Electronic Supplementary Information for

Preparation and photophysical properties of fluorescent difluoroboronated β-diketones having phenanthrene studied by emission and transient absorption measurements

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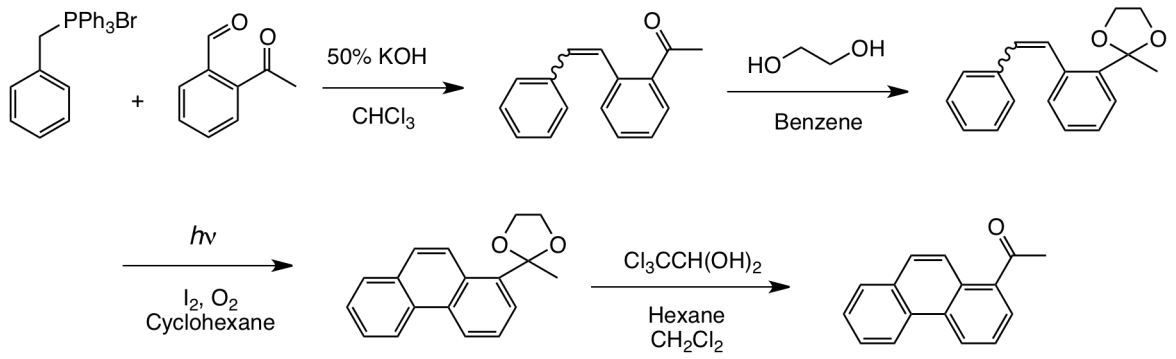
1. Procedure for the compound preparations and analytical data

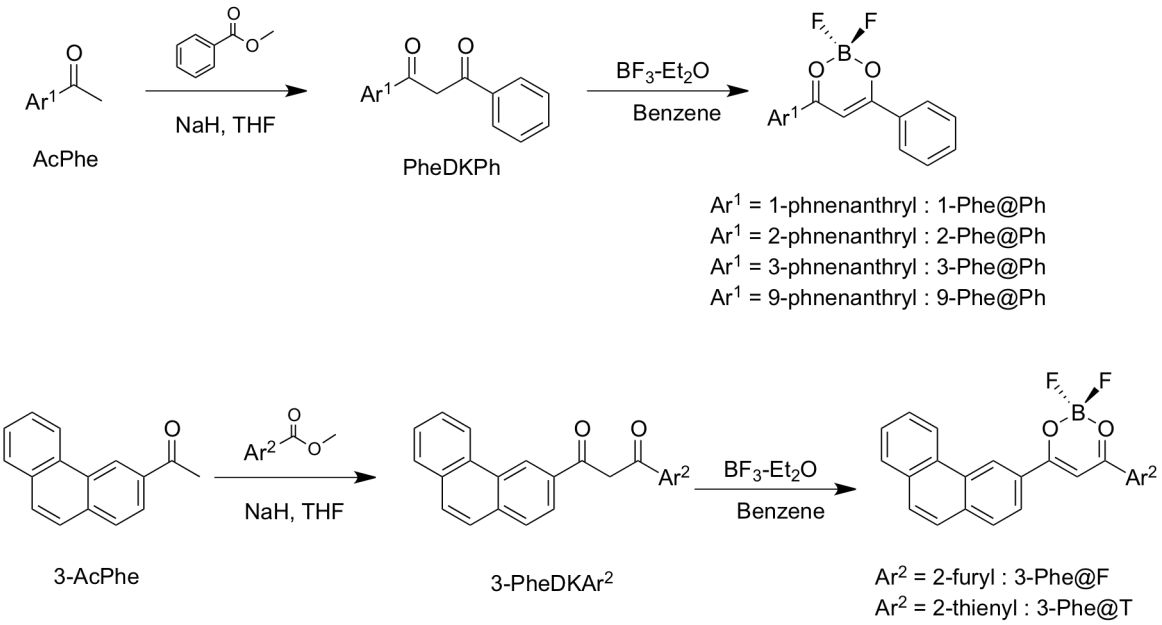
Synthesis of 1-acethylphenanthrene, β-diketones and difluoroboronated β-diketones. Acetylphenathrenes (AcPhe) are the key precursors to the desired boron complexes. 2-, 3-, and 9-Acetylphenathrenes (2-AcPhe, 3-AcPhe and 9-AcPhe, respectively) are commercially available whereas 1-acetylphenanthren (1-AcPhe) was synthesized by using photocyclization of a stilbene derivative. The synthesis procedures are illustrated in Scheme S1.



Scheme S1. Synthetic procedures to 1-acetylphenanthrene.

We performed acetal protection of the carbonyl group in *o*-acetylstilbene as it did not undergo photocyclization in the presence of iodine in aerated cyclohexane. The acetaled stilbene was subjected to photocyclization to form the phenanthrene derivative with the protected acetyl group. The deprotection of the acetal provided the desired 1-acetylphenanthrene.

General procedures for preparing the diketones. The used diketones were prepared by Claisen condensation between appropriate aromatic acetyl compounds and aromatic methyl ethers (Ar^1CO_2Me, Scheme S2). Acetyl compounds of phenyl, 2-naphthyl, 2-anthryl and phenanthryl rings (3.0 mmol) and methyl ethers (methyl benzoate, methyl 2-furoate and methyl thiophene-2-carboxylate) (3.3 mmol) were refluxed for 4 h in THF (15 ml) in the presence of NaH. After cooling to room temperature, HCl was added. The product was extracted with ethyl acetate, and the solution was washed with aqueous NH_4Cl and brine. The product was purified by silica-gel chromatography using a mixture of hexane and ethyl acetate to give the desired compound.



Scheme S2. Preparation of BF_2DKs.

Analytical Data for the employed compounds

2-NpDKPh. Yield 85 %. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.00 (s, 1H), 7.49-7.61 (m, 5H), 7.88-8.04 (m, 6H), 8.54 (brs, 1H).The ^{1}H NMR spectral data were agreed with those reported in the literature.[1]

2-AntDKPh. Yield 52 %. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.75 (s, 1H), 8.60 (s, 1H), 8.46 (s, 1H), 8.07-7.97 (m, 7H), 7.68-7.51 (m, 5H), 7.00 (s, 1H). The ^{1}H NMR spectral data were agreed with those reported in the literature.[2]

1-PheDKPh. Yield 48 %. mp 142–143 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 16.80 (brs, 1H), 8.85 (d, 1H, J = 8.3 Hz), 8.71 (d, 1H, J = 8.3 Hz), 8.38 (d, 1H, J = 9.1 Hz), 7.99 (d, 2H, J = 7.6 Hz), 7.91 (d, 1H, J = 7.3 Hz), 7.88 (d, 1H, J = 7.3 Hz), 7.83 (d, 1H, J = 9.1 Hz), 7.72–7.66 (two triplets overlapped, 2H), 7.63 (t, 1H, J = 7.3 Hz), 7.56 (t, 1H, J = 7.6 Hz), 7.48 (t, 2H, J = 7.6 Hz), 6.72 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 191.0, 184.6, 136.0, 135.1, 132.8, 131.9, 131.0, 130.2, 129.2, 128.9, 128.7, 128.4, 127.4, 127.2, 127.1, 125.9, 125.8, 123.8, 123.0, 98.8; HRMS (FAB-TOF) m/z calcd. for $C_{23}H_{17}O_2$ 325.1229 [M+1], found 325.1249.

2-PheDKPh. Yield 76 %. mp 117–118 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 17.02 (s, 1H), 8.77 (d, 1H, J = 8.7 Hz), 8.73 (d, 1H, J = 8.1 Hz), 8.55 (d, 1H, J = 1.5 Hz), 8.21 (dd, 1H, J = 8.7, 1.5 Hz), 8.06 (m, 2H), 7.93 (d, 1H, J = 7.7 Hz), 7.85 (d, 1H, J = 8.9 Hz), 7.82 (d, 1H, J = 8.9 Hz), 7.59 (m, 1H), 7.70 (ddd, 1H, J = 7.7, 7.1, 1.4 Hz), 7.68 (ddd, 1H, J = 7.7, 7.1, 1.0 Hz), 7.60 (m, 1H), 7.53 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 186.0, 185.5, 135.7, 138.4, 138.2, 133.0, 132.7, 131.8, 129.9, 128.9, 128.4, 128.1, 127.8, 127.40, 127.38 (overlapped), 127.2, 124.5, 123.4 (overlapped), 93.6. HRMS (FAB-TOF) m/z calcd. for $C_{23}H_{17}O_2$ 325.1229 [M+1], found 325.1227.

3-PheDKPh. Yield 60 %. mp 123–125 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 17.1 (s, 1H), 8.83 (d, 2H J = 8.3 Hz), 8.13 (dd, 1H, J = 8.2, 1.5 Hz), 8.08–8.05 (m, 2H), 7.97 (d, 1H, J = 8.2 Hz), 7.93 (brd, 1H, J = 7.9 Hz), 7.85 (d, 2H, J = 8.7 Hz), 7.78 (d, 2H, J = 8.7 Hz), 7.74 (ddd, 1H, J = 8.3, 7.1, 1.3 Hz), 7.65 (ddd, 1H, J = 7.9, 7.1, 1.3 Hz), 7.61–7.56 (m, 1H), 7.57–7.51 (m, 2H), 7.07 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 186.0, 185.8, 135.8, 134.8, 133.4, 132.7, 132.4, 130.7, 130.2, 129.6, 129.1, 129.0, 128.9 (overlapped), 127.40, 127.35, 126.5, 124.5, 123.0, 122.7, 93.7. HRMS (FAB-TOF) m/z calcd. for $C_{23}H_{17}O_2$ 325.1229 [M+1], found 325.1247.

9-PheDKPh. Yield 82 %. mp 172–174 °C.^{1}H NMR (600 MHz, $CDCl_3$) δ_H 16.82(brs, 1H), 8.76 (d, 1H, J = 8.3 Hz), 8.71 (d, 1H, J = 8.3 Hz), 8.54 (d, 1H, J = 8.3 Hz), 8.10 (s, 1H), 8.02 (m, 2H), 7.97

(d, 1H, J = 7.8 Hz), 7.77–7.70 (m, 2H), 7.70–7.63 (m, 4H), 7.57 (t, 1H, J = 7.4 Hz), 7.51 (t, 2H, J = 7.4 Hz), 6.80(s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 191.0, 184.6, 135.1, 134.2, 132.7, 131.6, 130.9, 130.5, 129.7, 128.9, 128.8, 128.6, 128.5, 127.35(two lines overlapped), 127.26 (two lines overlapped), 126.9, 123.1, 1232.8, 98.4; HRMS (FAB-TOF) m/z calcd. for $C_{23}H_{17}O_2$ 325.1229 [M+1], found 325.1242.

3-PheDKF. Yield 50 %. mp 216–217 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 16.40(brs, 1H), 9.31 (s, 1H), 8.79 (d, 1H, J = 8.3 Hz), 8.08 (dd, 1H, J = 8.3, 1.6 Hz), 7.92 (d, 1H, J = 8.4), 7.90 (d, 1H, J = 7.8 Hz), 7.82 (d, 1H, J = 7.8 Hz), 7.75–7.70 (m, 2H), 7.68–7.62 (m, 2H), 7.30 (d, 1H, J = 3.4 Hz), 6.95 (s, 1H), 6.95(s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 182.5.0, 177.7, 151.2, 146.3, 134.7, 132.4, 132.3, 130.6, 130.1, 129.5, 129.0, 128.9, 127.32, 127.28, 126.4, 124.3, 122.9, 122.4,116.0, 122.9, 93.2. HRMS (FAB-TOF) m/z calcd. for $C_{21}H_{14}O_3$ 314.0943 [M+1], found 314.0944.

3-PheDKT. Yield 56 %. mp 235–238 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 16.54(brs, 1H), 9.27 (s, 1H), 8.02 (dd, 1H, J = 8.5, 1.2 Hz), 7.92–786 (m, 2H), 7.86 (dd, 1H, J = 3.7, 0.8 Hz), 7.81 (d, 1H, J = 8.7 Hz), 7.74–7.69 (m, 3H), 7.66–7.61 (m, 2H), 7.19 (dd, 1H, J = 4.9, 3.8 Hz), 6.84 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 183.1, 180.7, 142.5, 134.6, 132.8, 132.3, 132.1, 130.5, 130.1, 129.4, 129.0, 128.9, 128.4, 127.30, 127.27, 126.4, 124.1, 122.9, 122.2, 93.6. HRMS (FAB-TOF) m/z calcd. for $C_{21}H_{14}O_2S$ 3304.0715 [M+1], found 330.0719.

General procedures for BF_2DKs. The prepared diketone compound was refluxed in benzene for 1 h in the presence of boron trifluoride diethyl etherate. The desired product was filtrated and washed with benzene.

Ph@Ph. Yield 86 %. ^{1}H NMR ($CDCl_3$, 400 MHz,) δ_H 7.20 (s, 1H), 7.56 (t, 4H, J = 7.33), 7.70 (t, 2H, J = 7.33), 8.16 (d, 4H, J = 7.33). The ^{1}H NMR spectral data were agreed with those reported in the literature.[3]

2-Np@Ph. Yield 85 %. ^{1}H NMR ($CDCl_3$, 400 MHz,) δ_H 7.00 (s, 1H), 7.49–7.61 (m, 5H), 7.88–8.04 (m, 6H), 8.54 (brs, 1H). The ^{1}H NMR data were agreed with those reported in the literature.[1]

2-Ant@Ph. Yield 48 %. ^{1}H NMR (DMSO-d_6, 400 MHz) δ_H 8.92 (s, 1H), 8.70 (s, 1H), 8.41 (dd, 2H, J=1.37, 8.70), 8.29–8.11 (m, 5H), 7.85–7.81 (m, 1H), 7.70–7.59 (m, 4H), 7.32 (s, 1H). The ^{1}H NMR data were agreed with those reported in the literature.[2]

1-Phe@Ph. Yield 47 %. mp 210–211 °C. H NMR (600 MHz, $CDCl_3$) δ_H 8.97 (d, 1H, J = 8.4 Hz), 8.70 (d, 1H, J = 8.2 Hz), 8.38 (d, 1H, J = 9.3 Hz), 8.17 (m, 2H), 8.04 (dd, 1H, J = 7.3, 1.0 Hz), 7.95 (dd, 1H, J = 7.8, 1.0 Hz), 7.91 (d, 1H, J = 9.3 Hz), 7.77–7.68 (m, 4H), 7.57 (m, 2H), 7.11 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 187.8, 183.3, 135.7, 132.0, 131.8, 131.4, 130.0, 129.9, 129.8, 129.4, 129.34, 129.29, 128.9, 128.6, 127.7, 127.5, 125.7, 123.04, 122.95, 99.0. HRMS (FAB-TOF) m/z calcd. for $C_{23}H_{15}BF_2O_2$ 372.1133 [M^+], found 372.1149.

2-Phe@Ph. Yield 27%. mp 261–263 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 8.97 (d, 1H, J = 8.4 Hz), 8.70 (d, 1H, J = 8.2 Hz), 8.38 (d, 1H, J = 9.3 Hz), 8.17 (m, 2H), 8.04 (dd, 1H, J = 7.3, 1.0 Hz), 7.95 (dd, 1H, J = 7.8, 1.0 Hz), 7.91 (d, 1H, J = 9.3 Hz), 7.77–7.68 (m, 4H), 7.57 (m, 2H), 7.11 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 187.8, 183.3, 135.7, 132.0, 131.8, 131.4, 130.0, 129.9, 129.8, 129.4, 129.34, 129.29, 128.9, 128.6, 127.7, 127.5, 125.7, 123.04, 122.95, 99.0. HRMS (FAB-TOF) m/z calcd. for $C_{23}H_{15}BF_2O_2$ 372.1133 [M^+], found 372.1135.

3-Phe@Ph. Yield 60 %. mp 258–260 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ_H 9.80 (d, 1H, J = 1.2 Hz), 9.21 (d, 1H, J = 8.3 Hz), 8.51–8.48 (m, 3H). 8.30 (s, 1H), 8.25 (d, 1H, J = 8.5 Hz), 8.12 (d, 1H, J = 8.5 Hz), 8.10 (d, 1H, J = 8.7 Hz), 8.00 (d, 1H, J = 7.7 Hz), 7.90–7.84 (two triplets overlapped, 2H), 7.78 (t, 1H, J = 7.7 Hz), 7.34, t, 2H, J = 7.7 Hz). ^{13}C NMR (150 MHz, DMSO-d_6) δ_C 182.5, 182.3, 136.3, 135.9, 131.9, 131.5, 131.4, 130.0, 129.8, 129.6, 129.50, 129.47, 129.27, 129.0, 127.9, 126.3, 125.9, 125.5, 123.7, 95.0. HRMS (FAB-TOF) m/z calcd. for $C_{23}H_{15}BF_2O_2$ 372.1133 [M^+], found 372.1170.

