Supplementary Information

Activity of *N,N′*-dialkyl-2-trifluoromethylthioimidazolium salts as phase-transfer catalysts for the alkylation of active methylene compounds

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1. General Information

All NMR spectra were recorded on Varian 500PS spectrometers. ^{1}H ^{13}C and ^{19}F NMR spectra are reported as chemical shifts (δ) in parts per million (ppm) relative to the solvent peak using tetramethylsilane, and trichlorofluoromethane (^{19}F) as an internal standard. Chemical shifts (δ) are quoted in parts per million (ppm) and coupling constants (*J*) are measured in hertz (Hz). The following abbreviations are used to describe multiplicities s=singlet, d=doublet, t=triplet, q=quartet,

quint.=quintet, sext.=sextet, sept.=septet br=broad, m=multiplet. NMR spectra were processed in ACD/SpecManager. High resolution mass spectra (HRMS, *m*/*z*) were obtained on JEOL JMS-700N for FAB using m-nitrobenzylalcohol as a matrix or on JEOL JMS-T100TD for electrospray ionization (ESI+).

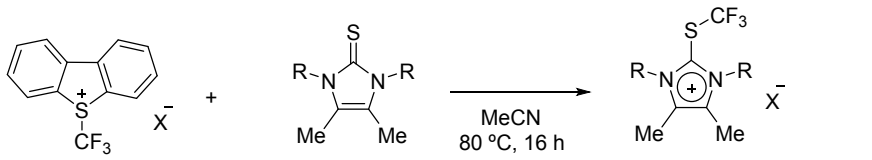
All reactions were performed in apparatuses with magnetic stirring under an inert atmosphere. Flash column chromatography was performed over Fuji Silysia Chemical Ltd. silica gel C60 (50-200 μm) using an eluent system as described for each experiment. Thin-layer chromatography was performed using TLC Silica gel 60 F_{254} aluminum sheets (Merck) and silica gel F_{254} glass plates (Merck).

Materials.

Imidazole-2(3*H*)-thiones **3**, Methyl 1-indanone-2-carboxylate **5** and Methyl 1-methyl-2-oxoindoline-3-carboxylate **6** were known compounds and were prepared according literature procedures.[1-3] Unless noted otherwise, all starting materials and reagents were obtained from commercial suppliers and were used without further purification. All chemicals were purchased from Aldrich, Nacalai tesque, Tokyo Chemical Industry and Wako Pure Chemical Industries and used as received. All solvents were purchased from Wako Pure Chemical Industries.

2. Experimental Procedures and Characterization Data

2-1. General procedure for synthesis of *N,N′*-dialkyl-2-trifluoromethylthioimidazolium salts



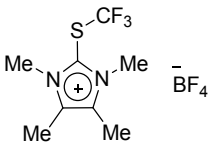
1; X=BF_4
2; X=OTf

3
3a; R = Me
3b; R = butyl
3c; R = *i*-Pr
3d; R = *c*-hexyl

4a; R = Me, X = BF_4, 64%
4b; R = butyl, X = BF_4, 43%
4c; R = *i*-Pr, X = BF_4, 46%
[*1 gram scale*]
4d; R = *i*-Pr, X = OTf, 31%
4e; R = *c*-hexyl, X = BF_4, 67%

A 30 mL test tube was charged with a solution of imidazole-2(3*H*)-thiones **3** (1.0 mmol) and *S*-(trifluoromethyl)dibenzothiophenium salts **1** (1.0 mmol) in MeCN (5.0 mL). After a cap is mounted, the mixture was heated to 80 °C and stirred for 16 h. The reaction mixture was cooled to room temperature followed by evaporation to remove the solvent. The residue was purified by SiO_2 gel column chromatography to afford the corresponding *N,N′*-dialkyl-2-trifluoromethylthioimidazolium salts.

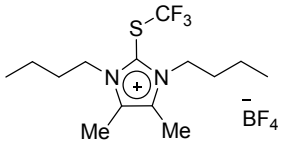
***1,3,4,5-Tetramethyl-2-trifluoromethylthioimidazolium tetrafluoroborate (*4a)**



4a

Synthesized following procedure. A mixture of imidazole-2(3*H*)-thiones **3a** (150 mg, 1.0 mmol), and *S*-(trifluoromethyl)dibenzothiophenium salts **1a** (340 mg, 1.0 mmol) in MeCN (5.0 mL) was stirred at 80 °C for 16hr. Purified by SiO_2 gel column chromatography (DCM : MeOH=90 : 10) to give 200 mg (64% yield) of the title compounds as a brown solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.39 (s, 6H), 3.91 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 9.43, 34.2, 126.7 (m), 126.9 (q, *J* = 313Hz), 132.8; **^{19}F NMR** (470 MHz, $CDCl_3$) δ –40.3(s, 3F, S-CF_3), –155.2 (s, $^{10}BF_4$), –155.2 (s, $^{11}BF_4$); **HRMS** (FAB) *m/z* Calcd for $C_8H_{12}F_3N_2S$ $[M]^+$ 225.0668, found 225.0672.

***1,3-Dibutyl-4,5-dimethyl-2-trifluoromethylthioimidazolium tetrafluoroborate (*4b)**

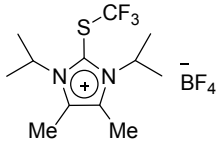


4b

Synthesized following procedure. A mixture of imidazole-2(3*H*)-thiones **3b** (381 mg, 1.5 mmol), and *S*-(trifluoromethyl)dibenzothiophenium salts **1a** (510 mg, 1.5 mmol) in MeCN (8.0 mL) was stirred at 80 °C for 16hr. Purified by SiO_2 gel column chromatography (DCM : MeOH=95 : 5) to give 257 mg (43% yield) of the title compounds as a brown oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.01 (t, *J* = 7.6 Hz, 6H), 1.47 (q, *J* = 7.4 Hz, 4H), 1.75–1.85 (m, 4H), 2.41 (s, 6H). 4.29 (t, *J* = 8.3 Hz, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 9.61, 13.3, 19.8, 31.0, 47.9, 124.8 (m), 126.5 (q, *J* = 313 Hz), 132.9; **^{19}F NMR** (470 MHz, $CDCl_3$) δ –39.4(s, 3F, S-CF_3), –154.6 (s, $^{10}BF_4$), –154.6 (s, $^{11}BF_4$); **HRMS** (FAB) *m/z* Calcd for $C_{14}H_{24}F_3N_2S$ $[M]^+$ 309.1607, found 309.1612.

***1,3-Diisopropyl-4,5-dimethyl-2-trifluoromethylthioimidazolium tetrafluoroborate (*4c)**



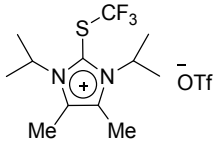
4c

Synthesized following procedure. A mixture of imidazole-2(3*H*)-thiones **3c** (1.0 g, 4.7 mmol), and *S*-(trifluoromethyl)dibenzothiophenium salts **1a** (1.6 g, 1.5 mmol) in MeCN (25.0 mL) was stirred at 80 °C for 16hr. Purified by SiO_2 gel column chromatography (DCM : MeOH=95 : 5) to give 796 mg (46 % yield) of the title compound as a white solid. Single crystals suitable for X-ray crystallography were grown from a mixture solution of MeOH/DCM.

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.63 (d, *J* = 4.9 Hz, 6H), 1.75 (d, *J* = 5.2 Hz, 6H), 2.51 (s, 6H), 5.37 (sept., 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 10.7, 20.5, 20.7, 54.6, 126.6 (q, *J* =313Hz), 133.0; **^{19}F NMR** (470 MHz, $CDCl_3$) δ –40.6(s, 3F, S-CF_3), –153.6 (s, $^{10}BF_4$), –153.6 (s, $^{11}BF_4$); **HRMS** (FAB) *m/z* Calcd for $C_{12}H_{20}F_3N_2S$ $[M]^+$ 281.1294, found 281.1299.

1,3-Diisopropyl-4,5-dimethyl-2-trifluoromethylthioimidazolium trifluoromethanesulfonate

(4d)

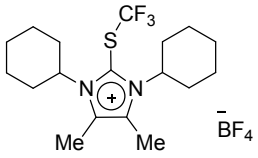


4d

Synthesized following procedure. A mixture of imidazole-2(3*H*)-thiones **3c** (212 mg, 1.0 mmol), and *S*-(trifluoromethyl)dibenzothiophenium salts **1b** (402 mg, 1.0 mmol) in MeCN (5.0 mL) was stirred at 80 °C for 16hr. Purified by SiO_2 gel column chromatography (DCM : MeOH=95 : 5) to give 134 mg (31 % yield) of the title compound as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.60–1.76 (m, 12H), 2.50 (s, 6H), 5.35 (sept., 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 10.8, 20.5, 20.9, 54.6, 126.6 (q, *J* =313Hz), 132.7; **^{19}F NMR** (470 MHz, $CDCl_3$) δ –40.6(s, 3F, S-CF_3), –78.4 (s, OTf); **HRMS** (FAB) *m/z* Calcd for $C_{12}H_{20}F_3N_2S$ $[M]^+$ 281.1294, found 281.1297.

1,3-Dicyclohexyl-4,5-dimethyl-2-trifluoromethylthioimidazolium tetrafluoroborate (4e)

Synthesized following procedure. A mixture of imidazole-2(3*H*)-thiones **3d** (439 mg, 1.5 mmol), and *S*-(trifluoromethyl)dibenzothiophenium salts **1a** (510 mg, 1.5 mmol) in MeCN (8.0 mL) was stirred at 80 °C for 16hr. Purified by SiO_2 gel column chromatography (DCM : MeOH=95 : 5) to give 302 mg (67% yield) of the title compounds as a brown oil.

