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Suppoting Information for

Redox-economical radical generation from organoborates and carboxylic acids by organic photoredox catalysis

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Contents:

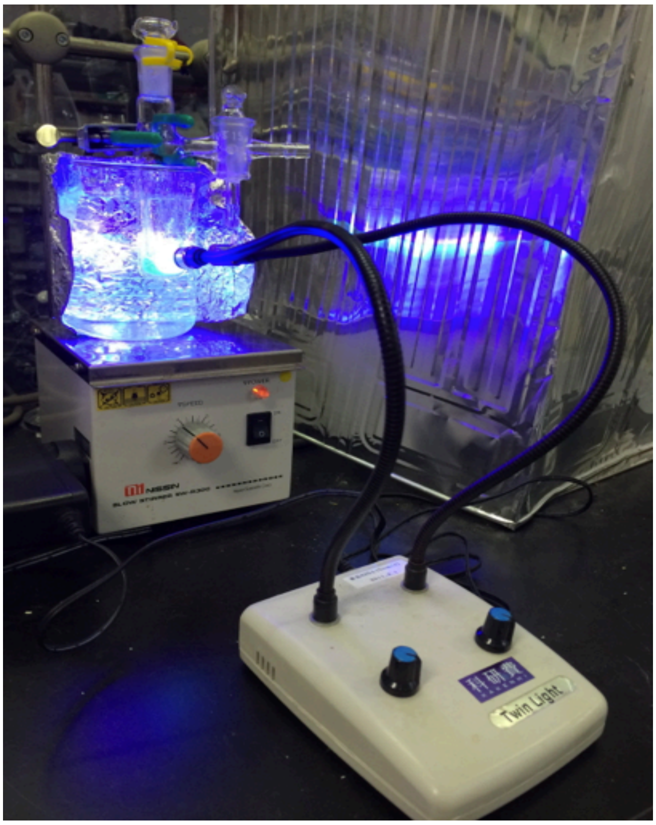
1. Materials and methods

9-Mesityl-10-methyl acridinium perchlorate ([Acr$^+$-Mes]ClO_4) (**1d**), pivalic acid (**3b**), 1-adamantanecarboxylic acid (**3c**), cyclohexanecarboxylic acid (**3f**), 2-methylbutyric acid (**3j**), benzyl acrylate (**4c**), benzyl methacrylate (**4d**), 2-cyclopenten-1-one (**4e**) and diethyl maleate (**4f**) were purchased from TCI. Potassium phenethyltrifluoroborate (**2a**), potassium cyclobutyltrifluoroborate (**2d**), potassium *sec*-butyltrifluoroborate (**2j**), potassium *n*-butyltrifluoroborate (**2m**), dimethyl 2-ethylidenemalonate (**4a**), diethyl 2-ethylidenemalonate (**4b**) and diethyl 2-benzylidenemalonate (**4g**) were purchased from Aldrich. Photocatalysts $[Ru(bpy)_3](PF_6)_2$ (**1a**)[1a], $[Ir(dF(CF_3)ppy)_2(bpy)](PF_6)$ (**1b**)[1b], and $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF_6)$ (**1c**)[1c] were prepared according to the literature procedures. Potassium organotrifluoroborates **2b**[2a], **2h**[2b], **2i**[2b], **2n**[2c] and **2o**[2d] were prepared according to the literature procedures. Catalytic reactions were performed under N_2 atmosphere using standard Schlenk techniques unless otherwise noted. Acetone was dried by K_2CO_3, distilled and stored under N_2 atmosphere. Anhydrous MeOH was purchased from KANTO CHEMICAL CO., INC. and degassed by supersonic waves. THF and Et_2O were purified through two columns containing alumina and alumina-Cu catalyst and stored under N_2 atmosphere. Thin-layer chromatography was performed on Merck TLC plate with 60 F_{254}. Preparative thin-layer chromatography (PTLC) plates were prepared through mixing Merck silica-gel 60 PF_{254} of 150 g with water of 430 mL, expanding on glass plate, and sintering at 100 °C for 5 h in oven. Flash column chromatography was carried out using silica gel 60 (40-63 μm) purchased from Aldrich. NMR spectra were acquired on a Bruker AVANCE-400 (400 MHz) and Bruker AVANCE-HD500 (500 MHz). NMR chemical shifts were referred to residual protio impurities in the deuterated solvent. CD_3OD solvent (99.8 atom% deuterated) was purchased from CIL. CD_3OH solvent (99.8 atom% deuterated) was perchased from ISOTEC. ^{19}F NMR chemical shifts were referenced to external 1,4-difluorobenzene (-118.8 ppm). ^{11}B NMR chemical shifts were referenced to external $BF_3 \cdot OEt_2$ (0.0 ppm). Electrochemical measurements were recorded on a Hokutodenkou HZ-5000 analyzer (observed in 0.004 M MeCN; $[N(Bu)_4](PF_6)$ = 0.1 M; Ag/AgCl = electrode; reported with respect to the $[FeCp_2]/[FeCp_2]^+$ couple). HRMS (ESI-TOF Mass and FAB-Mass) spectra were obtained with a Bruker micrOTOF Ⅱ and JEOL The MStation JMS-700, respectively, at Technical Department of Tokyo Institute of Technology. GC-MS(EI) spectra were auquired on a SHIMADZU GC-2010 (column: Rxi®-5ms) with a SHIMADZU PARVUM2.

2. Reaction apparatus

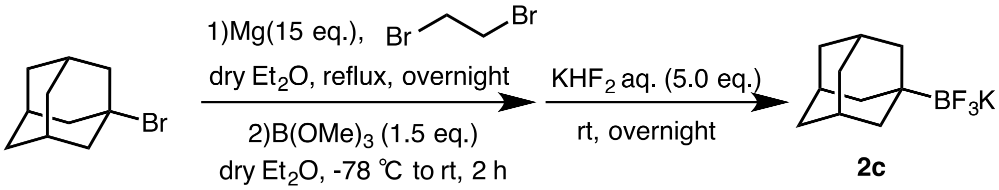
Irradiation of visible light was performed with a Relyon LED lamp (3 W x 2; λ_{max} = 425 ± 15 nm).

Cylindrical vessel was used for photoreaction under sunlight.



3. Synthesis of potassium organotrifluoroborates

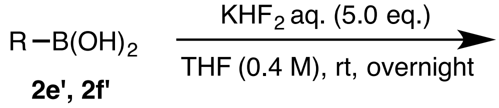
Synthesis of potassium 1-adamantyltrifluoroborate (2c)



A 100 mL two neck flask equipped with stirring bar was charged with magnesium turnings (3.65 g, 150 mmol) and 1-bromoadamantane (2.15 g, 10.0 mmol) under N_2 atmosphere. The solid mixture was stirred for 1 h, then the stirring bar was removed. To the flask, dry Et_2O (15.0 mL) and 1,2-dibromoethane (40.0 μL) were added. The reaction mixture was heated at reflux temperature without stirring overnight. This resulting reaction mixture was added to a 50 mL round-bottom teflon flask charged with trimethylborate (1.52 g, 14.6 mmol) through cannula tube at -78 ℃ under N_2. Then, the mixture was allowed to warm up to room temperature and stirred for 2 h. Under air at room temperature, KHF_2 aq. (3.90 g, 49.9 mmol, H_2O 11.0 mL) was added dropwise to this mixture, and stirred at room temperature overnight, then concentrated under vacuum. The residue was dissolved in hot acetone, and filtered. The volatile compounds were removed *in vacuo* and the crude product was washed with diethyl ether for several times and purified by recrystallization (acetone/MeOH(1/1) and Et_2O) to afford the title compound **2c** as a white solid (415 mg, 17% yield). Spectral data are shown below.

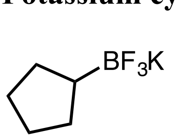
^{1}H NMR (400 MHz, DMSO-*d*$_6$, rt): δ 1.73-1.68 (br, 3H; $(C\mathit{H}CH_2)_3CBF_3K$), 1.68-1.58 (m, 6H; $(C\mathit{H_2}CHCH_2)_3CBF_3K$), 1.48-1.40 (m, 6H; $(C\mathit{H_2})_3CBF_3K$). **^{13}C NMR** (125 MHz, DMSO-*d*$_6$, rt): δ 45.2, 35.9, 30.0. **^{11}B NMR** (128 MHz, DMSO-*d*$_6$, rt): δ 5.07. **^{19}F NMR** (376 MHz, DMSO-*d*$_6$, rt): δ -152.6. **HRMS** (ESI-TOF-MS) : calculated for $[C_{10}H_{15}BF_3]^-$ requires 203.1215, found 203.1218.

General procedure for preparation of potassium organotrifluoroborates (2e and 2f) from the corresponding organoboronic acids (2e' and 2f').



A 50 mL round-bottom teflon flask was charged with boronic acid (**2e'** and **2f'**) (1.0 eq.) and dry THF under air at room temperature, then, KHF_2 aq. (5.0 eq.) was added dropwise to the reaction mixture. The resulting reaction solution was stirred at room temperature overnight. The mixture was concentrated under vacuum. The residue was dissolved in hot acetone, and filtered. The volatile compounds were removed and the crude product was washed with diethyl ether for several times to afford the potassium organotrifluoroborate (**2e** and **2f**) as a white solid.

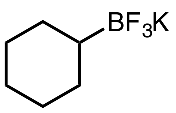
Potassium cyclopentyltrifluoroborate (2e)



According to the general procedure, cyclopentaneboronic acid (**2e'**) (0.390 g, 3.42 mmol), KHF_2 aq. (1.37 g, 17.6 mmol, H_2O 3.9 mL) and THF (9.0 mL) afforded **2e** as a white solid (396 mg, 66% yield). Spectral data are in agreement with the literature[3a].

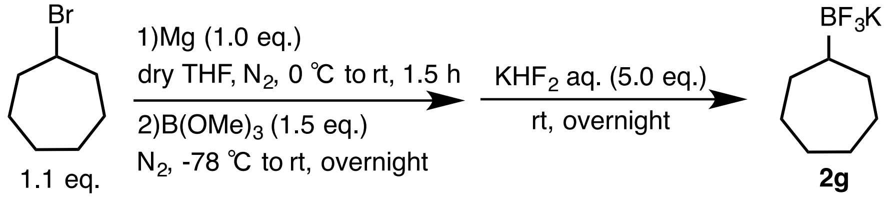
^{1}H NMR (400 MHz, DMSO-*d*$_6$, rt): δ 1.46-1.35 (m, 4H), 1.33-1.21 (m, 2H), 1.21-1.07 (m, 2H), 0.40 (br, 1H; $C\mathit{H}BF_3K$).

Potassium cyclohexyltrifluoroborate (2f)



According to the general procedure, cyclohexaneboronic acid (**2f'**) (1.92 g, 15.0 mmol), KHF_2 aq. (5.87 g, 75.2 mmol, H_2O 16.7 mL) and THF (40.0 mL) afforded **2f** as a white solid (909 mg, 32% yield). Spectral data are in agreement with the literature[3a]. **^{1}H NMR** (400 MHz, DMSO-*d*$_6$, rt): δ 1.65-1.56 (m, 3H), 1.56-1.44 (m, 2H), 1.18-0.98 (m, 3H), 0.98-0.82 (m, 2H), 0.64 (br, 1H; C*H*BF_3K).

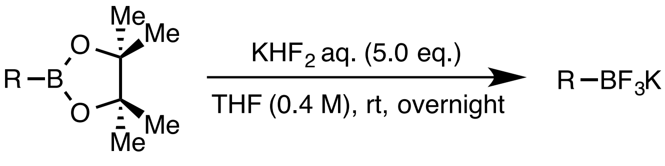
Synthesis of potassium cycloheptyltrifluoroborate (2g)



A 50 mL Schlenk tube equipped with stirring bar was charged with magnesium turnings (314 mg, 12.9 mmol, 1.0 eq.), flame-dried *in vacuo*, and backfilled with N_2, followed by the addition of dry THF (9.0 mL) and 1-bromocycloheptane (2.52 g, 14.2 mmol, 1.1 eq.) under N_2. The reaction solution was stirred at room temperature for 1.5 h. The resulting white slurry was diluted by dry THF (12.0 mL) and added dropwise via syringe to a 50 mL round-bottom teflon flask charged with trimethylborate (2.00 g, 19.3 mmol, 1.5 eq.) at -78 ℃ under N_2. The reaction mixture was allowed to warm up to room temperature and stirred overnight. Under air at room temperature, KHF_2 aq. (5.02 g, 64.3. mmol, H_2O 14.4 mL) was added dropwise to this mixture, and stirred at room temperature overnight, then concentrated under vacuum. The residue was dissolved in hot acetone, and filtered. The volatile compounds were removed *in vacuo* and the crude product was washed with diethyl ether for several times to afford the title compound as a white solid (693 mg, 26% yield). Spectral data are shown below.

^{1}H NMR (400 MHz, DMSO-*d*$_6$, rt): δ 1.63-1.53 (m, 4H), 1.53-1.43 (m, 2H), 1.43-1.30 (m, 2H), 1.30-1.17 (m, 2H), 1.08-0.96 (m, 2H), 0.06 (br, 1H; C*H*BF_3K). **^{13}C NMR** (125 MHz, DMSO-*d*$_6$, rt): δ 30.4, 29.8, 28.6. **^{11}B NMR** (128 MHz, DMSO-*d*$_6$, rt): δ 5.72. **^{19}F NMR** (376 MHz, DMSO-*d*$_6$, rt): δ -143.7. **HRMS** (ESI-TOF-MS) : calculated for $[C_7H_{13}BF_3]^-$ requires 165.1058, found 165.1057.

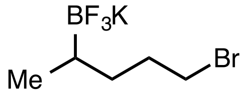
General procedure for preparation of potassium organotrifluoroborates (2k and 2l) from the corresponding organoboronic acid pinacol esters (2k’ and 2l’).



2k', 2l' **2k, 2l**

Boronic acid pinacol esters (**2k’**[3b] and **2l’**[3c]) were prepared according to the literatures, respectively. Potassium organotrifluoroborates (**2k** and **2l**) were synthesized from them. A 50 mL round-bottom teflon flask was charged with boronic acid pinacol ester **2’** (1.0 eq.) and dry THF under air at room temperature, then, KHF_2 aq. (5.0 eq.) was added dropwise to the reaction mixture. The resulting reaction solution was stirred at room temperature overnight. The mixture was concentrated under vacuum. The residue was dissolved in hot acetone, and filtered. The volatile compounds were removed and the crude product was washed with diethyl ether for several times to afford the potassium organotrifluoroborate **2** as a white solid. If required, the product was further purified by recrystallization.

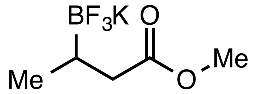
Potassium 4-bromo-1-methylbutane-2-trifluoroborate (2k)



According to the general procedure, 2-(5-bromopentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2k’**) (0.409 g, 1.48 mmol), KHF_2 aq. (0.583 g, 7.46 mmol, H_2O 1.7 mL) and THF (3.8 mL) afforded **2k** as a white solid (260 mg, 69% yield). Spectral data are shown below.

^{1}**H NMR** (400 MHz, DMSO-d_6, rt): δ 3.50-3.38 (m, 2H; $\mathrm{C}\mathit{H}_2\mathrm{Br}$), 1.90-1.65 (m, 2H; $\mathrm{C}\mathit{H}_2\mathrm{CH_2Br}$), 1.35 (m, 1H; $\mathrm{C}\mathit{H}\mathrm{HCH_2CH_2Br}$), 1.02 (m, 1H; $\mathrm{CH}\mathit{H}\mathrm{CH_2CH_2Br}$), 0.64 (d, J = 6.8 Hz, 3H; $\mathrm{C}\mathit{H}_3\mathrm{CHBF_3K}$), 0.10 (br, 1H; $\mathrm{CH_3C}\mathit{H}\mathrm{BF_3K}$). ^{13}**C NMR** (125 MHz, DMSO-d_6, rt): δ 36.8, 32.6, 32.5, 16.6. ^{11}**B NMR** (128 MHz, DMSO-d_6, rt): δ 5.36. ^{19}**F NMR** (376 MHz, DMSO-d_6, rt): δ -143.1. **HRMS** (FAB-MS) : calculated for $[C_5H_{10}BrBF_3]^-$ requires 217.0011, found 217.0014.

Potassium 1-methylbutanoate-3-trifluoroborate (2l)



According to the general procedure, methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (**2l’**) (0.948 g, 4.16 mmol), KHF_2 aq. (1.63 g, 20.8 mmol, H_2O 4.8 mL) and THF (10.7 mL) were utilized. This crude product was purified by recrystallization (acetone and pentane) to yield **2l** as a white solid (610 mg, 71% yield). Spectral data are shown below.

^{1}H NMR (400 MHz, DMSO-d_6, rt): δ 3.50 (s, 3H; OC*H*$_3$), 2.22 (dd, ^2J = 14.4 Hz, ^3J = 4.0 Hz, 1H; C*H*HCO$_2$CH$_3$), 1.71 (dd, ^2J = 14.4 Hz, ^3J = 4.0 Hz, 1H; CH*H*CO$_2$CH$_3$), 0.63 (d, J = 6.8 Hz, 3H; C*H*$_3$CHBF$_3$K), 0.53 (br, 1H; CH$_3$C*H*BF$_3$K). **^{13}C NMR** (125 MHz, DMSO-d_6, rt): δ 176.2 (*C*O$_2$Me), 50.4, 38.3, 15.9. **^{11}B NMR** (128 MHz, DMSO-d_6, rt): δ 5.00. **^{19}F NMR** (376 MHz, DMSO-d_6, rt): δ -145.6. **HRMS** (FAB-MS) : calculated for $[C_5H_9O_2BF_3]^-$ requires 169.0648, found 169.0645.

4. Typical NMR experiments for photoredox-catalyzed reactions

Reaction of organotrifluoroborates with electron-deficient alkenes

[Acr$^+$-Mes]ClO$_4$ (**1d**) (0.4 mg, 1.0 μmol) was weighted in an NMR tube under N$_2$, and potassium phenethyltrifluoroborate (**2a**) (12.7 mg, 59.9 μmol), acetone-d_6 (0.25 mL), dimethyl 2-ethylidenemalonate (**4a**) (7.9 mg, 50 μmol), tetraethylsilane as an internal standard, and CD$_3$OD (0.25 mL) were added to the NMR tube. The reaction mixture was degassed by three freeze-pump-thaw cycles, then irradiated for 24 h at room temperature (water bath) by 3 W LED lamps ($h\nu = 425 \pm 15$ nm, placed at a distance of ~3 cm from the reaction mixture).

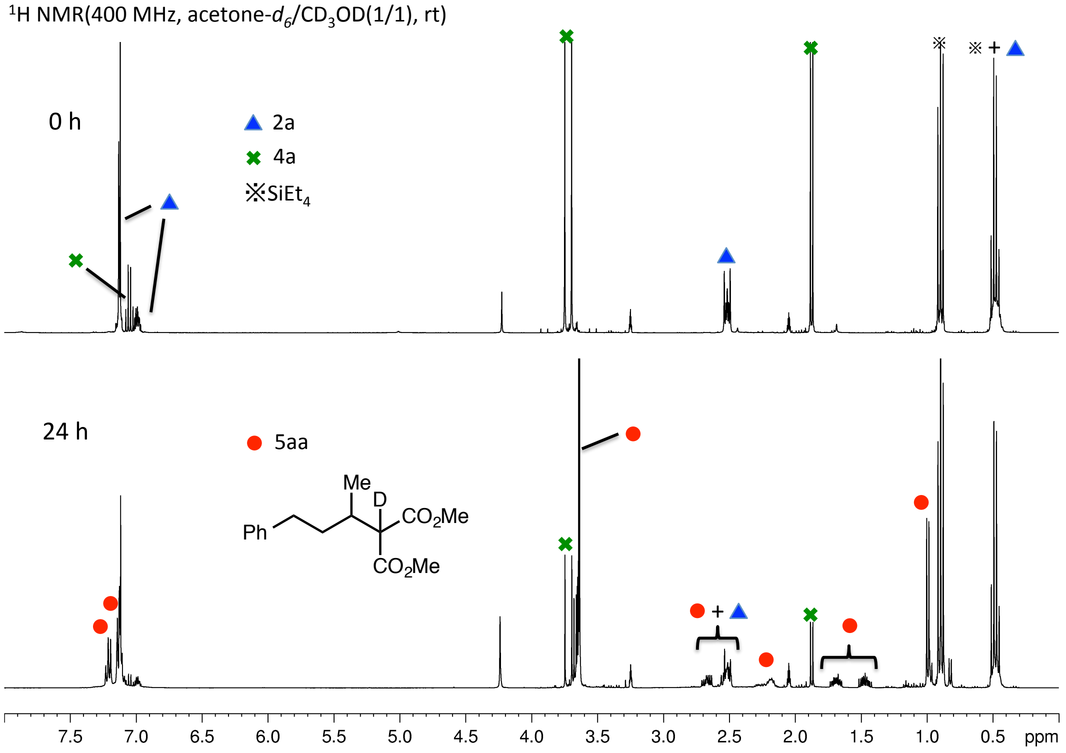
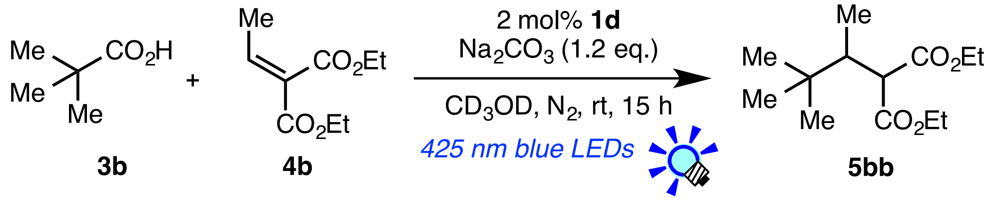


Figure S1-1. NMR spectra for the reaction of **2a** with **4a** in the presence of **1d**.

Reaction of carboxylic acids with electron-deficient alkenes



[Acr$^+$-Mes]ClO$_4$ (**1d**) (0.4 mg, 1.0 μmol) , Na_2CO_3 (6.4 mg, 60 μmol) was weighted in an NMR tube under N_2, and pivalic acid (**3b**) (6.1 mg, 60 μmol), diethyl 2-ethylidenemalonate (**4b**) (9.3 mg, 50 μmol), tetraethylsilane as an internal standard, and CD_3OD (0.50 mL) were added to the NMR tube. The reaction mixture was degassed by three freeze-pump-thaw cycles, then irradiated for 15 h at room temperature (water bath) by 3 W LED lamps ($h\nu$ = 425 ± 15 nm, placed at a distance of ∼ 3 cm from the reaction mixture).

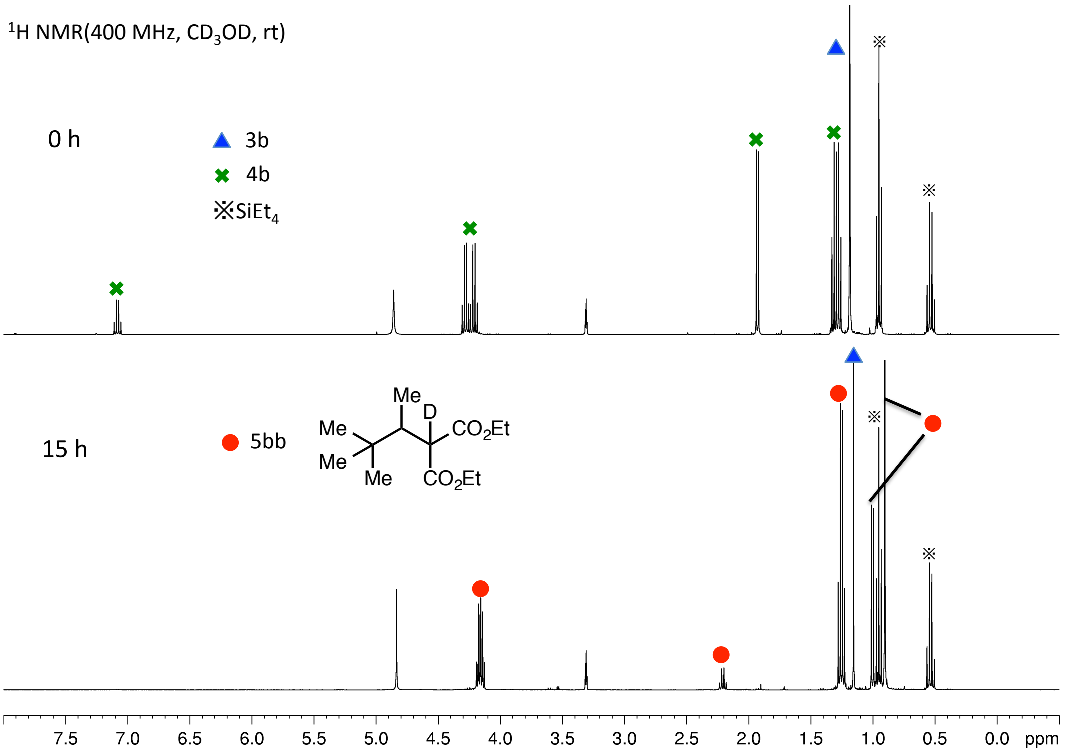


Figure S1-2. NMR spectra for the reaction of **3b** with **4b** in the presence of **1d**.

5. Optimization of photocatalytic radical reaction of pivalic acid (3b) with diethyl 2-ethylidenemalonate (4b)

According to the above-mentioned NMR experiment procedure, reaction conditions were investigated (Table S1).

3b **4b** **5bb**

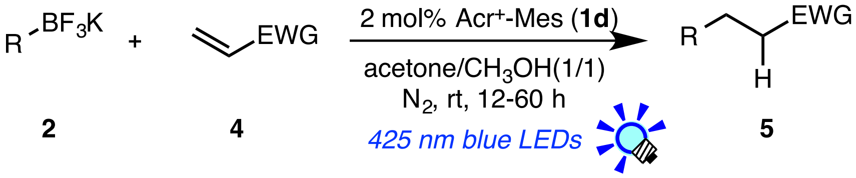
entry	solvent	base	NMR yield of **5bb**/%
1	acetone-d_6	Na_2CO_3	11
2	CD_3OD	Na_2CO_3	92
3	CD_3CN	Na_2CO_3	33
4	DMSO-d_6	Na_2CO_3	30
5	acetone-d_6/CD_3OD (1/1)	Na_2CO_3	55
6	CD_3OD	K_2HPO_4	48
7	CD_3OD	2,6-lutidine	31
8	CD_3OD	$NaHCO_3$	58
9 [a]	CD_3OD	Na_2CO_3	91
10	CD_3OD	None	0
11 [b]	CD_3OD	Na_2CO_3	0
12 [c]	CD_3OD	Na_2CO_3	0

[a] 0.1 eq. of base was used and reaction time was 18 h.
[b] Reaction was conducted in the dark.
[c] Reaction was conducted without catalyst.

Table S1. Optimization of photocatalytic radical reaction of pivalic acid (**3b**) with diethyl 2-ethylidenemalonate (**4b**).