9-Phe@Ph. Yield 92 %. mp 172–174 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ_H 9.08 (d, 1H, J = 8.0 Hz), 8.96 (d, 1H, J = 8.3 Hz), 8.79 (s, 1H), 8.05 (dd, 1H, J = 7.8, 1.5 Hz), 8.41 (d, 2H, J = 7.8 Hz), 8.23 (d, 1H, J = 7.8 Hz), 7.93–7.79 (m, 6H), 7.72 (t, 2H, J = 7.8 Hz).^{13}C NMR (150 MHz, DMSO-d_6) δ_C 187.0, 182.9, 136.2, 134.0, 132.0, 131.2, 130.6, 130.5, 130.3, 129.6, 129.5 (two lines

overlapped), 129.0, 128.0, 127.93, 127.91, 127.3, 125.6, 123.9, 123.3, 99.0. HRMS (FAB-TOF) *m/z* calcd. for $C_{23}H_{15}BF_2O_2$ 372.1133 [M^+], found 372.1133.

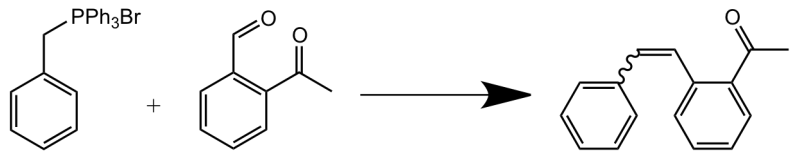
3-Phe@F. Yield 92 %. mp 216–217 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ_H 9.69 (bs, 1H), 9.15 (d, 1H, J = 8.4 Hz), 8.44 (m, 1H), 8.41 (dd, 1H, J = 8.3, 1.3 Hz), 8.28 (d, 1H, J = 3.6 Hz), 8.24 (d, 1H, J = 8.5 Hz), 8.10 (two doublets, 2H), 8.00 (two doublets, 2H), 7.85 (ddd, J = 8.4, 7.2, 1.1 Hz), 7.77 (t, 1H, J = 7.6 Hz), 7.06 (dd, 1H, 3.6, 1.5 Hz). ^{13}C NMR (150 MHz, DMSO-d_6) δ_C 180.7, 170.8, 152.5, 147.3, 136.0, 131.9, 131.2, 129.9, 129.8, 129.6, 129.3, 129.0, 127.90, 127.88, 126.3, 125.24, 125.18, 124.9, 123.6, 115.1, 93.9. HRMS (FAB-TOF) *m/z* calcd. for $C_{21}H_{13}BF_2O_3$ 362.0926 [M^+], found 362.0917.

3-Phe@T. Yield 72 %. mp 235–238 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ_H 9.71 (bs, 1H), 9.16 (d, 1H, J = 8.3 Hz), 8.86 (d, 1H, J = 4.1 Hz), 8.46 (dd, 1H, J = 4.8, 1.2 Hz), 8.44 (dd, 1H, J = 8.5, 1.2 Hz), 8.25 (d, 1H, J = 8.5 Hz), 8.19 (s, 1H), 8.11 (two doublets, 2H), 8.00 (d, J = 7.8 Hz), 7.86 (t, 1H, J = 7.6 Hz), 7.77 (t, 1H, 7.3 Hz), 7.56 (dd, 1H, J = 4.8, 4.1 Hz). ^{13}C NMR (150 MHz, DMSO-d_6) δ_C 180.7, 170.8, 152.5, 147.3, 136.0, 131.9, 131.1, 129.9, 129.8, 129.6, 129.3, 129.0, 127.89, 127.88, 126.3, 125.24, 125.18, 124.9, 123.6, 115.1, 93.9. HRMS (FAB-TOF) *m/z* calcd. for $C_{21}H_{13}BF_2O_2S$ 378.0697 [M^+], found 378.0695.

Detailed procedures

1.1. Preparation of 1-Phe@Ph

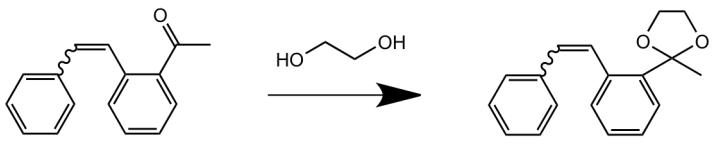
1.1.1 Synthesis of compound 1.



1

To 60 ml chloroform solution of benzyltriphenylphosphonium bromide (2.5 g, 5.77 mmol) and 2-acetylbenzaldehyde (780 mg, 5.25 mmol), 30 ml of aqueous KOH (50 %) was dropwise added. After the solution was stirred for 30 min at room temperature, 100 ml chloroform was added. The organic layer was separated, washed with brine, and evaporated under reduced pressure. The product was purified by silica gel chromatography using hexane/ethyl acetate (9:1, v/v) providing compound **1** (913 mg, 76 %).

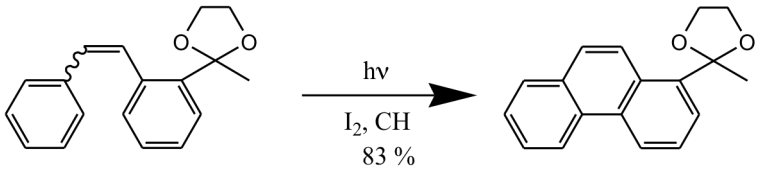
1.1.2 Synthesis of compound 2.



1 **2**

To 200 ml benzene (Bz), compound **1** (1.3 g, 5.85 mmol), 30 ml ethylene glycol and *p*-toluenesulfonic acid (0.77 g, 4.0 mmol) were added, the solution was refluxed for 48 h. After cooling to room temperature, the solution was washed with water and brine. The product was separated by silica-gel chromatography using hexane/ethyl acetate (3:1, v/v) providing compound **2** (1.42 g, 91%).

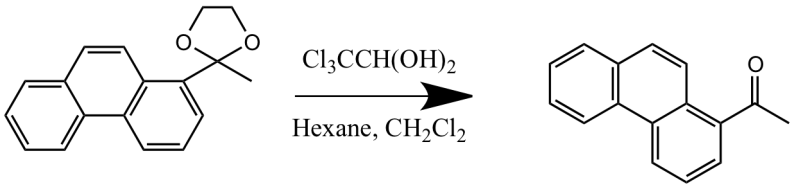
1.1.3 Synthesis of compound 3.



2 3

A cyclohexane (CH) solution (1000 ml) of compound **2** (600 mg, 2.26 mmol) and 50 mg I_2 was photolyzed using with a home-made microflow photoreactor.[4] The photolyzed solution was washed with aqueous $Na_2S_2O_3$ and brine. After usual work-up, crude compound **3** was obtained (500 mg, 83 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H, 8.75-8.71 (m, 3H), 8.01 (d, 1H, J = 7.33), 7.95-7.92 (m, 1H), 7.85 (d, 1H, J = 9.39), 7.69-7.63 (m, 3H), 4.14-4.13 (m,2H), 3.85-3.83 (m, 2H), 2.04 (s, 3H).

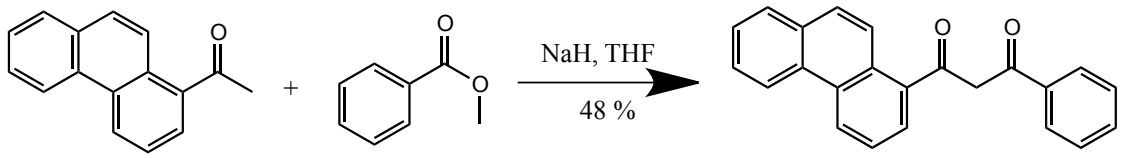
1.1.4 Synthesis of 1-AcPhe



3 1-AcPhe

Compound **3** (1.0 g, 3.78 mmol) and chloral hydrate (3.8 g, 22.7 mmol) was added in a mixture of 6 ml hexane and 0.5 ml CH_2Cl_2. The solution was stirred at room temperature under N_2 atmosphere for 2 h. After adding CH_2Cl_2 (100 ml), the solution was washed with water and brine. After evaporating the solvent, the residue was chromatographed on silica-gel using hexane/ethyl acetate (3:1, v/v) to give 1-AcPhe (600 mg, 72 %).

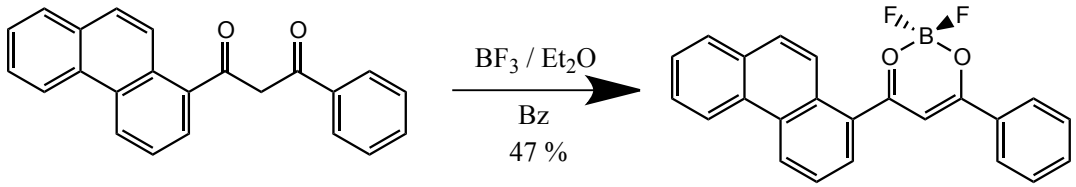
1.1.5 Synthesis of compound 1-PheDKPh



1-AcPhe 1-PheDKPh

To 25 ml of dry THF, 1-AcPhe (550 mg, 2.5 mmol) and NaH (60 % in oil, 720 mg, 18 mmol) were added, and the mixture was stirred for 5 min at room temperature. Methyl benzoate (0.40 ml, 3.0 mmol) was added to the solution, which was refluxed for 5 h. After cooling to room temperature, aqueous NH_4Cl (20 %, 30 ml) was added. The product was extracted with ethyl acetate, and the solution was washed with aqueous NH_4Cl and brine. The product was purified by silica-gel chromatography using hexane/ethyl acetate (3:1, v/v) to give 1-PheDKPh (390 mg, 48 %).

1.1.6 Synthesis of 1-Phe@Ph

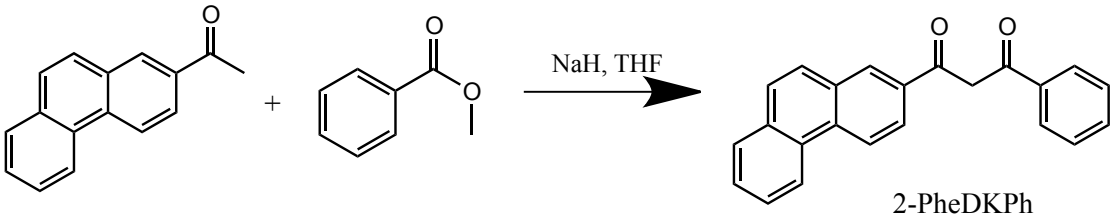


1-PheDKPh 1-Phe@Ph

1-PheDKPh (240 mg, 0.74 mmol) and a Et_2O solution of boron trifluoride diethyl etherate (46 %, 0.30 ml, 1.1 mmol) were added to 7 ml of benzene, and the solution was refluxed for 1 h. The precipitated 1-Phe@Ph was collected by filtration and washed with benzene (130 mg, 47 %).

1.2 Preparation of 2-Phe@Ph

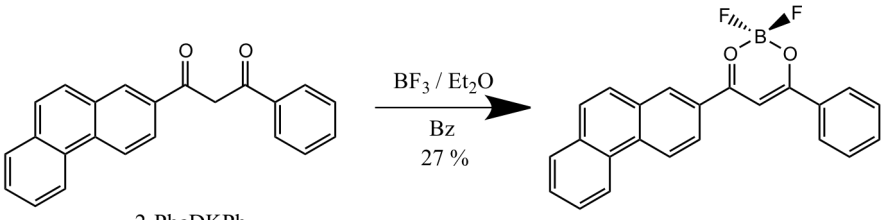
1.2.1 Synthesis of 2-PheDKPh



2-PheDKPh

To 20 ml of dry THF, 2-acetylphenanthrene (507 mg, 2.3 mmol) and NaH (60 % in oil, 720 mg, 18 mmol) were added, and the mixture was stirred for 5 min at room temperature. Methyl benzoate (0.34 ml, 2.5 mmol) was added to the solution, which was refluxed for 3 h. After cooling to room temperature, aqueous NH_4Cl (20 %, 30 ml) was added. The product was extracted with ethyl acetate, and the solution was washed with aqueous NH_4Cl and brine. After removal of the solvent, the product was purified by silica-gel chromatography using hexane/ethyl acetate (3:1, v/v) to give 2-PheDKPh (576 mg, 76 %).

1.2.2 Synthesis of 2-Phe@Ph

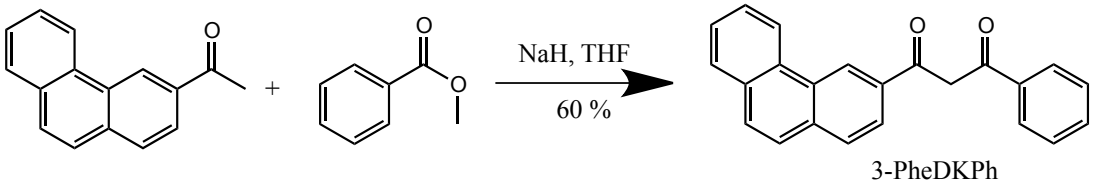


2-PheDKPh 2-Phe@Ph

2-PheDKPh (324 mg, 1.0 mmol) and boron trifluoride diethyl etherate (46 %, 0.41 ml, 1.5 mmol) were added to 7 ml of benzene, and the solution was refluxed for 1 h. The precipitated 2-Phe@Ph was collected by filtration and washed with benzene (100 mg, 27 %).

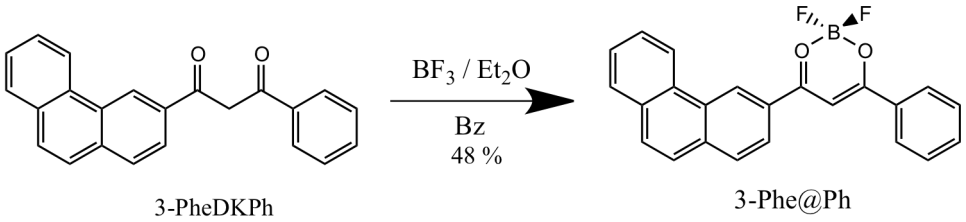
1.3 Preprarion of 3-Phe@Ph

1.3.1 Synthesis of 3-PheDKPh



To 20 ml of dry THF, 3-acetylphenanthrene (507 mg, 2.3 mmol) and NaH 700 mg (60 % in oil, 720 mg, 18 mmol) were added, and the mixture was stirred for 5 min at room temperature. Methyl benzoate 0.34 ml (2.5 mmol) was added to the mixture, which was then refluxed for 3 h. After cooling to room temperature, aqueous NH_4Cl (20 %, 30 ml) was added. The product was extracted with ethyl acetate, and the solution was washed with aqueous NH_4Cl and brine. After removal of the solvent, the product was purified by silica-gel chromatography using hexane/ethyl acetate (3:1, v/v) to give 3-PheDKPh (444 mg, 60 %).

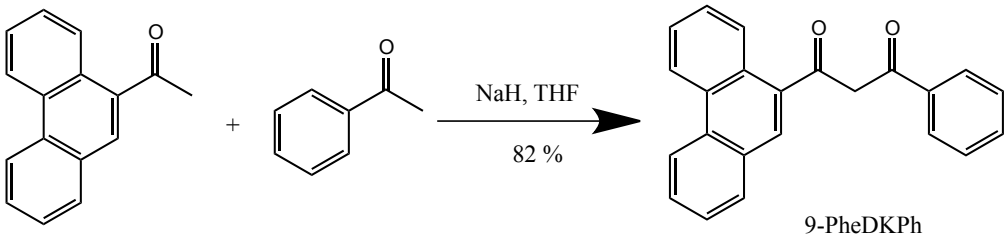
1.3.2 Synthesis of 3-Phe@Ph



3-PheDKPh (324 mg, 1.0 mmol) and boron trifluoride diethyl etherate (46 %, 0.41 ml, 1.5 mmol) were added to 10 ml benzene, and the solution was refluxed for 1 h. The precipitated product was filtrated and washed with benzene to give 3-Phe@Ph (100 mg, 48 %).

