Supporting Information

for

Direct C–H trifluoromethylation of di- and trisubstituted alkenes by photoredox catalysis

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Experimental procedures and NMR spectra

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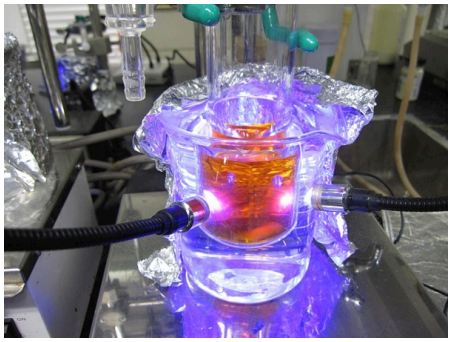
Materials and methods

$[Ru(bpy)_3](PF_6)_2$[1] and *fac*-$Ir(ppy)_3$[2] were prepared according to the literature procedures. Umemoto's reagent (**1a**) was purchased from Aldrich. Alkenes **2b**, **2c**, **2d**, **2e**, **2f**, **2g**, **2h**, **2j**, and **2k** were prepared by Wittig reactions. (*E*)-1,2-diphenyl-1-(4-methoxyphenyl)ethylene (**2m**) prepared according to the literature procedure[3]. Catalytic reactions were performed under an atmosphere of nitrogen using standard Schlenk techniques unless otherwise noted. All solvents were dried over molecular sieves, degassed and stored under N_2. Thin-layer chromatography was performed on Merck TLC plate with 60 F_{254}. Visible light irradiations were performed with a Relyon LED lamp (3 W x 2; λ_{max} = 425 ± 15 nm). Japan Analytical Industry LC-9201 was utilized for recycling preparative HPLC (GPC). The ^1H NMR was acquired on Bruker AVANCE-400 (400 MHz). NMR chemical shifts were referenced to residual protio impurities in the deuterated solvent. HRMS (ESI-TOF mass spectra) were obtained with a Bruker micrOTOF II.

Reaction apparatus

Irradiation of visible light was performed with a Relyon LED lamp (3 W x 2; λ_{max} = 425 nm).



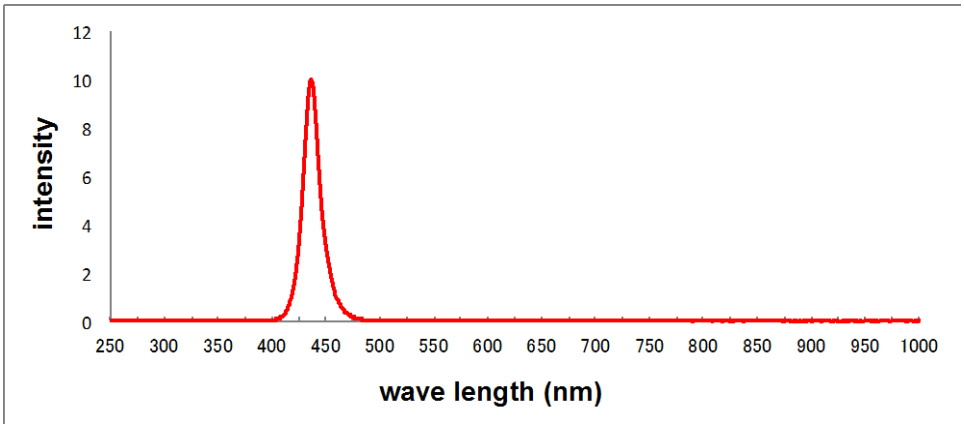
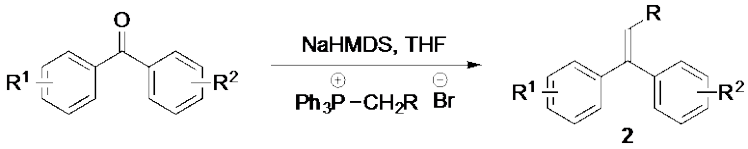


Figure S1: The emission spectrum of a Relyon LED lamp.

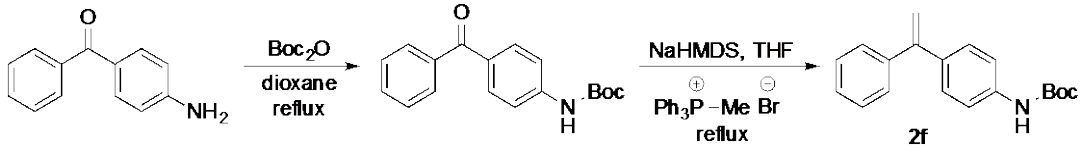
Synthesis of alkene 2

General procedure for the synthesis of alkenes (2b, 2c, 2d, 2e, 2g, 2h, 2j and 2k) by Wittig reaction



Under N_2, a 2-neck 100 mL round-bottom flask was charged with Wittig reagent (6 mmol) and dry THF (25 mL). Then sodium hexamethyldisilazide (1 M THF solution, 6 mL) was added into the solution and stirred at room temperature for 1 h. To the solution, benzophenone derivative (5 mmol) was added and stirred at room temperature overnight. Et_2O was added into the reaction mixture and filtered. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel to afford the product.

The synthesis of *N*-(*tert*-butoxycarbonyl)-4-(1-phenylvinyl)aniline (2f)



***N*-(*tert*-Butoxycarbonyl)-4-benzoylaniline:** A 2-neck 100 mL round-bottom flask was charged with 4-aminobenzophenone (1.97 g, 10 mmol), di-*tert*-butyl dicarbonate (2.84 g, 13 mmol), and 1,4-dioxane (30 mL). The solution was refluxed overnight and cooled to room temperature. The reaction mixture was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 4:1) to afford *N*-(*tert*-butoxycarbonyl)-4-benzoylaniline (1.35 g, 46% yield).

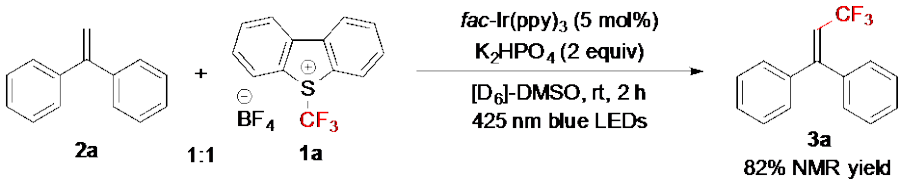
***N*-(*tert*-Butoxycarbonyl)-4-(1-phenylvinyl)aniline (2f):** Under N_2, a 2-neck 100 mL round-bottom flask was charged with methyltriphenylphosphonium bromide (1.07 g, 3 mmol) and dry THF (15 mL). Then sodium hexamethyldisilazide (1 M THF solution, 3 mL) was added into the solution and stirred at room temperature for 1 h. To the yellow solution, *N*-(*tert*-butoxycarbonyl)-4-benzoylaniline (0.53 g, 1.8 mmol) was added and refluxed overnight. After cooling to room temperature, Et_2O was added into the reaction mixture and filtered. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 4:1) to afford *N*-(*tert*-butoxycarbonyl)-4-(1-phenylvinyl)aniline (0.23 g, 44% yield).

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.34-7.26 (m, 9 H, Ar), 6.48 (brs, 1 H, N*H*), 5.41 (d, *J* = 1.2 Hz, C=C*H*H), 5.38 (d, *J* = 1.2 Hz, C=CH*H*), 1.53 (s, 9 H, C(CH_3)$_3$). **^{13}C NMR** (100 MHz, $CDCl_3$, rt): δ 152.8, 149.6, 141.7, 138.1, 136.4, 129.0, 128.4, 128.3, 127.8, 118.3, 113.6, 80.7,

28.5. **HRMS** (ESI-TOF): calculated for $[C_{19}H_{21}NO_2+Na]^+$ requires 318.1465, found 318.1464.

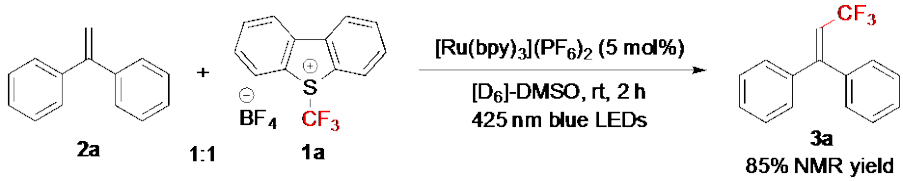
Typical NMR experimental procedures and NMR spectra

NMR experimental procedure (entry 1 in Table 1)



Under N_2, *fac*-Ir(ppy)$_3$ (0.8 mg, 1.3 μmol), Umemoto's reagent (**1a**, 8.5 mg, 25 μmol), K_2HPO_4 (8.7 mg, 50 μmol), 1,1-diphenylethylene (**2a**, 4.3 μL, 25 μmol), $SiEt_4$ (~1 μL) as an internal standard, and [D_6]-DMSO (0.5 mL) were added to an NMR tube. The reaction was carried out at room temperature (water bath) under irradiation of visible light (placed at a distance of ~3 cm from a blue LED lamp: $h\nu$ = 425 ± 15 nm).

NMR experimental procedure (entry 8 in Table 1) and NMR spectra



Under N_2, [Ru(bpy)$_3$](PF$_6$)$_2$ (1.1 mg, 1.3 μmol), Umemoto's reagent (**1a**) (8.5 mg, 25 μmol), 1,1-diphenylethylene (**2a**) (4.3 μL, 25 μmol), $SiEt_4$ (~1 μL) as an internal standard, and [D_6]-DMSO (0.5 mL) were added to an NMR tube. The reaction was carried out at room temperature (water bath) under irradiation of visible light (placed at a distance of ~3 cm from blue LED lamp: $h\nu$ = 425 ± 15 nm).