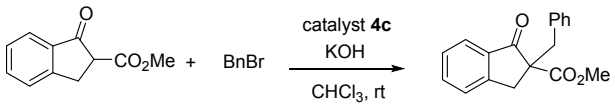


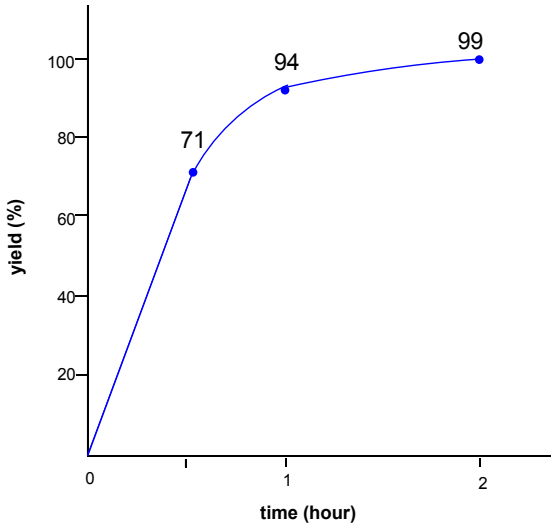
4e

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22–1.28 (m, 2H), 1.40–1.46 (m, 4H), 1.77–2.29 (m, 14H), 2.50 (s, 6H), 4.82–4.97 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 11.2, 24.3, 24.8, 25.4, 25.8, 25.9, 26.1, 30.1, 30.7, 32.6, 62.9, 126.5 (q, *J* = 313Hz), 133.1; **^{19}F NMR** (470 MHz, $CDCl_3$) δ –41.0 (s, 3F, S-CF_3), –153.6 (s, $^{10}BF_4$), –153.7 (s, $^{11}BF_4$); **HRMS** (FAB) *m/z* Calcd for $C_{18}H_{28}F_3N_2S$ $[M]^+$ 361.1920, found 361.1924.

2-2. Experiment of benzylation of 5 in the presence of 4c

To verify the catalytic activity of **4c**, the benzylation of indanone carboxylate **5** with KOH as base in the presence of a catalytic amount of **4c** was performed. The rate of reaction to convert **5** into benzylation product **6** was confirmed. The reaction was completed within 2 hrs. In contract, the reaction in the absence of catalyst afford the product **6** in 47% after 24 h duration. These results demonstrated the efficacy of **4c** as phase- transfer catalyst.

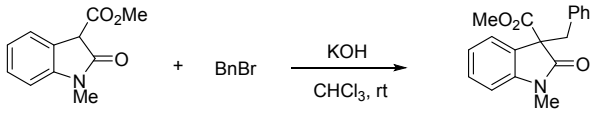


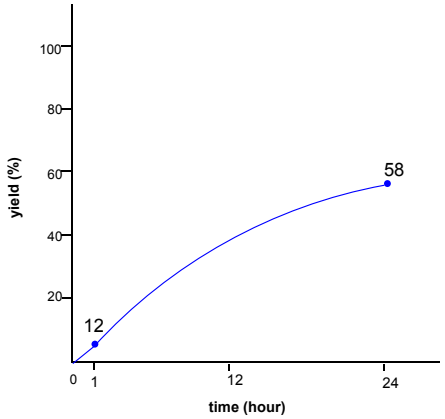


Indanone **5** (47.5 mg, 0.25 mmol), benzylbromide (45 µl, 0.38 mmol), **4c** (9.2 mg, 0.025 mmol), and KOH (42 mg, 0.75 mmol) in $CHCl_3$ (1.2 mL) was stirred for 2hrs.

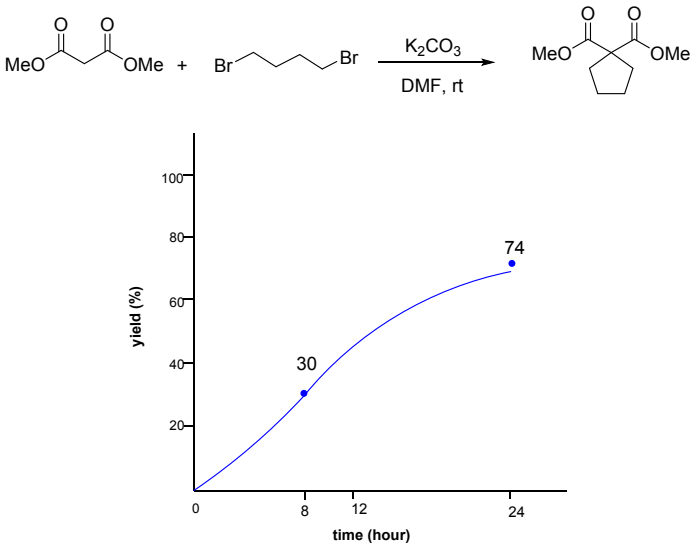
2-3. Experiment of benzylation of 7 and reaction of diethylmalonate and 1,4-dibromobutane without imidazolium salt catalyst 4c

These experiments that includes a comparison of reaction under conditions without catalyst **4c** perfomed, and these results demonstrated the efficacy of **4c** as phase- transfer catalyst in comparison with that showed in Table 1.





Indanone **7**(41 mg, 0.20 mmol), benzylbromide (26 µl, 0.22 mmol) and KOH (34 mg, 0.60 mmol) in $CHCl_3$ (1.0 mL) was stirred for 24hrs. When the reaction was stirred for 1hr, the isolated yield was 12%. The duration 24 hrs gave the product in 58% yield.



A mixture of dimethylmalonate (39.0 mg, 0.30 mmol), 1,4-dibromobutane (39 μl, 0.33 mmol) and K_2CO_3 (104 mg, 0.75 mmol) in DMF (1.5 mL) was stirred for 24 hrs. When the reaction was stirred for 8hr, the isolated yield was 30%. The duration 24 hrs gave the product in 74% yield. In contract, the reaction using catalyst **4c** stirring for 8 hour afford the product **10** in 83% duration (Table 1).

2-4. General procedure for the alkylation of *α*-keto esters

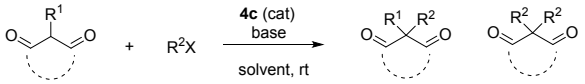
General procedure A: GP-A

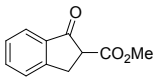
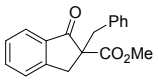
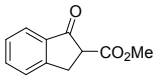
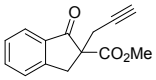
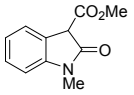
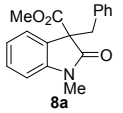
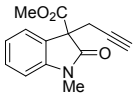
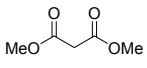
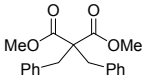
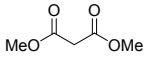
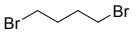
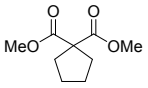
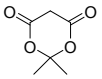
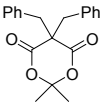
To a stirred suspension of active methylene compounds, **4c** (10 mol%), and KOH (3.0 equiv) in $CHCl_3$ (0.2 M) was added alkyl halide (1.5 equiv) at room temperature. After the reaction completed, the mixture was diluted with sat. NH_4Cl solution and extracted EtOAc. The organic layers were dried over $MgSO_4$, filtered, concentrated. The residue was purified by column chromatography on SiO_2 gel to afford the alkylation product.

General procedure A: GP-B

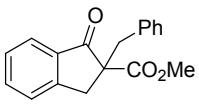
To a stirred suspension of active methylene compounds, **4c** (10 mol%), and K_2CO_3 (3.0 equiv) in DMF (0.2 M) was added alkyl halide (1.5 equiv) at room temperature. After the reaction completed, the mixture was diluted with sat. NH_4Cl solution and extracted EtOAc. The organic layers were dried over $MgSO_4$, filtered, concentrated. The residue was purified by column chromatography on SiO_2 gel to afford the alkylation product.

Table 1. Alkylation of a variety of active methylene compounds using **4c** as a catalyst



Substrate	R^2X	method	Time (h)	Product	Yield (%)
 **5**	benzyl bromide	GP-A	1	 **6a**	94
 **5**	propargyl bromide	GP-A	6	 **6b**	95
 **7**	benzyl bromide	GP-A	0.5	 **8a**	95
7	propargyl bromide	GP-A	1	 **8b**	96
	benzyl bromide	GP-B	10	 **9**	99
		GP-B	8	 **10**	83
	benzyl bromide	GP-B	8	 **11**	92

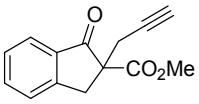
Methyl 2-benzyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (6a)


6a

Synthesized following GP-A (0.25 mmol scale). A mixture of indanone **5** (47.5 mg, 0.25 mmol), benzylbromide (45 µl, 0.38 mmol), **4c** (9.2 mg, 0.025 mmol) and KOH (42 mg, 0.75 mmol) in $CHCl_3$ (1.2 mL) was stirred for 1hr. Purified by SiO_2 gel column chromatography (acetone : n-hexane=1 : 9) to give 65.8 mg (94 % yield) of the title compound as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.18 (d, *J* = 17.1 Hz, 1H), 3.30 (d, *J* = 14.1 Hz, 1H), 3.50 (d, *J* = 14.0 Hz, 1H), 3.63 (d, *J* = 17.1 Hz, 1H), 3.73 (s, 3H), 7.13–7.20 (m, 5H), 7.34–7.37 (m, 2H), 7.54 (dt, *J* = 1.2 , 7.6 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 35.4, 39.7, 52.9, 61.7, 124.7, 126.2, 126.8, 127.6, 128.3, 129.9, 135.3, 136.3, 153.1, 171.2, 202.1. NMR data were corresponded with those previously described.[4]

Methyl 1-oxo-2-(prop-2-yn-1-yl)-2,3-dihydro-1H-indene-2-carboxylate (6b)

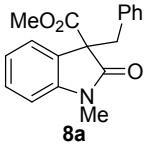


6b

Synthesized following GP-A (0.25 mmol scale). A mixture of indanone **5** (47.5 mg, 0.25 mmol), propargyl bromide (28 µl, 0.38 mmol), **4c** (9.2 mg, 0.025 mmol) and KOH (42 mg, 0.75 mmol) in $CHCl_3$ (1.2 mL) was stirred for 6hrs. Purified by SiO_2 gel column chromatography (EtOAc : n-hexane=1 : 4) to give 54.0 mg (95 % yield) of the title compound as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.82 (t, *J* = 2.7 Hz, 1H), 2.84 (dd, *J* = 2.7, 16.9 Hz, 1H), 3.01 (dd, *J* = 2.7, 16.9 Hz, 1H), 3.39 (d, *J* = 17.3 Hz, 1H), 3.68 (s, 3H), 3.70 (d, *J* = 17.3 Hz, 1H), 7.39–7.42 (m, 1H), 7.52 (dt, *J* = 1.0, 7.8 Hz, 1H), 7.65 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.78–7.79 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 23.9, 36.6, 52.9 , 58.9 , 70.5, 79.2, 124.8, 126.3, 127.8, 135.6, 153.3, 170.4, 200.8.

