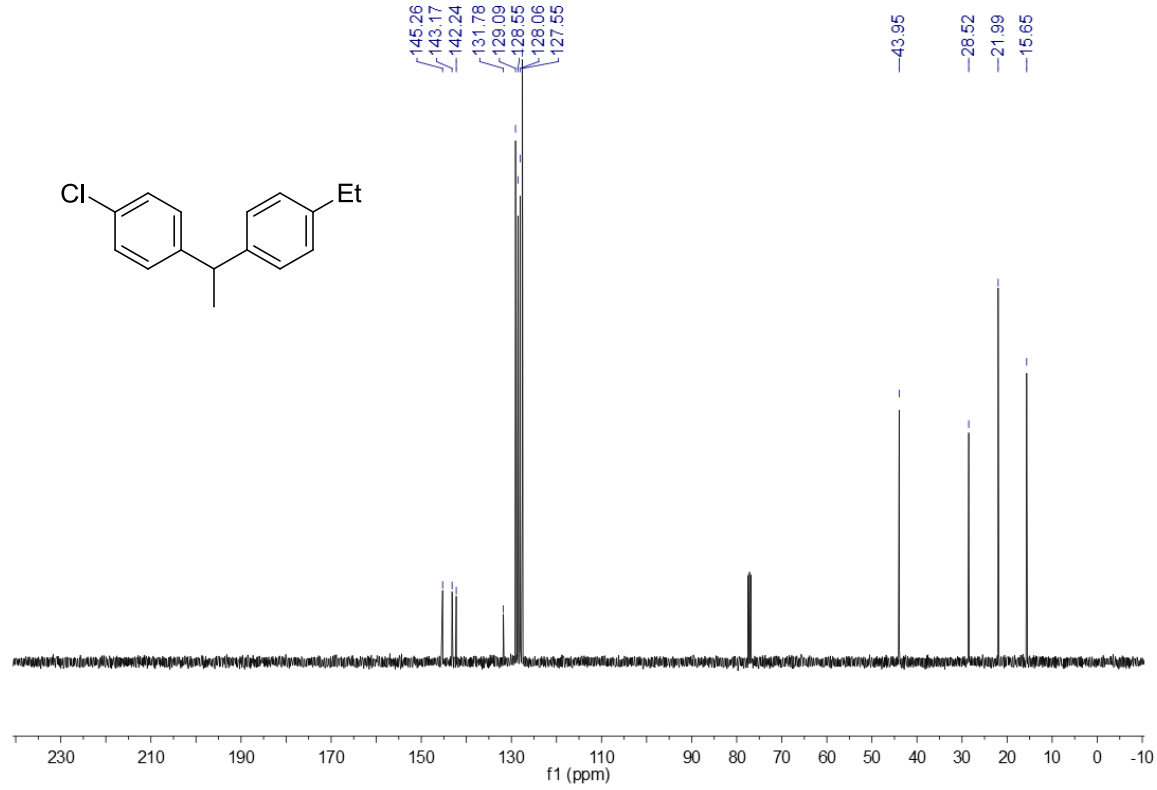


Fig. S96. $^{13}C\{^{1}H\}$ NMR spectrum of 1-(4-chlorophenyl)-1-(4-ethylphenyl)ethane in $CDCl_3$

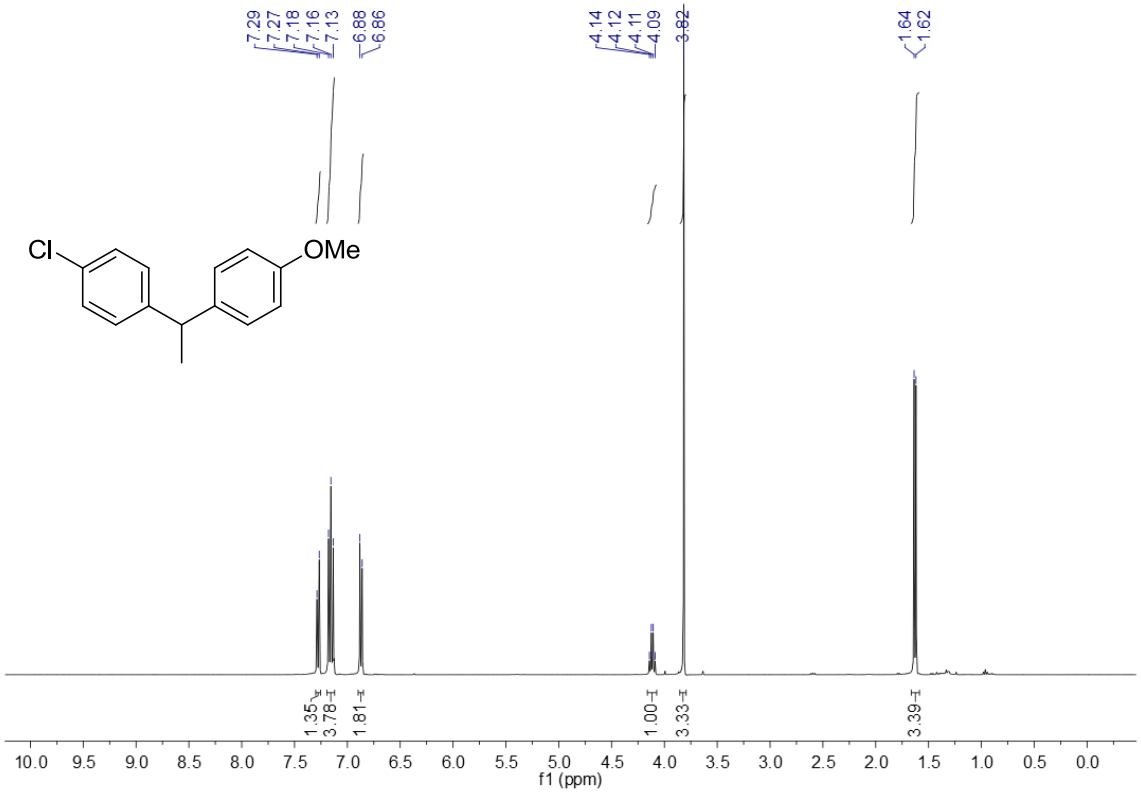


Fig. S97. ^{1}H NMR spectrum of 1-(4-chlorophenyl)-1-(4-methoxyphenyl)ethane in $CDCl_3$

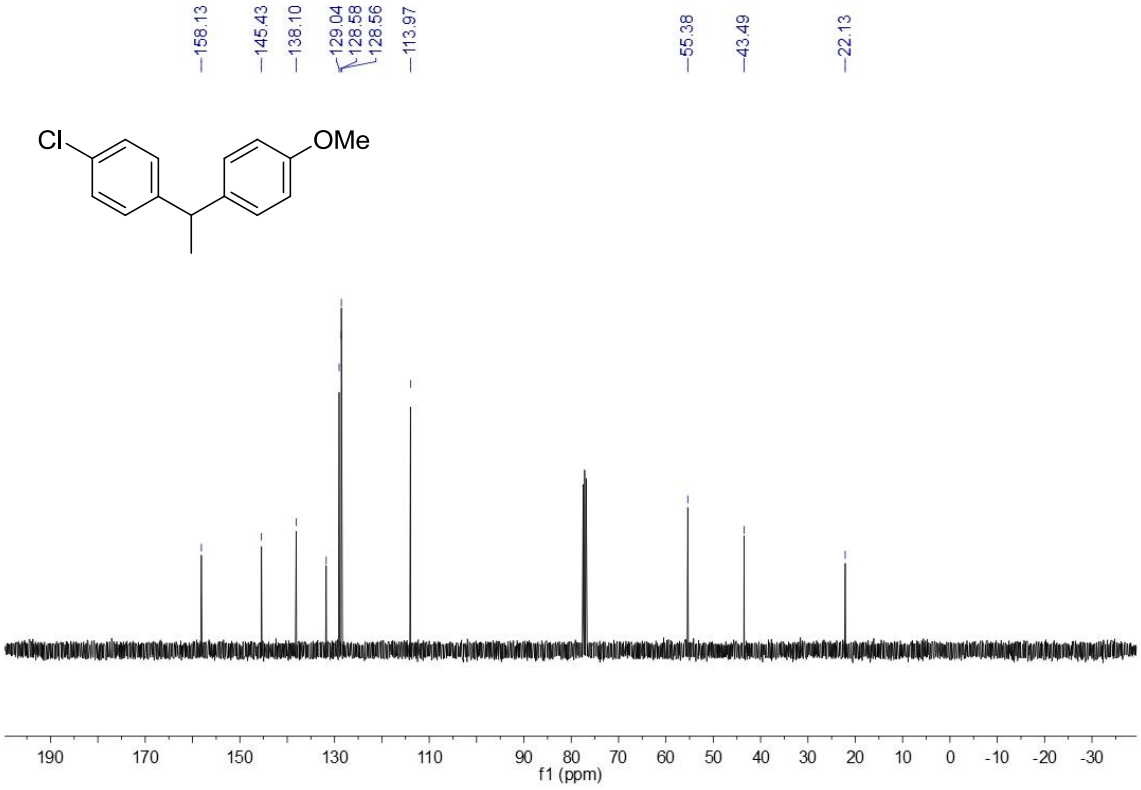


Fig. S98. ^{13}C{^{1}H} NMR spectrum of 1-(4-chlorophenyl)-1-(4-methoxyphenyl)ethane in $CDCl_3$

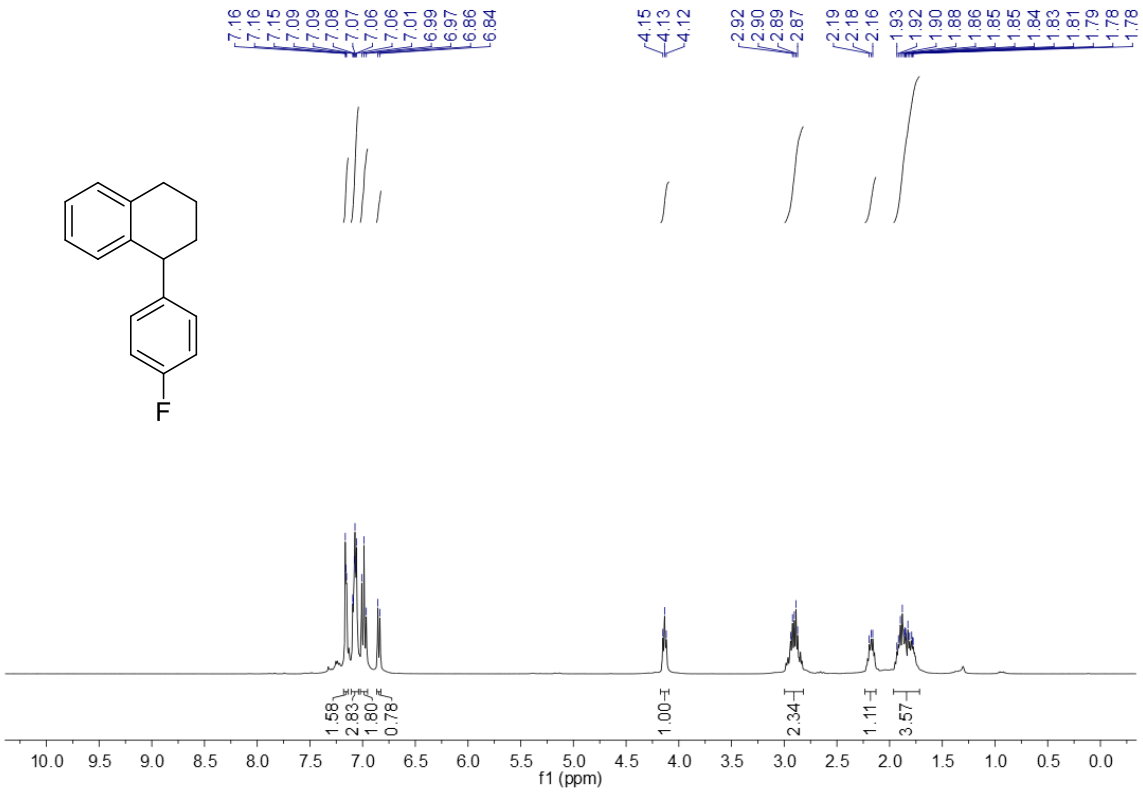


Fig. S99. ^{1}H NMR spectrum of 1-(4-fluorophenyl)-1,2,3,4-tetrahydronaphthalene in $CDCl_3$