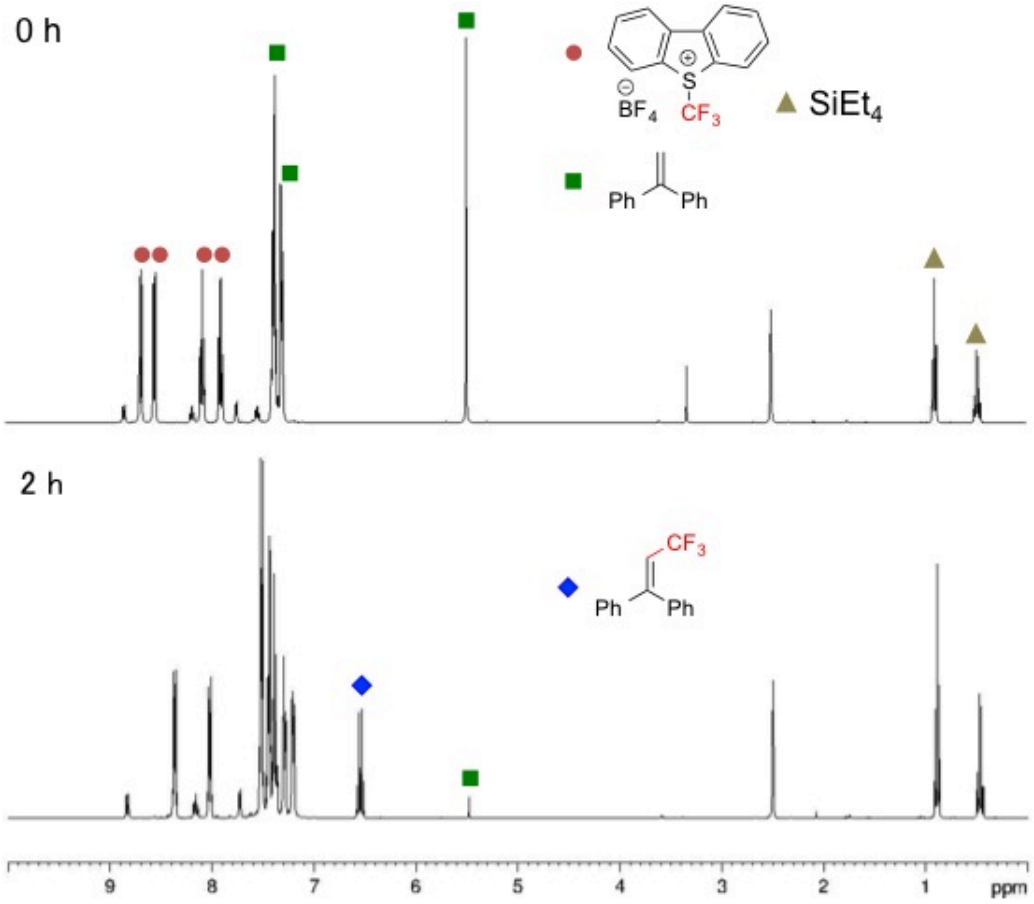
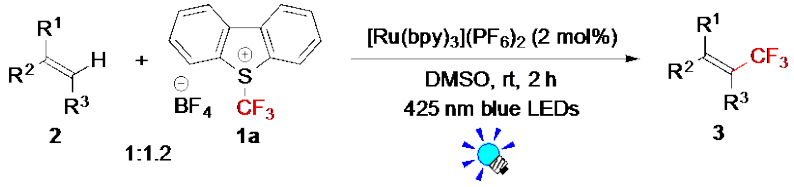


Figure S2. ^{1}H NMR spectra (400 MHz, [D_6]-DMSO, rt)

General procedure for the photocatalytic C−H trifluoromethylation of alkenes (Table 2, 3a–e, g–m)



A 20 mL-Schlenk tube was charged with Umemoto's reagent (**1a**, 102 mg, 0.3 mmol, 1.2 equiv.), $[Ru(bpy)_3](PF_6)_2$ (4.3 mg, 2 mol %), alkene **2** (0.25 mmol), and DMSO (2.5 mL) under N_2. The tube was irradiated for 2 h at room temperature (water bath) with stirring by 3 W blue LED lamps ($h\nu$ = 425 nm ± 15 nm) placed at a distance of 2−3 cm. After the reaction, H_2O was added. The resulting mixture was extracted with Et_2O, washed with H_2O, dried (Na_2SO_4), and filtered. The filtrate was concentrated in vacuo. The product was purified in two ways as described below.

For products **3b**, **3e**, **3g**, **3h**, **3k** and **3m**, the residue was purified by flash column chromatography on silica gel (eluent: hexane and Et_2O) to afford the corresponding product **3**.

For products **3a**, **3c**, **3d**, **3i**, **3j** and **3l**, the residue was treated by mCPBA (74 mg, ca. 0.3 mmol)

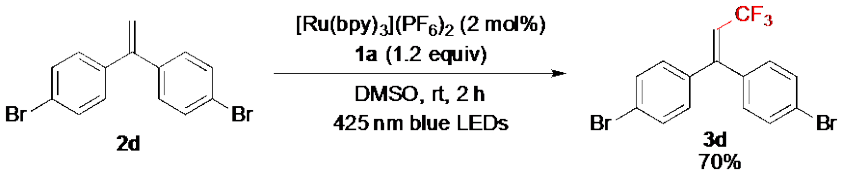
in CH_2Cl_2 to convert the dibenzothiophene to sulfoxide, which was more easily separated from the products. After the solution was stirred at room temperature for 2 h, an aqueous solution of $Na_2S_2O_3 \cdot 5H_2O$ was added to the solution, which was extracted with CH_2Cl_2. The organic layer was washed with H_2O, dried (Na_2SO_4), and filtered. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (eluent: hexane) to afford the corresponding product **3**. Further purification of **3c** and **3d** by GPC provided pure **3c** and **3d**. **3a**[4], **3b**[5], **3e**[5], **3j**[6], **3l**[7] and **3m**[7] were confirmed by published data.

1,1-Bis(4-chlorophenyl)-3,3,3-trifluoropropene (3c)

According to the general procedure, the title compound was synthesized from 1,1-bis(4-chlorophenyl)ethylene (**2c**, 62 mg, 0.25 mmol). The product was purified by silica gel flash column chromatography (hexane) to afford **3c** (82%) as a product mixture with bis(trifluoromethyl)alkene **4c** (8%). The yields were determined by ^{19}F NMR using α,α,α-trifluorotoluene as an internal standard. Further purification by GPC provided pure **3c** in 53% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.38 (d, J = 8.8 Hz, 2 H, Ar), 7.32 (d, J = 8.8 Hz, 2 H, Ar), 7.16 (d, J = 8.4 Hz, 4 H, Ar), 6.12 (q, J = 8.1 Hz, 1 H, C=C*H*CF_3). **^{13}C NMR** (100 MHz, $CDCl_3$, rt): δ 150.4 (q, J = 5.4 Hz), 138.3, 136.1, 135.3, 135.2, 130.6, 129.3, 129.0, 128.7, 122.9 (q, J = 269 Hz), 116.5 (q, J = 33.9 Hz). **^{19}F NMR** (376.5 MHz, $CDCl_3$, rt): δ -55.76 (d, J = 7.91 Hz, 3 F). **HRMS** (ESI-TOF): calculated for $[C_{15}H_9Cl_2F_3+Na]^+$ requires 338.9926, found 338.9967.

1,1-Bis(4-bromophenyl)-3,3,3-trifluoropropene (3d)

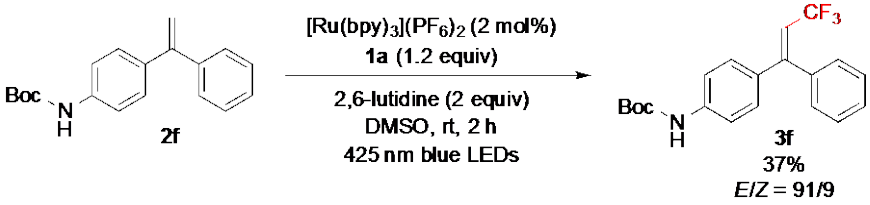


According to the general procedure, the title compound was synthesized from 1,1-bis(4-bromophenyl)ethylene (**2d**, 85 mg, 0.25 mmol). The product was purified by silica gel flash column chromatography (hexane) to afford **3d** (84%) as a product mixture with bis(trifluoromethyl)alkene **4d** (6%). The yields were determined by ^{19}F NMR using α,α,α-trifluorotoluene as an internal standard. Further purification by GPC provided pure **3d** in

70% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.54 (d, *J* = 8.4 Hz, 2 H, Ar), 7.47 (d, *J* = 8.4 Hz, 2 H, Ar), 7.10 (d, *J* = 8.4 Hz, 4 H, Ar), 6.12 (q, *J* = 8.1 Hz, 1 H, C=C*H*CF_3). **^{13}C NMR** (100 MHz, $CDCl_3$, rt): δ 150.4 (q, *J* = 5.4 Hz), 138.6, 135.7, 132.0, 131.7, 130.9, 129.6, 124.3, 123.4, 122.9 (q, *J* = 269 Hz), 116.5 (q, *J* = 34.0 Hz). **^{19}F NMR** (376.5 MHz, $CDCl_3$, rt): δ -55.72 (d, *J* = 7.91 Hz, 3 F). **HRMS** (ESI-TOF): calculated for $[C_{15}H_9Br_2F_3+Na]^+$ requires 426.8915, found 426.9055.

***N*-(*tert*-Butoxycarbonyl)-4-(1-phenyl-3,3,3-trifluoropropenyl)aniline (3f)**



A 20 mL-Schlenk tube was charged with Umemoto's reagent (**1a**, 102 mg, 0.3 mmol, 1.2 equiv.), $[Ru(bpy)_3](PF_6)_2$ (4.3 mg, 2 mol %), *N*-(*tert*-butoxycarbonyl)-4-(1-phenylvinyl)aniline (**2f**, 74 mg, 0.25 mmol), 2,6-lutidine (58 μL, 0.5 mmol, 2 equiv) and DMSO (2.5 mL) under N_2. The tube was irradiated for 2 h at room temperature (water bath) with stirring by 3 W blue LED lamps (*hν* = 425 nm ± 15 nm) placed at a distance of 2−3 cm. After the reaction, H_2O was added. The resulting mixture was extracted with Et_2O, washed with H_2O, dried (Na_2SO_4), and filtered. The filtrate was concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane→hexane/EtOAc = 9:1) to afford **3f** (60 mg, 59% yield, *E*/*Z* = 91:9) as a product mixture with bis(trifluoromethyl)alkene **4f** (21%). The yields were determined by ^{19}F NMR using α,α,α-trifluorotoluene as an internal standard. Further purification by GPC provided pure **3f** in 37% isolated yield. The stereochemistry was confirmed by ^{1}H NOESY NMR.

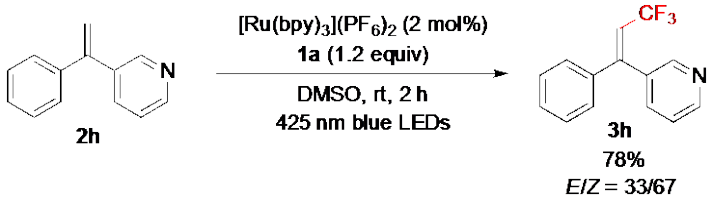
^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.38 (m, 3 H, Ar), 7.32 (d, *J* = 8.8 Hz, 2 H, Ar), 7.22 (m, 2H, Ar), 7.17 (d, *J* = 8.4 Hz, 2 H, Ar), 6.53 (brs, 1 H, N*H*), 6.08 (q, *J* = 8.4 Hz, 1 H, C=C*H*CF_3 in *E*-isomer), 6.06 (q, *J* = 8.0 Hz, 1 H, C=C*H*CF_3 in *Z*-isomer), 1.53 (s, 9 H, C(CH_3)$_3$ in *Z*-isomer), 1.52 (s, 9 H, C(CH_3)$_3$ in *E*-isomer). **^{13}C NMR** (100 MHz, $CDCl_3$, rt): δ 152.6, 152.0 (q, *J* = 5.3 Hz), 139.8, 137.5, 134.7, 129.3, 128.9, 128.6, 128.1, 123.4 (q, *J* = 269 Hz), 118.32, 114.2 (q, *J* = 33.6 Hz), 81.1, 28.4. **^{19}F NMR** (376.5 MHz, $CDCl_3$, rt): δ -55.32 (d, *J* = 8.28 Hz, 3 F, *E*-isomer), -55.56 (d, *J* = 9.04 Hz, 3 F, *Z*-isomer). **HRMS** (ESI-TOF): calculated for $[C_{20}H_{20}F_3NO_2+Na]^+$ requires 386.1338, found 386.1332.