Methyl 3-benzyl-1-methyl-2-oxoindoline-3-carboxylate (8a)

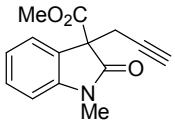


8a

Synthesized following GP-A (0.20 mmol scale). A mixture of **7** (41.0 mg, 0.20 mmol), benzyl bromide (36 µl, 0.30 mmol), **4c** (7.4 mg, 0.02 mmol) and KOH (34 mg, 0.60 mmol) in $CHCl_3$ (1.0 mL) was stirred for 30 min. Purified by SiO_2 gel column chromatography (EtOAc : n-hexane=1 : 2) to give 56.0 mg (95 % yield) of the title compound as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.95 (s, 3H), 3.56 (s, 2H), 3.71 (s, 3H), 6.58 (d, *J* =7.8 Hz, 1H), 6.84 –6.89 (m, 2H), 6.99–7.05 (m, 3H), 7.08 (dt, *J* = 1.0, 7.6 Hz, 1H), 7.23 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.33–7.35 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 26.1, 40.0, 53.2, 60.7, 108.1, 122.5, 123.9, 126.7, 127.2, 127.5, 129.0, 129.9, 134.2, 143.9, 169.7, 173.3. NMR data were corresponded with those previously described.[5]

Methyl 1-methyl-2-oxo-3-(prop-2-yn-1-yl)indoline-3-carboxylate (8b)



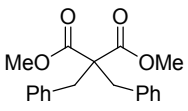
8b

Synthesized following GP-A (0.20 mmol scale). A mixture of **7** (41.0 mg, 0.20 mmol), propargyl bromide (23 µl, 0.30 mmol), **4c** (7.4 mg, 0.02 mmol) and KOH (34 mg, 0.60 mmol) in $CHCl_3$ (1.0 mL) was stirred for 30 min. Purified by SiO_2 gel column chromatography (EtOAc : n-hexane=1 : 4) to give 46.6 mg (96 % yield) of the title compound as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.78 (t, *J* = 2.7 Hz, 1H), 3.04 (dd, *J* = 2.7, 16.6 Hz, 1H), 3.20 (dd, *J* = 2.7, 16.6 Hz. 1H), 3.27 (s, 3H), 3.67 (s, 3H), 6.90 (d, *J* = 7.8 Hz, 1H), s7.11 (dt, *J* = 0.8, 7.6 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.38 (dt, *J* = 1.3, 7.6 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 24.2, 26.5, 53.2, 57.8, 70.6, 77.9, 108.4, 123.0, 123.5, 127.0, 129.5, 168.6, 172.8.

Dmethyl 2,2-dibenzylmalonate (9)

Synthesized following GP-B (0.25 mmol scale). A mixture of dimethylmalonate (33.0 mg, 0.25 mmol), benzyl bromide (89 µl, 0.75 mmol), **4c** (9.2 mg, 0.025 mmol) and K_2CO_3 (104 mg, 0.75

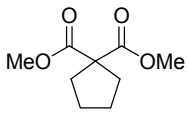


9

mmol) in DMF (1.2 mL) was stirred for 10 hrs. Purified by SiO_2 gel column chromatography (EtOAc : n-hexane=1 : 4) to give 77.3 mg (99 % yield) of the title compound as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.23 (s, 4H), 3.64 (s, 6H), 7.16 (d, *J* = 7.1Hz, 4H), 7.24–7.29 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 39.2, 52.2, 60.4, 127.0, 128.2, 130.0, 136.1, 171.2. NMR data were corresponded with those previously described.[6]

Dimethyl cyclopentane-1,1-dicarboxylate (10)

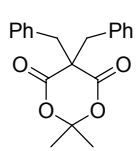


10

Synthesized following GP-B (0.20 mmol scale). A mixture of dimethylmalonate (39.0 mg, 0.30 mmol), 1,4-dibromobutane (39 μl, 0.33 mmol), **4c** (11.0 mg, 0.03 mmol) and K_2CO_3 (104 mg, 0.75 mmol) in DMF (1.5 mL) was stirred for 8 hrs. Purified by SiO_2 gel column chromatography (EtOAc : n-hexane=1 : 4) to give 46.3 mg (83 % yield) of the title compound as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.67–1.70, 2.18–2.20, 3.72 (s, 6H). NMR data were corresponded with those previously described.[7]

5,5-Dibenzyl-2,2-dimethyl-1,3-dioxane-4,6-dione (11)



11

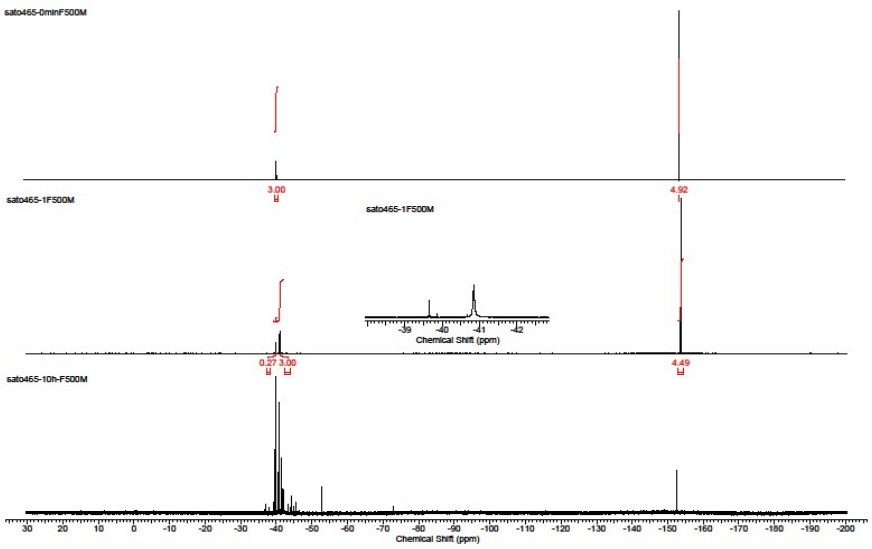
Synthesized following GP-B (0.25 mmol scale). A mixture of Merdrum's acid (36.0 mg, 0.25 mmol), benzyl bromide (89 μl, 0.75 mmol), **4c** (9.2 mg, 0.025 mmol) and K_2CO_3 (104 mg, 0.75 mmol) in DMF (1.2 mL) was stirred for 8 hrs. Purified by SiO_2 gel column chromatography (EtOAc : n-hexane=1 : 2) to give 74.3 mg (92 % yield) of the title compound as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.63 (s, 6H), 3.46 (s, 4H), 7.20–7.28 (m, 10H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 28.5, 44.9, 60.0, 105.8, 127.7, 128.8, 130.1, 134.8, 168.1. NMR data were corresponded with those previously described.[8]

2-5. Experiment of equilibrium between 4c with KOH

Imidazolium salt **4c** (11.0 mg, 0.03 mmol), KOH (16.8 mg 0.30 mmol) and $CHCl_3$ (1.0 mL) were placed in a vial which was equipped with a magnetic stir bar. The mixture was stirred for 1 and 10 hrs. The reaction mixture was quenched with 1M HCl aq., and the aqueous phase was extracted with AcOEt. The combined organic phases were washed with water and brine, then dried over $MgSO_4$, filtered and concentrated *in vacuo*. The relative intensity of peaks was determined by ^{19}F NMR analysis of the crude mixture. The result indicated that most of **4c** remained and ca.10% of 4c converted into likely ion exchange compound when stirring for 1hour. Besides, trace amount of thiourea ($[M+1]^+$ = 213) and unidentified products (243, 393) were detectable by Mass spectrometry, but not urea derivative. When stirring for stirring 10 hours, the reaction resulted in the

decomposition to give multi-compounds. In addition, the characterization of **4c** for sufficient alkaline stability was not ascertained.



(top) ^{19}F NMR spectrum of **4c**. (middle) ^{19}F NMR spectrum of crude mixture for while stirring for 1h. (bottom) ^{19}F NMR spectrum of crude mixture for while stirring for 10 hrs.

3. Crystal data for 4c

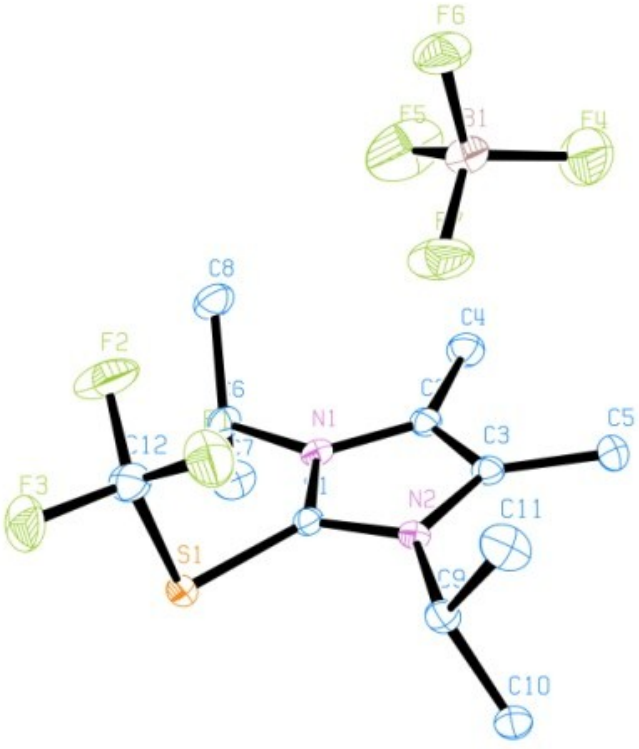


Figure1. ORTEP drawing of the X-ray structure of **4c**. Hydrogen atoms are omitted for clarity and ellipsoids displayed at 50% probability. Selected bond distances (Å), angles [deg] and torsional Angles[deg] in **4c**, C1–S1, 1.732 (2); S1–C12, 1.808 (3); F1–C12, 1.323(3); F2–C12, 1.342(3); F3–C12, 1.333(3); C1–S1–C12, 97.48 (11); C12–S1–C1-N1, –93.99 (19); C12–S1–C1-N2, 89.66 (19)

A. Crystal Data

Empirical Formula	$C_{12}H_{20}BF_7N_2S$
Formula Weight	368.16
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.150 X 0.070 X 0.040 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 7.926(2) Å b = 15.738(5) Å c = 13.422(4) Å β = 100.404(3) ° V = 1646.7(8) Å^3
Space Group	$P2_1/n$ (#14)
Z value	4
D_{calc}	1.485 g/cm^3
F_{000}	760.00
μ(MoKα)	2.643 cm^{-1}

B. Intensity Measurements

Diffractometer	Saturn724
Radiation	MoKα (λ = 0.71075 Å) multi-layer mirror monochromated
Voltage, Current	50kV, 24mA
Temperature	-180.0°C
Detector Aperture	72.8 x 72.8 mm
Data Images	720 exposures
ω oscillation Range (χ=45.0, ϕ=0.0)	-110.0 - 70.0°
Exposure Rate	16.0 sec./°

Detector Swing Angle	-20.09°
ω oscillation Range (χ=45.0, ϕ=90.0)	-110.0 - 70.0°
Exposure Rate	16.0 sec./°
Detector Swing Angle	-20.09°
Detector Position	44.99 mm
Pixel Size	0.141 mm
$2\theta_{max}$	54.9°
No. of Reflections Measured	Total: 13471
	Unique: 3722 (R_{int} = 0.0402)
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.873 - 0.989)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SHELXS2013)
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w (Fo^2 - Fc^2)^2
Least Squares Weights	w = 1/ [$\sigma^2(Fo^2)$ + (0.0576 · P)^2
	+ 1.0654 · P]
	where P = (Max(Fo^2,0) + 2Fc^2)/3
$2\theta_{max}$ cutoff	54.9°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	3722
No. Variables	214
Reflection/Parameter Ratio	17.39
Residuals: R1 (I>2.00σ(I))	0.0516
Residuals: R (All reflections)	0.0685
Residuals: wR2 (All reflections)	0.1267
Goodness of Fit Indicator	1.074
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	0.60 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.34 $e^-/Å^3$

4. References

1) N. Kuhn, T. Kratz, *Synthesis* 1993, 561.