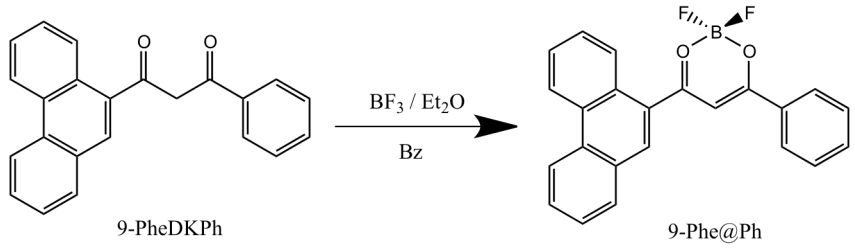
1.4 Preparation of 9-Phe@Ph

1.4.1 Synthesis of 9-PheDKPh



To 25 ml of dry THF, 9-acetylphenanthrene (500 mg, 2.3 mmol) and NaH 700 mg (60 % in oil, 720 mg, 18 mmol) were added, and the solution was stirred for 5 min at room temperature. Methyl benzoate (0.34 ml, 2.7 mmol) was added to the solution, which was refluxed for 24 h. After cooling to room temperature, aqueous NH_4Cl (20 %, 30 ml) was added. The product was extracted with ethyl acetate, and the solution was washed with aqueous NH_4Cl and brine. After removal of the solvent, the product was purified by silica-gel chromatography using hexane/ethyl acetate (3:1, v/v) to give 9-PheDKPh (600 mg, 82 %).

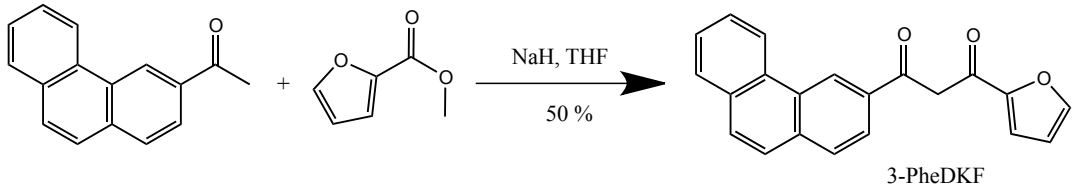
1.4.2 Synthesis of 9-Phe@Ph



9-PheDKPh **(**300 mg, 0.92 mmol) and boron trifluoride diethyl etherate (46 %, 0.41 ml, 1.5 mmol) were added to 10 ml of benzene, and the solution was refluxed for 1 h. The precipitated product was filtrated and washed with benzene to give 9-Phe@Ph (305 mg, 92 %).

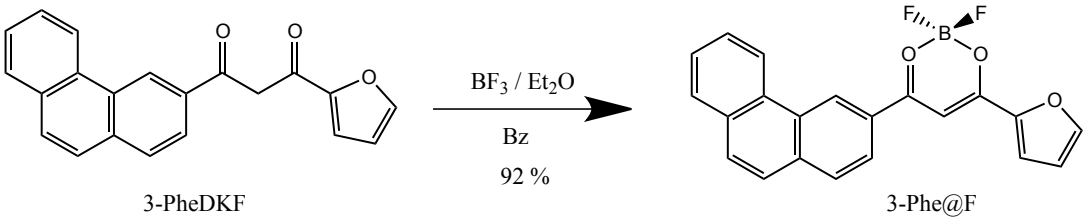
1.5 Preparation of 3-Phe@F

1.5.1 Synthesis of 3-PheDKF



To 25 ml of dry THF, 3-acetylphenanthrene (500 mg,2.3 mmol) and NaH (60 % in oil, 720 mg, 18 mmol) were added, and the mixture was stirred for 5 min at room temperature. Methyl 2-furoate (0.40 ml, 3.9 mmol) was added to the solution, which was refluxed for 5 h. After cooling to room temperature, aqueous NH_4Cl (20 %, 30 ml) was added. The product was extracted with ethyl acetate, and the solution was washed with aqueous NH_4Cl and brine. After removal of the solvent, the product was purified by silica-gel chromatography using hexane/ethyl acetate (3:1, v/v) to give 3-PheDKF (358 mg, 50 %).

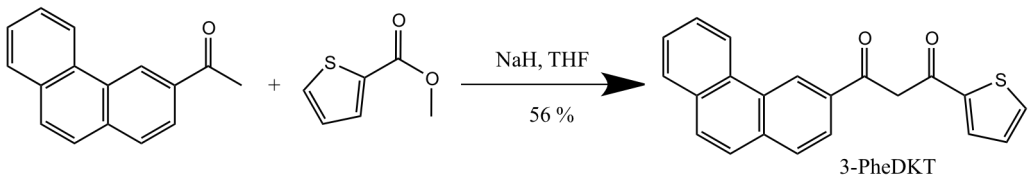
1.5.2 Synthesis of 3-Phe@F



3-PheDKF (300 mg, 0.95 mmol) and boron trifluoride diethyl etherate (46 %, 0.41 ml, 1.5 mmol) were added to 6 ml benzene, then the solution was refluxed for 1 h. The precipitated product was filtrated and washed with benzene to give 3-Phe@F (320 mg, 92 %).

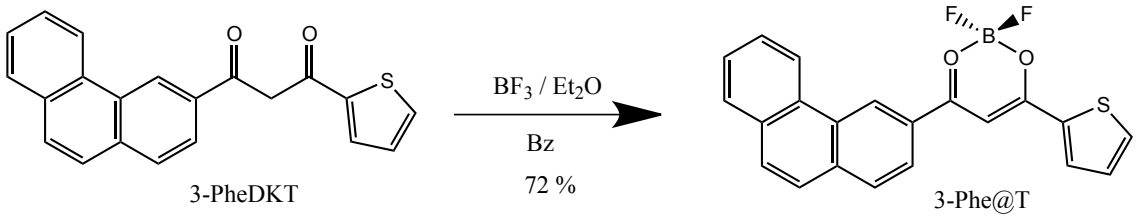
1.6. Preparation of 3-Phe@T

1.6.1 Synthesis of compound 3-PheDKT



To 25 ml of dry THF, 3-acetylphenanthrene (500 mg, 2.3 mmol) and NaH 700 mg (60 % in oil, 720 mg, 18 mmol) were added, and the mixture was stirred for 15 min at room temperature. Methyl 2-thiophenecarboxylate (0.35 ml, 3.0 mmol) was added to the mixture, which was refluxed for 3 h. After cooling to room temperature, aqueous NH_4Cl (20 %, 30 ml) was added. The product was extracted with ethyl acetate, and the solution was washed with aqueous NH_4Cl and brine. After removal of the solvent, the product was purified by silica-gel chromatography using hexane/ethyl acetate (3:1, v/v) to give 3-PheDKT (426 mg, 56 %).

1.6.2 Synthesis of 3-Phe@T



3-PheDKF (376 mg, 1.14 mmol) and boron trifluoride diethyl etherate (46 %, 0.41 ml, 1.5 mmol) were added to 6 ml of benzene, then the solution was refluxed for 1 h. The precipitated product was filtrated and washed with benzene to give 3-Phe@T (309 mg, 72 %).

2. Absorption and fluorescence spectra in ACN

Figure S1 shows absorption and fluorescence spectra of the used compounds in acetonitrile (ACN). All the compounds show stokes shifts. The fluorescence spectrum of Ph@Ph has vibrational structures while others show structureless emission bands.

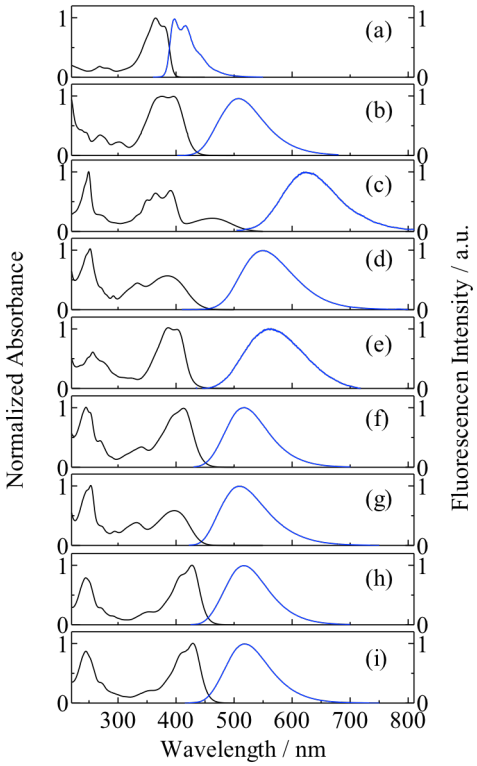


Figure S1. Absorption (black) and fluorescence (blue) spectra in ACN for Ph@Ph (a), 2-Np@Ph (b), 2-Ant@Ph (c), 1-Phe@Ph (d), 2-Phe@Ph (e), 3-Phe@Ph (f), 9-Phe@Ph (g), 3-Phe@F (h) and 3-Phe@T (i). The fluorescence spectra are not corrected.

3. Transient absorption spectra in ACN

Figure S2 shows transient absorption spectra obtained upon 355 and 400 nm laser pulsing in the ACN solution of the DF_2DKs.

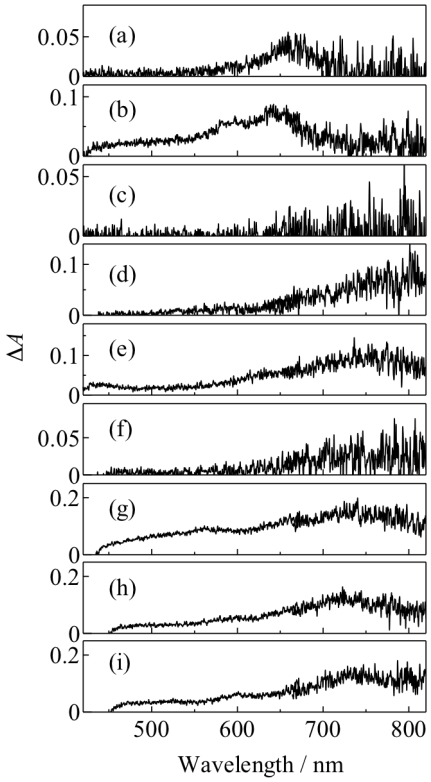


Figure S2. Transient absorption spectra obtained at 200 ns upon laser pulsing in the Ar-purged ACN solution of Ph@Ph (a), 2-Np@Ph (b), 2-Ant@Ph (c), 1-Phe@Ph (d), 2-Phe@Ph (e), 3-Phe@Ph (f), 9-Phe@Ph (g), 3-Phe@F (h) and 3-Phe@T (i) at 295 K. A 355 nm Laser pulse was used for Ph@Ph whereas 400 nm laser pulses were employed for exciting the other BF_2DK.

4. Results of DFT and TD-DFT calculations (atom coordinates and sum of electronic and zero-point energies)

The calculation was carried out at the DFT level, using the Gaussian 09 software package.[5] The geometries of the difluoroboronated β-diketones were fully optimized by using the 6-31G(d) base set at the B3LYP method considering a dielectric constant of CF in the CPCM model. Atom coordinates for the optimized geometries of the difluoroboronated β-diketones in vaccum and chloroform are as follows.

Table S1. Atom coordinates for the optimized geometry of 1-Phe@Ph in vacuum.

	X	Y	Z
C	−5.57662	1.21084	−1.40909
C	−6.73661	0.47573	−1.26593
C	−6.71366	−0.75171	−0.56427
C	−5.53449	−1.22196	−0.01991
C	−4.32699	−0.48511	−0.15314
C	−4.35565	0.74193	−0.85552
C	−3.06719	−0.95796	0.41035
C	−1.88902	−0.18477	0.23964
C	−1.96551	1.06988	−0.47857
C	−3.13789	1.51012	−0.99829
C	−2.99650	−2.17620	1.13200
C	−1.80000	−2.62557	1.66016
C	−0.62364	−1.87531	1.47668
C	−0.66145	−0.67501	0.77461
C	0.61450	0.06335	0.60682
C	1.78877	−0.55963	0.17022
C	2.98315	0.15899	0.04047
C	4.26597	−0.42467	−0.40381
C	4.32040	−1.71538	−0.95828
C	5.54387	−2.24548	−1.36984
C	6.71722	−1.49423	−1.23221
C	6.66802	−0.20834	−0.68466
C	5.44727	0.32874	−0.27274
O	0.57060	1.32204	0.90214
O	3.04780	1.42459	0.31920
B	1.81713	2.18454	0.77909
F	2.09017	2.64773	2.00309
F	1.55370	3.09115	−0.17066
H	−5.58506	2.15843	−1.94728
H	−7.67525	0.83171	−1.68822
H	−7.63625	−1.32098	−0.45796
H	−5.52350	−2.16919	0.52085
H	−1.05533	1.67167	−0.57346
H	−3.19226	2.46006	−1.53341
H	−3.90772	−2.76422	1.27189

H	−1.75780	−3.55899	2.22067
H	0.31446	−2.24084	1.89964
H	1.76507	−1.61731	−0.08349
H	3.40713	−2.30230	−1.07265
H	5.58579	−3.24538	−1.80041
H	7.67146	−1.91295	−1.55427
H	7.58152	0.37747	−0.58024
H	5.39652	1.33785	0.15211

Sum of electronic and zero-point energies = -1260.62705140 Hartree

Table S2. Atom coordinates for the optimized geometry of 1-Phe@Ph in chloroform.

	X	Y	Z
C	−5.70865	1.33807	−1.02252
C	−6.86930	0.60226	−0.87128
C	−6.79983	−0.70195	−0.34009
C	−5.58077	−1.24797	0.02801
C	−4.37356	−0.51871	−0.11305
C	−4.45212	0.79966	−0.65061
C	−3.06799	−1.05604	0.26204
C	−1.89766	−0.24331	0.11796
C	−2.03261	1.07265	−0.44569
C	−3.25034	1.56263	−0.81295
C	−2.92417	−2.37336	0.75825
C	−1.68559	−2.89518	1.08784
C	−0.53438	−2.10968	0.94313
C	−0.62399	−0.79596	0.48445
C	0.62977	−0.01669	0.42706
C	1.83014	−0.57549	−0.02091
C	3.01775	0.15966	0.07635
C	4.34533	−0.36924	−0.27583
C	4.55116	−1.73801	−0.53920
C	5.81932	−2.20623	−0.87624
C	6.89827	−1.31835	−0.95624
C	6.70483	0.04230	−0.69328
C	5.43936	0.51524	−0.35283
O	0.58128	1.21626	0.85735
O	2.99757	1.39320	0.50869
B	1.73205	2.15822	0.70518
F	1.84245	2.91290	1.85911
F	1.50871	2.95307	−0.41836
H	−5.74442	2.34589	−1.42958
H	−7.82864	1.02425	−1.15816
H	−7.70796	−1.28586	−0.21639
H	−5.57130	−2.25329	0.43404
H	−1.15252	1.68690	−0.58217
H	−3.32436	2.55974	−1.24052
H	−3.79693	−3.00389	0.88256
H	−1.60464	−3.90938	1.46745
H	0.42983	−2.51563	1.23233
H	1.83014	−1.57528	−0.42724
H	3.73171	−2.44508	−0.46827

H	5.96709	-3.26418	-1.07280
H	7.88574	-1.68647	-1.22095
H	7.53980	0.73428	-0.75542
H	5.28517	1.56945	-0.15196

Sum of electronic and zero-point energies = -1260.65477731 Hartree

Table S3. Atom coordinates for the optimized geometry of 2-Phe@Ph in vacuum.

