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CF_3-Substituted semisquarate: A pluripotent building block for the divergent synthesis of trifluoromethylated functional molecules

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General Experimental

General methods: All air- and moisture-sensitive reactions were performed under an argon (Ar) atmosphere in dried glassware. Analytical this layer chromatography was performed using 0.25 mm silica gel plate (Merck TLC Silica gel 60 F_{254}). Column chromatography was performed on silica gel (Cica silica gel 60N) with solvents specified below. For purification of carboxylic acid, SO_3H silica gel (CHROMATOREX®, Fuji Silysia Chemical LTD) was used. Bulb-to-bulb distillation was performed on SIBATA GTO-250RS. Melting points were recorded on SRS OptiMelt MPA100. NMR spectra were recorded on JEOL ESC-400 spectrometer (^{1}H/400 MHz, ^{13}C/100 MHz, and ^{19}F/376MHz) for samples in $CDCl_3$ solutions at 25 ˚C. ^{1}H NMR chemical shifts are reported in terms of chemical shift (δ, ppm) relative to the singlet at δ 7.26 ppm for chloroform. ^{13}C NMR spectra were fully decoupled and are reported in terms of chemical shift (δ, ppm) relative to the triplet at δ 77.0 ppm for $CDCl_3$. ^{19}F NMR spectra are reported in terms of chemical shift (δ, ppm) relative to the singlet at δ –63.7 ppm for α,α,α-trifluorobenzene as an external standard. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; sept, septet; m, multiplet. Coupling constants are reported in Hz. Infrared spectra were recorded on JASCO FT/IR-230 specrometer. High-resolution mass spectra were recorded on JEOL JMS-T100LP mass spectrometer.

Reagents and Solvents: Diisopropyl squarate **3a** (Aldrich), CF_3SiMe_3 (Fluorochem), Re_2O_7 (Strem Chemicals), Fe(pc) (TCI), $Pb(OAc)_4$ (TCI), *n*-BuLi (Mitsuwa), and isopropylmagnesium bromide (Wako) were purchased and used as received. Other Grignard reagents were also purchased from Aldrich and used as received with the following exceptions: *p*-ethoxycarbonylphenyl,[1] 2-furyl,[2] 2-thienyl,[2] 2-benzofuryl,[2] 2-benzothienyl,[2] *N*-Boc-3-indolyl,[3] and *N*-Boc-2-indolyl[4] Grignard reagents were prepared according to the reported procedures. Other solvents and reagents were purchased from chemical suppliers (Aldrich, Kanto Chemical, TCI, and Wako) and

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[1] W. Dohle, D. M. Lindsay, and P. Knochel, *Org. Lett.*, 2001, **3**, 2871.
[2] (a) P. Jiao, M. Kawasaki, and H. Yamamoto, *Angew. Chem. Int. Ed.,* 2009, **48**, 3333. (b) L. I. Rosquete, M. G. Cabrera-Serra, J. E. Piñero, P. Martín-Rodríguez, L. Fernández-Pérez, J. G. Luis, G. McNaughton-Smith, and T. Abad-Grillo, *Bioorg. Med. Chem.*, 2010, **18**, 4530.
[3] M. Abarbri, F. Dehmel, and P. Knochel, *Tetrahedron Lett.*, 1999, **40**, 7449.
[4] J. T. Kuethe and D. L. Comins, *J. Org. Chem.*, 2004, **69**, 2863.

used as received. $Ph_3SiOReO_3$ was prepared according to the reported method.[5]

Reaction Mechanisms

Plausible mechanisms of transformations depicted in eqs 1–4 are proposed based on literatures.[6] The transformation of **2a** to **1a** catalyzed by Re_2O_7 (eq. 1) started with the reaction of **2a** with Re_2O_7. The resultant intermediate **S1** underwent [3,3] rearrangement to afford **1a** with extrusion of $^{i}PrOReO_3$ from **S2**. As shown in eq 2, thermal electrocyclic ring opening of **5a** generate vinylketene **S3**, which underwent 6π electrocyclization and subsequent tautomerization. The iron-catalyzed aerobic oxidation of the resultant hydroquinone **S4** afforded **6a**. Similarly, the transformation of **1a** to **9a** proceeded via thermal electrocyclic ring opening of the corresponding 4-hydroxycyclobutenone and subsequent 6π electrocyclization of the resultant vinylketene intermediate. Radical-mediated ring transformation of **5a** to **7a** proceeded via a sequential process involving two single-electron oxidations (eq 3). The first singe-electron oxidation of **5a** generated oxy radical **S5**. Spontaneous ring opening of **S5** generated **S6**, which underwent ionic ring closure to produce **S7**. The second single-electron oxidation of **S7** was followed by the capture of the resultant cationic intermediate with acetate to afford **7a**. Finally, the ring expansion of **1a** to **11** is shown in eq 4. Adduct **S8** underwent ring expansion in a similar manner with pinacol rearrangement to generate **S9**, which was protonated to afford **11**.

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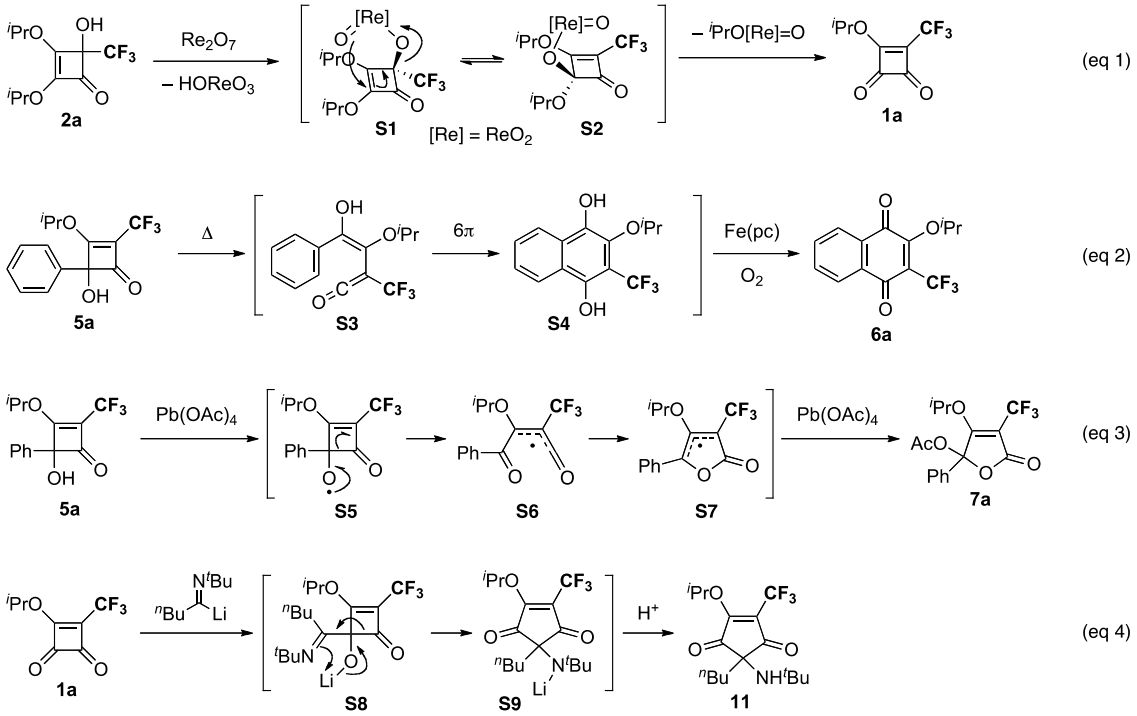
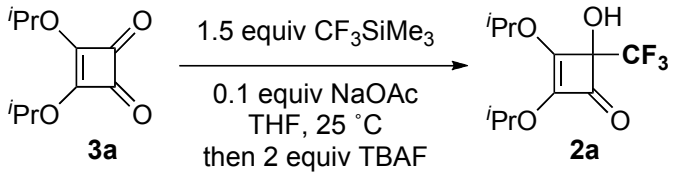
[5] C. Morrill, G. L. Beutner, and G. N. Grubbs, *J. Org. Chem.*, 2006, **71**, 7813.

