Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Photoactive perylenediimide metal-organic framework for boosting iodoperfluoroalkylation of alkenes and oxidative coupling of amines

Zhengfen Liu, Chao Li, Jian Chen, Xiaobo Li, Fumang Luo, Feixiang Cheng* and Jian-Jun Liu*

College of Chemistry and Environmental Science, Qujing Normal University, Qujing 655011, China. E-mail: chengfx2019@163.com (F.-X Cheng); jjliu302@163.com (J.-J. Liu)

Supplementary Methods:

General methods

All air- and moisture-sensitive solutions and chemicals were handled under an argon atmosphere of a glovebox and solutions were transferred via "Titan" brand pipettor. Anhydrous solvents were purchased from Sigma-Aldrich and used without further purification. Unless otherwise stated, all reagents were commercially available and used as received without further purification. Chemicals were obtained from Sigma-Aldrich, Acros, TCI and Alfa-Aesar. TLC was performed with Merck TLC Silica gel60 F_{254} plates with detection under UV light at 254 nm. Silica gel (200-300 mesh, Qingdao) was used for flash chromatography. Deactivated silica gel was prepared by addition of 15 mL Et_3N to 1 L of silica gel. Elemental analysis of the compound was recorded on Elementar Vario EL Cube elemental analyzer. Powder XRD measurements were performed at room temperature on a Bruker D8 ADVANCE X-Ray diffractometer using CuKα radiation in the range of 5–50°. Thermogravimetric analysis (TGA) of the sample was performed on a Mettler Toledo TGA2 thermogravimetric system in nitrogen atmosphere with a heating rate of 10 °C/min. NMR spectrum was measured on a Bruker 400 NMR spectrometer. Fourier transform infrared (FTIR) spectrum of the sample was taken on a Nicolet iS50 spectrometer. A Varian Cary 500 UV–Vis spectrophotometer equipped with an integrating sphere was used to recorded UV–vis diffuse reflectance spectra.

X-ray Data Collection and Structure Refinements

Suitable single crystal of MOF **1** was mounted on glass fibers for the X-ray measurement. Diffraction data were collected on Bruker APEX II diffractometer using graphite-monochromatic Mo Kα radiation at 100 K. The structure of MOF **1** was solved by direct methods and refined by full-matrix least-squares against F^2 using the SHELXS-2014 program. All the metal atom, C, N, and O atoms of the MOF **1** was located first and anisotropically refined. The hydrogen atoms of the organic ligands were generated theoretically onto the specific atoms. The diffraction data of MOF **1** was treated by the "SQUEEZE" method as implemented in PLATON to remove diffuse electron density associated with these badly disordered solvent molecules. Combined with TGA data, elemental analysis, and volume/count_electrons analysis, there are approximately three DMF molecule (only the DMF solvent was used) per formula was squeezed for MOF 1. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC 2108376 for MOF 1.

Procedure and characterization for iodoperfluoroalkylation of alkenes and oxidative coupling of amines

General Procedure A:

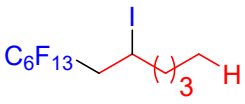
An oven-dried 10 mL reaction tube equipped with a stir bar was charged with alkenes (0.2 mmol), perfluoroalkyl iodides (0.4 mmol) and MOF 1 (1.24 mg, 0.001 mmol, 0.5 mol %) under an argon atmosphere in a glove box. A solution of sodium ascorbate (19.81 mg, 0.1 mmol) in 1.9 mL dry CH_3CN was added by a 1000 μL pipettor to the reaction tube at room temperature. The reaction tubel was sealed with a cap, removed from the glove box,and filled with 100 μL of H_2O from the cap using a micro-injector. The reaction mixture was stirred at room temperature under blue light-emitting diode (LED, λ = 450 nm) for 4 hours in total. The reaction opened to air and then extracted with ethyl acetate (3 x 20 mL). The organic phases were combined and washed with brine (10 mL) and then dried over sodium sulfate. The solvent was removed under reduced pressure and the crude material was purified by flash column chromatography to give the corresponding iodoperfluoroalkylation product.

General Procedure B:

An oven-dried 10 mL reaction vial equipped with a stir bar was charged with alkenes (0.2 mmol) and **MOF** 1 (1.24 mg, 0.001 mmol, 0.5 mol %) under a oxygen atmosphere. Anhydrous DMF (2.0 mL) was added by a 5 mL syringer to the reaction vial. Then, the vial was stirred for 6 hours under 300W Xe lamp with a cutoff below 420 nm at room temperature. The reaction mixture was opened in air, and the resulting biphasic solution was extracted with ethyl acetate (10 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, and the combined solutions were concentrated in vacuo. The crude material was loaded onto a deactivated silica gel column and purified by flash chromatography.

Product Characterization:

1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iododododecane (3a):

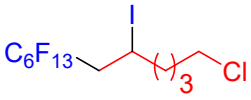


The reaction was performed following the General Procedure A with hex-1-ene **1a** (16.83 mg, 0.2 mmol) and 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-6-iodohexane **2a** (178.38 mg, 0.4 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product **3a** (103.90 mg, 98% yield) as a colorless oil.

1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodohexadecane (3b):

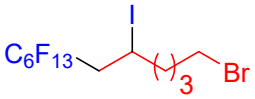
The reaction was performed following the General Procedure A with dec-1-ene **1b** (16.83 mg, 0.2 mmol) and 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-6-iodohexane **2a** (178.38 mg, 0.4 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product **3b** (112.55 mg, 96% yield) as a colorless oil.

12-chloro-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iododododecane (3c):



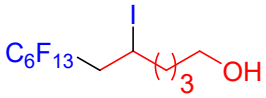
The reaction was performed following the General Procedure A with 6-chlorohex-1-ene **1c** (23.72 mg, 0.2 mmol) and 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-6-iodohexane **2a** (178.38 mg, 0.4 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product **3c** (106.14 mg, 94% yield) as a colorless oil.

12-bromo-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iododododecane (3d):



The reaction was performed following the General Procedure A with 6-bromohex-1-ene **1d** (32.61 mg, 0.2 mmol) and 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-6-iodohexane **2a** (178.38 mg, 0.4 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product **3d** (119.37 mg, 98% yield) as a colorless oil.

7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-5-iododododecan-1-ol (3e):



The reaction was performed following the General Procedure A with hex-5-en-1-ol **1e** (20.03 mg, 0.2 mmol) and 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-6-iodohexane **2a** (178.38 mg, 0.4 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc : hexanes = 1:10) to give the product **3e** (97.21 mg, 89% yield) as a colorless oil.

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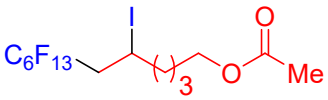
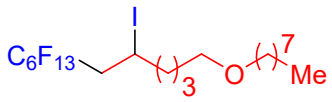
7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-5-iododododecyl acetate (3f):



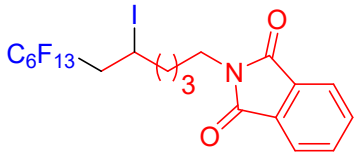
The reaction was performed following the General Procedure A with hex-5-en-1-yl acetate **1f** (28.44 mg, 0.2 mmol) and 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-6-iodohexane **2a** (178.38 mg, 0.4 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc : hexanes = 1:30) to give the product **3f** (107.04 mg, 91% yield) as a colorless oil.

1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodo-12-(octyloxy)dodecane (3g):



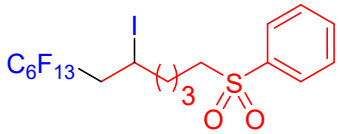
The reaction was performed following the General Procedure A with 1-(hex-5-en-1-yloxy)octane **1g** (42.48 mg, 0.2 mmol) and 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-6-iodohexane **2a** (178.38 mg, 0.4 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc : hexanes = 1:30) to give the product **3g** (127.72 mg, 97% yield) as a colorless oil.

2-(7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-5-iodododecyl)isoindoline-1,3-dione (3h):



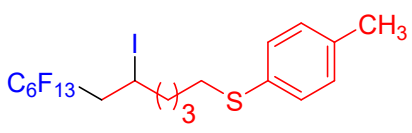
The reaction was performed following the General Procedure A with 2-(hex-5-en-1-yl)isoindoline-1,3-dione **1h** (45.86 mg, 0.2 mmol) and 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-6-iodohexane **2a** (178.38 mg, 0.4 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc : hexanes = 1:10) to give the product **3h** (132.34 mg, 97% yield) as a colorless oil.

((7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-5-iodododecyl)sulfonyl)benzene (3i):



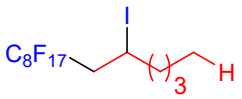
The reaction was performed following the General Procedure A with (hex-5-en-1-ylsulfonyl)benzene **1i** (44.86 mg, 0.2 mmol) and 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-6-iodohexane **2a** (178.38 mg, 0.4 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc : hexanes = 1:10) to give the product **3i** (127.35 mg, 95% yield) as a colorless oil.

***p*-tolyl(7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-5-iodododecyl)sulfane (3j):**



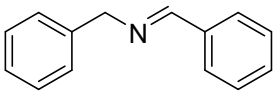
The reaction was performed following the General Procedure A with hex-5-en-1-yl(*p*-tolyl)sulfane **1j** (41.27 mg, 0.2 mmol) and 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-6-iodohexane **2a** (178.38 mg, 0.4 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc : hexanes = 1:10) to give the product **3j** (125.24 mg, 96% yield) as a colorless oil.

1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-10-iodotetradecane (3k):



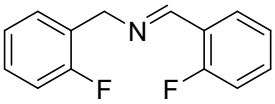
The reaction was performed following the General Procedure A with hex-1-ene **1a** (16.83 mg, 0.2 mmol) and 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-8-iodooctane **2b** (218.39 mg, 0.4 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product **3k** (117.20 mg, 93% yield) as a colorless oil.

(*E*)-*N*-benzyl-1-phenylmethanimine (5a):



The reaction was performed following the General Procedure B with phenylmethanamine **4a** (21.43 mg, 0.2 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with EtOAc : hexanes = 1:25) to give the product **5a** (37.88 mg, 97% yield) as a colorless oil.

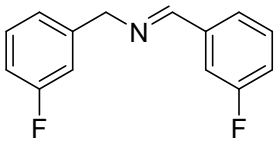
(*E*)-*N*-(2-fluorobenzyl)-1-(2-fluorophenyl)methanimine (5b):



The reaction was performed following the General Procedure B with (2-fluorophenyl)methanamine **4b** (25.03 mg, 0.2 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with EtOAc : hexanes = 1:25) to give the product **5b** (42.55 mg, 92% yield) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.72 (d, *J* = 1.6 Hz, 1H), 8.03 (td, *J* = 7.6, 1.6 Hz, 1H), 7.42–7.35 (m, 2H), 7.28 – 7.24 (m, 1H), 7.18 – 7.03 (m, 4H), 4.87 (t, *J* = 1.2 Hz, 2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 163.6, 162.0, 161.1, 159.6, 156.1 (d, $J_{C\text{-}F}$ = 5.0 Hz), 132.5 (d, $J_{C\text{-}F}$ = 8.5 Hz), 130.2 (d, $J_{C\text{-}F}$ = 4.4 Hz), 128.9 (d, $J_{C\text{-}F}$ = 8.1 Hz), 127.8 (d, $J_{C\text{-}F}$ = 2.8 Hz), 126.1 (d, $J_{C\text{-}F}$ = 14.8 Hz), 124.4 (d, $J_{C\text{-}F}$ = 3.2 Hz), 124.2 (d, $J_{C\text{-}F}$ = 3.7 Hz), 123.7 (d, $J_{C\text{-}F}$ = 9.0 Hz), 115.8 (d, $J_{C\text{-}F}$ = 21.2 Hz), 115.3 (d, $J_{C\text{-}F}$ = 21.3 Hz), 58.6 (d, $J_{C\text{-}F}$ = 2.9 Hz) ppm.

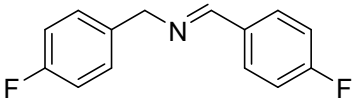
(*E*)-*N*-(3-fluorobenzyl)-1-(3-fluorophenyl)methanimine (5c):



The reaction was performed following the General Procedure B with (3-fluorophenyl)methanamine **4c** (25.03 mg, 0.2 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with EtOAc : hexanes = 1:25) to give the product **5c** (43.01 mg, 93% yield) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.35 (d, *J* = 1.6 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.38 (td, *J* = 8.0, 5.2 Hz, 1H), 7.30 (td, *J* = 8.0, 6.0 Hz, 1H), 7.15–7.09 (m, 2H), 7.05 (dt, *J* = 9.6, 2.0 Hz, 1H), 6.95 (td, *J* = 8.8, 2.8 Hz, 1H), 4.80 (s, 2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.3 (d, $J_{C\text{-}F}$ = 5.6 Hz), 161.8 (d, $J_{C\text{-}F}$ = 4.9 Hz), 161.1 (d, $J_{C\text{-}F}$ = 2.9 Hz), 141.6 (d, $J_{C\text{-}F}$ = 7.3 Hz), 138.3 (d, $J_{C\text{-}F}$ = 7.3 Hz), 130.2 (d, $J_{C\text{-}F}$ = 8.1 Hz), 130.0 (d, $J_{C\text{-}F}$ = 8.1 Hz), 124.5 (d, $J_{C\text{-}F}$ = 2.9 Hz), 123.4 (d, $J_{C\text{-}F}$ = 2.9 Hz), 117.9 (d, $J_{C\text{-}F}$ = 21.8 Hz), 114.8 (d, $J_{C\text{-}F}$ = 21.9 Hz), 114.4 (d, $J_{C\text{-}F}$ = 22.2 Hz), 114.0 (d, $J_{C\text{-}F}$ = 21.1 Hz), 64.2 (d, $J_{C\text{-}F}$ = 2.1 Hz).

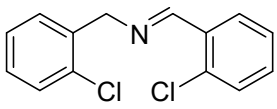
(*E*)-*N*-(4-fluorobenzyl)-1-(4-fluorophenyl)methanimine (5d):



The reaction was performed following the General Procedure B with (4-fluorophenyl)methanamine **4d** (25.03 mg, 0.2 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with EtOAc : hexanes = 1:25) to give the product **5d** (41.62 mg, 90% yield) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.34 (t, *J* = 1.6 Hz, 1H), 7.79 – 7.74 (m, 2H), 7.32 – 7.27 (m, 2H), 7.13 – 7.00 (m, 4H), 4.76 (s, 2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 165.7, 163.2 (d, $J_{C\text{-}F}$ = 4.3 Hz), 160.8, 160.6, 134.9 (d, $J_{C\text{-}F}$ = 3.3 Hz), 132.3 (q, $J_{C\text{-}F}$ = 3.0 Hz), 130.2 (d, $J_{C\text{-}F}$ = 8.8 Hz), 129.5 (d, $J_{C\text{-}F}$ = 8.1 Hz), 115.8 (d, $J_{C\text{-}F}$ = 21.9 Hz), 115.3 (d, $J_{C\text{-}F}$ = 21.3 Hz), 64.2 ppm.

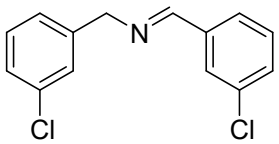
(*E*)-*N*-(2-chlorobenzyl)-1-(2-chlorophenyl)methanimine (5e):



The reaction was performed following the General Procedure B with (2-chlorophenyl)methanamine **4e** (28.32 mg, 0.2 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with EtOAc : hexanes = 1:25) to give the product **5e** (51.77 mg, 98% yield) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.87 (d, *J* = 1.6 Hz, 1H), 8.11 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.43 – 7.31 (m, 4H), 7.30 – 7.18 (m, 3H), 4.93 (d, *J* = 1.2 Hz, 2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 159.8, 136.9, 135.3, 133.4, 133.1, 131.8, 129.9, 129.7, 129.4, 128.5, 128.4, 127.1, 127.0, 62.2 ppm.

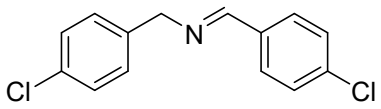
(*E*)-*N*-(3-chlorobenzyl)-1-(3-chlorophenyl)methanimine (5f):



The reaction was performed following the General Procedure B with (3-chlorophenyl)methanamine **4f** (28.32 mg, 0.2 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with EtOAc : hexanes = 1:25) to give the product **5f** (50.72 mg, 96% yield) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.32 (t, *J* = 1.6 Hz, 1H), 7.81 (t, *J* =1.6 Hz, 1H), 7.62 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.42 – 7.29 (m, 3H), 7.28 – 7.20 (m, 3H), 4.77 (d, *J* = 1.2 Hz, 2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 161.0, 141.0, 137.6, 134.9, 134.4, 131.0, 130.0, 129.8, 128.1, 128.0, 127.3, 126.7, 126.1, 64.3 ppm.

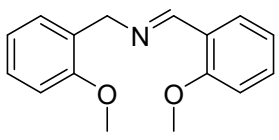
(*E*)-*N*-(4-chlorobenzyl)-1-(4-chlorophenyl)methanimine (5g):



The reaction was performed following the General Procedure B with (4-chlorophenyl)methanamine **4g** (28.32 mg, 0.2 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with EtOAc : hexanes = 1:25) to give the product **5g** (49.66 mg, 94% yield) as a colorless oil.

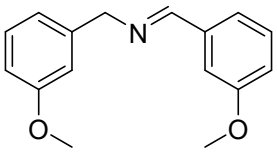
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.33 (t, *J* =1.2 Hz, 1H), 7.70 (dt, *J* =8.8, 2.4 Hz, 2H), 7.38 (dt, *J* =8.4, 2.4 Hz, 2H), 7.31 (dt, *J* =8.4, 2.4 Hz, 2H), 7.27 – 7.24 (m, 2H),4.86 (t, *J* =0.8 Hz,2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 160.9, 137.6, 136.9, 134.4, 132.9, 129.5, 129.3, 129.0, 128.7, 64.2 ppm.

(*E*)-*N*-(2-methoxybenzyl)-1-(2-methoxyphenyl)methanimine (5h):



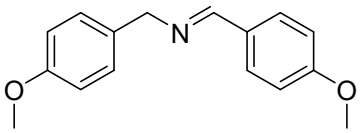
The reaction was performed following the General Procedure B with (2-methoxyphenyl)methanamine **4h** (27.44 mg, 0.2 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with EtOAc : hexanes = 1:25) to give the product **5h** (45.45 mg, 89% yield) as a colorless oil.

(*E*)-*N*-(3-methoxybenzyl)-1-(3-methoxyphenyl)methanimine (5i):



The reaction was performed following the General Procedure B with (3-methoxyphenyl)methanamine **4i** (27.44 mg, 0.2 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with EtOAc : hexanes = 1:25) to give the product **5i** (46.47 mg, 91% yield) as a colorless oil.

(*E*)-*N*-(4-methoxybenzyl)-1-(4-methoxyphenyl)methanimine (5j):



The reaction was performed following the General Procedure B with (4-methoxyphenyl)methanamine **4j** (27.44 mg, 0.2 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with EtOAc : hexanes = 1:25) to give the product **5j** (41.87 mg, 82% yield) as a colorless oil.