	X	Y	Z
C	-7.42023	-1.25577	0.04064
C	-6.50732	-2.32882	0.00734
C	-5.14439	-2.08699	-0.01217
C	-4.62916	-0.76754	0.00067
C	-5.55926	0.31634	0.03485
C	-3.20426	-0.47257	-0.01898
C	-2.77412	0.88920	-0.00380
C	-3.74658	1.94669	0.03178
C	-5.07897	1.67026	0.04990
C	-2.20470	-1.47724	-0.05563
C	-0.86103	-1.16460	-0.07041
C	-0.43097	0.18670	-0.05132
C	-1.39680	1.18933	-0.02260
C	0.99371	0.56217	-0.05789
C	2.03850	-0.35517	0.11706
C	3.36228	0.07296	-0.03834
C	4.52482	-0.83807	-0.01218
C	5.81486	-0.29140	0.11856
C	6.93188	-1.12367	0.15742
C	6.77897	-2.51011	0.05913
C	5.50143	-3.06262	-0.08037
C	4.38163	-2.23409	-0.11504
O	1.24322	1.82256	-0.25979
O	3.63985	1.32753	-0.23444
B	2.61179	2.41511	-0.03405
F	2.68856	2.84725	1.27702
F	2.82492	3.39921	-0.96098
H	-7.64322	0.87970	0.07997
H	-8.48930	-1.45025	0.05577
H	-6.87318	-3.35211	-0.00312
H	-4.46771	-2.93447	-0.03737
H	-3.39237	2.97436	0.04335
H	-5.80838	2.47639	0.07623
H	-2.48794	-2.52373	-0.07820
H	-0.13819	-1.97234	-0.11539
H	-1.07961	2.22708	-0.00832
H	1.82466	-1.38949	0.33557
H	5.92467	0.78474	0.19490
H	7.92240	-0.69036	0.26540
H	7.65109	-3.15814	0.08741
H	5.37858	-4.13865	-0.16809
H	3.40016	-2.67875	-0.24480

Sum of electronic and zero-point energies = -1260.66104196 Hartree

Table S4. Atom coordinates for the optimized geometry of 2-Phe@Ph in chloroform.

	X	Y	Z
C	2.77487	0.89354	−0.00366
C	1.39808	1.19534	−0.01791
C	3.20166	−0.47010	−0.01062
C	2.20072	−1.47475	−0.03384
C	0.85742	−1.16132	−0.04495
C	0.42991	0.19235	−0.03512
C	−0.99208	0.56153	−0.04182
C	−2.03617	−0.35728	0.11427
C	−3.36085	0.06673	−0.02947
C	−4.51940	−0.84236	−0.01060
C	−4.36811	−2.23797	−0.12902
C	−5.48449	−3.07138	−0.10274
C	−6.76527	−2.52651	0.04413
C	−6.92617	−1.14135	0.15875
C	−5.81339	−0.30318	0.12783
O	−1.24865	1.83172	−0.22548
O	−3.64015	1.33225	−0.20644
B	−2.61337	2.40185	−0.03655
F	−2.82462	3.37702	−0.99588
F	−2.71167	2.91631	1.25631
H	2.48060	−2.52197	−0.04814
H	0.13619	−1.97023	−0.07724
H	−1.82056	−1.39514	0.31058
H	−3.38592	−2.67843	−0.26325
H	−5.35608	−4.14540	−0.20188
H	−7.63383	−3.17904	0.06626
H	−7.91855	−0.71484	0.27366
H	−5.93437	0.77046	0.21937
H	1.08794	2.23502	−0.00848
C	3.74969	1.95036	0.01857
C	4.62606	−0.76784	0.00375
C	5.55893	0.31480	0.02418
C	5.08211	1.67081	0.03132
H	5.81362	2.47501	0.04724
H	3.39838	2.97900	0.02411
C	5.13679	−2.08984	−0.00147
C	6.94782	0.03933	0.03794
C	7.41602	−1.26249	0.03213
H	8.48450	−1.45980	0.04281
C	6.49999	−2.33425	0.01238
H	6.86340	−3.35826	0.00800
H	7.64531	0.87352	0.05331
H	4.45831	−2.93580	−0.01626

Sum of electronic and zero-point energies = -1260.63914126 Hartree

Table S5. Atom coordinates for the optimized geometry of 3-Phe@Ph in vacuum.

	X	Y	Z
C	−6.63909	0.12096	−0.34686
C	−6.64021	1.47538	−0.61529
C	−5.42038	2.18999	−0.65654
C	−4.22280	1.54014	−0.43107
C	−4.19474	0.14695	−0.15517
C	−5.41733	−0.56433	−0.11207
C	−2.94759	−0.56850	0.08333
C	−2.98156	−1.95828	0.35710
C	−4.25124	−2.64996	0.39621
C	−5.41202	−1.98374	0.17157
C	−1.69320	0.08764	0.05031
C	−0.51214	−0.61351	0.27050
C	−0.55550	−2.00475	0.54944
C	−1.76767	−2.65974	0.59215
C	0.77799	0.10420	0.21940
C	2.02162	−0.51486	0.04580
C	3.19977	0.23751	−0.00513
C	4.54925	−0.34269	−0.17987
C	5.66887	0.37347	0.27940
C	6.94920	−0.16254	0.12724
C	7.11821	−1.40562	−0.49056
C	6.00628	−2.11545	−0.95935
C	4.72291	−1.58862	−0.80587
O	0.66705	1.39161	0.33758
O	3.19626	1.52887	0.11241
B	1.89435	2.28395	0.30846
F	1.75129	3.09008	−0.74995
F	1.97168	2.87057	1.50880
H	−7.57486	−0.43583	−0.31210
H	−7.57465	2.00497	−0.79628
H	−5.43594	3.25944	−0.86760
H	−3.28442	2.09826	−0.46199
H	−4.24428	−3.71837	0.61135
H	−6.37297	−2.49996	0.19949
H	−1.64944	1.16720	−0.14995
H	0.37324	−2.54538	0.73772
H	−1.80828	−3.72713	0.80959
H	2.07234	−1.59671	−0.04868
H	5.52575	1.35178	0.75063
H	7.81572	0.39217	0.48711
H	8.11879	−1.82244	−0.61045
H	6.14295	−3.07991	−1.44715
H	3.85941	−2.13947	−1.18151

Sum of electronic and zero-point energies = -1260.62679147 Hartree

Table S6. Atom coordinates for the optimized geometry of 3-Phe@Ph in chloroform.

	X	Y	Z
C	−6.65582	0.13055	0.08332
C	−6.68768	1.51313	0.11170
C	−5.47855	2.23742	0.09771
C	−4.26189	1.57471	0.05608
C	−4.19706	0.16115	0.02703
C	−5.42455	−0.56833	0.04075
C	−2.93917	−0.57960	−0.01671
C	−2.96887	−2.00827	−0.04355
C	−4.22591	−2.69603	−0.02936
C	−5.40065	−2.00408	0.01127
C	−1.68300	0.05729	−0.03235
C	−0.48669	−0.66310	−0.06783
C	−0.53239	−2.08189	−0.09720
C	−1.74806	−2.72877	−0.08649
C	0.78543	0.07170	−0.07231
C	2.03520	−0.53337	0.10635
C	3.20056	0.22652	−0.03213
C	4.56025	−0.33793	0.01456
C	5.66190	0.53352	0.12165
C	6.95879	0.02679	0.17553
C	7.17604	−1.35418	0.11738
C	6.08880	−2.22809	0.00355
C	4.78979	−1.72653	−0.04688
O	0.69697	1.36220	−0.27405
O	3.13409	1.51800	−0.23027
B	1.85842	2.27854	−0.09188
F	1.81338	3.25377	−1.07367
F	1.80123	2.82990	1.18836
H	−7.58090	−0.44112	0.09343
H	−7.63776	2.03928	0.14460
H	−5.49714	3.32367	0.11946
H	−3.35166	2.16442	0.04587
H	−4.22502	−3.78283	−0.05084
H	−6.34922	−2.53573	0.02242
H	−1.61840	1.13719	−0.00906
H	0.37866	−2.66755	−0.14781
H	−1.78367	−3.81475	−0.11619
H	2.10032	−1.58811	0.31998
H	5.49007	1.60297	0.16952
H	7.79998	0.70830	0.26451
H	8.18779	−1.74839	0.15786
H	6.25346	−3.30034	−0.05095
H	3.96247	−2.41994	−0.15361

Sum of electronic and zero-point energies = -1260.65976304 Hartree

Table S7. Atom coordinates for the optimized geometry of 9-Phe@Ph in vacuum.

	X	Y	Z
C	−2.97146	3.11548	0.71705
C	−4.25649	3.62172	0.69983
C	−2.71729	1.76495	0.37135
C	−3.79269	0.90624	0.0022
C	−5.09786	1.45464	−0.00199
C	−5.32586	2.77828	0.33717
C	−1.38616	1.24944	0.40272
C	−1.09642	−0.05873	0.10781
C	−2.15830	−0.96880	−0.29486
C	−3.50172	−0.47866	−0.35345
C	0.31148	−0.49406	0.24679
C	1.37628	0.30182	−0.19377
C	2.69106	−0.08455	0.09771
C	3.87764	0.73947	−0.20759
C	3.76770	2.07512	−0.63739
C	4.90972	2.82121	−0.92059
C	6.17693	2.24576	−0.77914
C	6.29682	0.92054	−0.34937
C	5.15726	0.17155	−0.06309
O	0.52068	−1.63331	0.8343
O	2.93280	−1.21924	0.68407
B	1.88137	−2.29021	0.83831
F	2.06682	−2.92106	2.03667
F	1.94973	−3.12912	−0.26093
C	−4.52083	−1.36621	−0.77546
C	−4.24238	−2.67202	−1.13639
C	−2.91886	−3.14423	−1.0948
C	−1.89795	−2.30756	−0.68239
H	−2.13371	3.74910	1.00001
H	−4.44375	4.65831	0.96621
H	−5.94786	0.83766	−0.27064
H	−6.34080	3.16699	0.32509
H	−0.59103	1.91886	0.72059
H	1.16942	1.21103	−0.73762
H	2.79424	2.54349	−0.73962
H	4.81190	3.85265	−1.24784
H	7.06647	2.82935	−1.00146
H	7.27911	0.46965	−0.23853
H	5.24170	−0.85727	0.26879
H	−5.54759	−1.02222	−0.82912
H	−5.04755	−3.32782	−1.45714
H	−2.69247	−4.16656	−1.38484
H	−0.88551	−2.68877	−0.64812

Sum of electronic and zero-point energies = -1260.63191457 Hartree

Table S8. Atom coordinates for the optimized geometry of 9-Phe@Ph in chloroform.

	X	Y	Z
C	-4.54546	-1.35896	0.72882
C	-4.28227	-2.66788	1.09259
C	-3.51127	-0.47326	0.33849
C	-2.16818	-0.96816	0.31018
C	-1.92468	-2.30812	0.70490
C	-2.95888	-3.14374	1.08827
C	-3.78835	0.91683	-0.01069
C	-2.69968	1.77484	-0.34225
C	-1.37087	1.25392	-0.35219
C	-1.09283	-0.06050	-0.06649
C	0.31116	-0.49655	-0.20418
C	1.38169	0.30296	0.20786
C	2.69328	-0.08879	-0.08458
C	3.88106	0.73071	0.20537
C	3.77128	2.08117	0.59164
C	4.91437	2.83020	0.86253
C	6.18077	2.24437	0.75377
C	6.30044	0.90475	0.36764
C	5.16068	0.15231	0.09197
O	0.51778	-1.65430	-0.77401
O	2.92738	-1.24012	-0.65831
B	1.87334	-2.28197	-0.83013
F	2.03460	-2.87808	-2.06776
F	1.97895	-3.20417	0.21017
H	-0.91211	-2.69014	0.70431
H	-2.74384	-4.16629	1.38604
H	-0.56850	1.92399	-0.64735
H	1.18420	1.22324	0.73585
H	2.80008	2.55820	0.66697
H	4.81793	3.87192	1.15456
H	7.07030	2.83070	0.96743
H	7.28177	0.44677	0.28302
H	5.24940	-0.88680	-0.20454
H	-5.57183	-1.01150	0.75688
H	-5.09821	-3.32143	1.38894
C	-5.09150	1.46995	-0.03269
C	-2.93716	3.13202	-0.67677
C	-4.22089	3.64341	-0.68510
H	-4.39713	4.68425	-0.94142
C	-5.30344	2.79993	-0.36108
H	-6.31628	3.19362	-0.36939
H	-2.08961	3.76488	-0.92883
H	-5.95166	0.85550	0.20708

Sum of electronic and zero-point energies = -1260.65053126 Hartree

Table S9. Atom coordinates for the optimized geometry of 3-Phe@F in vacuum.

	X	Y	Z
C	6.39421	0.19581	0.03267
C	6.40721	1.57814	0.04602
C	5.18846	2.28487	0.03692
C	3.98174	1.60505	0.01486
C	3.93609	0.19095	0.00133
C	5.17347	-0.52079	0.01021
C	2.68823	-0.56609	-0.02172
C	2.73651	-1.99371	-0.03443
C	4.00301	-2.66367	-0.02561
C	5.16821	-1.95634	-0.00386
C	1.42347	0.05441	-0.03074
C	0.23732	-0.68016	-0.04824
C	0.30118	-2.09718	-0.06406
C	1.52483	-2.72904	-0.05790
C	-1.04457	0.04471	-0.04524
C	-2.28882	-0.57934	0.11175
C	-3.44860	0.18760	-0.03391
O	-0.96954	1.33257	-0.22365
O	-3.41686	1.47539	-0.22465
B	-2.14322	2.25599	-0.00167
F	-2.11697	2.68118	1.31371
F	-2.08259	3.27137	-0.91821
H	7.32761	-0.36277	0.03920
H	7.35028	2.11775	0.06332
H	5.19158	3.37152	0.04712
H	3.06241	2.18054	0.00802
H	4.01664	-3.75092	-0.03615
H	6.12427	-2.47506	0.00328
H	1.33990	1.13333	-0.01914
H	-0.60464	-2.69295	-0.09637
H	1.57434	-3.81518	-0.07540
H	-2.37468	-1.64135	0.28393
C	-4.77282	-0.39034	-0.01858
C	-6.02088	0.17841	-0.11129
C	-6.95806	-0.89062	-0.03185
H	-6.22068	1.23498	-0.21947
C	-6.21863	-2.03451	0.10491
H	-8.03656	-0.82385	-0.06849
H	-6.47682	-3.07850	0.20383
O	-4.89246	-1.75290	0.11426

Sum of electronic and zero-point energies = -1258.41789682 Hartree

Table S10. Atom coordinates for the optimized geometry of 3-Phe@F in chloroform.

	X	Y	Z
C	6.39564	0.18991	0.05616
C	6.41097	1.57271	0.08645
C	5.19307	2.28228	0.08062
C	3.98434	1.60486	0.04514
C	3.93637	0.19061	0.01438
C	5.17274	-0.52390	0.01975
C	2.68727	-0.56520	-0.02293
C	2.73422	-1.99326	-0.05298
C	3.99960	-2.66573	-0.04718
C	5.16616	-1.95980	-0.01199
C	1.42328	0.05652	-0.02952
C	0.23577	-0.67822	-0.06059
C	0.29856	-2.09629	-0.09323
C	1.52194	-2.72843	-0.09019
C	-1.04602	0.03936	-0.05529
C	-2.28812	-0.58476	0.09157
C	-3.45263	0.18005	-0.02555
O	-0.97427	1.33836	-0.21716
O	-3.41860	1.47847	-0.19841
B	-2.14615	2.24328	-0.03855
F	-2.10518	2.78248	1.24765
F	-2.09711	3.22982	-1.00958
H	7.32761	-0.37056	0.05992
H	7.35480	2.11030	0.11451
H	5.19857	3.36865	0.10381
H	3.06698	2.18353	0.04111
H	4.01165	-3.75243	-0.07067
H	6.12116	-2.47994	-0.00726
H	1.34559	1.13546	-0.00357
H	-0.60578	-2.69277	-0.13631
H	1.57044	-3.81390	-0.12067
H	-2.37099	-1.64937	0.24792
C	-4.77100	-0.39434	0.00622
C	-6.02595	0.16937	-0.06477
C	-6.95511	-0.90314	0.02045
H	-6.23970	1.22420	-0.16354
C	-6.20779	-2.04598	0.13839
H	-8.03415	-0.84156	-0.00046
H	-6.46151	-3.09150	0.23290
O	-4.88376	-1.75894	0.13094

Sum of electronic and zero-point energies = -1258.44014106 Hartree

Table S11. Atom coordinates for the optimized geometry of 3-Phe@T in vacuum.