[6] (a) I. Volchkov and D. Lee, *Chem. Soc. Rev.*, 2014, **43**, 4381. (b) H. W. Moore and B. R. Yerxa, *Chemtracts–Org. Chem.*, 1992, **5**, 273. (c) A. G. Birchler, F. Liu, and L. S. Liebeskind, *J. Org. Chem.*, 1994, **59**, 7737. (d) Y. Yamamoto, M. Ohno, and S. Eguchi, *J. Am. Chem. Soc.*, 1995, **117**, 9653. (e) L. Sun and L. S. Liebeskind, *J. Org. Chem.*, 1994, **59**, 6856.



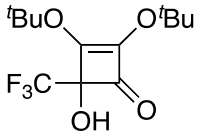
Experimental Procedures



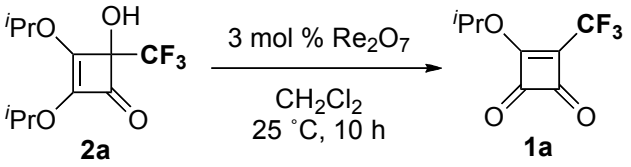
***Synthesis of 2a from 3a**:* To a degassed solution of **3a** (99.9 mg, 0.50 mmol), NaOAc (4.2 mg, 0.05 mmol), and $^{n}Bu_4NCl$ (13.8 mg, 0.05 mmol) in dry THF (1 mL) was added CF_3SiMe_3 (111 μL, 0.75 mmol) at room temperature under an argon atmosphere. The solution was stirred at room temperature for 20 min. To this solution was added TBAF (1 M THF solution, 1 mL, 1.0 mmol) and then H_2O (20 mL) at room temperature. The reaction mixture was extracted with Et_2O (3 × 20 mL). The combined organic layer was washed with brine (10 mL) and dried over $MgSO_4$. The solvents were evaporated *in vacuo*, and the obtained crude product was purified by silica gel column chromatography (hexane:AcOEt = 10:1) to afford **2a** (92.4 mg, 69% yield) as a colorless solid (mp 76.8–78.3 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.31 (d, J = 6.4 Hz, 3 H), 1.32 (d, J = 6.4 Hz, 3 H), 1.42 (d, J = 6.4 Hz, 6 H), 3.00 (s, 1 H), 4.94 (sept, J = 6.4 Hz, 1 H), 4.95 (sept, J = 6.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25

˚C): δ 22.1, 22.3, 22.46, 22.53, 74.7, 78.6, 84.8 (q, J = 33.4 Hz), 122.9 (q, J = 281.9 Hz), 135.3, 160.1, 176.9; ^{19}F NMR (376 MHz, $CDCl_3$, 25 ˚C): δ –76.7; IR (neat) 3380 (OH), 1781 (C=O), 1618 (C=C) cm^{-1}; HRMS (DART) *m/z* calcd for $C_{11}H_{15}F_3O_4$•NH_4 286.1266, found 286.1273 $[M+NH_4]^+$.

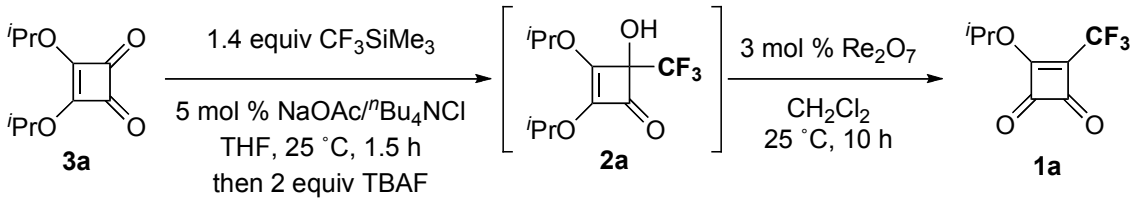
Compound **2b** was also obtained according to the above procedure.



Analytical data for 2b: colorless solid (mp 71.0–73.2 ˚C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.50 (s, 9 H), 1.55 (s, 9 H), 1.42 (d, J = 6.4 Hz, 6 H), 3.00 (br s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 28.2, 28.6, 82.0, 83.6 (q, J = 33.0 Hz), 85.7, 123.1 (q, J = 282.2 Hz), 133.3, 160.2, 177.1; ^{19}F NMR (376 MHz, $CDCl_3$, 25 ˚C): δ –76.9; IR (neat) 3379 (OH), 1772 (C=O), 1597 (C=C) cm^{-1}; HRMS (DART) *m/z* calcd for $C_{17}H_{16}O_3$•NH_4 314.1579, found 314.1594 $[M+NH_4]^+$.

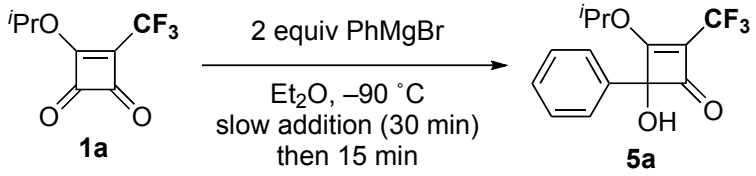


***Conversion of 2a into 1a**:* To a degassed solution of **2a** (128.5 mg, 0.48 mmol) in dry CH_2Cl_2 (25 mL) was added Re_2O_7 (7.8 mg, 0.016 mmol) at room temperature under an argon atmosphere. The solution was stirred at room temperature for 10 h. The reaction mixture was filtered through a pad of alumina under an argon stream. The filtrate was concentrated in vacuo to afford **1a** as yellow oil (99.2 mg, 99% yield), which was solidified in a freezer (mp 32.7–35.5 ˚C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.54 (d, J = 6.4 Hz, 6 H), 5.53 (sept, J = 6.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 22.5, 83.4, 118.8 (q, J = 268.9 Hz), 162.1 (q, J = 40.0 Hz), 184.8, 193.0, 195.6; ^{19}F NMR (376 MHz, $CDCl_3$, 25 ˚C): δ –63.9; IR (neat) 1817 (C=O), 1786 (C=O), 1631 (C=C) cm^{-1}; HRMS (DART) *m/z* calcd for $C_8H_7F_3O_3$•NH_4 226.0691, found 226.0700 $[M+NH_4]^+$.