3,3,3-Trifluoro-1-(4-nitrophenyl)-1-phenylpropene (3g)

According to the general procedure, the title compound was synthesized from 1-(4-nitrophenyl)-1-phenylethylene (**2g**, 56 mg, 0.25 mmol). The product was purified by silica gel flash column chromatography (hexane→hexane/Et_2O = 19:1) to afford **3g** (39 mg, 51% yield, *E*/*Z* = 17:83). The stereochemistry was confirmed by ^{1}H NOESY NMR.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.27 (d, *J* = 8.8 Hz, 2 H, Ar in *Z-isomer*), 8.19 (d, *J* = 8.8 Hz, 2 H, Ar in *E-isomer*), 7.45-7.35 (m, 5 H, Ar), 7.21 (d, *J* = 8.0 Hz, 2 H, Ar), 6.25 (q, *J* = 8.1 Hz, 1 H, C=C*H*CF_3 in *Z-isomer*), 6.22 (q, *J* = 8.0 Hz, 1 H, C=C*H*CF_3 in *Z-isomer*). **^{13}C NMR** (100 MHz, $CDCl_3$, rt): δ 150.4 (q, *J* = 5.4 Hz), 148.5, 148.2, 146.4, 144.1, 138.7, 136.1, 130.3, 130.2, 129.3, 129.1, 129.0, 128.6, 127.9, 123.9, 123.5, 122.8 (q, *J* = 269 Hz), 118.6 (q, *J* = 33.8 Hz, *E*-isomer), 117.1 (q, *J* = 34.0 Hz, *Z*-isomer). **^{19}F NMR** (376.5 MHz, $CDCl_3$, rt): δ -55.72 (d, *J* = 8.28 Hz, 3 F, *Z-isomer*), -56.23 (d, *J* = 8.00 Hz, 3 F, *E-isomer*). **HRMS** (ESI-TOF): calculated for $[C_{15}H_{10}F_3NO_2+Na]^+$ requires 316.0556, found 316.0553.

3,3,3-Trifluoro-1-phenyl-1-(3-pyridyl)propene (3h)



According to the general procedure, the title compound was synthesized from 1-phenyl-1-(3-pyridyl)ethylene (**2h**) (45 mg, 0.25 mmol). The product was purified by silica gel flash column chromatography (hexane→hexane/Et_2O = 1:1) to afford **3h** (48 mg, 78% yield, *E*/*Z* = 33:67). The stereochemistry was confirmed by ^{1}H NOESY NMR.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.66 (dd, *J* = 4.8, 1.6 Hz, 1H, Ar in *Z*-isomer), 8.60 (dd, *J* = 4.8, 1.2 Hz, 1H, Ar in *E-isomer*), 8.56 (d, *J* = 2.0 Hz, 1 H, Ar in *E-isomer*), 8.52 (d, *J* = 1.6 Hz, 1H, Ar in *Z-isomer)*, 7.57 (d, *J* = 7.8 Hz, 1 H, Ar in *Z-isomer*), 7.51 (d, *J* = 8.1 Hz, 1 H, Ar in *E-isomer*), 7.42-7.33 (m, 3 H, Ar), 7.28-7.22(m, 2 H, Ar), 6.23 (q, *J* = 8.1 Hz, 1 H, C=C*H*CF_3 in *Z-isomer*) 6.16 (q, *J* = 8.0 Hz, 1 H, C=C*H*CF_3 in *E-isomer*). **^{13}C NMR** (100 MHz, $CDCl_3$, rt): δ 150.5, 149.9, 149.6, 149.1 (q, *J* = 5.3 Hz), 148.8, 139.3, 136.6, 136.3, 136.0, 135.4, 133.3, 130.0, 129.1, 128.9, 128.5, 128.0, 123.4, 123.1, 122.9 (q, *J* = 269 Hz, *Z*-isomer), 122.8 (q, *J* = 270 Hz, *E*-isomer), 117.3 (q, *J* = 33.4 Hz, *Z*-isomer), 116.9 (q, *J* = 33.3 Hz, *E*-isomer). **^{19}F NMR**

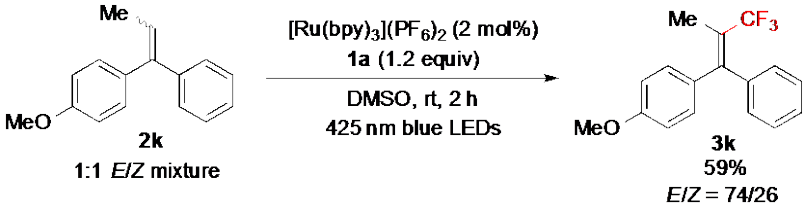
(376.5 MHz, $CDCl_3$, rt): δ -55.58 (d, *J* = 8.28 Hz, 3 F, *Z-isomer*), -55.99 (d, *J* = 8.28 Hz, 3 F, *E-isomer*). **HRMS** (ESI-TOF): calculated for $[C_{14}H_{10}F_3N+Na]^+$ requires 272.0658, found 272.0657.

1,1,1-Trifluoro-3,5-diphenyl-5-methyl-2-hexene (3i)

According to the general procedure, the title compound was synthesized from 2,4-diphenyl-4-methyl-1-pentene (**2i**, 59 mg, 0.25 mmol). The product was purified by silica gel flash column chromatography (hexane) to afford **3i** (45 mg, 58% yield, *E*/*Z* = 88:12). The stereochemistry was confirmed by ^{1}H NOESY NMR.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.21-7.10 (m, 9 H, Ar), 7.06 (t, *J* = 7.0 Hz, Ar), 5.66 (q, *J* = 8.8 Hz, 1 H, C=C*H*CF_3 in *E*-isomer), 5.37 (q, *J* = 8.4 Hz, 1 H, C=C*H*CF_3 in *Z*-isomer), 3.09 (d, *J* = 1.2 Hz, 2 H, CCH_2C in *E*-isomer), 2.80 (d, *J* = 1.2 Hz, 2 H, CCH_2C in *Z*-isomer), 1.24 (s, 6 H, CH_3 in *Z*-isomer), 1.21 (s, 6 H, CH_3 in *E*-isomer). **^{13}C NMR** (100 MHz, $CDCl_3$, rt): δ 152.7 (q, *J* = 5.4 Hz), 149.3, 141.8, 128.3, 128.0, 127.0, 125.8, 125.7, 123.4 (q, *J* = 269 Hz), 119.6 (q, *J* = 33.1 Hz), 44.5, 38.4, 28.8. **^{19}F NMR** (376.5 MHz, $CDCl_3$, rt): δ –55.87 (d, *J* = 8.28 Hz, 3 F, *Z*-isomer), -55.96 (d, *J* = 9.41 Hz, 3 F, *E*-isomer). **HRMS** (ESI-TOF): calculated for $[C_{19}H_{19}F_3+Na]^+$ requires 327.1331, found 327.1332.

3,3,3-Trifluoro-1-(4-methoxyphenyl)-2-methyl-1-phenylpropene (3k)



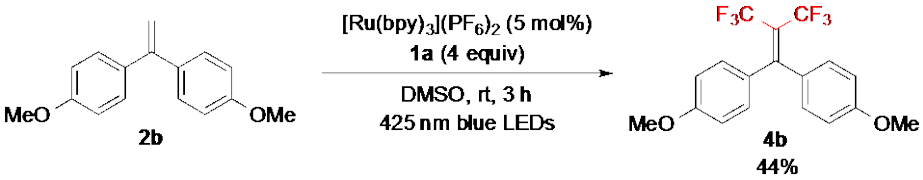
According to the general procedure, the title compound was synthesized from 1-methoxyphenyl-1-phenylpropene (**2k**). The product was purified by silica gel flash column chromatography (hexane→hexane/Et_2O = 29:1) to afford **3k** (45 mg, 59% yield, *E*/*Z* = 74/26). The stereochemistry was confirmed by ^{1}H NOESY NMR.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.34-7.27 (m, 3 H, Ar), 7.14 (d, *J* = 9.6 Hz, 2 H, Ar in *E-isomer*), 7.12 (d, *J* = 8.4 Hz, 2 H, Ar in *Z-isomer*), 7.08 (d, *J* = 8.8 Hz, 2 H, Ar in *Z-isomer*), 7.05 (d, *J* = 8.8 Hz, 2 H, Ar in *E-isomer*), 6.85 (d, *J* = 8.8 Hz, 2 H, Ar in *E-isomer*), 6.82 (d, *J* = 8.8 Hz, 2 H, Ar in *Z-isomer*), 3.80 (s, 3 H, CH_3O in *E-isomer*), 3.79 (s, 3 H, CH_3O in *Z-isomer*),

1.96 (s, 3 H, CH_3CCF_3 in *E-isomer*), 1.90 (s, 3 H, CH_3CCF_3 in *Z-isomer*). **^{13}C NMR** (100 MHz, $CDCl_3$, rt): δ 159.3, 159.3, 147.3, 147.3, 141.8, 141.4, 133.7, 133.4. 130.5, 130.0, 129.0, 128.7, 128.4, 128.0, 127.8, 127.6, 124.8 (q, J = 274 Hz), 123.0 (q, J = 27.9 Hz), 113.8, 113.5, 55.4, 55.3, 16.5. **^{19}F NMR** (376.5 MHz, $CDCl_3$, rt): δ -59.23 (s, 3 F, *E-isomer*), -59.36 (s, 3 F, *Z-isomer*). **HRMS** (ESI-TOF): calculated for $[C_{17}H_{15}F_3O+Na]^+$ requires 315.0967, found 315.0963.

Procedures for the photocatalytic double C−H trifluoromethylation of alkenes

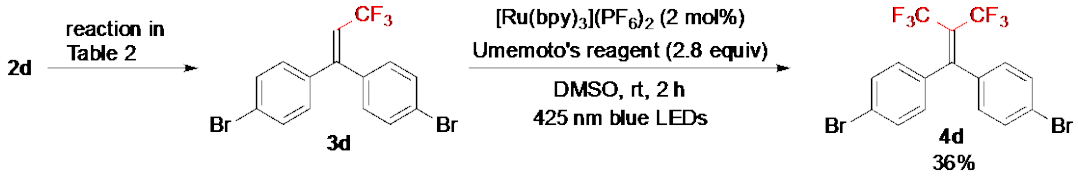
2-Trifluoromethyl-3,3,3-trifluoro-1-bis(4-methoxyphenyl)propene (4b)



A 20 mL-Schlenk tube was charged with Umemoto's reagent (**1a**, 340 mg, 1.0 mmol, 4 equiv), $[Ru(bpy)_3](PF_6)_2$ (10.7 mg, 5 mol %), **2b** (60 mg, 0.25 mmol), and DMSO (5 mL) under N_2. The tube was irradiated for 3 h at room temperature (water bath) with stirring by 3 W blue LED lamps ($h\nu$ = 425 nm ± 15 nm) placed at a distance of 2−3 cm. After the reaction, H_2O was added. The resulting mixture was extracted with Et_2O, washed with H_2O, dried (Na_2SO_4), and filtered. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexane→hexane/Et_2O = 29:1) to afford **4b** as a product mixture with **3b**. Further purification by GPC provided pure **4b** in 44% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.09 (d, J = 8.8 Hz, 4 H, Ar), 6.87 (d, J = 8.8 Hz, 4 H, Ar), 3.83 (s, 6 H, CH_3O). **^{13}C NMR** (100 MHz, $CDCl_3$, rt): δ 161.3, 160.1, 132.3, 131.2, 122.3, (q, J = 273 Hz), 115.7 (q, J = 30.1 Hz), 113.7, 55.4. **^{19}F NMR** (376.5 MHz, $CDCl_3$, rt): δ -54.80 (s, 6 F). **HRMS** (ESI-TOF): calculated for $[C_{18}H_{14}F_6O_2+Na]^+$ requires 399.0790, found 399.0795.