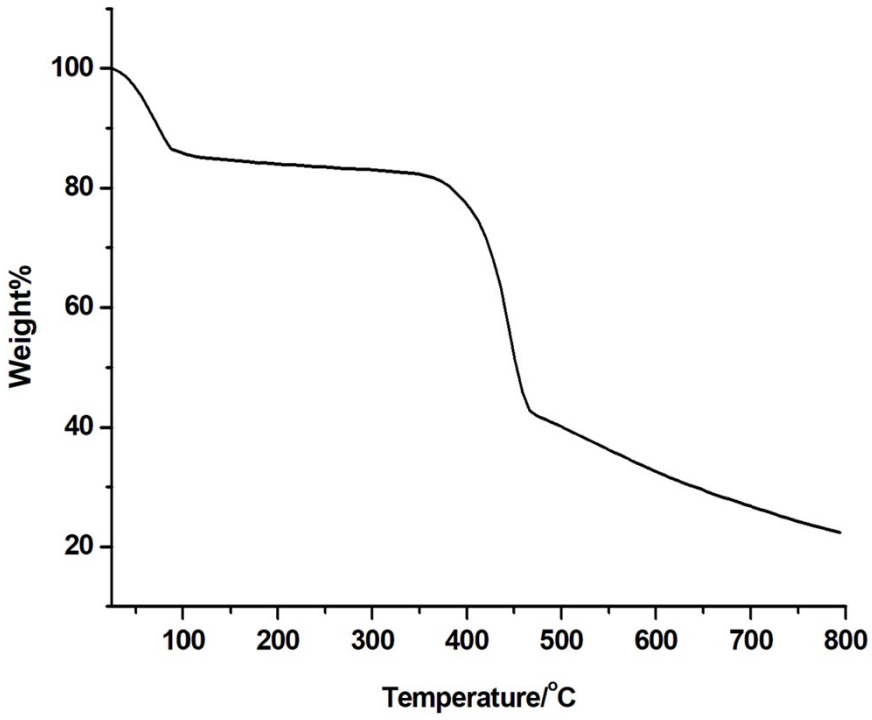


Figure S1. TGA curve of MOF 1 under N_2 atmosphere with a heating rate of 10 °C/min.

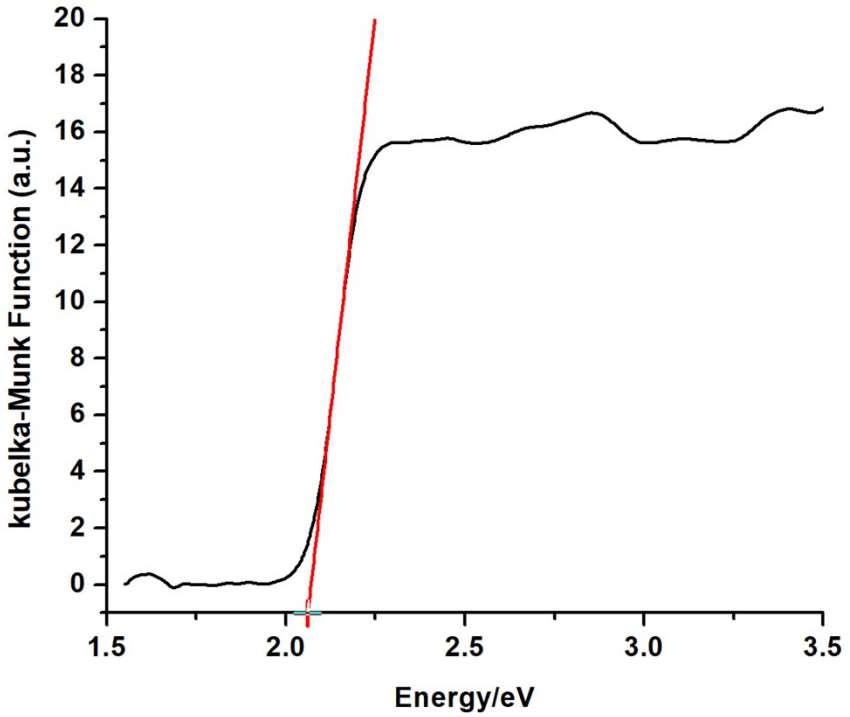


Figure S2. Optical absorption spectra of MOF 1.

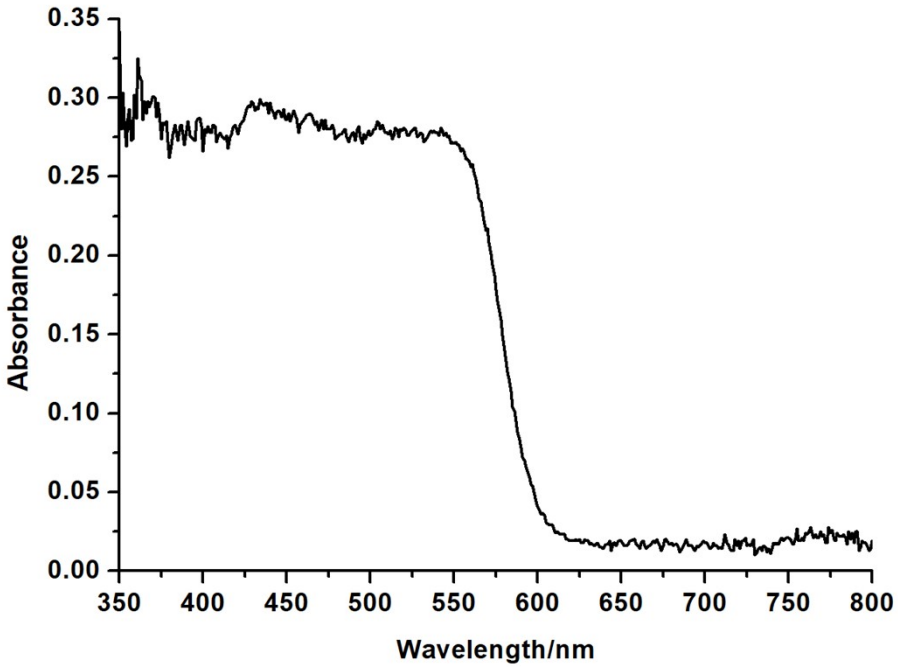


Figure S3. The soild-state UV-Vis spectrum of MOF 1.

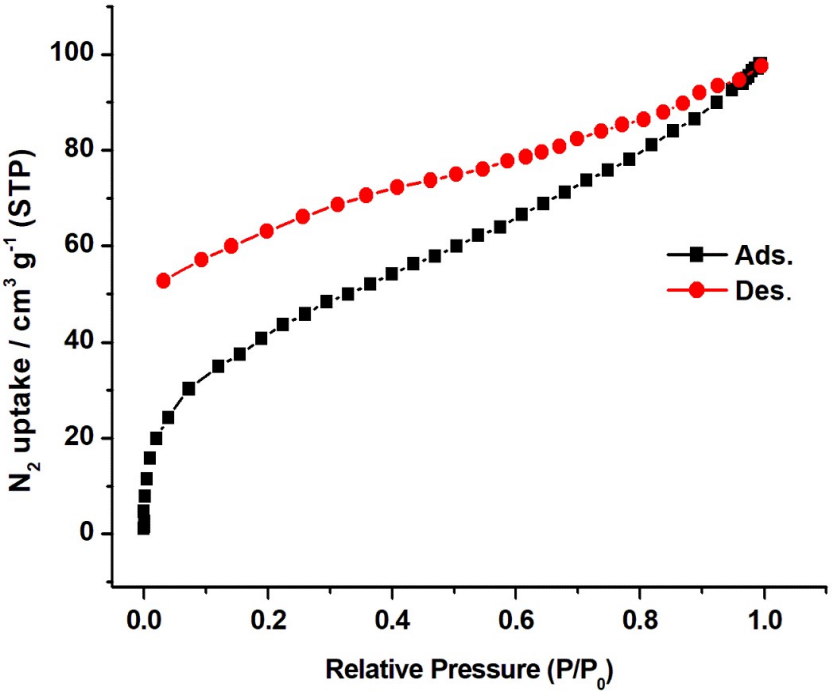


Figure S4. Nitrogen sorption isotherm for MOF 1 at 77 K.

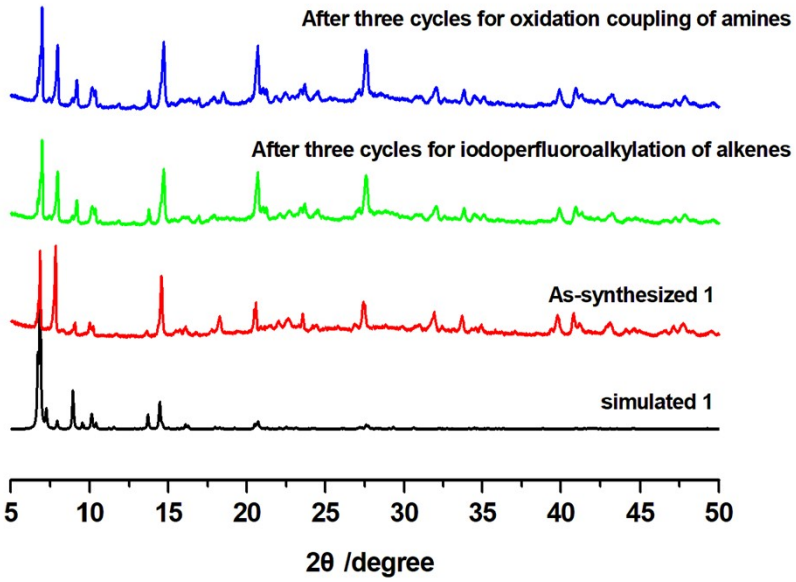


Figure S5. The PXRD patterns of MOF 1 after seven cycles.

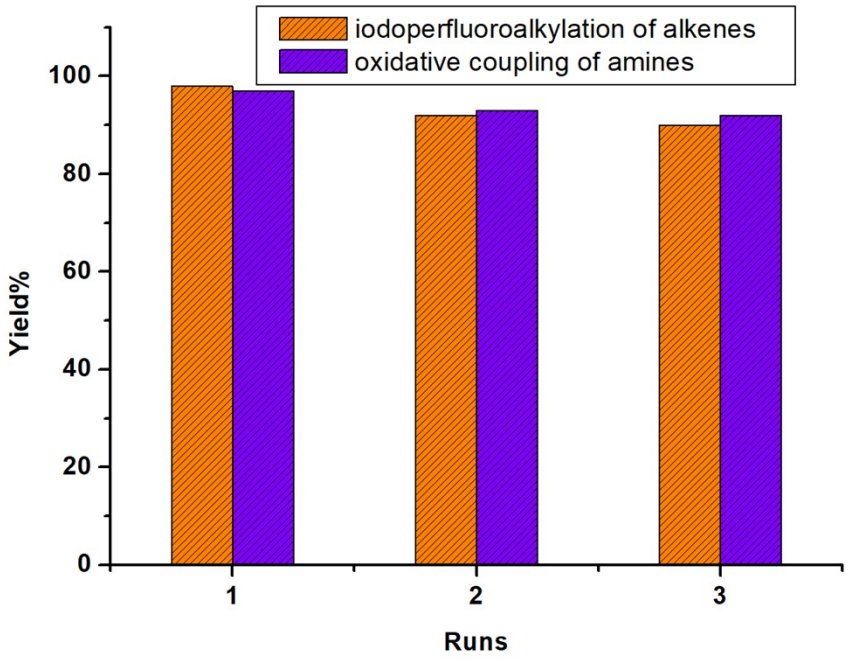


Figure S6. The recycle experiments for iodoperfluoroalkylation of alkenes and oxidative coupling of amines by using MOF 1 as catalyst.

Figure S7. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodododecane (3a):

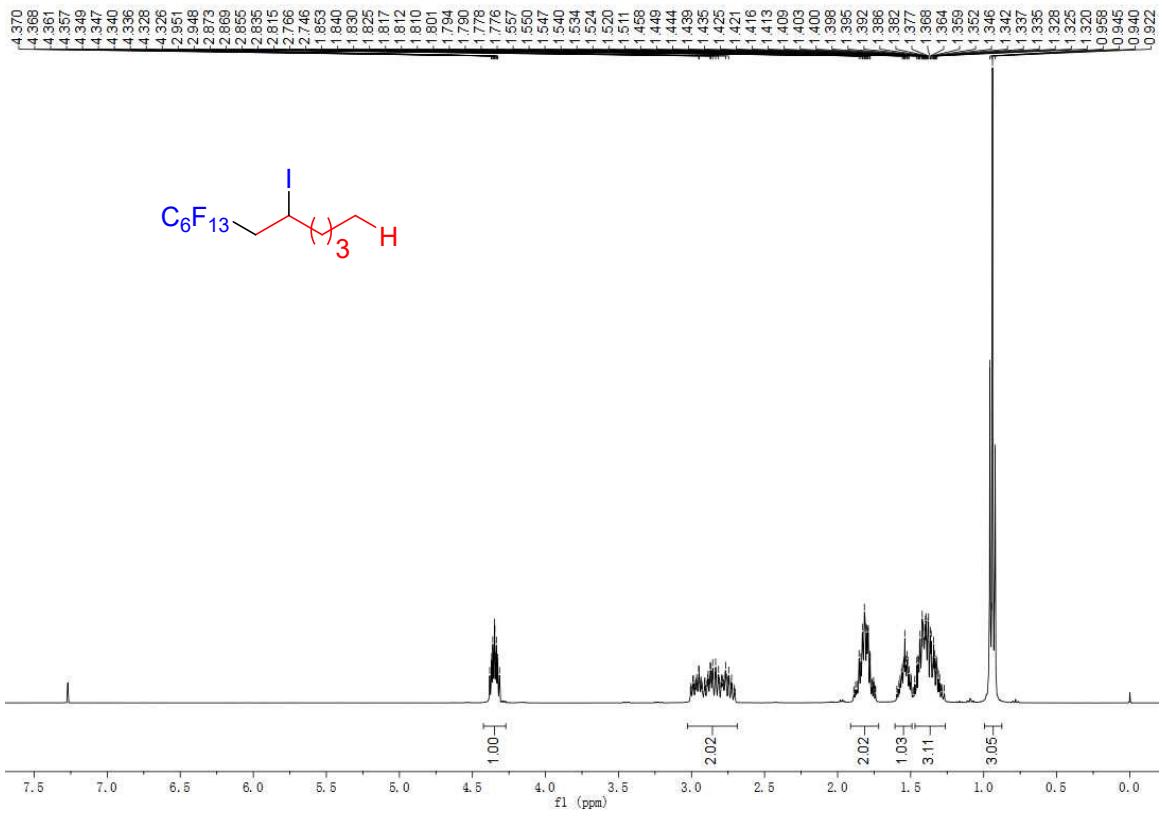


Figure S8. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodododecane (3a):

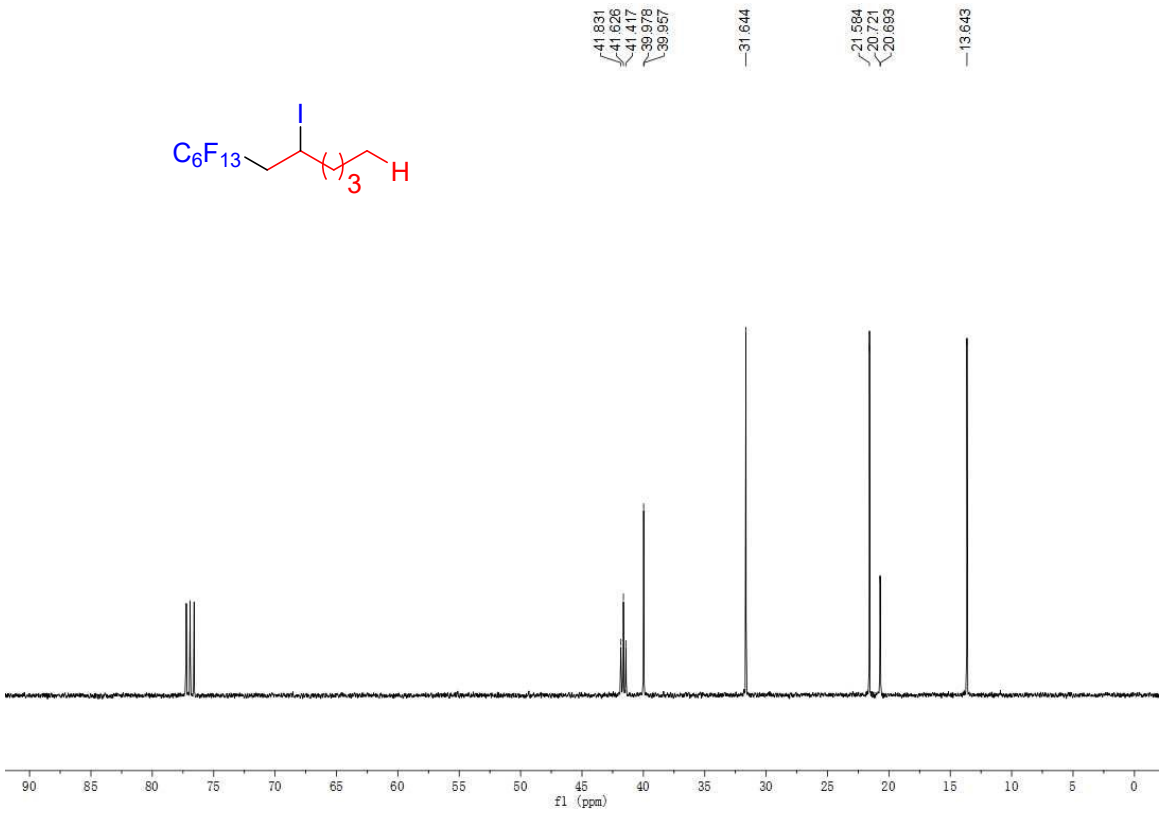


Figure S9. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodohexadecane (3b):

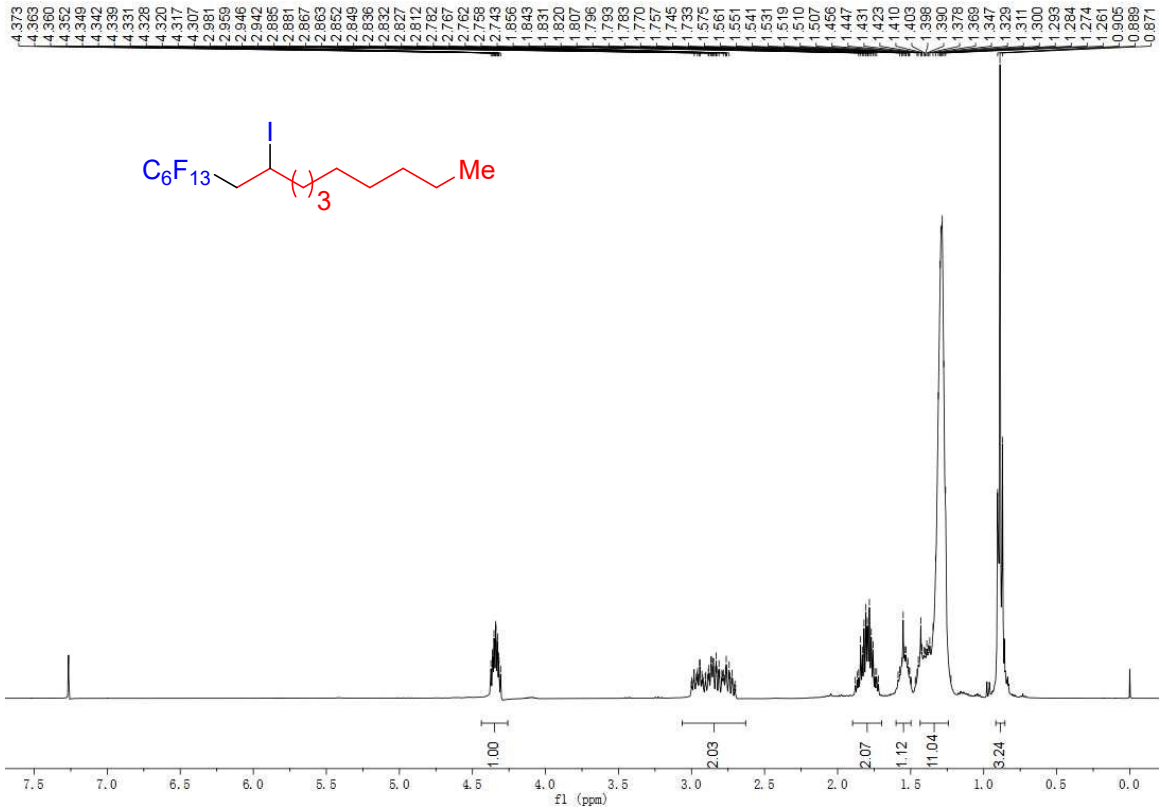


Figure S10. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodohexadecane (3b):