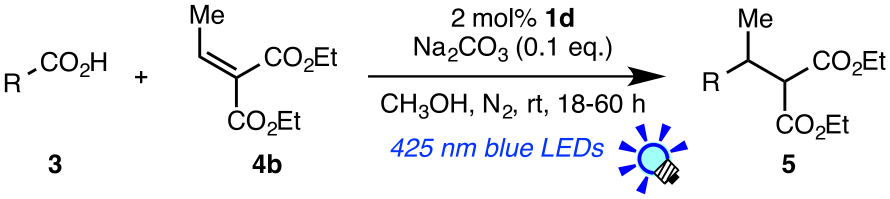
6. Photocatalytic reactions of organotrifluoroborates or carboxylic acids with electron-deficient alkenes

General procedure A (GP A) for photocatalytic reaction of organotrifluoroborates (2) with electron-deficient alkenes (4)



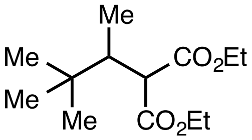
A 20 mL Schlenk tube was charged with potassium organotrifluoroborate salt (**2**) (0.36 mmol, 1.2 eq.), [Acr$^+$-Mes]ClO_4 (**1d**) (2.5 mg, 6.1 μmol, 2.0 mol%), dry acetone (1.5 mL), dry MeOH (1.5 mL) and electron-deficient alkenes (**4**) (0.30 mmol, 1.0 eq.) under N_2. The reaction mixture was degassed by three freeze-pump-thaw cycles, then stirred for 12-60 h at room temperature (water bath) under irradiation of 3 W LED lamps (*hν* = 425 ± 15 nm, placed at a distance of ~3 cm from the reaction mixture). The resulting mixture was concentrated *in vacuo*, followed by addition of water (15.0 mL) and CH_2Cl_2 (15.0 mL). The aqueous layer was extracted with CH_2Cl_2 for three times, dried over Na_2SO_4, and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by flash column chromatography or by PTLC to afford products (**5**).

General procedure B (GP B) for photocatalytic reaction of carboxylic acids (3) with diethyl 2-ethylidenemalonate (4b)



A 20 mL Schlenk tube was charged with [Acr$^+$-Mes]ClO_4 (**1d**) (2.5 mg, 6.1 μmol, 2.0 mol%), Na_2CO_3 (3.2 mg, 30 μmol, 0.1 eq.), dry MeOH (3.0 mL), carboxylic acid (**3**) (0.36 mmol, 1.2 eq.), and diethyl 2-ethylidenemalonate (**4b**) (56 mg, 0.30 mmol, 1.0 eq.) under N_2. Then the reaction mixture was stirred for 18-60 h at room temperature (water bath) under irradiation of 3 W LED lamps (*hν* = 425 ± 15 nm, placed at a distance of ~3 cm from the reaction mixture). The reaction mixture was diluted with sat. $NaHCO_3$ aq. (50.0 mL), and extracted with Et_2O for three times. The combined organic layer was washed with H_2O and brine, dried over Na_2SO_4, and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by flash column chromatography or by PTLC to afford products (**5**).

Diethyl (1,2,2-trimethylpropyl)malonate (5bb)

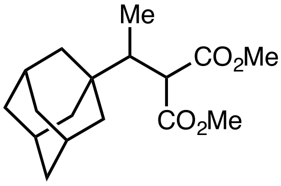


According to the GP A, potassium *tert*-butyltrifluoroborate (**2b**) (59.1 mg, 0.360 mmol), diethyl 2-ethylidenemalonate (**4b**) (55.9 mg, 0.300 mmol) and [Acr$^+$-Mes]ClO_4 (**1d**) (2.5 mg, 6.1 μmol) under blue LEDs irradiation for 24 h afforded **5bb** (44.4 mg, 61% yield) as a colorless oil after purification by flash column chromatography (hexane/EtOAc = 20/1). Spectral data are shown below.

According to the GP B, pivalic acid (**3b**) (36.6 mg, 0.358 mmol), diethyl 2-ethylidenemalonate (**4b**) (55.4 mg, 0.298 mmol), Na_2CO_3 (3.2 mg, 30 μmol) and [Acr$^+$-Mes]ClO_4 (**1d**) (2.5 mg, 6.1 μmol) under blue LEDs irradiation for 18 h afforded **5bb** (58.8 mg, 81% yield) as a colorless oil after purification by flash column chromatography (hexane/EtOAc = 20/1). Spectral data are shown below.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 4.22-4.13 (m, 4H; $CH(CO_2CH_2CH_3)_2$), 3.51 (d, J = 5.6 Hz, 1H; $CH(CO_2Et)_2$), 2.24 (m, 1H; $CHCH(CO_2Et)_2$), 1.30-1.22 (m, 6H; $CH(CO_2CH_2CH_3)_2$), 1.01 (d, J = 7.2 Hz, 3H; $CH_3CHCH(CO_2Et)_2$), 0.90 (s, 9H; ^{t}Bu). **^{13}C NMR** (125 MHz, $CDCl_3$, rt): δ 170.4 (CO_2Et), 169.7 (CO_2Et), 61.5, 61.1, 53.5, 42.8, 33.8, 27.7, 14.19, 14.16, 12.2. **HRMS** (ESI-TOF-MS): calculated for $[C_{13}H_{24}O_4+Na]^+$ requires 267.1567, found 267.1561

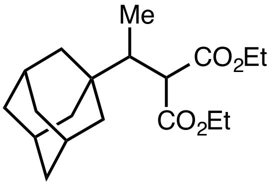
Dimethyl (1-adamantylethyl)malonate (5ca)



According to the GP A, potassium 1-adamantyltrifluoroborate (**2c**) (86.6 mg, 0.358 mmol), dimethyl 2-ethylidenemalonate (**4a**) (47.3 mg, 0.299 mmol) and [Acr$^+$-Mes]ClO_4 (**1d**) (2.5 mg, 6.1 μmol) under blue LEDs irradiation for 12 h afforded **5ca** (82.8 mg, 94% yield) as a pale yellow oil after purification by flash column chromatography (pentane/Et_2O = 10/1). Spectral data are shown below.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 3.73 (s, 3H; CO_2CH_3), 3.71 (s, 3H; CO_2CH_3), 3.61 (d, J = 5.2 Hz, 1H; $CH(CO_2Me)_2$), 2.09 (m, 1H, $CHCH(CO_2Me)_2$), 1.97 (s, 3H; Adamantyl group), 1.73-1.65 (m, 3H; Adamantyl group), 1.65-1.57 (m, 3H; Adamantyl group), 1.57-1.45(m, 6H; Adamantyl group), 0.97 (d, J = 7.6 Hz, 3H; $CH_3CHCH(CO_2Me)_2$). **^{13}C NMR** (125 MHz, $CDCl_3$, rt): δ 171.0 (CO_2Me), 170.3 (CO_2Me), 52.7, 52.2, 51.7, 43.4, 39.5, 37.1, 35.4, 28.8, 10.6. **HRMS** (ESI-TOF-MS): calculated for $[C_{17}H_{26}O_4+Na]^+$ requires 317.1723, found 317.1720.

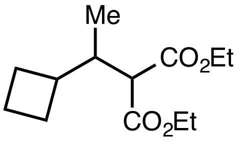
Diethyl (1-adamantylethyl)malonate (5cb)



According to the GP B, 1-adamantanecarboxylic acid (**3c**) (65.2 mg, 0.362 mmol), diethyl 2-ethylidenemalonate (**4b**) (55.4 mg. 0.298 mmol), Na_2CO_3 (3.3 mg, 31 μmol) and [Acr^+-Mes]ClO_4 (**1d**) (2.5 mg, 6.1 μmol) under blue LEDs irradiation for 60 h afforded **5cb** (82.8 mg, 86% yield) as a pale yellow oil after purification by flash column chromatography (pentane/Et_2O = 100/0→20/1→10/1). Spectral data are in agreement with the literature[4].

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 4.22-4.11 (m, 4H; $CH(CO_2CH_2CH_3)_2$), 3.57 (d, J = 5.2 Hz, 1H; $CH(CO_2Et)_2$), 2.06 (m, 1H, $CHCH(CO_2Et)_2$), 1.97 (s, 3H; Adamantyl group), 1.73-1.65 (m, 3H; Adamantyl group), 1.65-1.57 (m, 3H; Adamantyl group), 1.57-1.45(m, 6H; Adamantyl group), 1.33-1.22 (m, 6H; $CH(CO_2CH_2CH_3)_2$), 0.98 (d, J = 7.2 Hz, 3H; $CH_3CHCH(CO_2Et)_2$).

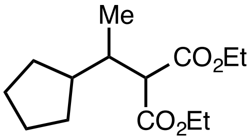
Diethyl (1-cyclobutylethyl)malonate (5db)



According to the GP A, potassium cyclobutyltrifluoroborate (**2d**) (58.3 mg, 0.360 mmol), diethyl 2-ethylidenemalonate (**4b**) (55.9 mg, 0.300 mmol) and [Acr^+-Mes]ClO_4 (**1d**) (2.5 mg, 6.1 μmol) under blue LEDs irradiation for 36 h afforded **5db** (42.1 mg, 58% yield) as a colorless oil after purification by flash column chromatography (pentane/Et_2O = 20/1). Spectral data are shown below.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 4.21-4.11 (m, 4H; $CH(CO_2CH_2CH_3)_2$), 3.21 (d, J = 6.0 Hz, 1H; $CH(CO_2Et)_2$), 2.29-2.11 (m, 2H), 2.03-1.87 (m, 2H; cyclobutyl group), 1.85-1.62 (m, 4H; cyclobutyl group), 1.26 (t, J = 7.2 Hz, 6H; $CH(CO_2CH_2CH_3)_2$), 0.91 (d, J = 6.8 Hz, 3H; $CH_3CHCH(CO_2Et)_2$). **^{13}C NMR** (100 MHz, $CDCl_3$, rt): δ 169.4 (CO_2Et), 168.8 (CO_2Et), 61.3, 61.1, 55.2, 40.3, 40.1, 27.4, 27.2, 17.6, 14.3, 14.2, 14.1. **HRMS** (ESI-TOF-MS): calculated for $[C_{13}H_{22}O_4+Na]^+$ requires 265.1410, found 265.1415

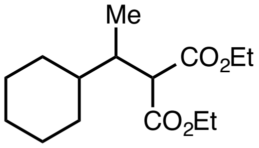
Diethyl (1-cyclopentylethyl)malonate (5eb)



According to the GP A, potassium cyclopentyltrifluoroborate (**2e**) (63.3 mg, 0.361 mmol), diethyl 2-ethylidenemalonate (**4b**) (56.3 mg, 0.302 mmol) and [Acr^+-Mes]ClO_4 (**1d**) (2.5 mg, 6.1 μmol) under blue LEDs irradiation for 24 h afforded **5eb** (66.1 mg, 85% yield) as a colorless oil after purification by flash column chromatography (pentane/Et_2O = 20/1). Spectral data are shown below.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 4.25-4.11(m, 4H; $CH(CO_2CH_2CH_3)_2$), 3.42 (d, J = 6.0 Hz, 1H; $CH(CO_2Et)_2$), 2.15 (m, 1H; $CHCH(CO_2Et)_2$), 1.85-1.70 (m, 3H; cyclopentyl group), 1.69-1.47 (m, 4H; cyclopentyl group), 1.30-1.24 (m, 6H; CH($CO_2CH_2C\mathit{H_3}$)$_2$), 1.24-1.08 (m, 2H; cyclopentyl group), 1.01 (d, *J* = 6.8 Hz, 3H; C*H*$_3$CHCH(CO_2Et)$_2$). **^{13}C NMR** (100 MHz, CDCl$_3$, rt): δ 169.6 (*C*O$_2$Et), 169.0 (*C*O$_2$Et), 61.3, 61.0, 56.5, 44.0, 38.6, 31.1, 29.8, 25.5, 25.4, 14.7, 14.3, 14.2. **HRMS** (ESI-TOF-MS): calculated for $[C_{14}H_{24}O_4+Na]^+$ requires 279.1567, found 279.1569

Diethyl (1-cyclohexylethyl)malonate (5fb)

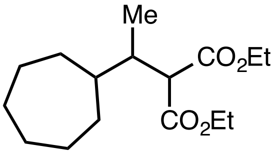


According to the GP A, potassium cyclohexyltrifluoroborate (**2f**) (68.5 mg, 0.360 mmol), diethyl 2-ethylidenemalonate (**4b**) (56.1 mg, 0.301 mmol) and [Acr$^+$-Mes]ClO$_4$ (**1d**) (2.5 mg, 6.1 μmol) under blue LEDs irradiation for 24 h afforded **5fb** (68.7 mg, 84% yield) as a pale yellow oil after purification by flash column chromatography (hexane/EtOAc = 10/1). Spectral data are in agreement with the literature.[4]

According to the GP B, cyclohexanecarboxylic acid (**3f**) (46.8 mg, 0.365 mmol), diethyl 2-ethylidenemalonate (**4b**) (55.2 mg, 0.296 mmol), Na$_2$CO$_3$ (3.2 mg, 30 μmol) and [Acr$^+$-Mes]ClO$_4$ (**1d**) (2.5 mg, 6.1 μmol) under blue LEDs irradiation for 60 h afforded **5fb** (31.8 mg, 40% yield) as a pale yellow oil after purification by flash column chromatography (hexane/EtOAc = 10/1). Spectral data are in agreement with the literature.[4]

^{1}H NMR (400 MHz, CDCl$_3$, rt): δ 4.23-4.14 (m, 4H; CH($CO_2C\mathit{H_2}CH_3$)$_2$), 3.39 (d, *J* = 9.2 Hz, 1H; C*H*(CO_2Et)$_2$), 2.17 (m, 1H; C*H*CH(CO_2Et)$_2$), 1.78-1.69 (m, 2H; cyclohexyl group), 1.68-1.55 (m, 3H; cyclohexyl group), 1.32-1.05 (m, 11H; CH($CO_2CH_2C\mathit{H_3}$)$_2$, cyclohexyl group), 1.01-0.88 (m, 4H; C*H*$_3$CHCH(CO_2Et)$_2$, cyclohexyl group).

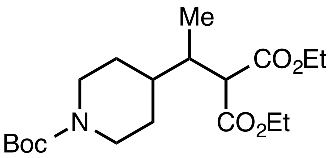
Diethyl (1-cycloheptylethyl)malonate (5gb)



According to the GP A, potassium cycloheptyltrifluoroborate (**2g**) (73.0 mg, 0.358 mmol), diethyl 2-ethylidenemalonate (**4b**) (55.4 mg, 0.298 mmol) and [Acr$^+$-Mes]ClO$_4$ (**1d**) (2.5 mg, 6.1 μmol) under blue LEDs irradiation for 18 h afforded **5gb** (69.0 mg, 82% yield) as a colorless oil after purification by flash column chromatography (hexane/EtOAc = 15/1). Spectral data are shown below.

^{1}H NMR (400 MHz, CDCl$_3$, rt): δ 4.24-4.14 (m, 4H; CH($CO_2C\mathit{H_2}CH_3$)$_2$), 3.32 (d, *J* = 10.4 Hz, 1H; C*H*(CO_2Et)$_2$), 2.29 (m, 1H; C*H*CH(CO_2Et)$_2$), 1.74-1.63 (m, 2H; cycloheptyl group), 1.63-1.30 (m, 10H; cycloheptyl group), 1.30-1.23 (m, 6H; CH($CO_2CH_2C\mathit{H_3}$)$_2$), 1.22-1.13 (m, 1H; cycloheptyl group), 0.86 (d, *J* = 6.8 Hz, 3H; C*H*$_3$CHCH(CO$_2$Et)$_2$). **^{13}C NMR** (125 MHz, CDCl$_3$, rt): *δ* 169.3 (*C*O$_2$Et), 169.2 (*C*O$_2$Et), 61.3, 56.9, 41.1, 39.8, 34.1, 28.3, 27.9, 27.8, 27.6, 27.4, 14.30, 14.26, 12.3. **HRMS** (ESI-TOF-MS): calculated for [C$_{16}$H$_{28}$O$_4$+Na]$^+$ requires 307.1880, found 307.1880.

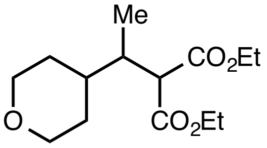
Diethyl (1-(*N*-Boc-4-piperidinyl)ethyl)malonate (5hb)



According to the GP A, potassium *N*-Boc-4-(trifluoroborato)piperidine (**2h**) (105 mg, 0.361 mmol), diethyl 2-ethylidenemalonate (**4b**) (56.2 mg, 0.302 mmol), and [Acr$^+$-Mes]ClO$_4$ (**1d**) (2.5 mg, 6.1 μmol) under blue LEDs irradiation for 36 h afforded **5hb** (64.5 mg, 58% yield) as a colorless oil after purification by flash column chromatography (hexane/EtOAc = 5/1). Spectral data are shown below.

^{1}H NMR (400 MHz, CDCl$_3$, rt): *δ* 4.30-4.02 (m, 6H; CH(CO$_2$C*H*$_2$CH$_3$)$_2$, C*H*H(NBoc)C*H*H), 3.38 (d, *J* = 8.8 Hz, 1H; C*H*(CO$_2$Et)$_2$), 2.71-2.48 (m, 2H; CH*H*(NBoc)CH*H*), 2.23 (m, 1H; C*H*CH(CO$_2$Et)$_2$), 1.70-1.50 (m, 3H; piperidinyl group), 1.44 (s, 9H; Boc), 1.38-1.22 (m, 7H; CH(CO$_2$CH$_2$C*H$_3$*)$_2$, piperidinyl group), 1.20- 1.07 (m, 1H; piperidinyl group), 0.92 (d, *J* = 6.8 Hz, 3H; C*H*$_3$CHCH(CO$_2$Et)$_2$). **^{13}C NMR** (125 MHz, CDCl$_3$, rt): *δ* 169.2 (*C*O$_2$Et), 168.8 (*C*O$_2$Et), 154.9 (*C*O$_2{}^t$Bu), 79.5, 61.5, 61.4, 55.5, 44.3, 44.1, 38.9, 37.9, 30.5, 28.6, 27.1, 14.3, 13.2. **HRMS** (ESI-TOF-MS): calculated for [C$_{19}$H$_{33}$NO$_6$+Na]$^+$ requires 394.2200, found 394.2195.

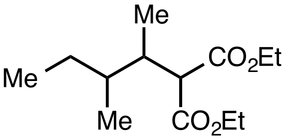
Diethyl (1-(tetrahydro-2*H*-4-pyranyl)ethyl)malonate (5ib)



According to the GP A, potassium 4-(trifluoroborato)tetrahydropyran (**2i**) (69.3 mg, 0.361 mmol), diethyl 2-ethylidenemalonate (**4b**) (56.0 mg, 0.301 mmol) and [Acr$^+$-Mes]ClO$_4$ (**1d**) (2.5 mg, 6.1 μmol) under blue LEDs irradiation for 36 h afforded **5ib** (55.7 mg, 68% yield) as a colorless oil after purification by flash column chromatography (hexane/EtOAc = 10/1→8/1). Spectral data are shown below.

^{1}H NMR (400 MHz, CDCl$_3$, rt): *δ* 4.25-4.16 (m, 4H; CH(CO$_2$C*H$_2$*CH$_3$)$_2$), 4.03-3.93 (m, 2H; CH*H*OCH*H*), 3.41 (d, *J* = 8.0 Hz, 1H; C*H*(CO$_2$Et)$_2$, 3.39-3.26 (m, 2H; C*H*HOC*H*H), 2.18 (m, 1H; C*H*CH(CO$_2$Et)$_2$), 1.62-1.44 (m, 4H; pyranyl group), 1.38 (m, 1H; O(CH$_2$CH$_2$)$_2$C*H*), 1.30-1.23(m, 6H; CH(CO$_2$CH$_2$C*H$_3$*)$_2$), 0.96 (d, 3H, *J* = 6.8 Hz, C*H*$_3$CHCH(CO$_2$Et)$_2$)). **^{13}C NMR** (125 MHz, CDCl$_3$, rt); *δ* 169.3 (*C*O$_2$Et), 168.9 (*C*O$_2$Et), 68.34, 68.26, 61.5, 61.3, 55.1, 38.2, 37.9, 31.2, 28.4, 14.3, 13.1. **HRMS** (ESI-TOF-MS): calculated for [C$_{14}$H$_{24}$O$_5$+Na]$^+$ requires 295.1516, found 295.1515.

Diethyl (1,2-dimethylbutyl)malonate (5jb)

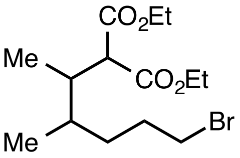


According to the GP A, potassium *sec*-butyltrifluoroborate (**2j**) (59.0 mg, 0.360 mmol), diethyl 2-ethylidenemalonate (**4b**) (55.9 mg, 0.300 mmol) and [Acr$^+$-Mes]ClO$_4$ (**1d**) (2.5 mg, 6.1 μmol) under blue LEDs irradiation for 24 h afforded **5jb** (1:1 diastereomer mixture, 49.5 mg, 68% yield) as a colorless oil after purification by flash column chromatography (hexane/EtOAc = 20/1). Spectral data are shown below.

According to the GP B, 2-methylbutyric acid (**3j**) (36.7 mg, 0.359 mmol), diethyl 2-ethylidenemalonate (**4b**) (55.6 mg, 0.299 mmol), Na$_2$CO$_3$ (3.3 mg, 31 μmol) and [Acr$^+$-Mes]ClO$_4$ (**1d**) (2.5 mg, 6.1 μmol) under blue LEDs irradiation for 60 h afforded **5jb** (1:1 diastereomer mixture, 40.1 mg, 55% yield) as a colorless oil after purification by flash column chromatography (hexane/EtOAc = 20/1). Spectral data are shown below.

^{1}H NMR (400 MHz, CDCl$_3$, rt): δ 4.23-4.12 (m, CH(CO$_2$C*H*$_2$CH$_3$)$_2$), 3.38, 3.31 (each d, J = 9.2 Hz, J = 10.4 Hz, (C*H*(CO$_2$Et)$_2$) of diastereomers), 2.37, 2.25 (each m, CH$_3$C*H*CH(CO$_2$Et)$_2$ of diastereomers), 1.47-1.20 (m, 8H; 1,2-dimethylbutyl group), 1.12-0.74 (m, 9H; CH(CO$_2$CH$_2$C*H*$_3$)$_2$, 1,2-dimethylbutyl group). **^{13}C NMR** (125 MHz, CDCl$_3$, rt): δ 169.4, 169.21,169.19, 169.1 (each *C*O$_2$Et of diastereomer), 61.3, 61.2, 57.0, 56.2, 38.9, 37.0, 36.6, 36.2, 28.2, 23.8, 17.6, 14.2, 13.5, 12.6, 12.2, 12.1, 11.3. **HRMS** (ESI-TOF-MS): calculated for [C$_{13}$H$_{24}$O$_4$+Na]$^+$ requires 267.1567, found 267.1565.

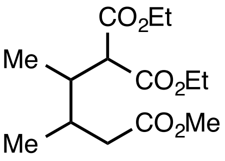
Diethyl (5-bromo-1,2-dimethylpentyl)malonate (5kb)



According to the GP A, potassium 4-bromo-1-methylbutane-2-trifluoroborate (**2k**) (93.0 mg, 0.362 mmol), diethyl 2-ethylidenemalonate (**4b**) (56.2 mg, 0.302 mmol), and [Acr$^+$-Mes]ClO$_4$ (**1d**) (2.5 mg, 6.1 μmol) under blue LEDs irradiation for 24 h afforded **5kb** (1:1 diastereomer mixture, 79.3 mg, 78% yield) as a pale yellow oil after purification by flash column chromatography (hexane/EtOAc = 10/1). Spectral data are shown below.

^{1}H NMR (400 MHz, CDCl$_3$, rt): δ 4.24-4.14 (m, CH(CO$_2$C*H*$_2$CH$_3$)$_2$), 3.44-3.34 (m, C*H*$_2$Br, C*H*(CO$_2$Et)$_2$), 3.30 (d, J = 10.4 Hz, C*H*(CO$_2$Et)$_2$), 2.34, 2.27 (each m, CH$_3$C*H*CH(CO$_2$Et)$_2$ of diastereomers), 2.00-1.83 (m, C*H*$_2$CH$_2$Br), 1.72 (m, CH*H*CH$_2$Br), 1.60-1.30 (m, *CH*$_2$(CH$_2$)$_2$Br, CH$_3$C*H*(CH$_2$)$_3$Br), 1.30-1.22 (m, 6H; CH(CO$_2$CH$_2$C*H*$_3$)$_2$), 1.14 (m, CH*H*(CH$_2$)$_2$Br), 0.95 (d, J = 6.8 Hz, C*H*$_3$CH(CH$_2$)$_3$Br), 0.90 (d, J = 7.2 Hz, C*H*$_3$CHCH(CO$_2$Et)$_2$), 0.86-0.78 (m, C*H*$_3$CH(CH$_2$)$_3$Br, CH_3CHCH(CO_2Et)$_2$). **^{13}C NMR** (125 MHz, $CDCl_3$, rt): δ 169.2, 169.02, 169.01, 168.96 (each *C*O_2Et of diastereomer), 61.45, 61.42, 61.3, 38.8, 36.4, 34.6, 34.1, 33.8, 33.7, 31.1, 30.7, 29.8, 18.1, 14.3, 13.9, 12.5, 11.2. **HRMS** (ESI-TOF-MS): calculated for $[C_{14}H_{25}BrO_4+Na]^+$ requires 359.0828, found 359.0826.

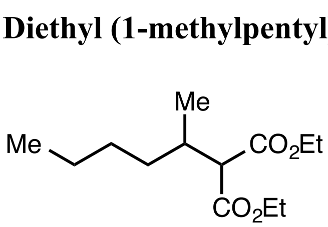
Diethyl (3-methoxycarbonyl-1,2-dimethylpropyl)malonate (5lb)



According to the GP A, potassium methyl 3-(trifluoroborato)butanoate (**2l**) (74.8 mg, 0.360 mmol), diethyl 2-ethylidenemalonate (**4b**) (55.2 mg, 0.296 mmol), and [Acr$^+$-Mes]ClO_4 (**1d**) (2.5 mg, 6.1 μmol) under blue LEDs irradiation for 60 h afforded **5lb** (1:1 diastereomer mixture, 63.8 mg, 75% yield) as a colorless oil after purification by flash column chromatography (pentane/Et_2O = 4/1). Spectral data are shown below.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 4.26-4.16 (m, CH(CO_2CH_2CH$_3$)$_2$), 3.67, 3.66 (each s, CO_2CH_3 of diastereomers), 3.31, 3.31 (each d, *J* = 9.2 Hz, *J* = 10.0 Hz, C*H*(CO_2Et)$_2$) of diastereomers), 2.44-2.26 (m, CH_3C*H*CH(CO_2Et)$_2$, CH_3CHC$H_2$$CO_2$Me), 2.26-2.17 (m, CH_3C*H*$CH_2$$CO_2$Me), 2.18-1.98 (m, CH_3C*H*CH(CO_2Et)$_2$, CH_3C*H*$CH_2$$CO_2$Me, CH_3CHCH*H*CO_2Me), 1.36-1.24 (m, 6H; CH($CO_2$$CH_2CH_3$)$_2$), 1.00 (d, *J* = 6.4 Hz, CH_3CH$CH_2$$CO_2$Me), 0.92 (d, *J* = 7.2 Hz, CH_3CHCH(CO_2Et)$_2$), 0.88 (d, *J* = 7.2 Hz, CH_3CHCH(CO_2Et)$_2$), 0.87 (d, *J* = 6.8 Hz, CH_3CH$CH_2$$CO_2$Me). **^{13}C NMR** (125 MHz, $CDCl_3$, rt): δ 173.6 (*C*O_2Me of diastereomer), 173.1 (*C*O_2Me of diastereomer), 169.0, 168.8, 168.74, 168.68 (each *C*O_2Et of diastereomer), 61.6, 61.4, 56.6, 56.1, 51.7, 40.3, 38.2, 37.0, 36.5, 32.4, 31.9, 18.6, 14.23, 14.19, 14.16, 13.8, 12.7, 11.7. **HRMS** (ESI-TOF-MS): calculated for $[C_{14}H_{24}O_6+Na]^+$ requires 311.1465, found 311.1468.