	X	Y	Z
C	−6.64411	0.09219	−0.04596
C	−6.69408	1.47357	−0.06722
C	−5.49476	2.21280	−0.05795
C	−4.27033	1.56576	−0.02788
C	−4.18688	0.15348	−0.00631
C	−5.40469	−0.59125	−0.01529
C	−2.91934	−0.56973	0.02508
C	−2.92947	−1.99797	0.04604
C	−4.17749	−2.70178	0.03712
C	−5.36108	−2.02604	0.00725
C	−1.67162	0.08450	0.03395
C	−0.46622	−0.61767	0.05879
C	−0.49242	−2.03573	0.08342
C	−1.69862	−2.70033	0.07781
C	0.79518	0.14283	0.05560
C	2.05474	−0.44417	−0.11620
C	3.20292	0.34427	0.03417
O	0.68455	1.42615	0.24688
O	3.12506	1.62847	0.23297
B	1.83192	2.37758	0.01460
F	1.78854	2.79817	−1.30194
F	1.75305	3.39406	0.92842
H	−7.56217	−0.49123	−0.05242
H	−7.65119	1.98760	−0.09082
H	−5.52701	3.29890	−0.07424
H	−3.36680	2.16575	−0.02103
H	−4.16200	−3.78892	0.05412
H	−6.30290	−2.57019	−0.00005
H	−1.61709	1.16520	0.01626
H	0.42837	−2.60768	0.12487
H	−1.71894	−3.78724	0.10281
H	2.14901	−1.50251	−0.31130
C	4.55304	−0.19401	0.01620
C	5.72108	0.54367	0.07942
C	6.88912	−0.25955	0.03437
H	5.71452	1.62488	0.15123
C	6.60275	−1.60120	−0.06194
H	7.89899	0.13396	0.06919
H	7.29803	−2.42954	−0.11322
S	4.90387	−1.90599	−0.09678

Sum of electronic and zero-point energies = -1581.39478595 Hartree

Table S12. Atom coordinates for the optimized geometry of 3-Phe@T in chloroform.

	X	Y	Z
C	6.64560	0.08717	0.06683
C	6.69740	1.46890	0.10496
C	5.49874	2.21056	0.09999
C	4.27262	1.56560	0.05758
C	4.18736	0.15333	0.01872
C	5.40429	-0.59375	0.02318
C	2.91872	-0.56874	-0.02584
C	2.92788	-1.99733	-0.06337
C	4.17496	-2.70327	-0.05848
C	5.35974	-2.02876	-0.01677
C	1.67170	0.08648	-0.03202
C	0.46516	-0.61609	-0.06891
C	0.49040	-2.03510	-0.10904
C	1.69656	-2.69964	-0.10713
C	-0.79646	0.13713	-0.06371
C	-2.05389	-0.45024	0.09877
C	-3.20655	0.33545	-0.02854
O	-0.68865	1.43148	-0.24100
O	-3.12570	1.63039	-0.21252
B	-1.83583	2.36339	-0.04911
F	-1.77816	2.88936	1.24228
F	-1.76642	3.35738	-1.01099
H	7.56245	-0.49774	0.06996
H	7.65506	1.98112	0.13857
H	5.53300	3.29626	0.12931
H	3.37080	2.16813	0.05460
H	4.15821	-3.78977	-0.08789
H	6.30059	-2.57403	-0.01282
H	1.62278	1.16699	-0.00094
H	-0.42901	-2.60763	-0.15965
H	1.71613	-3.78579	-0.14423
H	-2.14566	-1.51120	0.27867
C	-4.55122	-0.19842	0.00195
C	-5.72370	0.53943	-0.04592
C	-6.88821	-0.26486	0.00754
H	-5.72683	1.62090	-0.11228
C	-6.59661	-1.60782	0.09455
H	-7.89922	0.12585	-0.01498
H	-7.28957	-2.43795	0.14882
S	-4.90003	-1.91300	0.11118

Sum of electronic and zero-point energies = -1581.41669452 Hartree

5. ^{1}H and ^{13}C NMR spectra

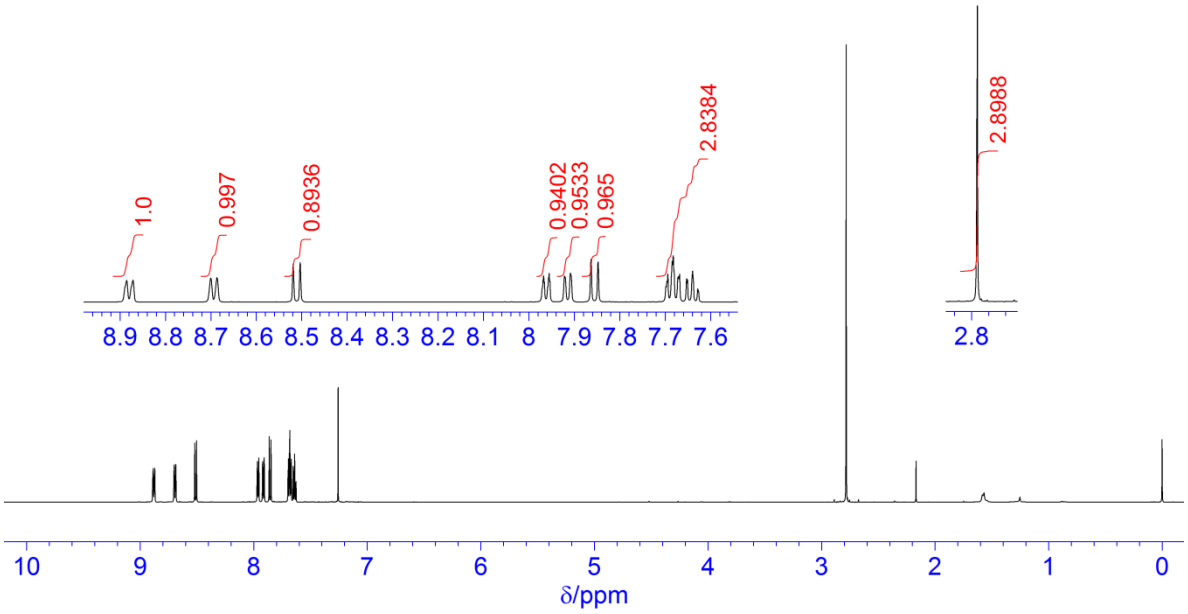


Figure S3. ^{1}H NMR spectrum of 1-AcPhe in $CDCl_3$.

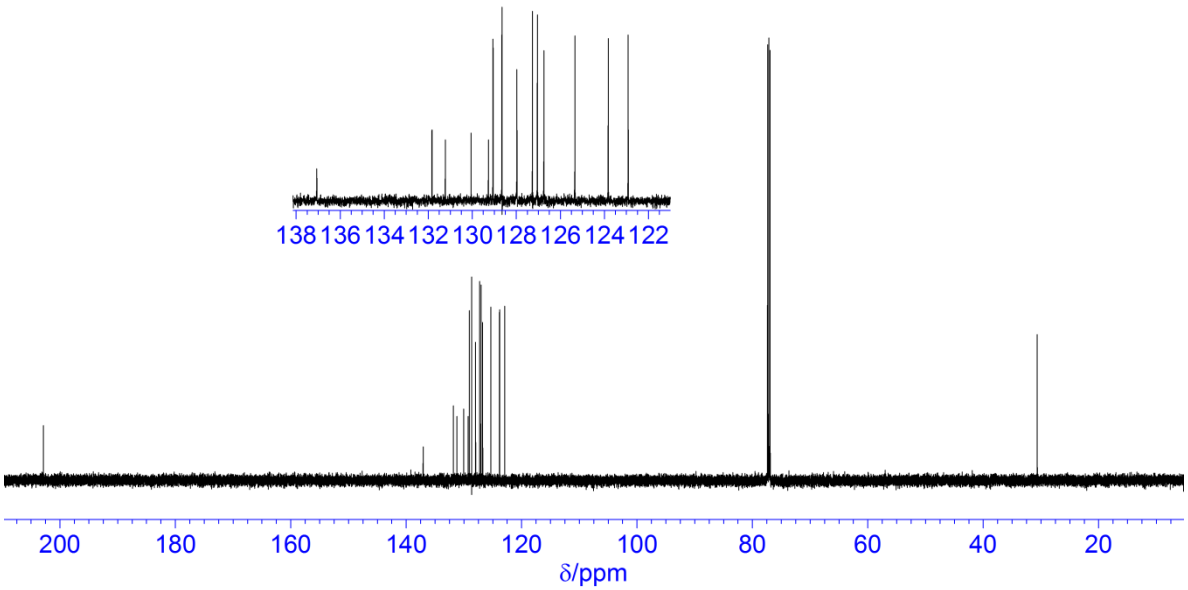


Figure S4. ^{13}C NMR spectrum of 1-AcPhe in $CDCl_3$.

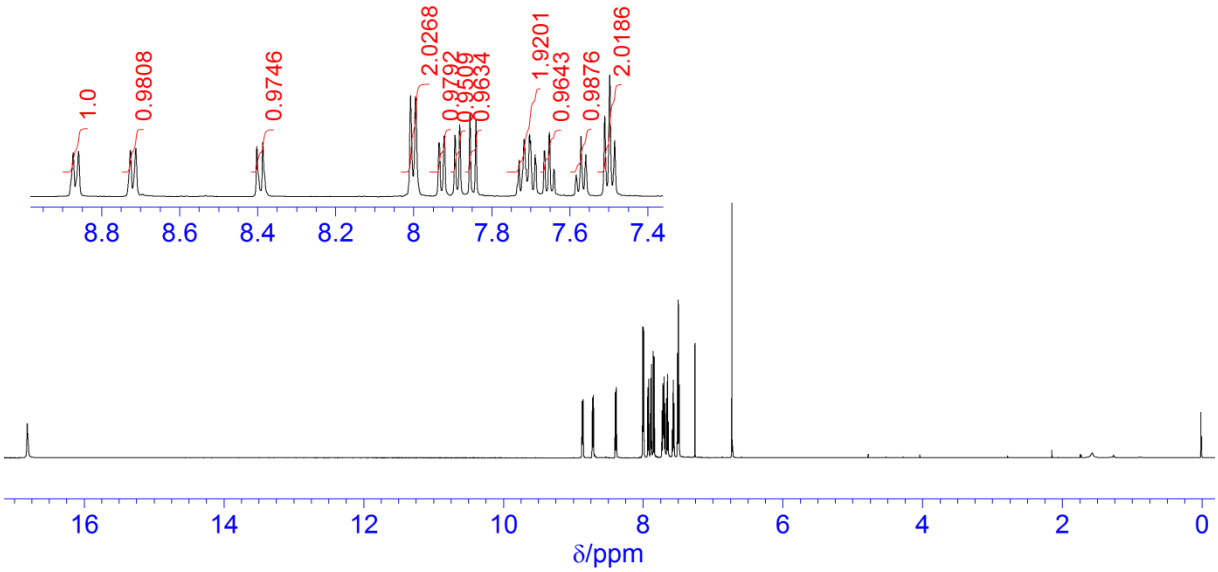


Figure S5. ^{1}H NMR spectrum of 1-PheDKPh in $CDCl_3$.

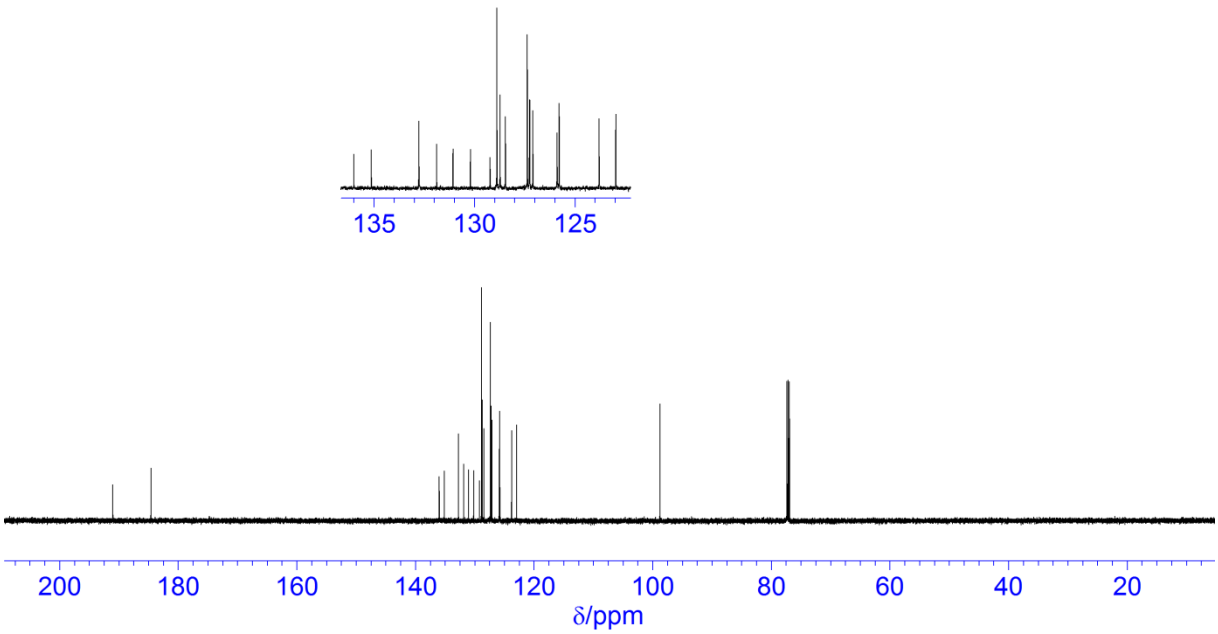


Figure S6. ^{13}C NMR spectrum of 1-PheDKPh in $CDCl_3$.

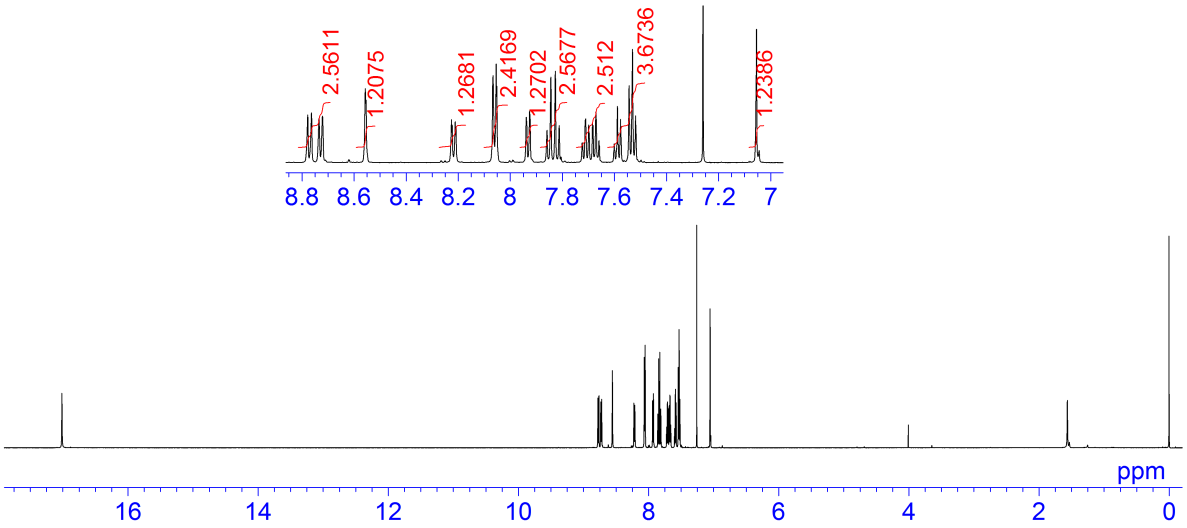


Figure S7. ^{1}H NMR spectrum of 2-PheDKPh in $CDCl_3$.

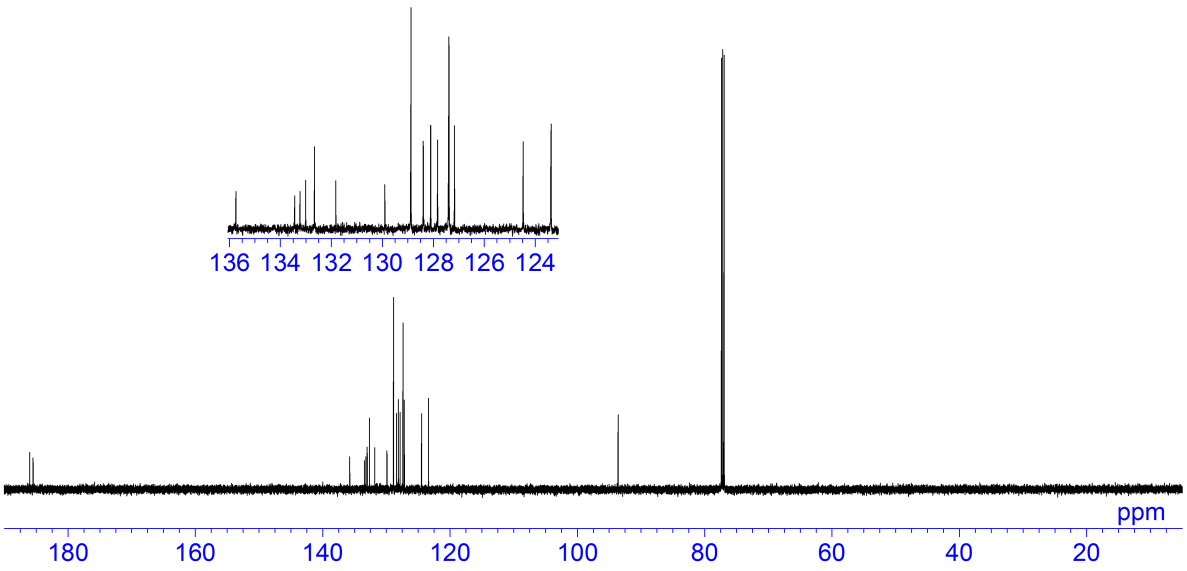


Figure S8. ^{13}C NMR spectrum of 2-PheDKPh in $CDCl_3$.