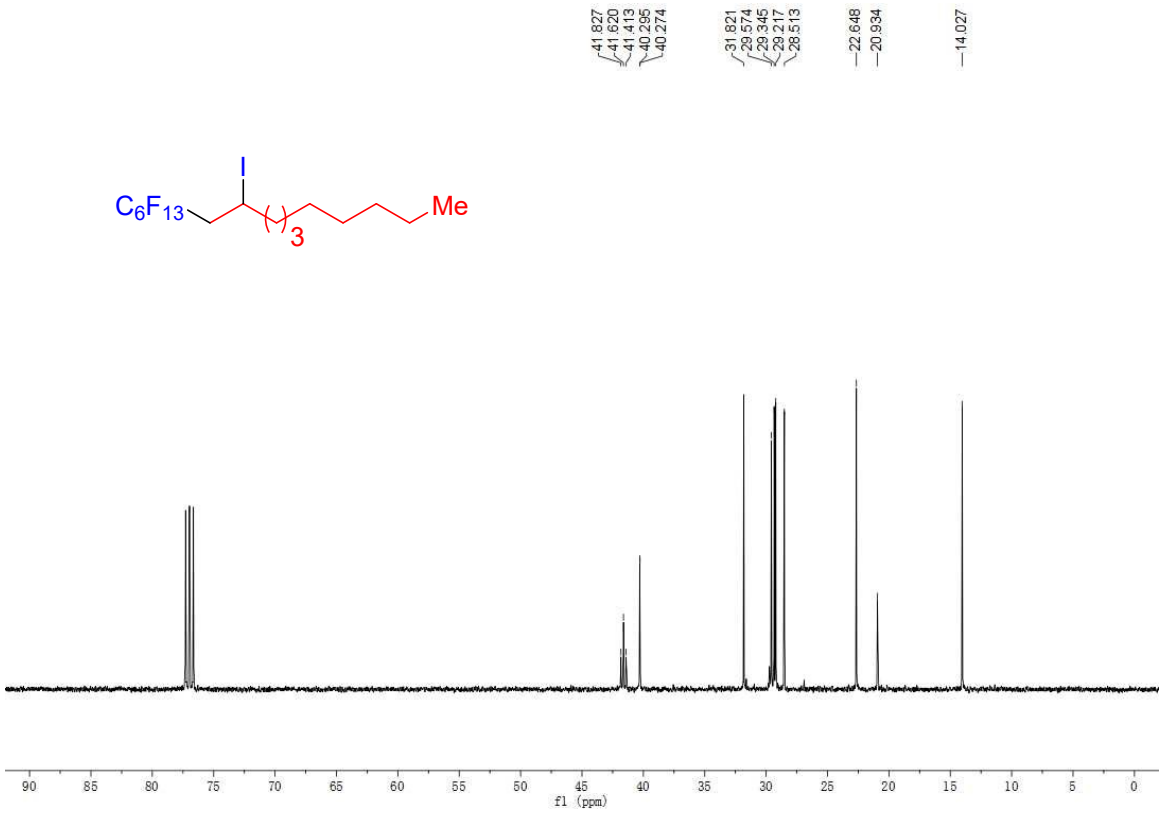


Figure S11. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of 12-chloro-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodododecane (3c):

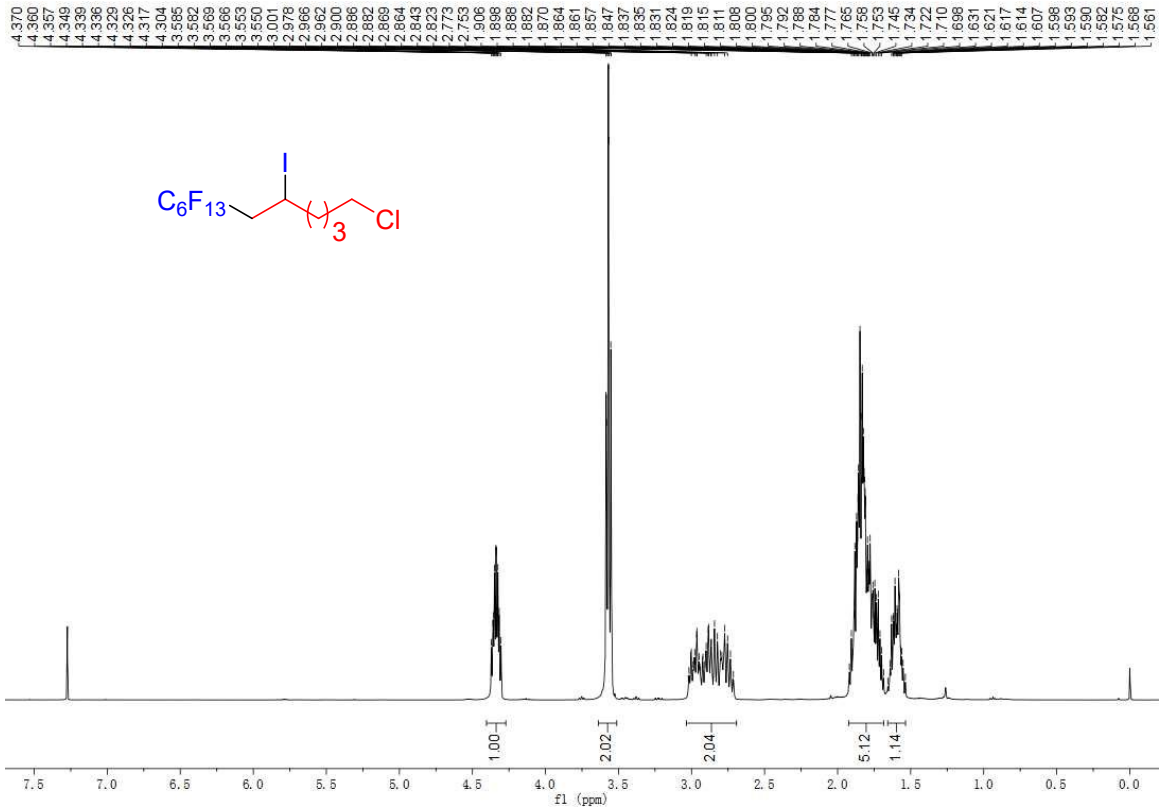


Figure S12. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of 12-chloro-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodododecane (3c):

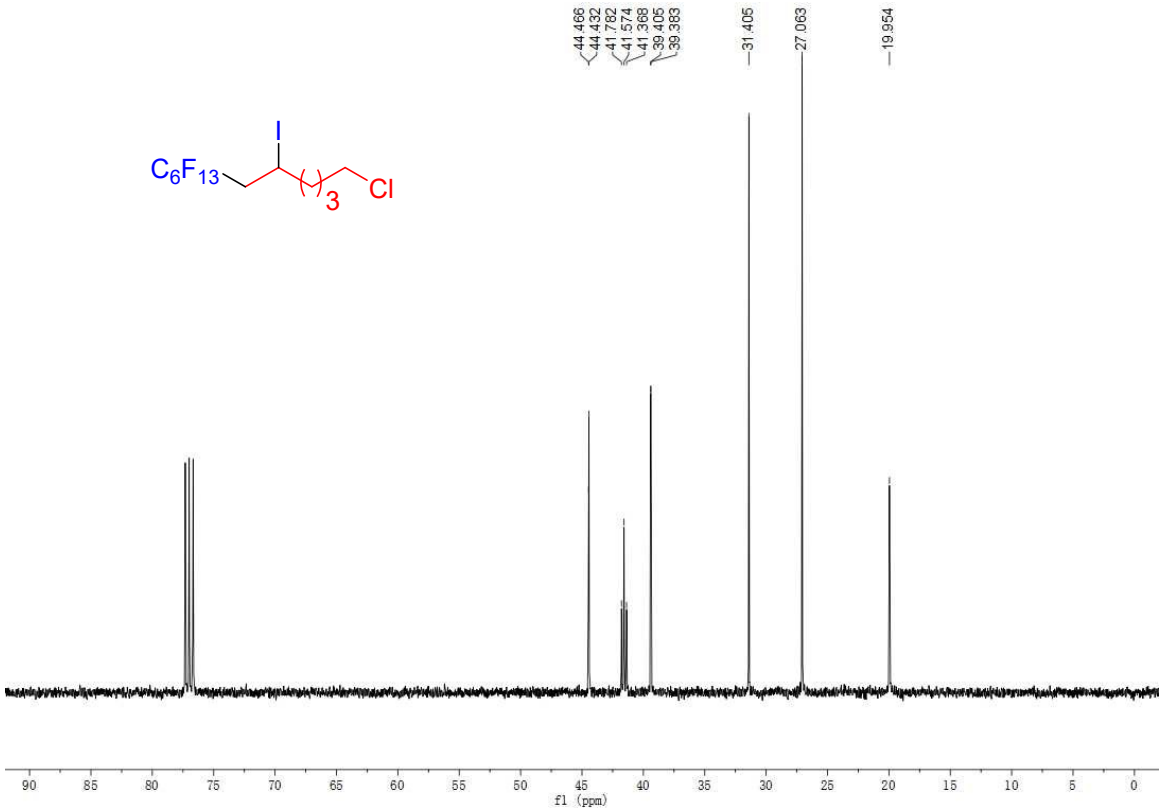


Figure S13. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of 12-bromo-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodododecane (3d):

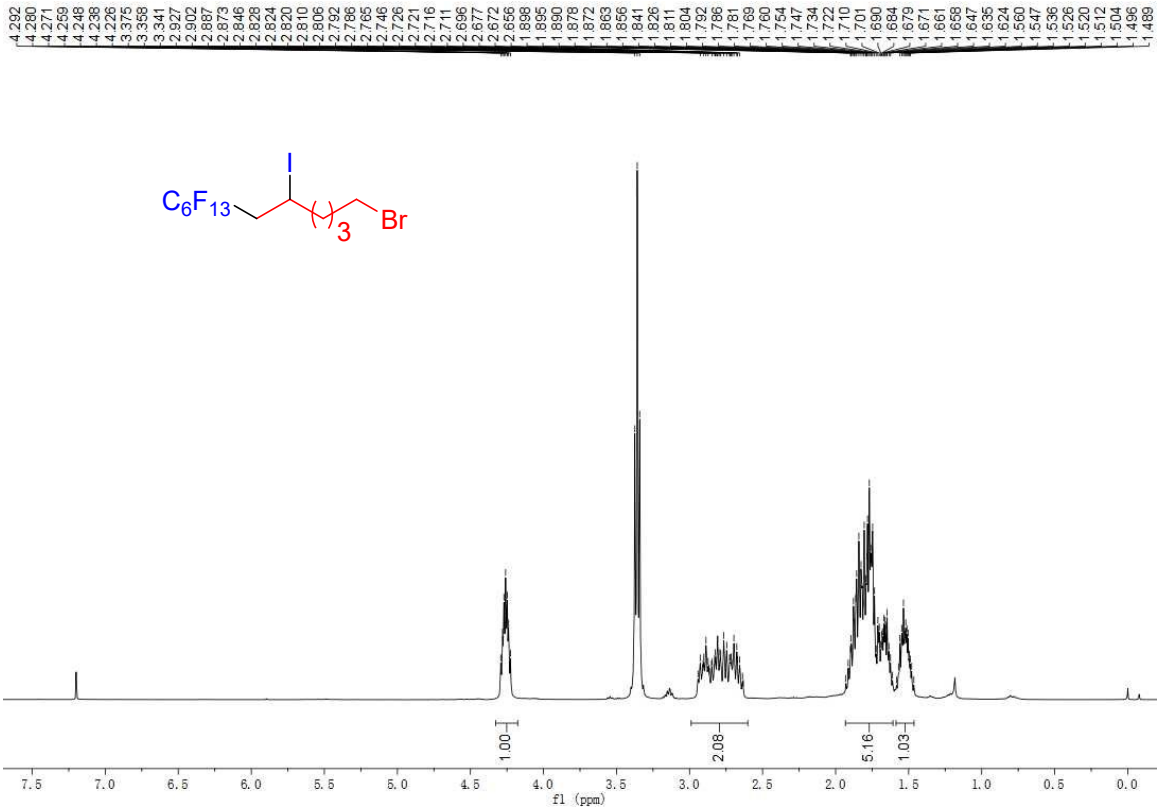


Figure S14. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of 12-bromo-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodododecane (3d):

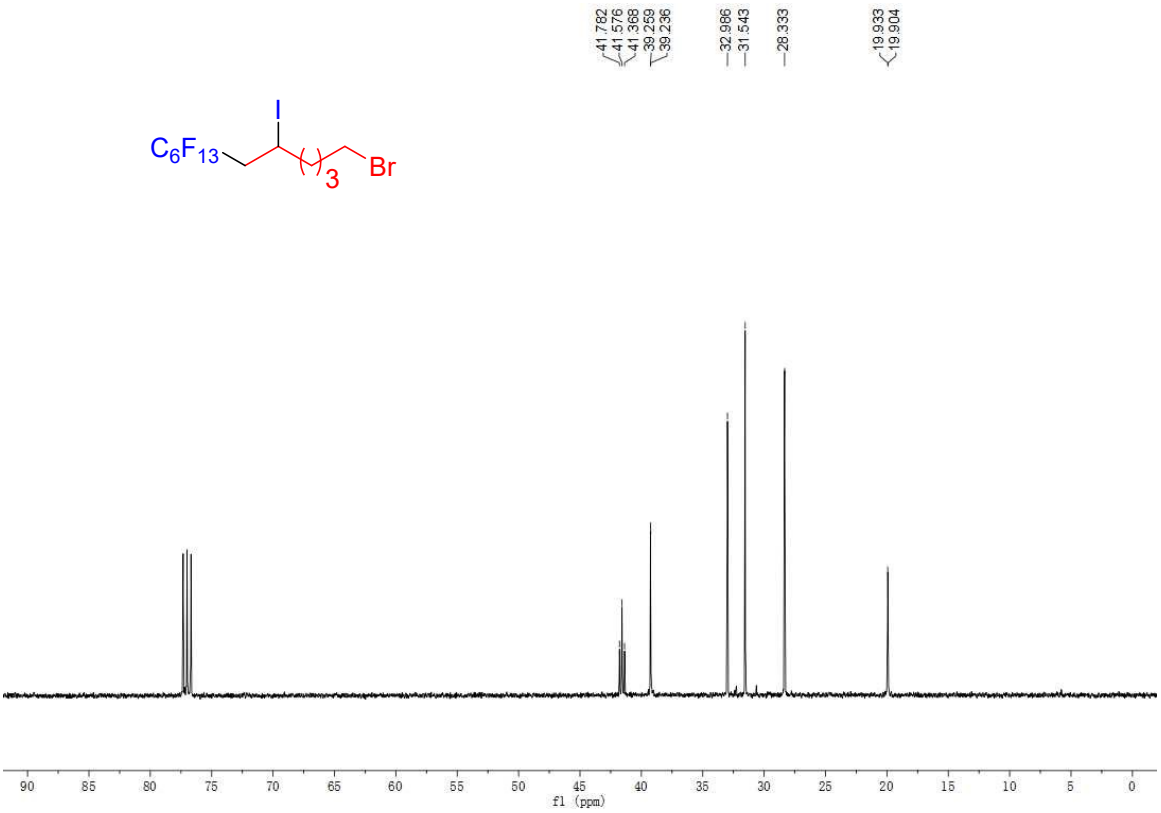


Figure S15. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of 7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-5-iodododecan-1-ol (3e):

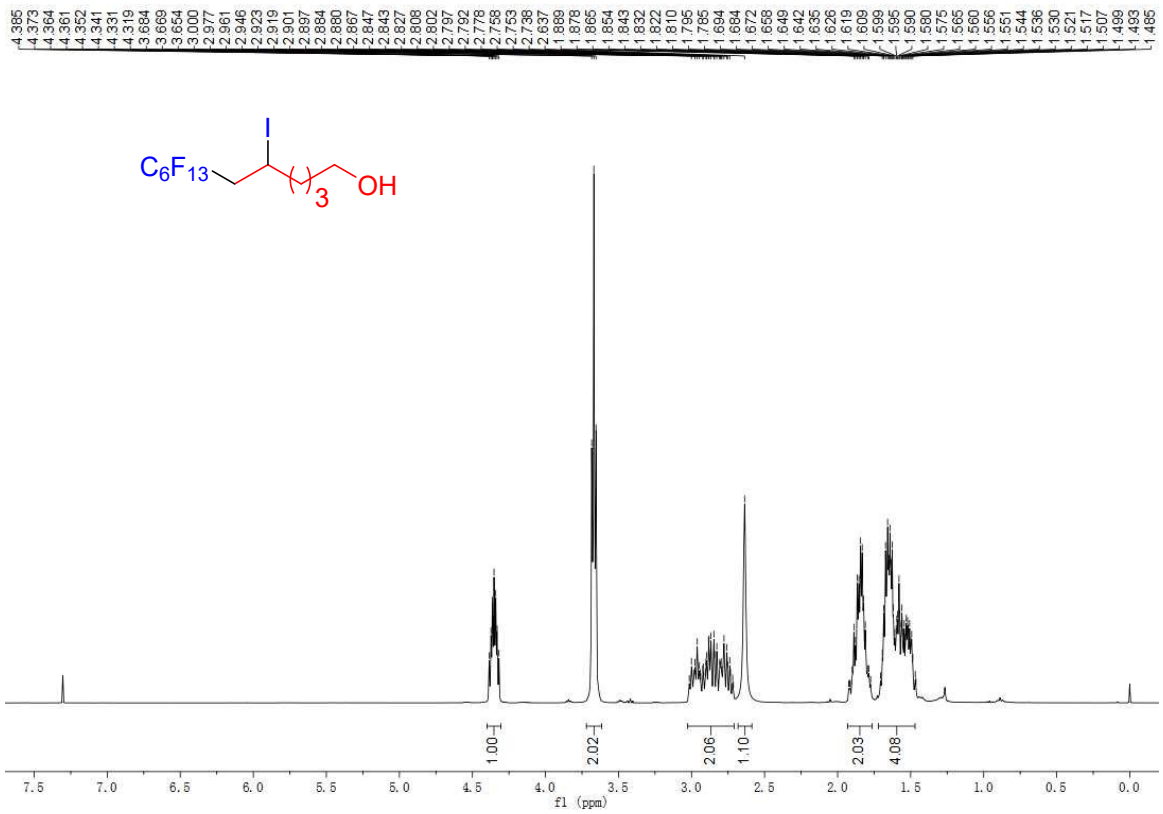


Figure S16. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of 7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-5-iodododecan-1-ol (3e):