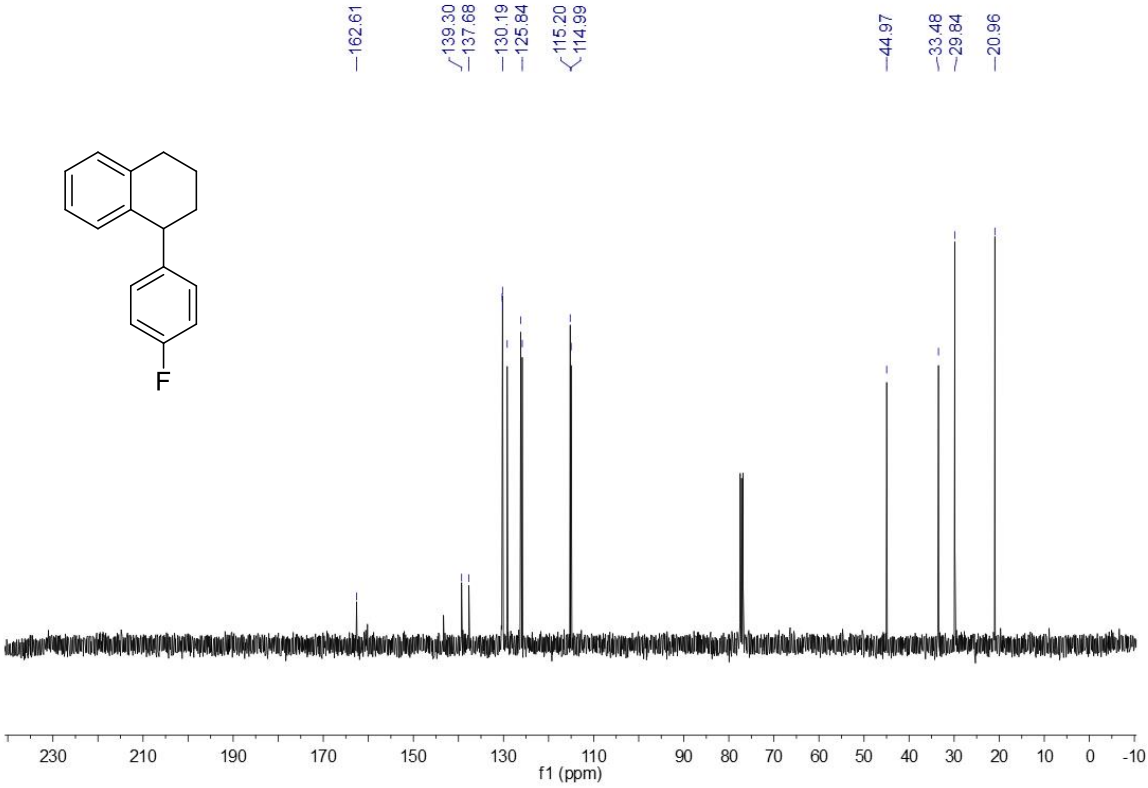


Fig. S100. $^{13}C\{^{1}H\}$ NMR spectrum of 1-(4-fluorophenyl)-1,2,3,4-tetrahydronaphthalene in $CDCl_3$

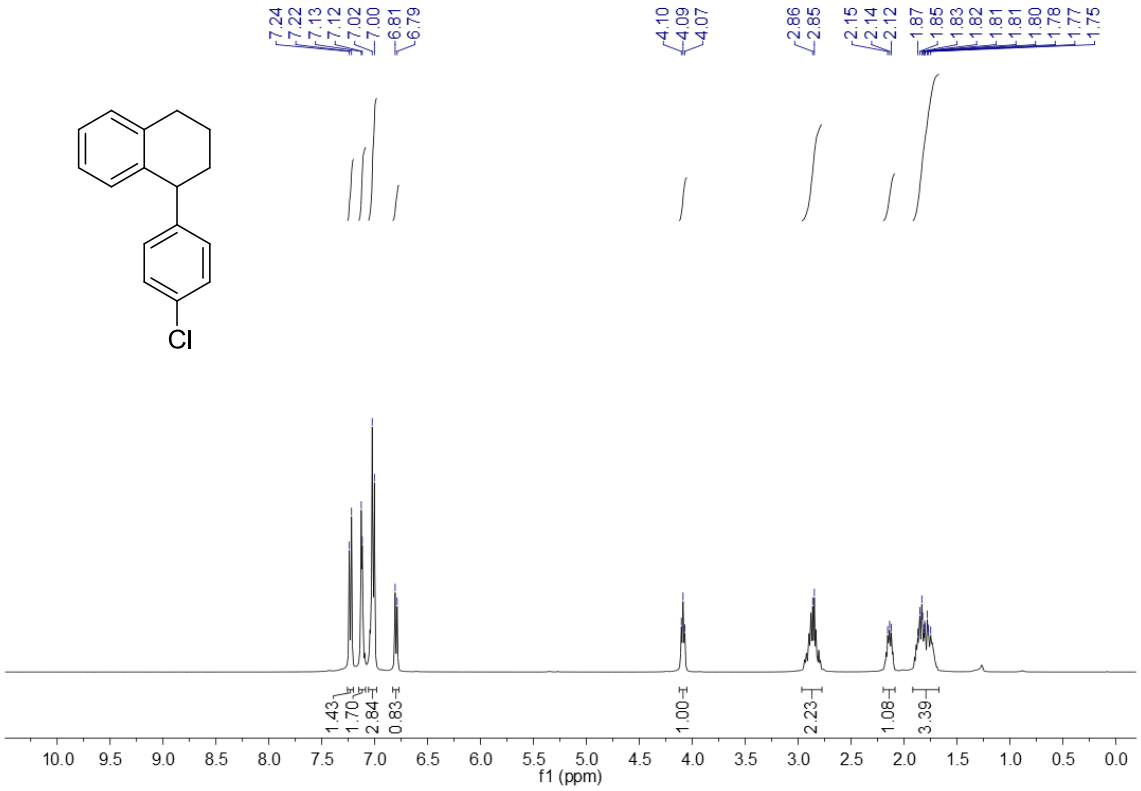


Fig. S101. ^{1}H NMR spectrum of 1-(4-chlorophenyl)-1,2,3,4-tetrahydronaphthalene in $CDCl_3$

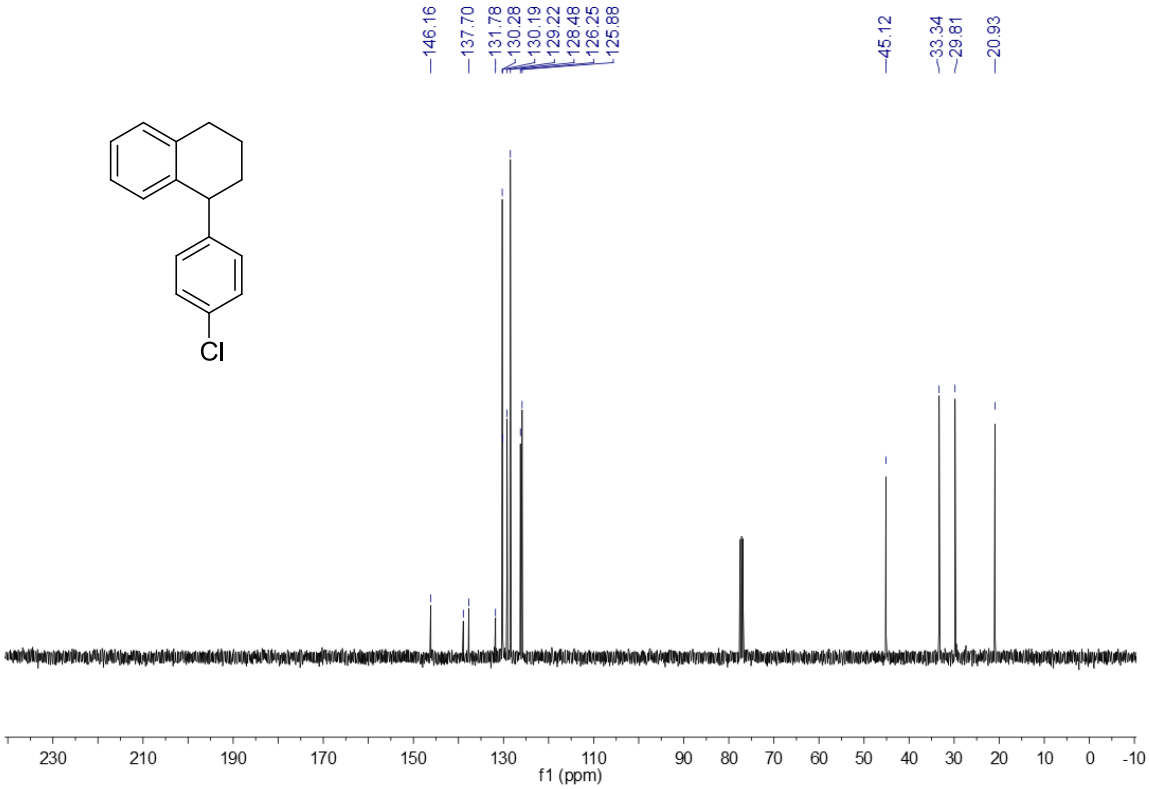


Fig. S102. $^{13}C\{^{1}H\}$ NMR spectrum of 1-(4-chlorophenyl)-1,2,3,4-tetrahydronaphthalene in $CDCl_3$

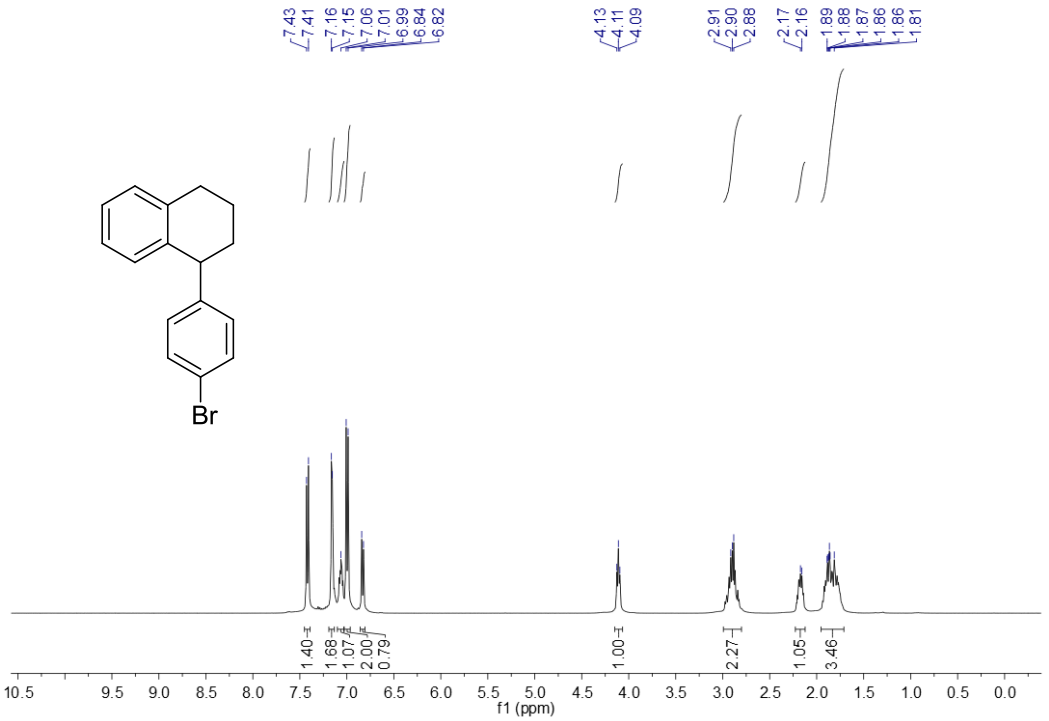


Fig. S103. ^{1}H NMR spectrum of 1-(4-bromophenyl)-1,2,3,4-tetrahydronaphthalene in $CDCl_3$

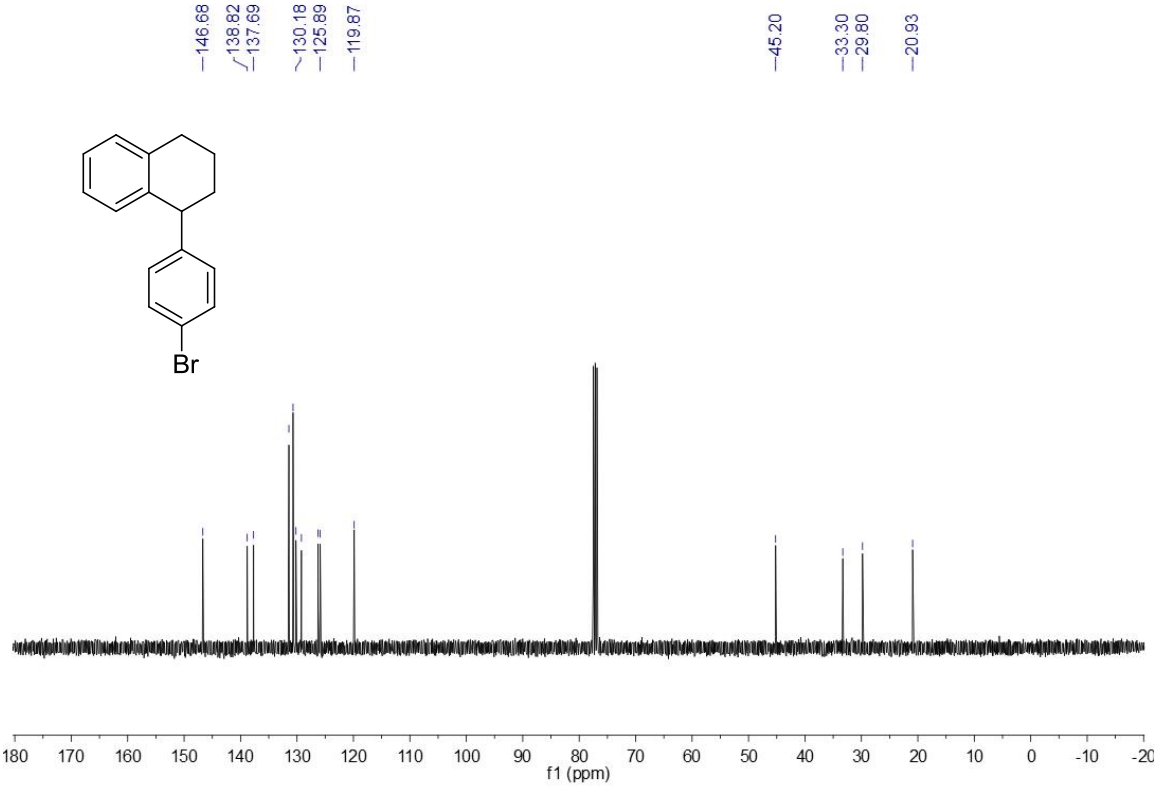


Fig. S104. $^{13}C\{^{1}H\}$ NMR spectrum of 1-(4-bromophenyl)-1,2,3,4-tetrahydronaphthalene in $CDCl_3$