Diethyl (1-methylpentyl)malonate (5mb)

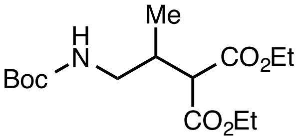


According to the GP A, potassium butyltrifluoroborate (**2m**) (58.3 mg, 0.355 mmol), diethyl 2-ethylidenemalonate (**4b**) (56.2 mg, 0.302 mmol) and [Acr$^+$-Mes]ClO_4 (**1d**) (2.5 mg, 6.1 μmol) under blue LEDs irradiation for 36 h afforded **5mb** (28.1 mg, 38% yield) as a pale yellow oil after purification by flash column chromatography (hexane/EtOAc = 18/1). Spectral data are shown below.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 4.19 (q, *J* = 7.2 Hz, 4H; CH(CO_2CH_2CH$_3$)$_2$), 3.22 (d, *J* = 8.0 Hz, 1H; C*H*(CO_2Et)$_2$), 2.24 (m, 1H; C*H*CH(CO_2Et)$_2$), 1.45-1.15 (m, 12H; CH($CO_2$$CH_2CH_3$)$_2$, 1-methylpentyl group), 0.98 (d, *J* = 6.8 Hz, 3H; CH_3CHCH(CO_2Et)$_2$), 0.93-0.86 (m, 3H;

1-methylpentyl group). **^{13}C NMR** (125 MHz, CDCl$_3$, rt): δ 169.2 (CO$_2$Et), 169.1 (CO$_2$Et), 61.3, 61.2, 58.0, 34.1, 33.5, 29.1, 22.8, 17.1, 14.28, 14.26, 14.2. **HRMS** (ESI-TOF-MS): calculated for [C$_{13}$H$_{24}$O$_4$+Na]$^+$ requires 267.1567, found 267.1563.

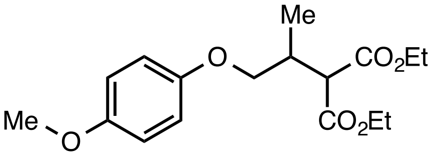
Diethyl (2-(*tert*-butoxycarbonyl)amino-1-methylethyl)malonate (5nb)



According to the GP A, potassium ((*tert*-butoxycarbonyl)aminomethyl)trifluoroborate (**2n**) (85.9 mg, 0362 mmol), diethyl 2-ethylidenemalonate (**4b**) (56.7 mg, 0.304 mmol) and [Acr$^+$-Mes]ClO$_4$ (**1d**) (2.5 mg, 6.1 μmol) under blue LEDs irradiation for 24 h afforded **5nb** (89.8 mg, 93% yield) as a pale yellow oil after purification by flash column chromatography (hexane/EtOAc = 10/1→8/1→6/1→5/1). Spectral data are in agreement with the literature[2d].

^{1}H NMR (400 MHz, CDCl$_3$, rt): δ 4.71 (br, 1H; BocNH), 4.23-4.14 (m, 4H; CH(CO$_2$CH_2CH$_3$)$_2$), 3.30 (d, J = 7.6 Hz, 1H; CH(CO$_2$Et)$_2$), 3.24-3.10 (m, 2H; BocNHCH_2), 2.45 (m, 1H; CHCH(CO$_2$Et)$_2$), 1.43 (s, 9H; *Boc*NH), 1.27 (t, J = 7.2 Hz, 6H; CH(CO$_2$CH$_2$CH_3)$_2$), 1.01 (d, J = 6.8 Hz, 3H; CH_3CHCH(CO$_2$Et)$_2$).

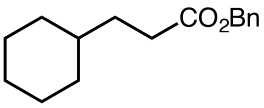
Diethyl (2-(4-methoxyphenoxy)-1-methylethyl)malonate (5ob)



According to the GP A, potassium (*p*-methoxyphenoxy)methyltrifluoroborate (**2o**) (87.8 mg, 0.360 mmol), diethyl 2-ethylidenemalonate (**4b**) (57.2 mg, 0.307 mmol) and [Acr$^+$-Mes]ClO$_4$ (**1d**) (2.5 mg, 6.1 μmol) under blue LEDs irradiation for 36 h afforded **5ob** (67.7 mg, 68% yield) as a pale yellow oil after purification by flash column chromatography (hexane/EtOAc = 10/1). Spectral data are in agreement with the literature.[5]

^{1}H NMR (400 MHz, CDCl$_3$, rt): δ 6.82 (s, 4H; Ar), 4.26-4.12 (m, 4H; CH(CO$_2$CH_2CH$_3$)$_2$, 3.96-3.85 (m, 2H; ArOCH_2CHCH$_3$), 3.76 (s, 3H; OCH_3), 3.58 (d, J = 8.0 Hz, 1H; CH(CO$_2$Et)$_2$), 2.71 (m, 1H; CHCH(CO$_2$Et)$_2$), 1.30-1.20 (m, 6H; CH(CO$_2$CH$_2$CH_3)$_2$), 1.14 (d, J = 6.8 Hz, 3H; CH_3CHCH(CO$_2$Et)$_2$).

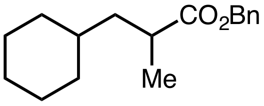
Benzyl 3-cyclohexylpropanoate (5fc)



According to the GP A, potassium cyclohexyltrifluoroborate (**2f**) (68.5 mg, 0.360 mmol), benzyl acrylate (**4c**) (48.9 mg, 0.301 mmol) and [Acr$^+$-Mes]ClO$_4$ (**1d**) (2.5 mg, 6.1 μmol) under blue LEDs irradiation for 15 h afforded **5fc** (28.1 mg, 38% yield) as a colorless oil after purification by PTLC (hexane/EtOAc = 15/1). Spectral data are shown below.

^{1}H NMR (500 MHz, CDCl$_3$, rt): δ 7.42-7.26 (m, 5H; phenyl group), 5.11 (s, 2H; benzyl), 2.37 (t, J = 8.0 Hz, 2H; CH_2CO$_2$Bn), 1.78-1.60 (m, 5H; cyclohexyl group), 1.55 (m, 2H; CH_2CH$_2$CO$_2$Bn), 1.32-1.08 (m, 4H; cyclohexyl group), 0.96-0.82 (m, 2H; cyclohexyl group). **^{13}C NMR** (125 MHz, CDCl$_3$, rt): δ 174.2 (CO$_2$Bn), 136.3, 128.7, 128.33, 128.30, 66.2, 37.3, 33.1, 32.5, 32.1, 26.7, 26.4. **HRMS** (ESI-TOF-MS): calculated for [$C_{16}H_{22}O_2$+Na]$^+$ requires 269.1512, found 269.1508.

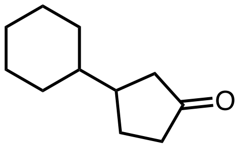
Benzyl 3-cyclohexyl-2-methylpropanoate (5fd)



According to the GP A, potassium cyclohexyltrifluoroborate (**2f**) (68.0 mg, 0.358 mmol), benzyl mathacrylate (**4d**) (53.0 mg, 0.301 mmol) and [Acr$^+$-Mes]ClO$_4$ (**1d**) (2.5 mg, 6.1 μmol) under blue LEDs irradiation for 24 h afforded **5fd** (68.1 mg, 88% yield) as a colorless oil after purification by flash column chromatography (hexane/EtOAc = 30/1). Spectral data are shown below.

^{1}H NMR (400 MHz, CDCl$_3$, rt): δ 7.42-7.28 (m, 5H; phenyl group), 5.09 (d, J = 12.4 Hz, 1H; CO$_2$CHHPh), 5.14 (d, J = 12.4 Hz, 1H; CO$_2$CHHPh), 2.60 (m, 1H; CH$_3$CHCO$_2$Bn), 1.80-1.53 (m, 6H; cyclohexyl group, CHHCH(CH$_3$)CO$_2$Bn), 1.31-1.06 (m, 8H; cyclohexyl group, CH_3CHCO$_2$Bn, CHHCH(CH$_3$)CO$_2$Bn), 0.93-0.77 (m, 2H; cyclohexyl group). **^{13}C NMR** (125 MHz, CDCl$_3$, rt): δ 177.2 (CO$_2$Bn), 136.4, 128.7, 128.2, 66.1, 41.8, 37.0, 35.5, 33.4, 33.3, 26.7, 26.4, 17.8. **HRMS** (ESI-TOF-MS): calculated for [$C_{17}H_{24}O_2$+Na]$^+$ requires 283.1669, found 283.1671.

3-cyclohexylcyclopentan-1-one (5fe)

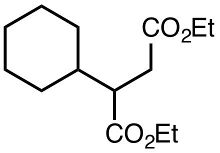


According to the GP A, potassium cyclohexyltrifluoroborate (**2f**) (68.3 mg, 0.359 mmol), 2-cyclopenten-1-one (**4e**) (24.6 mg, 0.300 mmol) and [Acr$^+$-Mes]ClO$_4$ (**1d**) (2.5 mg, 6.1 μmol) under blue LEDs irradiation for 15 h afforded **5fe** (30.3 mg, 61% yield) as a colorless oil after purification by flash column chromatography (hexane/EtOAc = 10/1). Spectral data are in agreement with the literature[6].

^{1}H NMR (400 MHz, CDCl$_3$, rt): δ 2.47-2.25 (m, 2H; cyclopentyl group), 2.23-2.07 (m, 2H;

cyclopentyl group), 1.95-1.57 (m, 7H; cyclopentyl group (2H) and cyclohexyl group (5H)), 1.48 (m, 1H; cyclopentyl group), 1.33-1.10 (m, 4H; cyclohexyl group), 1.02-0.89 (m, 2H; cyclohexyl group).

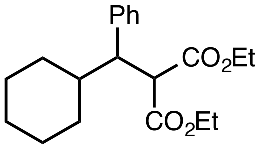
Diethyl 2-cyclohexylsuccinate (5ff)



According to the GP A, potassium cyclohexyltrifluoroborate (**2f**) (68.4 mg, 0.360 mmol), diethyl maleate (**4f**) (51.7 mg, 0.300 mmol) and [Acr$^+$-Mes]ClO_4 (**1d**) (2.5 mg, 6.1 μmol) under blue LEDs irradiation for 24 h afforded **5ff** (49.0 mg, 57% yield) as a pale yellow oil after purification by flash column chromatography (hexane/EtOAc = 7/1). Spectral data are shown below.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 4.22-4.07 (m, 4H; $CO_2CH_2CH_3$), 2.75-2.64 (m, 2H; CH_2CO_2Et), 2.42 (m, 1H; $CHCO_2Et$), 1.79-1.53 (m, 6H; cyclohexyl group), 1.32-0.96 (m, 11H; $CO_2CH_2CH_3$, cyclohexyl group). **^{13}C NMR** (125 MHz, $CDCl_3$, rt): δ 174.7 (CO_2Et), 172.7 (CO_2Et), 60.7, 60.5, 47.2, 40.1, 33.6, 30.7, 30.2, 26.5, 26.3, 14.4, 14.3. **HRMS** (ESI-TOF-MS): calculated for $[C_{14}H_{24}O_4+Na]^+$ requires 279.1567, found 279.1564.

Diethyl (1-cyclohexyl-1-phenyl)methylmalonate (5fg)



According to the GP A, potassium cyclohexyltrifluoroborate (**2f**) (68.0 mg, 0.358 mmol), diethyl 2-benzylidenemalonate (**4g**) (74.5 mg, 0.300 mmol) and [Acr$^+$-Mes]ClO_4 (**1d**) (2.5 mg, 6.1 μmol) under blue LEDs irradiation for 48 h afforded **5fg** (77.9 mg, 78% yield) as a colorless oil after purification by PTLC (hexane/EtOAc = 7/1). Spectral data are shown below.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.30-7.12 (m, 5H; Ph), 4.31-4.16 (m, 2H; $CO_2CH_2CH_3$), 3.97 (d, J = 11.6 Hz, 1H; $CH(CO_2Et)_2$), 3.92-3.79 (m, 2H; $CO_2CH_2CH_3$), 3.37 (dd, ^3J = 11.2 Hz, ^3J = 4.8 Hz, 1H; $PhCHCH(CO_2Et)_2$), 1.72-1.51 (m, 6H; cyclohexyl group), 1.29 (t, J = 7.2 Hz, 3H; $CO_2CH_2CH_3$), 1.27-1.05 (m, 2H; cyclohexyl group), 1.01-0.76 (m, 6H; $CO_2CH_2CH_3$, cyclohexyl group). **^{13}C NMR** (125 MHz, $CDCl_3$, rt): δ 169.0 (CO_2Et), 168.2 (CO_2Et), 139.1, 129.6, 127.8, 126.8, 61.7, 61.3, 55.5, 51.2, 40.9, 32.2, 28.4, 26.8, 26.6, 26.3, 14.3, 13.8. **HRMS** (ESI-TOF-MS): calculated for $[C_{20}H_{28}O_4+Na]^+$ requires 355.1891, found 355.1891.

7. Cyclic voltammogram of potassium phenethyltrifluoroborate (2a)

Electrochemical measurements were recorded on Hokutodenkou HZ-5000 analyzer (observed in 0.004 M MeCN; $[N(Bu)_4](PF_6)$ = 0.1 M; Ag/AgCl = electrode; reported with respect to the $[FeCp_2]/[FeCp_2]^+$ couple). (Figure. S2)

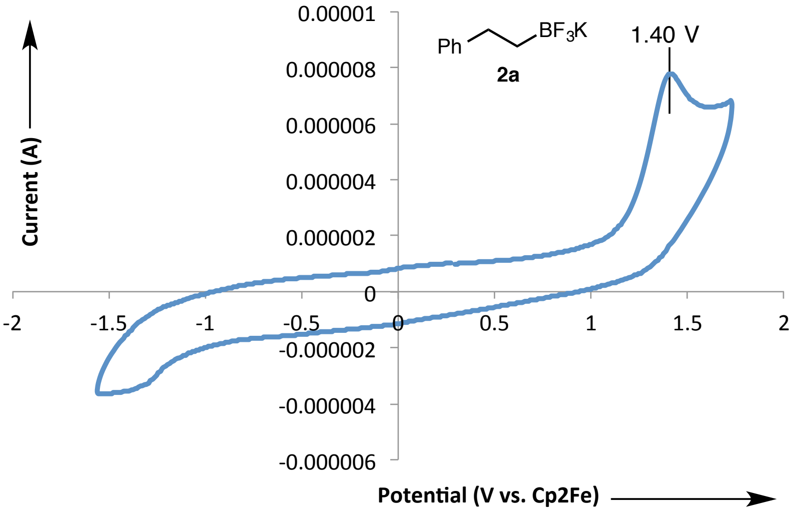
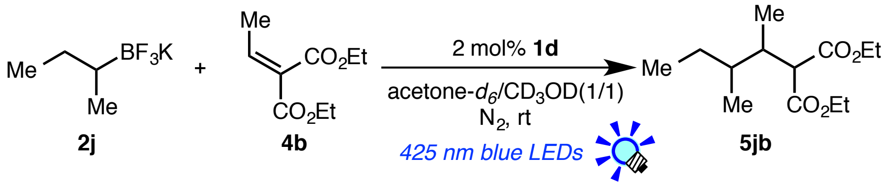


Figure S2. Cyclic Voltammogram of potassium phenethyltrifluoroborate (**2a**)

8. Time profile of photocatalytic radical reaction of potassium *sec*-butyltrifluoroborate (2j) with diethyl 2-ethylidenemalonate (4b)

The photocatalytic radical reaction of **2j** with **4b** using [Acr$^+$-Mes]ClO_4 (**1d**) was performed with/without visible light irradiation. The time profile is shown in Figure S3. As a result, continuous irradiation of visible light is necessary for efficient reaction. Furthermore, the result of this experiment suggests that radical chain propagation mechanism is not main component in this reaction.



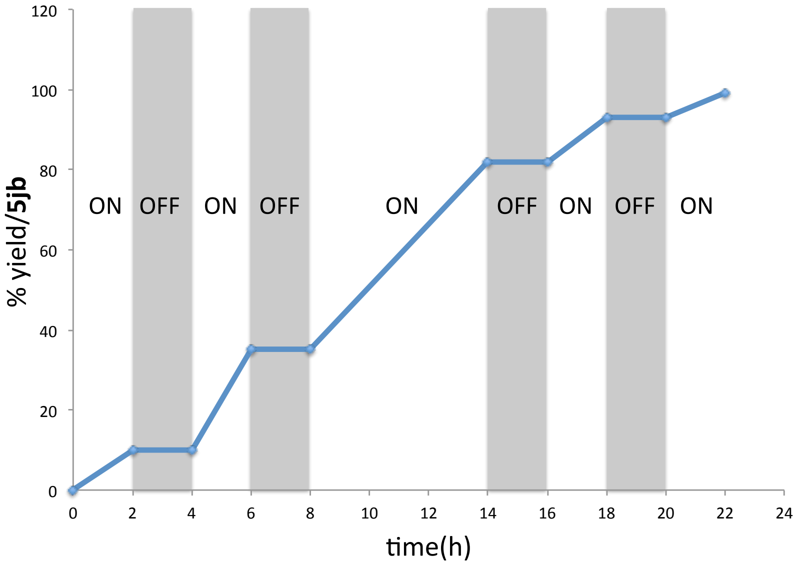
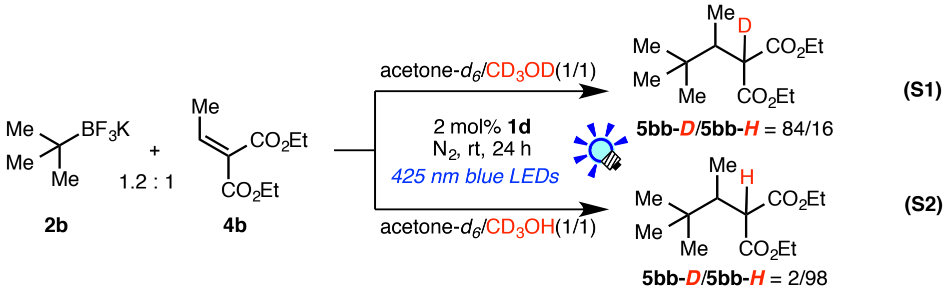


Figure S3. Time profile of photocatalytic radical reaction of potassium *sec*-butyltrifluoroborate (**2j**) with diethyl 2-ethylidenemalonate (**4b**)

9. Control experiments in a mixed solvent system of acetone-d_6 and CD_3OH

*Reaction of potassium tert-butyltrifluoroborate (**2b**) with diethyl 2-ethylidenemalonate (**4b**)*



[Acr$^+$-Mes]ClO_4 (**1d**) (0.4 mg, 1.0 μmol) was weighted in an NMR tube under N_2, and potassium *tert*-butyltrifluoroborate (**2a**) (9.8 mg, 60 μmol), acetone-d_6 (0.25 mL), diethyl 2-ethylidenemalonate (**4b**) (9.3 mg, 50 μmol), tetraethylsilane as an internal standard and CD_3OD (99.8 atom% deuterated, 0.25 mL) or CD_3OH (99.8 atom% deuterated, 0.25 mL) were added to the NMR tube. The reaction mixture was degassed by three freeze-pump-thaw cycles, then irradiated for 24 h at room temperature (water bath) by 3 W LED lamps ($h\nu = 425 \pm 15$ nm, placed at a distance of ~3 cm from reaction mixture). Then, each reaction mixtures were measured by GC-MS without further purification. The ratio of **5bb-D**/**5bb-H** is 84/16 in acetone-d_6/CD_3OD (1/1) solvent. In contrast, the ratio of **5bb-D**/**5bb-H** is 2/98 in acetone-d_6/CD_3OH (1/1) solvent. These ratios were calculated on the basis of the GC-MS spectrum for isolated **5bb** (retention time : 8.6 min., column : 50 ˚C (hold 2 min.)→300 ˚C (rate 15 ˚C/min. and hold 35 min.), peaks 229.00(73198), 230.05(10012)). These results suggest that the H atom in the product **5bb** derived not from hydrogen abstraction but from protonation (Figure S4-1.).

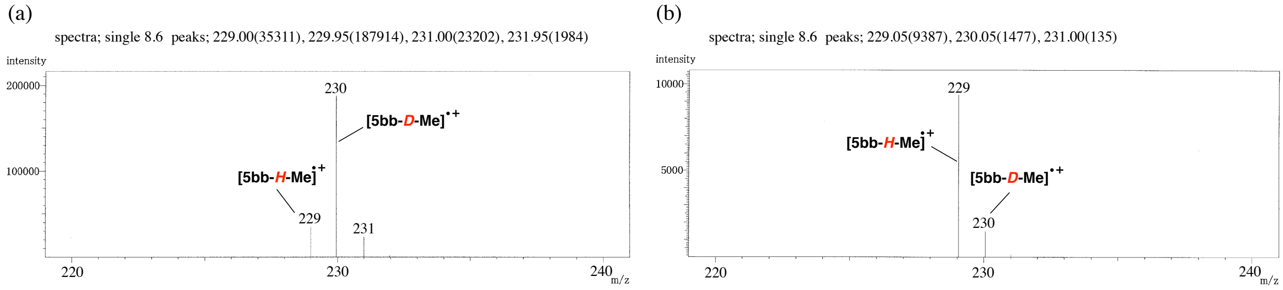
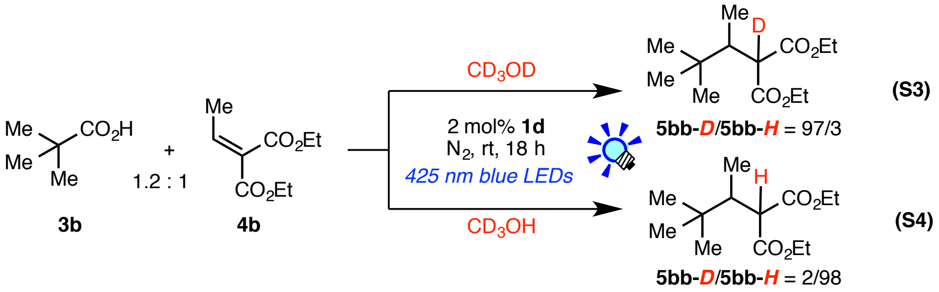


Figure S4-1. GC-MS spectra for control experiments. (a) eq. S1, (b) eq. S2. (inject: 300 ˚C, retention time : 8.6 min., column : 50 ˚C (hold 2 min.)→300 ˚C (rate 15 ˚C/min. and hold 35 min.)).

*Reaction of pivalic acid (**3b**) with diethyl 2-ethylidenemalonate (**4b**)*



[Acr$^+$-Mes]ClO$_4$ (**1d**) (0.4 mg, 1.0 μmol) was weighted in an NMR tube under N$_2$, pivalic acid (**3b**) (6.1 mg, 60 μmol), diethyl 2-ethylidenemalonate (**4b**) (9.3 mg, 50 μmol), tetraethylsilane as an internal standard and CD$_3$OD (99.8 atom% deuterated, 0.50 mL) or CD$_3$OH (99.8 atom% deuterated, 0.50 mL) were added to the NMR tube. The reaction mixture was degassed by three freeze-pump-thaw cycles, then irradiated for 18 h at room temperature (water bath) by 3 W LED lamps ($h\nu$ = 425 ± 15 nm, placed at a distance of ~3 cm from reaction mixture). Then, each reaction mixtures were measured by GC-MS without further purification. The ratio of **5bb-D**/**5bb-H** is 97/3 in CD$_3$OD solvent. In contrast, the ratio of **5bb-D**/**5bb-H** is 2/98 in CD$_3$OH solvent. These ratios were calculated on the basis of the GC-MS spectrum for isolated **5bb** (retention time : 8.6 min., column : 50 ˚C (hold 2 min.)→300 ˚C (rate 15 ˚C/min. and hold 35 min.), peaks 229.00(73198), 230.05(10012)). These results suggest that the H atom in the product **5bb** derived not from hydrogen abstraction but from protonation (Figure S4-2.).

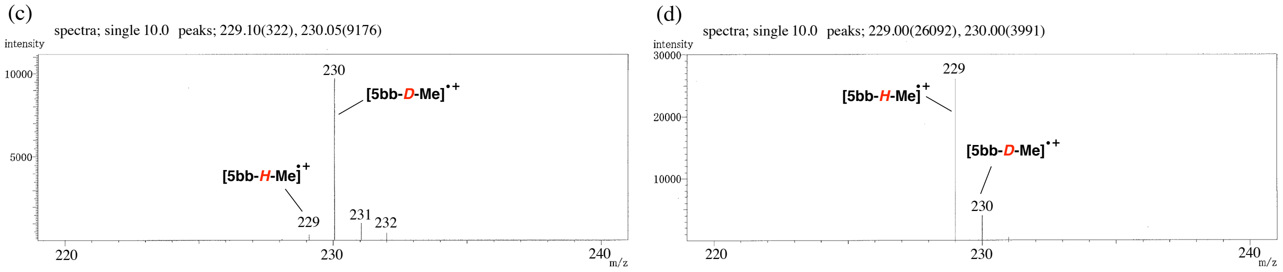
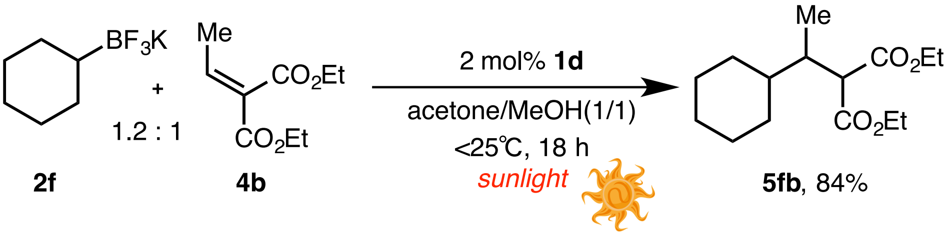


Figure S4-2. GC-MS spectra for control experiments. (c) eq. S3, (d) eq. S4. (inject : 300 ˚C, retention time : 10.0 min., column : 50 ˚C (hold 2 min.)→300 ˚C (rate 20 ˚C/min. and hold 40 min.)).