2) S.Jia , A.brahim Alkhalila , Y.Sua, X. Xiaa , S. Chonga , K.-H. Wanga , D. Huanga , Y. Fua , Y. Hu, *Synlett* 2015, 1725.

3) S. Ghosh, S. Chaudhuri, A. Bisai, *Org. Lett.* 2015,**17**, 1373.

4) K. Umemura, *J. Org. Chem.* 1989, **54**, 2374.

5) S. Ghosh, S. De, B. N. Kakde, S. Bhunia, A. Adhikary, A.Bisai, *Org. Lett.* **14**, 5864.

6) T. Ohkita, Y. Tsuchiya, H. Togo, *Tetrahedron*, 2012, **68**, 7247.

7) S. Muthusamy, B. Gnanaprakasam, *Tetrahedron Lett.* 2005, **46**, 635.

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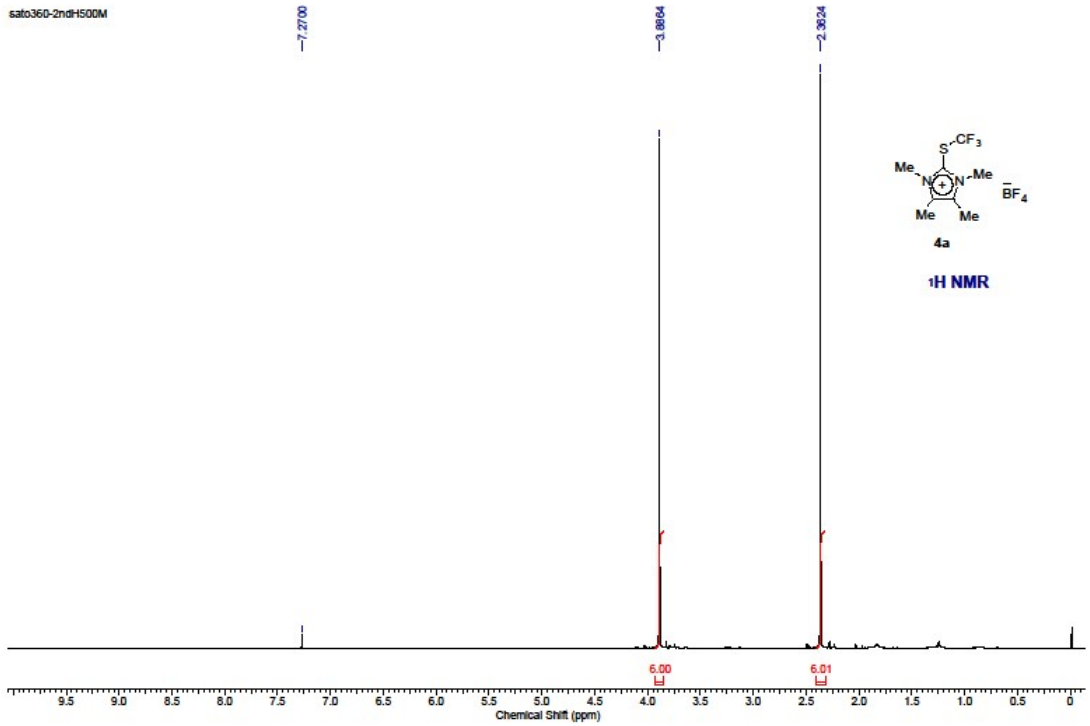
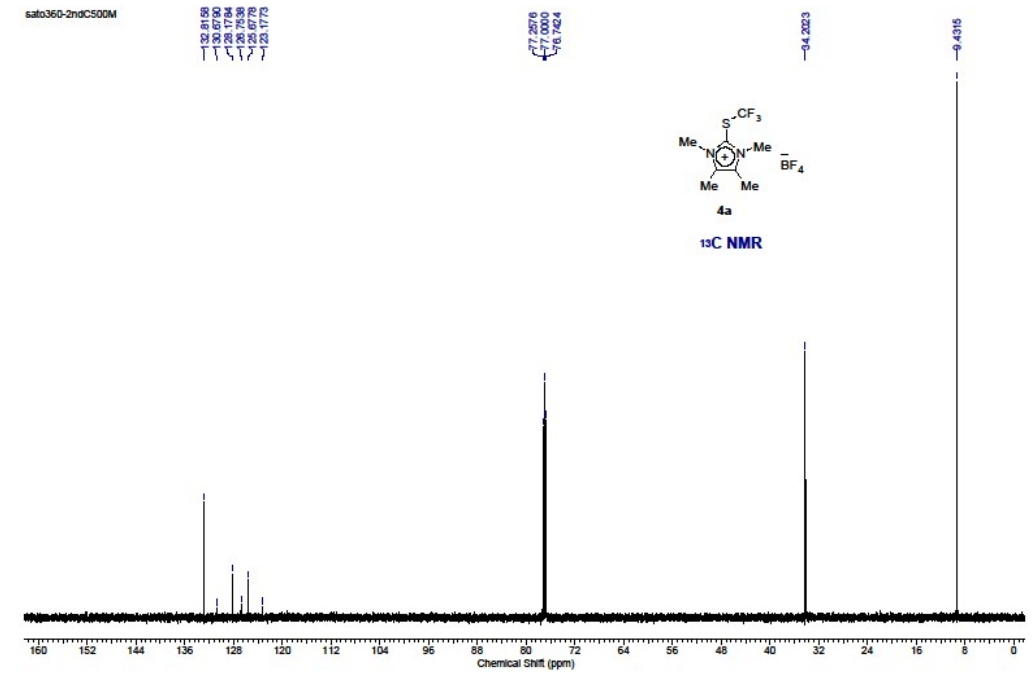
5. NMR spectra