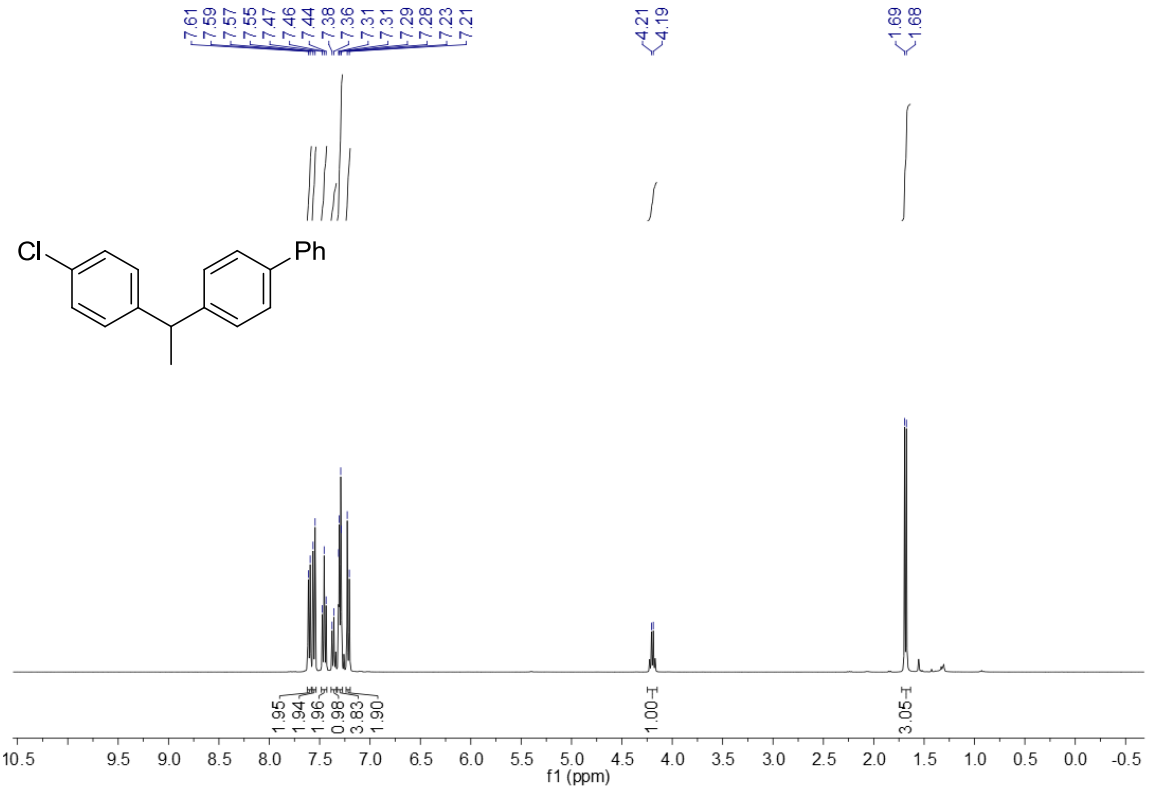


Fig. S105. ^{1}H NMR spectrum of 1-(4-chlorophenyl)-1-(4-phenylphenyl)ethane in $CDCl_3$

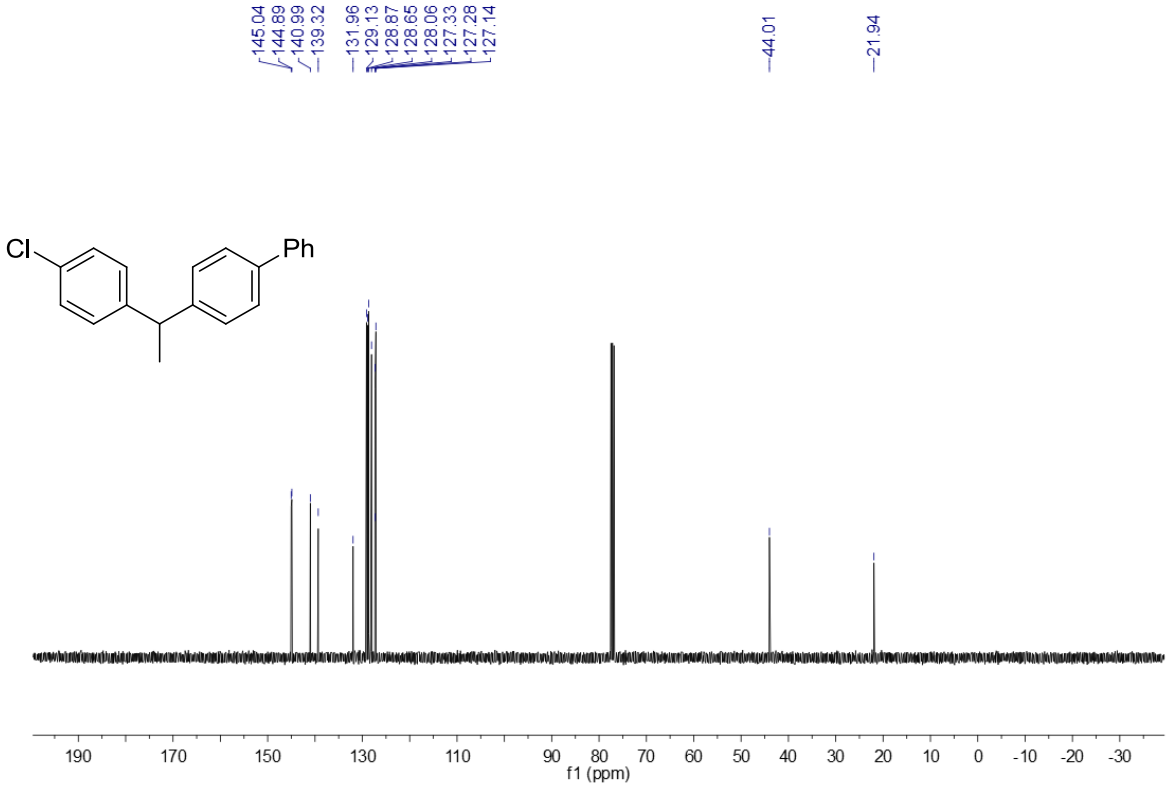


Fig. S106. $^{13}C\{^{1}H\}$ NMR spectrum of 1-(4-chlorophenyl)-1-(4-phenylphenyl)ethane in $CDCl_3$

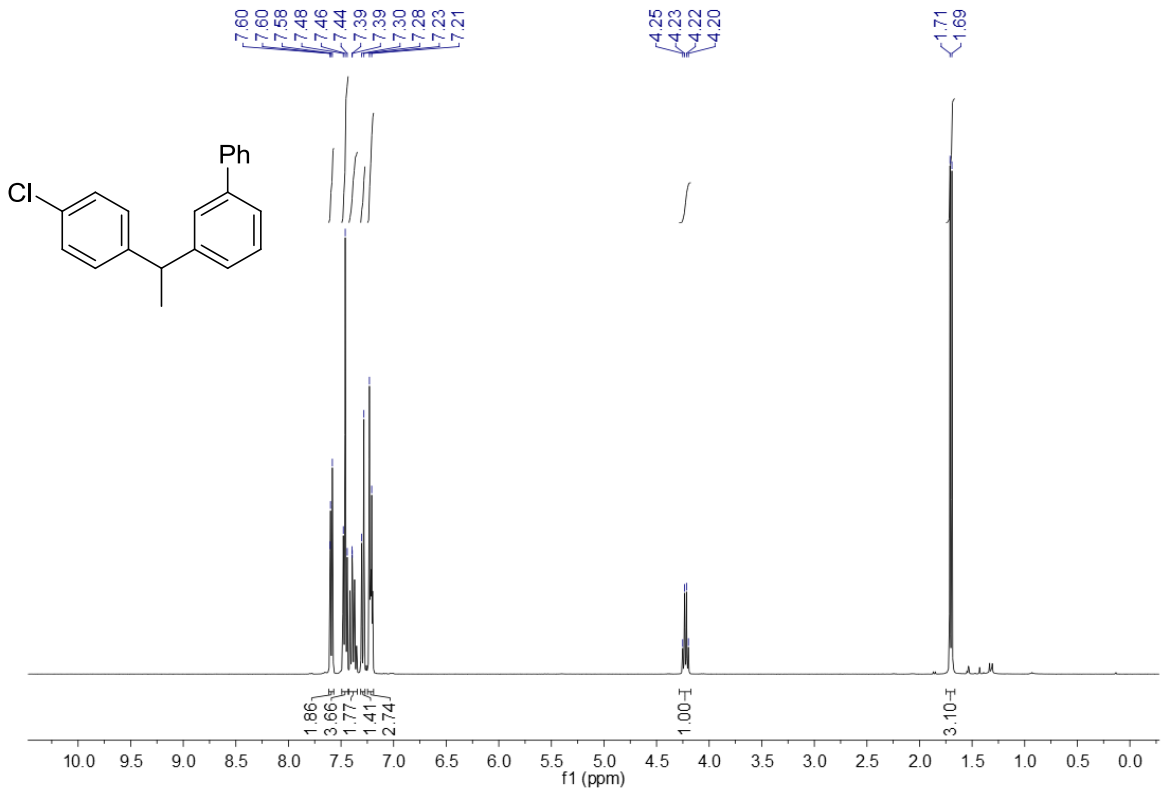


Fig. S107. ^{1}H NMR spectrum of 1-(4-chlorophenyl)-1-(3-phenylphenyl)ethane in $CDCl_3$

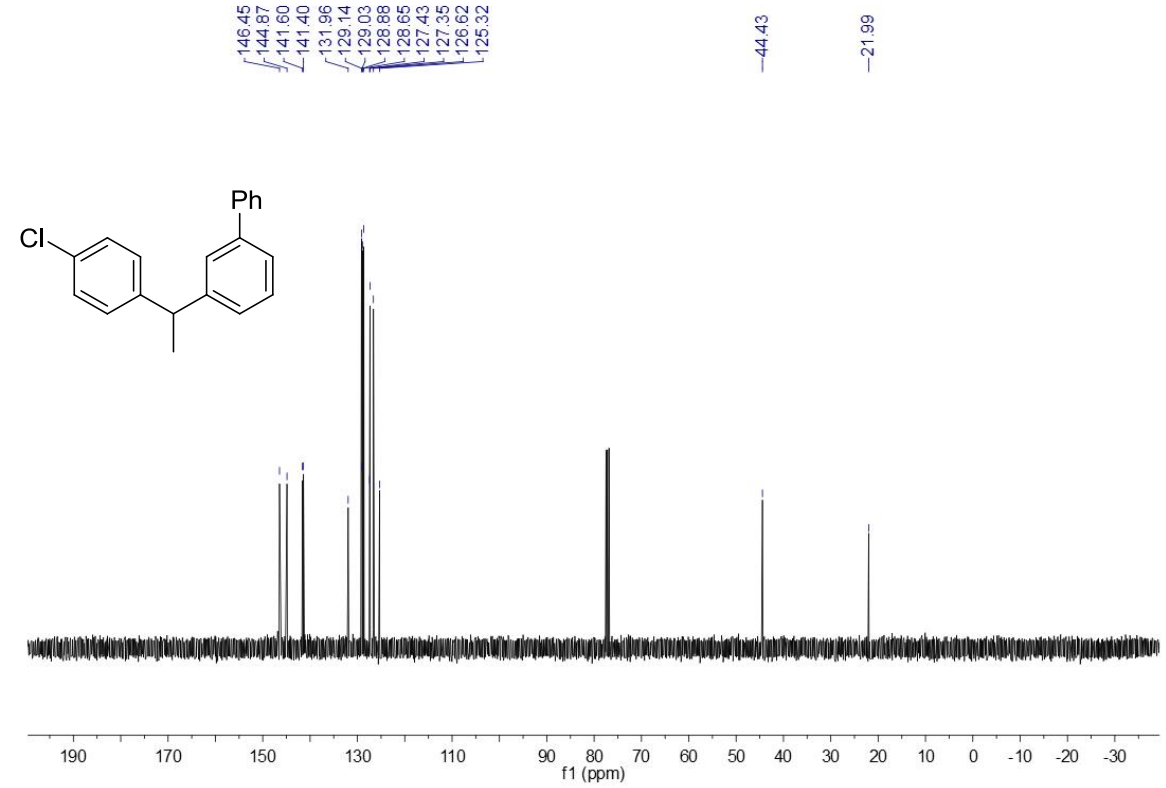


Fig. S108. $^{13}C\{^{1}H\}$ NMR spectrum of 1-(4-chlorophenyl)-1-(3-phenylphenyl)ethane in $CDCl_3$