10. Sunlight-driven reaction

Cylindrical vessel was used for photoreaction under sunlight. To a mixture of acetone (2.5 mL) and MeOH (2.5 mL) of [Acr$^+$-Mes]ClO_4 (**1d**) (4.1 mg, 10 μmol) in the vessel, potassium cyclohexyltrifluoroborate (**2f**) (116 mg, 0.610 mmol) and diethyl 2-ethylidenemalonate (**4b**) (93.9 mg, 0.504 mmol) were added under N_2. The reaction mixture was exposed to sunlight (11/18-20/2013) below under 25 ℃. After work up, **5fb** was obtained as a pale yellow oil (115 mg, 84% yield).



2f **4b** **5fb**, 84%

11. References

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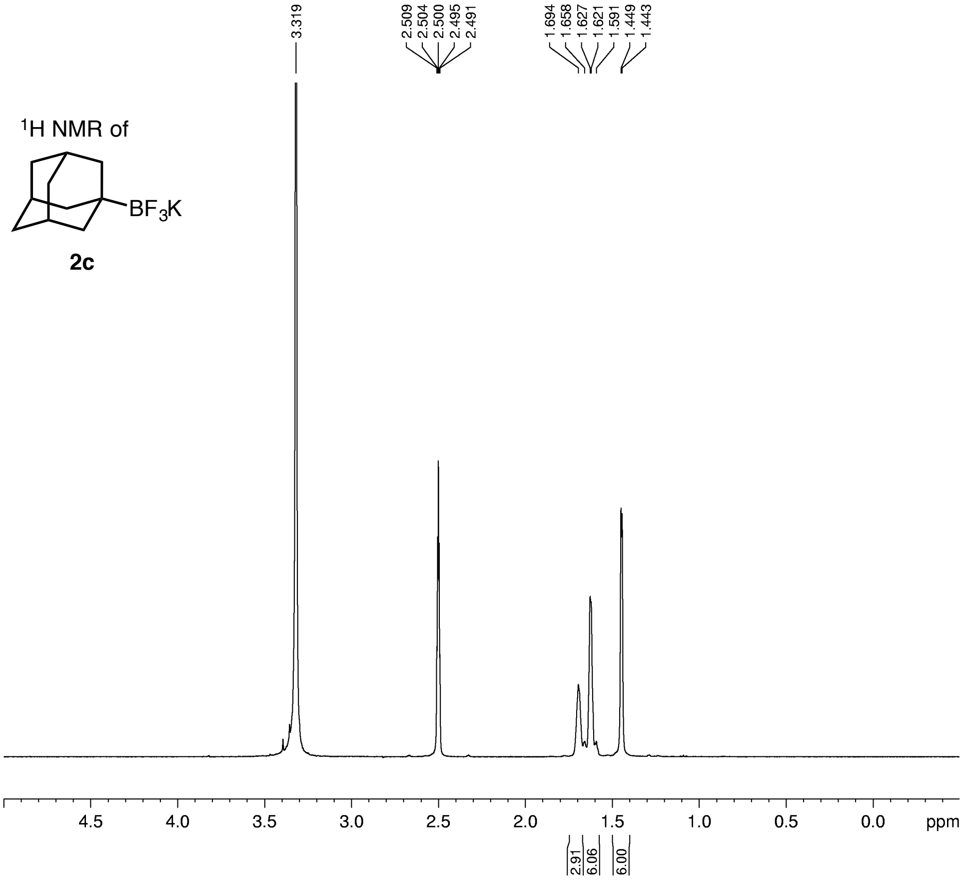
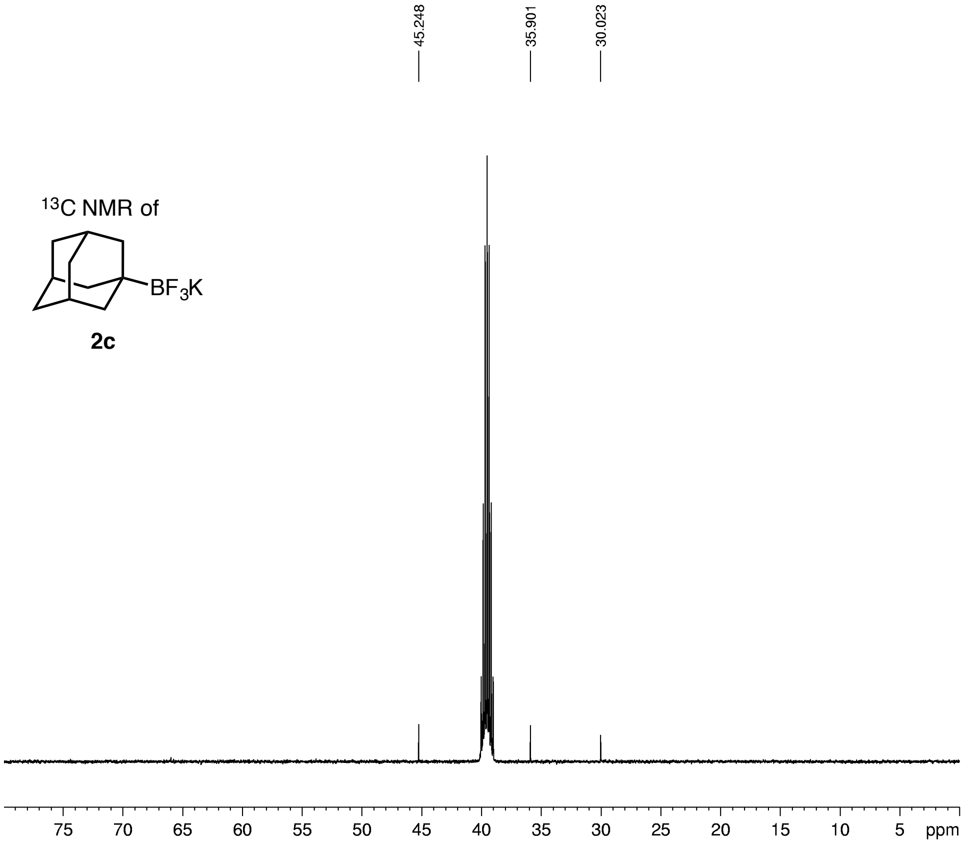
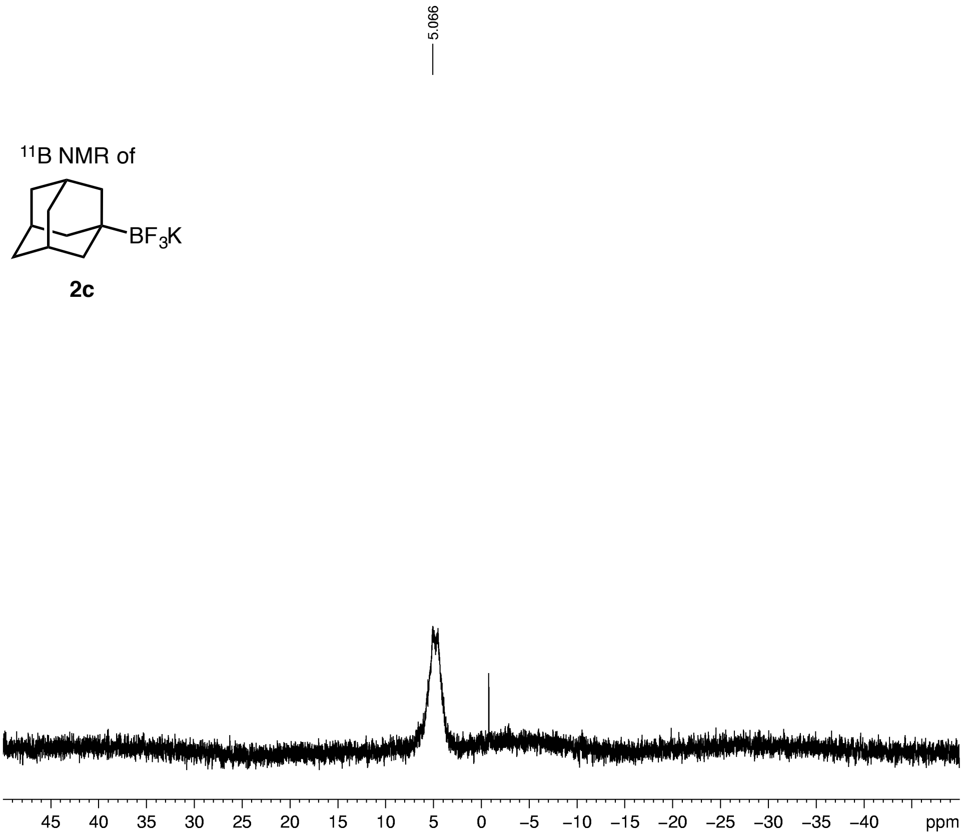
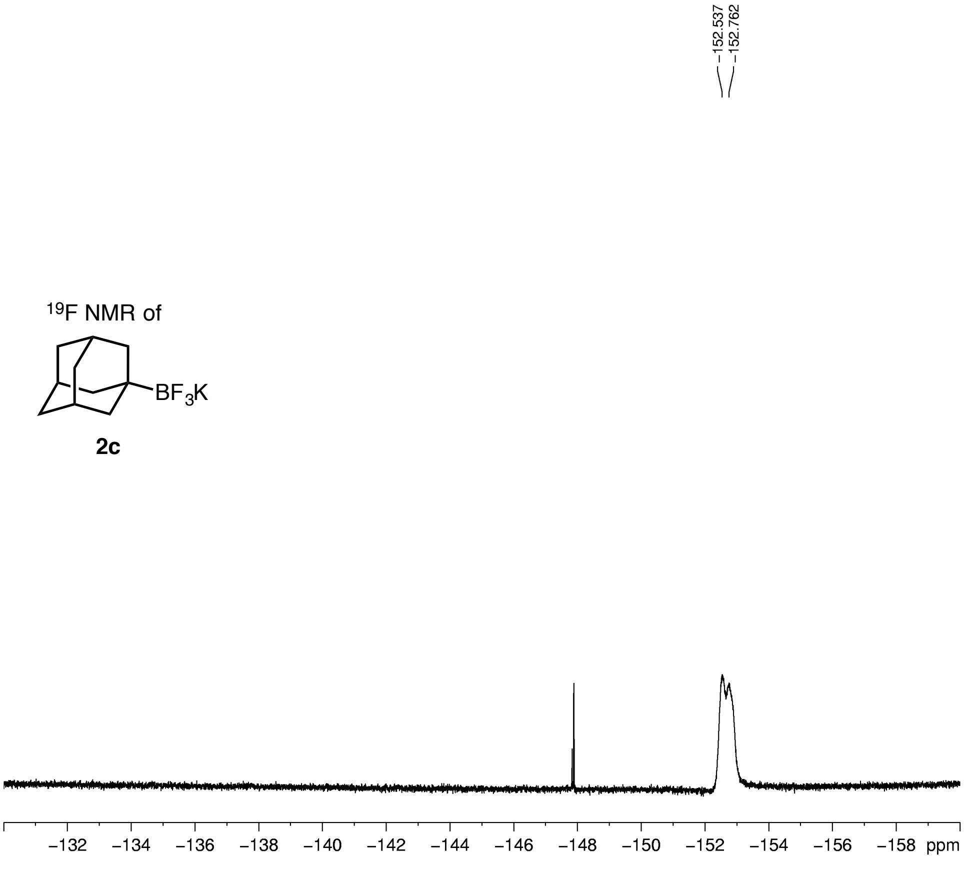
[6] P. Jones, C. K. Reddy and P. Knochel, *Tetrahedron,* **1998**, *54*, 1471.

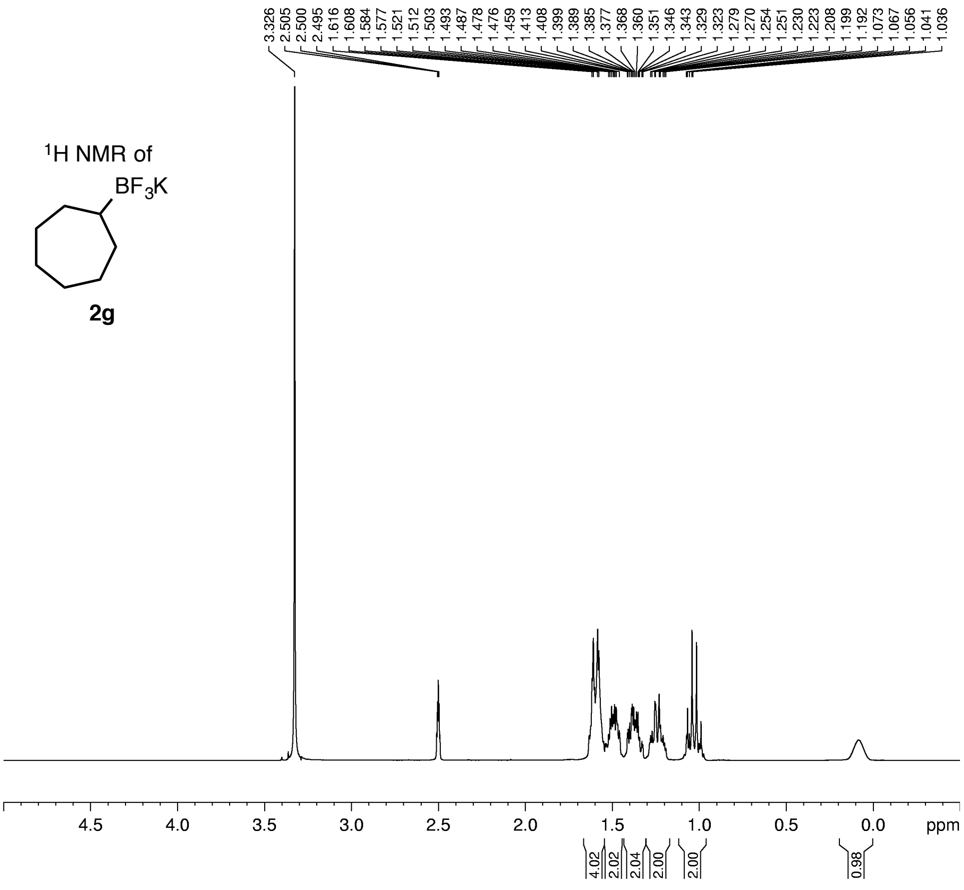
12. ^{1}H, ^{13}C, ^{11}B and ^{19}F NMR spectra



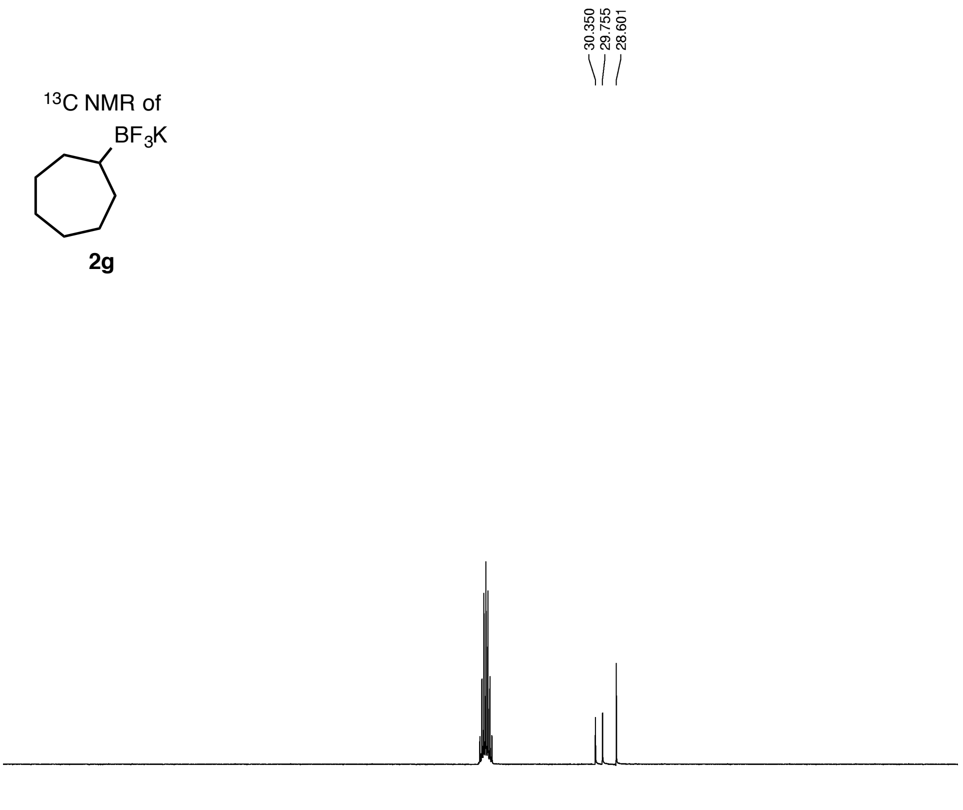



5.066
11B NMR of
BF3K
2c
45 40 35 30 25 20 15 10 5 0 −5 −10 −15 −20 −25 −30 −35 −40 ppm

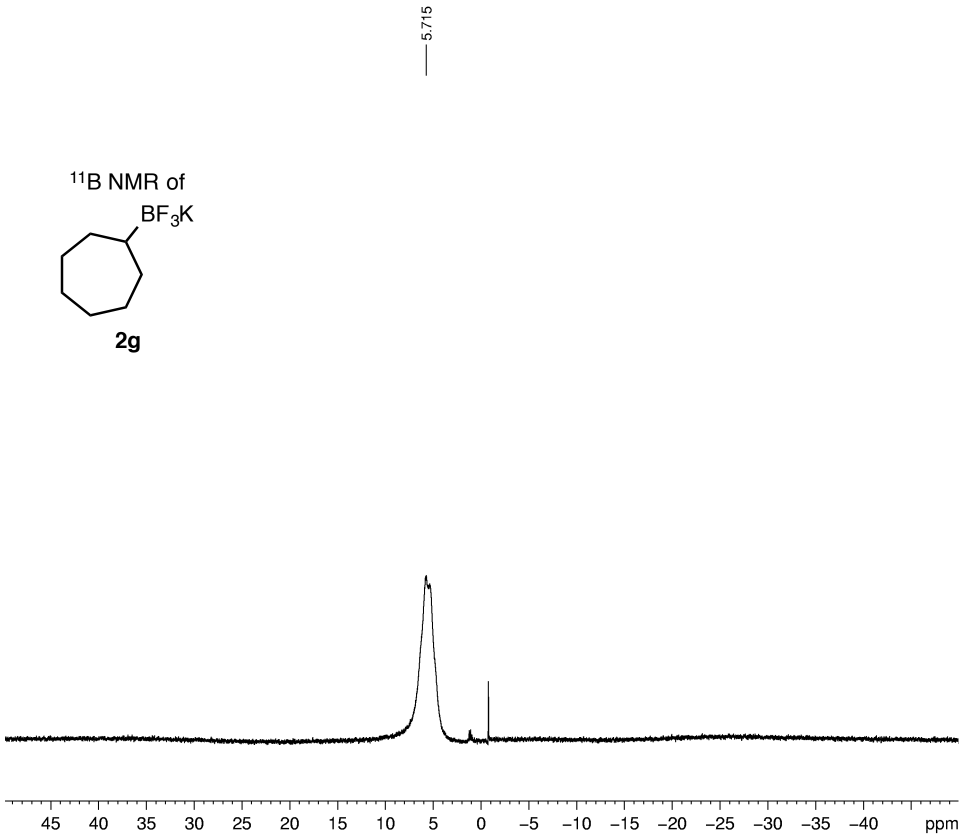

−152.537
−152.762
19F NMR of
BF3K
2c
−132 −134 −136 −138 −140 −142 −144 −146 −148 −150 −152 −154 −156 −158 ppm

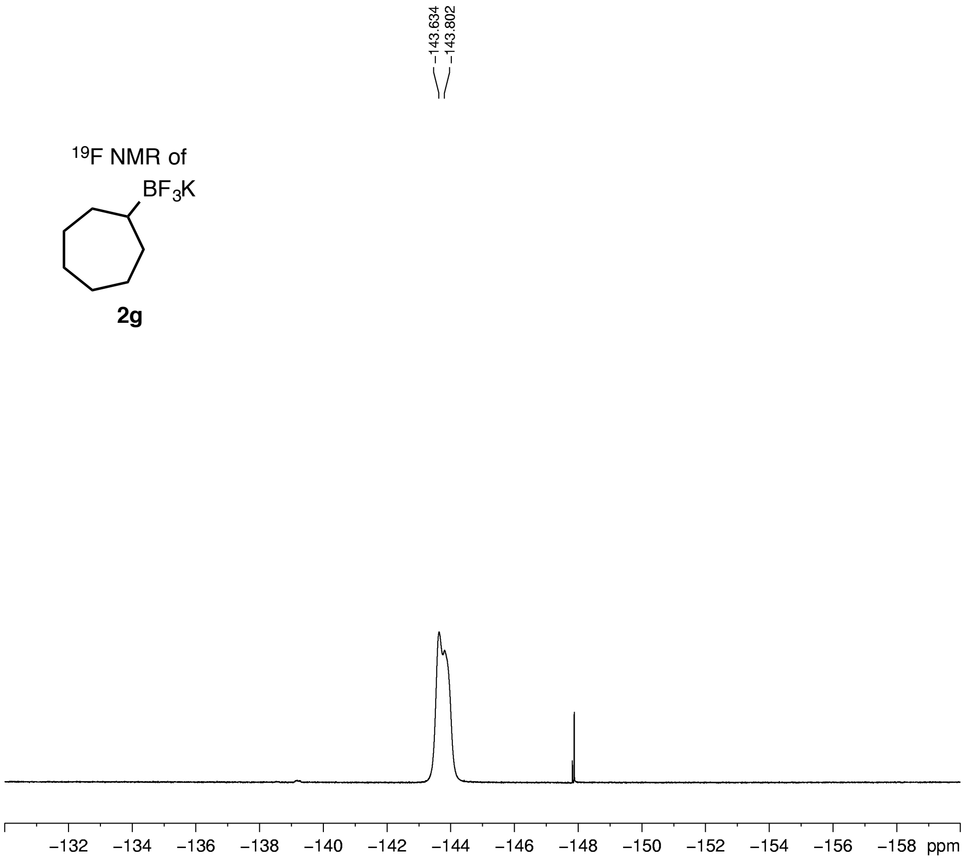


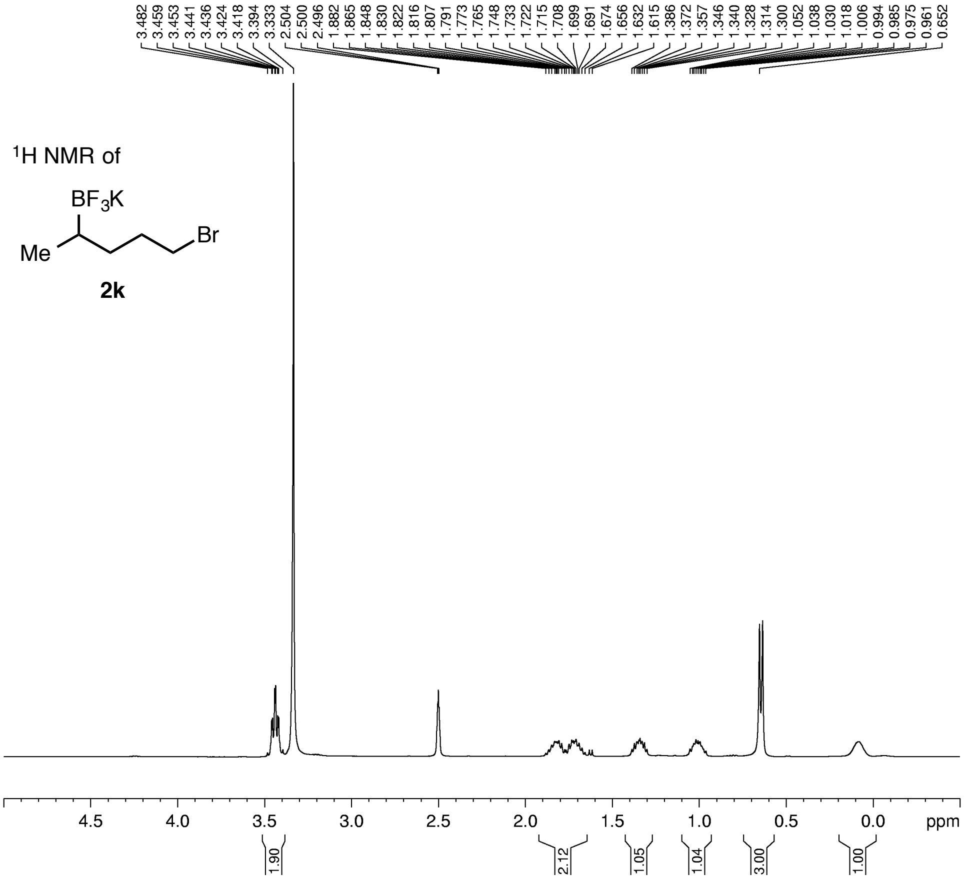
^{1}H NMR of
BF_3K
2g
3.326
2.505
2.500
2.495
1.616
1.608
1.584
1.577
1.521
1.512
1.503
1.493
1.487
1.478
1.476
1.459
1.413
1.408
1.399
1.389
1.385
1.377
1.368
1.360
1.351
1.346
1.343
1.329
1.323
1.279
1.270
1.254
1.251
1.230
1.223
1.208
1.199
1.192
1.073
1.067
1.056
1.041
1.036
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
4.02
2.02
2.04
2.00
2.00
0.98



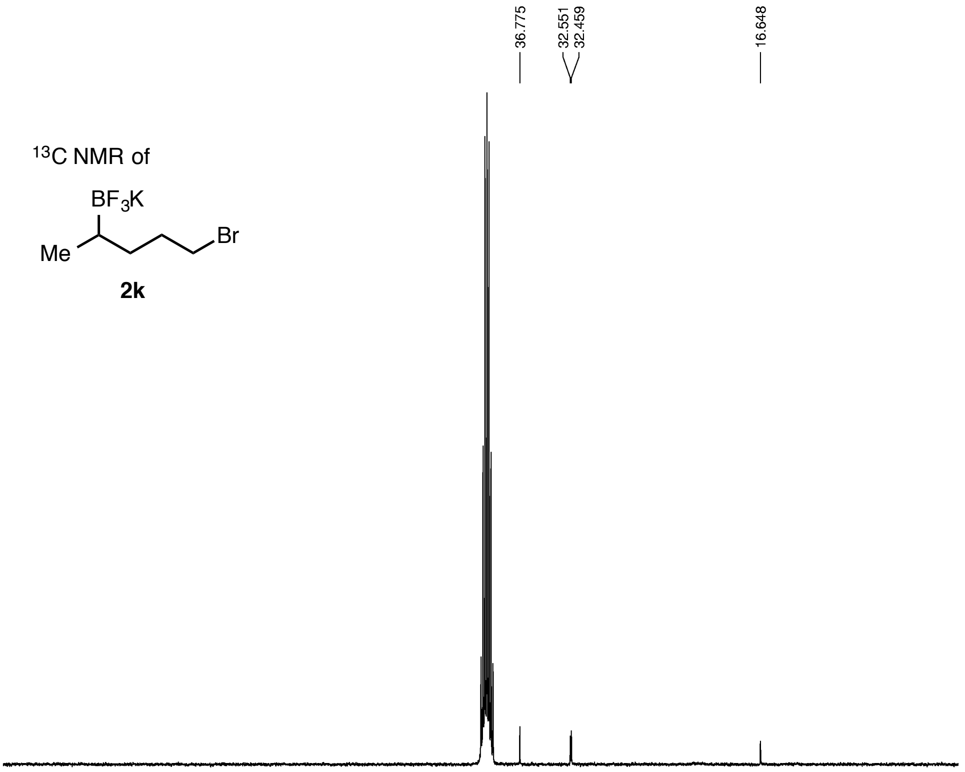
30.350
29.755
28.601
^{13}C NMR of
BF_3K
2g
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
ppm