1-Bis(4-bromophenyl)-2-trifluoromethyl-3,3,3-trifluoropropene (4d)



Two-step reactions were conducted. According to the procedure in Table 2, **2d** (85 mg, 0.25 mmol) was converted into the mixture of **3d** and a small amount of **4d** (90 mg). To the mixture, Umemoto's reagent (**1a**, 238 mg), $[Ru(bpy)_3](PF_6)_2$ (4.3 mg) and DMSO (5 mL) were added under N_2. The solution was placed at a distance of 2−3 cm from the 3 W blue LED lamp ($h\nu$ =

425 nm ± 15 nm) and stirred at room temperature (water bath) for 2 h. After the reaction, H_2O was added. The resulting mixture was extracted with Et_2O, washed with H_2O, dried (Na_2SO_4), and filtered. The filtrate was concentrated in vacuo. The residue was treated by mCPBA (0.17 g, ca. 0.7 mmol) in CH_2Cl_2 to convert the dibenzothiophene to sulfoxide, which was more easily separated from the products. After the solution was stirred at room temperature for 2 h, an aqueous solution of $Na_2S_2O_3 \cdot 5H_2O$ was added to the solution, which was extracted with CH_2Cl_2. The organic layer was washed with H_2O, dried (Na_2SO_4), and filtered. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel (eluent: hexane) to afford **4d** as a product mixture with **3d**. Further purification by GPC provided pure **4d** in 36% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.51 (d, J = 8.4 Hz, 4 H, Ar), 7.01 (d, J = 8.4 Hz, 4 H, Ar).

^{13}C NMR (100 MHz, $CDCl_3$, rt): δ 157.9, 137.7, 131.9, 130.3, 124.9, 121.5 (q, J = 276 Hz), 119.4 (q, J = 31.0 Hz), **^{19}F NMR** (376.5 MHz, $CDCl_3$, rt): δ -55.31 (s, 6 F). **HRMS** (ESI-TOF): calculated for $[C_{16}H_8Br_2F_6+Na]^+$ requires 474.8950, found 474.8953.

Time profile of the photocatalytic C−H trifluoromethylation of 2a

The trifluoromethylation of **2a** was performed with/without visible light irradiation. The time profile is shown in Figure S3. As a result, continuous irradiation of visible light is essential for efficient reaction. Furthermore, the result of this experiment suggests that radical chain propagation is not the main component in this reaction.

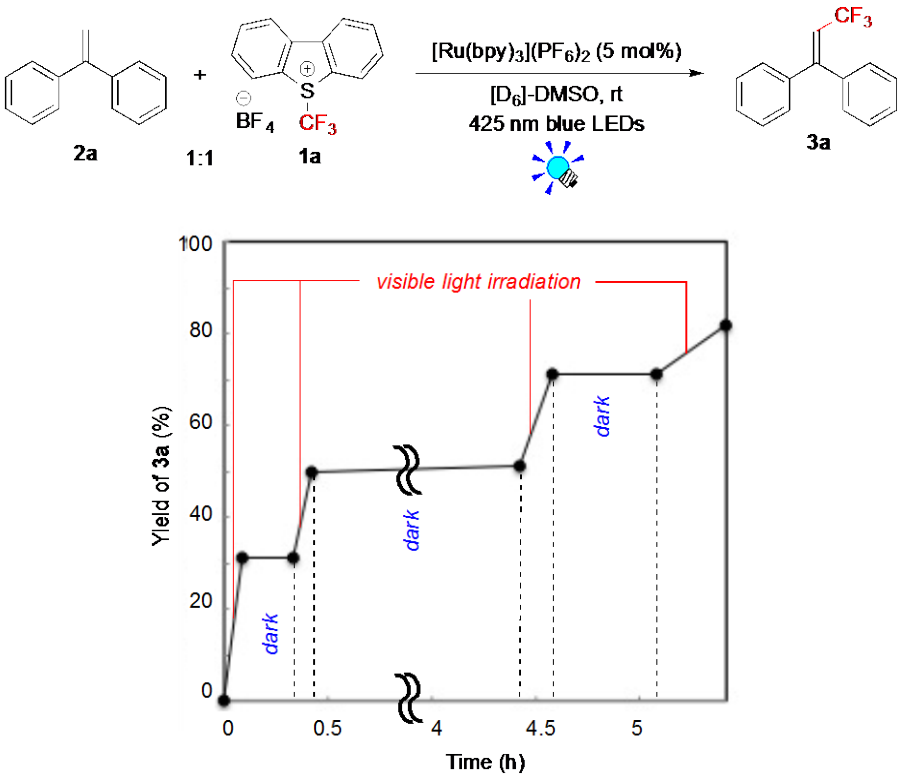
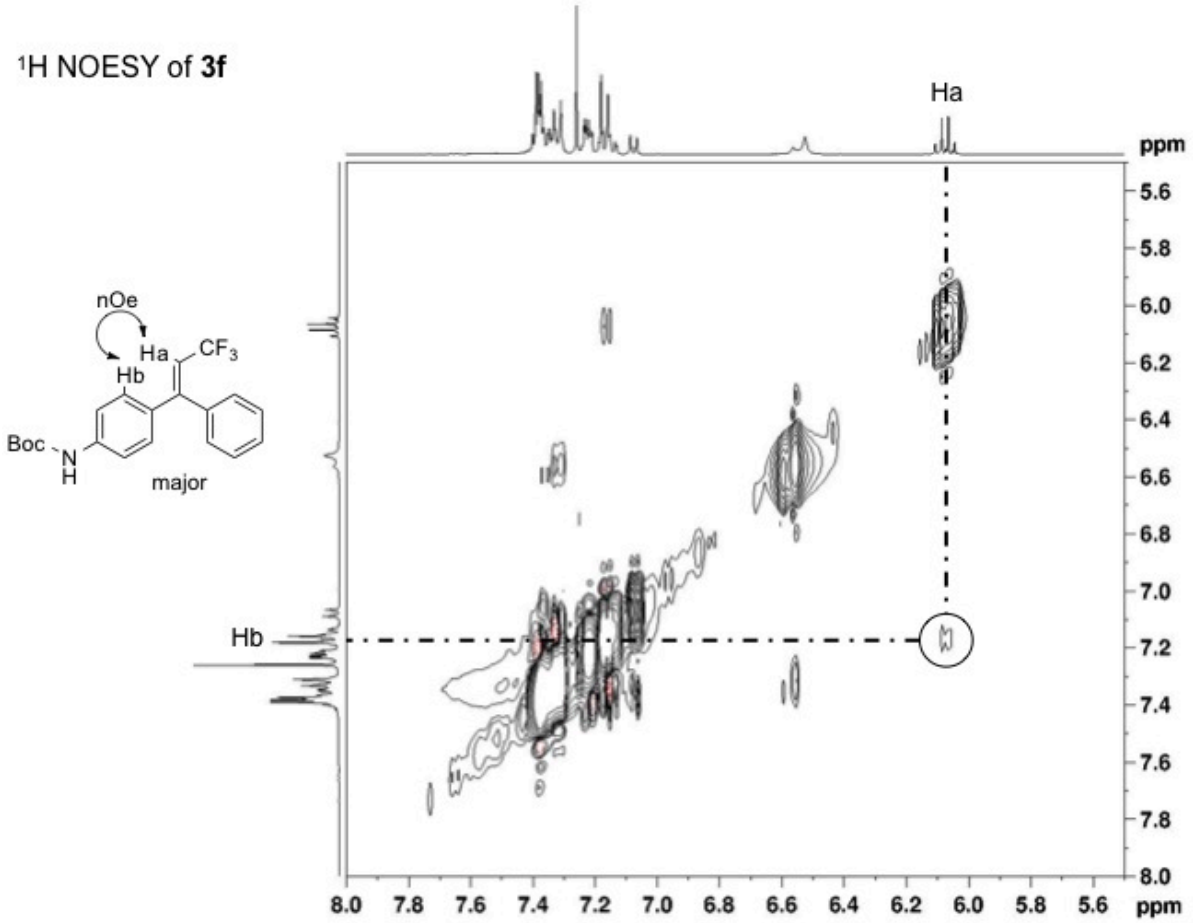
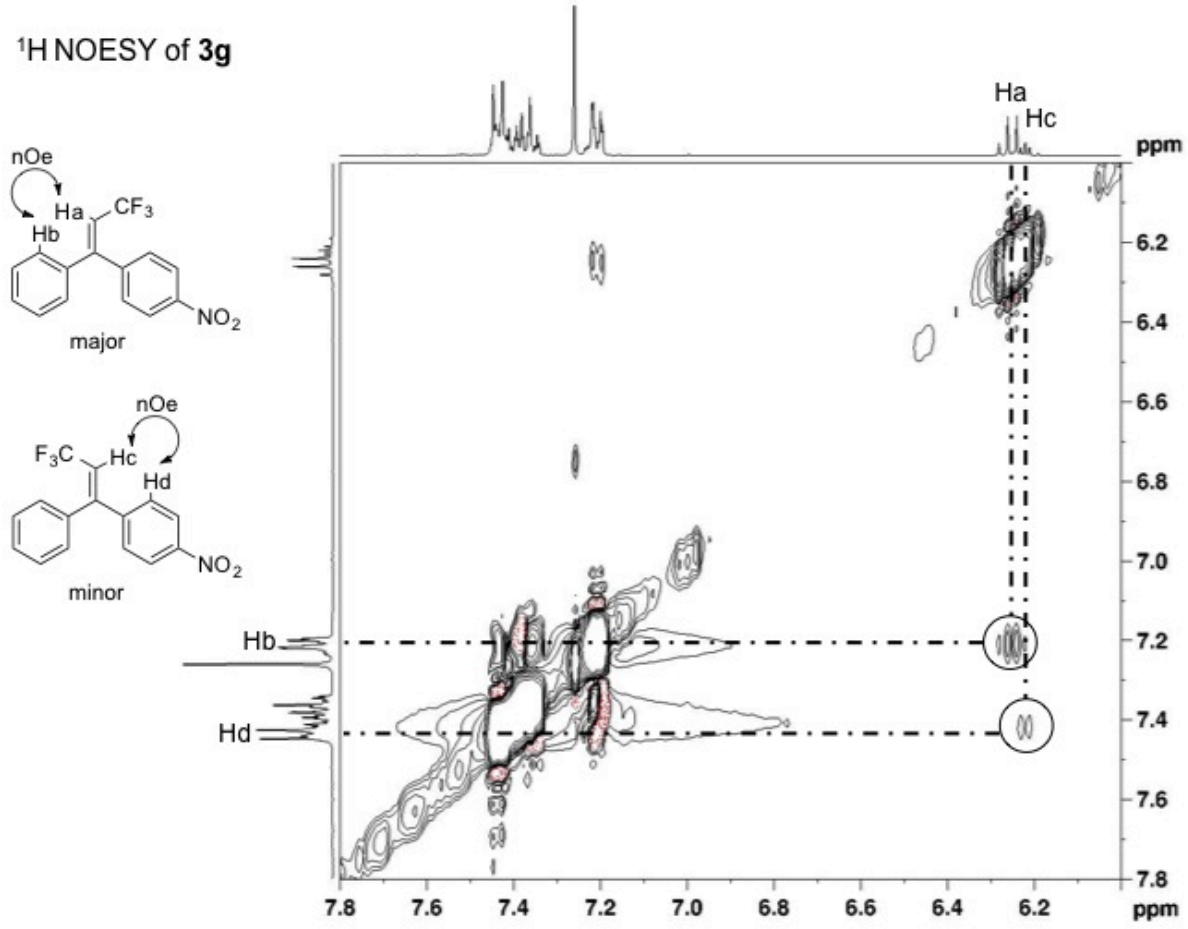