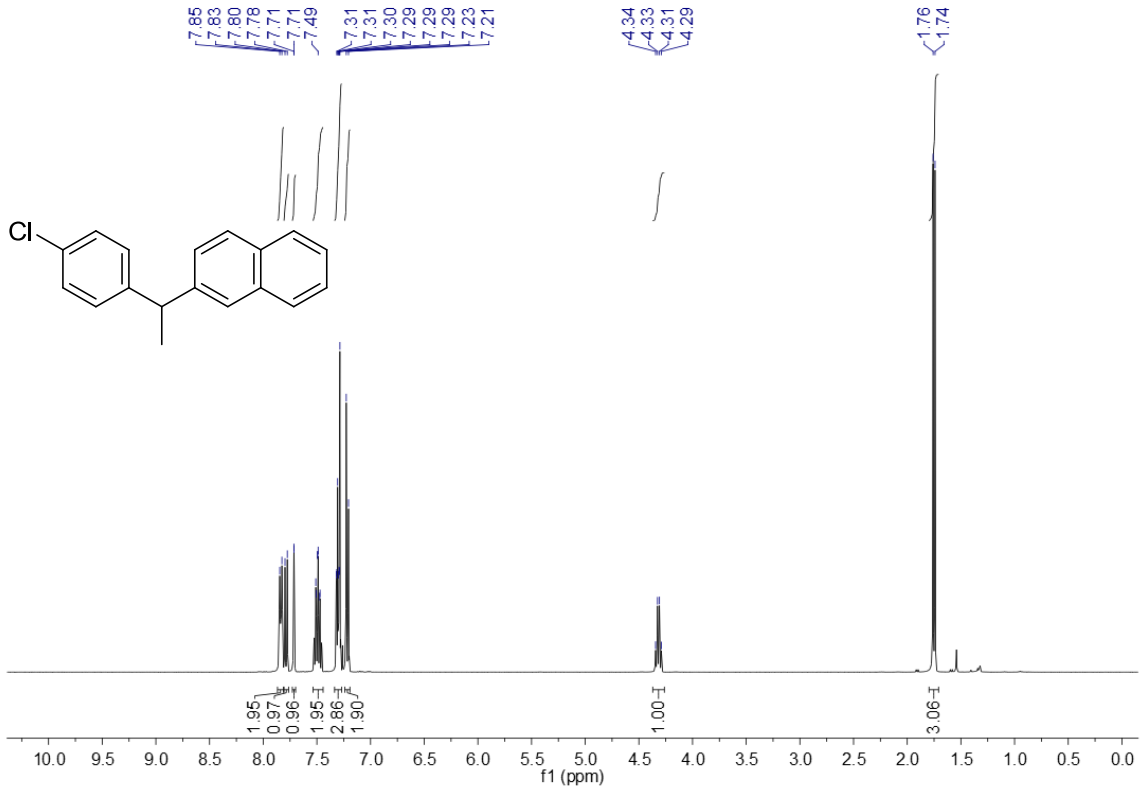


Fig. S109. $^{13}C\{^{1}H\}$ NMR spectrum of 1-(4-chlorophenyl)-1-(2-naphthyl)ethane in $CDCl_3$

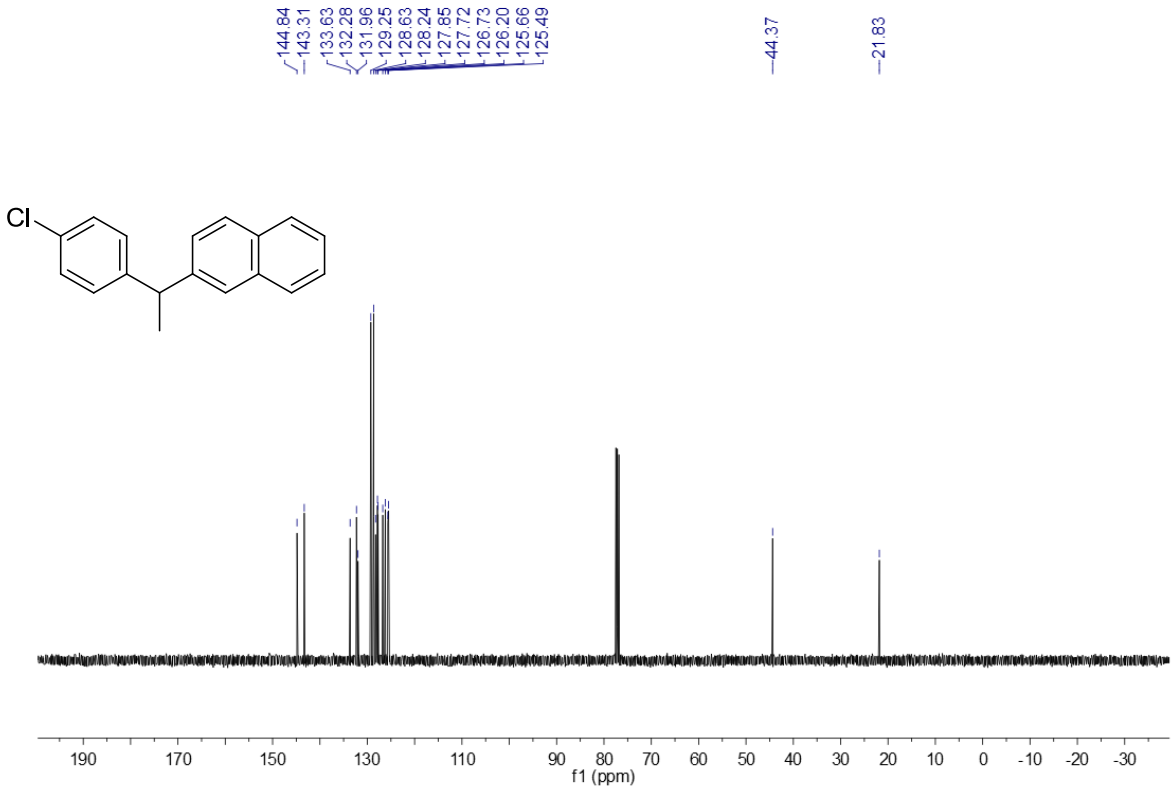


Fig. S110. $^{13}C\{^{1}H\}$ NMR spectrum of 1-(4-chlorophenyl)-1-(2-naphthyl)ethane in $CDCl_3$

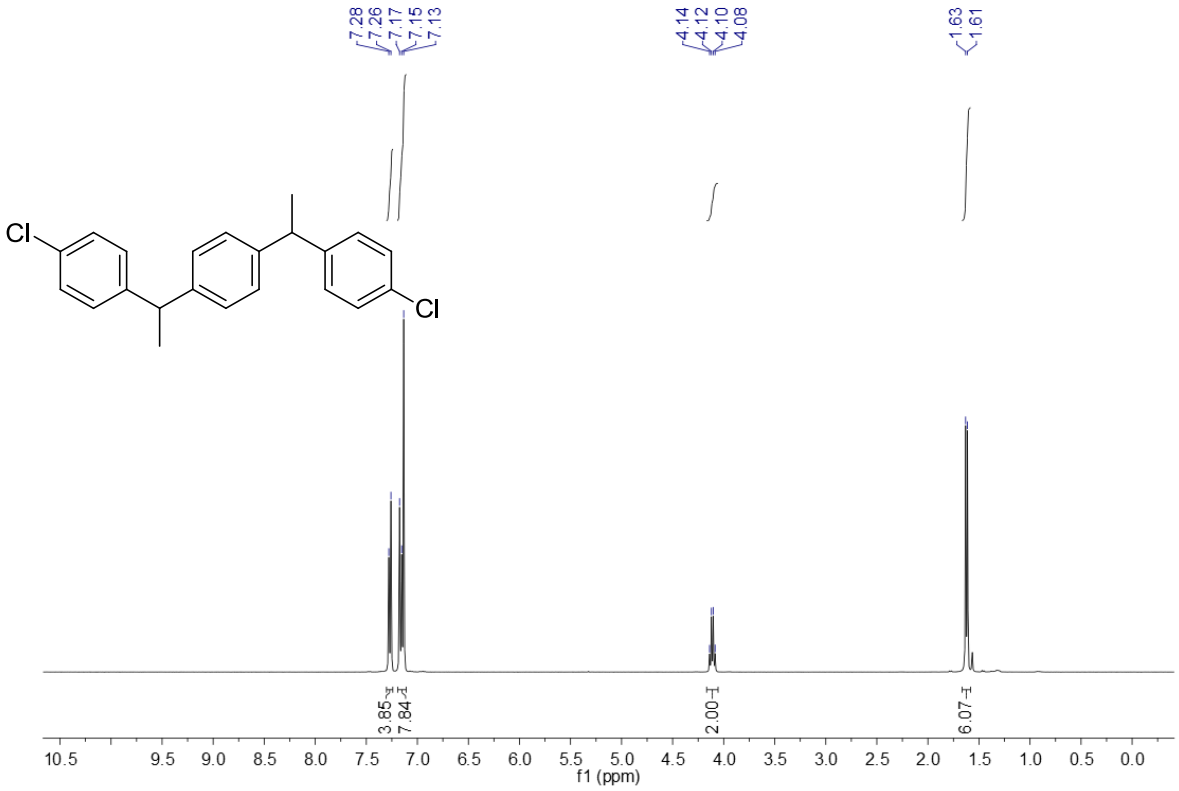


Fig. S111. ^{1}H NMR spectrum of 1,4-bis(1-(4-chlorophenyl)ethyl)benzene in $CDCl_3$

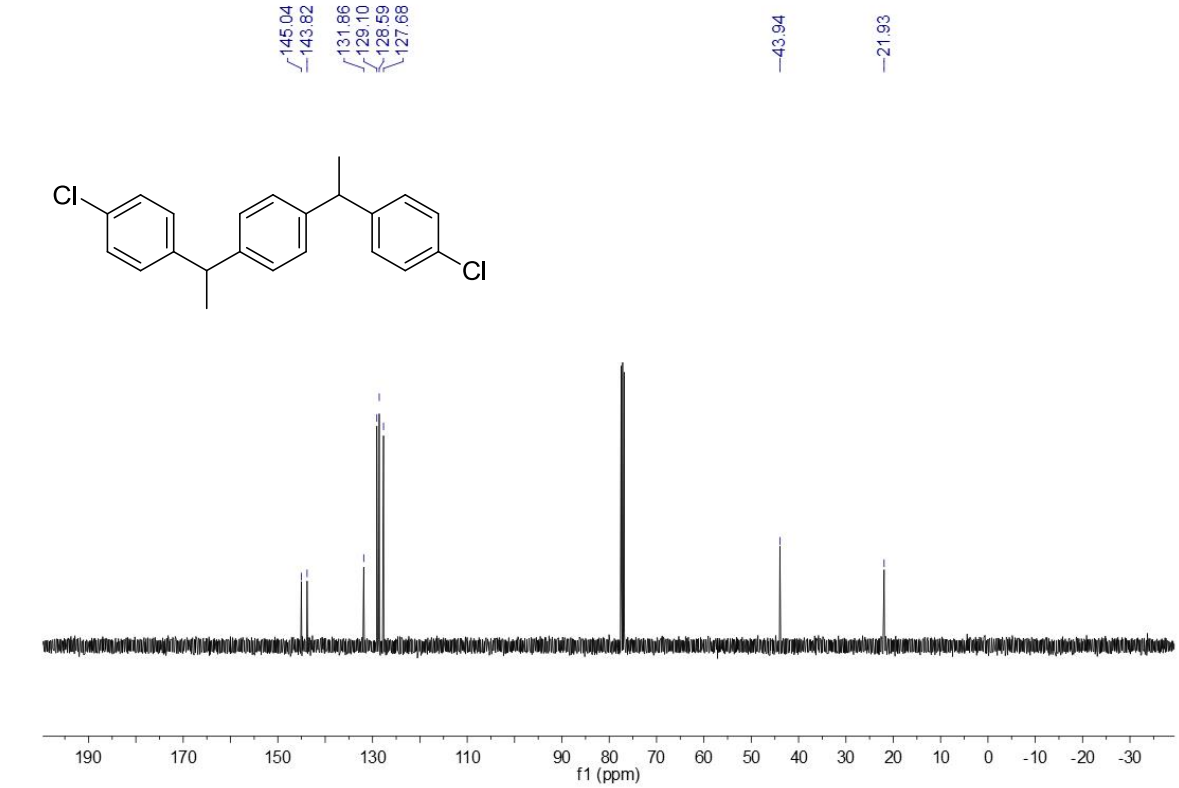


Fig. S112. $^{13}C\{^{1}H\}$ NMR spectrum of 1,4-bis(1-(4-chlorophenyl)ethyl)benzene in $CDCl_3$

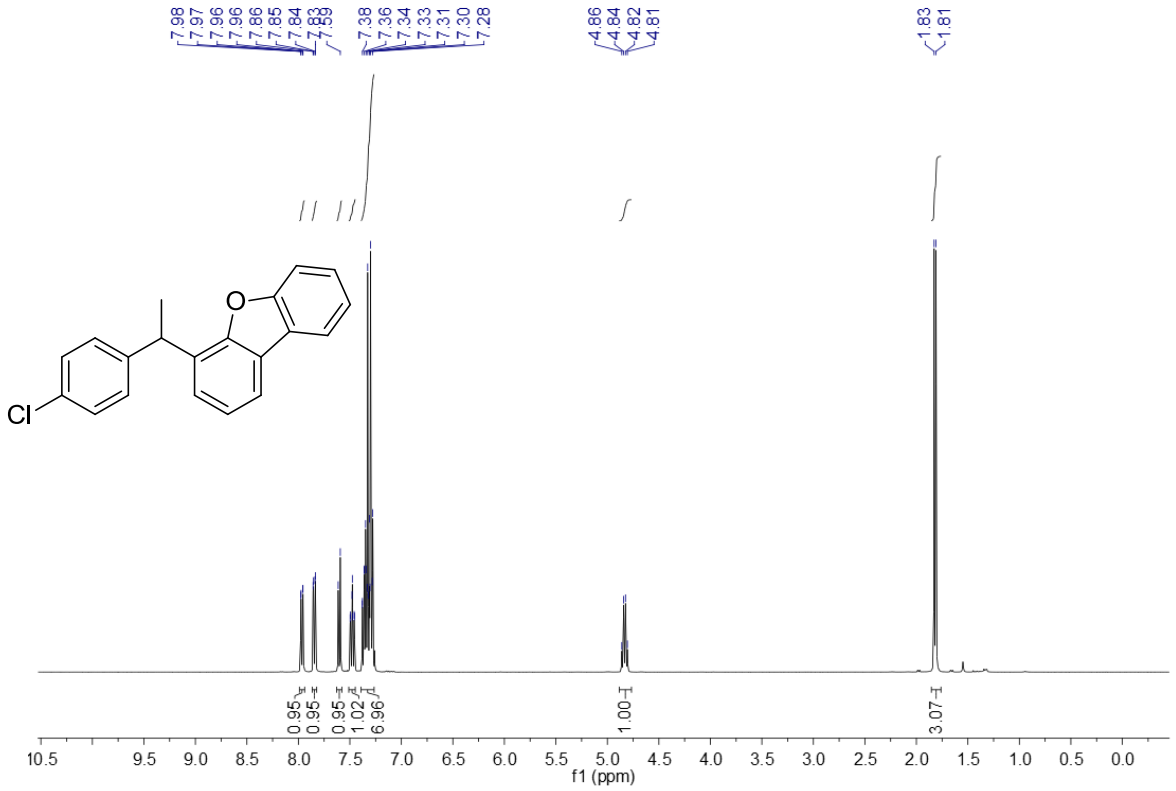


Fig. S113. ^{1}H NMR spectrum of 1-(4-chlorophenyl)-1-(4-dibenzofuryl)ethane in $CDCl_3$