5.715
11B NMR of
BF3K
2g
45 40 35 30 25 20 15 10 5 0 −5 −10 −15 −20 −25 −30 −35 −40 ppm


−143.634
−143.802
19F NMR of
BF3K
2g
−132 −134 −136 −138 −140 −142 −144 −146 −148 −150 −152 −154 −156 −158 ppm

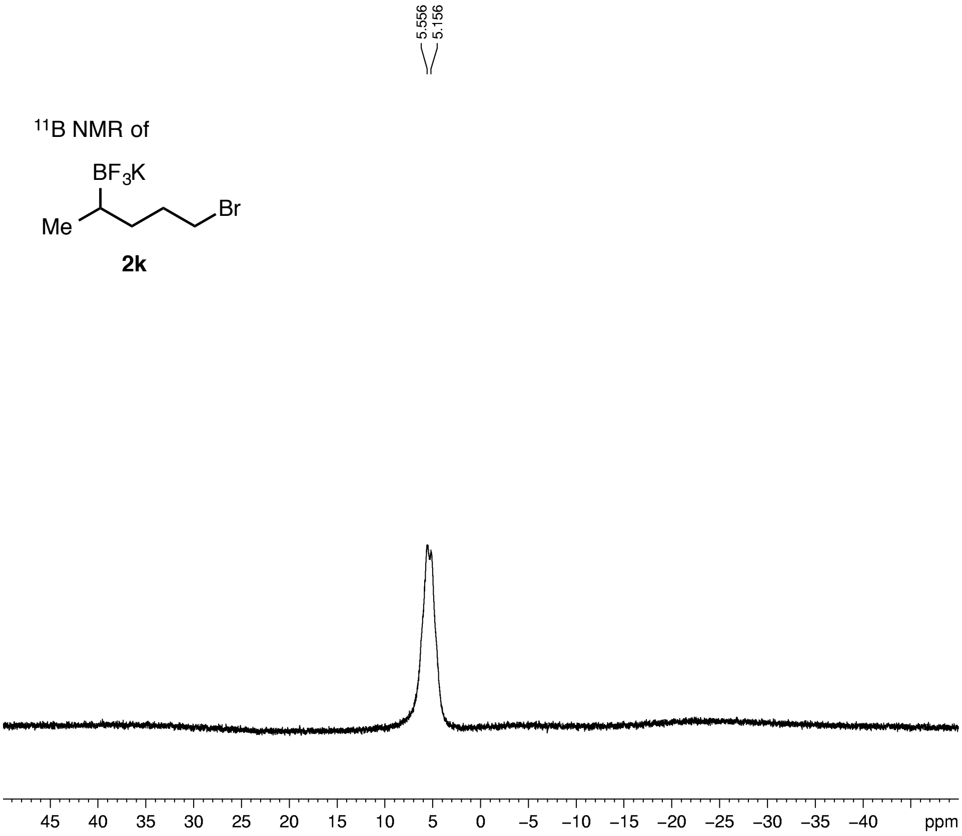


3.482
3.459
3.453
3.441
3.436
3.424
3.418
3.394
3.333
2.504
2.500
2.496
1.882
1.865
1.848
1.830
1.822
1.816
1.807
1.791
1.773
1.765
1.748
1.733
1.722
1.715
1.708
1.699
1.691
1.674
1.656
1.632
1.615
1.386
1.372
1.357
1.346
1.340
1.328
1.314
1.300
1.052
1.038
1.030
1.018
1.006
0.994
0.985
0.975
0.961
0.652
^{1}H NMR of
BF$_3$K
Me
Br
2k
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.90
2.12
1.05
1.04
3.00
1.00



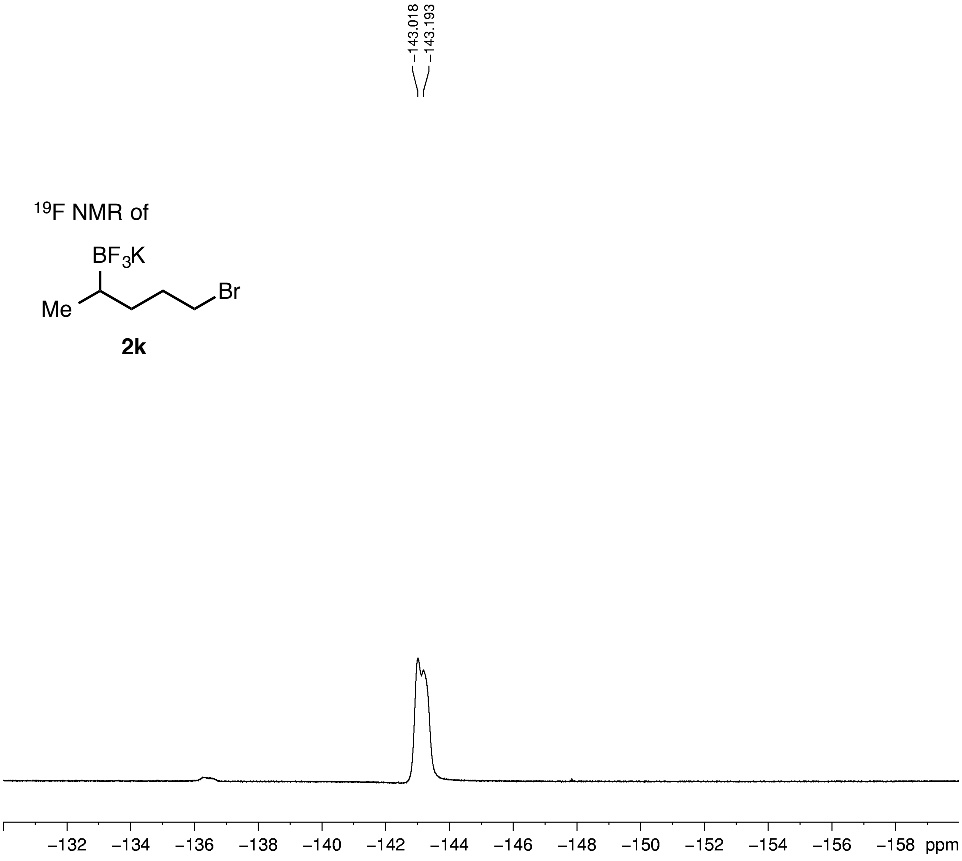
36.775
32.551
32.459
16.648
^{13}C NMR of
BF$_3$K
Me
Br
2k
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
ppm

^{11}B NMR of

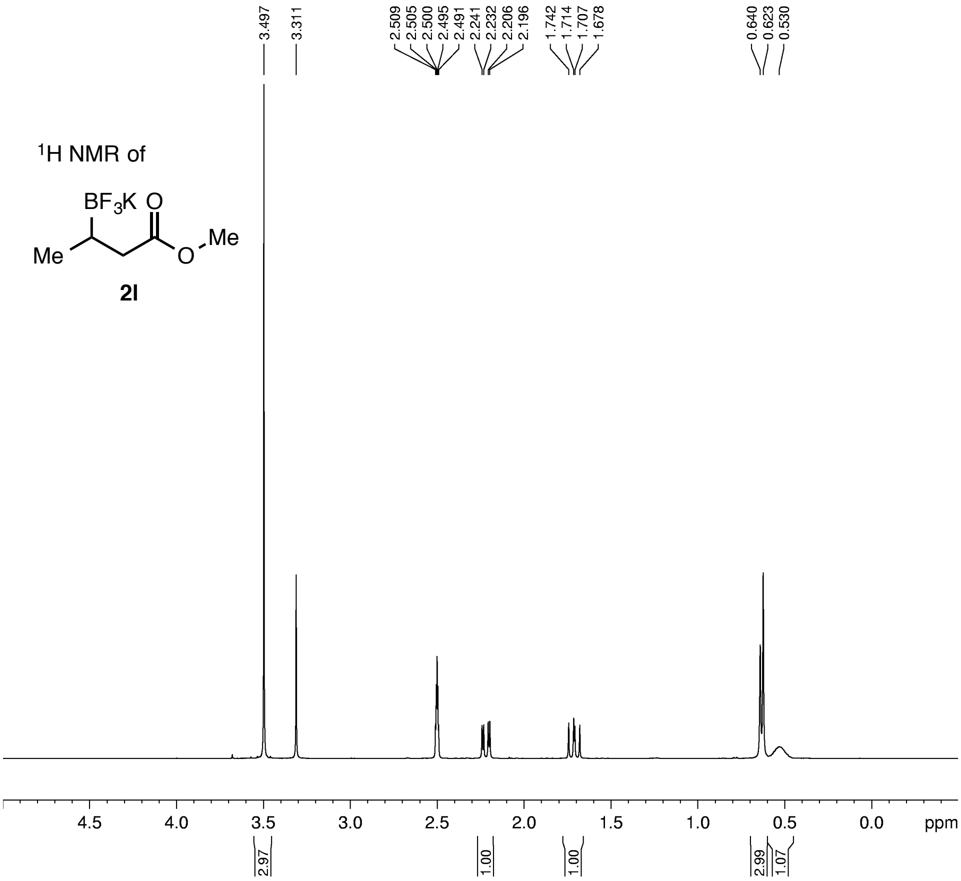


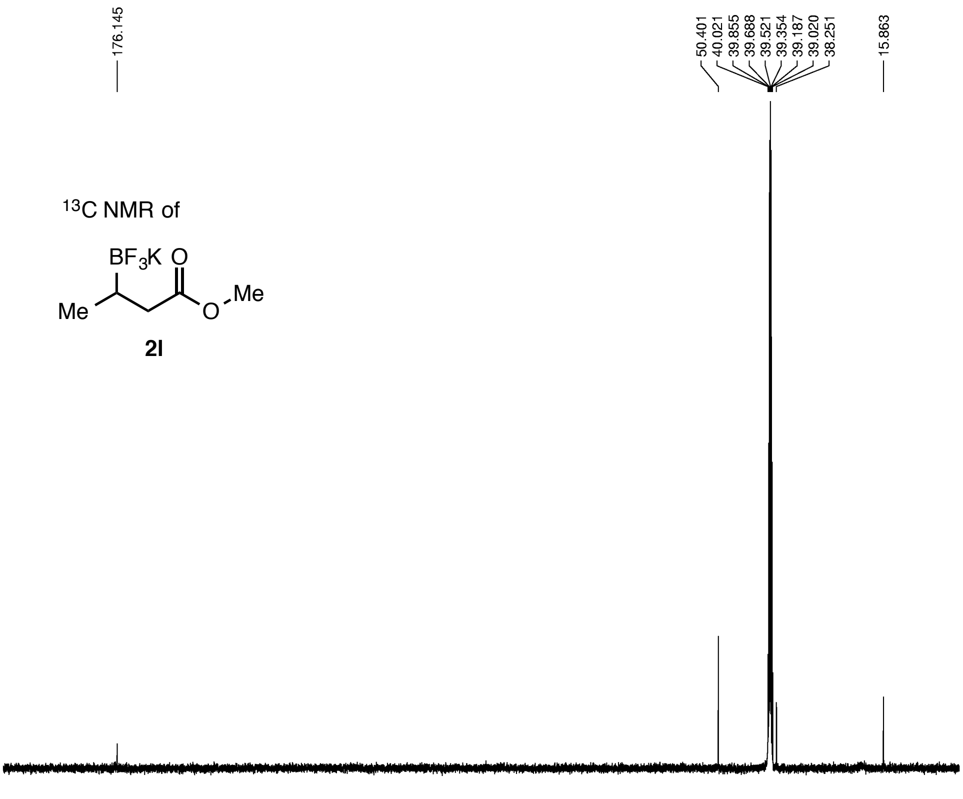
2k

^{19}F NMR of

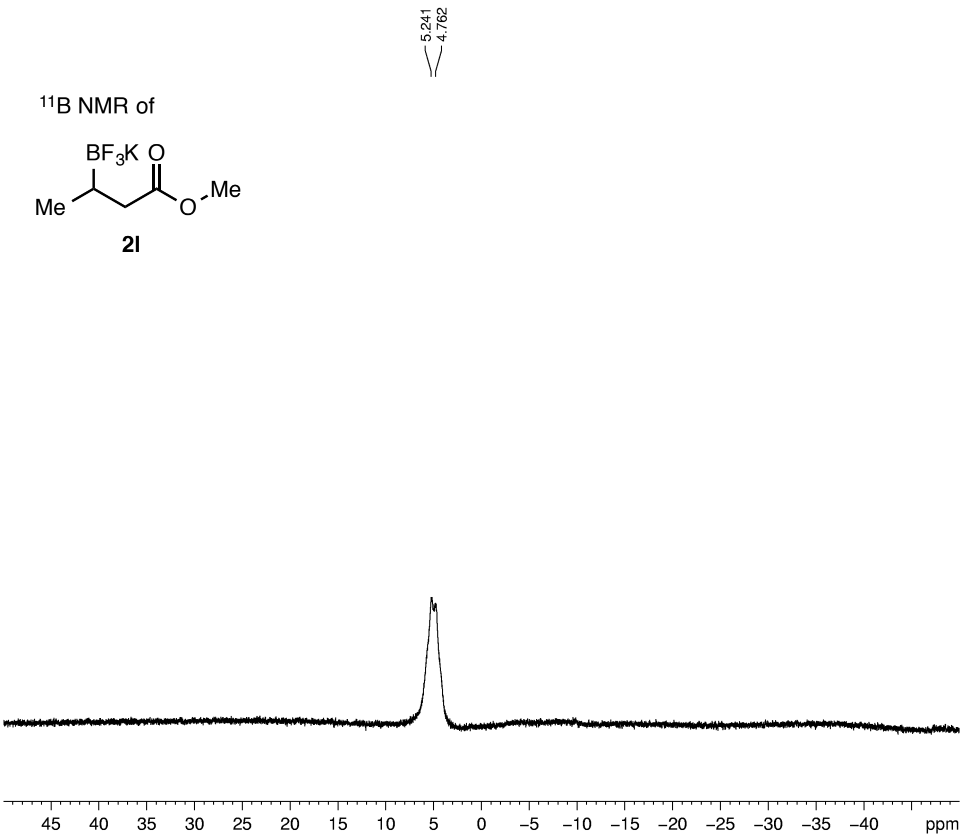


2k

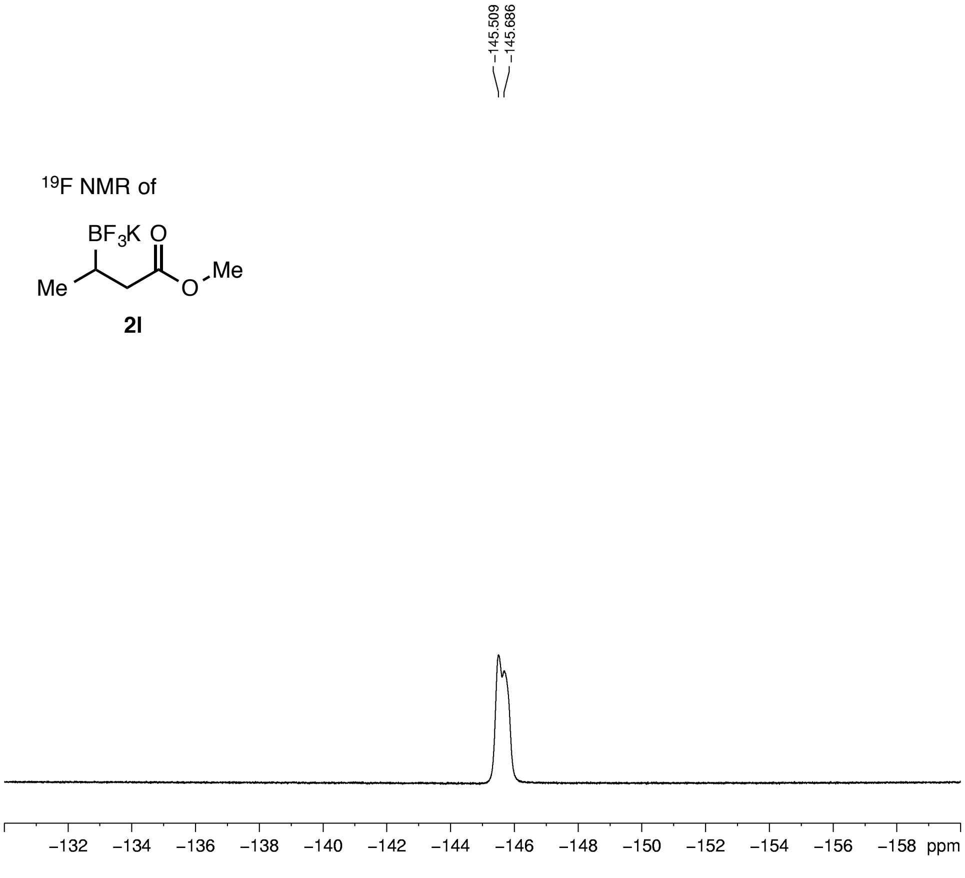

1H NMR of
BF3K O
Me
O
Me
2l
3.497
3.311
2.509
2.505
2.500
2.495
2.491
2.241
2.232
2.206
2.196
1.742
1.714
1.707
1.678
0.640
0.623
0.530
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.97
1.00
1.00
2.99
1.07

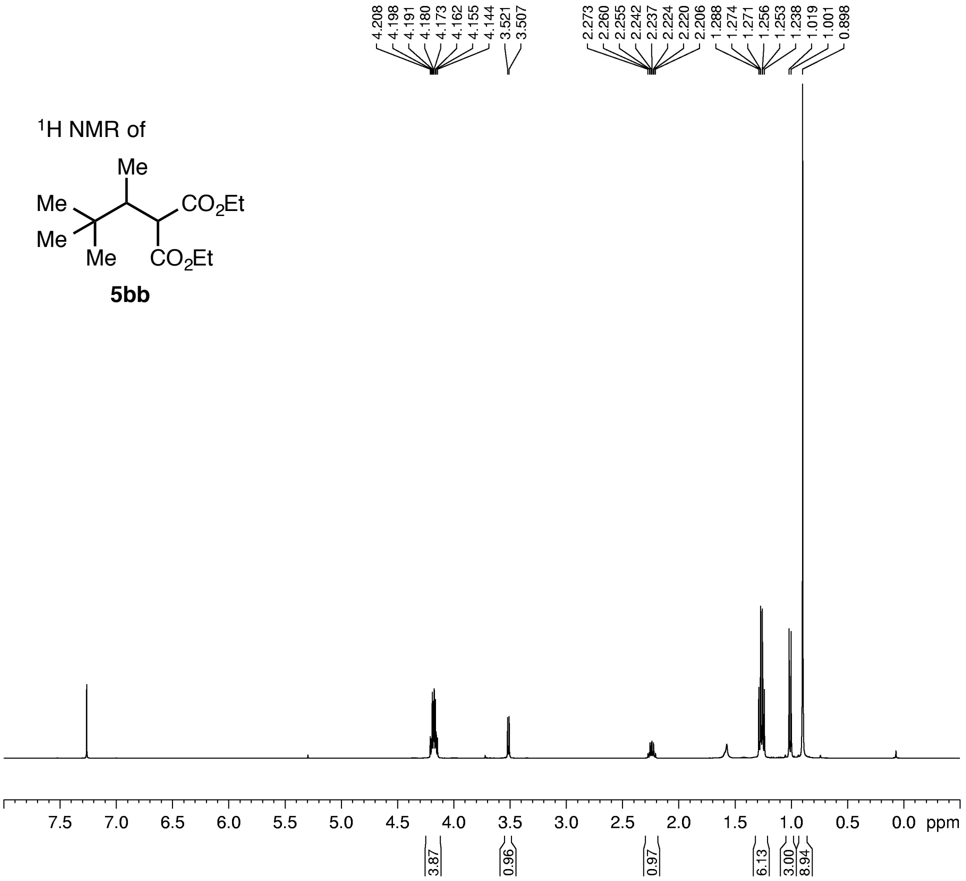

13C NMR of
BF3K O
Me
O
Me
2l
176.145
50.401
40.021
39.855
39.688
39.521
39.354
39.187
39.020
38.251
15.863
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