Figure S3: Time profile of the photocatalytic C−H trifluoromethylation of **2a**

^{1}H, ^{13}C NMR spectra

Assignment of stereochemistry of product 3

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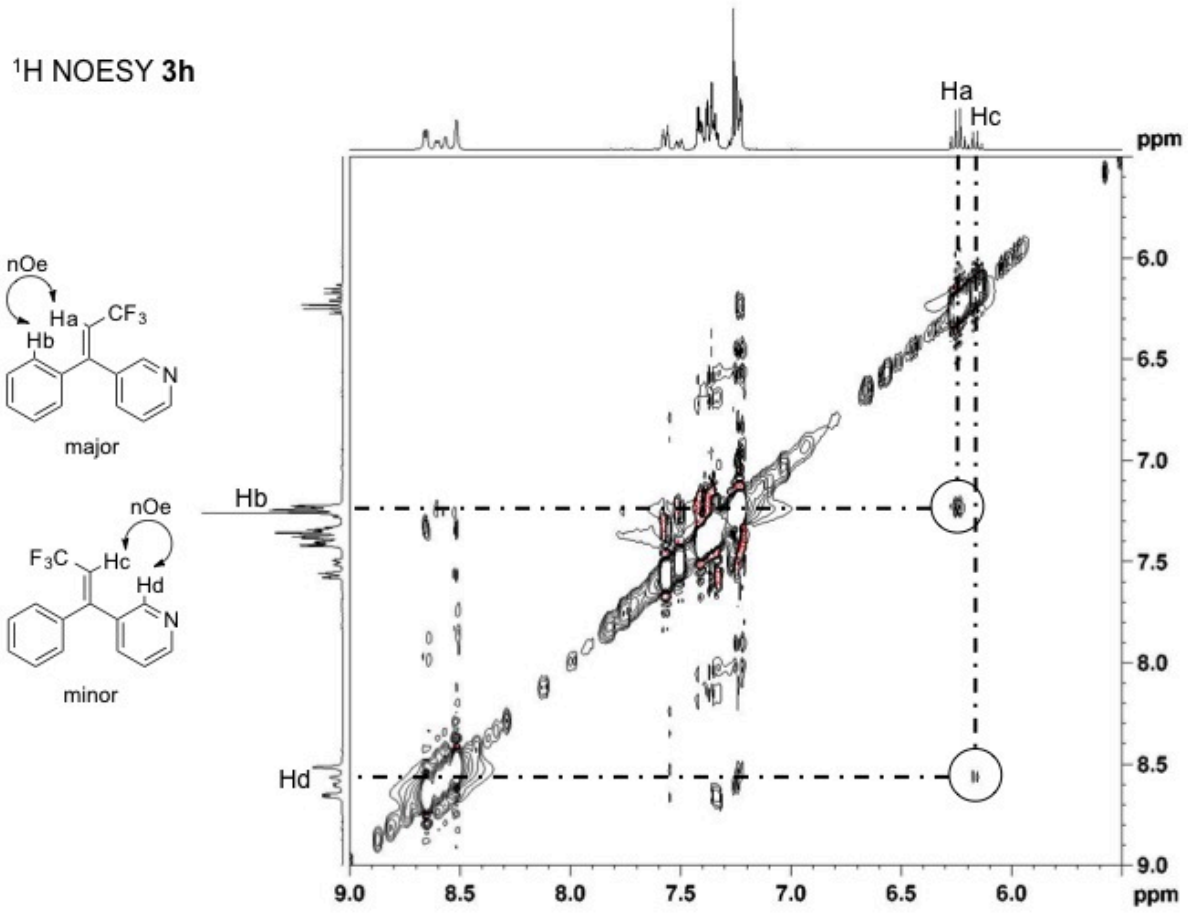
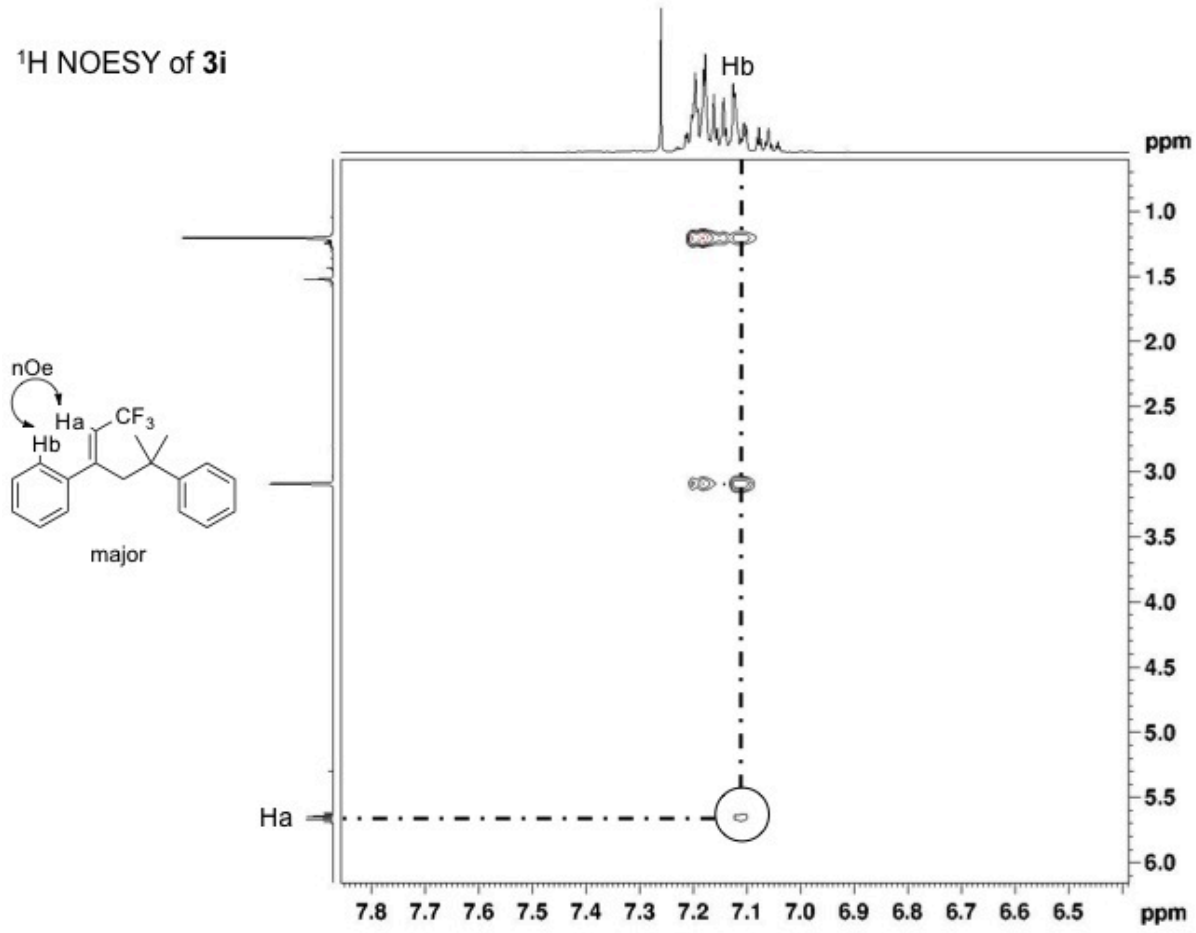
nOe
Ha
CF_3
Hb
NO_2
major
nOe
F_3C
Hc
Hd
NO_2
minor
Ha
Hc
ppm
Hb
Hd
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
ppm


1H NOESY 3h
nOe
Ha
CF3
Hb
N
major
nOe
F3C
Hc
Hd
N
minor
Ha
Hc
ppm
Hb
Hd
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.0
8.5
8.0
7.5
7.0
6.5
6.0
ppm


1H NOESY of 3i
Hb
ppm
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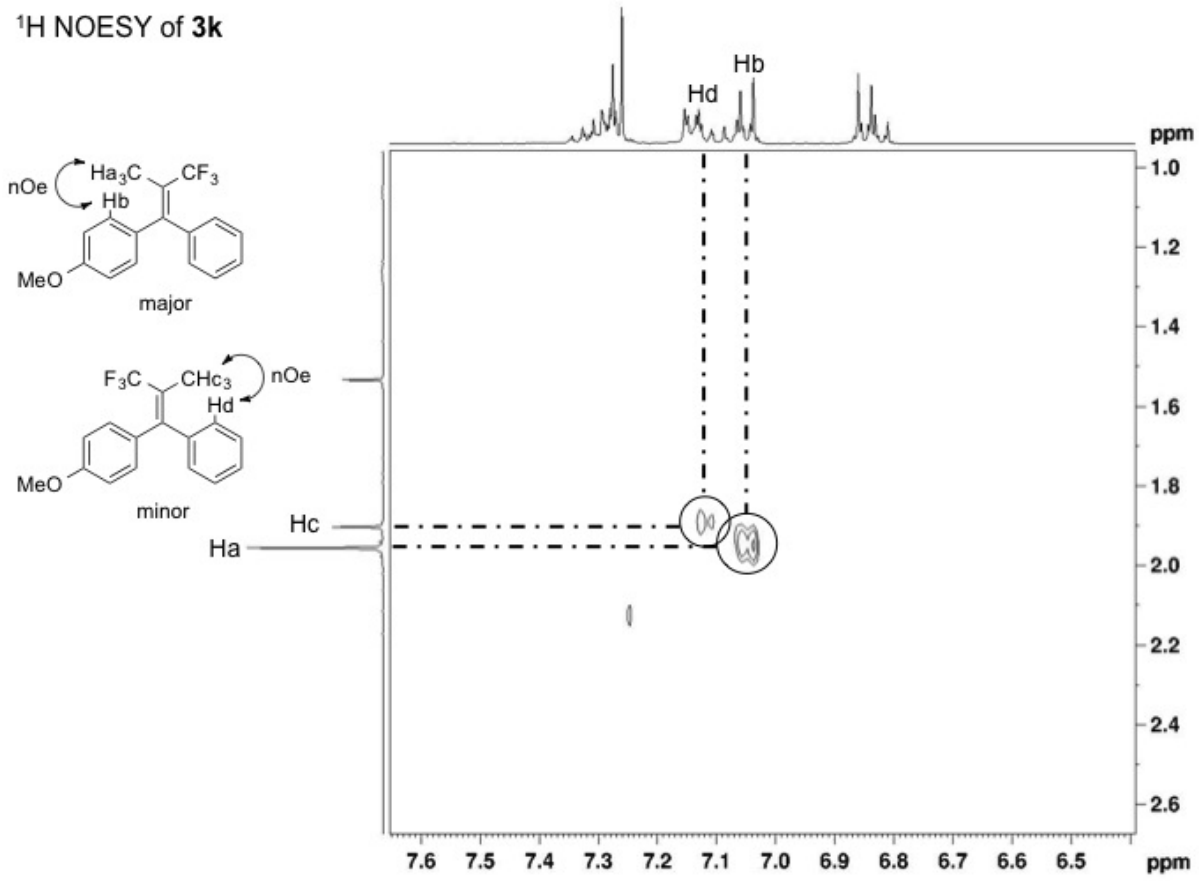
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
nOe
Ha
CF3
Hb
major
Ha
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
ppm