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128.1784
126.7538
125.6778
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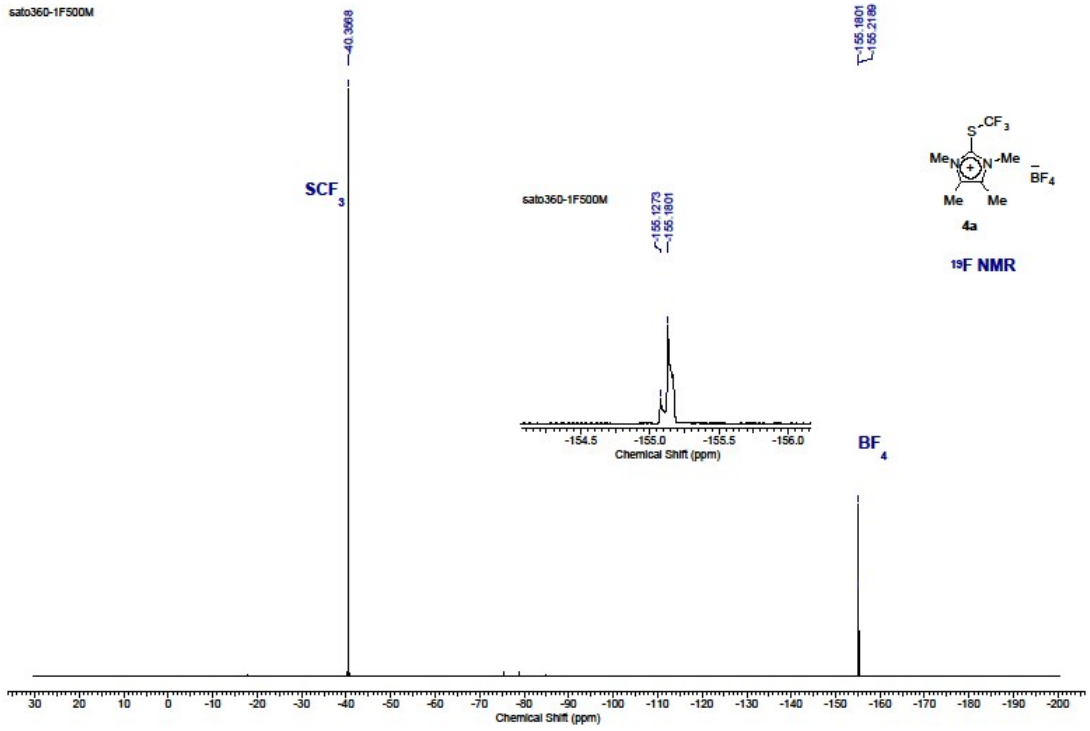
77.2576
77.0000
76.7424
34.2323
9.4315
Me
Me
Me
Me
CF3
BF4
4a
13C NMR
160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)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156.2189
sato360-1F500M
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155.1801
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Chemical Shift (ppm)
BF4
Me
Me
Me
Me
CF3
BF4
4a
19F NMR
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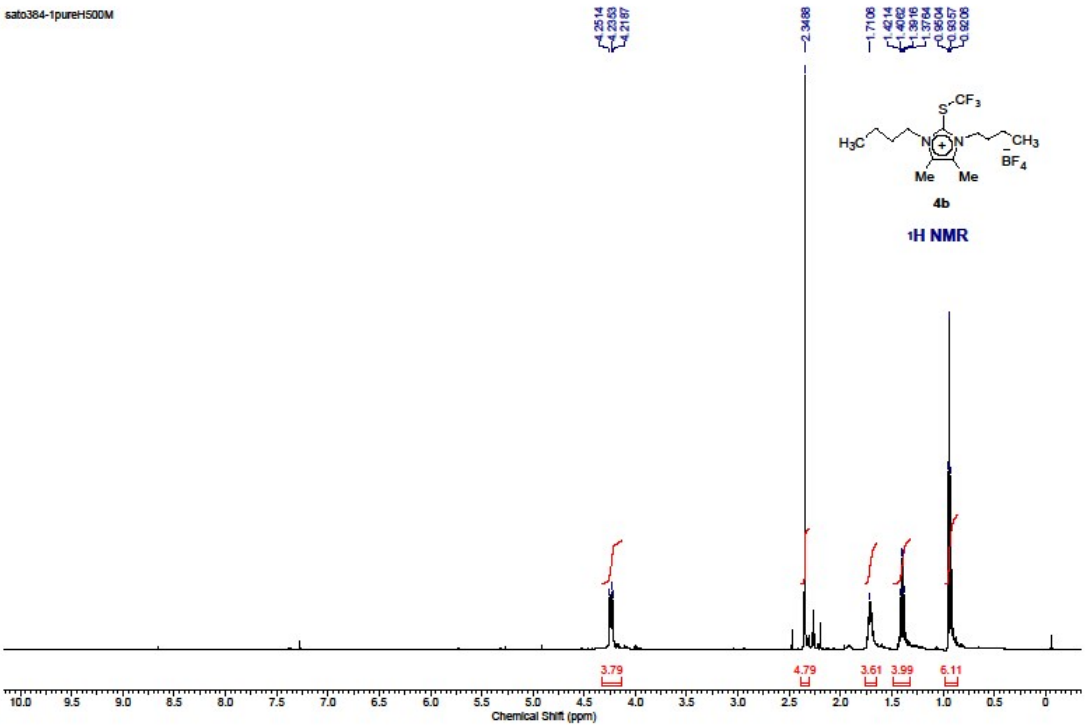
Chemical Shift (ppm)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3.99