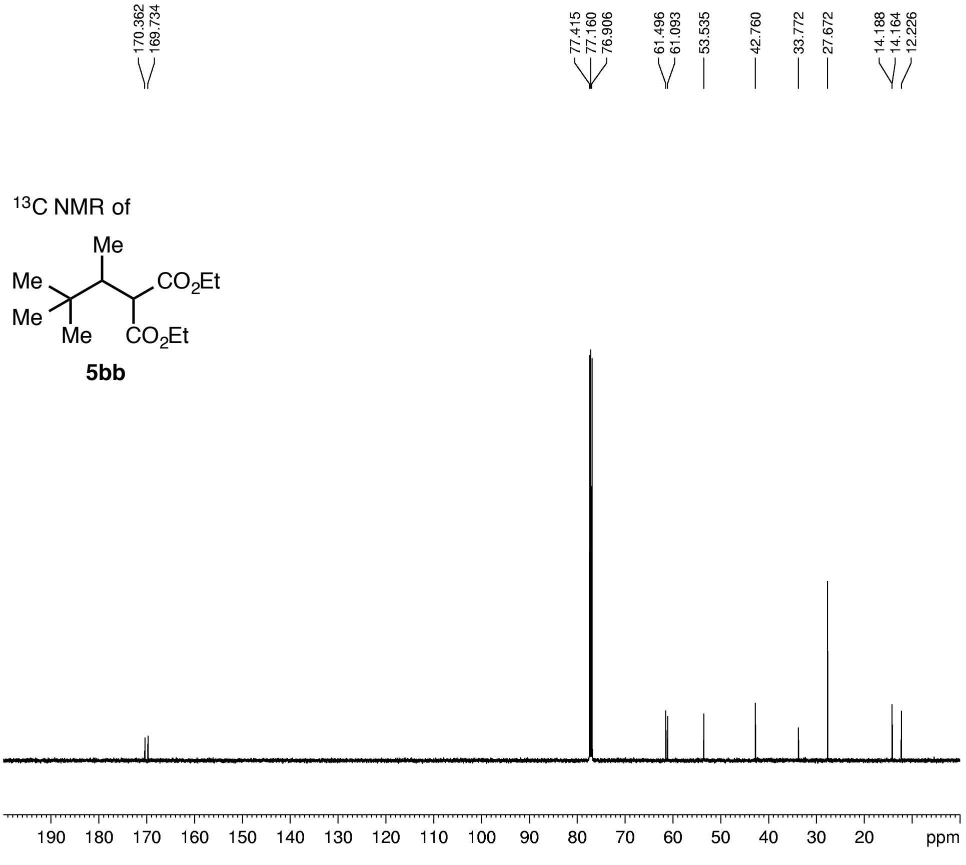
^{11}B NMR of

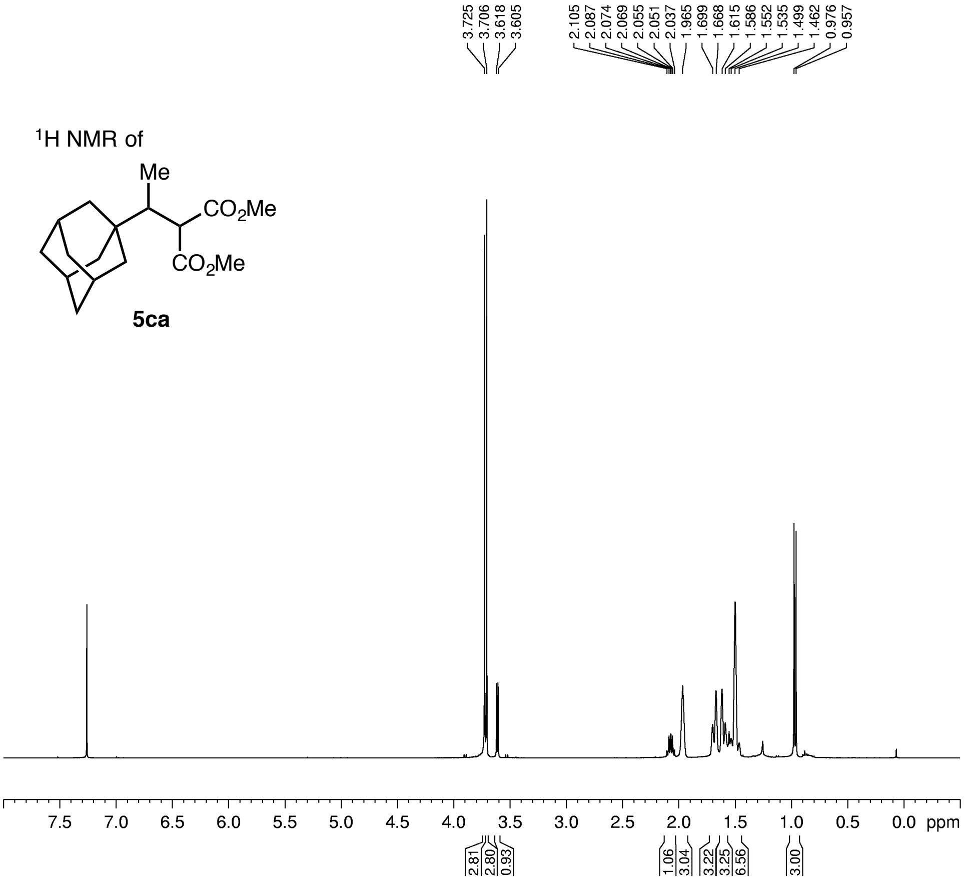


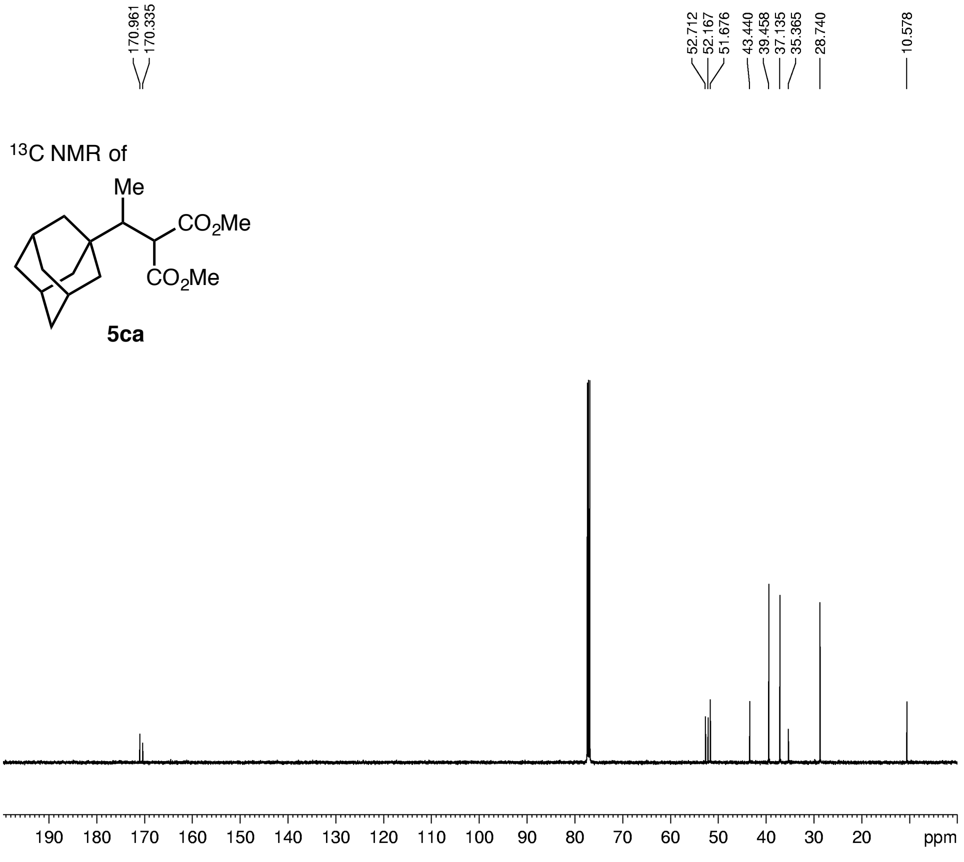
^{19}F NMR of

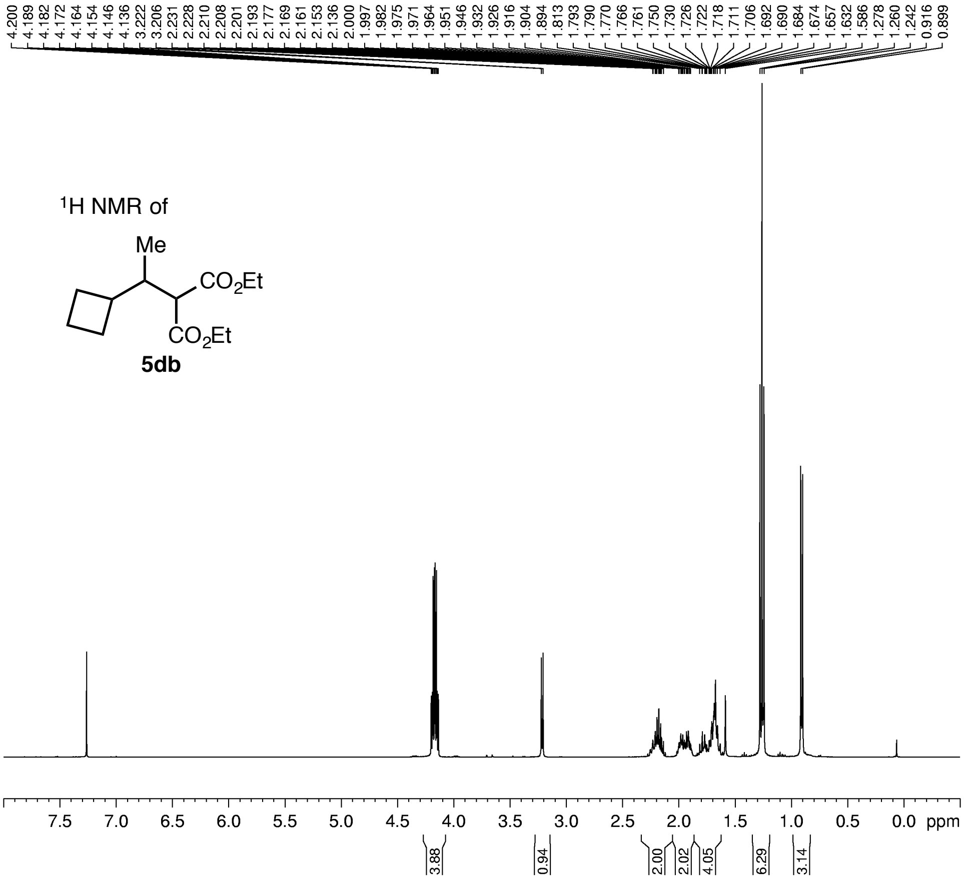


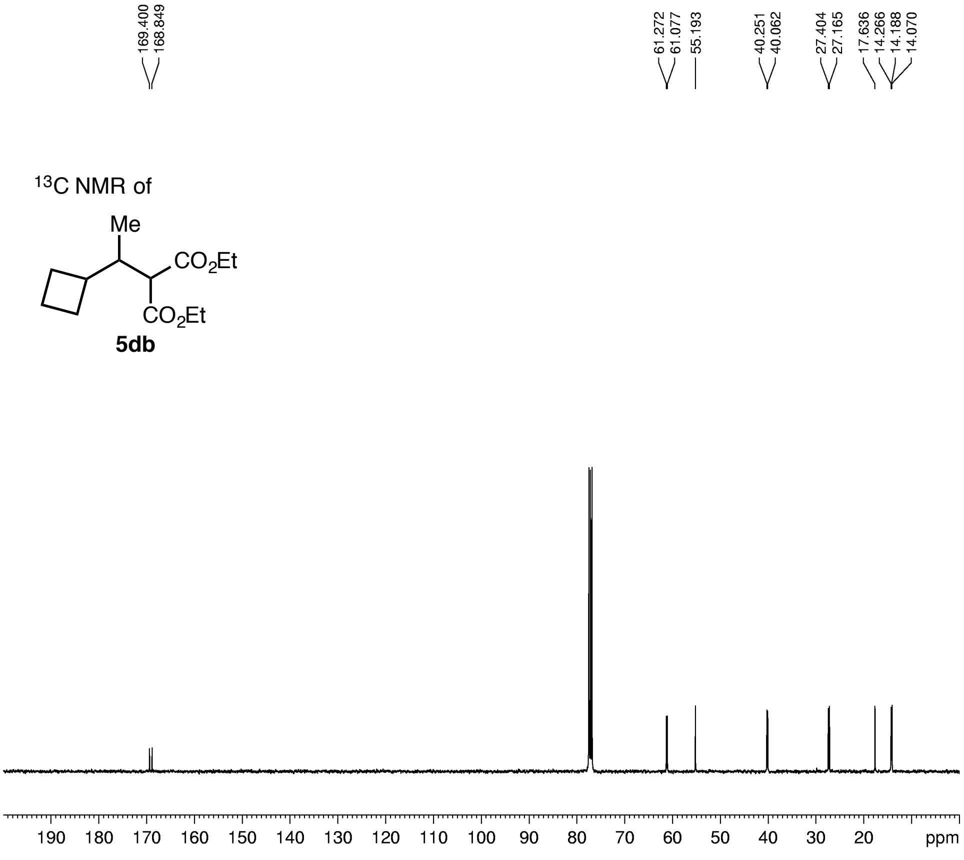

1H NMR of
Me
Me
Me
Me
CO2Et
CO2Et
5bb
4.208
4.198
4.191
4.180
4.173
4.162
4.155
4.144
3.521
3.507
2.273
2.260
2.255
2.242
2.237
2.224
2.220
2.206
1.288
1.274
1.271
1.256
1.253
1.238
1.019
1.001
0.898
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
3.87
0.96
0.97
6.13
3.00
8.94

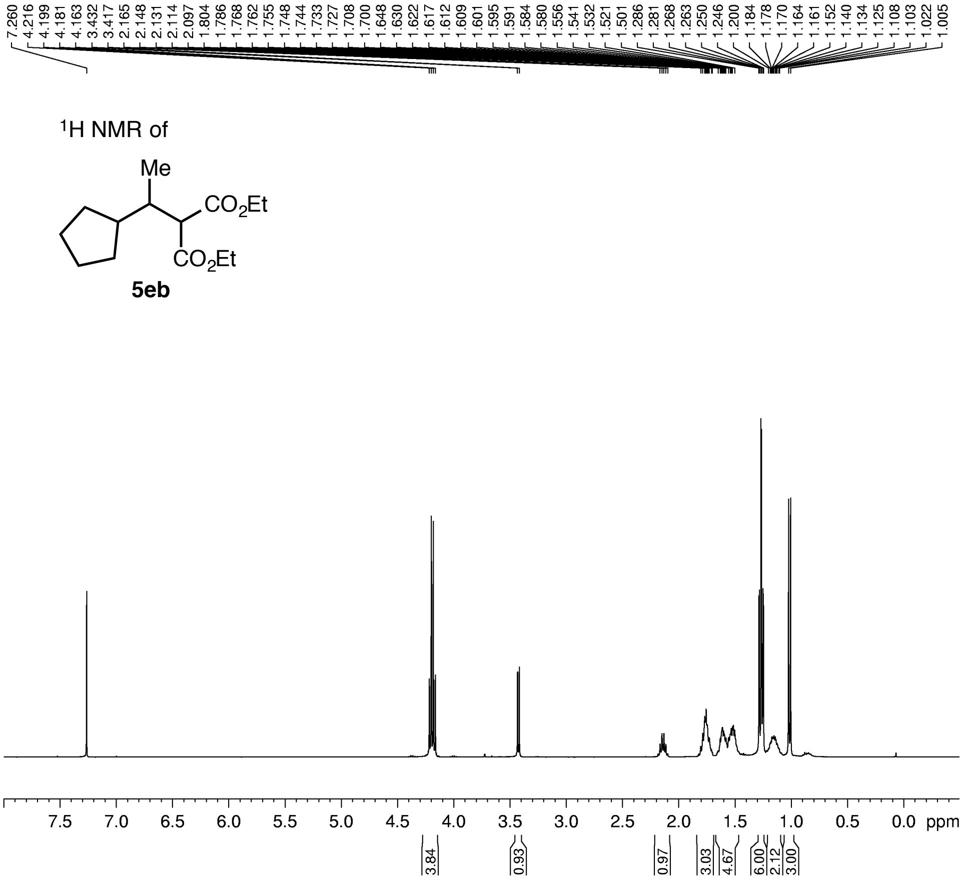

13C NMR of
Me
Me
Me
Me
CO2Et
CO2Et
5bb
170.362
169.734
77.415
77.160
76.906
61.496
61.093
53.535
42.760
33.772
27.672
14.188
14.164
12.226
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

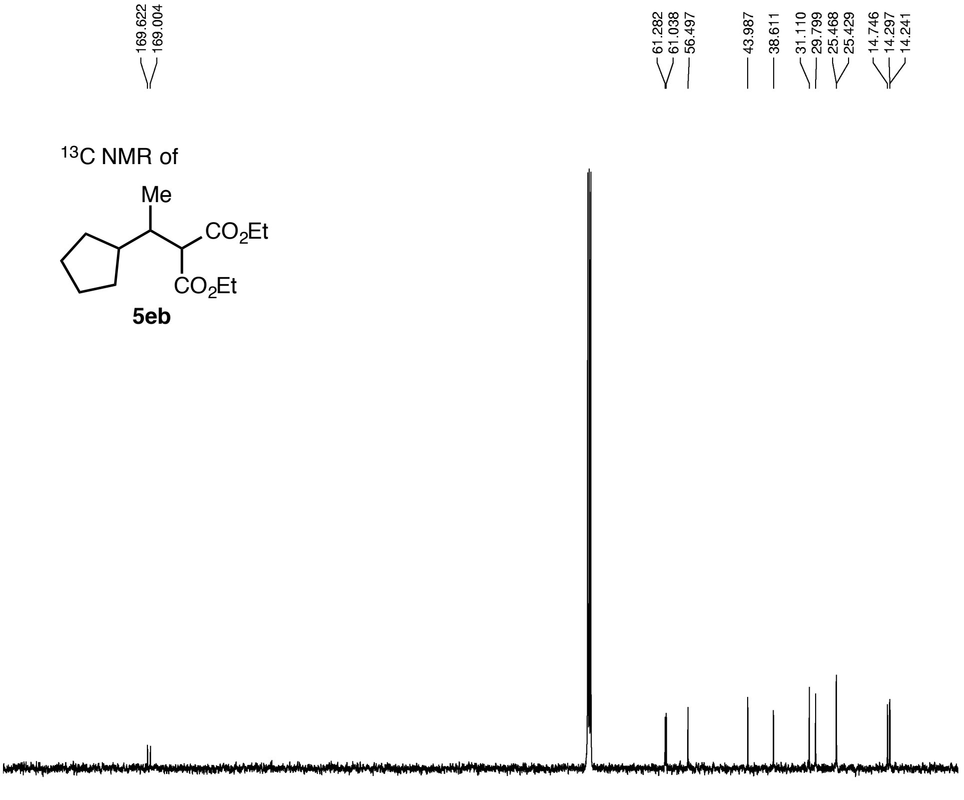

3.725
3.706
3.618
3.605
2.105
2.087
2.074
2.069
2.055
2.051
2.037
1.965
1.699
1.668
1.615
1.586
1.552
1.535
1.499
1.462
0.976
0.957
^{1}H NMR of
Me
CO$_2$Me
CO$_2$Me
5ca
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.81
2.80
0.93
1.06
3.04
3.22
3.25
6.56
3.00


170.961
170.335
52.712
52.167
51.676
43.440
39.458
37.135
35.365
28.740
10.578
^{13}C NMR of
Me
CO$_2$Me
CO$_2$Me
5ca
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


4.200
4.189
4.182
4.172
4.164
4.154
4.146
4.136
3.222
3.206
2.231
2.228
2.210
2.208
2.201
2.193
2.177
2.169
2.161
2.153
2.136
2.000
1.997
1.982
1.975
1.971
1.964
1.951
1.946
1.932
1.926
1.916
1.904
1.894
1.813
1.793
1.790
1.770
1.766
1.761
1.750
1.730
1.726
1.722
1.718
1.711
1.706
1.692
1.690
1.684
1.674
1.657
1.632
1.586
1.278
1.260
1.242
0.916
0.899
^{1}H NMR of
Me
CO$_2$Et
CO$_2$Et
5db
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
3.88
0.94
2.00
2.02
4.05
6.29
3.14


169.400
168.849
61.272
61.077
55.193
40.251
40.062
27.404
27.165
17.636
14.266
14.188
14.070
^{13}C NMR of
Me
CO$_2$Et
CO$_2$Et
5db
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.260
4.216
4.199
4.181
4.163
3.432
3.417
2.165
2.148
2.131
2.114
2.097
1.804
1.786
1.768
1.762
1.755
1.748
1.744
1.733
1.727
1.708
1.700
1.648
1.630
1.622
1.617
1.612
1.609
1.601
1.595
1.591
1.584
1.580
1.556
1.541
1.532
1.521
1.501
1.286
1.281
1.268
1.263
1.250
1.246
1.200
1.184
1.178
1.170
1.164
1.161
1.152
1.140
1.134
1.125
1.108
1.103
1.022
1.005
^{1}H NMR of
Me
CO$_2$Et
CO$_2$Et
5eb
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
3.84
0.93
0.97
3.03
4.67
6.00
2.12
3.00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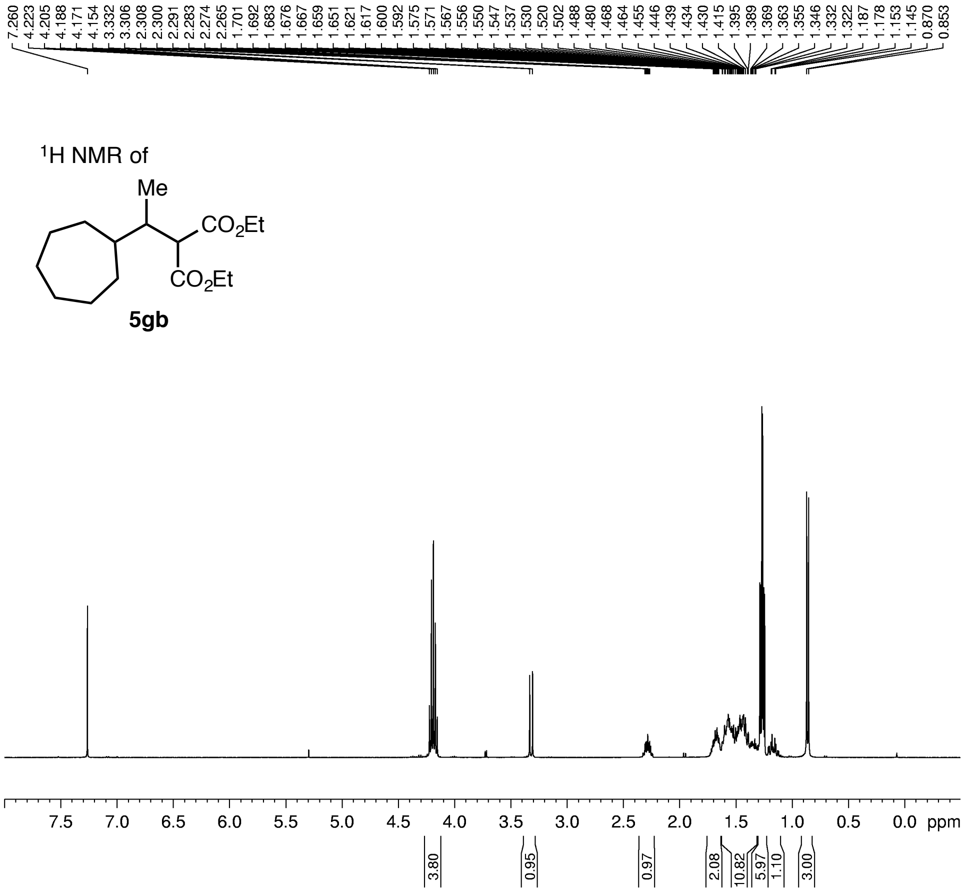
169.004
61.282
61.038
56.497
43.987
38.611
31.110
29.799
25.468
25.429
14.746
14.297
14.241
^{13}C NMR of
Me
CO$_2$Et
CO$_2$Et
5eb
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.260
4.223
4.205
4.188
4.171
4.154
3.332
3.306
2.308
2.300
2.291
2.283
2.274
2.265
1.701
1.692
1.683
1.676
1.667
1.659
1.651
1.621
1.617
1.600
1.592
1.575
1.571
1.567
1.556
1.550
1.547
1.537
1.530
1.520
1.502
1.488
1.480
1.468
1.464
1.455
1.446
1.439
1.434
1.430
1.415
1.395
1.389
1.369
1.363
1.355
1.346
1.332
1.322
1.187
1.178
1.153
1.145
0.870
0.853
1H NMR of
Me
CO2Et
CO2Et
5gb
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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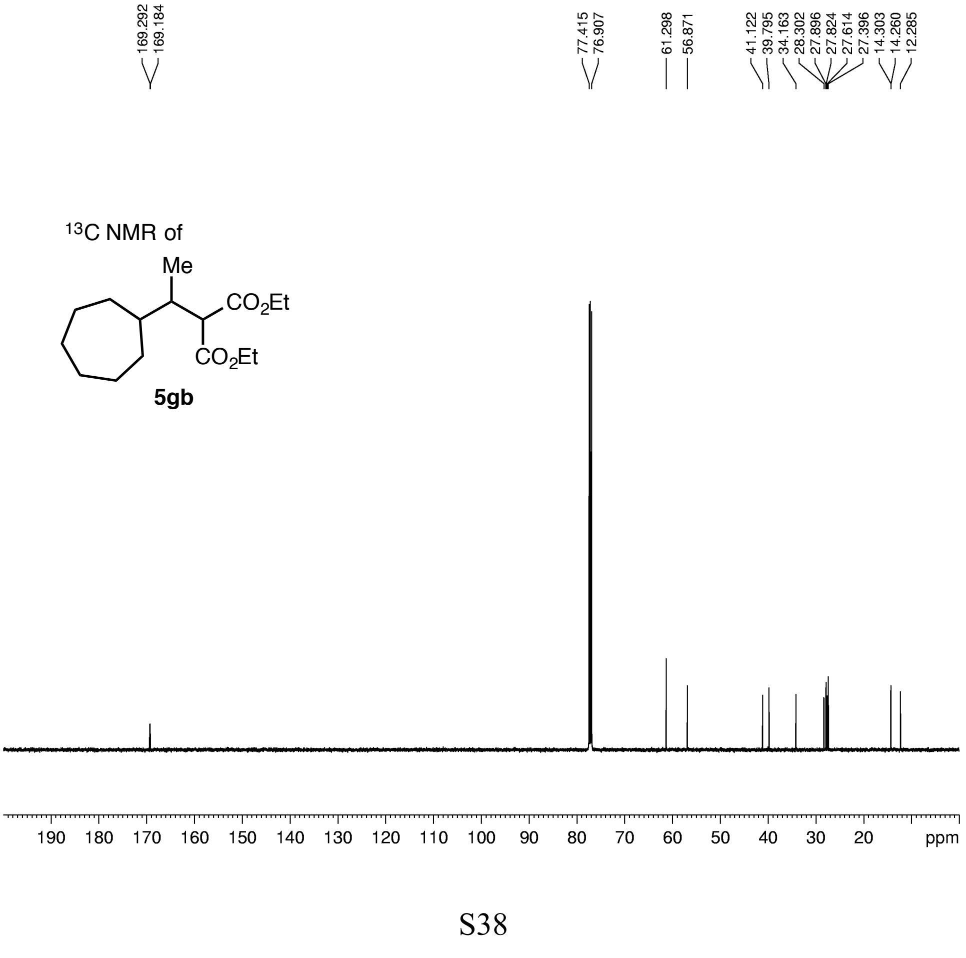
0.95
0.97
2.08
10.82
5.97
1.10
3.00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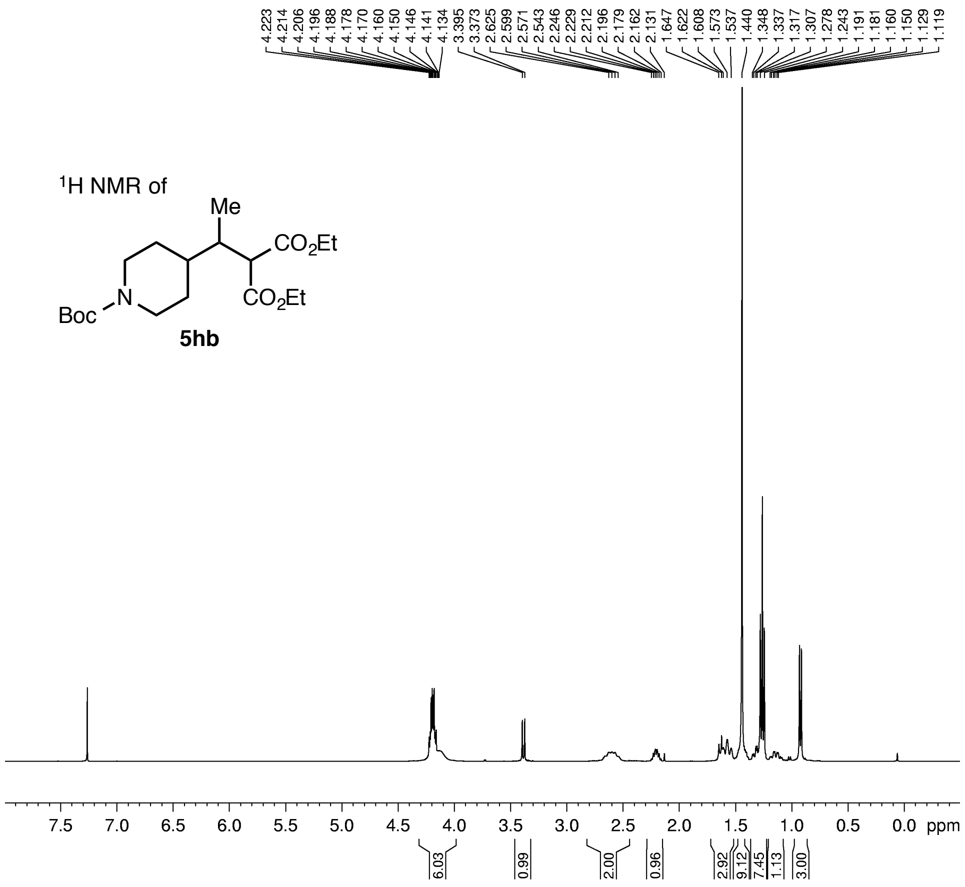
169.184
77.415
76.907
61.298
56.871
41.122
39.795
34.163
28.302
27.896
27.824
27.614
27.396
14.303
14.260
12.285
13C NMR of
Me
CO2Et
CO2Et
5gb
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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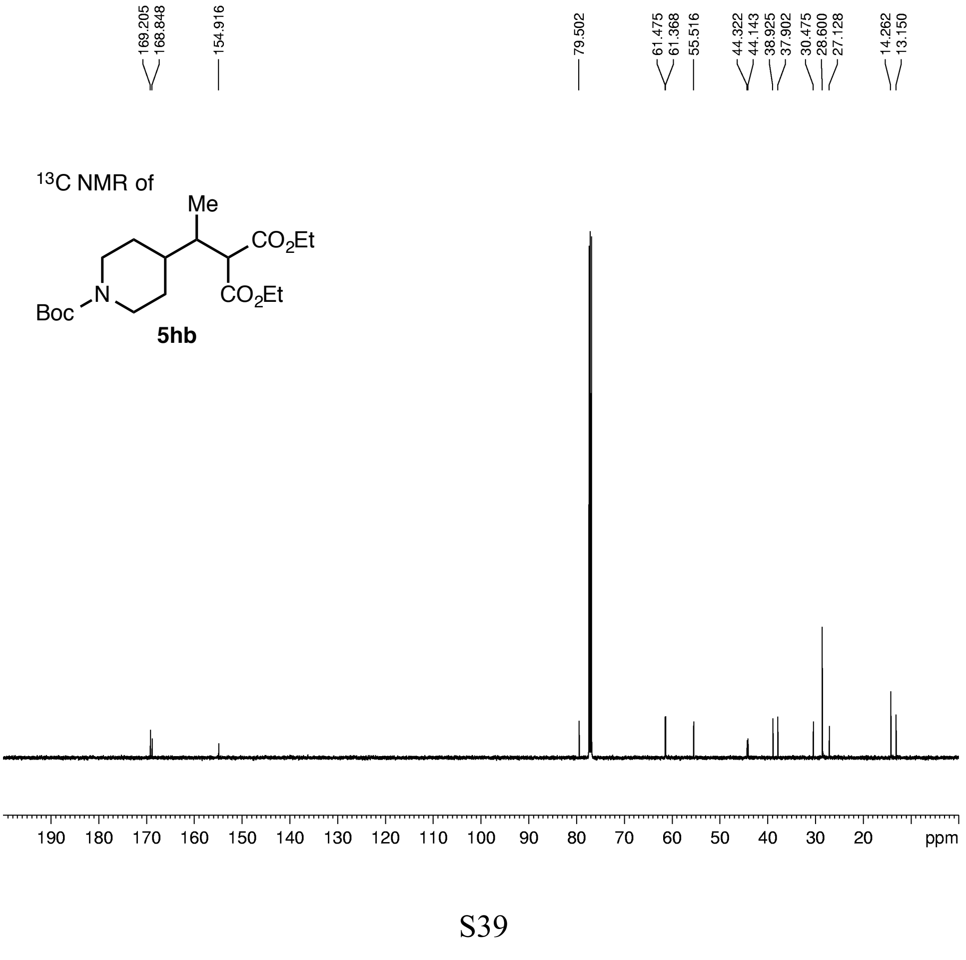
4.214
4.206
4.196
4.188
4.178
4.170
4.160
4.150
4.146
4.141
4.134
3.395
3.373
2.625
2.599
2.571
2.543
2.246
2.229
2.212
2.196
2.179
2.162
2.131
1.647
1.622
1.608
1.573
1.537
1.440
1.348
1.337
1.317
1.307
1.278
1.243
1.191
1.181
1.160
1.150
1.129
1.119
^{1}H NMR of
Me
CO$_2$Et
CO$_2$Et
N
Boc
5hb
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
6.03
0.99
2.00
0.96
2.92
9.12
7.45
1.13
3.00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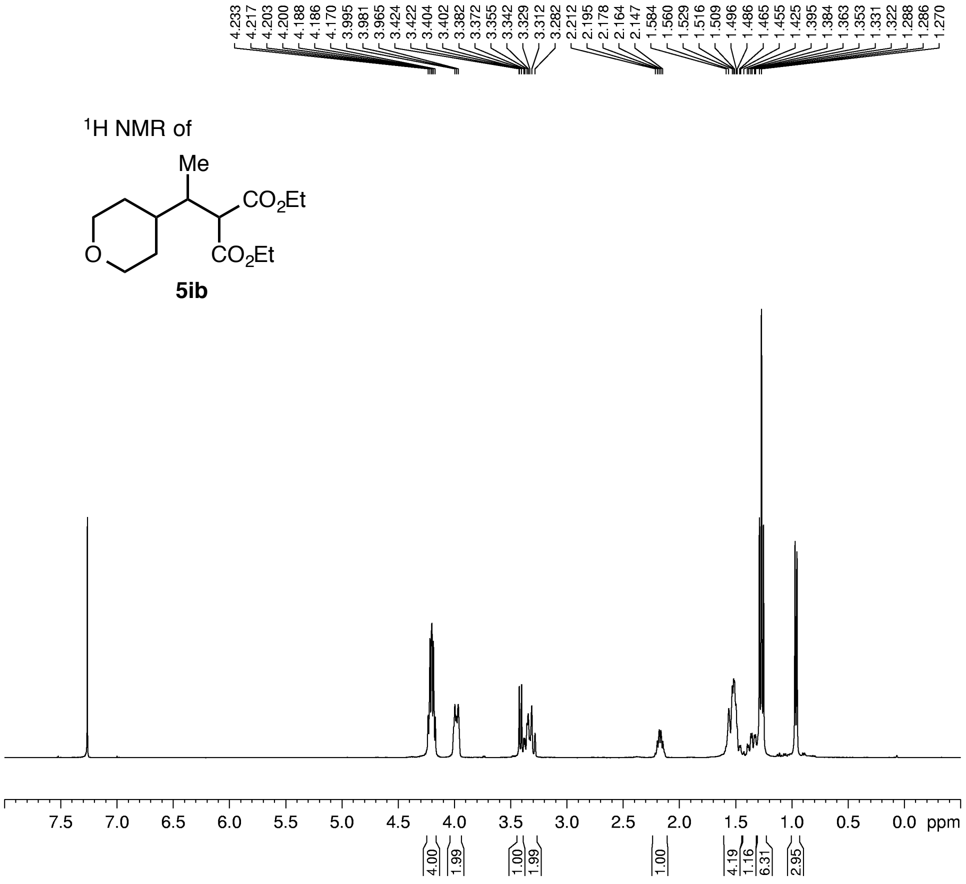
168.848
154.916
79.502
61.475
61.368
55.516
44.322
44.143
38.925
37.902
30.475
28.600
27.128
14.262
13.150
^{13}C NMR of
Me
CO$_2$Et
CO$_2$Et
N
Boc
5hb
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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4.217
4.203
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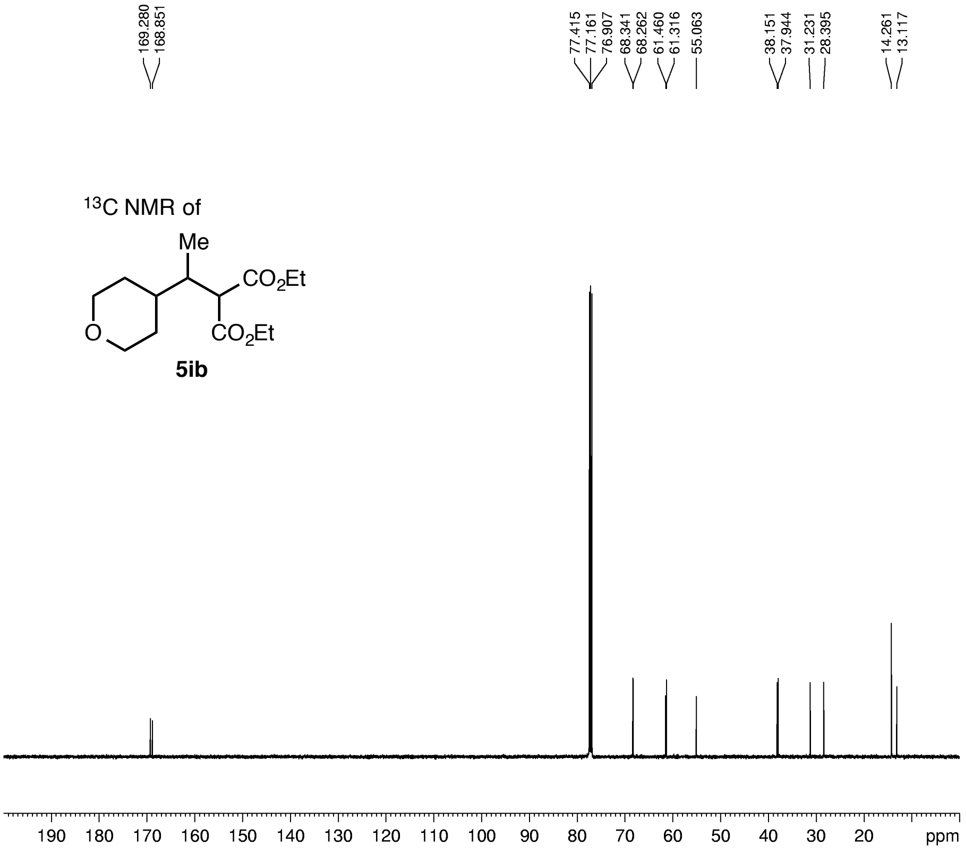
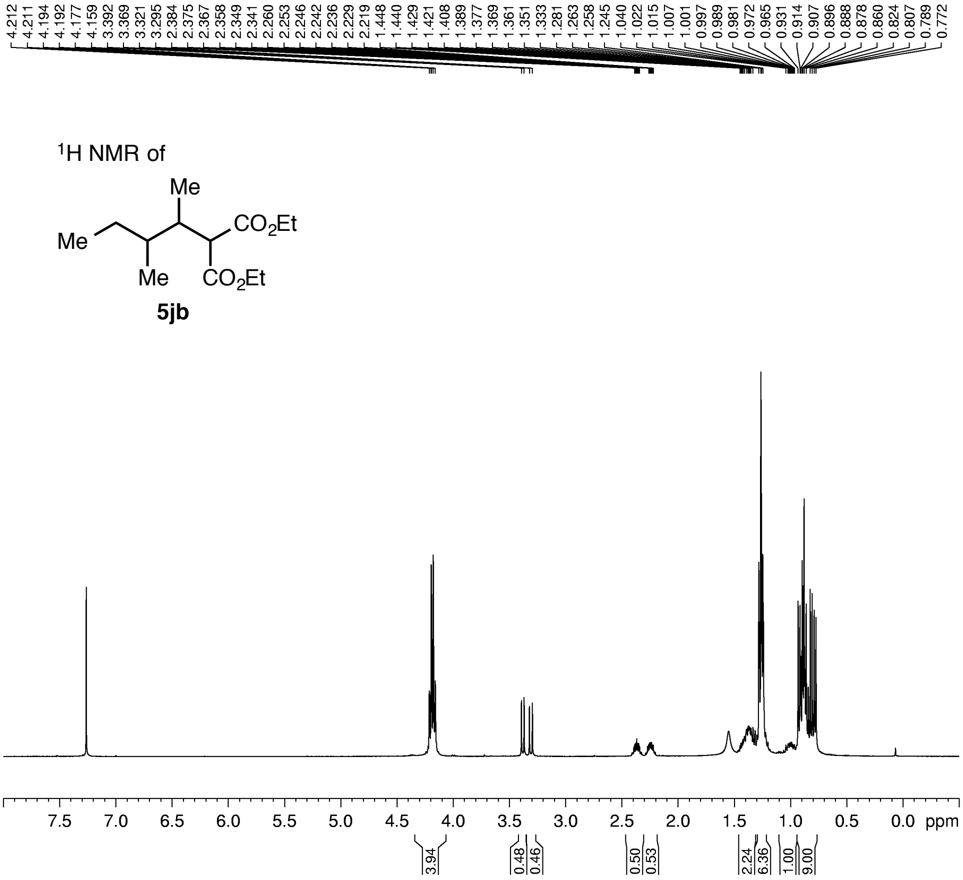
4.186
4.170
3.995
3.981
3.965
3.424
3.422
3.404
3.402
3.382
3.372
3.355
3.342
3.329
3.312
3.282
2.212
2.195
2.178
2.164
2.147
1.584
1.560
1.529
1.516
1.509
1.496
1.486
1.465
1.455
1.425
1.395
1.384
1.363
1.353
1.331
1.322
1.288
1.286
1.270
¹H NMR of
Me
CO₂Et
O
CO₂Et
5ib
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
4.00
1.99
1.00
1.99
1.00
4.19
1.16
6.31
2.95