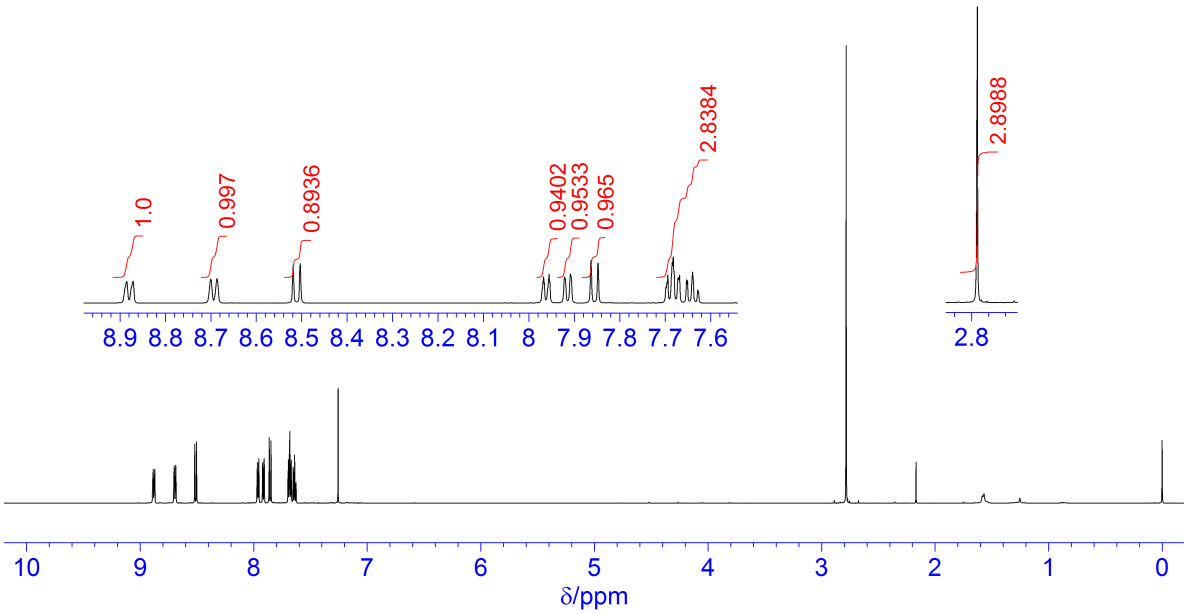


Figure S9. ^{1}H NMR spectrum of 3-PheDKPh in $CDCl_3$.

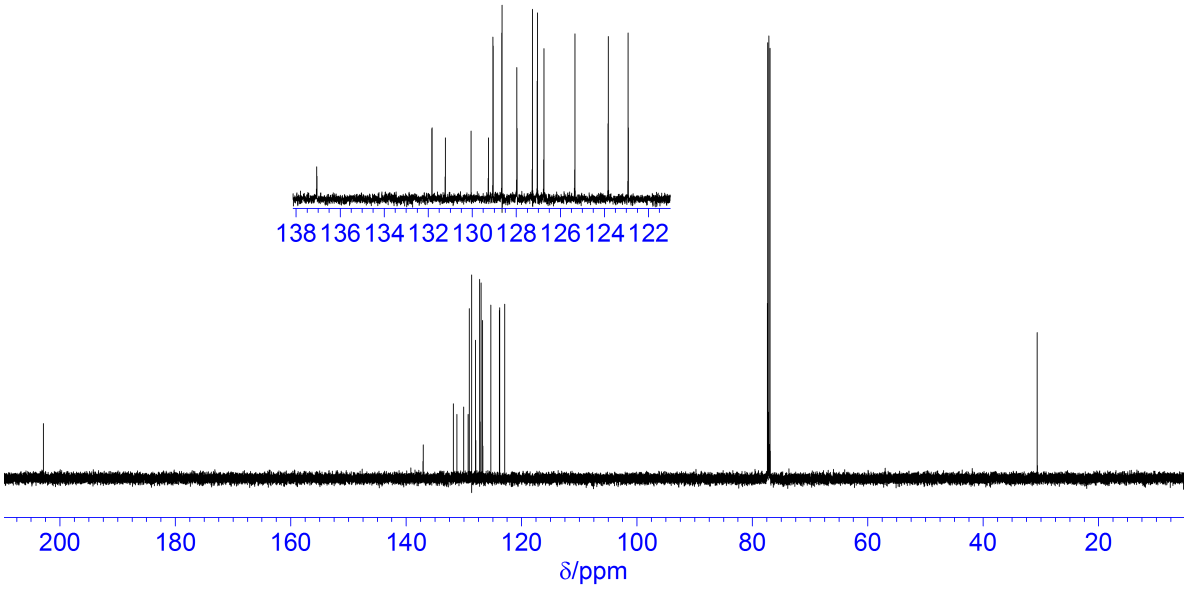


Figure S10. ^{13}C NMR spectrum of 3-PheDKPh in $CDCl_3$.

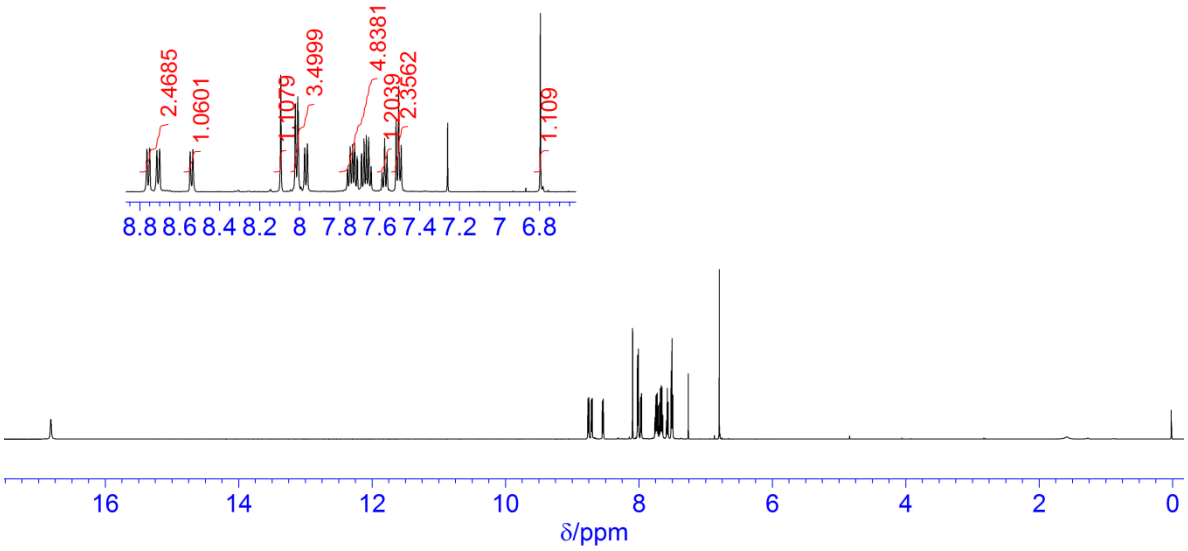


Figure S11. ^{1}H NMR spectrum of 9-PheDKPh in $CDCl_3$.

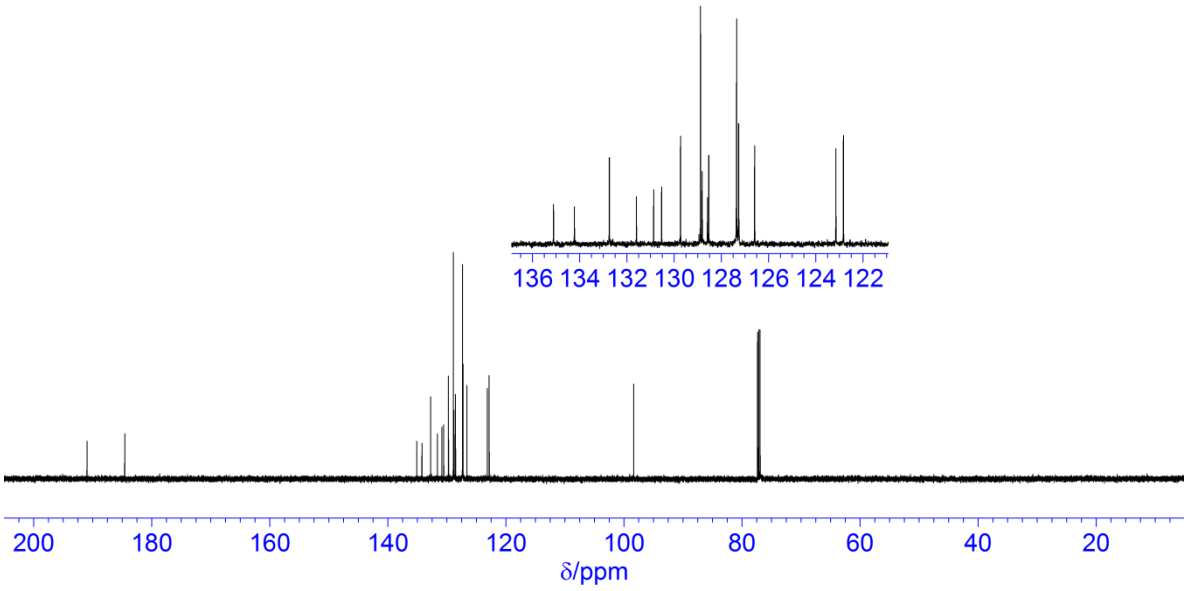


Figure S12. ^{13}C NMR spectrum of 9-PheDKPh in $CDCl_3$.

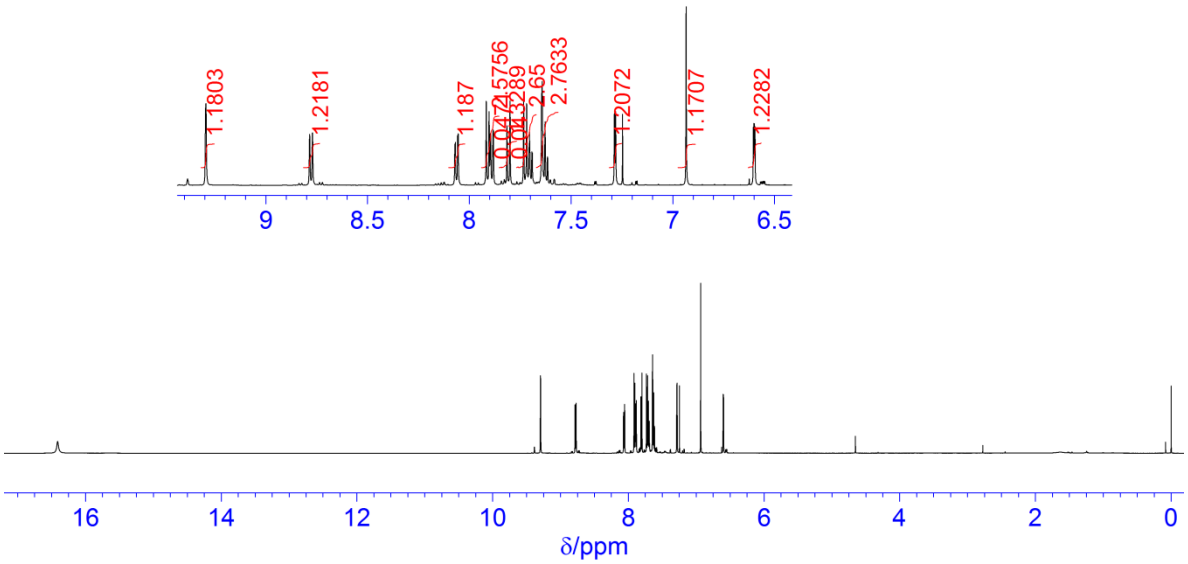


Figure S13. ^{1}H NMR spectrum of 3-PheDKF in $CDCl_3$.

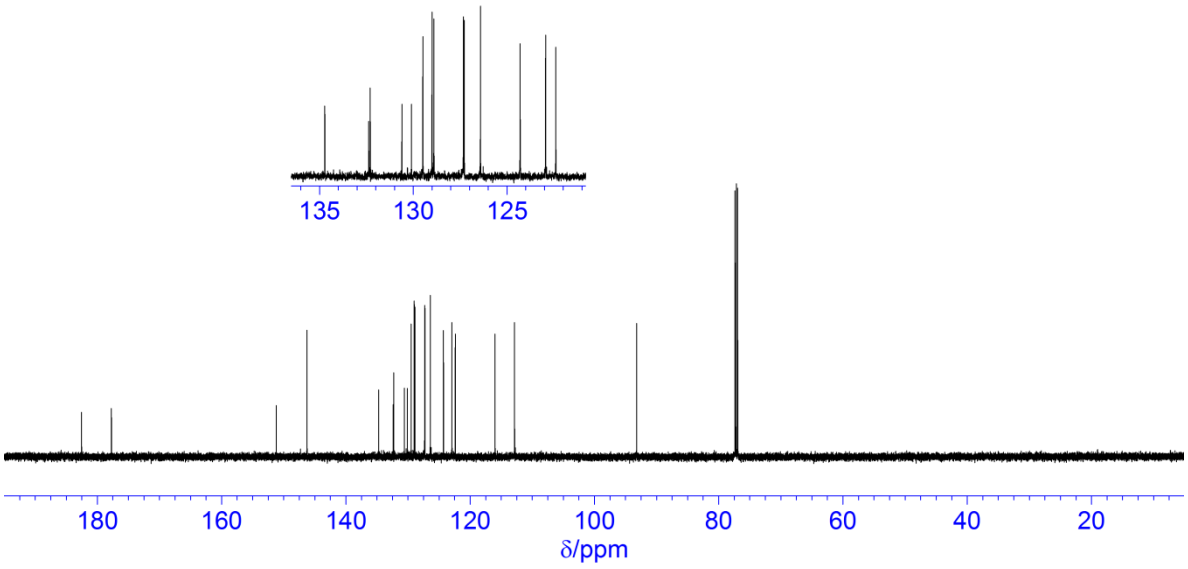


Figure S14. ^{13}C NMR spectrum of 3-PheDKF in $CDCl_3$.

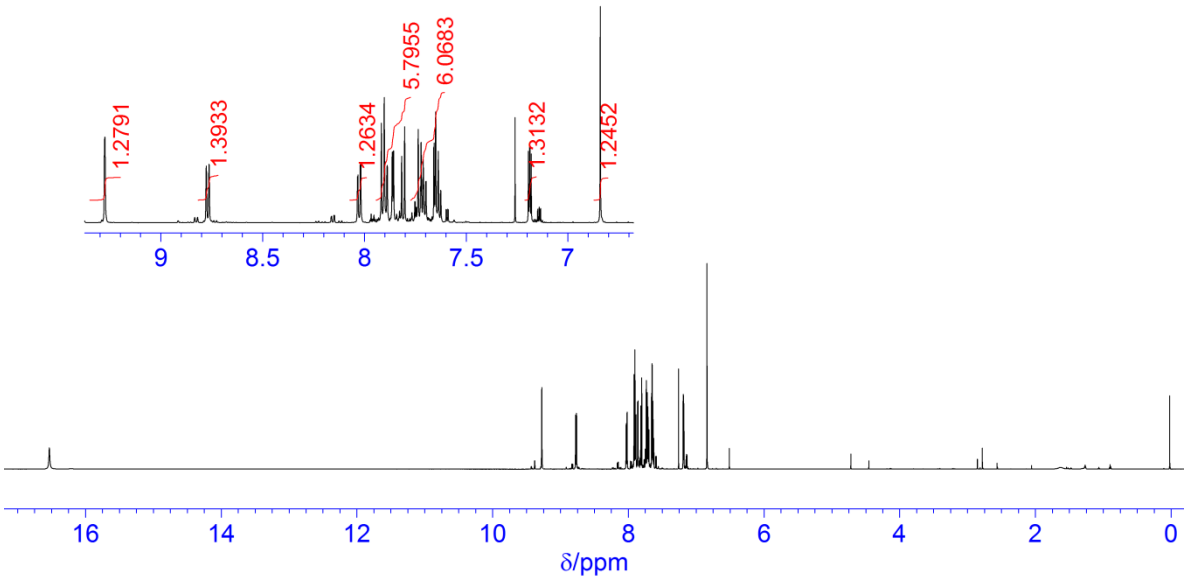


Figure S15. ^{1}H NMR spectrum of 3-PheDKT in $CDCl_3$.