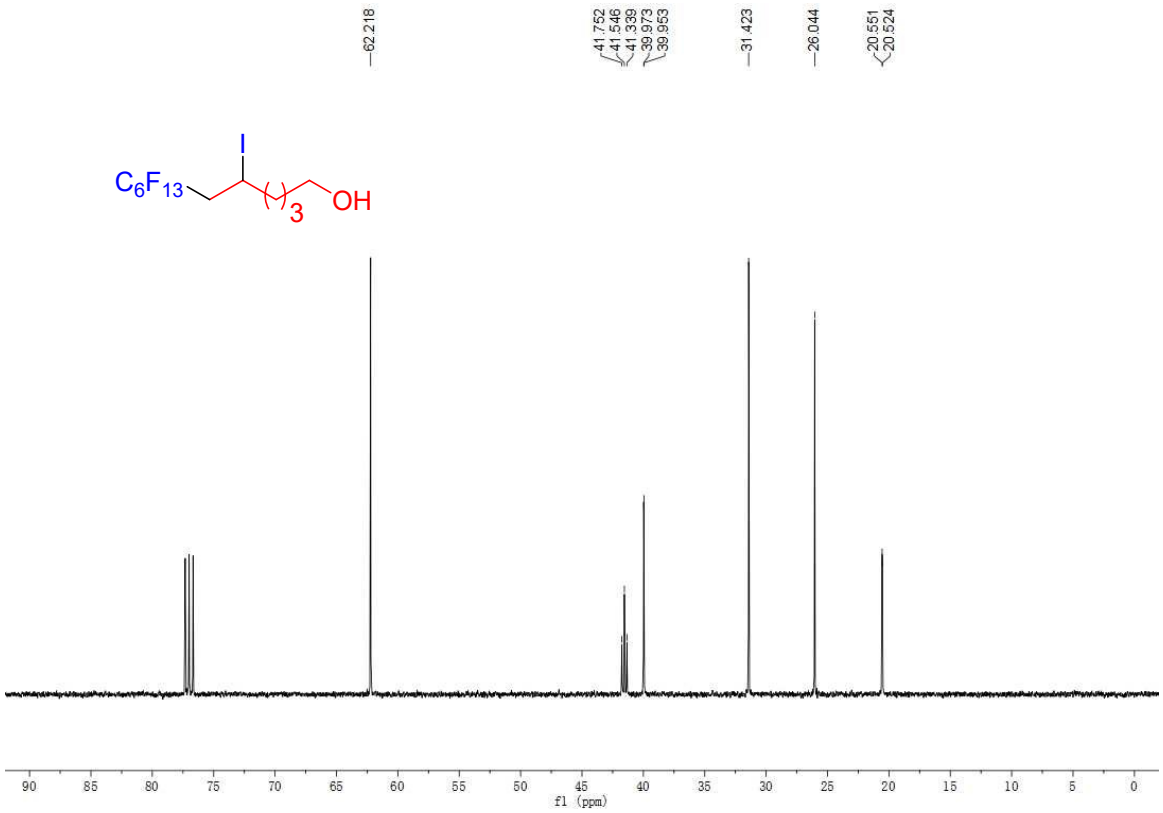


Figure S17. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of 7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-5-iodododecyl acetate (3f):

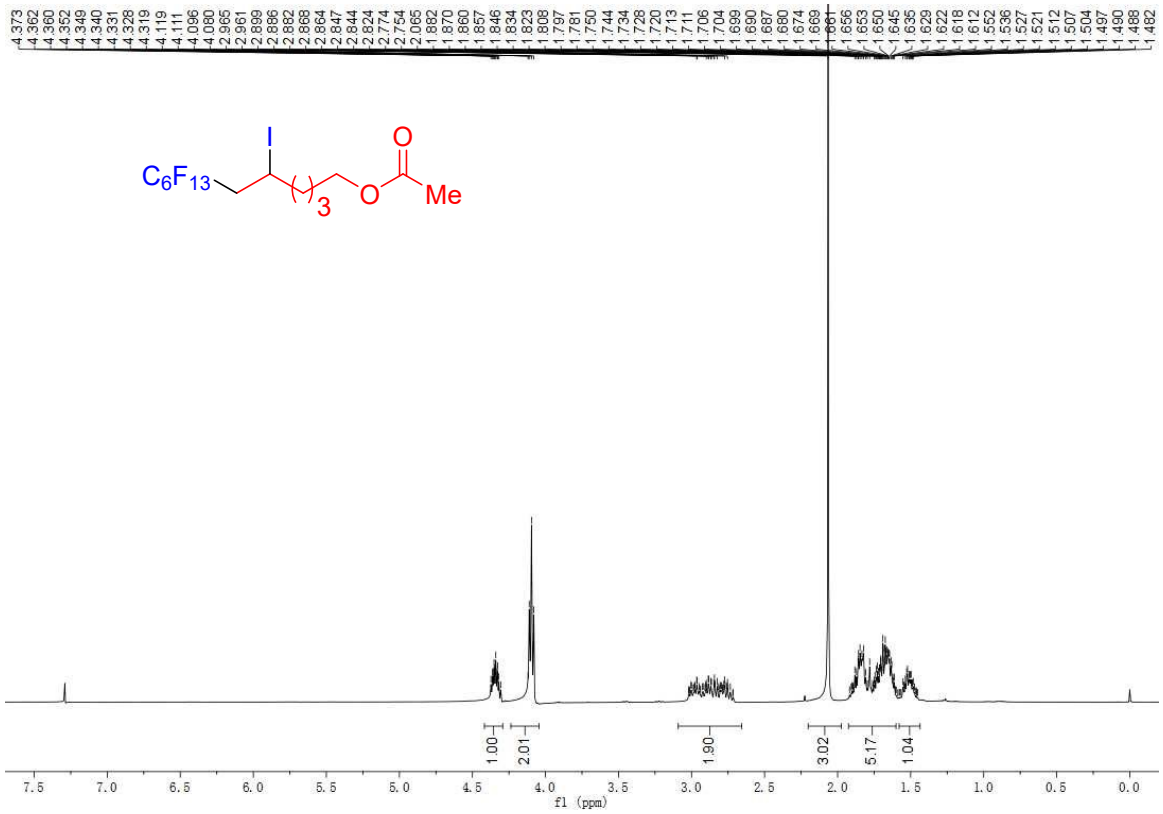


Figure S18. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of 7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-5-iodododecyl acetate (3f):

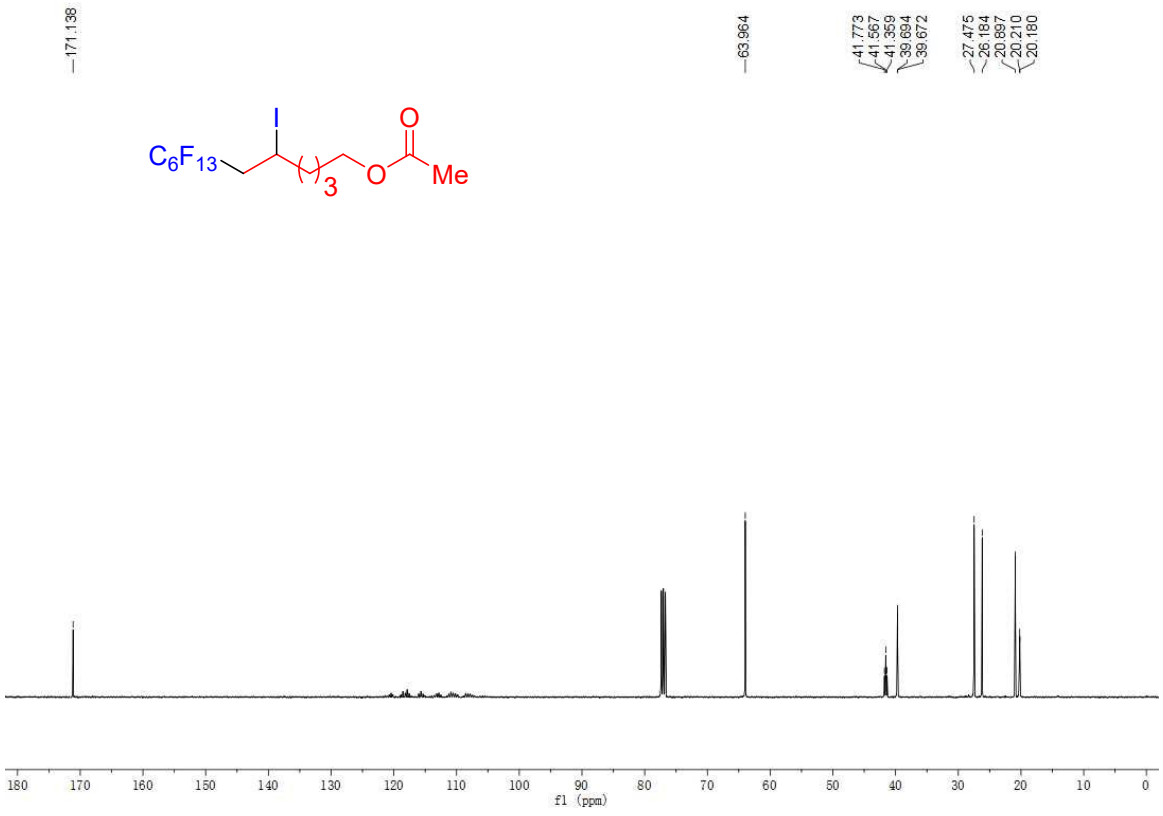


Figure S19. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodo-12-(octyloxy)dodecane (3g):

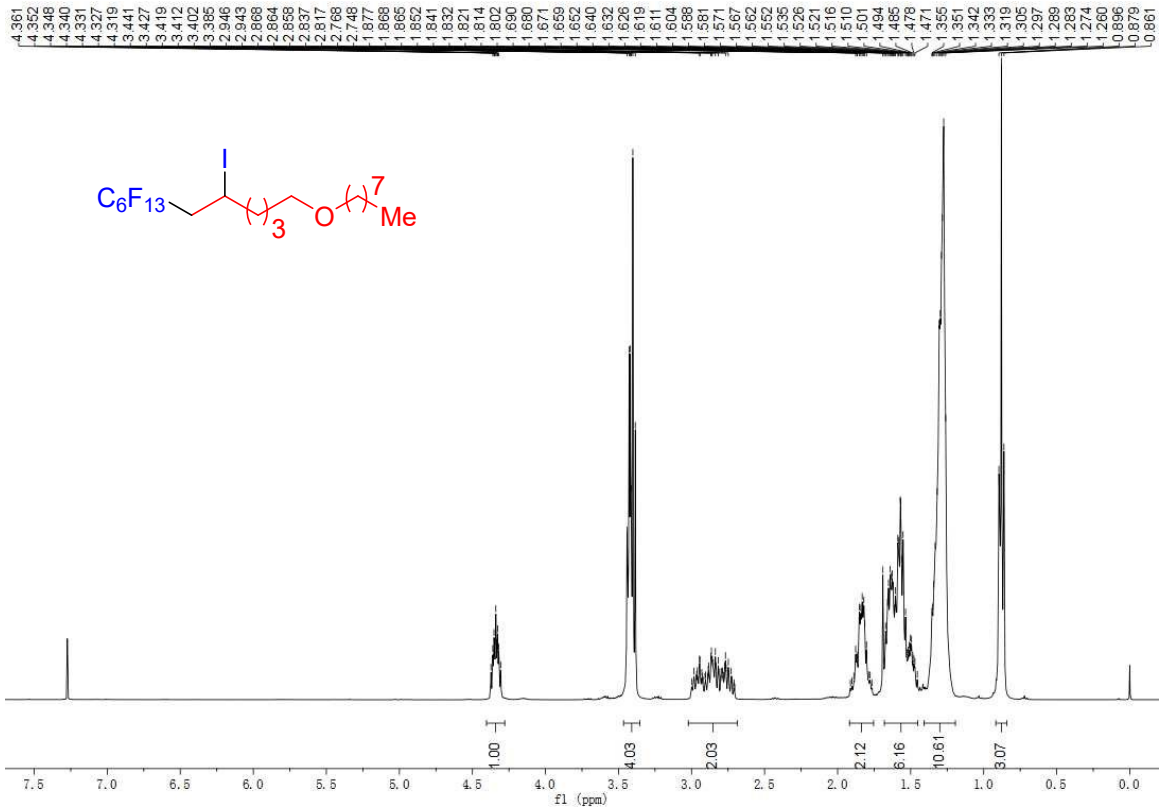


Figure S20. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodo-12-(octyloxy)dodecane (3g):

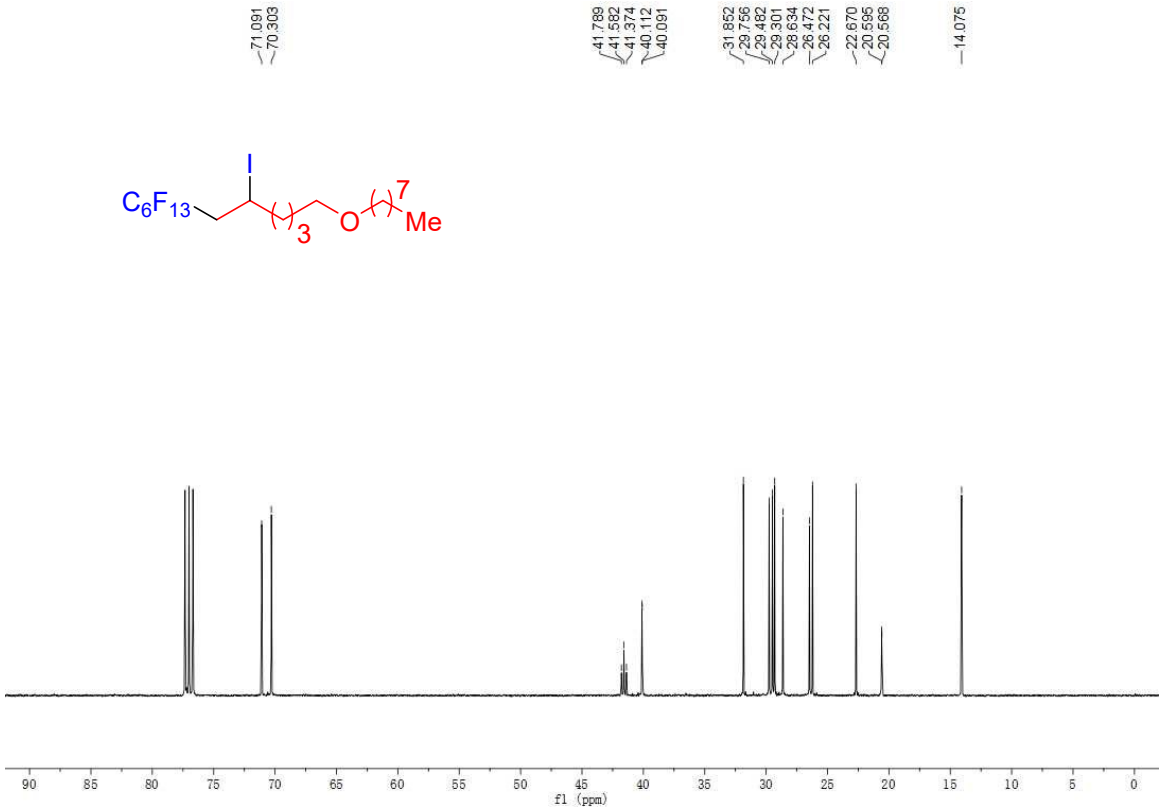


Figure S21. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of 2-(7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-5-iodododecyl)isoindoline-1,3-dione (3h):

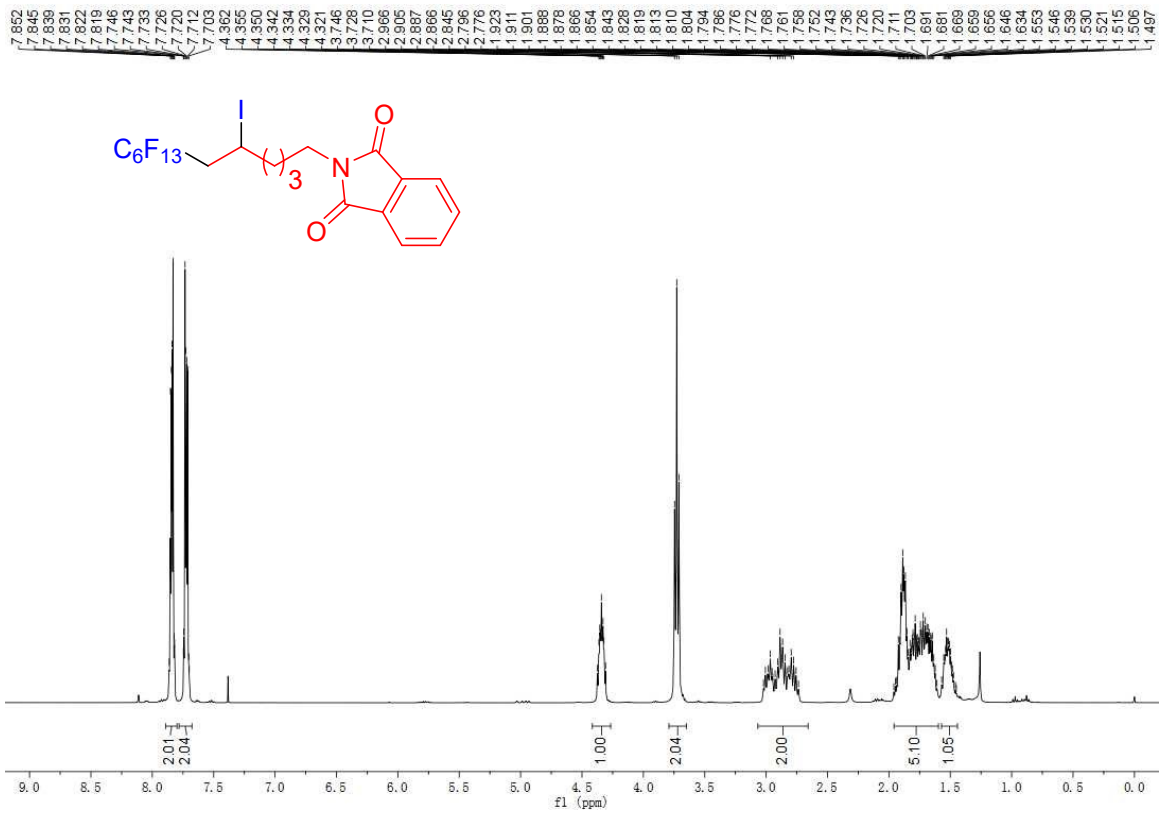


Figure S22. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of 2-(7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-5-iodododecyl)isoindoline-1,3-dione (3h):

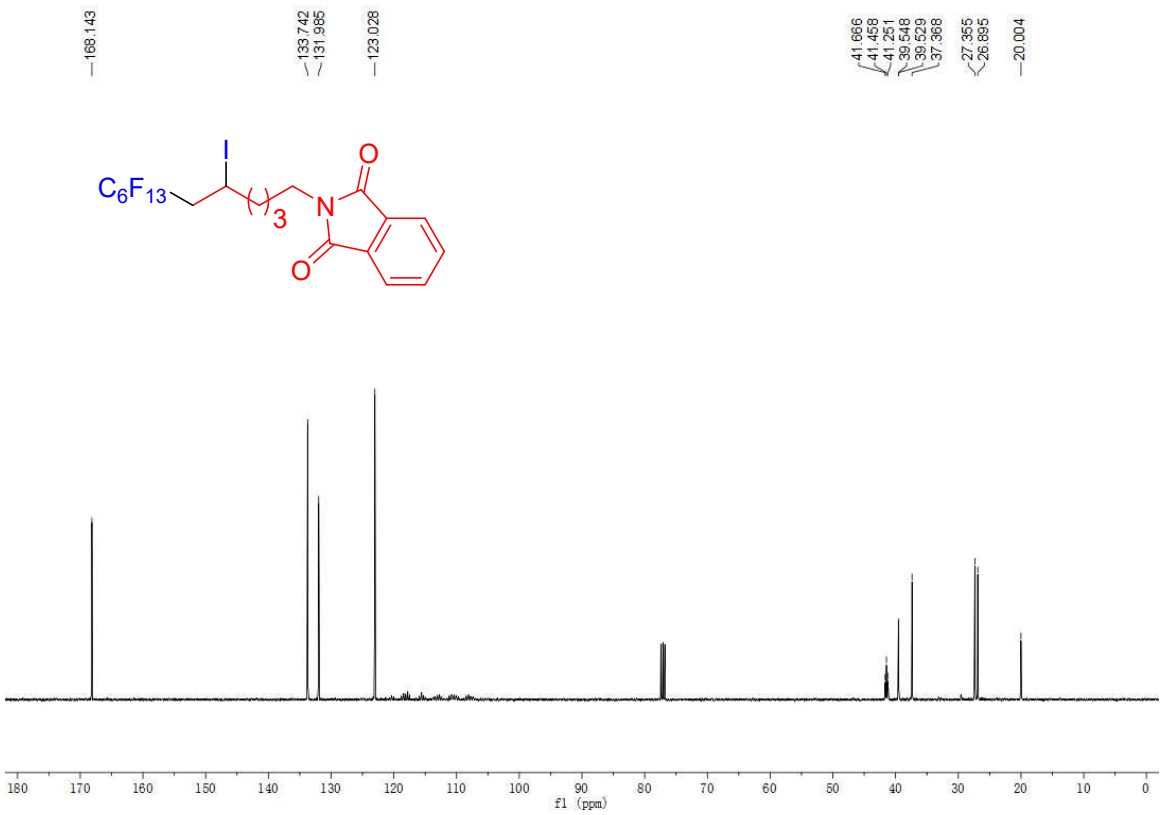


Figure S23. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of ((7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-5-iododododecyl)sulfonyl)benzene (3i):