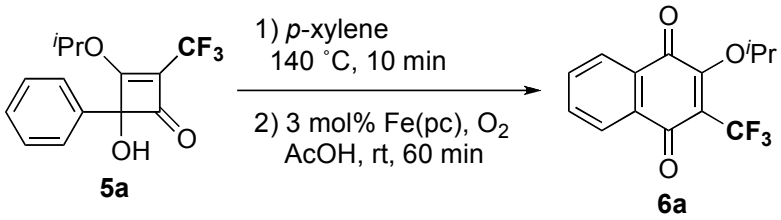
Sequential Procedure for Conversion of 3a into 1a: To a degassed solution of **3a** (2.98 g, 15.0 mmol), NaOAc (61.0 mg, 0.74 mmol), and $^{n}Bu_4NCl$ (206.2 mg, 0.74 mmol) in dry THF (15 mL) was added CF_3SiMe_3 (3.1 □L, 21.0 mmol) at room temperature under an argon atmosphere. The solution was stirred at room temperature for 90 min. To this solution was added TBAF (1 M THF solution, 21 mL, 21.0 mmol) and the mixture was stirred for 15 min at room temperature. After addition of H_2O (30 mL), the reaction mixture was extracted with Et_2O (3 × 30 mL). The combined organic layer was washed with brine (30 mL) and dried over Na_2SO_4. The solvents were evaporated *in vacuo* to obtain crude products, which was dried under reduced pressure for 2 h.

To a degassed solution of the above crude products in dry CH_2Cl_2 (35 mL) was added Re_2O_7 (218 mg, 0.45 mmol) at room temperature under an argon atmosphere. The solution was stirred at room temperature for 10 h. The reaction mixture was concentrated in vacuo and the obtained crude product was purified by bulb-to-bulb distillation (bp. 70 ˚C/3 hPa) to afford **1a** as a yellow solid (2.61 g, 84% yield).

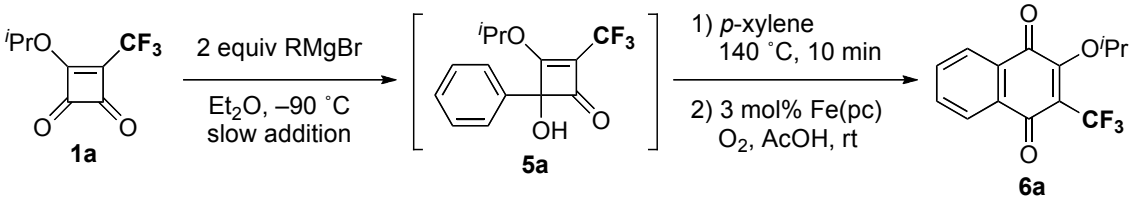


Synthesis of 5a from 1a: To a degassed solution of **1a** (104.1 mg, 0.50 mmol) in dry Et_2O (2 mL) was added PhMgBr (0.1 M in Et_2O, 10 □L, 1.0 mmol) at –90 ˚C under an argon atmosphere via syringe pump (20 mL/h). After stirring for 30 min, the reaction was quenched with sat. NH_4Cl (2 mL) at –90 ˚C. After addition of H_2O (20 mL) at room temperature, the reaction mixture was extracted with Et_2O (3 × 20 mL). The combined organic layer was washed with brine (10 mL) and dried over Na_2SO_4. The solvents were evaporated *in vacuo*, and the obtained crude product was purified by silica gel column chromatography (hexane:AcOEt = 10:1) to afford **5a** (112.0 mg, 78% yield) as a colorless solid (mp 113.1–114.2 ˚C); ^1H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ

1.14 (d, J = 6.4 Hz, 3 H), 1.43 (d, J = 6.4 Hz, 3 H), 4.87 (sept, J = 6.4 Hz, 1 H), 5.09 (br s, 1 H), 7.34–7.43 (m, 3 H), 7.45–7.49 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 22.0, 22.4, 82.4, 93.4, 114.2 (q, J = 37.8 Hz), 117.3 (q, J = 268.9 Hz), 125.3, 128.9, 129.0, 134.6, 183.5, 184.2; ^{19}F NMR (376 MHz, $CDCl_3$, 25 ˚C): δ –61.0; IR (neat) 3378 (OH), 1775 (C=O), 1637 (C=C), 1621 (C=C) cm^{-1}; HRMS (DART) *m/z* calcd for $C_{14}H_{13}F_3O_3$•H 287.0895, found 287.0889 $[M+H]^+$.



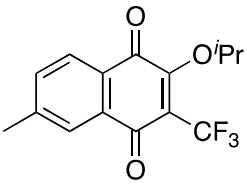
***Conversion of 5a into 6a**:* A solution of **5a** (143.2 mg, 0.5 mmol) in *p*-xylene (10 mL) was stirred at 140 ˚C under an Ar atmosphere for 10 min. After cooling to room temperature, to this solution was added Fe(II) phthalocyanine complex (8.5 mg, 0.015 mmol) and AcOH (1 mL). The solution was stirred at room temperature under an O_2 atmosphere for 1 h. The solution was filtered through a pad of celite, and the filtrate was concentrated *in vacuo*. The obtained crude product was purified by silica gel column chromatography (hexane:AcOEt = 10:1) to afford **6a** (121.0 mg, 85% yield) as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.43 (d, J = 6.4 Hz, 6 H), 5.44 (sept, J = 6.4 Hz, 1 H), 7.76 (dt, J = 7.2, 1.6 Hz, 1 H), 7.82 (dt, J = 7.2, 1.6 Hz, 1 H), 8.08 (dd, J = 7.2, 1.6 Hz, 1 H), 8.15 (dd, J = 7.2, 1.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 22.9, 79.7, 120.6 (q, J = 27.3 Hz), 122.0 (q, J = 275.6 Hz), 126.5, 126.6, 130.6, 131.7, 133.7, 135.0, 159.8, 180.4, 181.4; ^{19}F NMR (376 MHz, $CDCl_3$, 25 ˚C): δ –58.2; IR (neat) 1684 (C=O), 1666 (C=O), 1603 (C=C), 1580 (C=C) cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{14}H_{11}F_3O_3$•H 285.0739, found 285.0748 $[M+H]^+$.



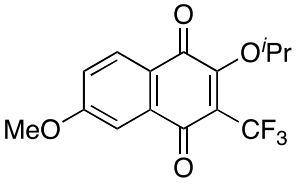
***Sequential Procedure for Conversion of 1a into 6a**:* To a degassed solution of **1a** (104.2 mg, 0.50 mmol) in dry Et_2O (2 mL) was added PhMgBr (0.1 M in Et_2O, 10 □L,

1.0 mmol) at –90 ˚C under an argon atmosphere via syringe pump (20 mL/h). After stirring for 30 min, the reaction was quenched with sat. NH_4Cl (2 mL) at –90 ˚C. The reaction mixture was extracted with Et_2O (3 × 10 mL). The combined organic layer was washed with brine (10 mL) and dried over Na_2SO_4. The organic layer was diluted with *p*-xylene (10 mL) and Et_2O was evaporated *in vacuo*. The obtained solution of crude **5a** in *p*-xylene (ca. 10 mL) was stirred at 140 ˚C under an Ar atmosphere for 10 min. After cooling to room temperature, to this solution was added Fe(II) phthalocyanine complex (8.4 mg, 0.015 mmol) and AcOH (0.5 mL). The solution was stirred at room temperature under an O_2 atmosphere for 1 h. The solution was filtered through a pad of celite, and the filtrate was concentrated *in vacuo*. The obtained crude product was purified by silica gel column chromatography (hexane:AcOEt = 10:1) to afford **6a** (103.8 mg, 73% yield) as yellow oil.