References

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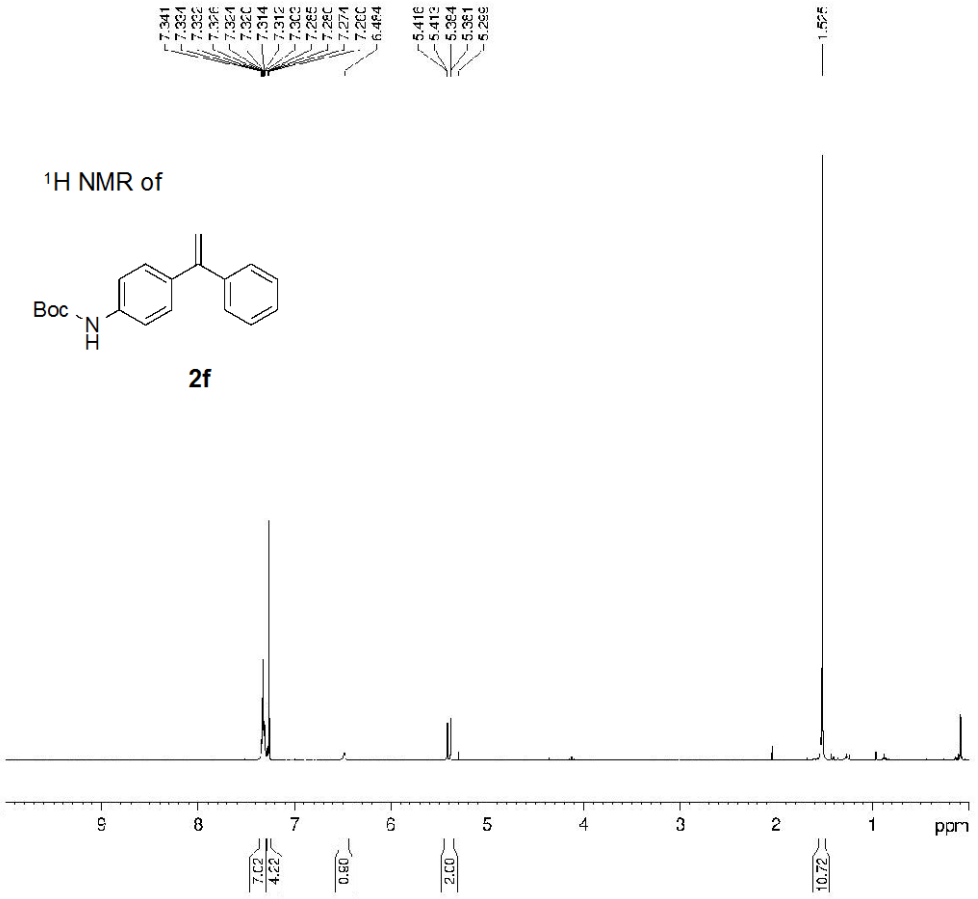
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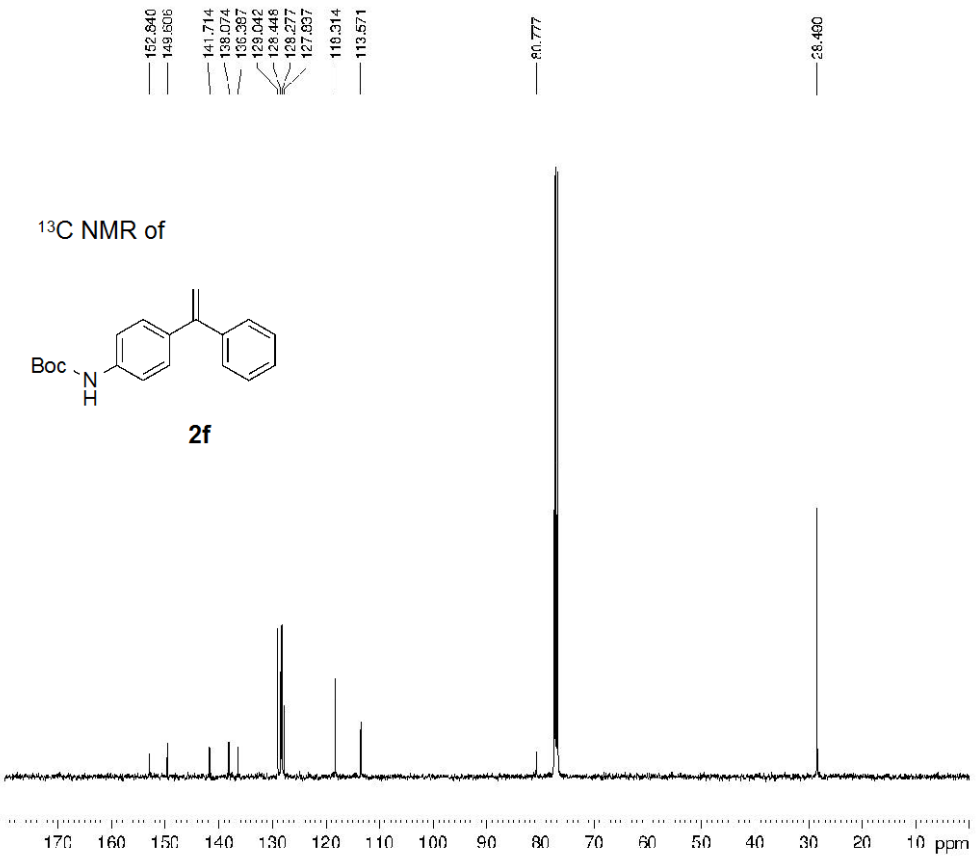
7.334
7.332
7.326
7.321
7.320
7.314
7.312
7.305
7.285
7.280
7.274
7.260
6.484
5.416
5.413
5.384
5.381
5.289
1.525
1H NMR of
Boc
N
H
2f
9
8
7
6
5
4
3
2
1
ppm
7.02
4.22
0.80
2.00
10.72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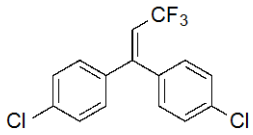
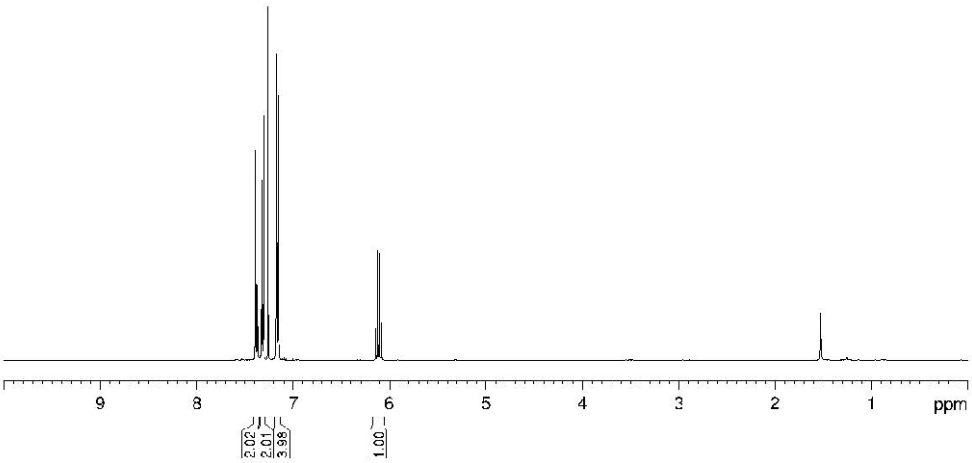
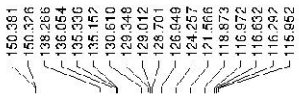
149.606
141.714
138.074
136.397
129.042
128.446
128.277
127.937
116.314
113.571
80.777
28.490
13C NMR of
Boc
N
H
2f
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

^{1}H NMR of

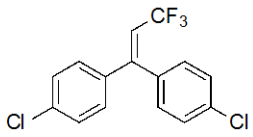


3c





^{13}C NMR of



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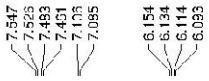
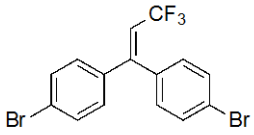
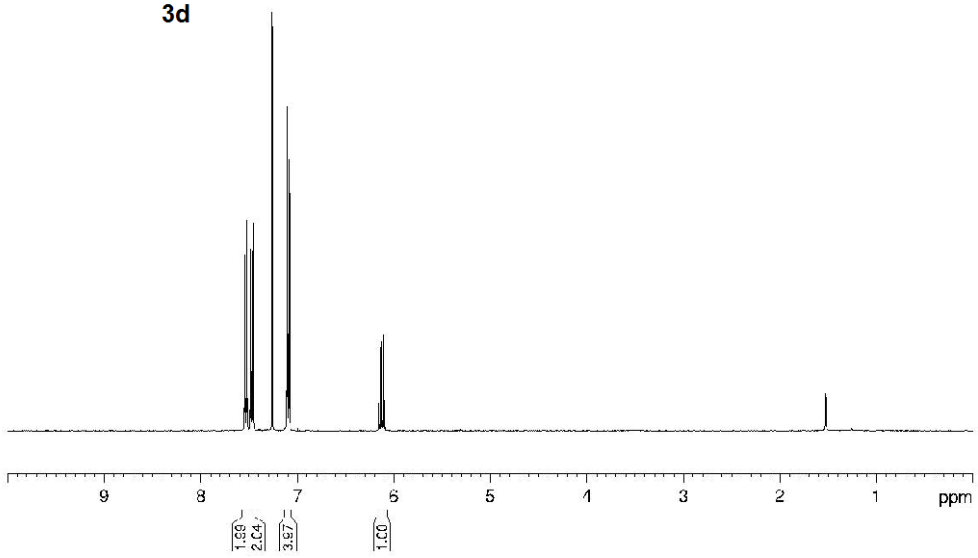
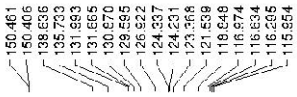