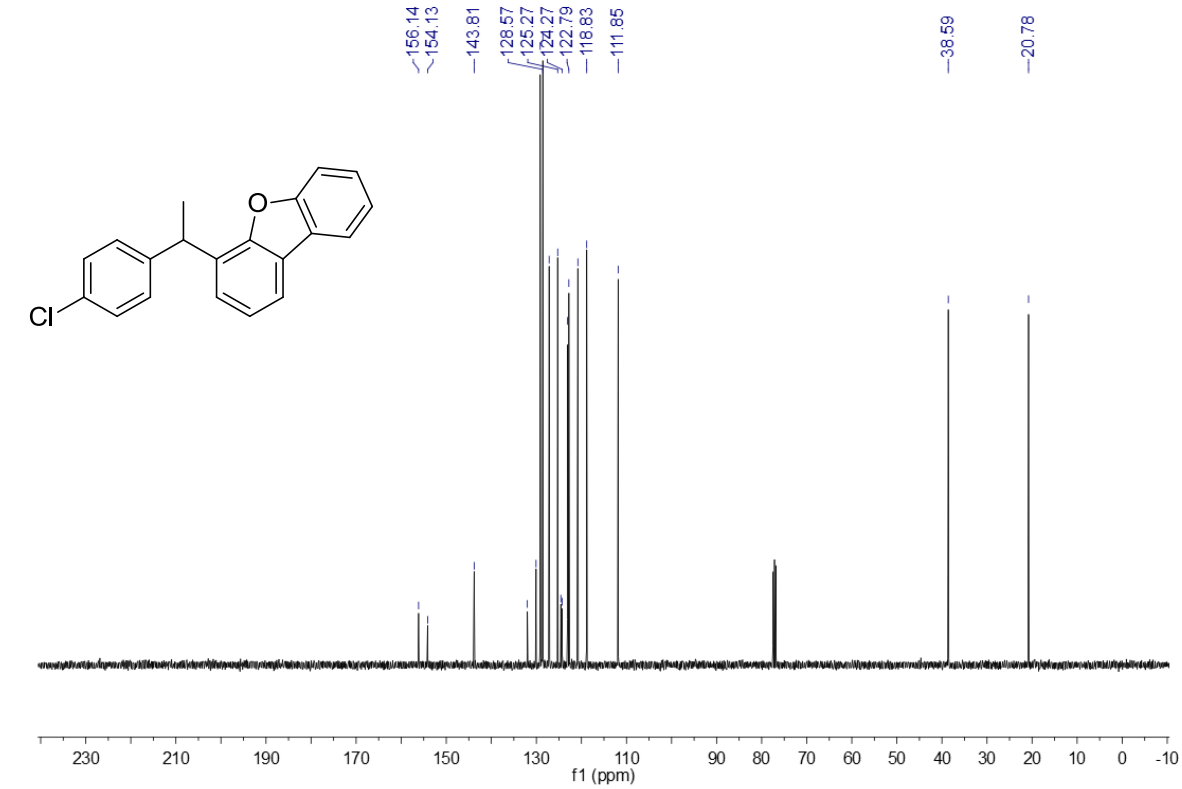


Fig. S114. $^{13}C\{^{1}H\}$ NMR spectrum of 1-(4-chlorophenyl)-1-(4-dibenzofuryl)ethane in $CDCl_3$

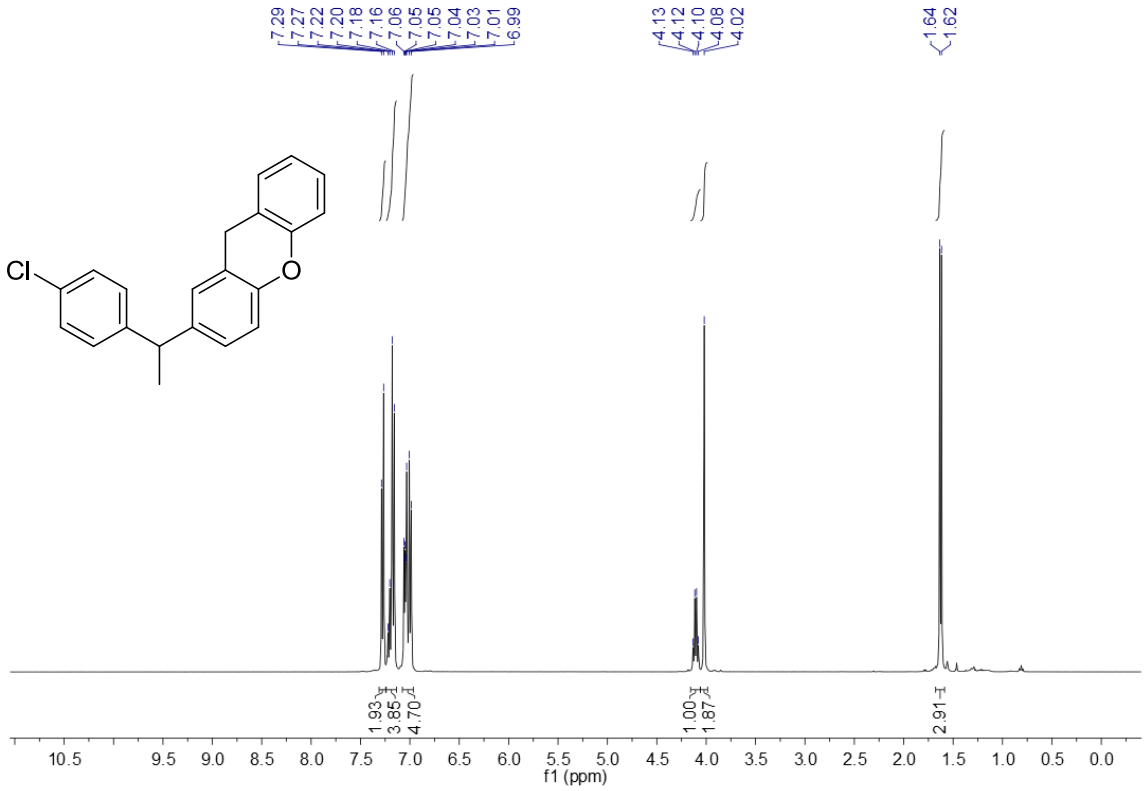


Fig. S115. ^{1}H NMR spectrum of 1-(4-chlorophenyl)-1-(3-xanthyl)ethane in $CDCl_3$

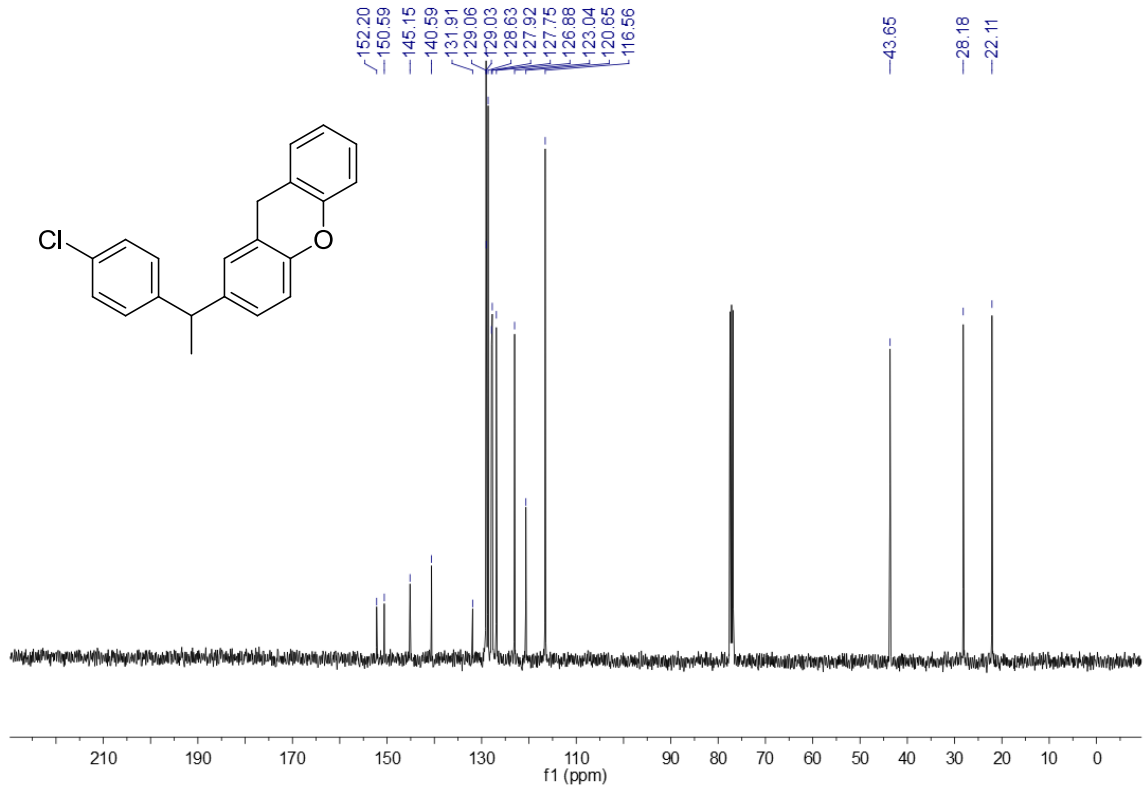


Fig. S116. ^{13}C{^{1}H} NMR spectrum of 1-(4-chlorophenyl)-1-(3-xanthyl)ethane in $CDCl_3$