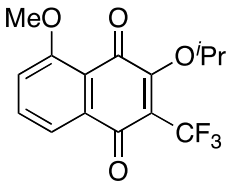
Other quinones were synthesized according to the above procedure.



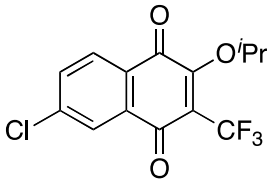
Analytical data for 6b: yellow solid (mp 89.2–92.3 ˚C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.41 (d, *J* = 6.4 Hz, 6 H), 2.51 (s, 3 H), 5.42 (sept, *J* = 6.4 Hz, 1 H), 7.53 (d, *J* = 7.6 Hz, 1 H), 7.91 (s, 1 H), 7.94 (d, *J* = 7.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 22.0, 22.9, 79.6, 120.5 (q, *J* = 27.0 Hz), 122.0 (q, *J* = 275.5 Hz), 126.8, 127.0, 128.4, 131.6, 134.4, 146.6, 159.9, 180.7, 181.1; ^{19}F NMR (376 MHz, $CDCl_3$, 25 ˚C): δ –58.1; IR (neat) 1682 (C=O), 1665 (C=O), 1597 (C=C) cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{15}H_{13}F_3O_3$•H 299.0895, found 299.0914 $[M+H]^+$.



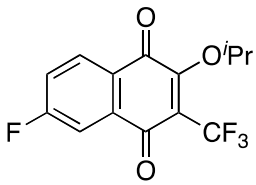
Analytical data for 6c: yellow solid (mp 69.7–73.5 ˚C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.41 (d, *J* = 6.4 Hz, 6 H), 3.96 (s, 3 H), 5.47 (sept, *J* = 6.4 Hz, 1 H), 7.19 (dd, *J* = 8.4, 2.4 Hz, 1 H), 7.55 (d, *J* = 2.4 Hz, 1 H), 8.00 (d, *J* = 8.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 23.0, 56.2, 79.8, 109.9, 120.3 (q, *J* = 27.0 Hz), 120.6, 122.2 (q, *J* = 275.5 Hz), 124.2, 129.3, 134.1, 160.4, 165.2, 180.1, 180.5; ^{19}F NMR (376 MHz, $CDCl_3$, 25 ˚C): δ –58.2; IR (neat) 1675 (C=O), 1594 (C=C) cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{15}H_{13}F_3O_4$•H 315.0844, found 315.0825 $[M+H]^+$.



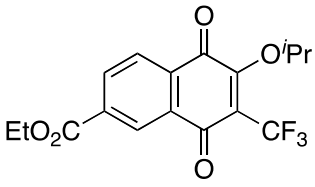
Analytical data for 6d: yellow solid (mp 113.0–114.7 ˚C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.42 (d, J = 6.4 Hz, 6 H), 4.02 (s, 3 H), 5.33 (sept, J = 6.4 Hz, 1 H), 7.26–7.32 (m, 1 H), 7.68–7.76 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 22.9, 56.5, 79.5, 117.2, 118.6 (q, J = 27.7 Hz), 118.9, 119.1, 121.9 (q, J = 275.2 Hz), 134.0, 136.0, 159.6, 161.0, 179.4, 180.3; ^{19}F NMR (376 MHz, $CDCl_3$, 25 ˚C): δ –59.5; IR (neat) 1676 (C=O), 1588 (C=C) cm^{-1}; HRMS (DART) *m/z* calcd for $C_{15}H_{13}F_3O_4$•H 315.0844, found 315.0870 $[M+H]^+$.



Analytical data for 6e: yellow-brown solid (mp 93.2–94.2 ˚C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.42 (d, J = 6.4 Hz, 6 H), 5.45 (sept, J = 6.4 Hz, 1 H), 7.70 (dd, J = 8.4, 2.0 Hz, 1 H), 8.00 (d, J = 8.4 Hz, 1 H), 8.07 (d, J = 2.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 23.0, 80.1, 120.5 (q, J = 27.6 Hz), 121.8 (q, J = 275.9 Hz), 126.8, 128.3, 128.8, 132.9, 133.8, 142.3, 159.9, 179.2, 180.5; ^{19}F NMR (376 MHz, $CDCl_3$, 25 ˚C): δ –58.3; IR (neat) 1685 (C=O), 1667 (C=O), 1586 (C=C) cm^{-1}; HRMS (DART) *m/z* calcd for $C_{14}H_{10}ClF_3O_3$•H 319.0349, found 319.0369 $[M+H]^+$.

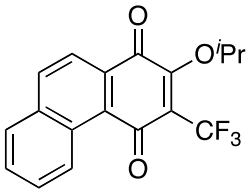


Analytical data for 6f: yellow solid (mp 80.1–81.2 ˚C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.41 (d, J = 6.4 Hz, 6 H), 5.45 (sept, J = 6.4 Hz, 1 H), 7.40 (dt, J = 8.4, 2.4 Hz, 1 H), 7.73 (dd, J = 8.8, 1.6 Hz, 1 H), 8.09 (dd, J = 8.4, 5.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 22.9, 80.1, 113.5 (d, J = 23.9 Hz), 120.6 (q, J = 27.7 Hz), 121.1 (d, J = 22.9 Hz), 121.8 (q, J = 275.9 Hz), 127.2 (d, J = 2.9 Hz), 130.0 (d, J = 8.6 Hz), 134.5 (d, J = 8.6 Hz), 160.0, 166.8 (d, J = 258.4 Hz), 179.1, 180.0; ^{19}F NMR (376 MHz, $CDCl_3$, 25 ˚C): δ –59.4, –101.0; IR (neat) 1670 (C=O), 1586 (C=C) cm^{-1}; HRMS (DART) *m/z* calcd for $C_{14}H_{10}F_4O_3$•NH_4 320.0910, found 320.0907 $[M+NH_4]^+$.

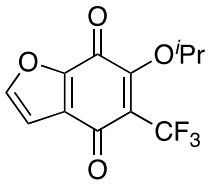


Analytical data for 6g: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.42 (d, J = 6.4 Hz, 6 H), 1.43 (t, J = 7.2 Hz, 3 H), 4.43 (q, J = 7.2 Hz, 2 H), 5.43 (sept, J = 6.4 Hz, 1 H), 8.11 (d, J = 8.0 Hz, 1 H), 8.36 (dd, J = 8.0, 1.6 Hz, 1 H), 8.21

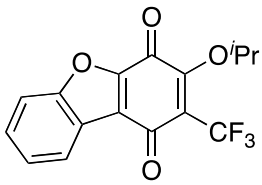
(d, J = 1.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 14.2, 22.9, 62.0, 80.0, 121.0 (q, J = 27.3 Hz), 121.9 (q, J = 275.9 Hz), 126.8, 127.9, 131.8, 133.1, 134.2, 136.3, 159.8, 164.6, 179.5, 181.1; ^{19}F NMR (376 MHz, $CDCl_3$, 25 ˚C): δ –59.3; IR (neat) 1727 (C=O), 1686 (C=O), 1668 (C=O), 1604 (C=C) cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{17}H_{15}F_3O_5$•NH_4 374.1215, found 374.1190 $[M+ NH_4]^+$.