169.280
168.851
77.415
77.161
76.907
68.341
68.262
61.460
61.316
55.063
38.151
37.944
31.231
28.395
14.261
13.117
¹³C NMR of
Me
CO₂Et
O
CO₂Et
5ib
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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4.211
4.194
4.192
4.177
4.159
3.392
3.369
3.321
3.295
2.384
2.375
2.367
2.358
2.349
2.341
2.260
2.253
2.246
2.242
2.236
2.229
2.219
1.448
1.440
1.429
1.421
1.408
1.389
1.377
1.369
1.361
1.351
1.333
1.281
1.263
1.258
1.245
1.040
1.022
1.015
1.007
1.001
0.997
0.989
0.981
0.972
0.965
0.931
0.914
0.907
0.896
0.888
0.878
0.860
0.824
0.807
0.789
0.772
^{1}H NMR of
Me
CO$_2$Et
Me
Me
CO$_2$Et
5jb
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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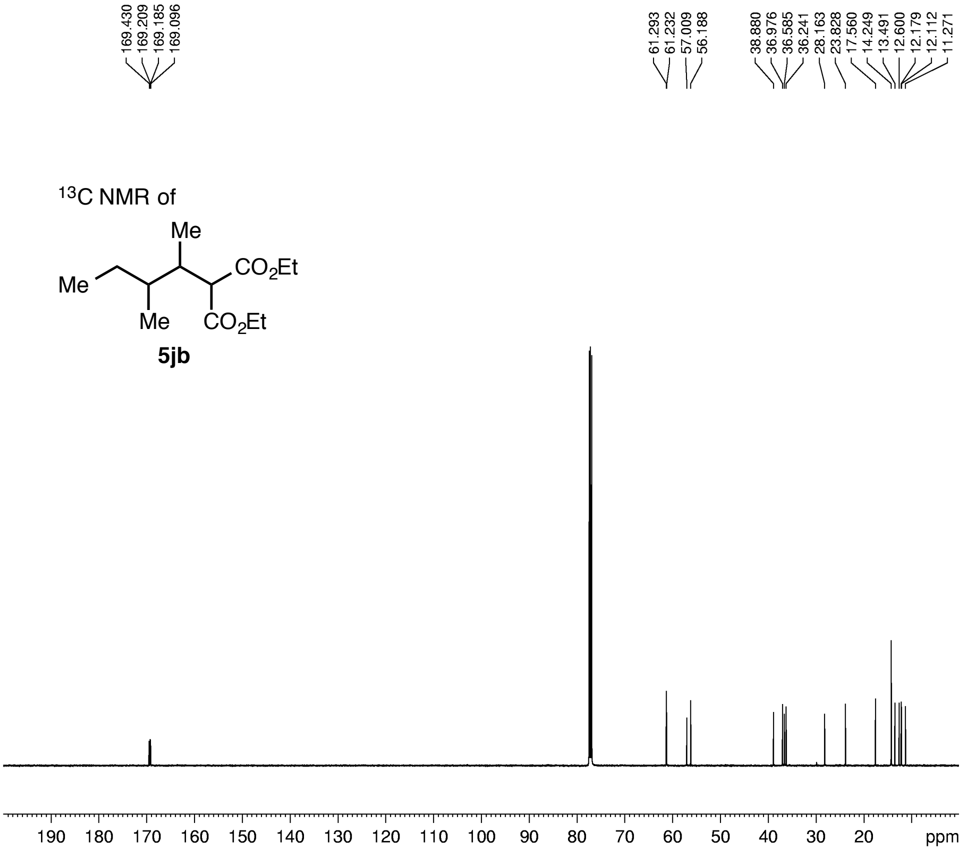
0.46
0.50
0.53
2.24
6.36
1.00
9.00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169.209
169.185
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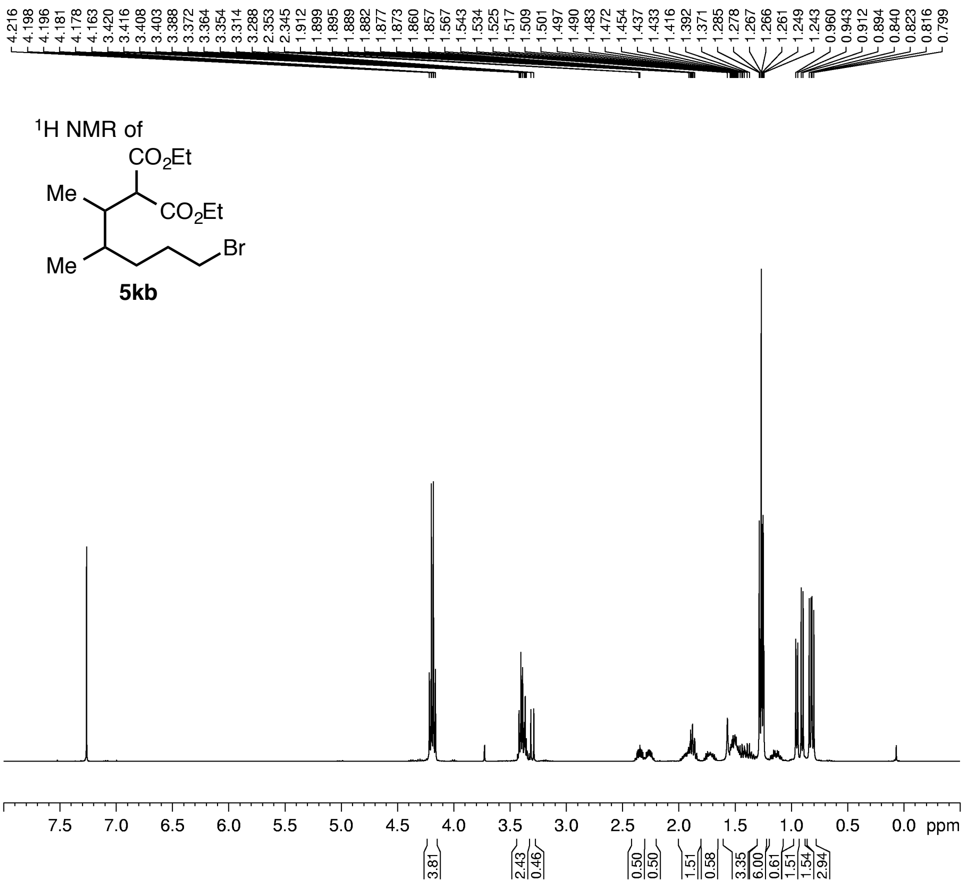
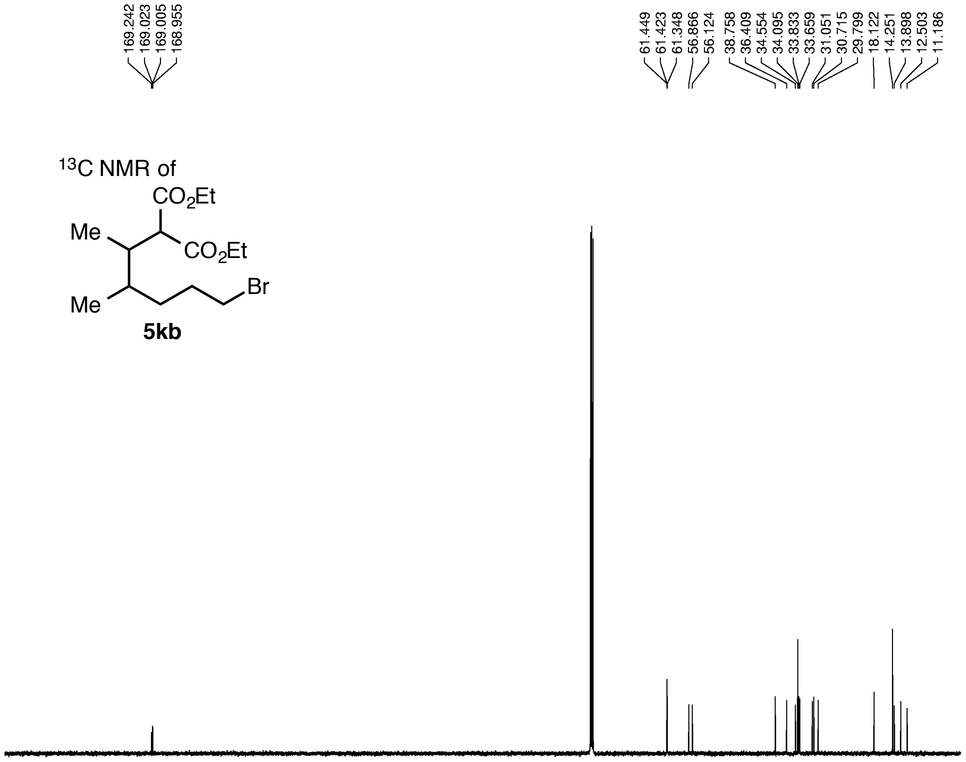
61.293
61.232
57.009
56.188
38.880
36.976
36.585
36.241
28.163
23.828
17.560
14.249
13.491
12.600
12.179
12.112
11.271
^{13}C NMR of
Me
CO$_2$Et
Me
Me
CO$_2$Et
5jb
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