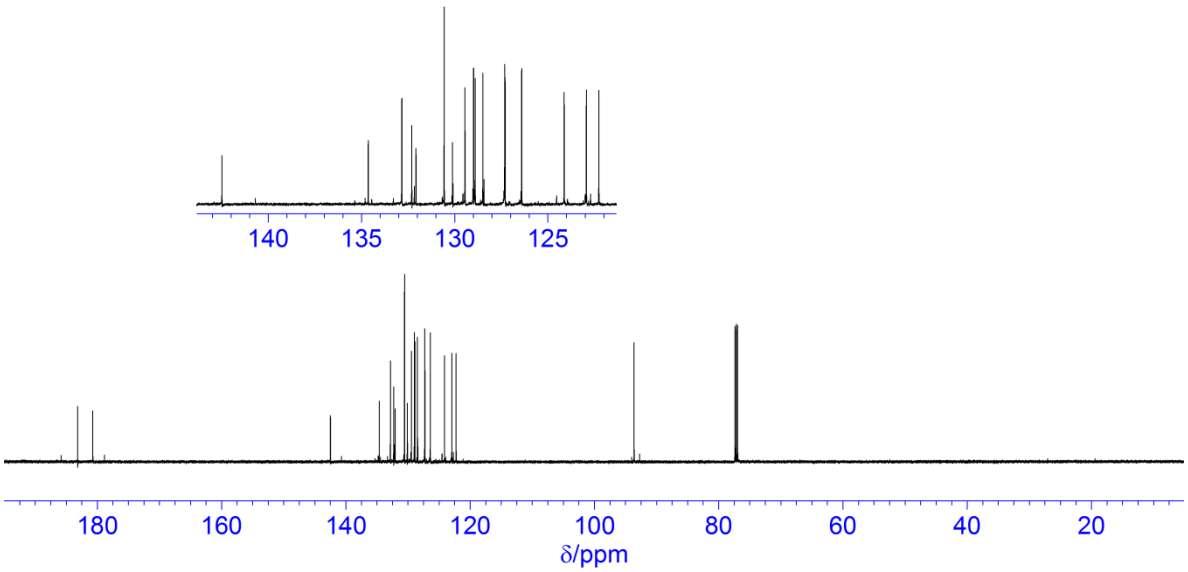


Figure S16. ^{13}C NMR spectrum of 3-PheDKT in $CDCl_3$.

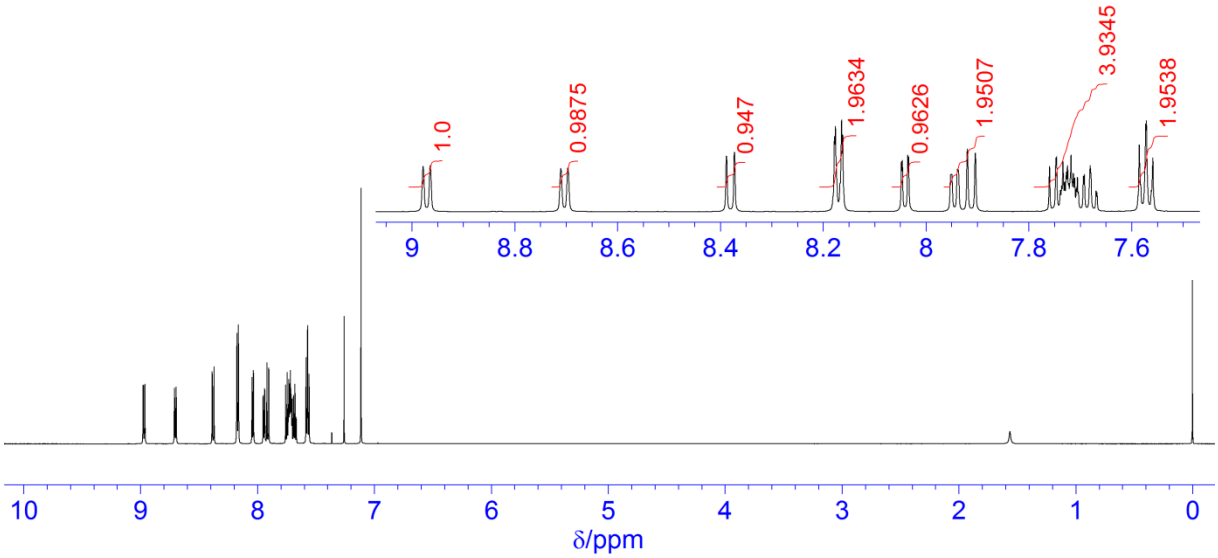


Figure S17. ^{1}H NMR spectrum of 1-Phe@Ph in $CDCl_3$.

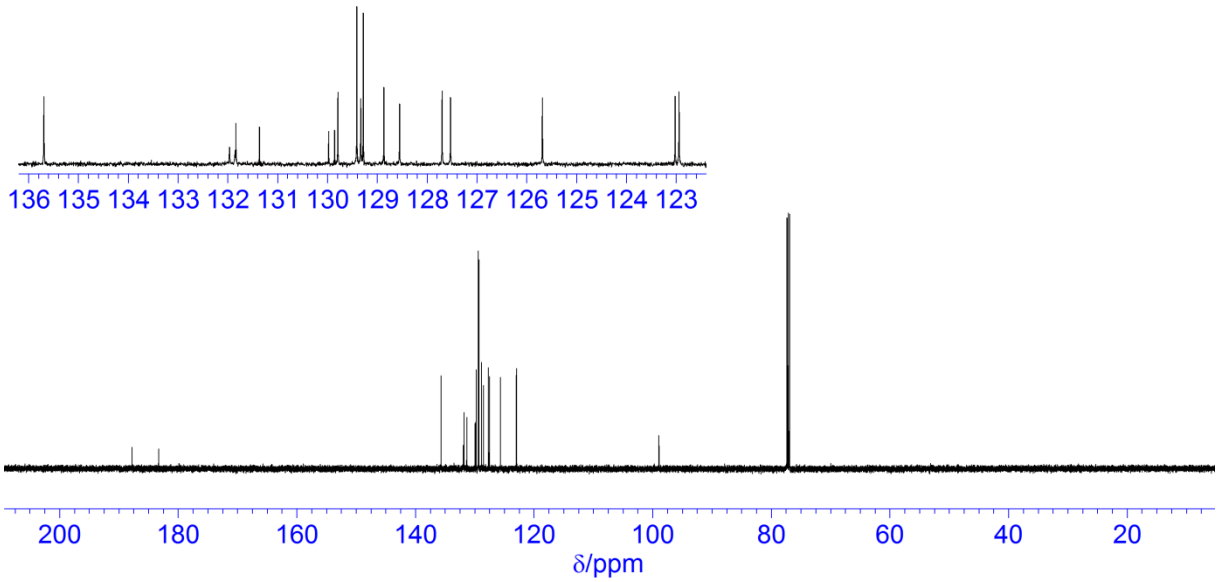


Figure S18. ^{13}C NMR spectrum of 1-Phe@Ph in $CDCl_3$.

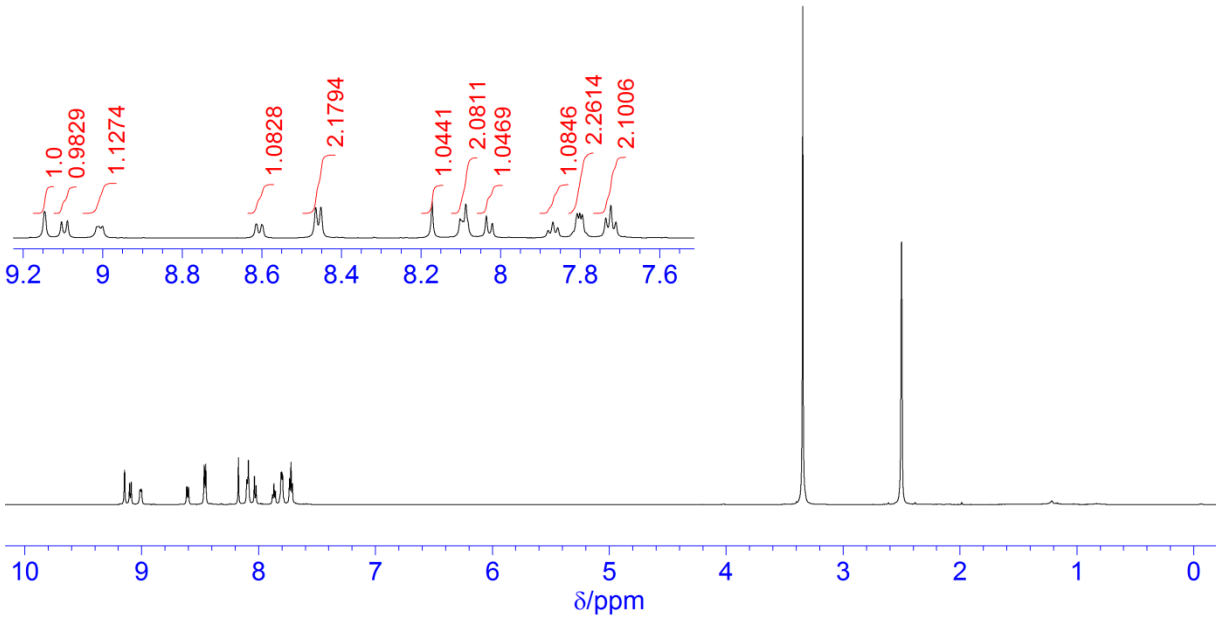


Figure S19. ^{1}H NMR spectrum of 2-Phe@Ph in DMSO-d_6.

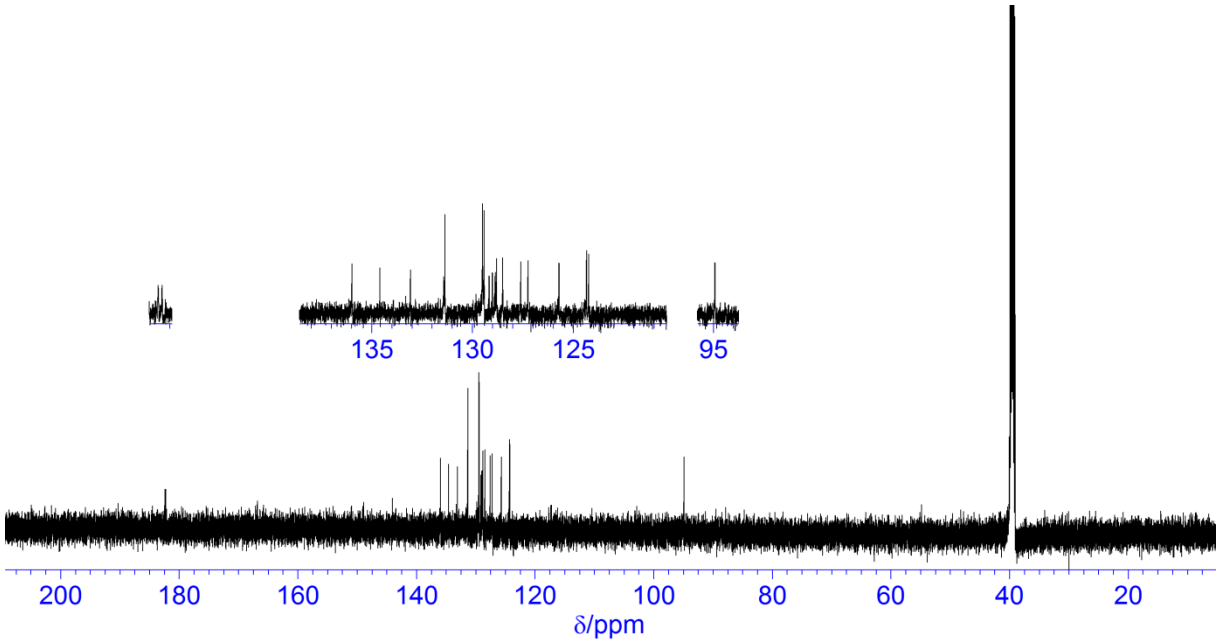


Figure S20. ^{13}C NMR spectrum of 2-Phe@Ph in DMSO-d_6.

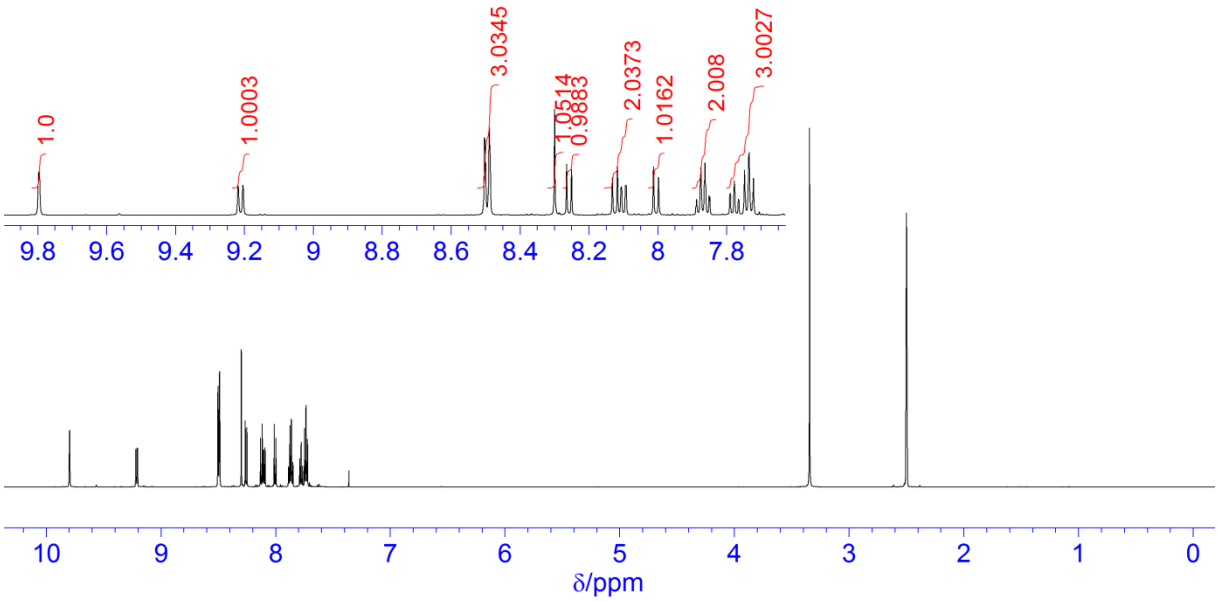


Figure S21. [1]H NMR spectrum of 3-Phe@Ph in DMSO-d_6.