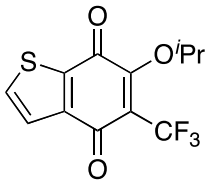
Analytical data for 6h: yellow solid (mp 112.7–114.5 ˚C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.43 (d, J = 6.4 Hz, 6 H), 5.36 (sept, J = 6.4 Hz, 1 H), 7.60–7.69 (m, 2 H), 7.84 (d, J = 7.6 Hz, 1 H), 7.99 (d, J = 8.0 Hz, 1 H), 8.06 (d, J = 8.0 Hz, 1 H), 9.25 (d, J = 8.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 22.9, 79.2, 121.2, 121.5 (q, J = 27.0 Hz), 122.0 (q, J = 275.2 Hz), 127.8, 128.2, 128.6, 129.2, 130.0, 130.5, 134.6, 136.9, 157.4, 182.2, 183.5; ^{19}F NMR (376 MHz, $CDCl_3$, 25 ˚C): δ –58.2; IR (neat) 1680 (C=O), 1654 (C=O), 1605 (C=C), 1591 (C=C) cm^{-1}; HRMS (DART) *m/z* calcd for $C_{18}H_{13}F_3O_3$•H 335.0895, found 335.0903 $[M+H]^+$.



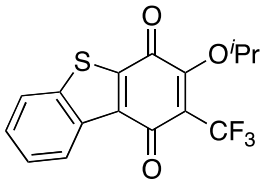
Analytical data for 6i: dark-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.41 (d, J = 6.4 Hz, 6 H), 5.42 (sept, J = 6.4 Hz, 1 H), 6.89 (d, J = 2.0 Hz, 1 H), 7.76 (d, J = 2.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 23.0, 80.6, 108.9, 118.8 (q, J = 27.7 Hz), 122.0 (q, J = 275.5 Hz), 129.7, 148.9, 150.0, 159.5, 170.1, 177.3; ^{19}F NMR (376 MHz, $CDCl_3$, 25 ˚C): δ –57.8; IR (neat) 1692 (C=O), 1674 (C=O) cm^{-1}; HRMS (DART) *m/z* calcd for $C_{12}H_9F_3O_4$•NH_4 292.0797, found 292.0778 $[M+NH_4]^+$.



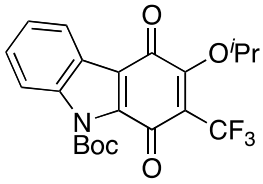
Analytical data for 6j: orange solid (mp 128.1–129.9 ˚C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.44 (d, J = 6.4 Hz, 6 H), 5.43 (sept, J = 6.4 Hz, 1 H), 7.47 (ddd, J = 8.0, 6.8, 1.2 Hz, 1 H), 7.59 (dt, J = 6.8, 1.6 Hz, 1 H), 7.64 (d, J = 8.4 Hz, 1 H), 8.18 (d, J = 8.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 22.8, 80.5, 112.8, 118.7 (q, J = 27.3 Hz), 121.9 (q, J = 275.5 Hz), 122.0, 122.8, 123.9, 126.4, 130.3, 149.3, 157.0, 158.8, 172.1, 178.3; ^{19}F NMR (376 MHz, $CDCl_3$, 25 ˚C): δ –57.6; IR (neat) 1686 (C=O), 1670 (C=O) cm^{-1}; HRMS (DART) *m/z* calcd for $C_{16}H_{11}F_3O_4$•NH_4 342.0953, found 342.0953 $[M+NH_4]^+$.



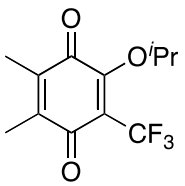
Analytical data for 6k: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.40 (d, J = 6.4 Hz, 6 H), 5.41 (sept, J = 6.4 Hz, 1 H), 7.54 (d, J = 4.6 Hz, 1 H), 7.77 (d, J = 4.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 22.8, 80.2, 119.1 (q, J = 27.3 Hz), 122.0 (q, J = 275.5 Hz), 126.6, 135.9, 140.0, 141.7, 160.4, 175.2, 176.9; ^{19}F NMR (376 MHz, $CDCl_3$, 25 ˚C): δ –57.9; IR (neat) 1662 (C=O), 1590 (C=C) cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{12}H_9F_3O_3S$•H 291.0303, found 291.0307 $[M+H]^+$.



Analytical data for 6l: orange solid (mp 158.6–161.1 ˚C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.44 (d, J = 6.4 Hz, 6 H), 5.40 (sept, J = 6.4 Hz, 1 H), 7.52–7.58 (m, 2 H), 7.85–7.92 (m, 1 H), 8.68–8.75 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 22.9, 80.1, 119.7 (q, J = 27.0 Hz), 122.0 (q, J = 275.5 Hz), 122.9, 127.3, 127.5, 130.0, 133.9, 135.4, 142.1, 142.9, 159.1, 177.1, 178.2; ^{19}F NMR (376 MHz, $CDCl_3$, 25 ˚C): δ –57.7; IR (neat) 1666 (C=O), 1655 (C=O) cm^{-1}; HRMS (DART) *m/z* calcd for $C_{16}H_{11}F_3O_3S$•H 341.0459, found 341.0469 $[M+H]^+$.

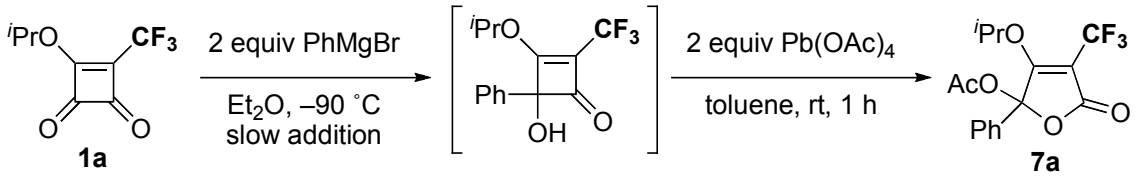


Analytical data for 6m: orange solid (mp 230.8–233.8 ˚C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.44 (d, J = 6.4 Hz, 6 H), 1.66 (s, 9 H), 5.47 (sept, J = 6.4 Hz, 1 H), 7.42 (t, J = 7.6 Hz, 1 H), 7.51 (t, J = 7.6 Hz, 1 H), 8.02 (d, J = 8.8 Hz, 1 H), 8.20 (d, J = 7.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 23.0, 27.4, 79.7, 86.6, 114.5, 118.6 (q, J = 28.0 Hz), 119.3, 122.0 (q, J = 274.9 Hz), 122.7, 122.9, 125.8, 128.8, 136.0, 138.5, 148.0, 158.8, 173.5, 178.5; ^{19}F NMR (376 MHz, $CDCl_3$, 25 ˚C): δ –58.0; IR (neat) 1759 (C=O), 1748 (C=O), 1669 (C=O) cm^{-1}; HRMS (DART) *m/z* calcd for $C_{21}H_{20}F_3NO_5$•H 424.1372, found 424.1393 $[M+H]^+$.