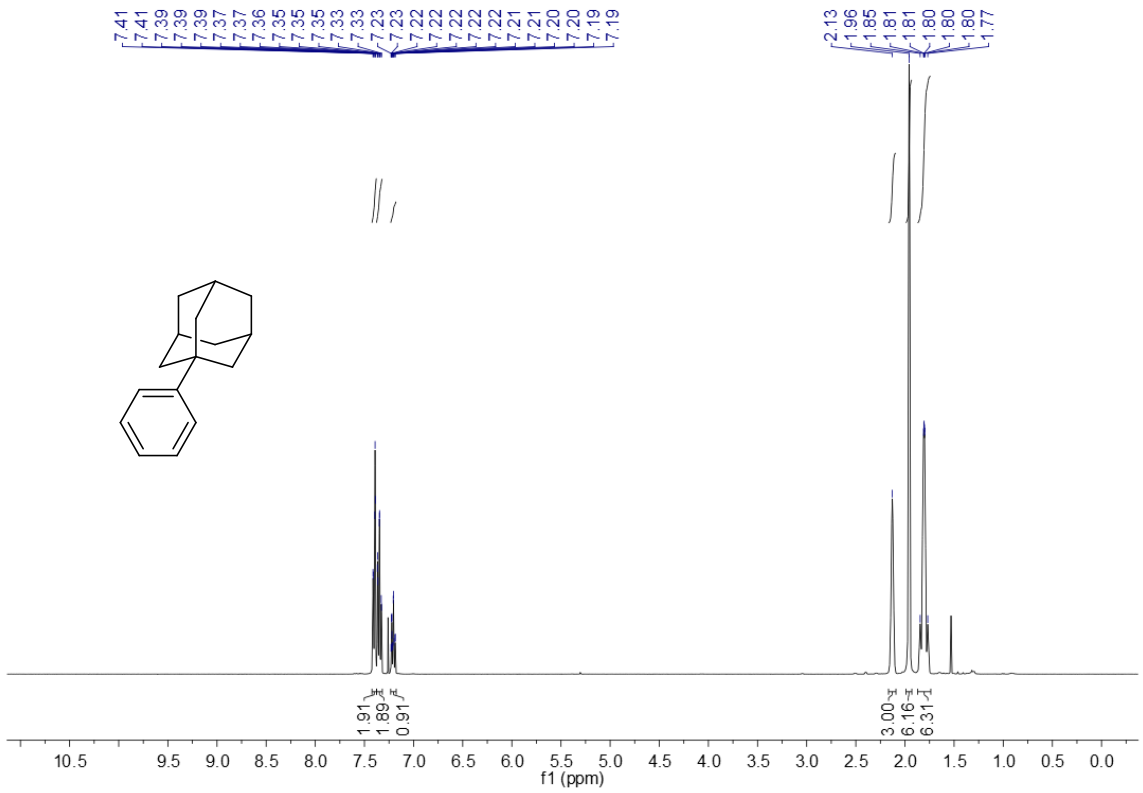


Fig. S117. ^{1}H NMR spectrum of 1-phenyladamantane in $CDCl_3$

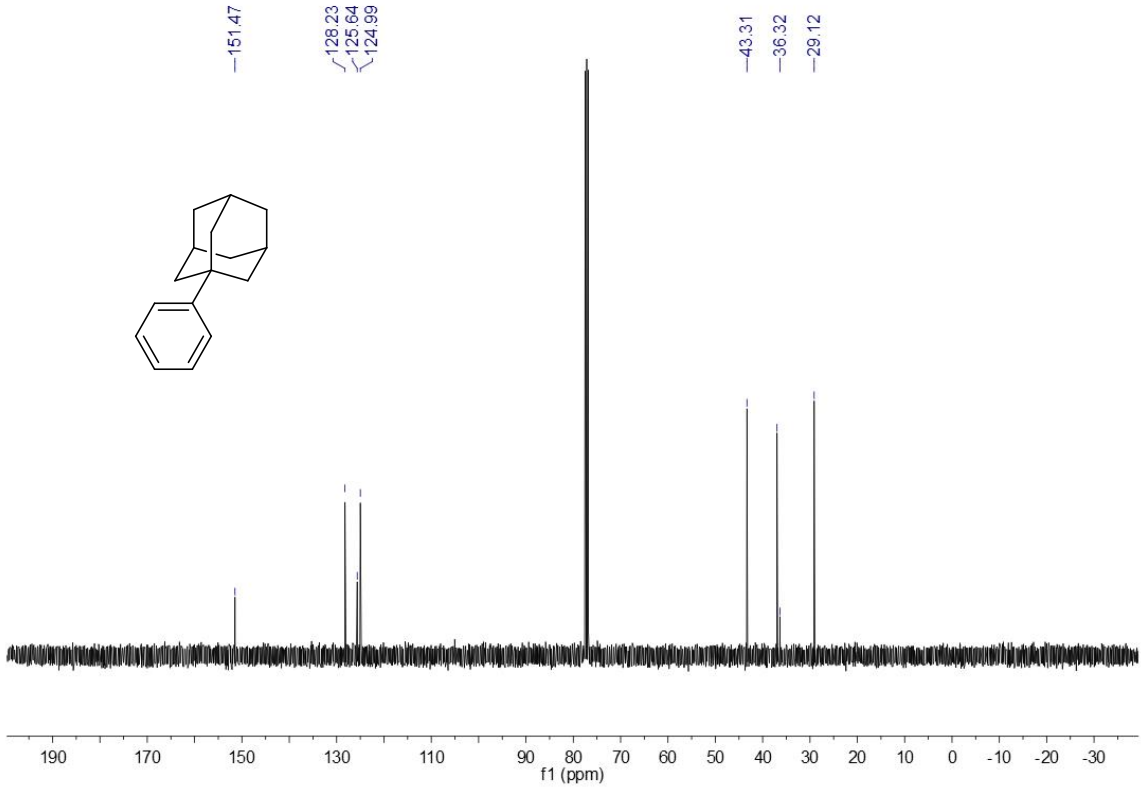


Fig. S118. $^{13}C\{^{1}H\}$ NMR spectrum of 1-phenyladamantane in $CDCl_3$

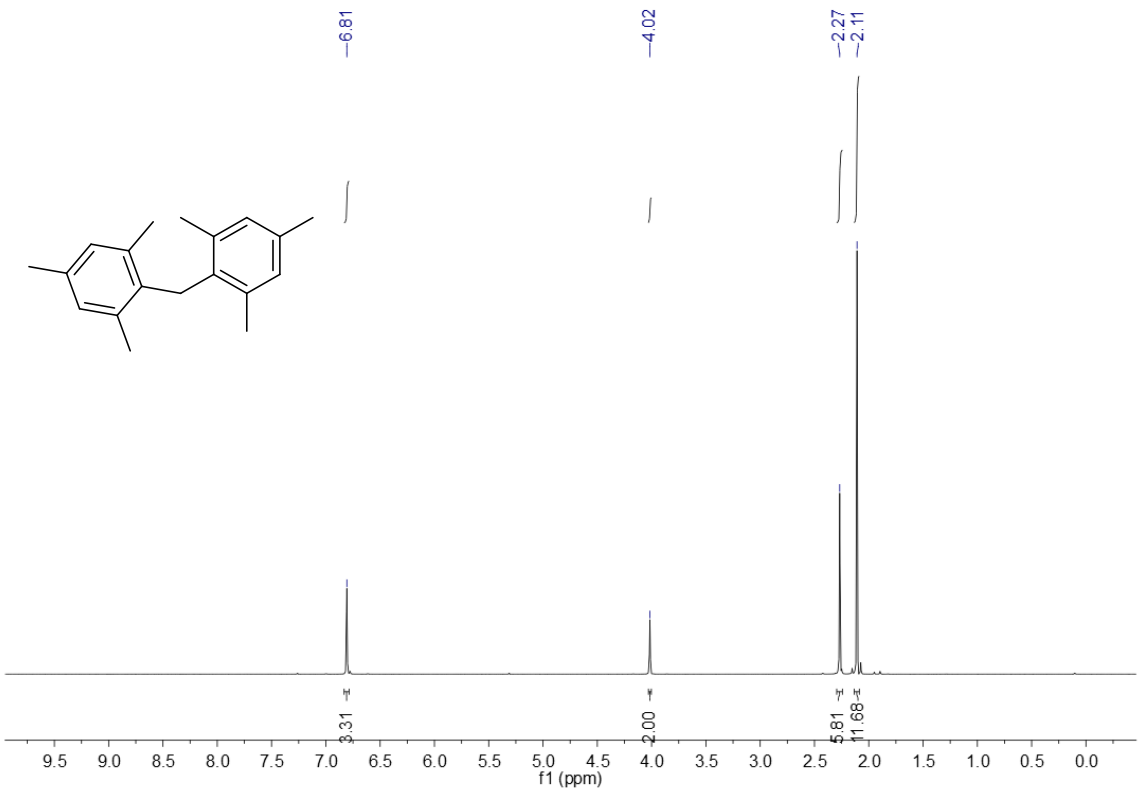


Fig. S119. ^{1}H NMR spectrum of dimesitylmethane in $CDCl_3$

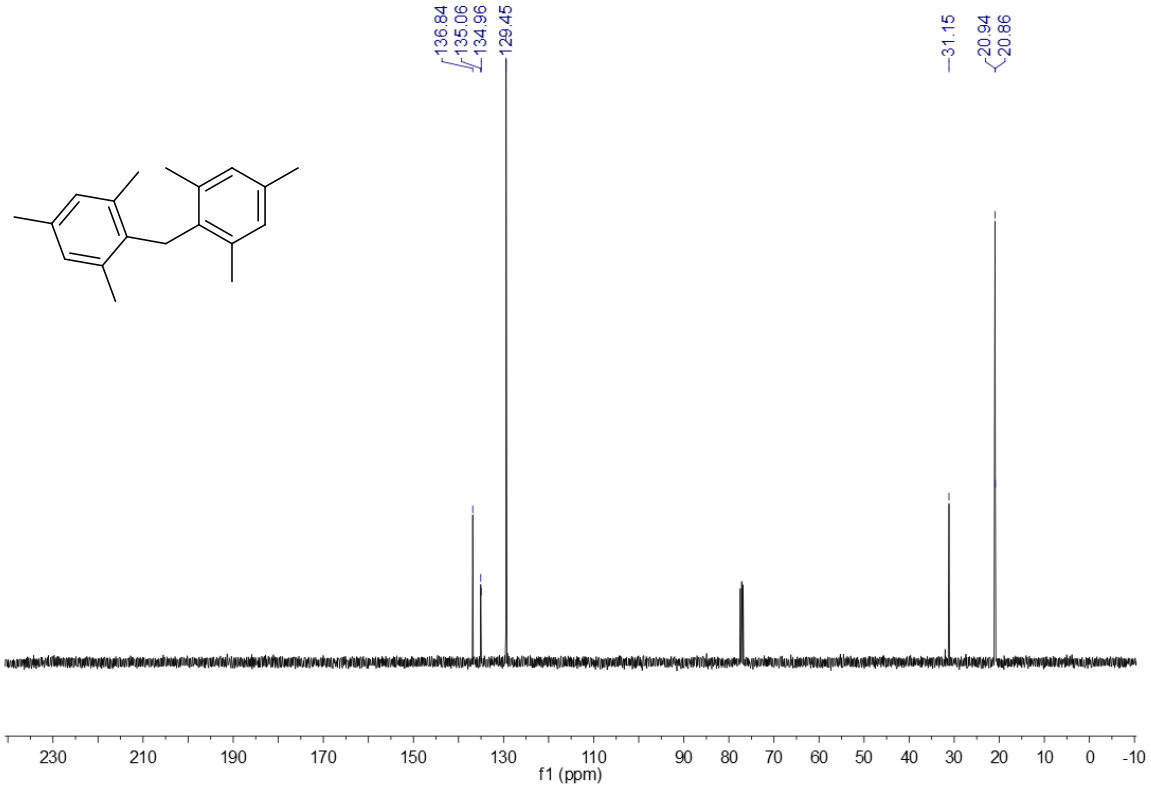


Fig. S120. $^{13}C\{^{1}H\}$ NMR spectrum of dimesitylmethane in $CDCl_3$

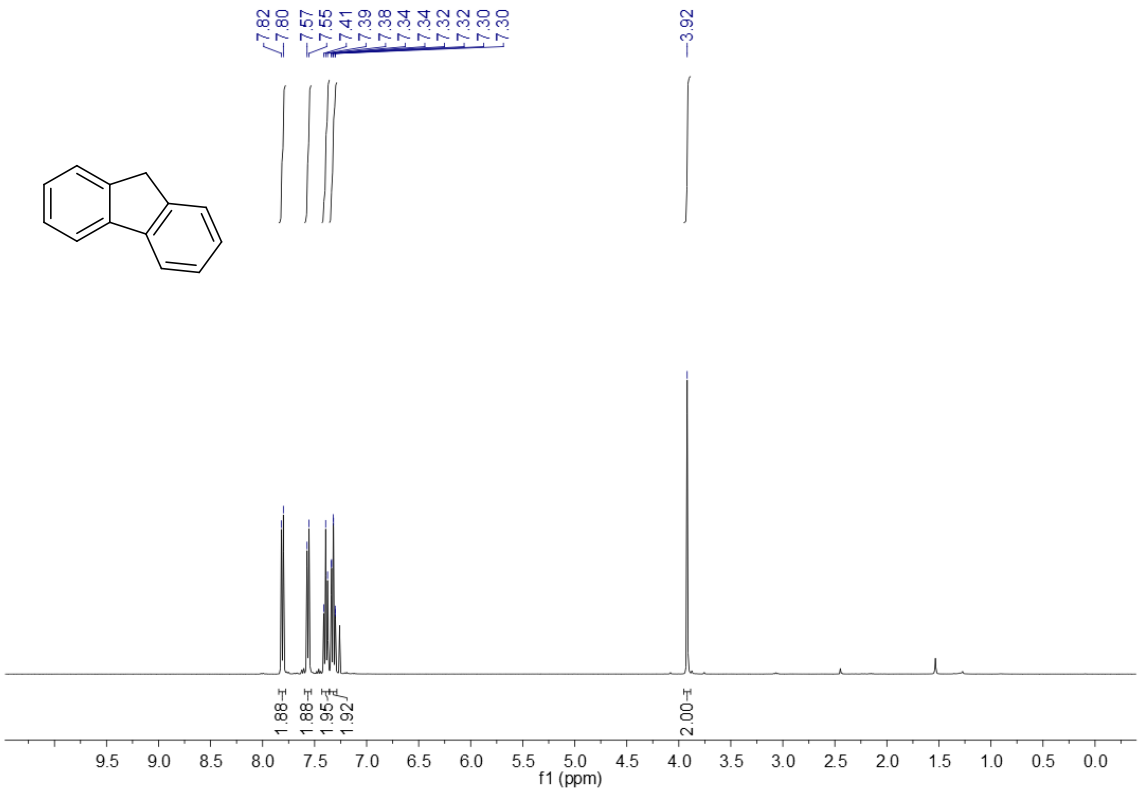


Fig. S121. ^{1}H NMR spectrum of 9H-fluorene in $CDCl_3$

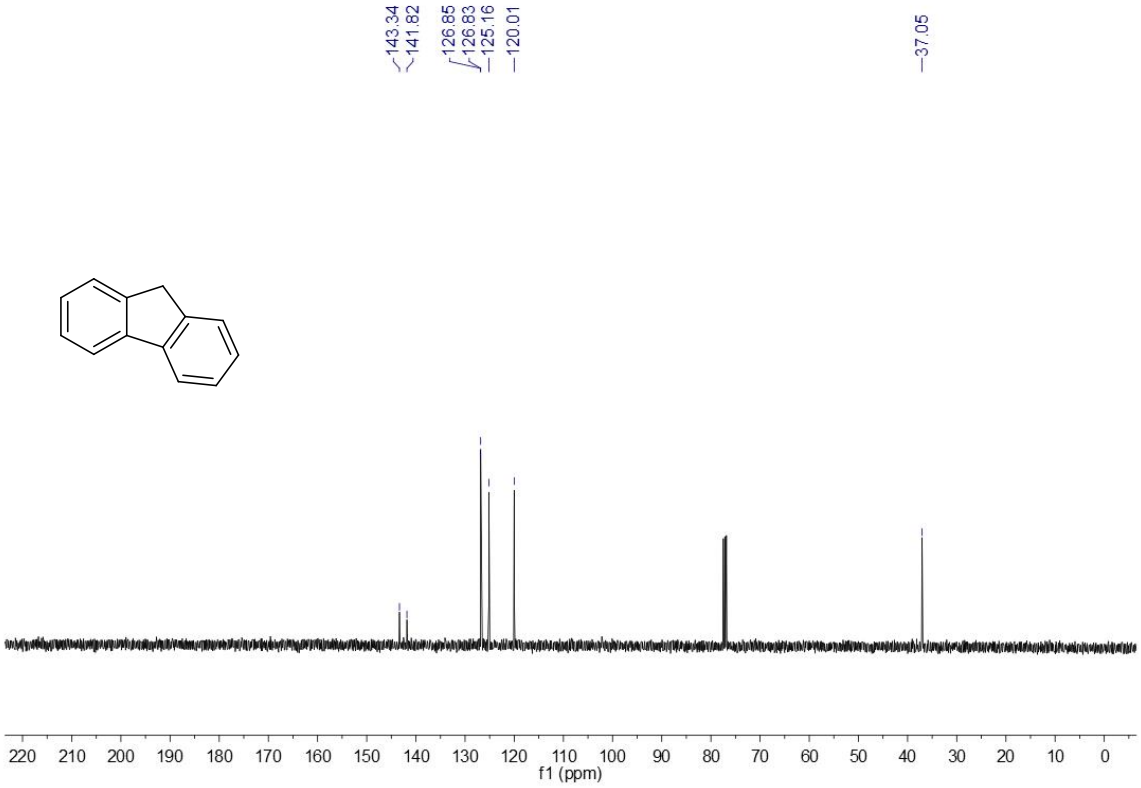


Fig. S122. $^{13}C\{^{1}H\}$ NMR spectrum of 9H-fluorene in $CDCl_3$

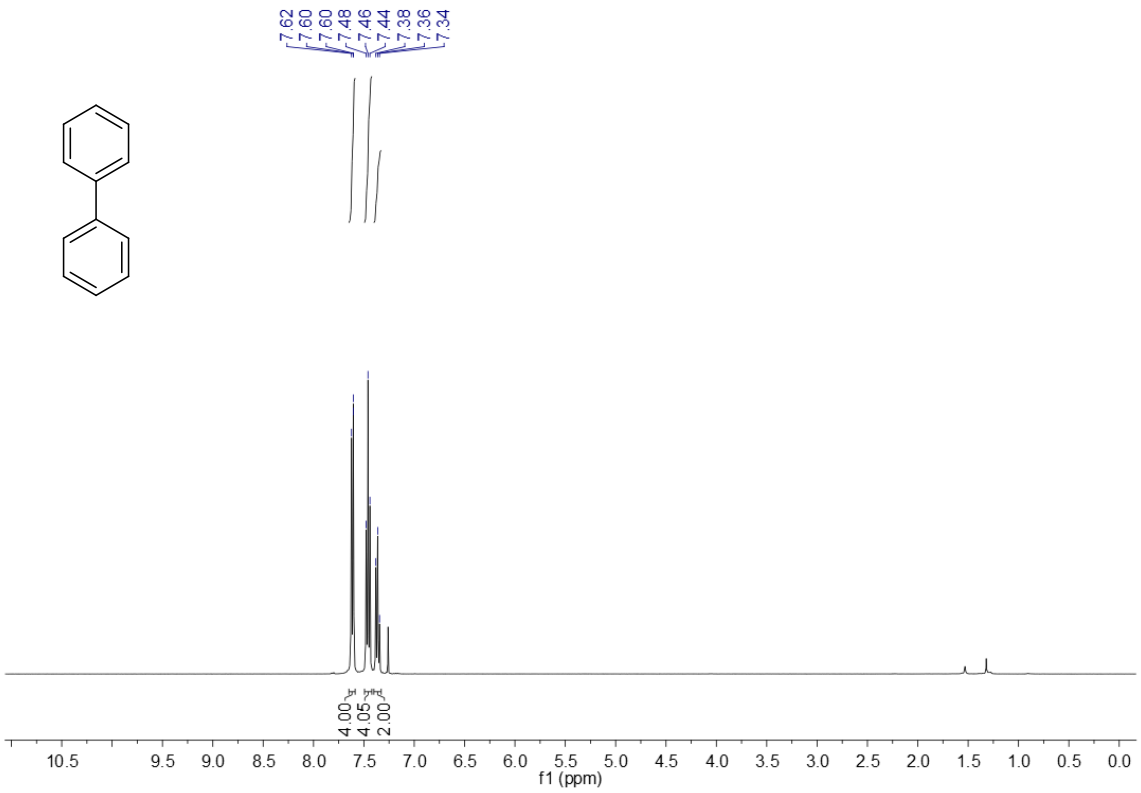


Fig. S123. ^{1}H NMR spectrum of biphenyl in $CDCl_3$

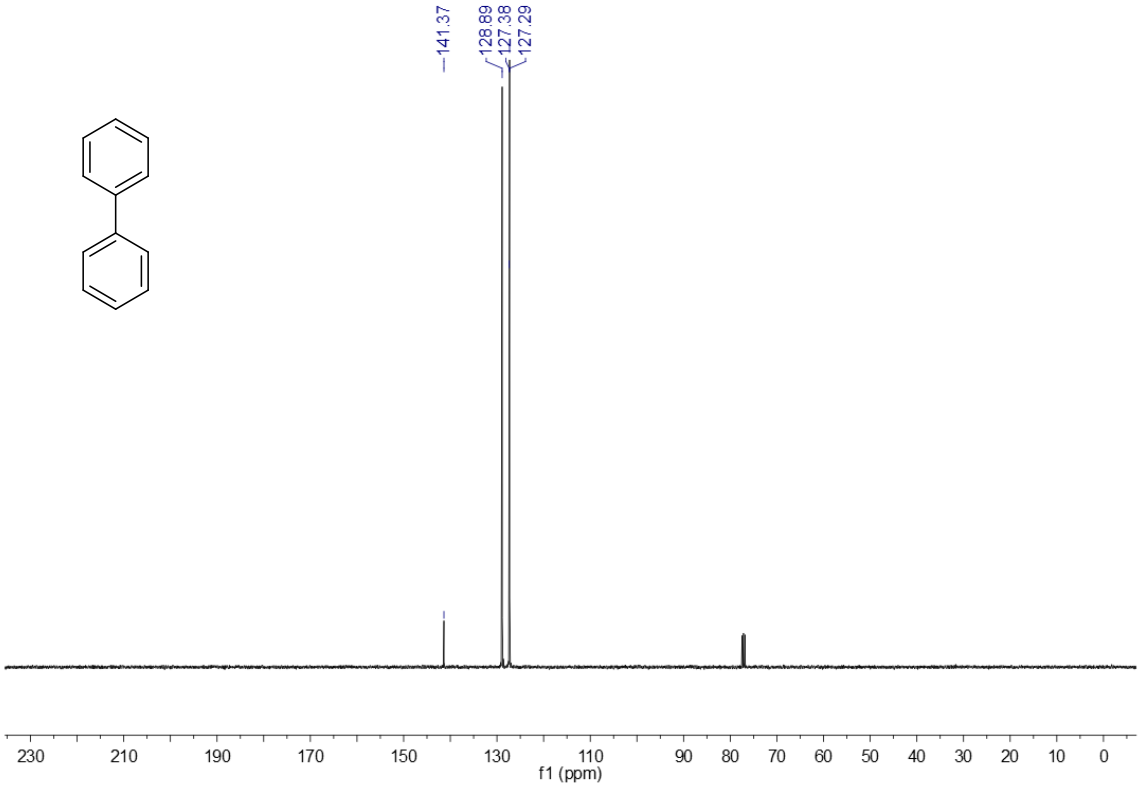


Fig. S124. $^{13}C\{^{1}H\}$ NMR spectrum of biphenyl in $CDCl_3$

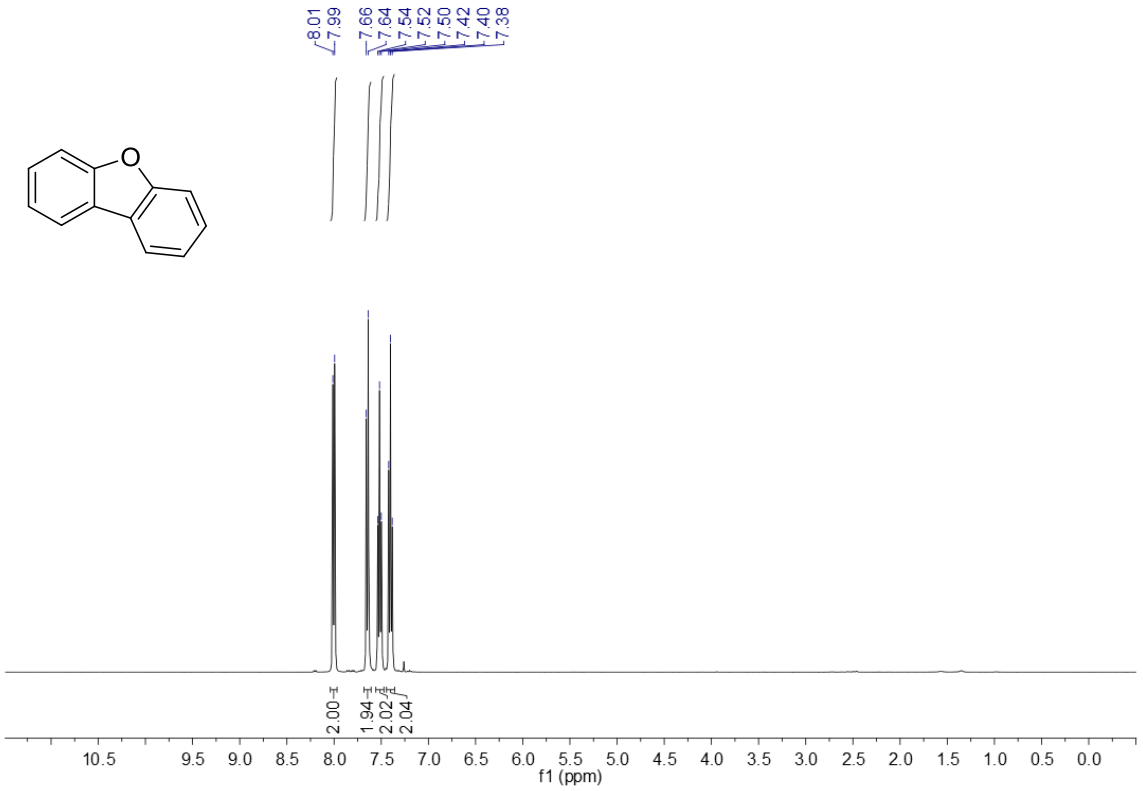


Fig. S125. ^{1}H NMR spectrum of dibenzofuran in $CDCl_3$

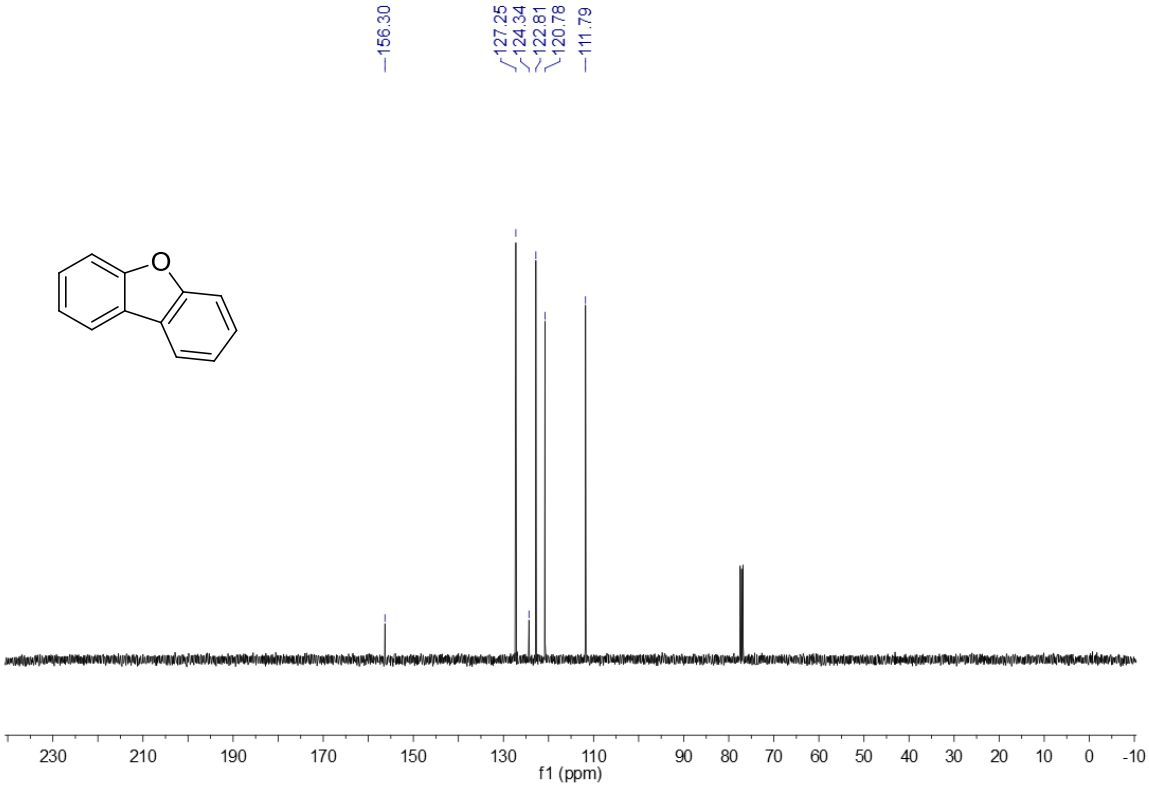


Fig. S126. $^{13}C\{^{1}H\}$ NMR spectrum of dibenzofuran in $CDCl_3$

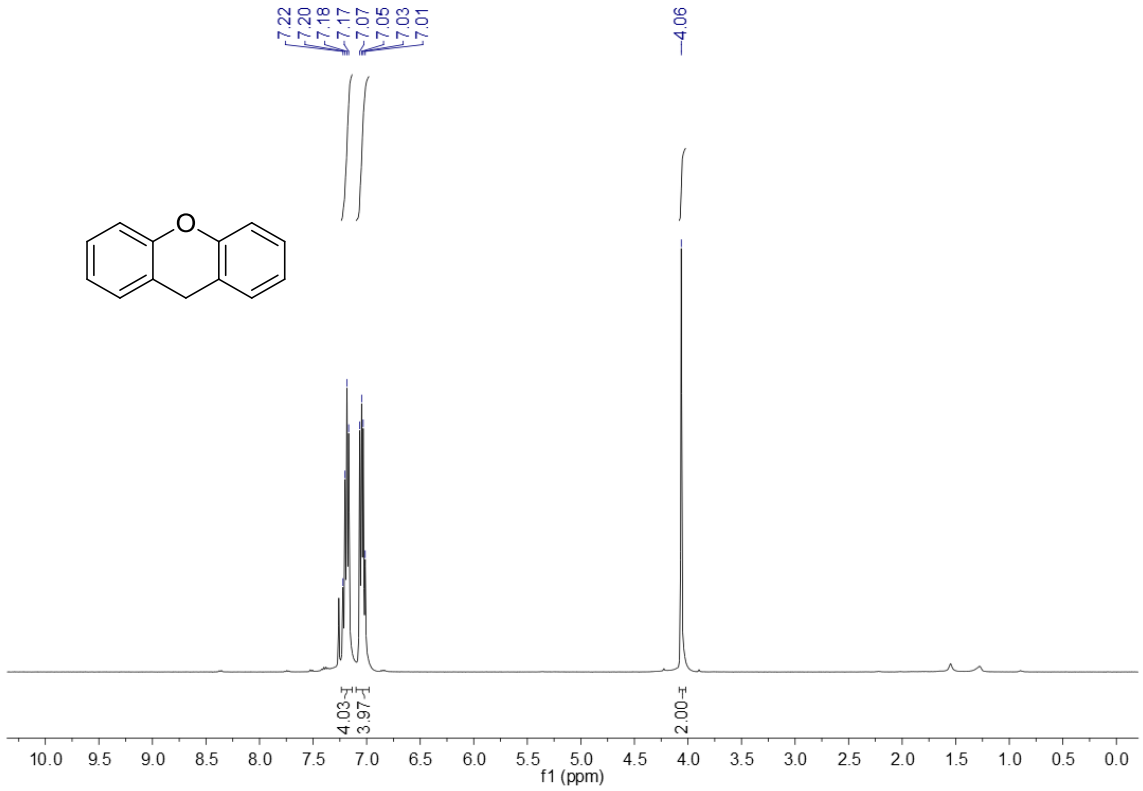


Fig. S127. ^{1}H NMR spectrum of xanthene in $CDCl_3$

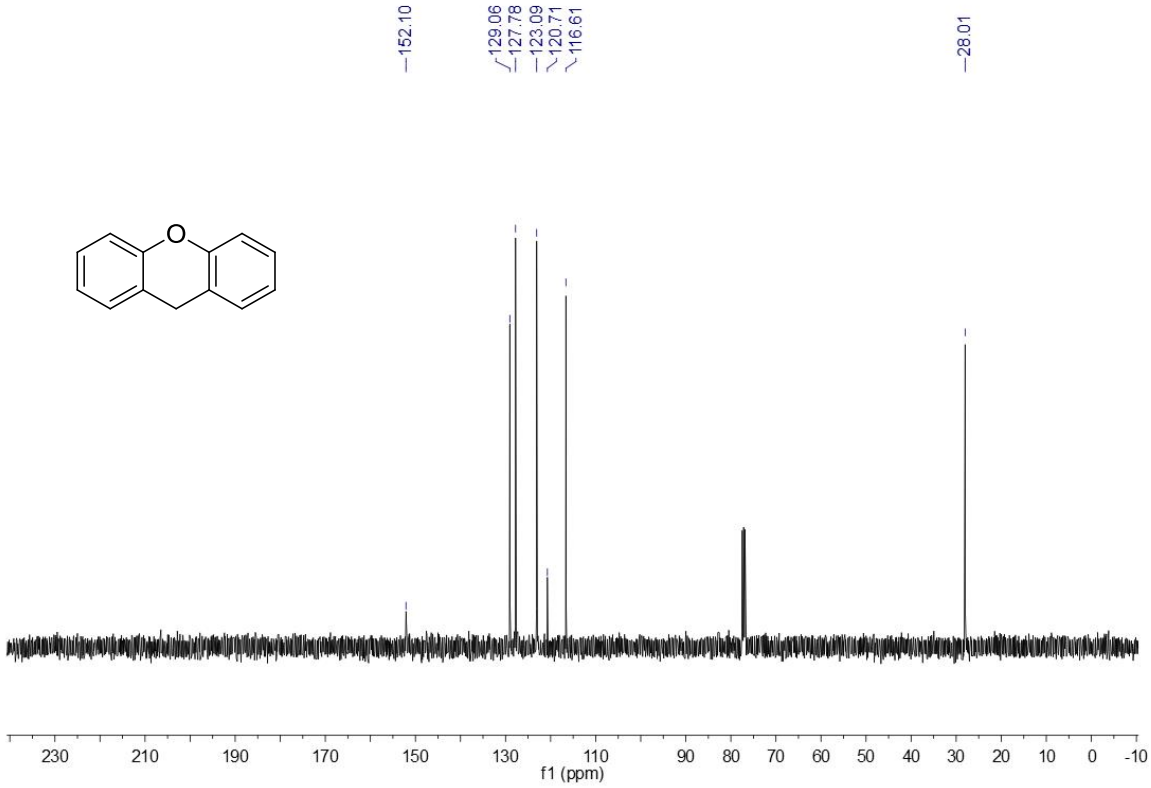


Fig. S128. $^{13}C\{^{1}H\}$ NMR spectrum of xanthene in $CDCl_3$

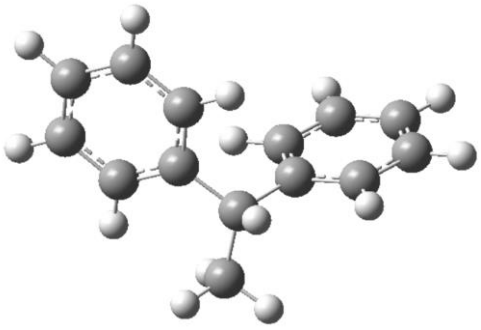
8. Computation details