4.216
4.198
4.196
4.181
4.178
4.163
3.420
3.416
3.408
3.403
3.388
3.372
3.364
3.354
3.314
3.288
2.353
2.345
1.912
1.899
1.895
1.889
1.882
1.877
1.873
1.860
1.857
1.567
1.543
1.534
1.525
1.517
1.509
1.501
1.497
1.490
1.483
1.472
1.454
1.437
1.433
1.416
1.392
1.371
1.285
1.278
1.267
1.266
1.261
1.249
1.243
0.960
0.943
0.912
0.894
0.840
0.823
0.816
0.799
1H NMR of
CO2Et
Me
CO2Et
Br
Me
5kb
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
3.81
2.43
0.46
0.50
0.50
1.51
0.58
3.35
6.00
0.61
1.51
1.54
2.94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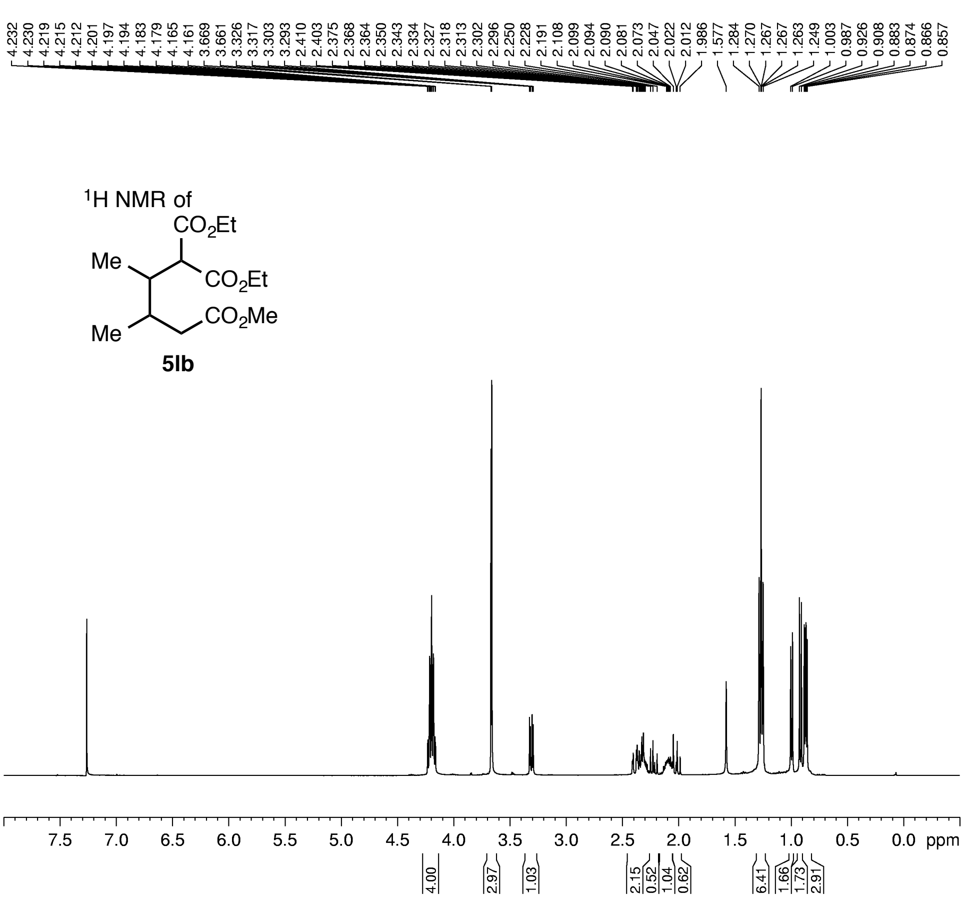
169.023
169.005
168.955
61.449
61.423
61.348
56.866
56.124
38.758
36.409
34.554
34.095
33.833
33.659
31.051
30.715
29.799
18.122
14.251
13.898
12.503
11.186
13C NMR of
CO2Et
Me
CO2Et
Me
Br
5kb
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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4.230
4.219
4.215
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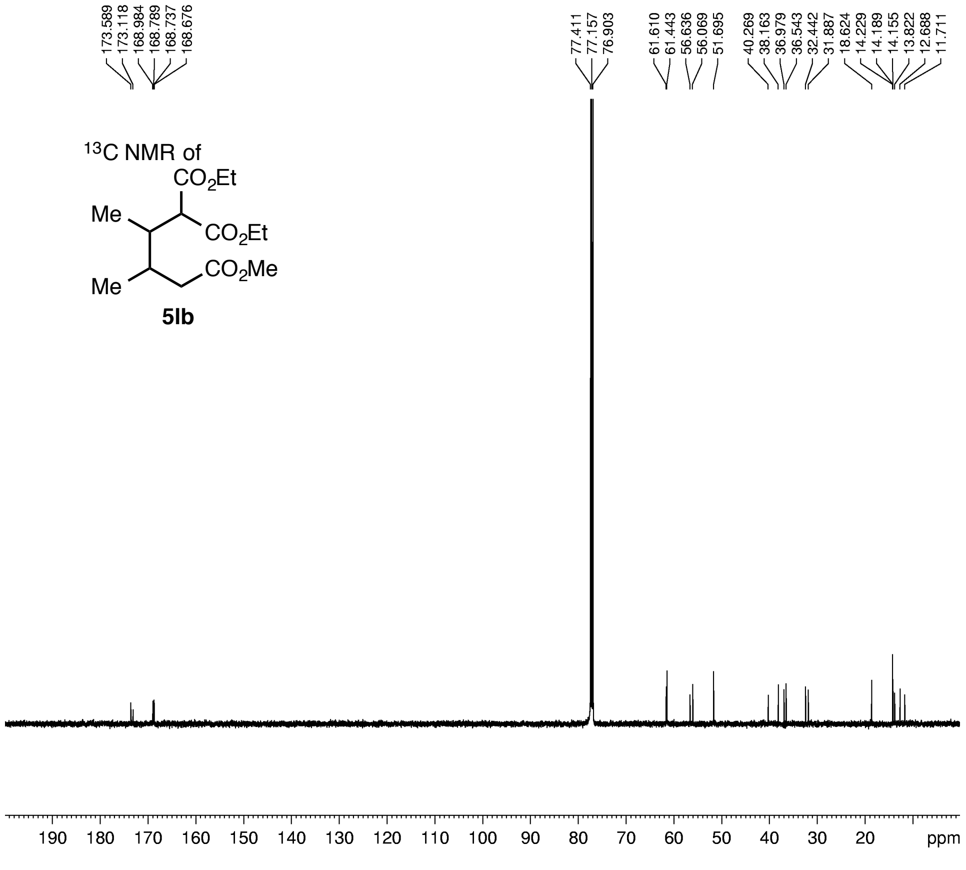
4.201
4.197
4.194
4.183
4.179
4.165
4.161
3.669
3.661
3.326
3.317
3.303
3.293
2.410
2.403
2.375
2.368
2.364
2.350
2.343
2.334
2.327
2.318
2.313
2.302
2.296
2.250
2.228
2.191
2.108
2.099
2.094
2.090
2.081
2.073
2.047
2.022
2.012
1.986
1.577
1.284
1.270
1.267
1.267
1.263
1.249
1.003
0.987
0.926
0.908
0.883
0.874
0.866
0.857
^{1}H NMR of
CO_2Et
Me
CO_2Et
CO_2Me
Me
5lb
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
4.00
2.97
1.03
2.15
0.52
1.04
0.62
6.41
1.66
1.73
2.91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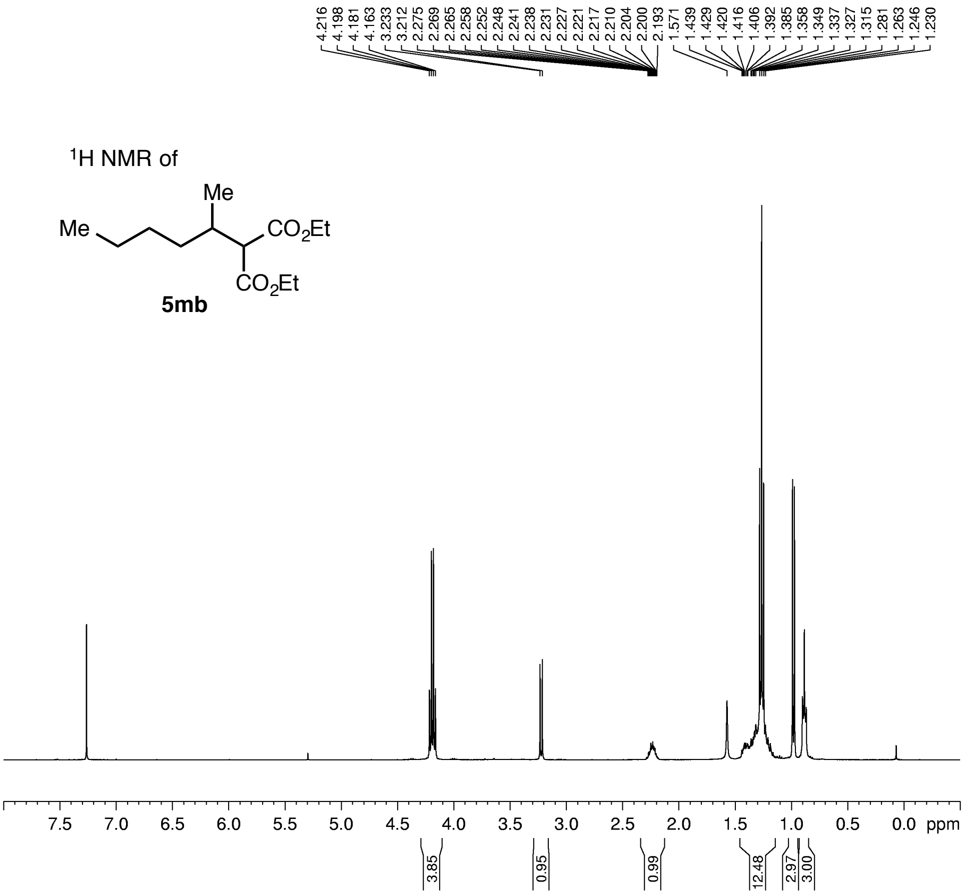
173.118
168.984
168.789
168.737
168.676
77.411
77.157
76.903
61.610
61.443
56.636
56.069
51.695
40.269
38.163
36.979
36.543
32.442
31.887
18.624
14.229
14.189
14.155
13.822
12.688
11.711
^{13}C NMR of
CO_2Et
Me
CO_2Et
CO_2Me
Me
5lb
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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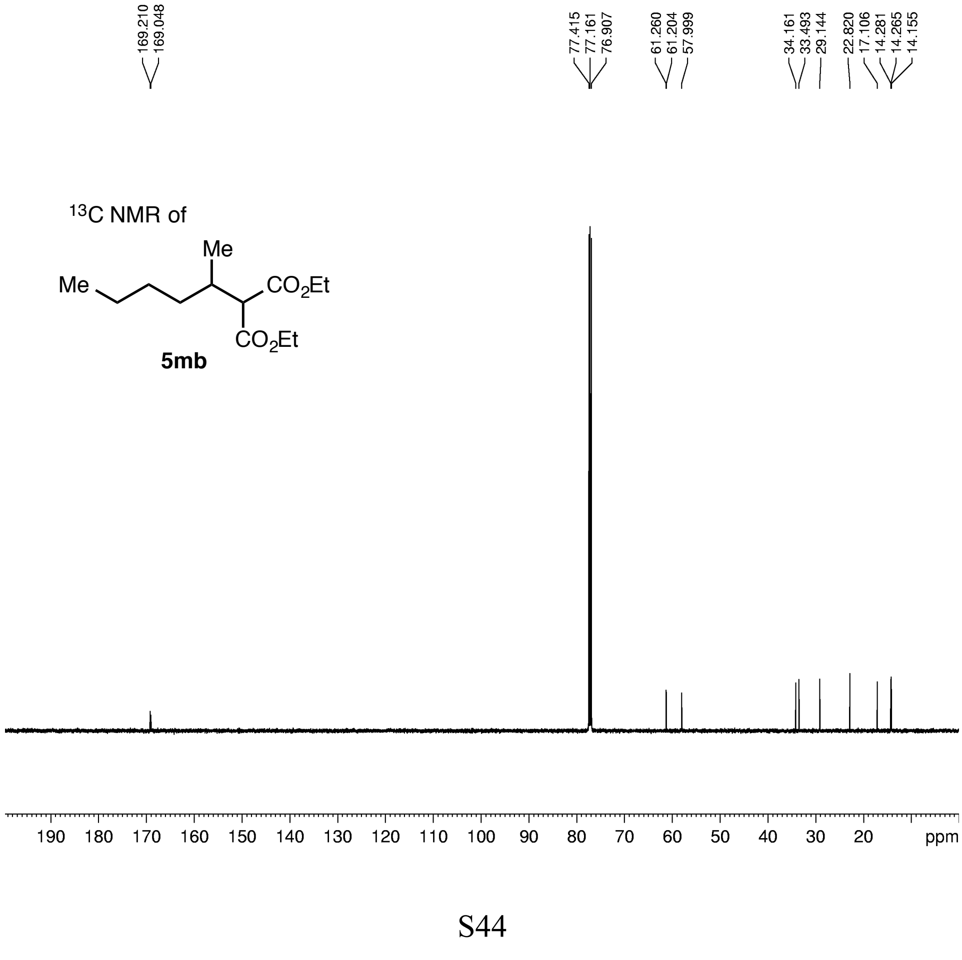
4.198
4.181
4.163
3.233
3.212
2.275
2.269
2.265
2.258
2.252
2.248
2.241
2.238
2.231
2.227
2.221
2.217
2.210
2.204
2.200
2.193
1.571
1.439
1.429
1.420
1.416
1.406
1.392
1.385
1.358
1.349
1.337
1.327
1.315
1.281
1.263
1.246
1.230
¹H NMR of
Me
Me
CO2Et
CO2Et
5mb
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
3.85
0.95
0.99
12.48
2.97
3.00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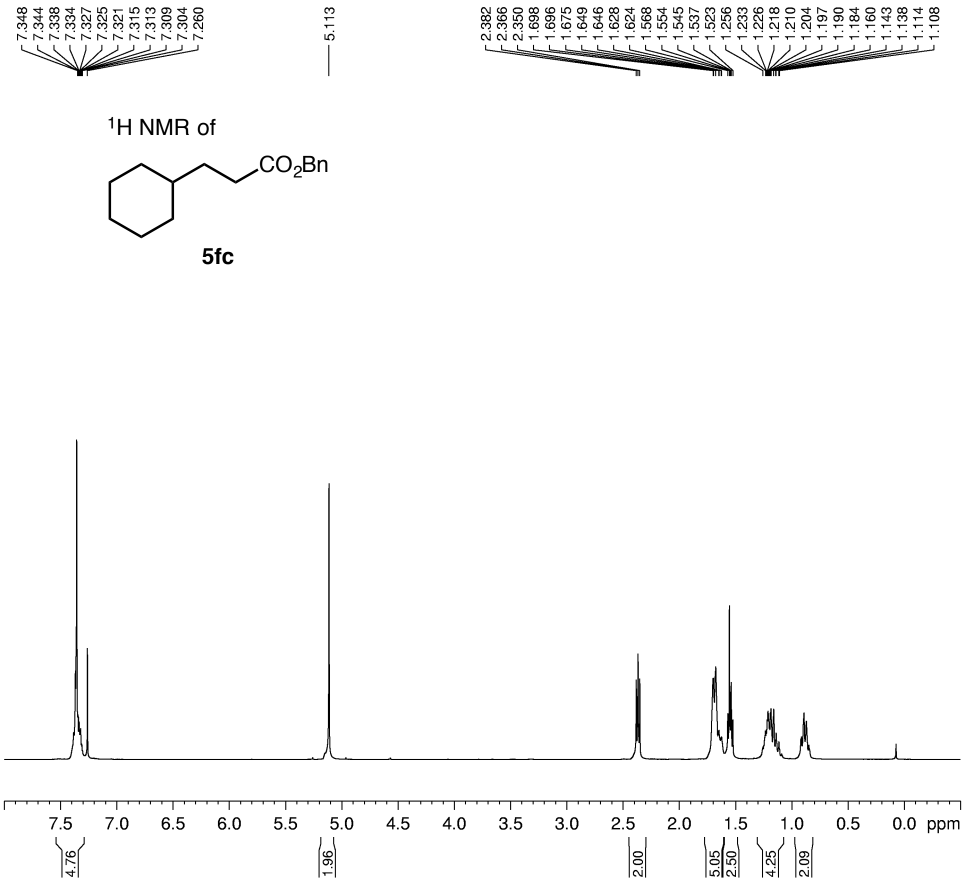
169.048
77.415
77.161
76.907
61.260
61.204
57.999
34.161
33.493
29.144
22.820
17.106
14.281
14.265
14.155
¹³C NMR of
Me
Me
CO2Et
CO2Et
5mb
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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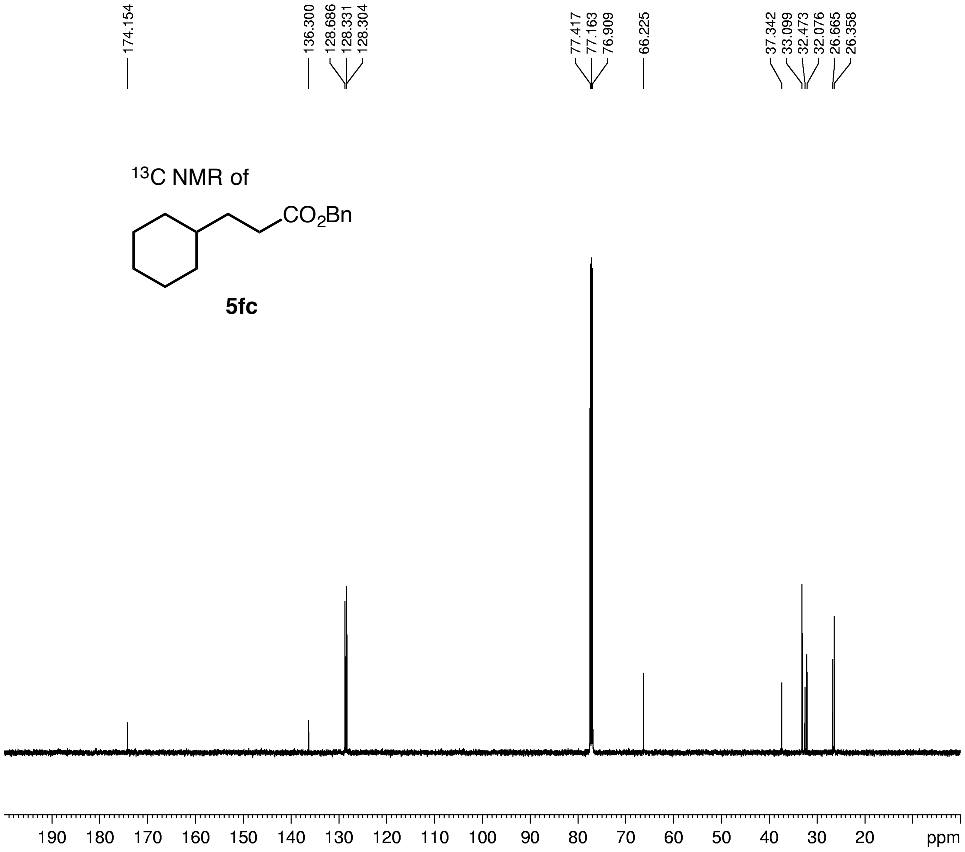
7.338
7.334
7.327
7.325
7.321
7.315
7.313
7.309
7.304
7.260
5.113
2.382
2.366
2.350
1.698
1.696
1.675
1.649
1.646
1.628
1.624
1.568
1.554
1.545
1.537
1.523
1.256
1.233
1.226
1.218
1.210
1.204
1.197
1.190
1.184
1.160
1.143
1.138
1.114
1.108
¹H NMR of
CO₂Bn
5fc
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
4.76
1.96
2.00
5.05
2.50
4.25
2.09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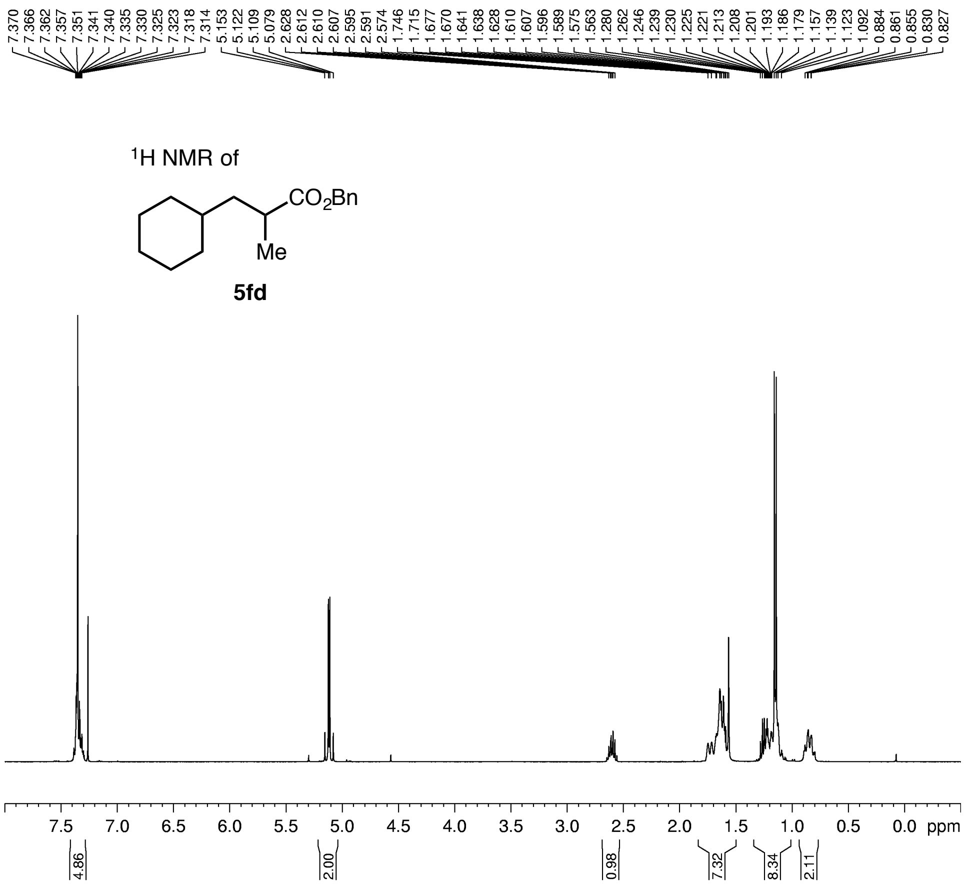
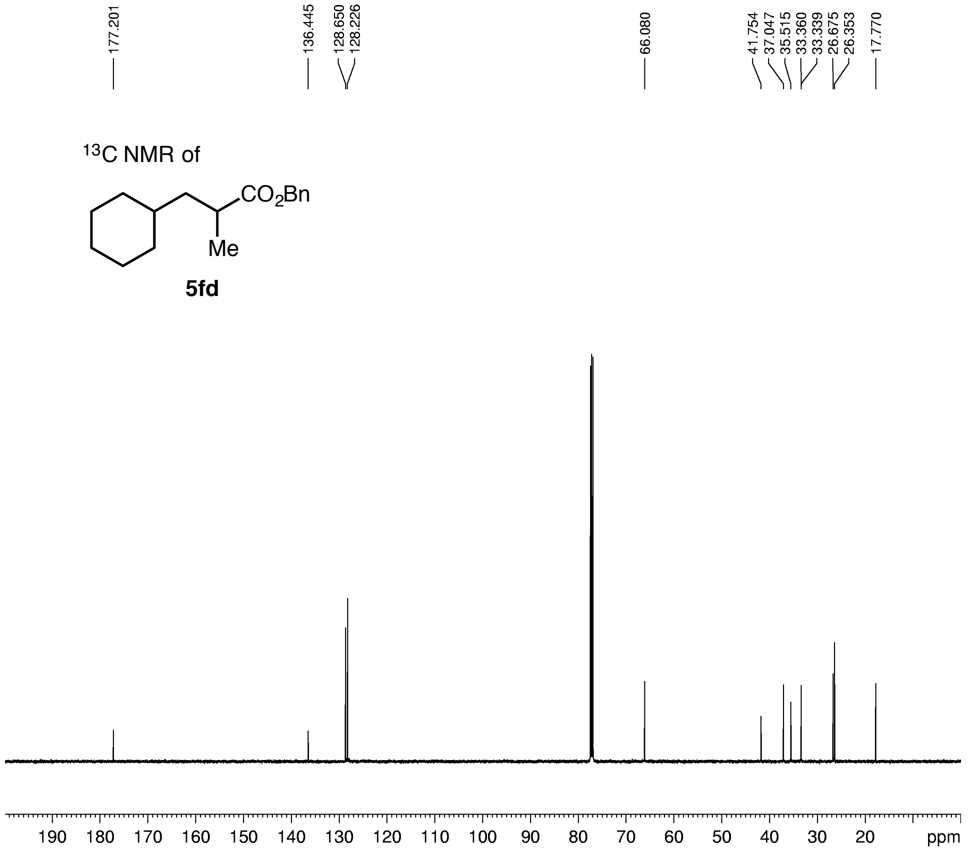
136.300
128.686
128.331
128.304
77.417
77.163
76.909
66.225
37.342
33.099
32.473
32.076
26.665
26.358
¹³C NMR of
CO₂Bn
5fc
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.370
7.366
7.362
7.357
7.351
7.341
7.340
7.335
7.330
7.325
7.323
7.318
7.314
5.153
5.122
5.109
5.079
2.628
2.612
2.610
2.607
2.595
2.591
2.574
1.746
1.715
1.677
1.670
1.641
1.638
1.628
1.610
1.607
1.596
1.589
1.575
1.563
1.280
1.262
1.246
1.239
1.230
1.225
1.221
1.213
1.208
1.201
1.193
1.186
1.179
1.157
1.139
1.123
1.092
0.884
0.861
0.855
0.830
0.827
1H NMR of
CO2Bn
Me
5fd
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
4.86
2.00
0.98
7.32
8.34
2.11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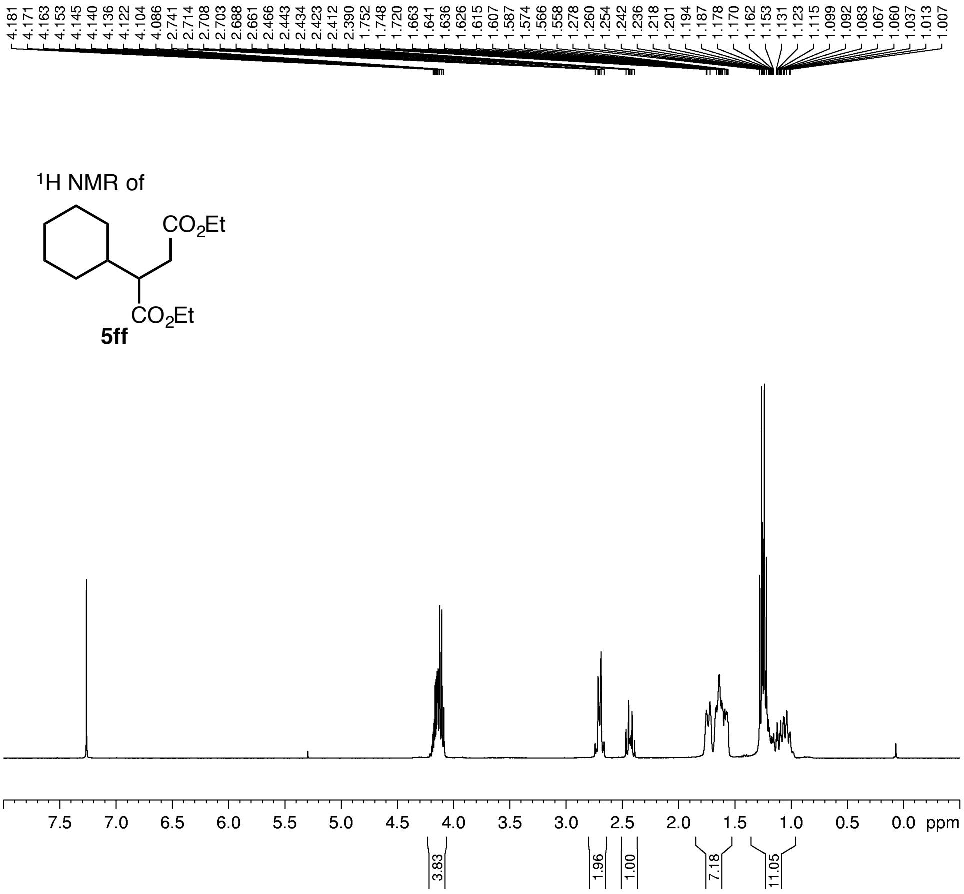
128.650
128.226
66.080
41.754
37.047
35.515
33.360
33.339
26.675
26.353
17.770
13C NMR of
CO2Bn
Me
5fd
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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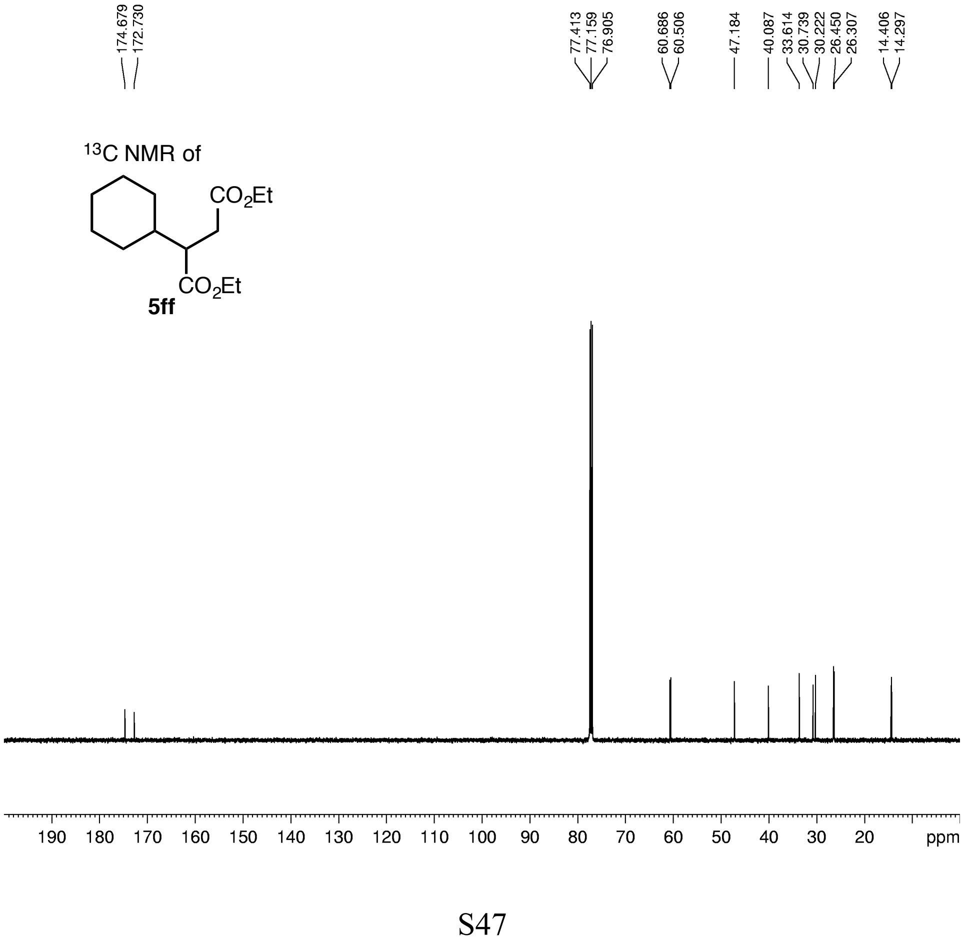
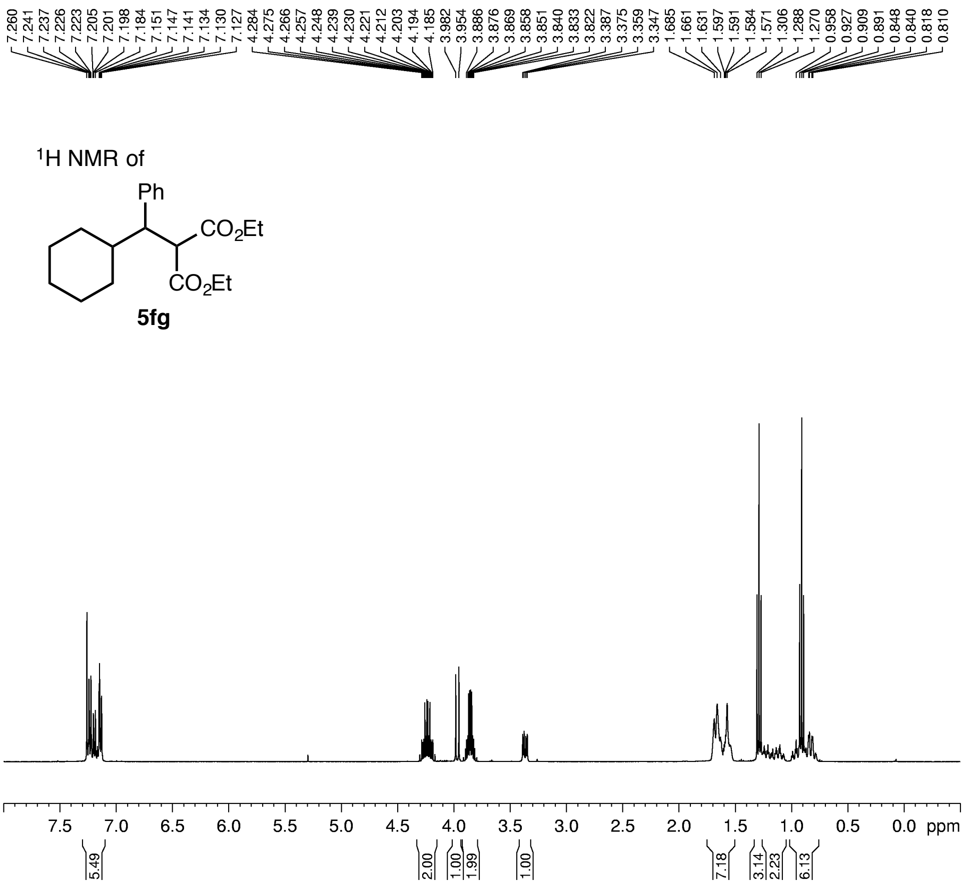
4.163
4.153
4.145
4.140
4.136
4.122
4.104
4.086
2.741
2.714
2.708
2.703
2.688
2.661
2.466
2.443
2.434
2.423
2.412
2.390
1.752
1.748
1.720
1.663
1.641
1.636
1.626
1.615
1.607
1.587
1.574
1.566
1.558
1.278
1.260
1.254
1.242
1.236
1.218
1.201
1.194
1.187
1.178
1.170
1.162
1.153
1.131
1.123
1.115
1.099
1.092
1.083
1.067
1.060
1.037
1.013
1.007
^{1}H NMR of
CO$_2$Et
CO$_2$Et
5ff
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
3.83
1.96
1.00
7.18
11.05


174.679
172.730
77.413
77.159
76.905
60.686
60.506
47.184
40.087
33.614
30.739
30.222
26.450
26.307
14.406
14.297
^{13}C NMR of
CO$_2$Et
CO$_2$Et
5ff
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

^{1}H NMR of **5fg**



^{13}C NMR of **5fg**