^{1}H NMR of



3d





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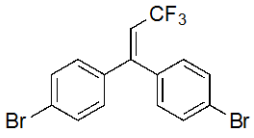
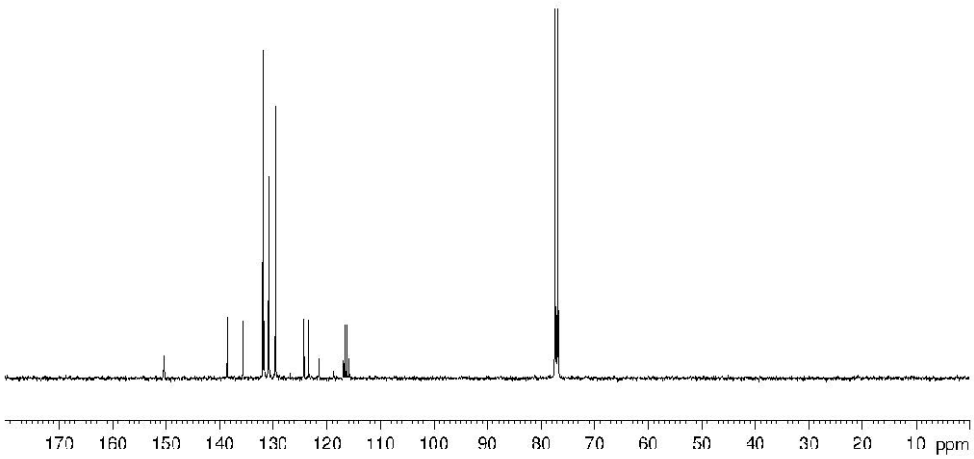
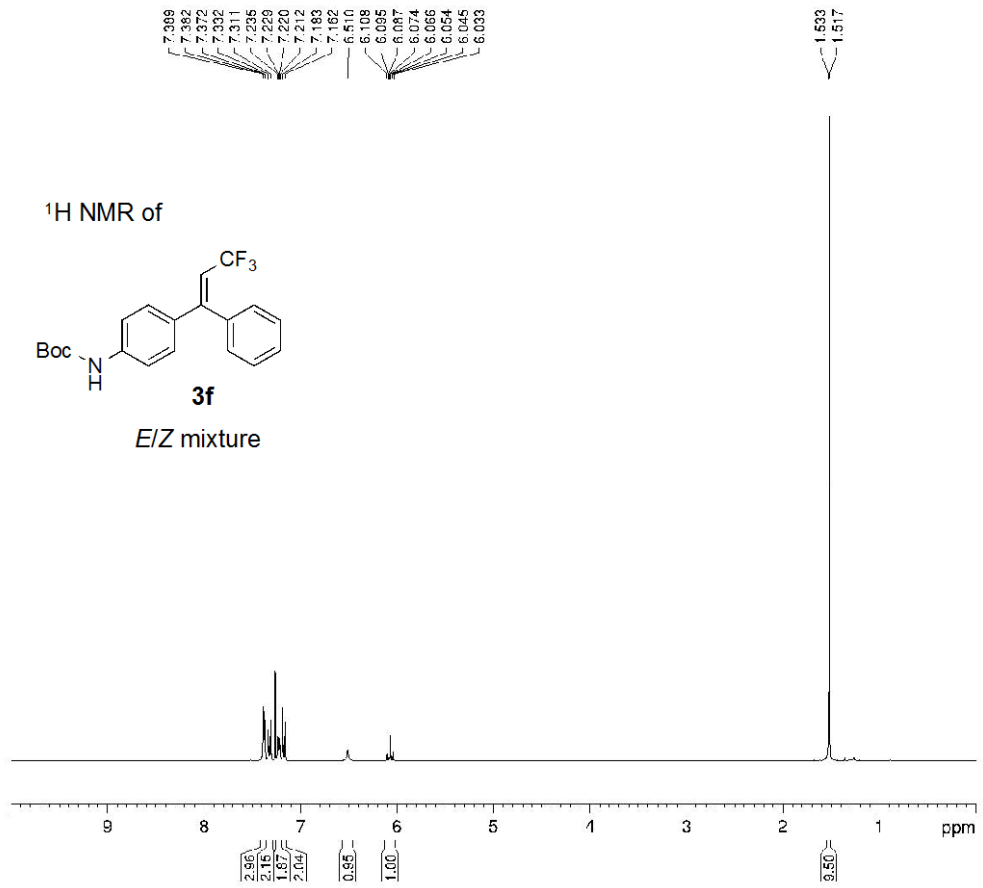


3d

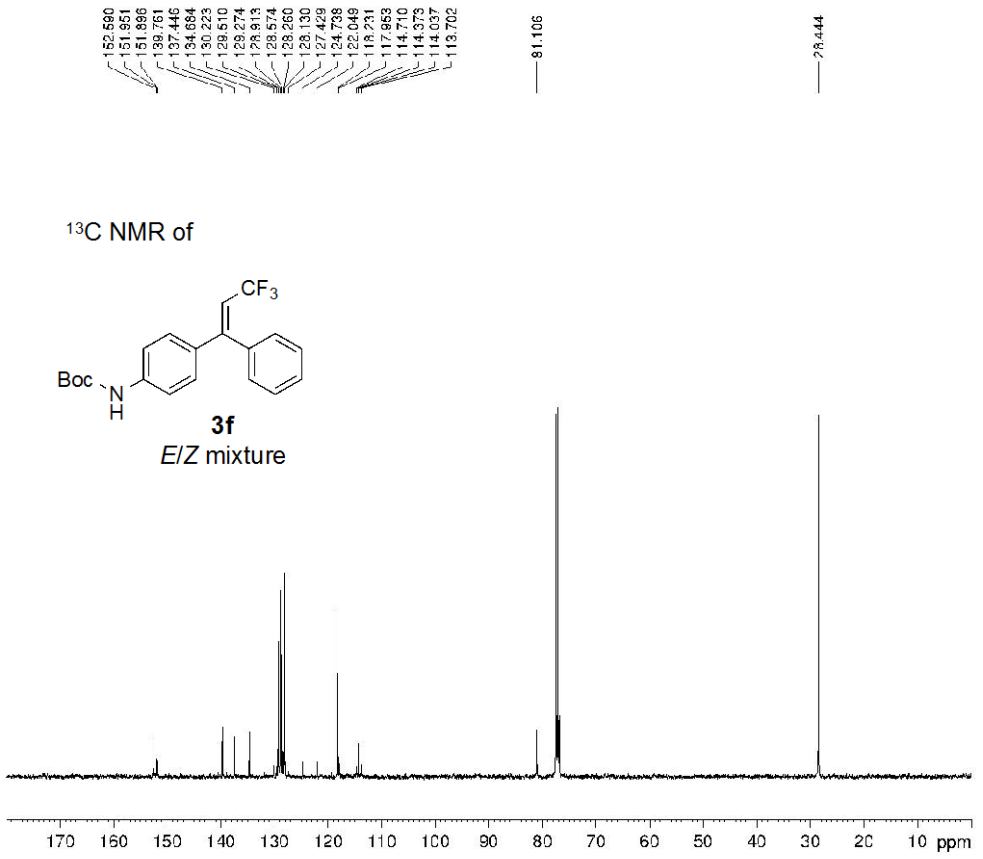




^{1}H NMR of

3f

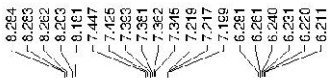
E/*Z* mixture



^{13}C NMR of

3f

E/*Z* mixture



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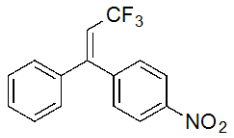
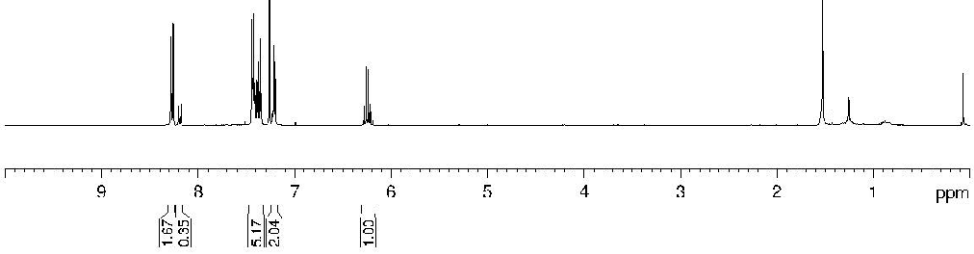
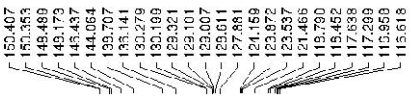


3g

E/*Z* mixture





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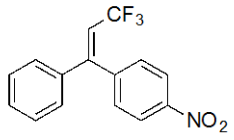
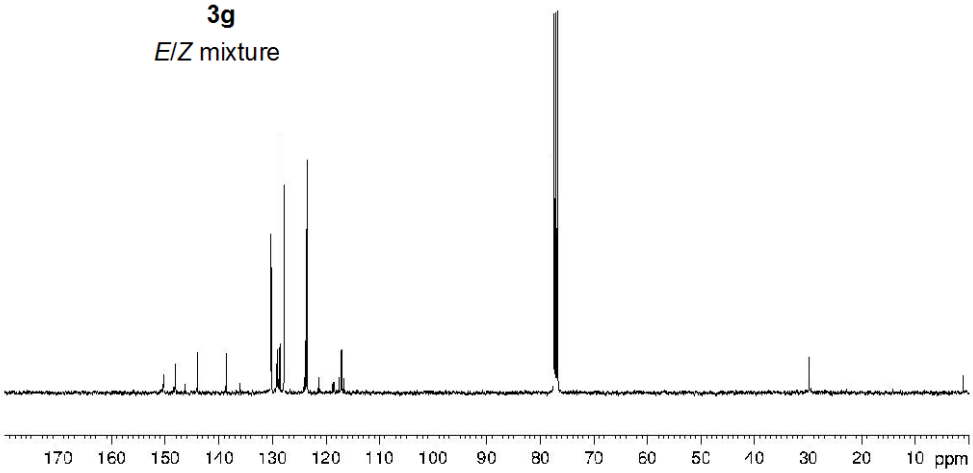
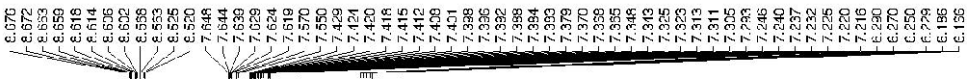


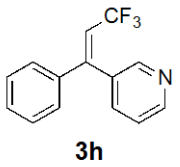
3g

E/*Z* mixture



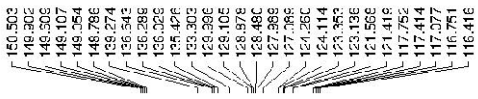


^{1}H NMR of



3h

E/*Z* mixture



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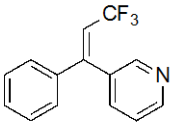
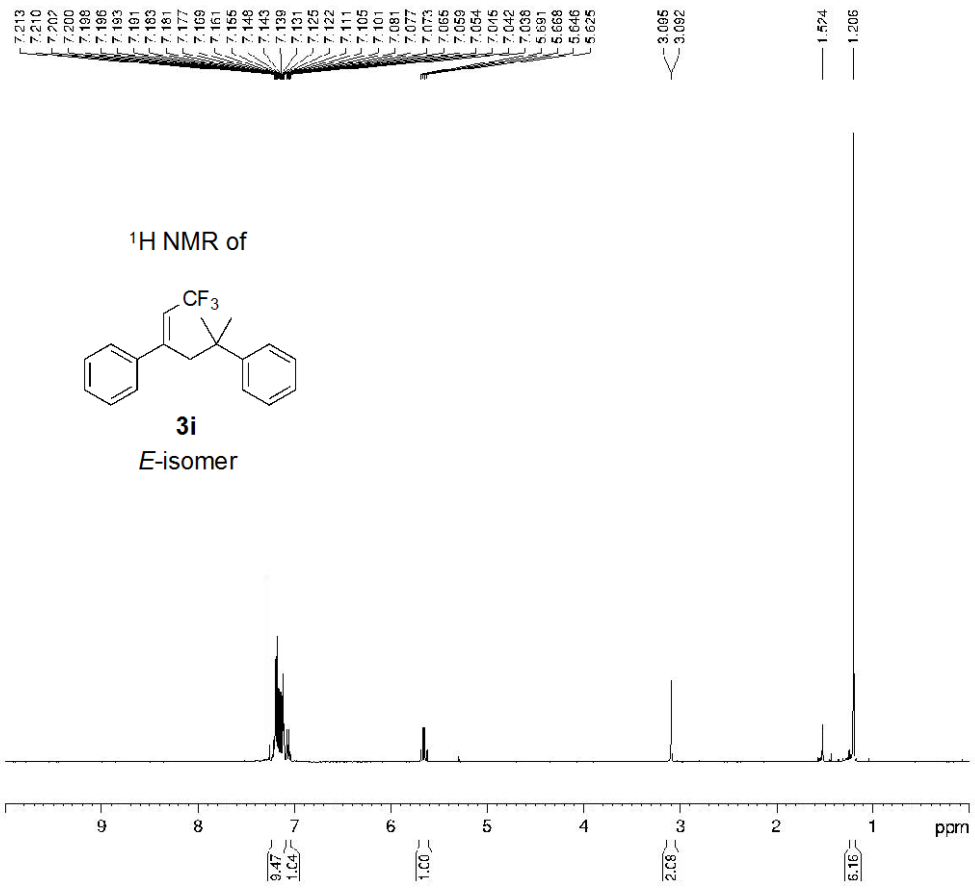