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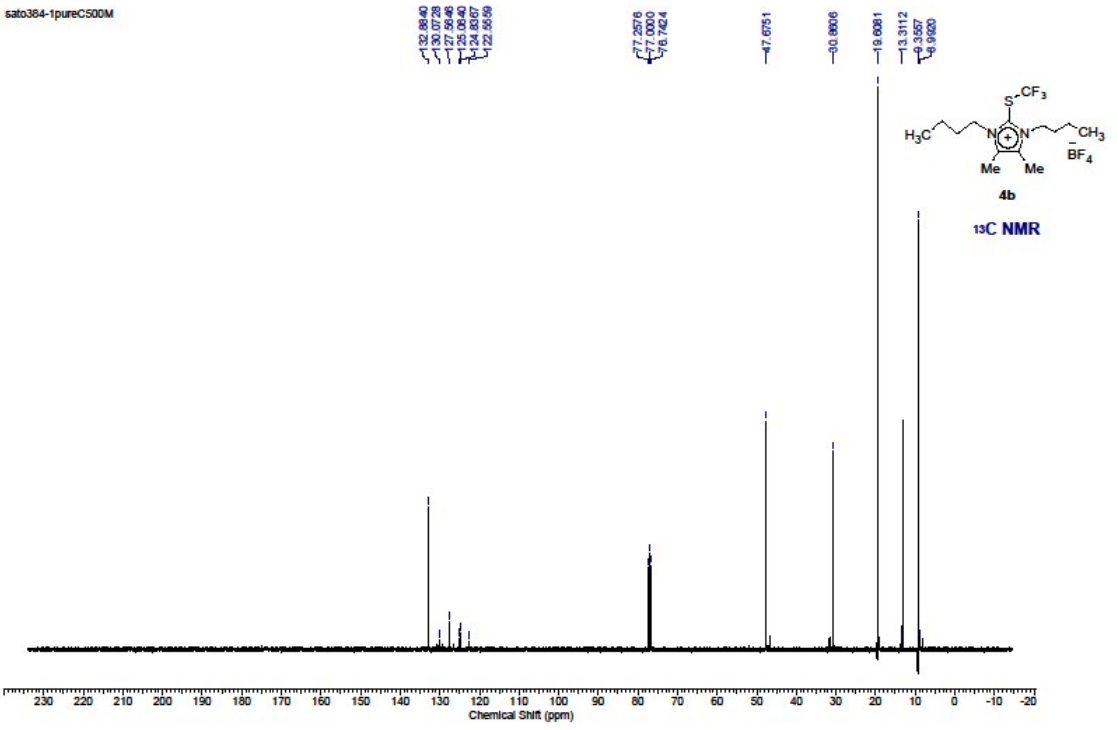
Chemical Shift (ppm)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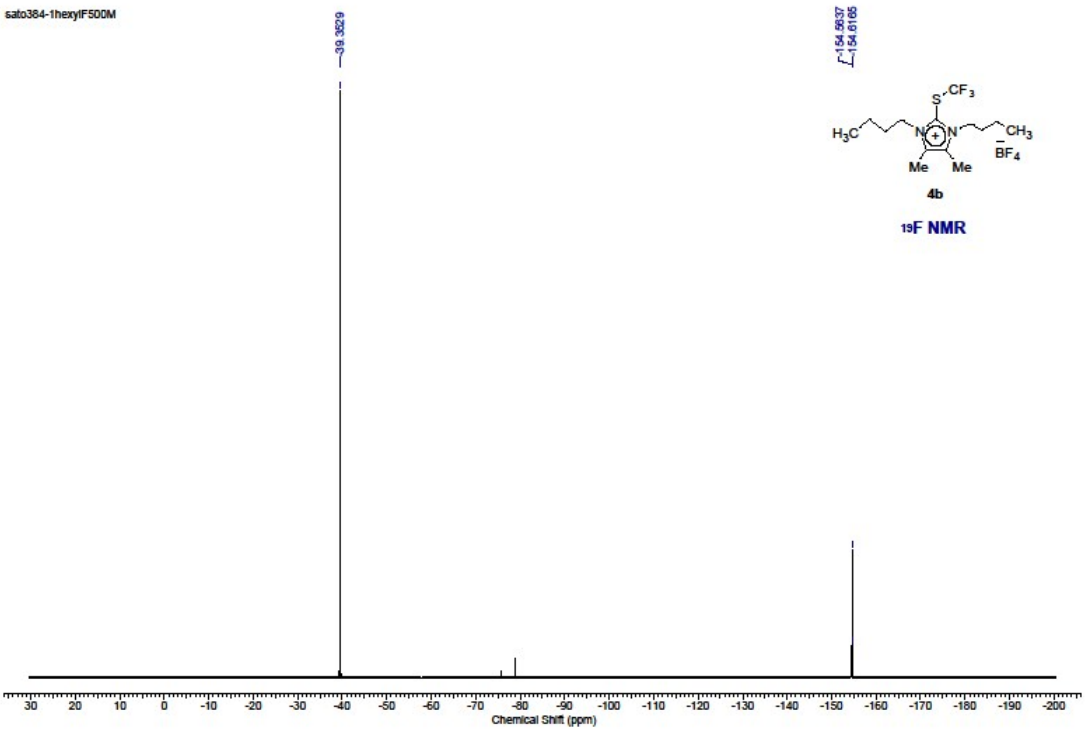
Chemical Shift (ppm)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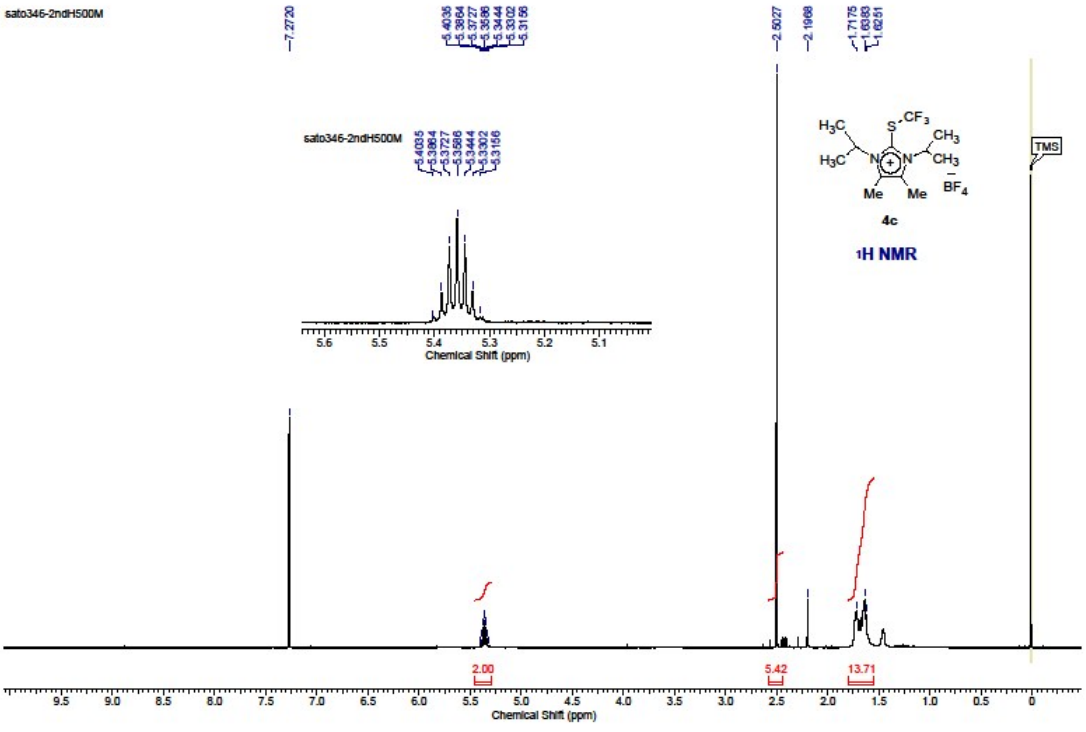
Chemical Shift (ppm)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5.3302
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2.5927
2.1968
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Me
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2.00
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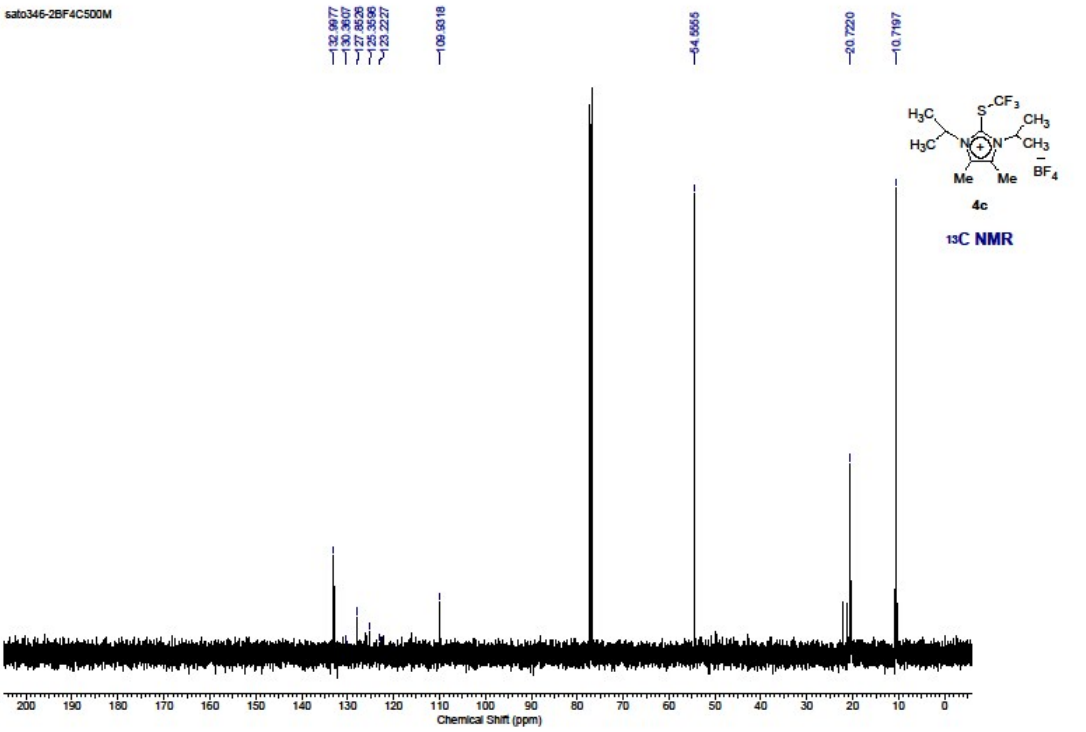
Chemical Shift (ppm)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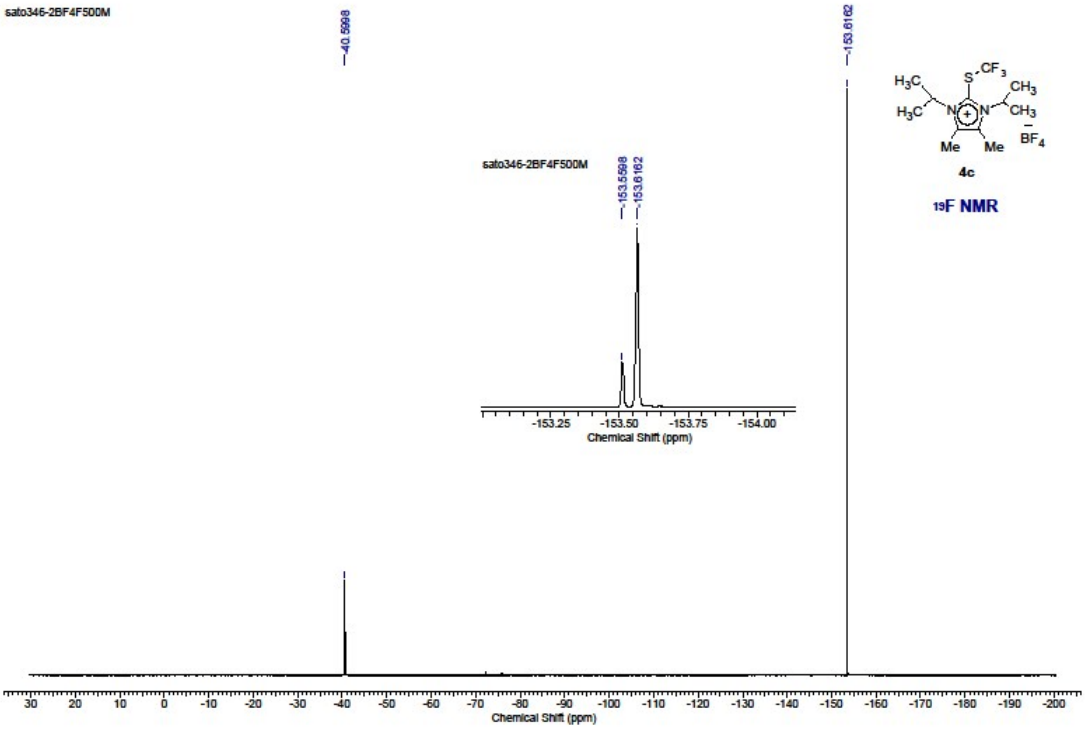