Quantum chemical calculations were all performed at the density functional theory (DFT) level using the hybrid meta-GGA M06-2x functional (*16*,*17*), which has been proven to give reliable results to the reaction energy barriers involving organic molecules and their geometries. A moderate basis set, which was a combined basis set, in which the 6-31+G(d,p) basis set (*18*,*19*) was employed for the atoms of the reaction center (the two H atoms of dihydrogen, the borenium center and the two C atoms and H atom around it, the two *ipso*-carbon of phenyl rings and the CH moiety in **6**) and the 6-31G(d) basis set (*18*,*19*) was employed for the other atoms, was used for geometry optimization. Single-point energies were performed with a larger basis set, the 6-311++G(d,p) basis set (*18*,*19*) on the geometries optimized with the moderate basis set to provide more accurate energetic results. All calculations were performed in the bromobenzene solution which was modelled by the polarizable continuum solvation model (IEFPCM) (*20*) with radii and non-electrostatic terms for Truhlar and coworkers' SMD solvation model (*21*). This solvation model is by far the most reliable one in predicting solvation free energies. This procedure has been well validated in our previous studies.

The convergence criteria used for the geometry optimization were 4.50×10^{-4} au. for gradients, and 1.80×10^{-3} au. for displacements. Harmonic vibrational analyses were carried out to confirm if the optimized structure is a local minimum structure or a first order transition state and to provide zero-point vibrational energy corrections and thermal corrections to various thermodynamic properties. Transition states were further confirmed by IRC calculations (*22*,*23*). All the calculations were performed by using the Gaussian 09 software package (*24*).

9. Geometries and Cartesian coordinates of some important species optimized at the M06-2x level in the bromobenzene solution

1,1-diphenylethane (6)



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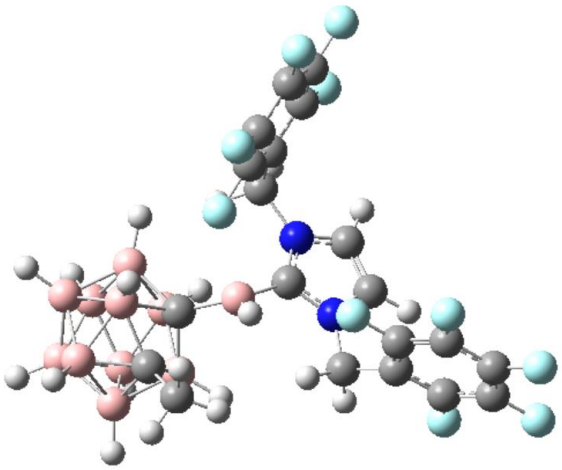
1a



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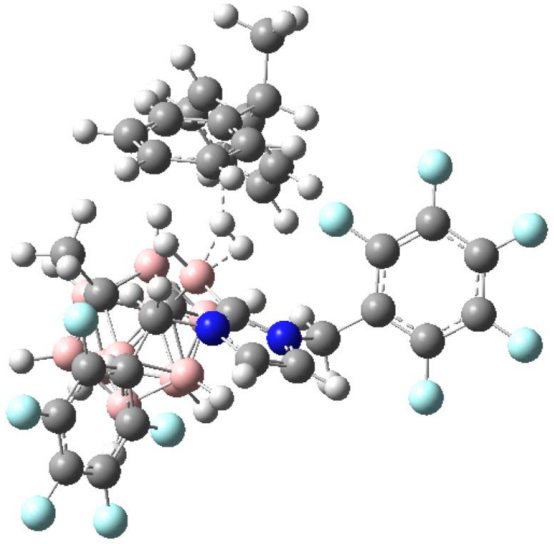

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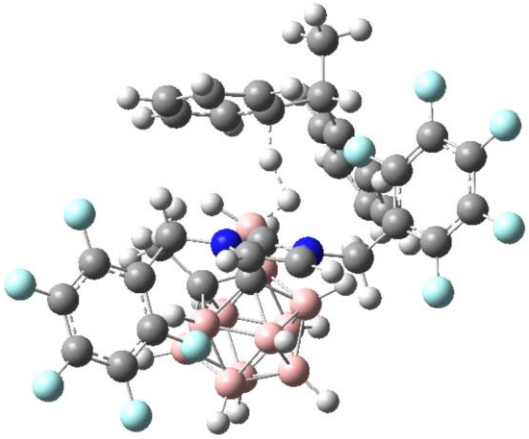
TS1



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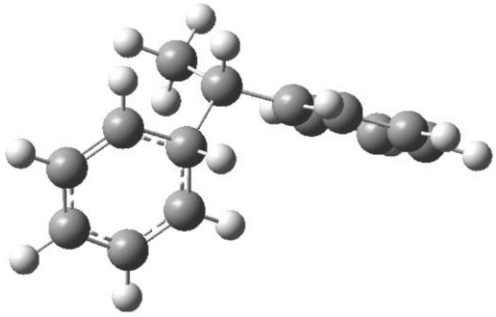

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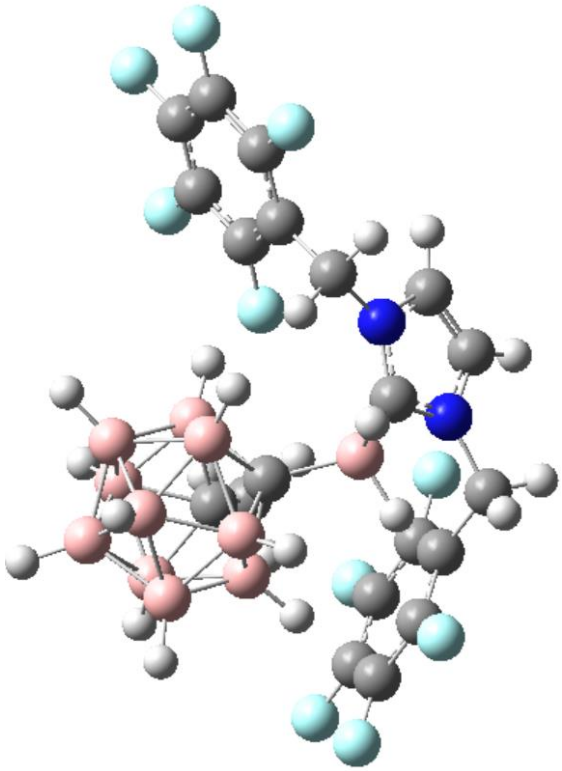

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TS2

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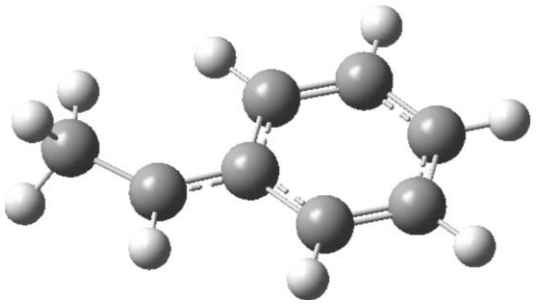

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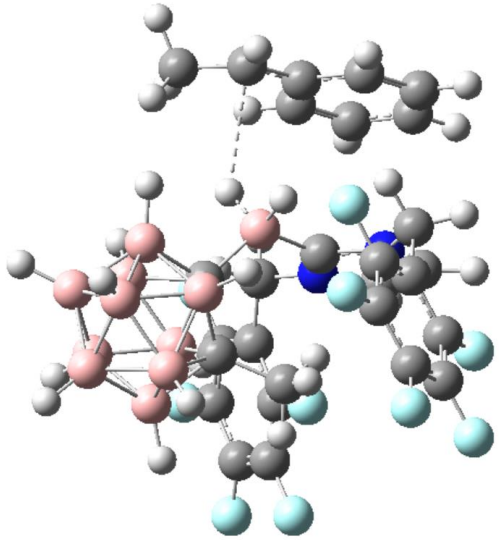
TS3



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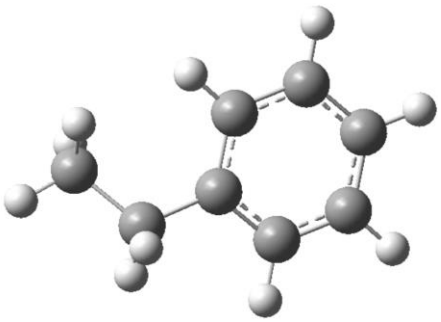
Ethylbenzene



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