3h

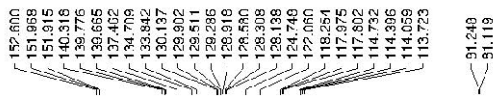
E/*Z* mixture



^{1}H NMR of

3i

E-isomer



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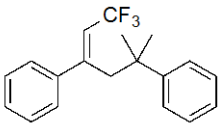

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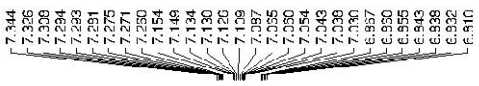
E-isomer



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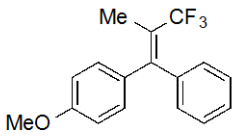
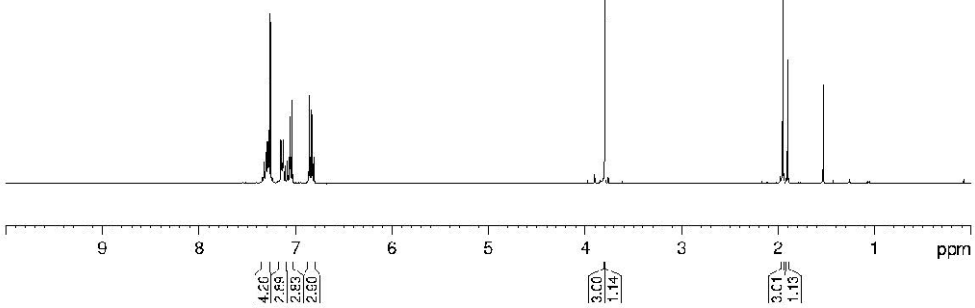
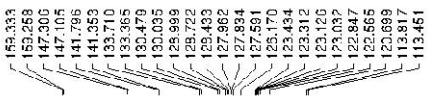


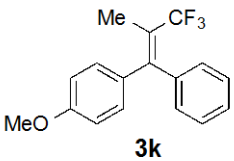
3k

E/*Z* mixture



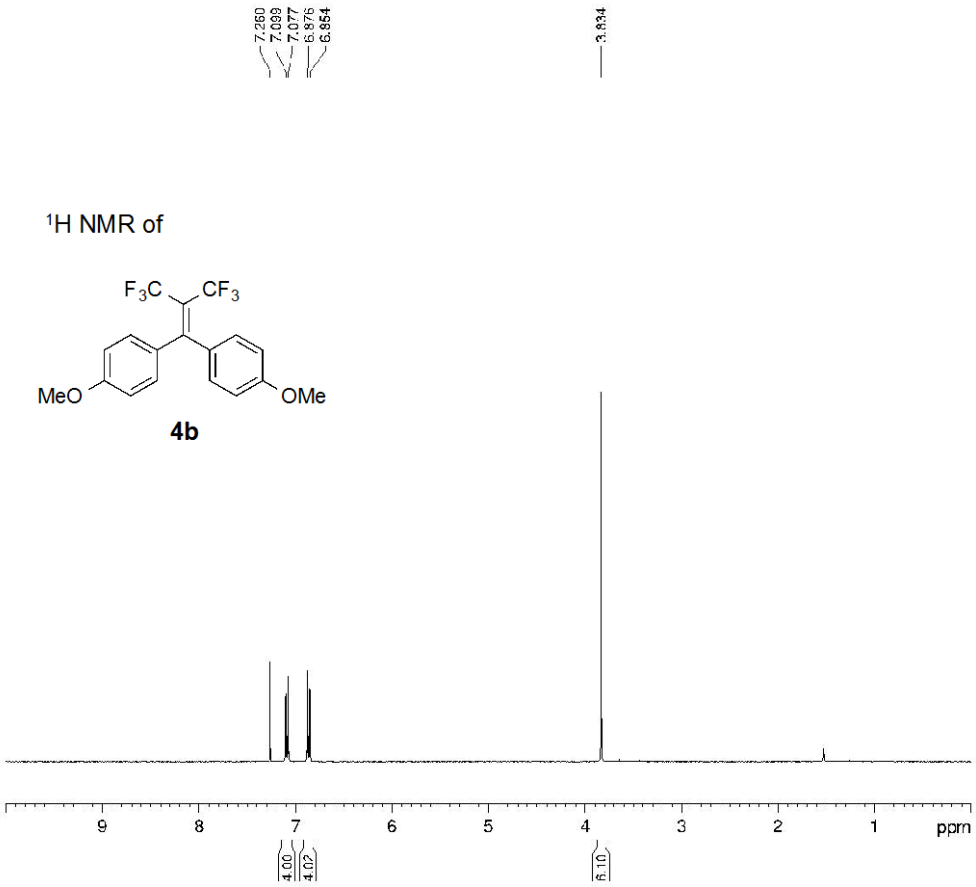


^{13}C NMR of



3k

E/*Z* mixture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7.077
6.876
6.854
3.834
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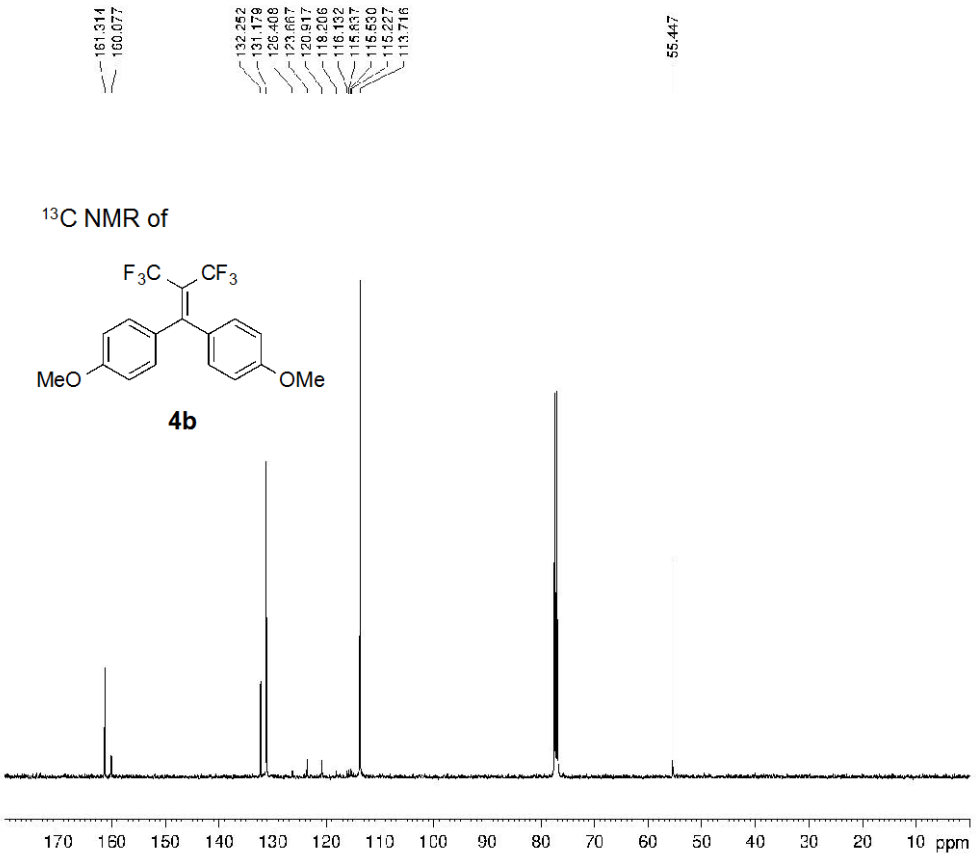
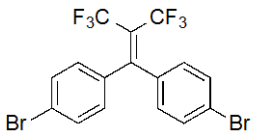
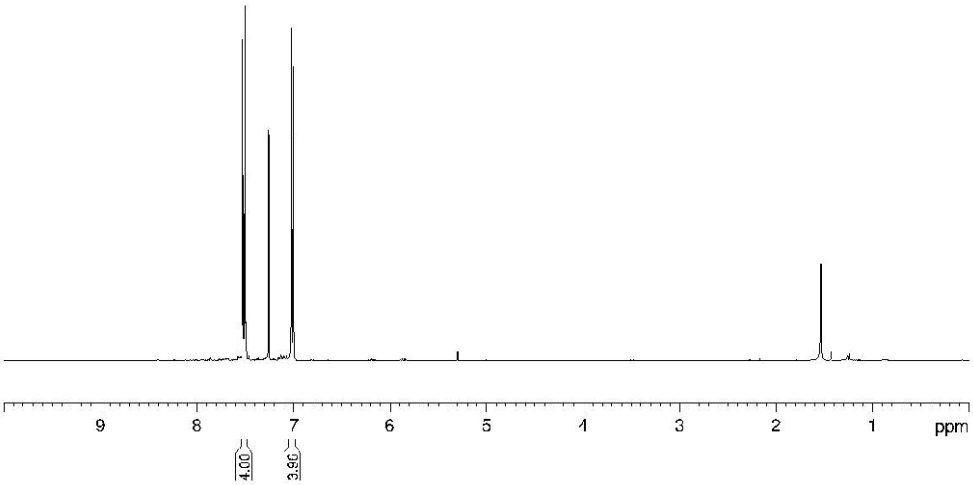
F_3C
CF_3
MeO
OMe
4b
9
8
7
6
5
4
3
2
1
ppm
4.00
4.02
6.10

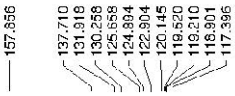

161.314
160.077
132.252
131.179
125.408
123.667
120.917
118.206
116.132
115.837
115.530
115.227
113.716
55.447
^{13}C NMR of
F_3C
CF_3
MeO
OMe
4b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

^{1}H NMR of

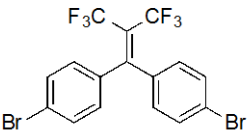


4d





^{13}C NMR of



4d