13C NMR
Chemical Shift (ppm)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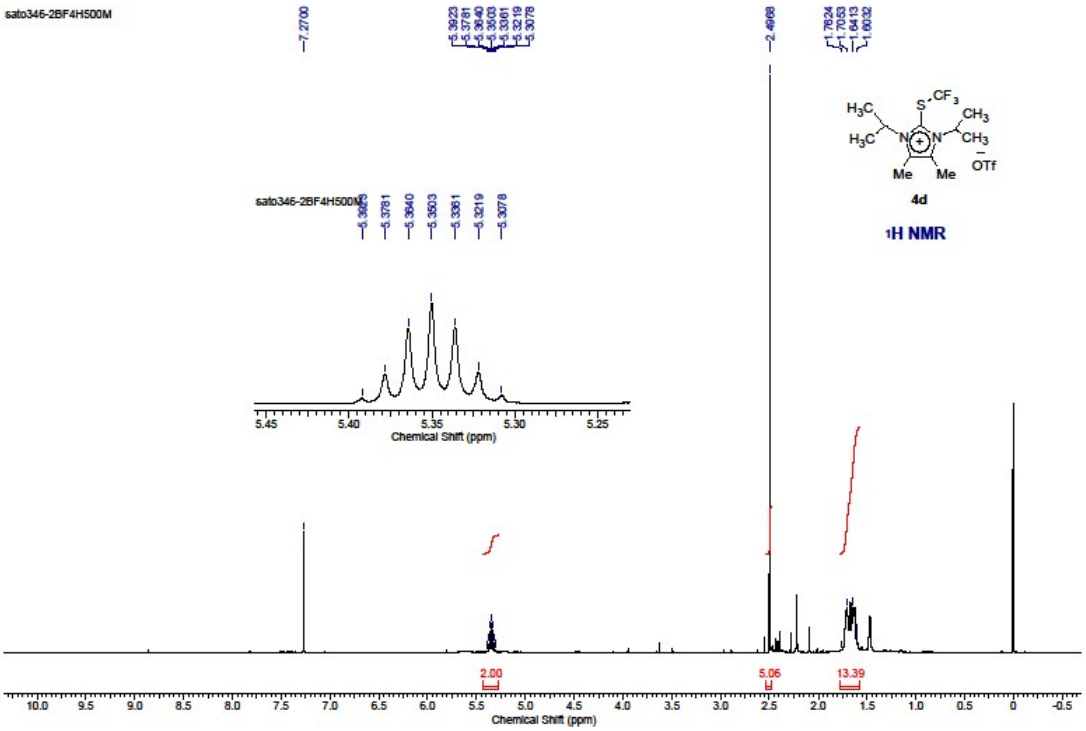
Chemical Shift (ppm)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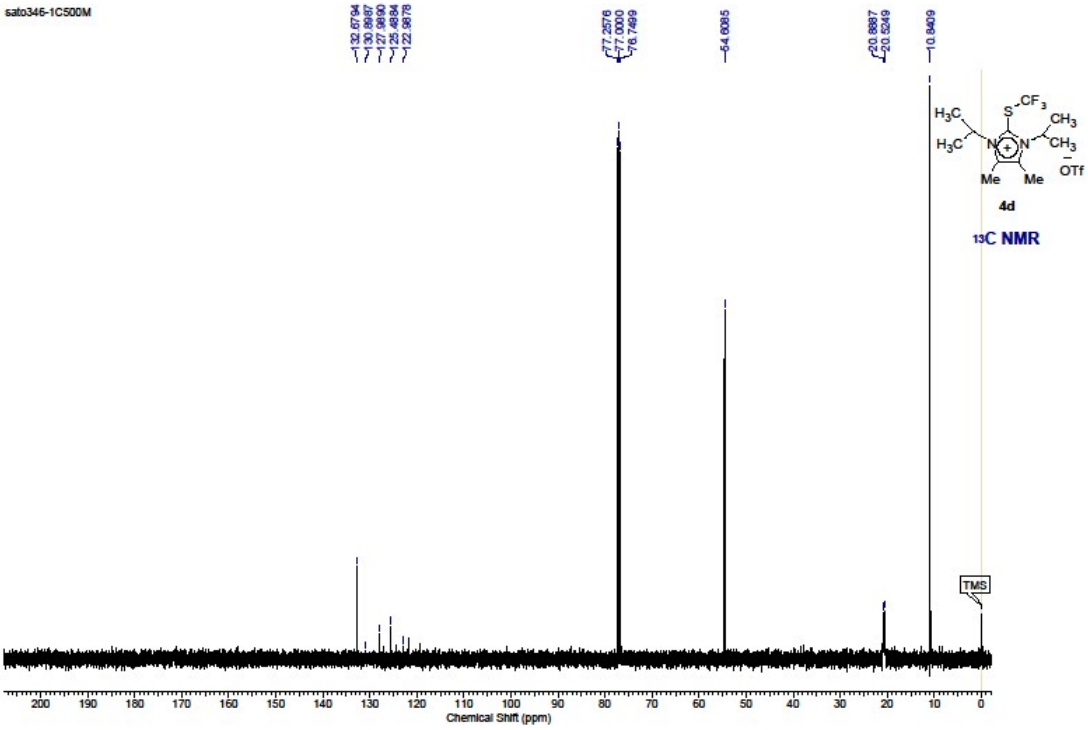
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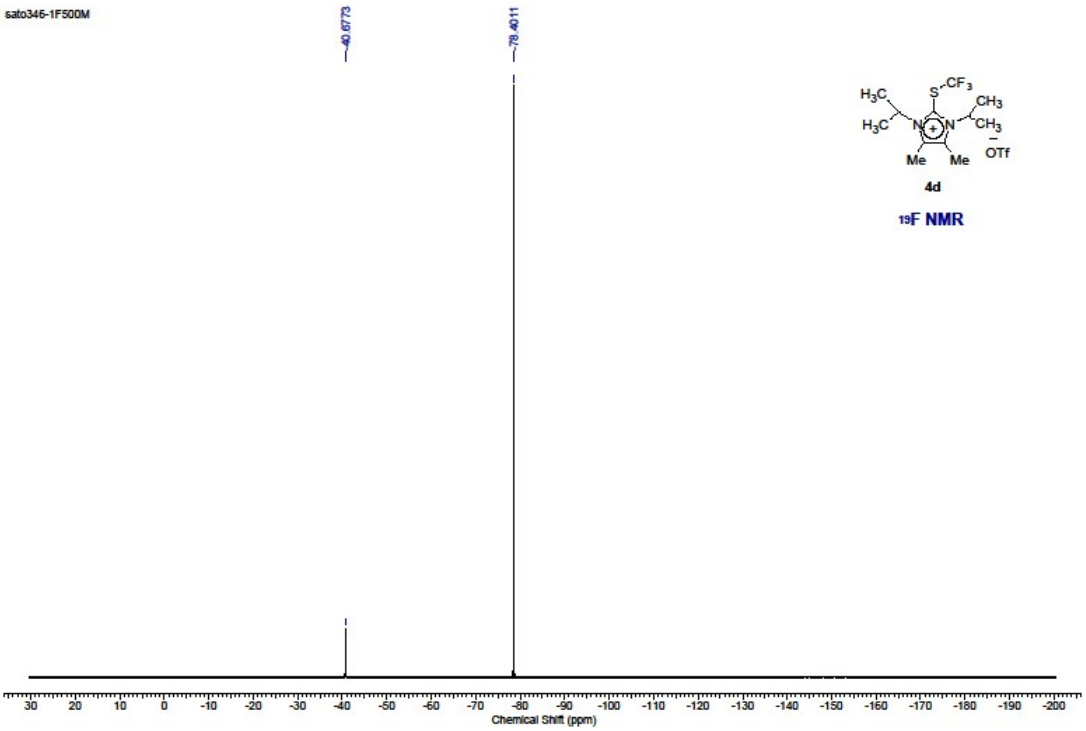
Chemical Shift (ppm)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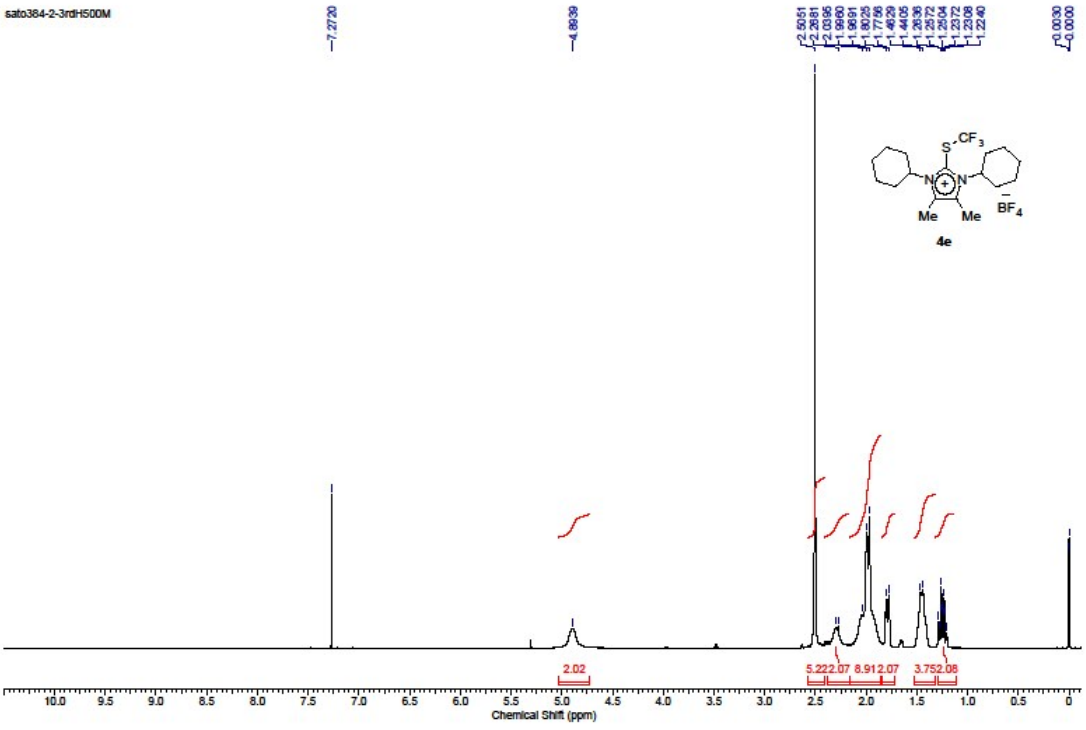
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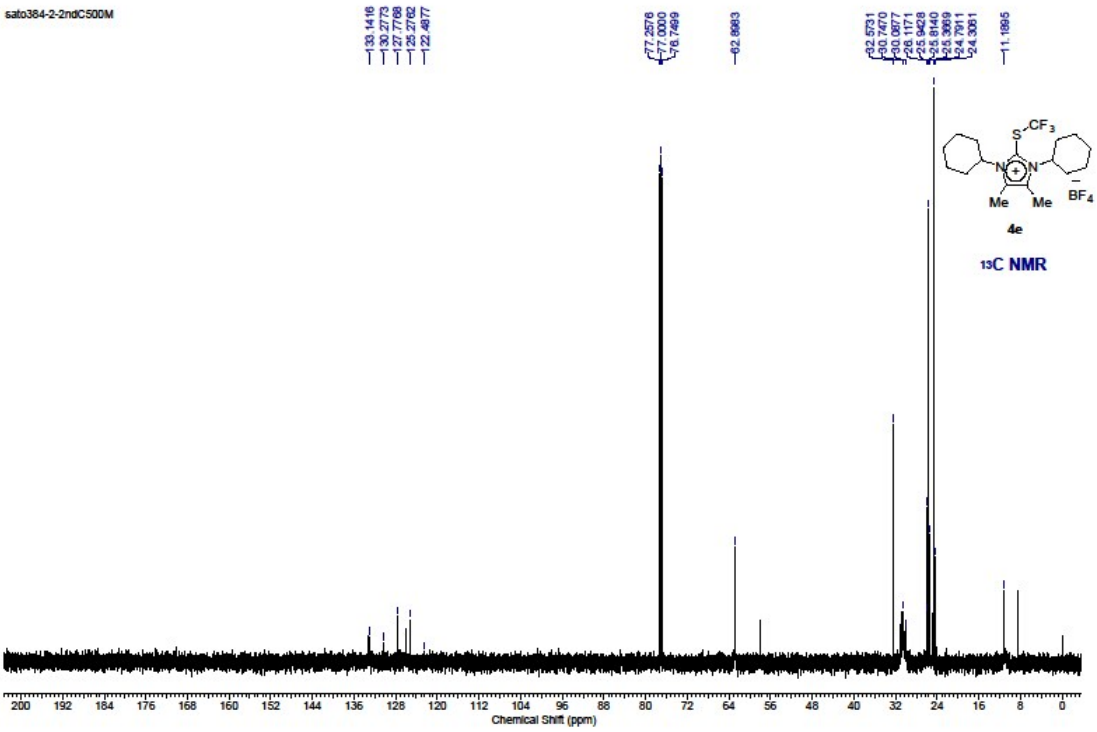
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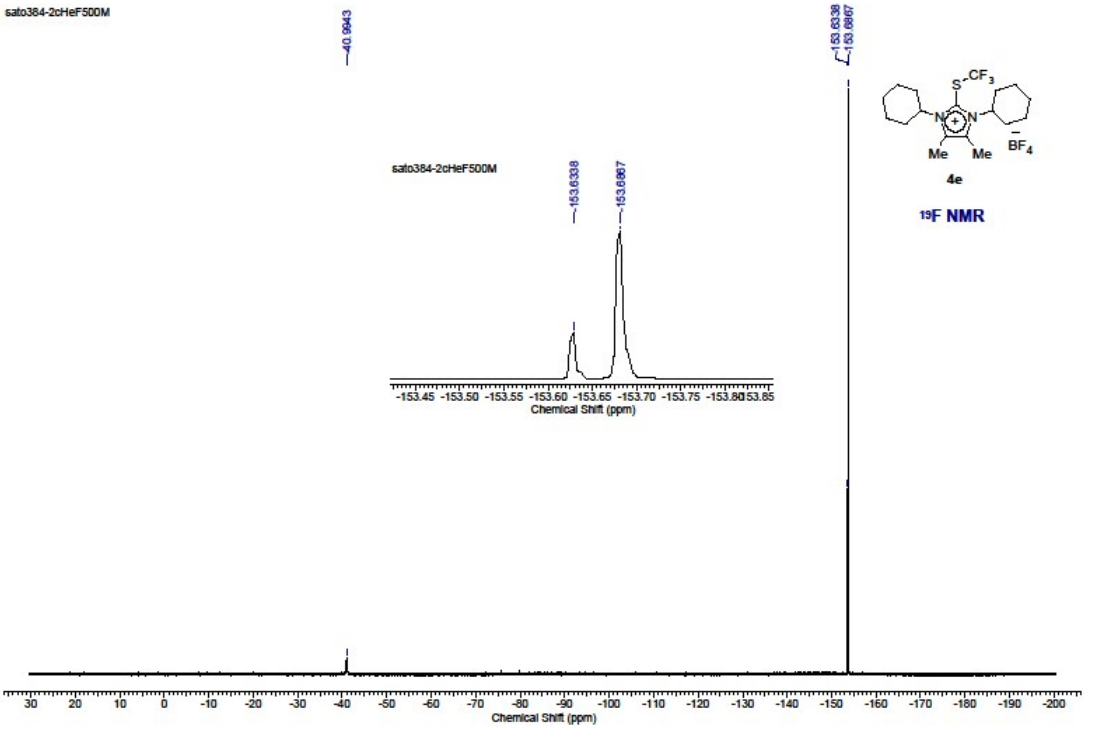
Chemical Shift (ppm)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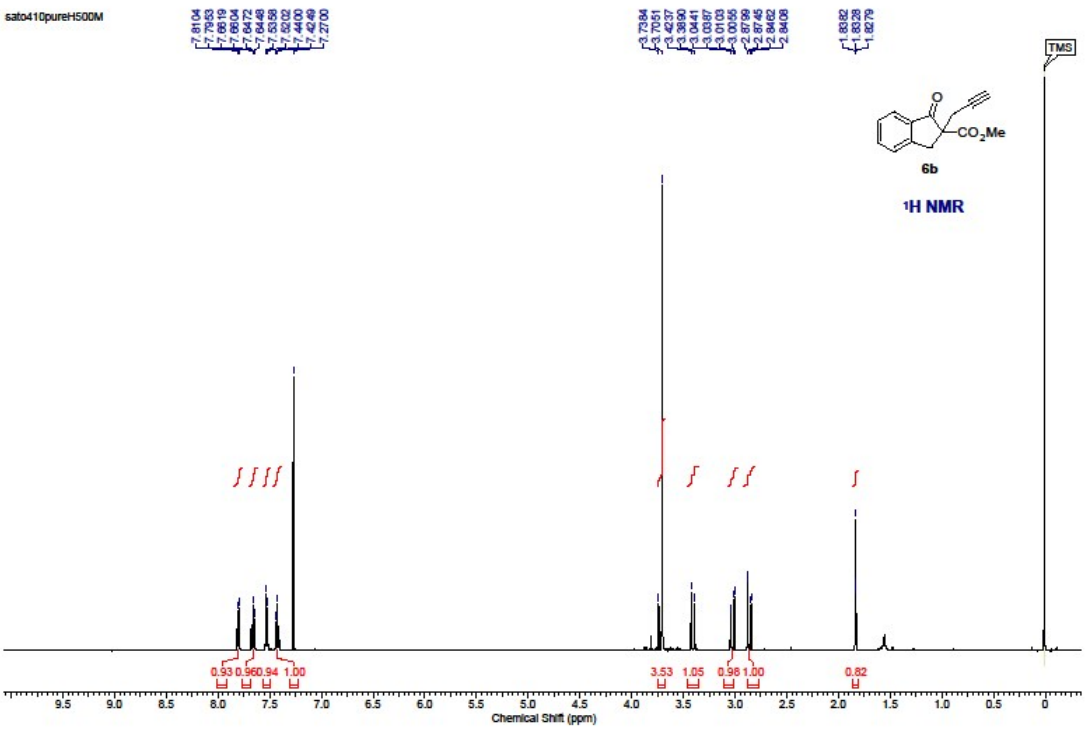