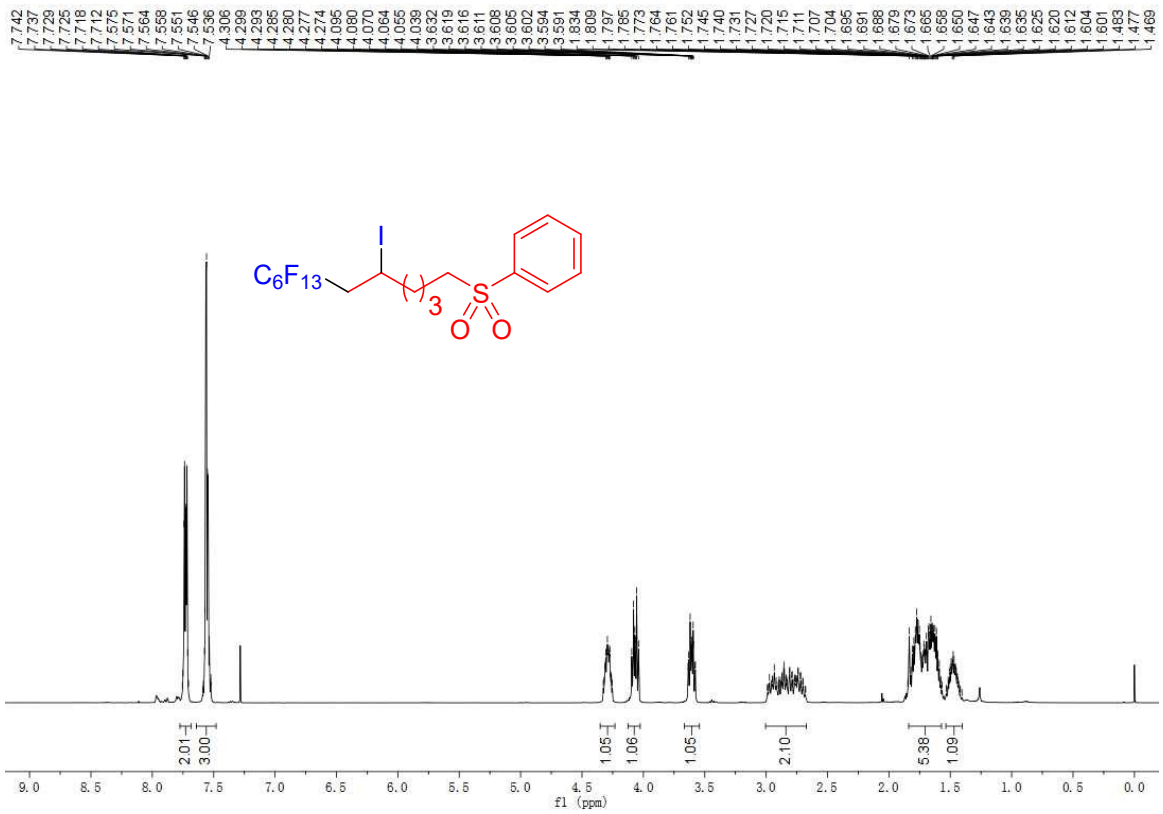


Figure S24. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of ((7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-5-iododododecyl)sulfonyl)benzene (3i):

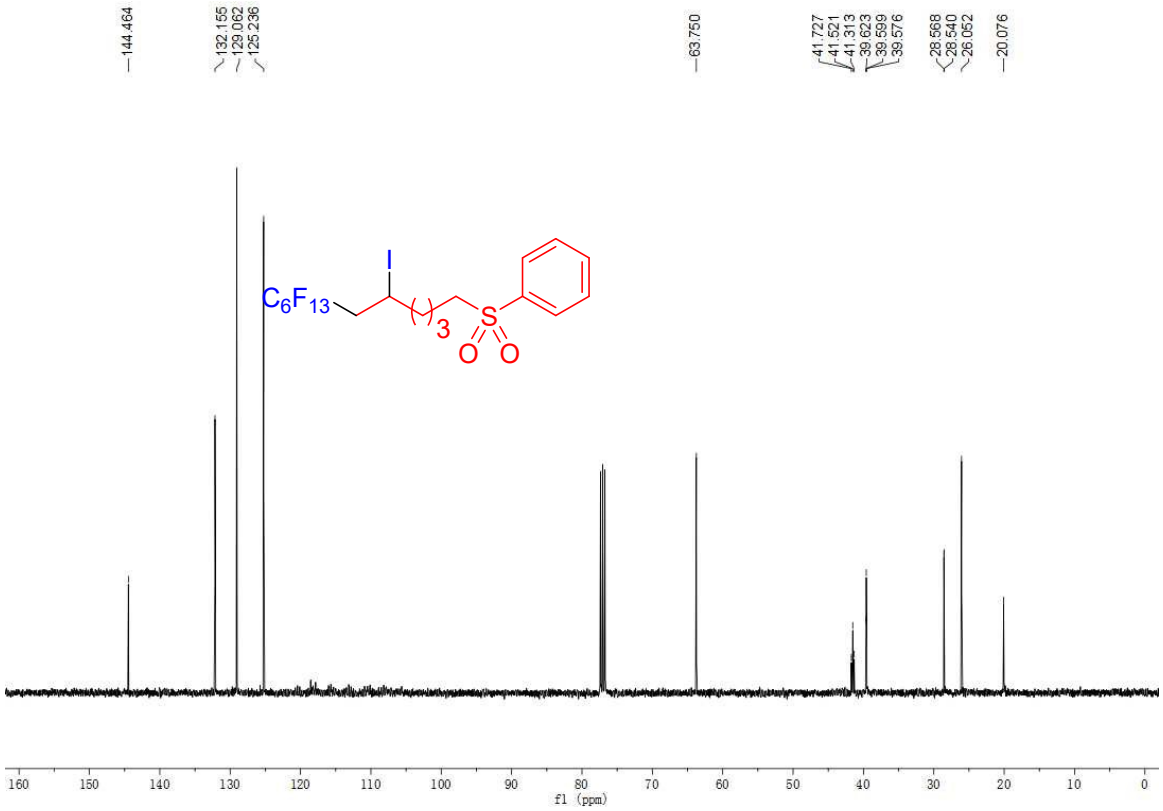


Figure S25. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *p*-tolyl(7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-5-iodododecyl)sulfane (3j):

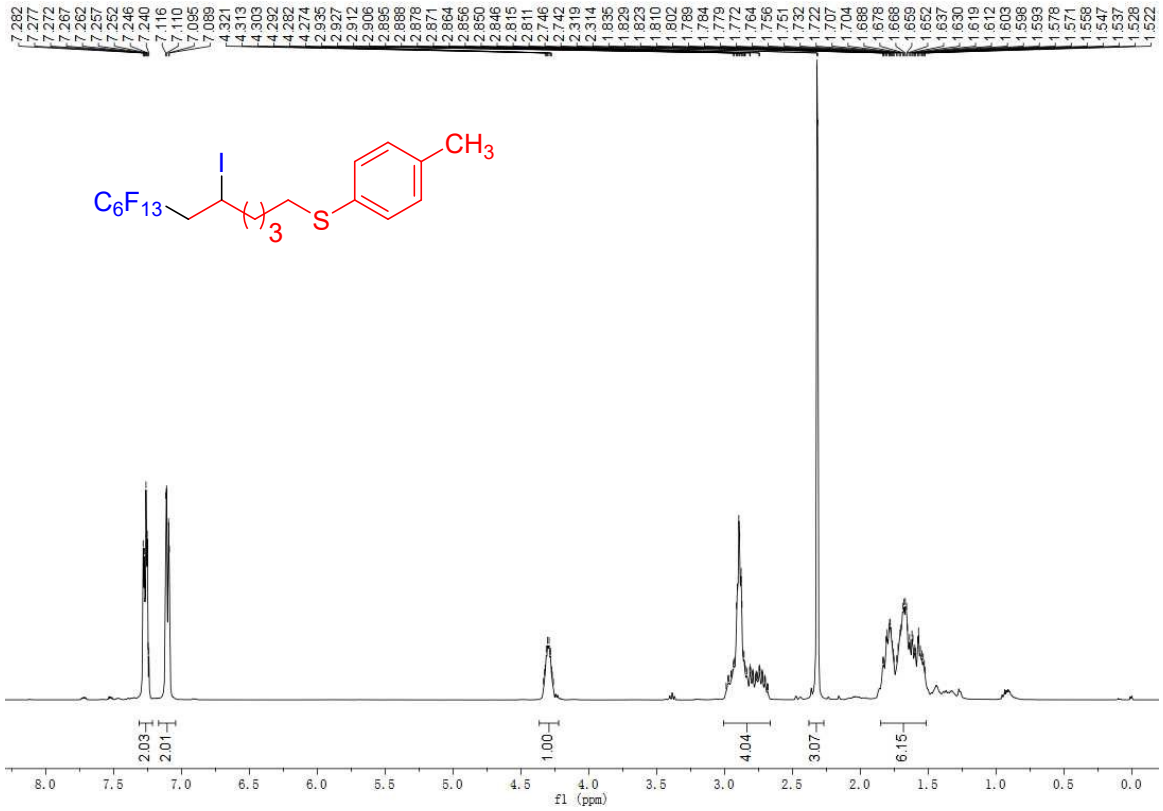


Figure S26. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of *p*-tolyl(7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-5-iodododecyl)sulfane (3j):

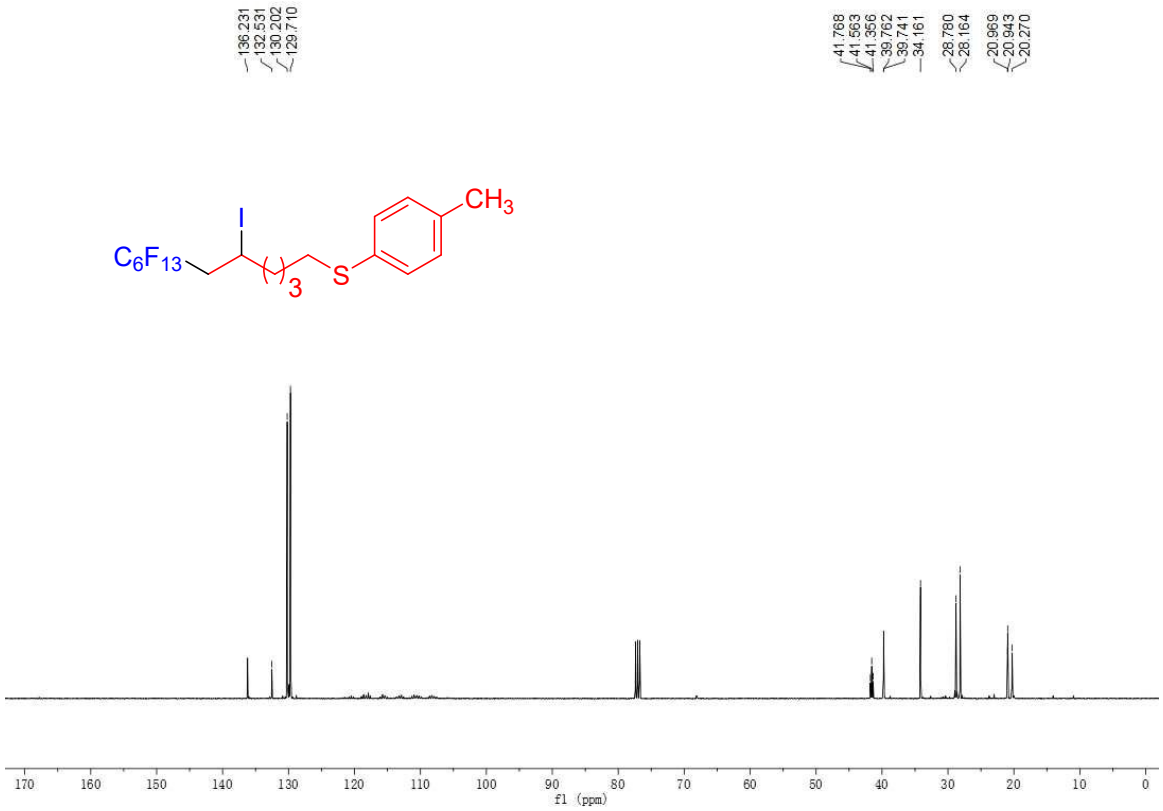


Figure S27. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-10-iodotetradecane (3k):

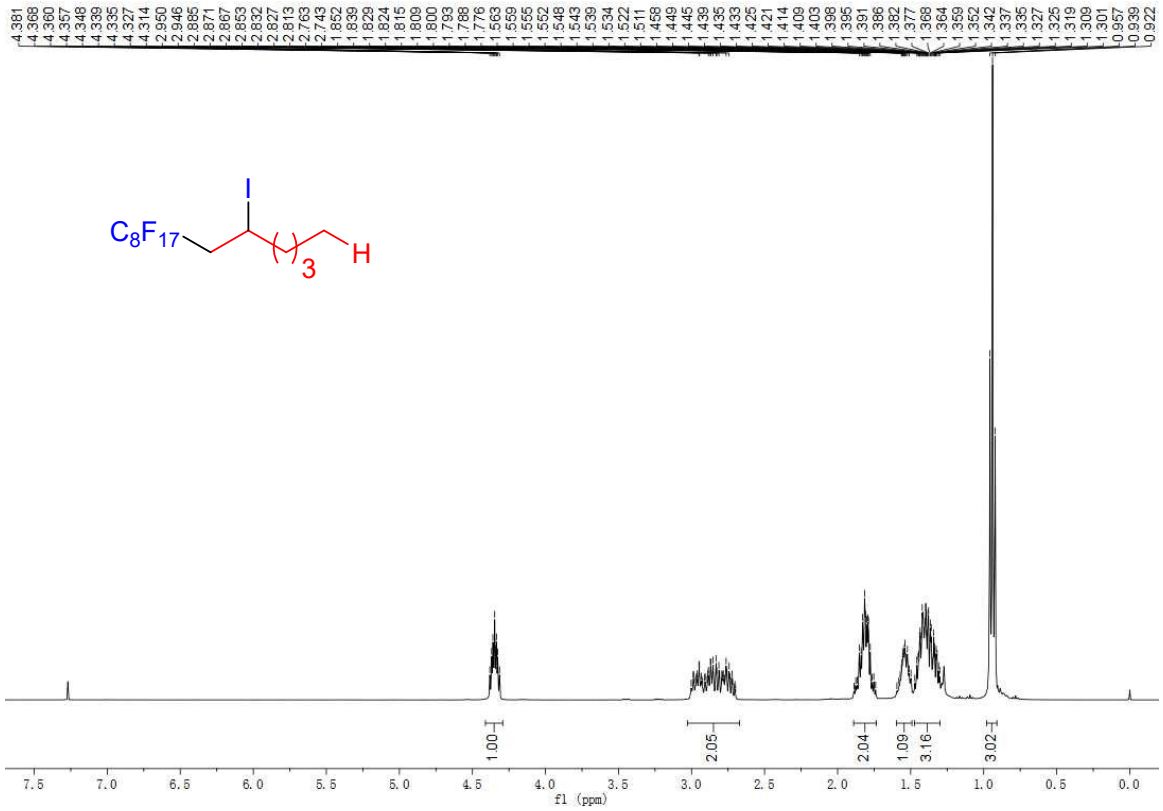


Figure S28. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of 1,1,1,2,2,3,3,4,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-10-iodotetradecane (3k):

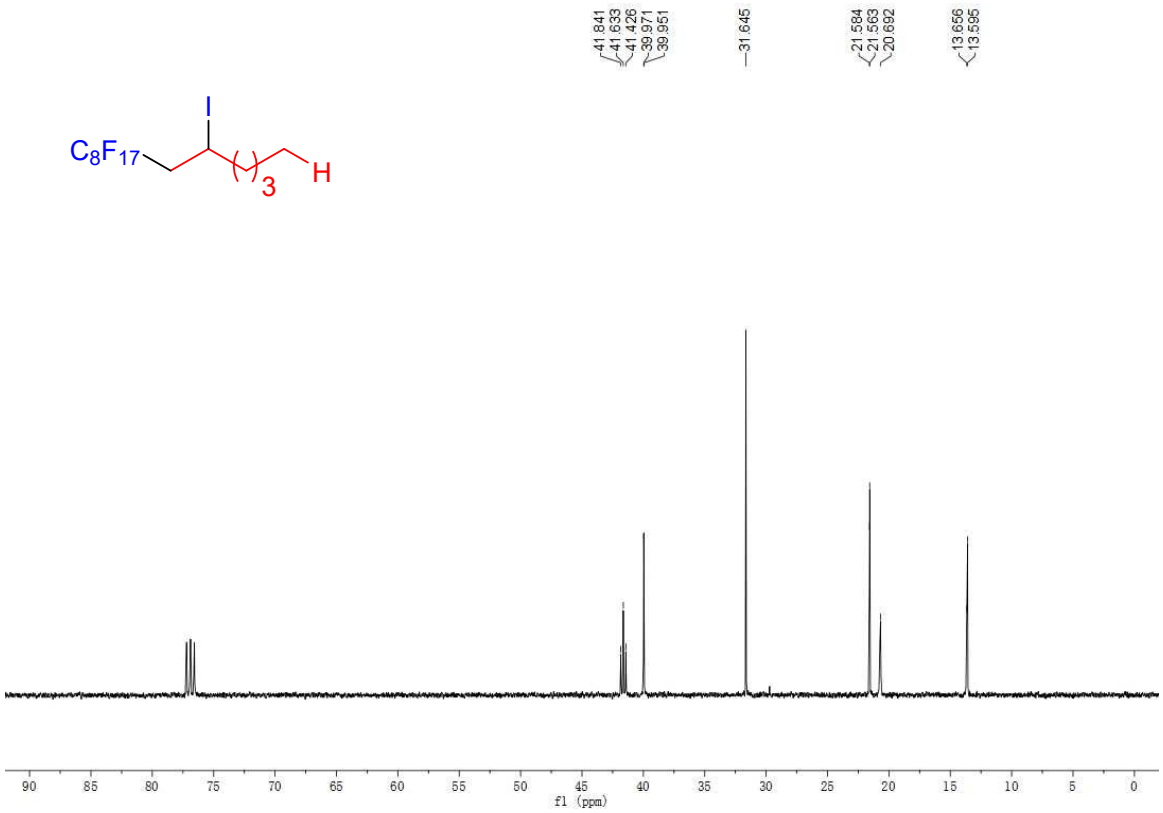


Figure S29. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of (*E*)-*N*-benzyl-1-phenylmethanimine (5a):