Analytical data for 6n: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.36 (d, J = 6.4 Hz, 6 H), 2.04 (s, 3 H), 2.05 (d, J = 1.2 Hz, 3 H), 5.17 (sept, J = 6.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 12.1, 12.5, 22.8, 79.3, 118.3 (q, J = 27.7 Hz), 121.8 (q, J = 274.9 Hz), 139.3, 142.1, 157.3, 182.6, 183.1; ^{19}F NMR (376 MHz, $CDCl_3$, 25 ˚C): δ –58.4; IR

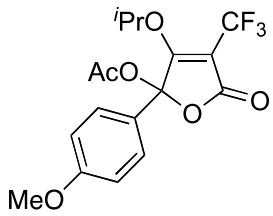
(neat) 1658 (C=O), 1610 (C=C) cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{12}H_{13}F_3O_3 \bullet NH_4$ 280.1161, found 280.1151 $[M+NH_4]^+$.



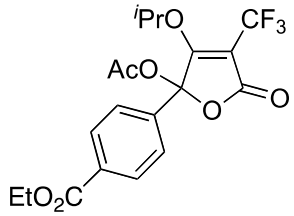
***Synthesis of 7a from 1a**:* To a degassed solution of **1a** (104.3 mg, 0.50 mmol) in dry Et_2O (2 mL) was added PhMgBr (0.1 M in Et_2O, 10 □L, 1.0 mmol) at –90 ˚C under an argon atmosphere via syringe pump (20 mL/h). After stirring for 30 min, the reaction was quenched with sat. NH_4Cl (10 mL) at –90 ˚C. The reaction mixture was extracted with Et_2O (3 × 10 mL). The combined organic layer was washed with brine (10 mL) and dried over Na_2SO_4. The solvent was removed *in vacuo*, and the obtained crude product was diluted with toluene (1 mL).

To a suspension of $Pb(OAc)_4$ (445.2 mg, 1.0 mmol) in toluene (2 mL) was added the above obtained solution. The reaction mixture was stirred under an Ar atmosphere for 1 h. After adding H_2O (10 mL), the reaction mixture was filtered through a pad of celite, and the residue was washed with CH_2Cl_2. The filtrate was separated and the aqueous solution was extracted with CH_2Cl_2 (3 × 10 mL). The conbined organic layer was washed with brine (10 mL) and dried over Na_2SO_4. The solvent was removed *in vacuo*. The obtained crude product was purified by silica gel column chromatography (hexane:AcOEt = 6:1) to afford **7a** (131.9 mg, 77% yield) as colorless oil; ^1H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.18 (d, *J* = 6.0 Hz, 3 H), 1.27 (d, *J* = 6.0 Hz, 3 H), 2.21 (s, 3 H), 4.92 (sept, *J* = 6.0 Hz, 1 H), 7.41–7.47 (m, 3 H), 7.50–7.55 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 21.2, 22.0, 22.1, 80.9 (q, *J* = 2.9 Hz), 93.7 (q, *J* = 37.5 Hz), 99.9, 120.7 (q, *J* = 267.9 Hz), 125.5, 128.8, 128.9, 130.4, 133.4, 164.3, 167.9, 175.0; ^{19}F NMR (376 MHz, $CDCl_3$, 25 ˚C): δ –58.4; IR (neat) 1792 (C=O), 1658 (C=C) cm^{-1}; HRMS (DART) *m/z* calcd for $C_{16}H_{15}F_3O_5 \bullet NH_4$ 362.1215, found 362.1202 $[M+NH_4]^+$.

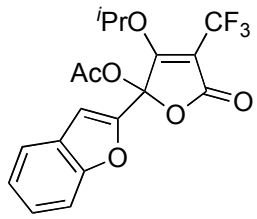
Similarly, **7b**–**c** were obtained according to the above procedure.



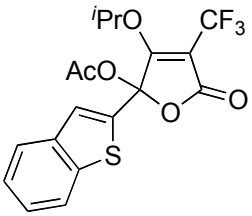
Analytical data for 7b: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.18 (d, *J* = 6.0 Hz, 3 H), 1.23 (d, *J* = 6.0 Hz, 3 H), 2.18 (s, 3 H), 3.80 (s, 3 H), 4.90 (sept, *J* = 6.0 Hz, 1 H), 6.90–6.94 (m, 2 H), 7.40–7.45 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 21.1, 22.0, 22.1, 55.3, 80.8 (q, *J* = 2.8 Hz), 93.5 (q, *J* = 37.2 Hz), 100.0, 114.1, 120.7 (q, *J* = 267.9 Hz), 125.1, 126.9, 161.1, 164.3, 167.9, 175.2; ^{19}F NMR (376 MHz, $CDCl_3$, 25 ˚C): δ –58.7; IR (neat) 1787 (C=O), 1762 (C=O), 1653 (C=C) cm^{-1}; HRMS (DART) *m/z* calcd for $C_{17}H_{17}F_3O_6 \bullet NH_4$ 392.1321, found 392.1309 $[M+NH_4]^+$.



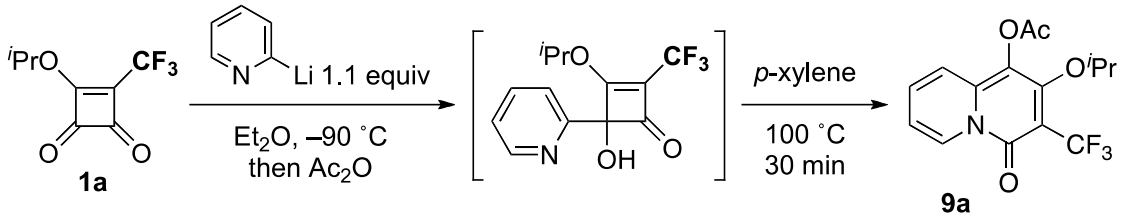
Analytical data for 7c: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.15 (d, *J* = 6.0 Hz, 3 H), 1.29 (d, *J* = 6.0 Hz, 3 H), 1.38 (t, *J* = 7.2 Hz, 3 H), 2.20 (s, 3 H), 4.38 (q, *J* = 7.2 Hz, 2 H), 4.92 (sept, *J* = 6.0 Hz, 1 H), 7.58 (d, *J* = 8.0 Hz, 2 H), 8.09 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 14.2, 21.0, 21.8, 22.0, 61.3, 81.3 (q, *J* = 3.8 Hz), 93.6 (q, *J* = 37.5 Hz), 99.6, 120.5 (q, *J* = 267.9 Hz), 125.6, 129.9, 132.3, 137.8, 164.0, 165.6, 167.7, 174.5; ^{19}F NMR (376 MHz, $CDCl_3$, 25 ˚C): δ –58.3; IR (neat) 1794 (C=O), 1722 (C=O), 1659 (C=C) cm^{-1}; HRMS (DART) *m/z* calcd for $C_{19}H_{19}F_3O_7 \bullet NH_4$ 434.1427, found 434.1411 $[M+NH_4]^+$.