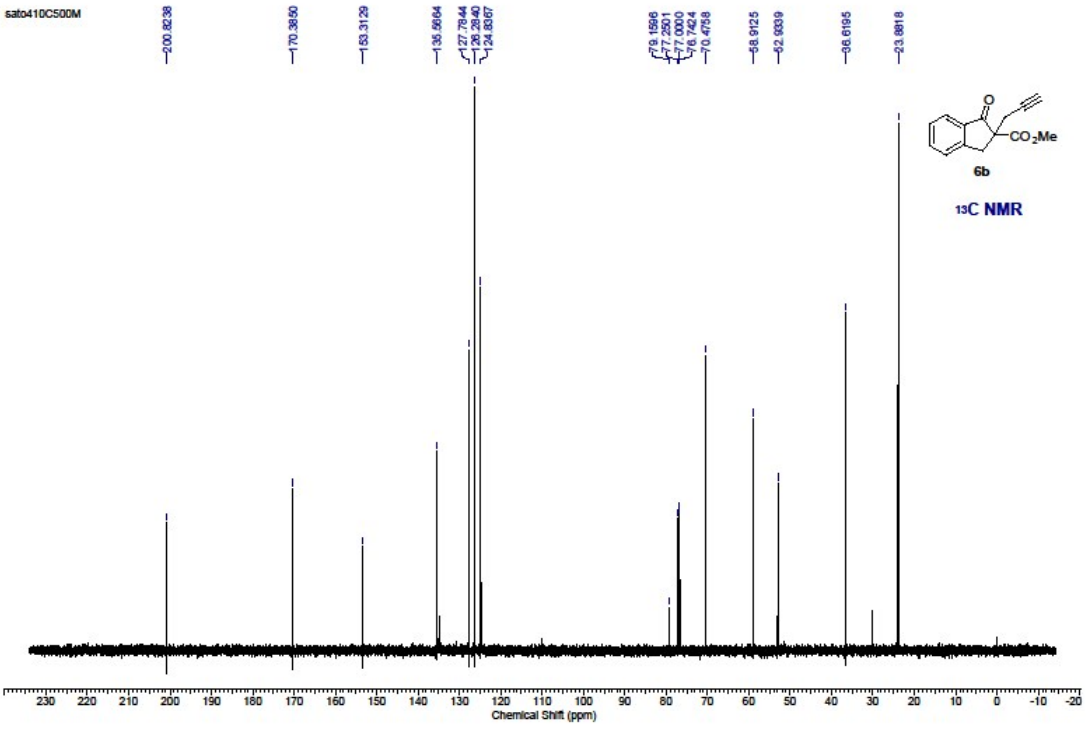
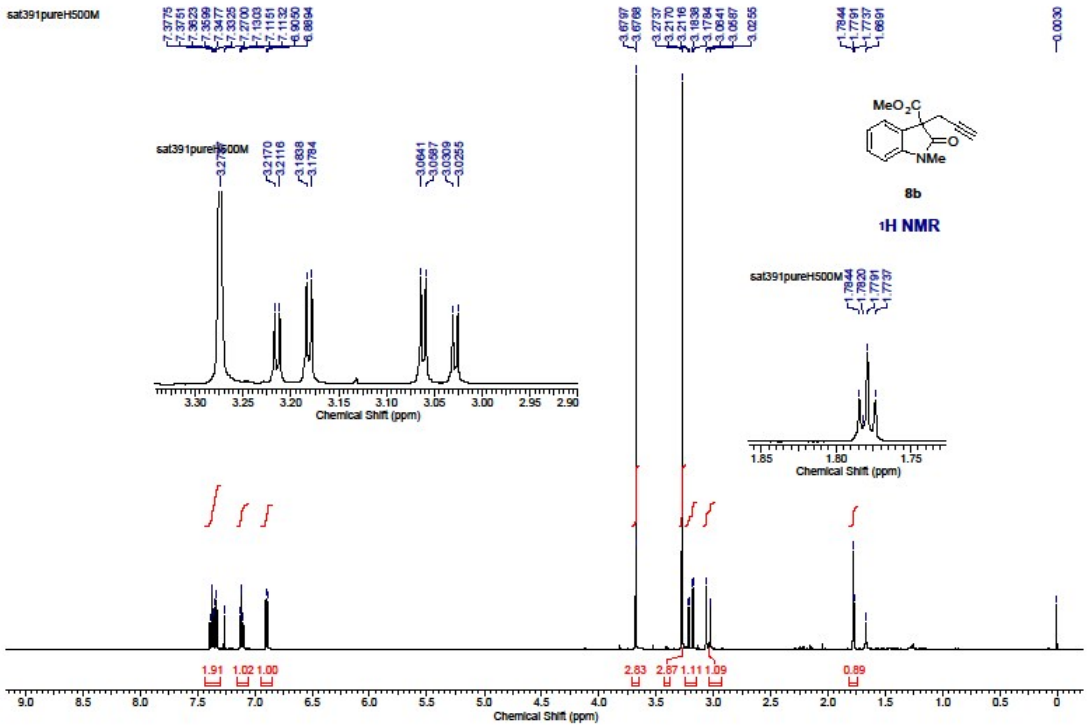
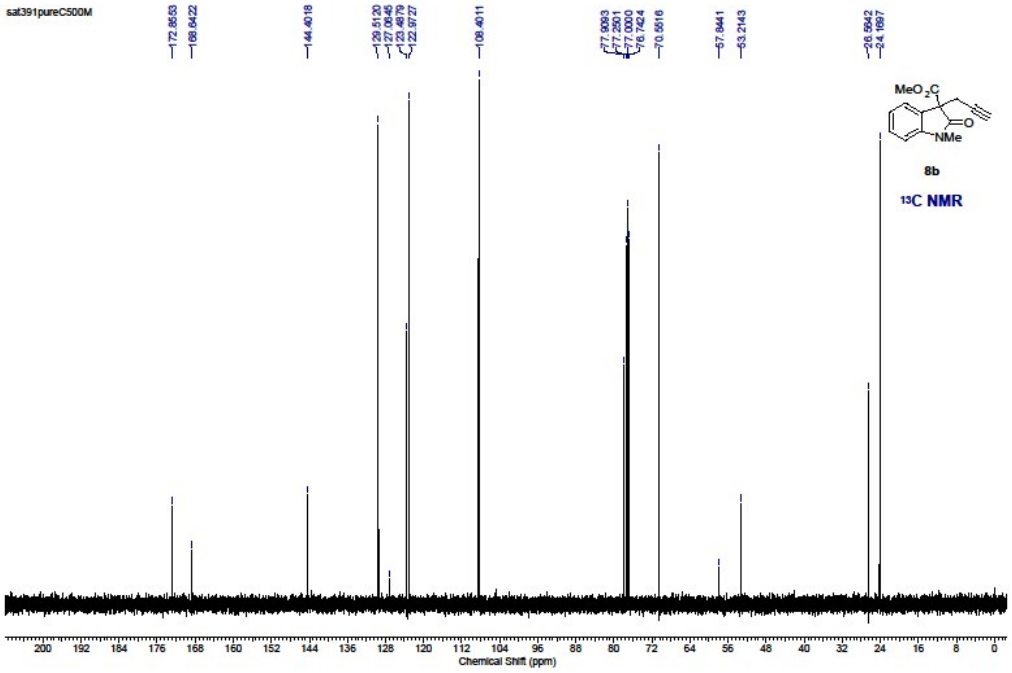
19F NMR
Chemical Shift (ppm)


sato410pureH500M
7.8104
7.7953
7.6619
7.6604
7.6472
7.6448
7.5398
7.5202
7.4400
7.4249
7.2700
3.7384
3.7051
3.4237
3.3890
3.3441
3.0167
3.0103
3.0055
2.8798
2.8745
2.8462
2.8406
1.8382
1.8329
1.8279
TMS
O
CO2Me
6b
1H NMR
0.93 0.96 0.94 1.00
3.53 1.05 0.98 1.00
0.82
Chemical Shift (ppm)


sato410CS00M
200.8238
170.3850
153.3129
135.5664
127.7844
126.2940
124.8367
79.1586
77.2551
77.0000
76.7424
70.4758
58.9125
52.9339
36.6195
23.8818
O
CO2Me
6b
13C NMR
Chemical Shift (ppm)


sat391pureH500M
MeO2C
O
NMe
8b
1H NMR
Chemical Shift (ppm)


sat391pureC500M
MeO2C
O
NMe
8b
13C NMR
Chemical Shift (ppm)