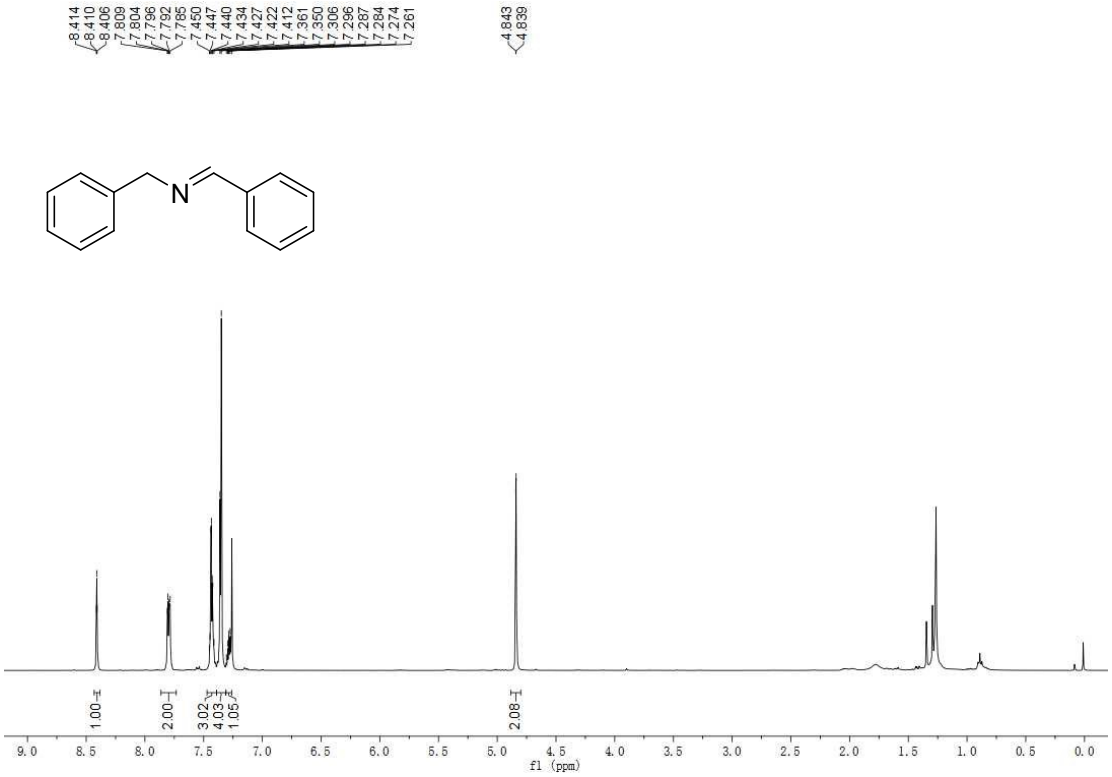


Figure S30. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of (*E*)-*N*-benzyl-1-phenylmethanimine (5a):

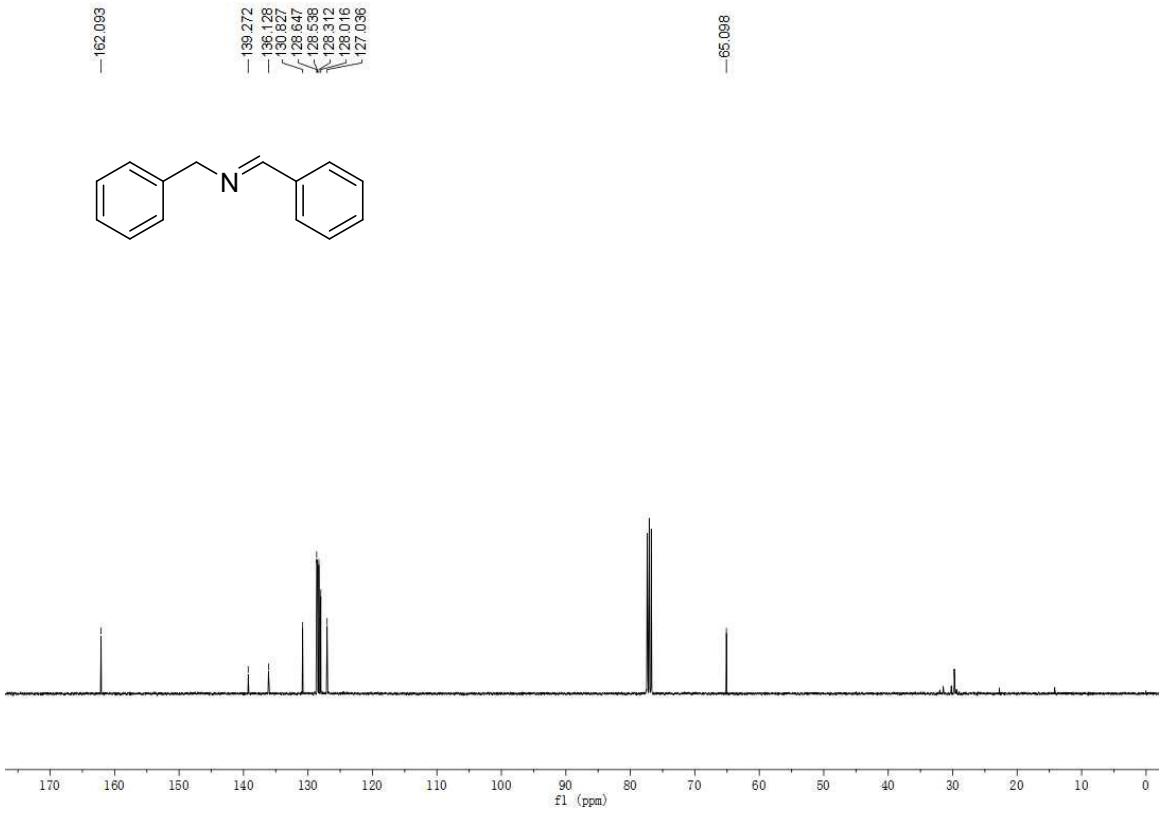


Figure S31. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of (*E*)-*N*-(2-fluorobenzyl)-1-(2-fluorophenyl)methanimine (5b):

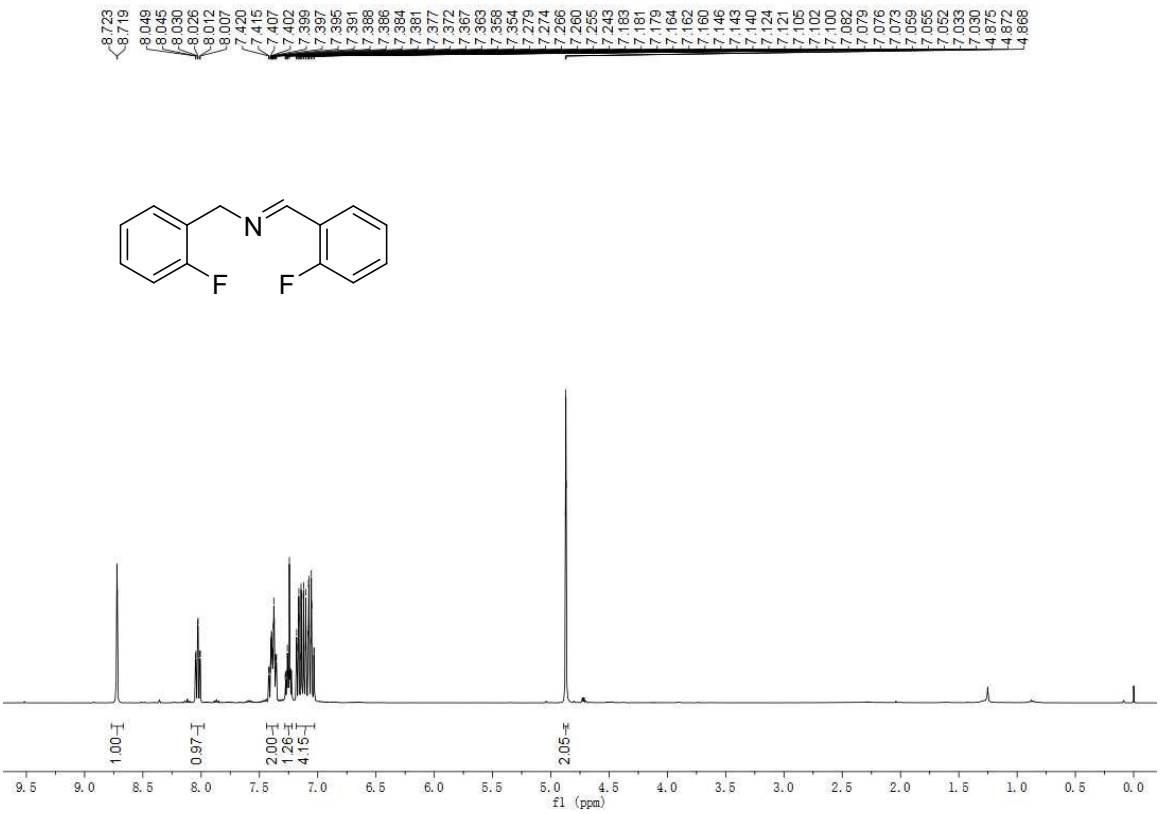


Figure S32. ^{13}C{^{1}H} NMR spectra (400 MHz, Chloroform-*d*) of (*E*)-*N*-(2-fluorobenzyl)-1-(2-fluorophenyl)methanimine (5b):

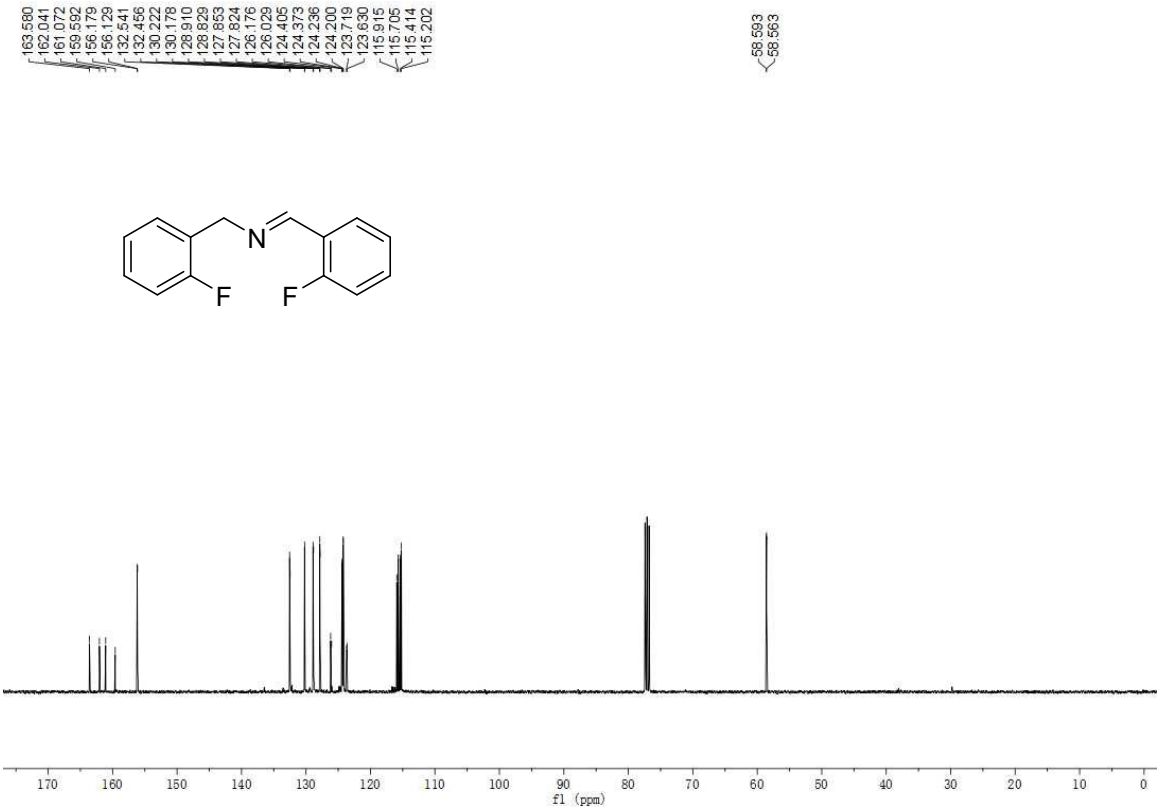


Figure S33. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of (*E*)-*N*-(3-fluorobenzyl)-1-(3-fluorophenyl)methanimine (5c):

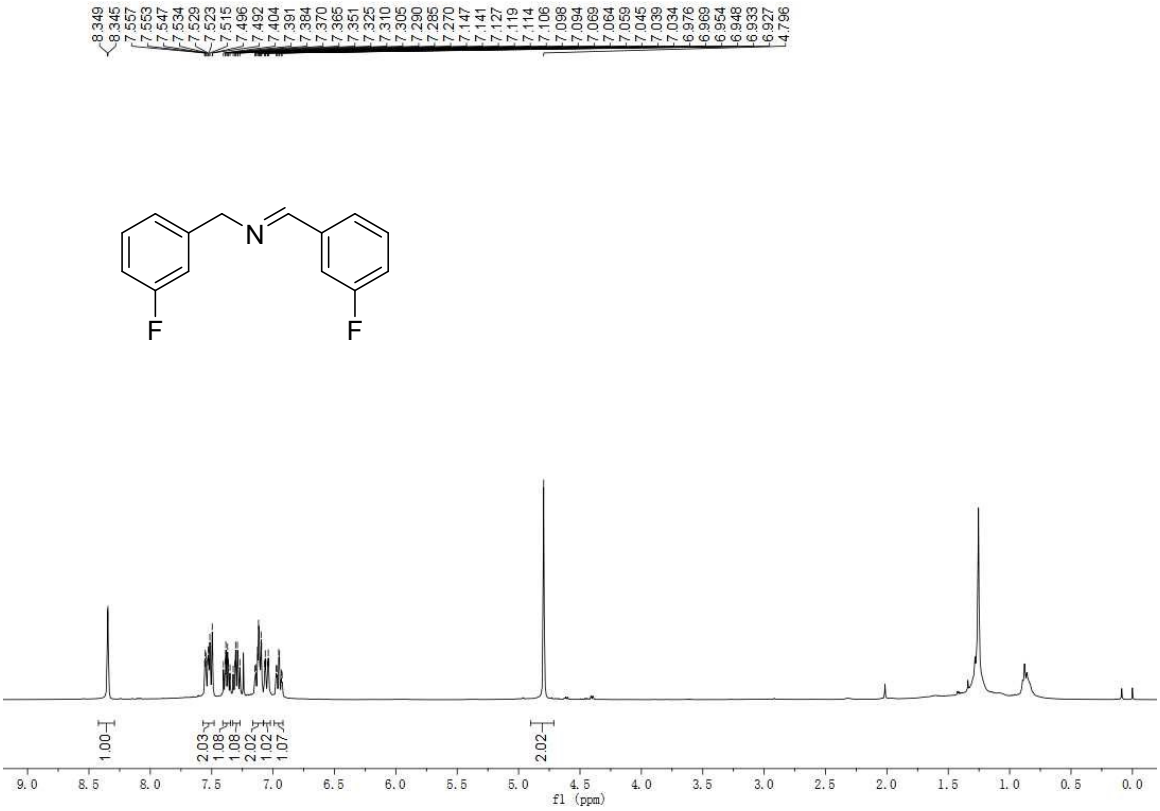


Figure S34. ^{13}C{^{1}H} NMR spectra (400 MHz, Chloroform-*d*) of (*E*)-*N*-(3-fluorobenzyl)-1-(3-fluorophenyl)methanimine (5c):

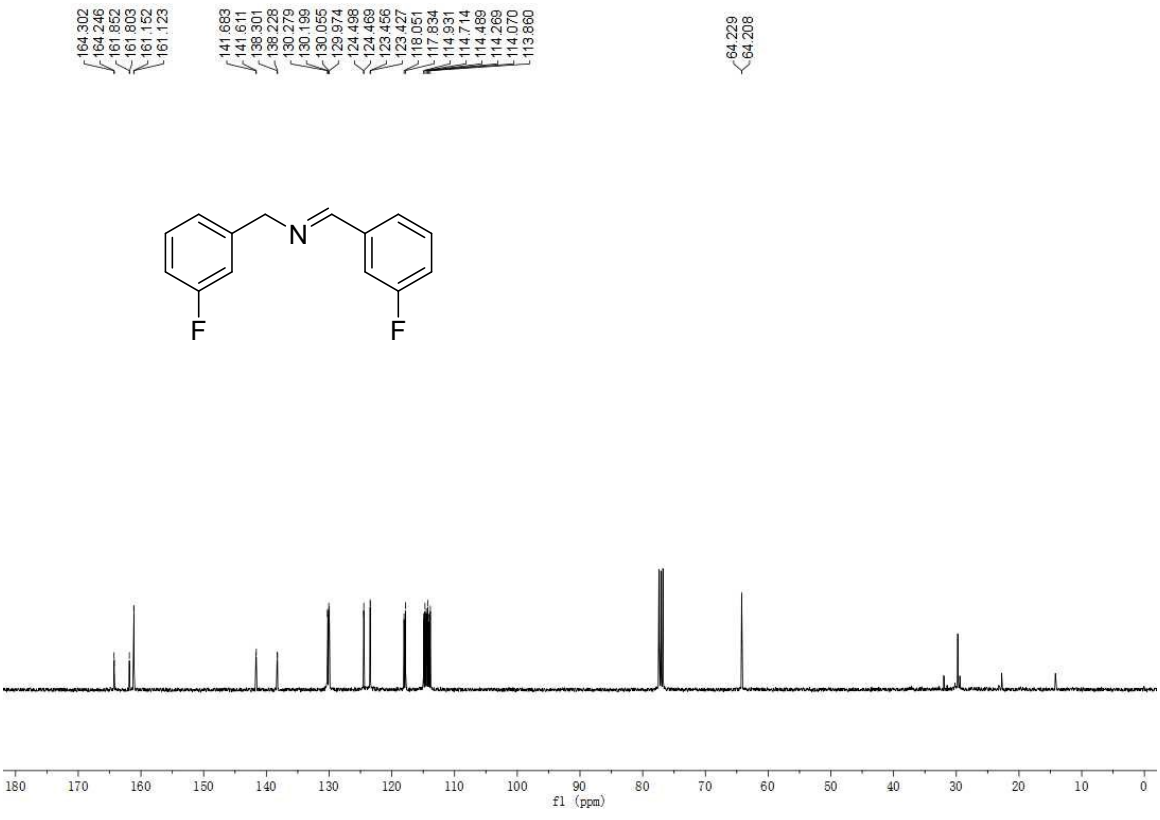


Figure S35. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of (*E*)-*N*-(4-fluorobenzyl)-1-(4-fluorophenyl)methanimine (5d):