Analytical data for 7d: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.26 (d, *J* = 6.0 Hz, 3 H), 1.29 (d, *J* = 6.0 Hz, 3 H), 2.25 (s, 3 H), 5.11 (sept, *J* = 6.0 Hz, 1 H), 7.10 (s, 1 H), 7.29 (dt, *J* = 8.0, 1.0 Hz, 1 H), 7.37 (dt, *J* = 8.0, 1.0 Hz, 1 H), 7.51 (d, *J* = 8.0 Hz, 1 H), 7.63 (d, *J* = 8.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 21.0, 22.1, 22.2, 81.2 (q, *J* = 2.9 Hz), 95.0 (q, *J* = 37.2 Hz), 96.4, 107.4, 111.7, 120.5 (q, *J* = 267.9 Hz), 122.0, 123.7, 126.0, 126.8, 147.3, 155.2, 163.4, 167.3, 173.1; ^{19}F NMR (376 MHz, $CDCl_3$, 25 ˚C): δ –59.3; IR (neat) 1794 (C=O), 1664 (C=C) cm^{-1}; HRMS (DART) *m/z* calcd for $C_{18}H_{15}F_3O_6 \bullet NH_4$ 402.1164, found 402.1172 $[M+NH_4]^+$.



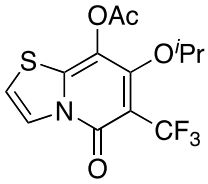
Analytical data for 7e: pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.33 (d, *J* = 6.4 Hz, 3 H), 1.35 (d, *J* = 6.4 Hz, 3 H), 2.22 (s, 3 H), 5.05 (sept, *J* = 6.0 Hz, 1 H), 7.37–7.44 (m, 2 H), 7.54 (s, 1 H), 7.77–7.87 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 21.1, 22.1, 22.2, 81.5 (q, *J* = 3.8 Hz), 93.5 (q, *J* = 37.5 Hz), 98.7, 120.6 (q, *J* = 268.0 Hz), 122.3, 123.9, 124.5, 124.9, 125.8, 136.2, 138.4, 140.1, 163.4, 167.6, 173.9; ^{19}F NMR (376 MHz, $CDCl_3$, 25 ˚C): δ –58.4; IR (neat) 1789 (C=O), 1771 (C=O), 1658 (C=C) cm^{-1}; HRMS (DART) *m/z* calcd for $C_{18}H_{15}F_3O_5S•NH_4$ 418.0936, found 418.0933 $[M+NH_4]^+$.



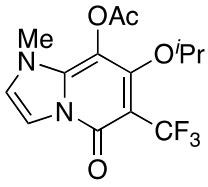
Synthesis of 9a from 1a: To a degassed solution of **1a** (104.6 mg, 0.50 mmol) in dry Et_2O (8 mL) was added 2-lithiopyridine (0.3 M in THF, 1.8 mL, 0.55 mmol), which was prepared by adding *n*-BuLi (1.6 M in hexane, 580 μL, 0.93 mmol) to a solution of 2-bromopyridine (93 μL, 0.96 mmol) in THF (2.5 mL), at –90 ˚C under an argon atmosphere. After stirring for 30 min, Ac_2O (103 mL, 1.1 mmol) was added to the reaction mixture. The reaction mixture was stirred for 1 h at –90 ˚C and then, quenched with sat. NH_4Cl (10 mL). The reaction mixture was extracted with AcOEt (3 × 20 mL). The combined organic layer was washed with brine (10 mL) and dried over Na_2SO_4. The organic layer was diluted with *p*-xylene (10 mL) and AcOEt was evaporated *in vacuo*. The resultant crude product solution was stirred at 100 ˚C under an Ar atmosphere for 30 min. After cooling to room temperature, the reaction mixture was concentrated *in vacuo*. The obtained crude product was purified by silica gel column chromatography (hexane:AcOEt = 2:1) to afford **9a** (88.1 mg, 54% yield) as a brown oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.32 (d, *J* = 6.4 Hz, 6 H), 2.40 (s, 3 H), 4.67 (sept, *J* = 6.4 Hz, 1 H), 7.03 (dd, *J* = 7.2, 6.4 Hz, 1 H), 7.42 (d, *J* = 8.8 Hz, 1 H), 7.52 (dd *J* = 8.8, 6.4 Hz, 1 H), 9.09 (d, *J* = 7.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 20.3, 22.3, 79.0, 100.9 (q, *J* = 28.6 Hz), 115.1, 118.5, 120.6, 123.7 (q, *J* = 272.1 Hz), 128.1, 133.6, 138.5, 154.9, 157.7, 168.3; ^{19}F NMR (376 MHz, $CDCl_3$,

25 ˚C): δ –58.8; IR (neat) 1781 (C=O), 1675 (C=O), 1631 (C=C) cm^{-1}; HRMS (DART) *m/z* calcd for $C_{15}H_{14}F_3NO_4$•H 330.0953, found 330.0946 $[M+H]^+$.

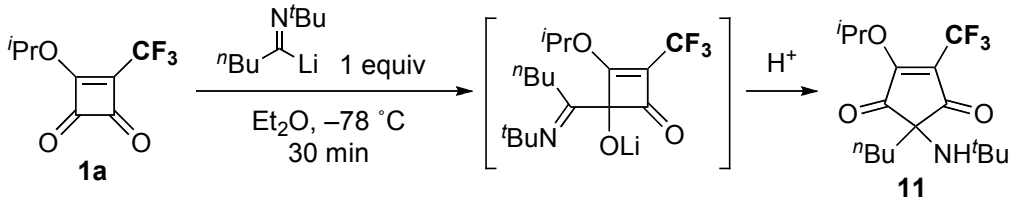
Similarly, **9b** and **9c** were obtained according to the above procedure.



Analytical data for 9b: brown oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.33 (d, *J* = 6.4 Hz, 6 H), 2.37 (s, 3 H), 4.65 (sept, *J* = 6.4 Hz, 1 H), 7.00 (d, *J* = 4.8 Hz, 1 H), 8.15 (d, *J* = 4.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 20.2, 22.3, 79.1, 102.0 (q, *J* = 29.2 Hz), 112.0, 121.7, 123.5 (q, *J* = 272.1 Hz), 125.4, 145.9, 155.0, 159.0, 167.1; ^{19}F NMR (376 MHz, $CDCl_3$, 25 ˚C): δ –58.8; IR (neat) 1784 (C=O), 1661 (C=O), 1577 (C=C) cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{13}H_{12}F_3NO_4S$•H 336.0517, found 336.0515 $[M+H]^+$.