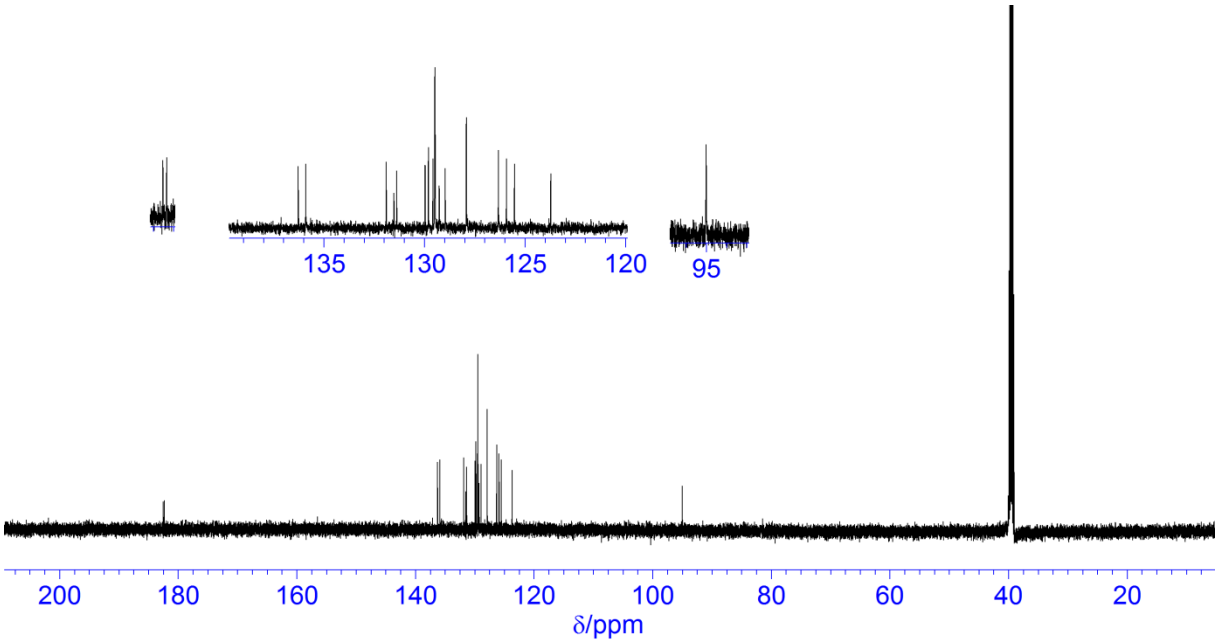


Figure S22. [13]C NMR spectrum of 3-Phe@Ph in DMSO-d_6.

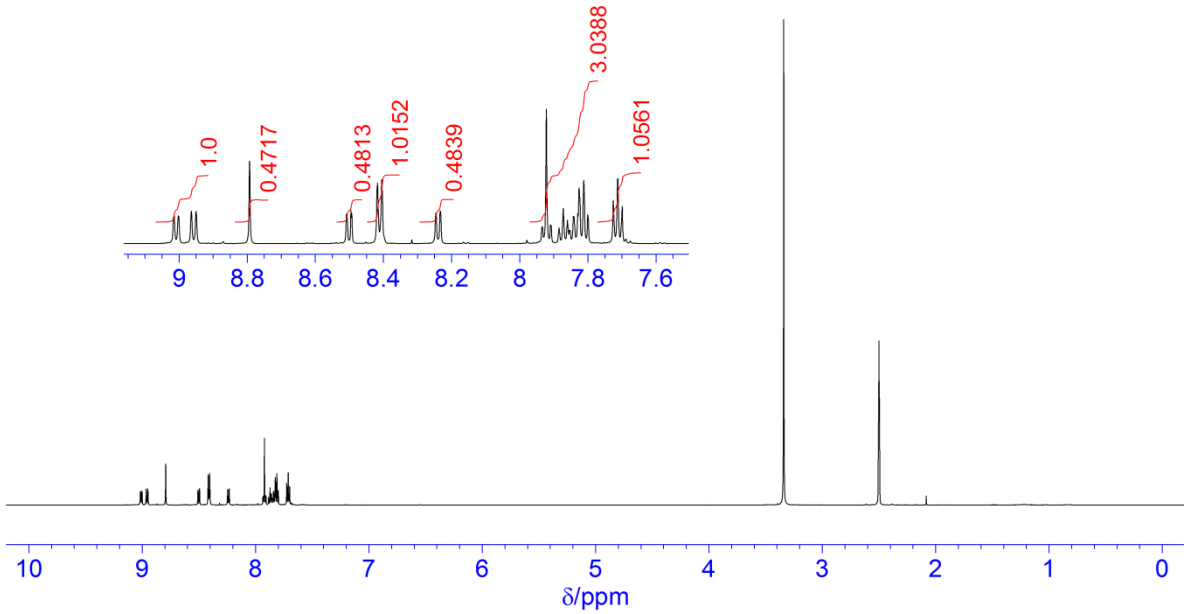


Figure S23. ^{1}H NMR spectrum of 9-Phe@Ph in DMSO-d_6.

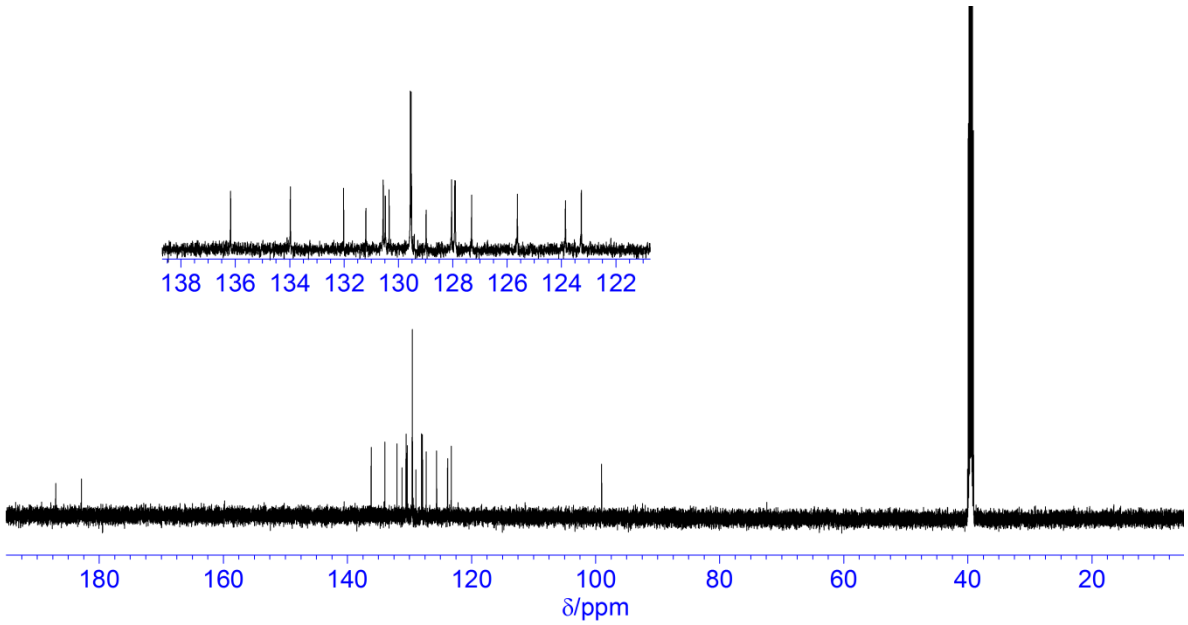


Figure S24. ^{13}C NMR spectrum of 9-Phe@Ph in DMSO-d_6.

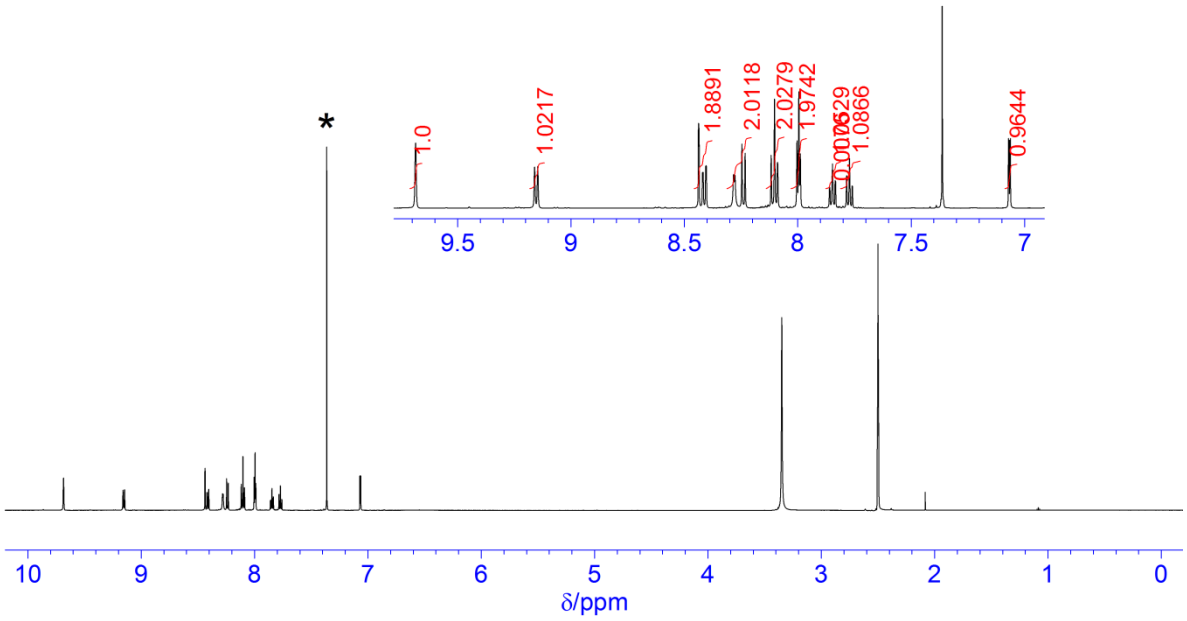


Figure S25. ^{1}H NMR spectrum of 3-Phe@F in DMSO-d_6.

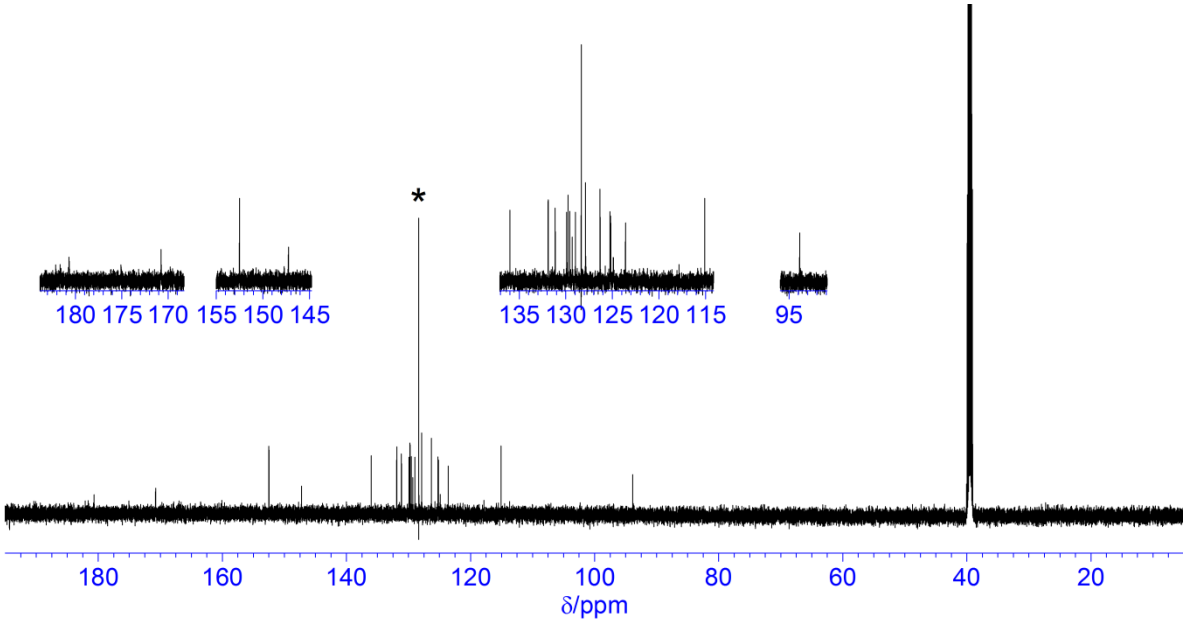


Figure S26. ^{13}C NMR spectrum of 3-Phe@F in DMSO-d_6. * Benzene.

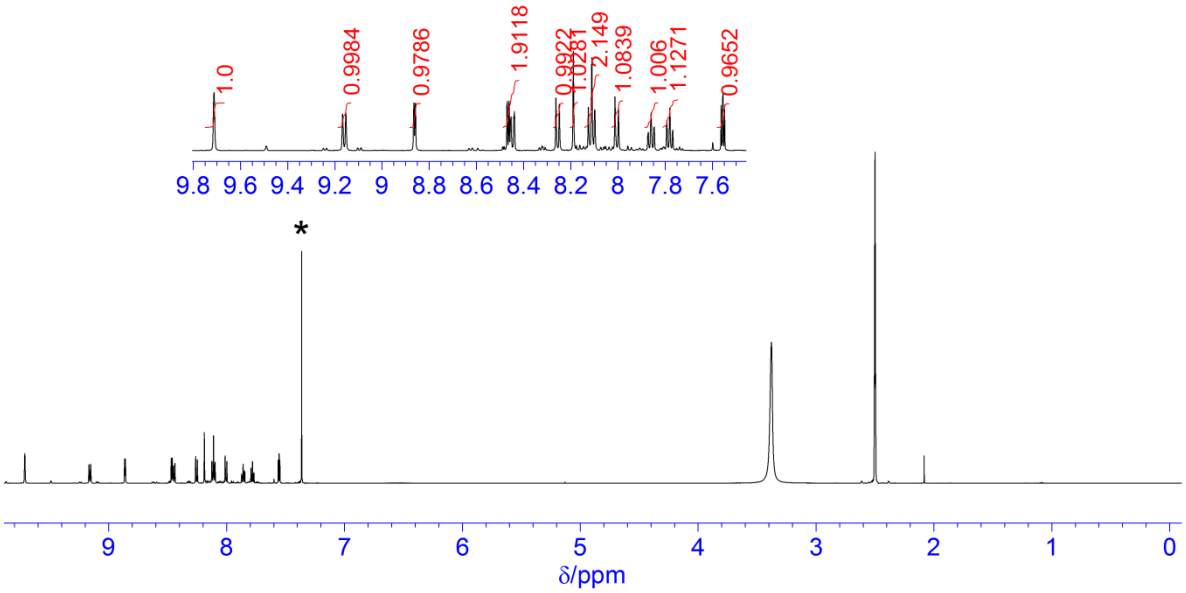


Figure S27. [1]H NMR spectrum of 3-Phe@T in DMSO-d_6.

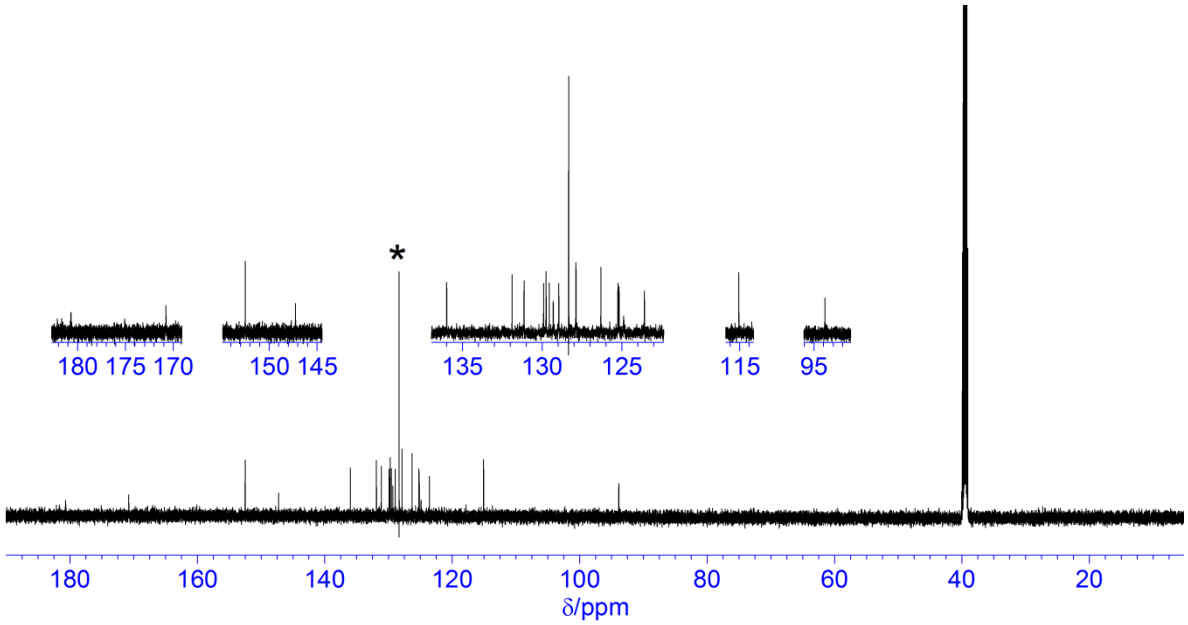


Figure S28. [13]C NMR spectrum of 3-Phe@T in DMSO-d_6. * Benzene.

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