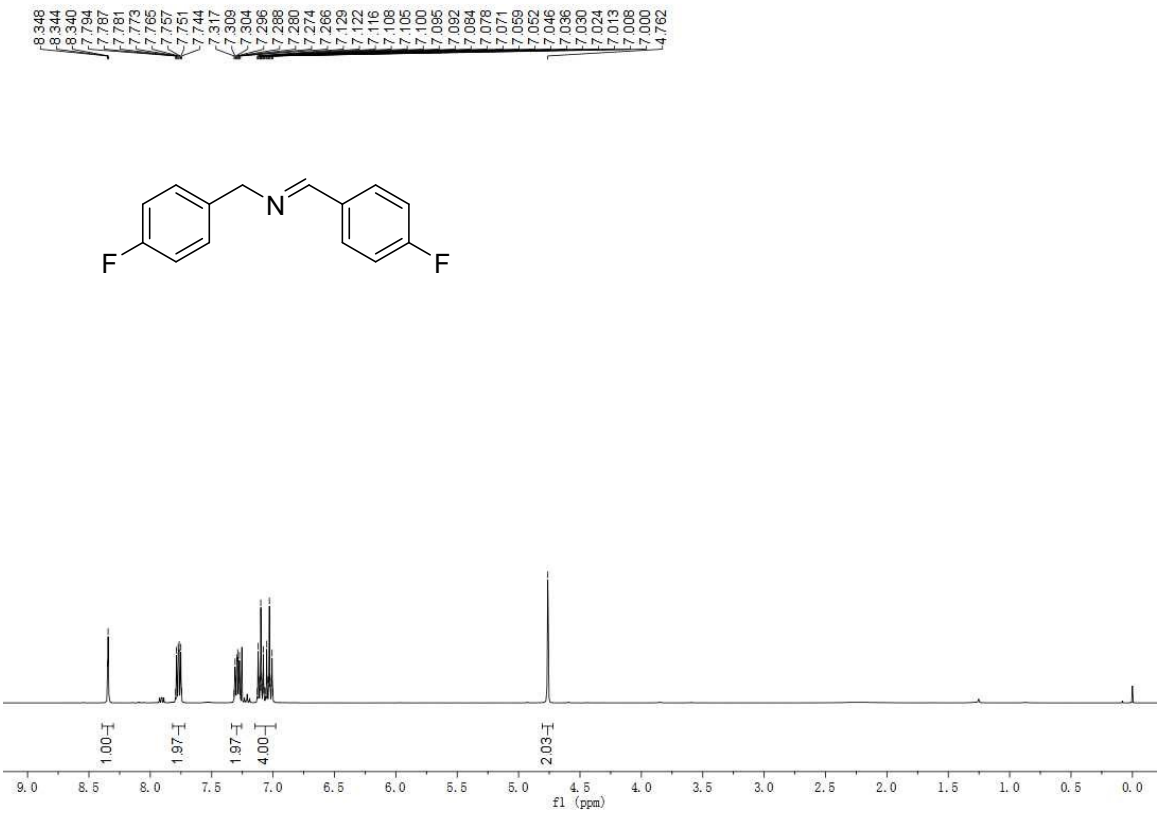


Figure S36. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of (*E*)-*N*-(4-fluorobenzyl)-1-(4-fluorophenyl)methanimine (5d):

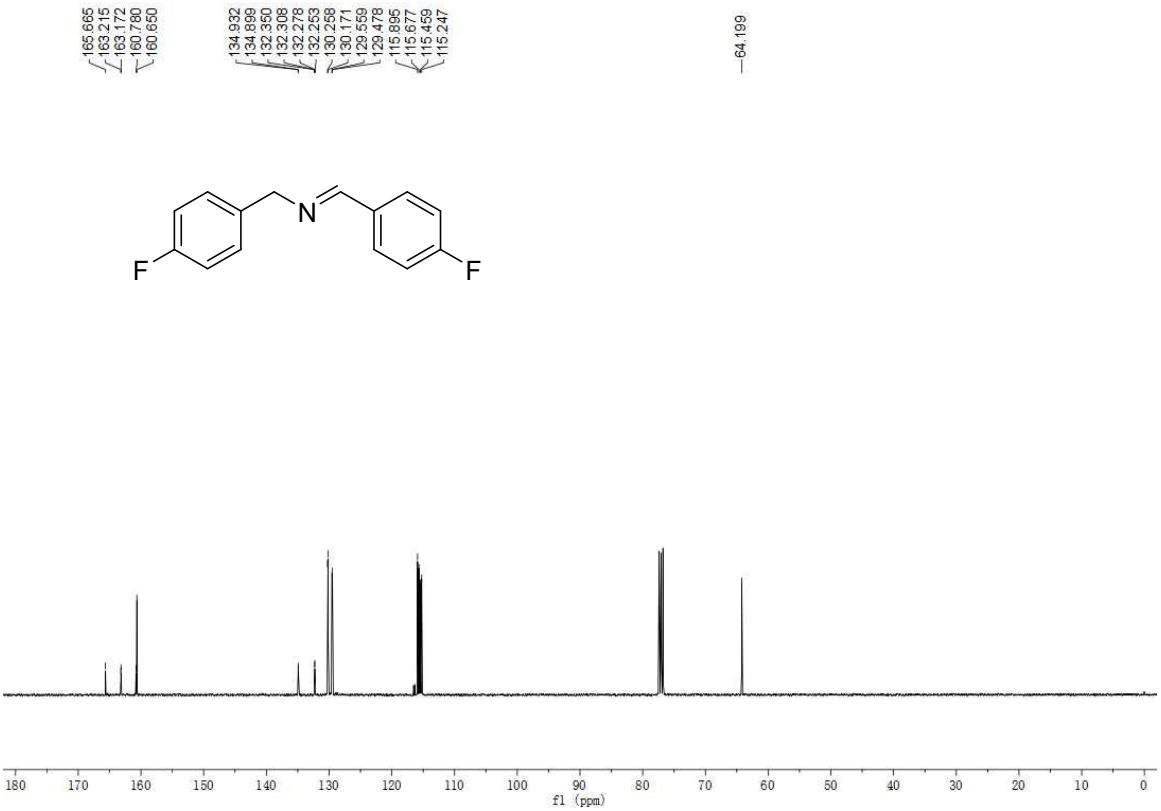


Figure S37. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of (*E*)-*N*-(2-chlorobenzyl)-1-(2-chlorophenyl)methanimine (5e):

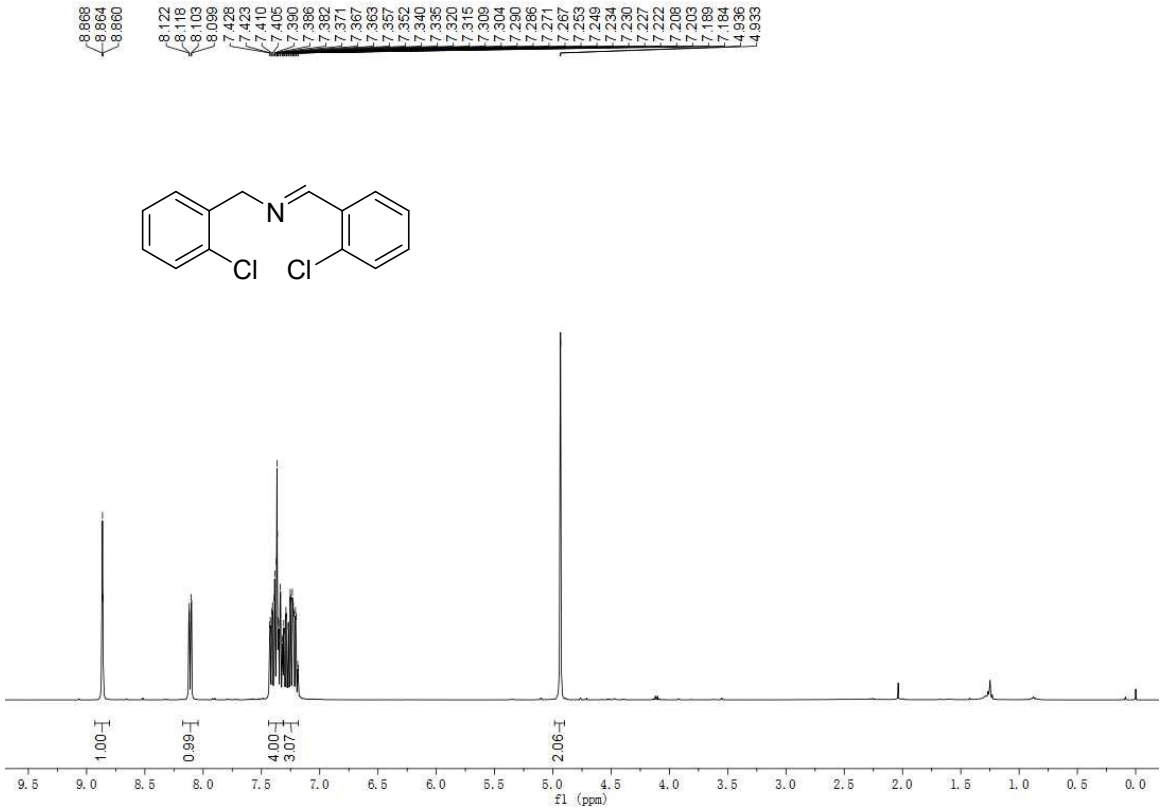


Figure S38. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of (*E*)-*N*-(2-chlorobenzyl)-1-(2-chlorophenyl)methanimine (5e):

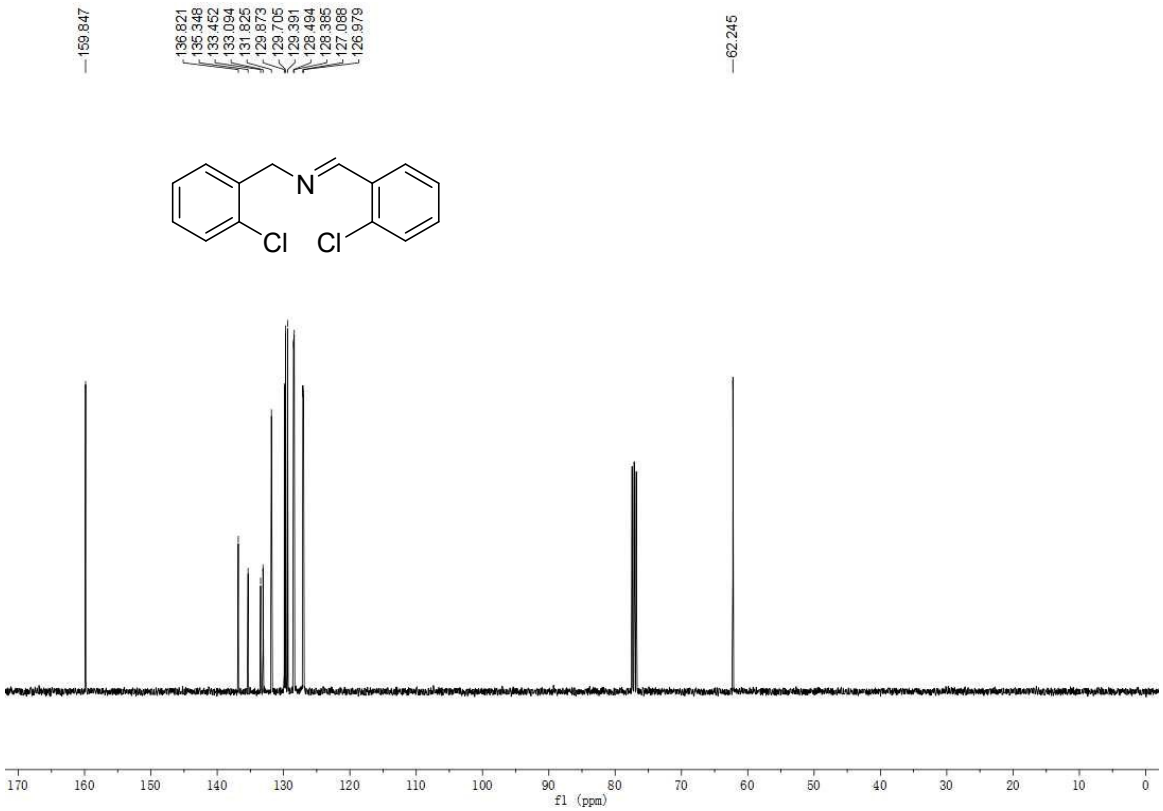


Figure S39. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of (*E*)-*N*-(3-chlorobenzyl)-1-(3-chlorophenyl)methanimine (5f):

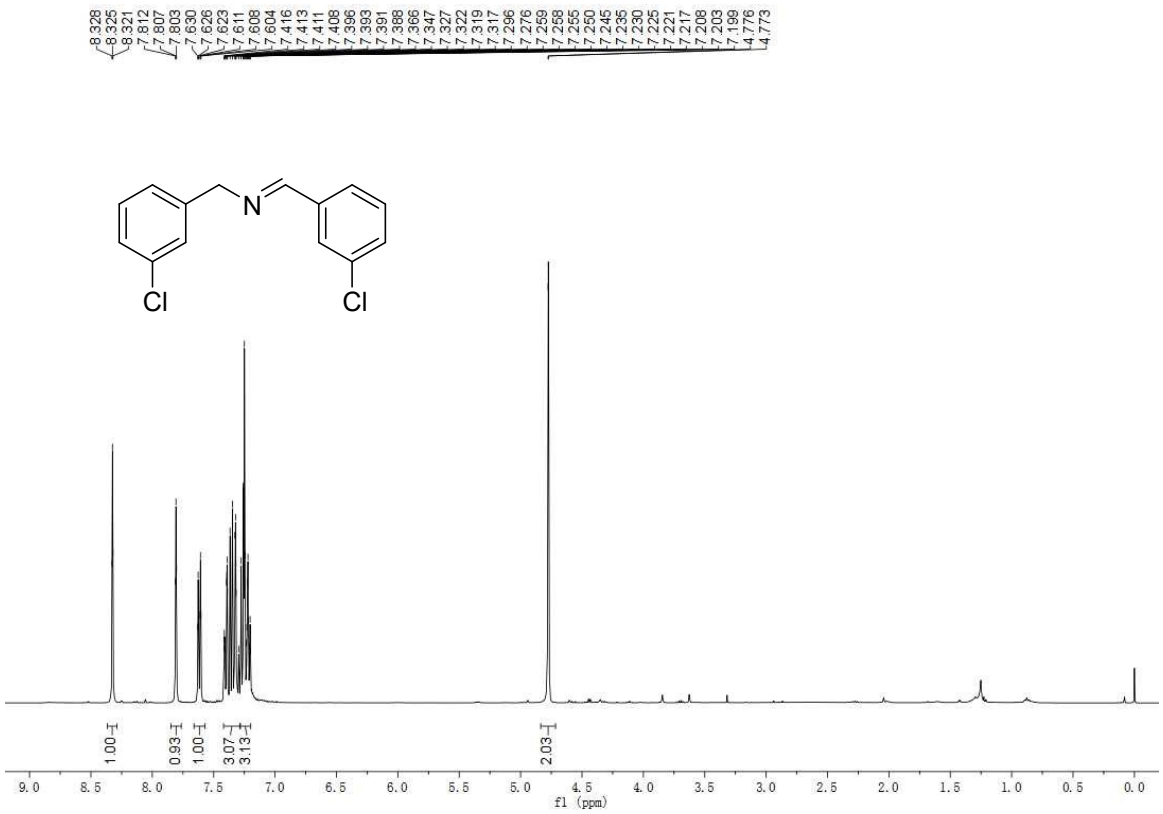


Figure S40. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of (*E*)-*N*-(3-chlorobenzyl)-1-(3-chlorophenyl)methanimine 5f):

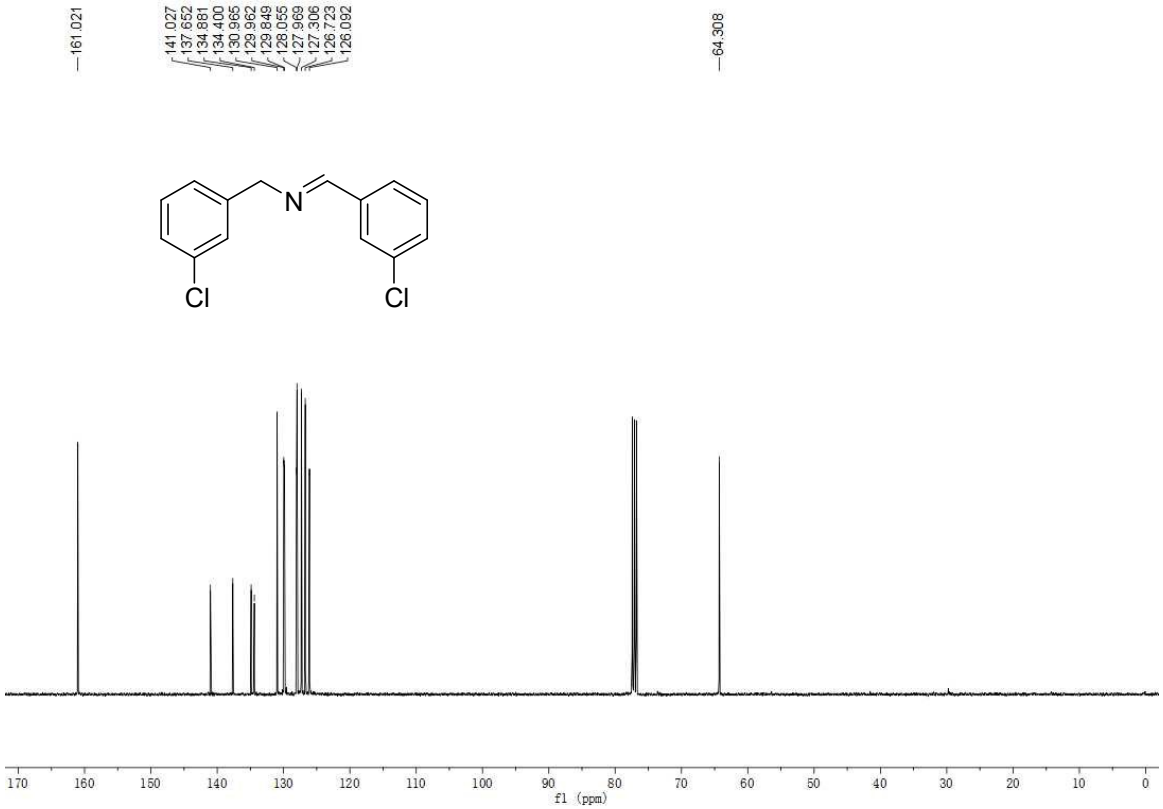


Figure S41. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of (*E*)-*N*-(4-chlorobenzyl)-1-(4-chlorophenyl)methanimine (5g):

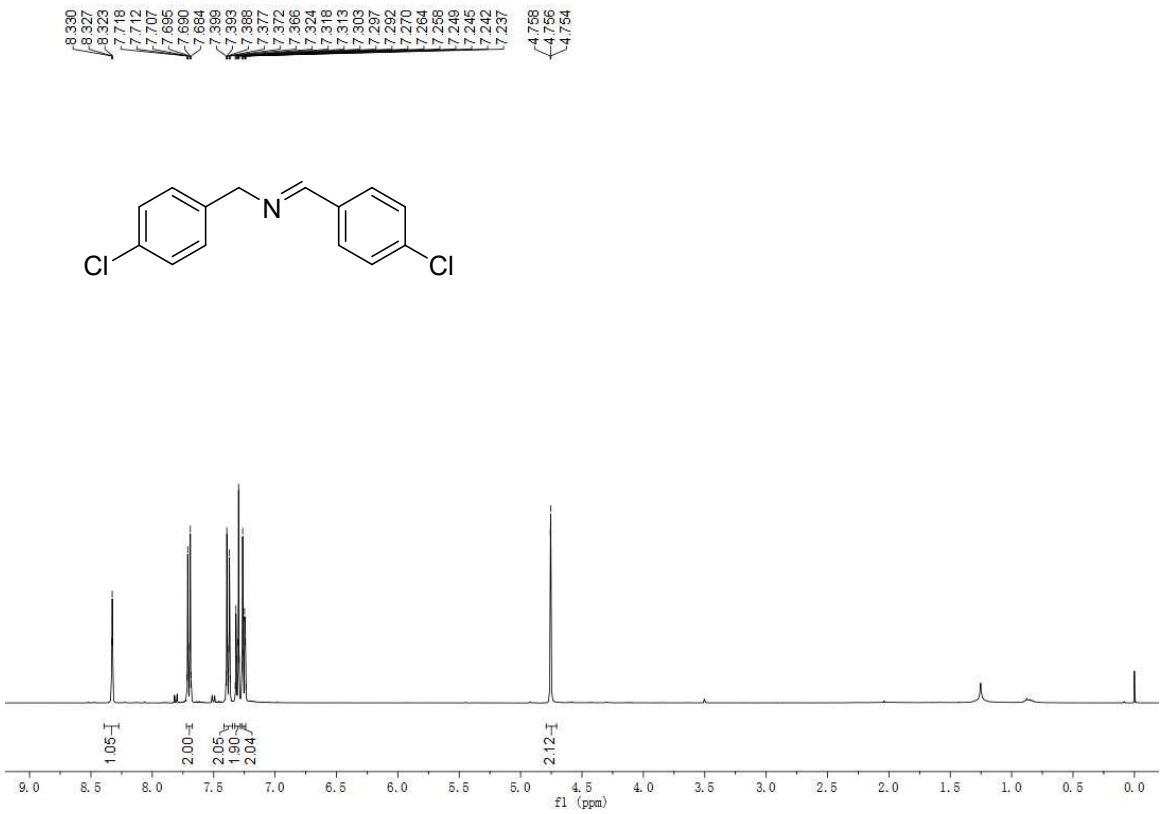


Figure S42. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of (*E*)-*N*-(4-chlorobenzyl)-1-(4-chlorophenyl)methanimine (5g):

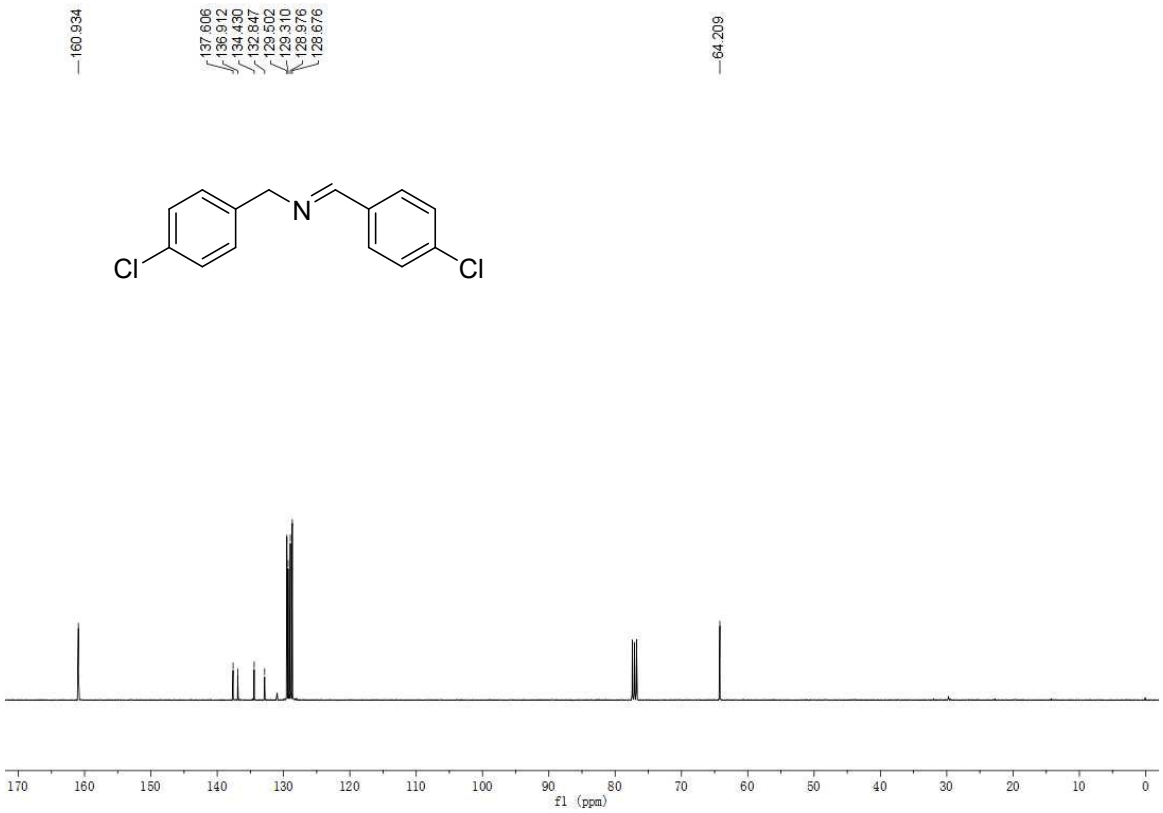


Figure S43. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of (*E*)-*N*-(2-methoxybenzyl)-1-(2-methoxyphenyl)methanimine (5h):

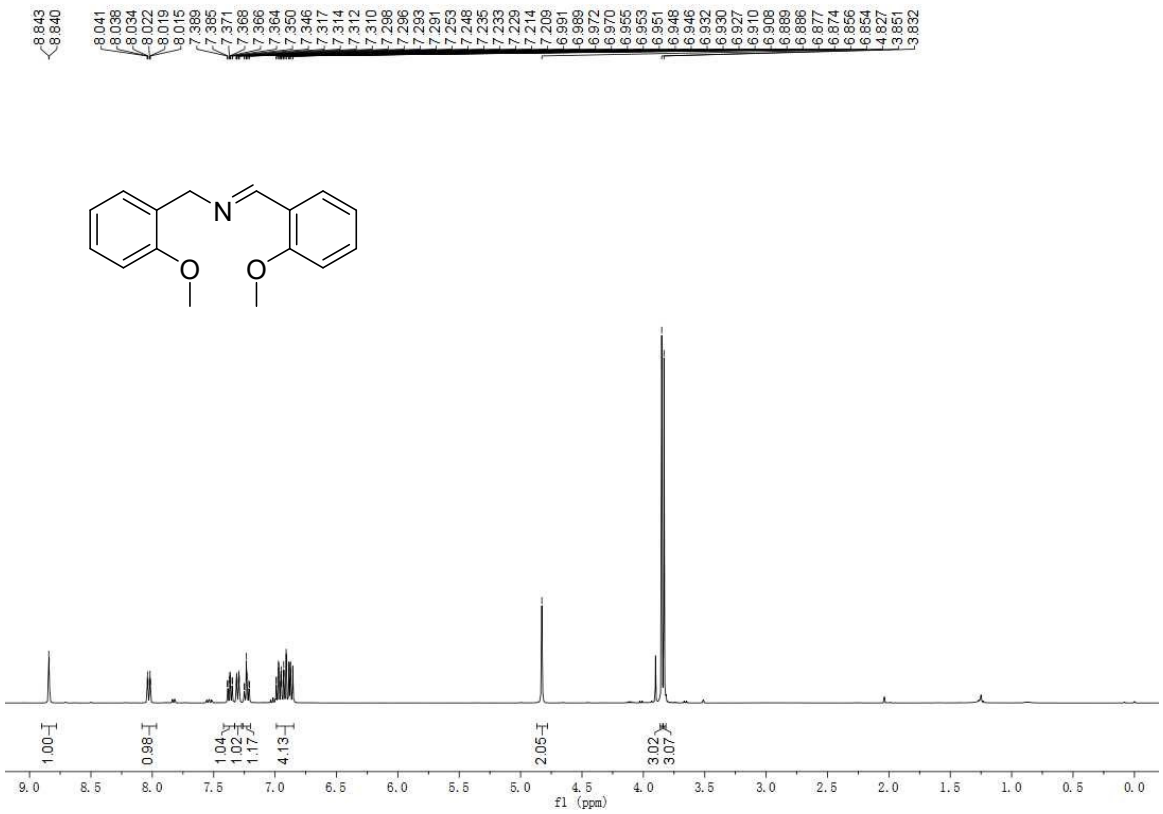


Figure S44. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of (*E*)-*N*-(2-methoxybenzyl)-1-(2-methoxyphenyl)methanimine (5h):

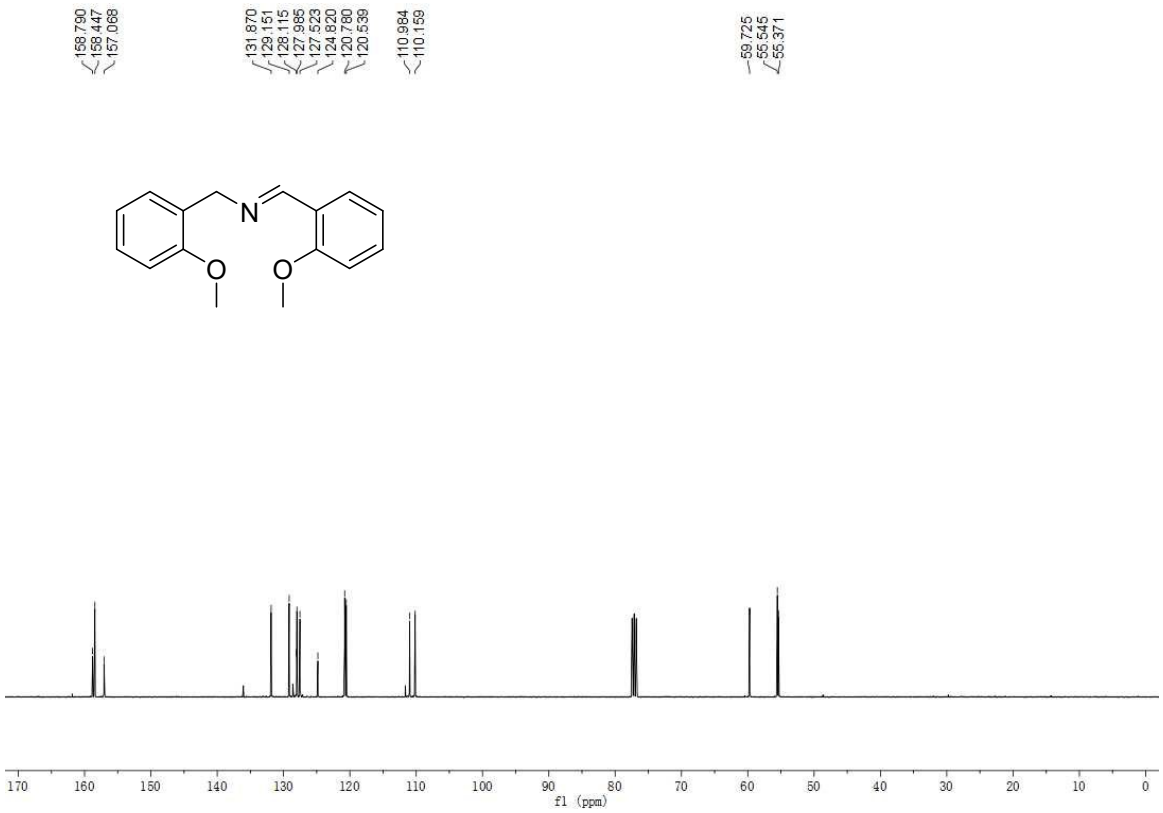


Figure S45. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of (*E*)-*N*-(3-methoxybenzyl)-1-(3-methoxyphenyl)methanimine (5i):

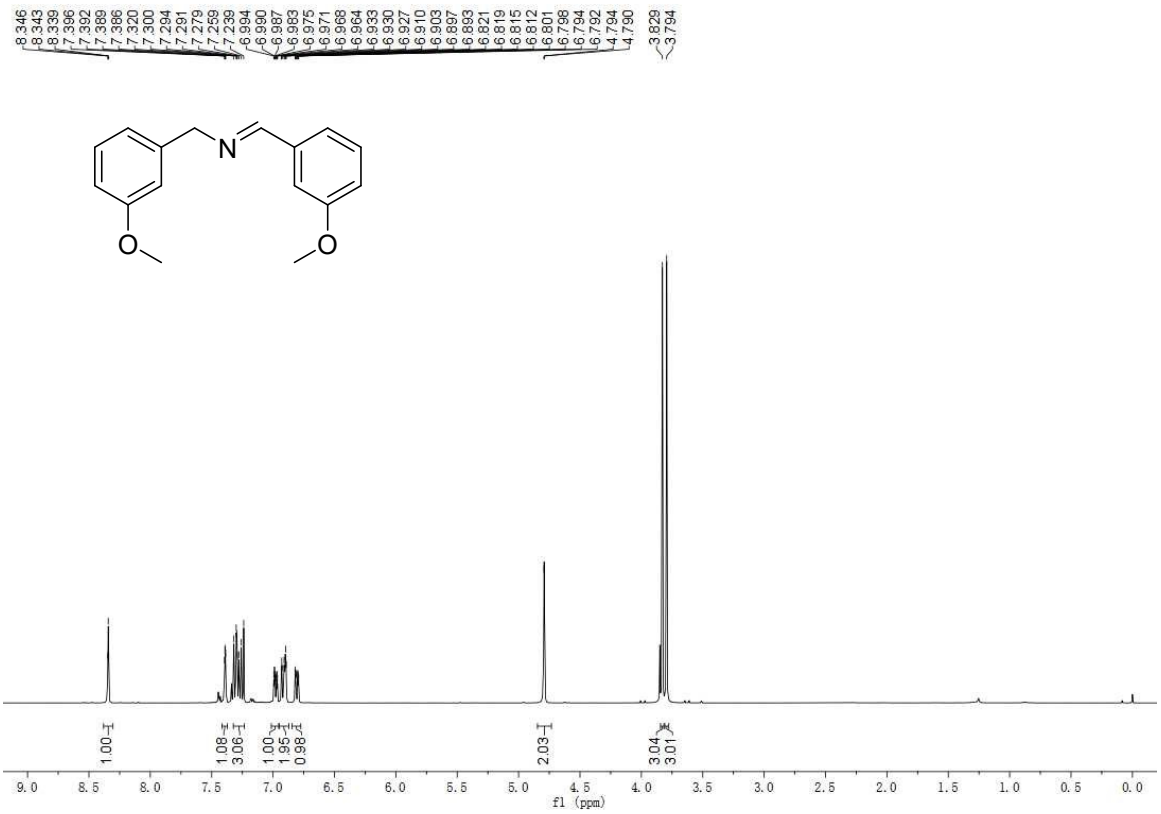


Figure S46. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of (*E*)-*N*-(3-methoxybenzyl)-1-(3-methoxyphenyl)methanimine (5i):

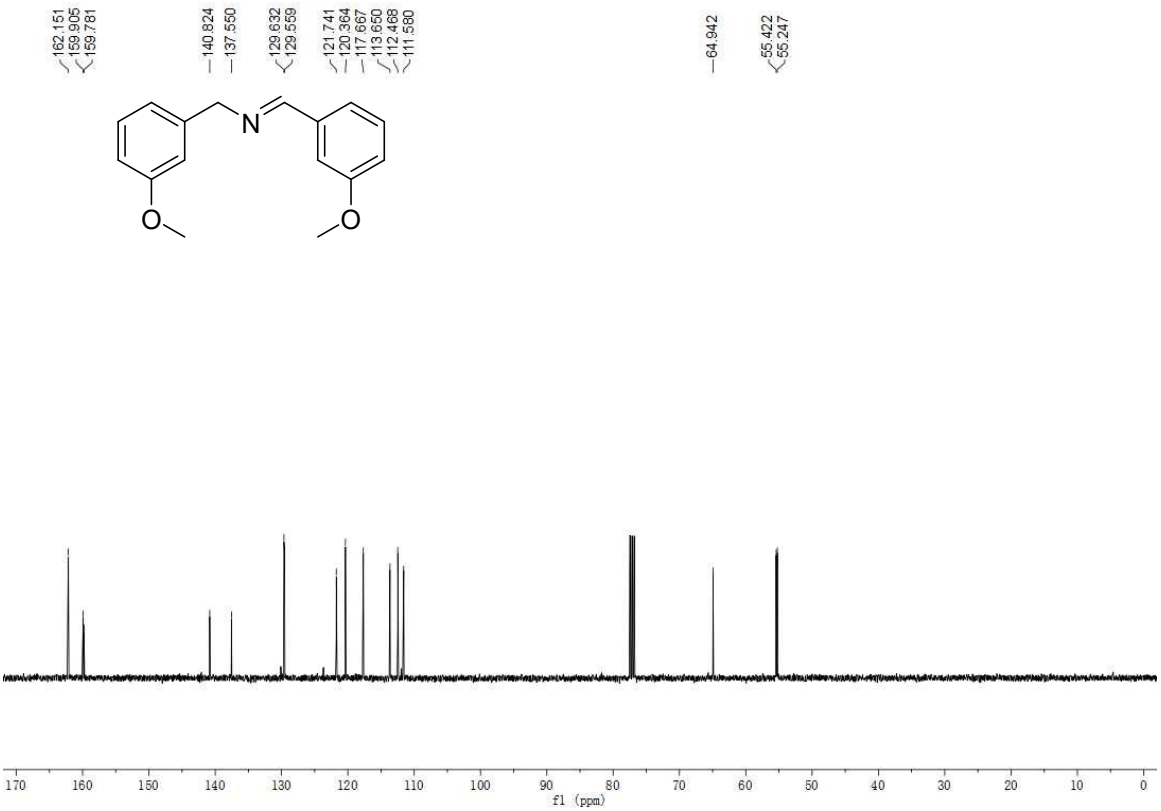


Figure S47. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of (*E*)-*N*-(4-methoxybenzyl)-1-(4-methoxyphenyl)methanimine (5j):

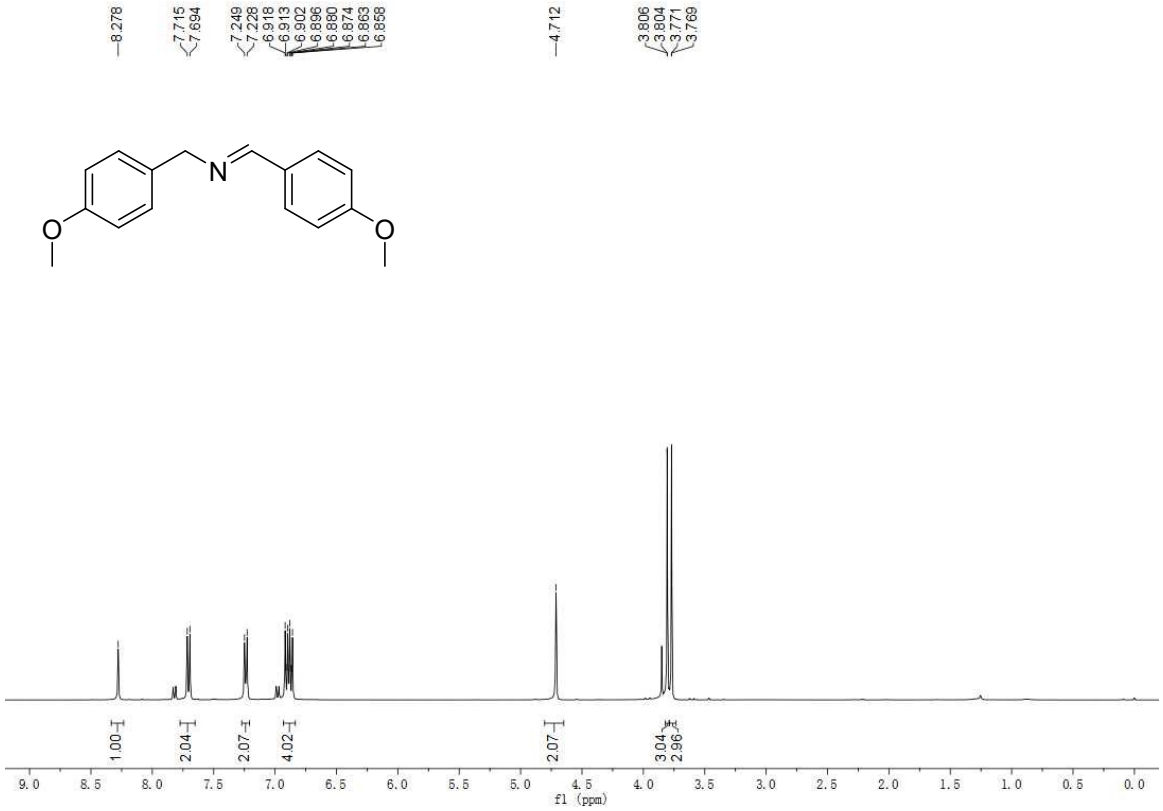


Figure S48. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of (*E*)-*N*-(4-methoxybenzyl)-1-(4-methoxyphenyl)methanimine (5j):