Analytical data for 9c: pale-brown oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.28 (d, *J* = 6.4 Hz, 6 H), 2.34 (s, 3 H), 3.75 (s, 3 H), 4.53 (sept, *J* = 6.4 Hz, 1 H), 6.88 (d, *J* = 2.2 Hz, 1 H), 6.67 (d, *J* = 2.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 20.2, 22.2, 34.7, 78.2, 94.1 (q, *J* = 28.9 Hz), 109.9, 111.0, 122.5, 124.6 (q, *J* = 270.8 Hz), 136.4, 152.4, 157.4, 169.1; ^{19}F NMR (376 MHz, $CDCl_3$, 25 ˚C): δ –57.3; IR (neat) 1780 (C=O), 1666 (C=O), 1589 (C=C) cm^{-1}; HRMS (DART) *m/z* calcd for $C_{14}H_{15}F_3N_2O_4$•H 333.1062, found 333.1069 $[M+H]^+$.



Synthesis of 11 from 1a: A 0.3 M solution of 1-(*tert*-Butylimino)pentyllithium was prepared by the addition of *n*-BuLi (1.6 M in hexane, 480 μL, 0.75 mmol) to *tert*-BuNC (85 μL, 0.75 mmol) in Et_2O (2.0 mL) at –15 ˚C and the solution was stirred at this temperature for 30 min. To a degassed solution of **1a** (104.3 mg, 0.50 mmol) in dry Et_2O (10 mL) was added 1-(*tert*-butylimino)pentyllithium (0.3 M in Et_2O/hexane, 1.7 mL, 0.51 mmol) at –78 ˚C under an argon atmosphere. After stirring for 30 min, the

reaction was quenched with sat. NH_4Cl (10 mL). The reaction mixture was extracted with Et_2O (3 × 10 mL). The combined organic layer was washed with brine (10 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The obtained crude product was purified by silica gel column chromatography (hexane:AcOEt = 6:1) to afford **11** (87.2 mg, 50% yield) as a dark-red solid (mp 61.6–63.4 ˚C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 0.83 (t, *J* = 7.2 Hz, 3 H), 1.01 (s, 9 H), 1.02–1.27 (m, 4 H), 1.41 (d, *J* = 6.0 Hz, 3 H), 1.42 (d, *J* = 6.0 Hz, 3 H), 1,57 (br s, 1 H), 1.66 (dt, *J* = 9.8, 7.2 Hz, 1 H), 1.68 (dt, *J* = 9.8, 7.2 Hz, 1 H), 2.68 (dd, *J* = 14.0, 7.2 Hz, 1 H), 5.91 (sept, *J* = 6.0 Hz, 1 H),; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 13.5, 22.7, 23.0, 23.2, 25.4, 31.9, 38.7, 52.4, 66.0, 78.0, 120.8 (q, *J* = 272.7 Hz), 122.1 (q, *J* = 31.8 Hz), 165.1, 196.7, 203.9; ^{19}F NMR (376 MHz, $CDCl_3$, 25 ˚C): δ –63.0; IR (neat) 3449 (NH), 1713 (C=O), 1619 (C=C) cm^{-1}; HRMS (DART) *m/z* calcd for $C_{17}H_{26}F_3NO_3$•H 350.1943, found 350.1945 $[M+H]^+$.

Single Crystal X-Ray Diffraction

Single crystals of **6m** was mounted on a glass fiber, and diffraction data were collected in θ ranges specified in Table S1 at 103 K on a Brucker D8 QUEST diffractomter with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å). The absorption correction was made using SADABS. The structure was solved by direct methods and refined by the full-matrix least-squares on F^2 by using SHELXL-2013.[7] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions. Final refinement details are compiled in Table S1. The supplementary crystallographic data for this paper (CCDC 1416765) can also be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

[7] Sheldrick, G. M. SHELXL-2013, Bruker AXS Inc., Madison, Wisconsin, **2013**.

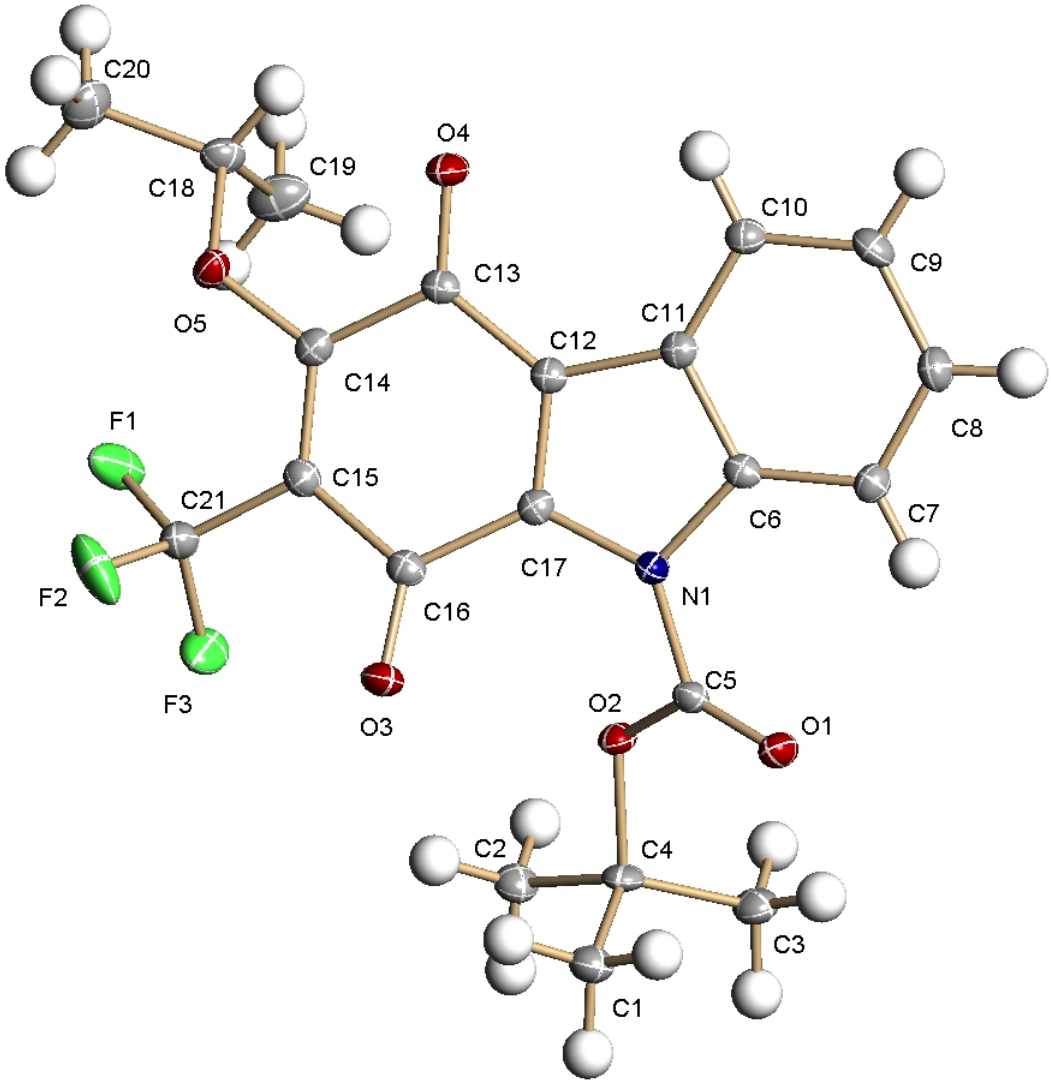


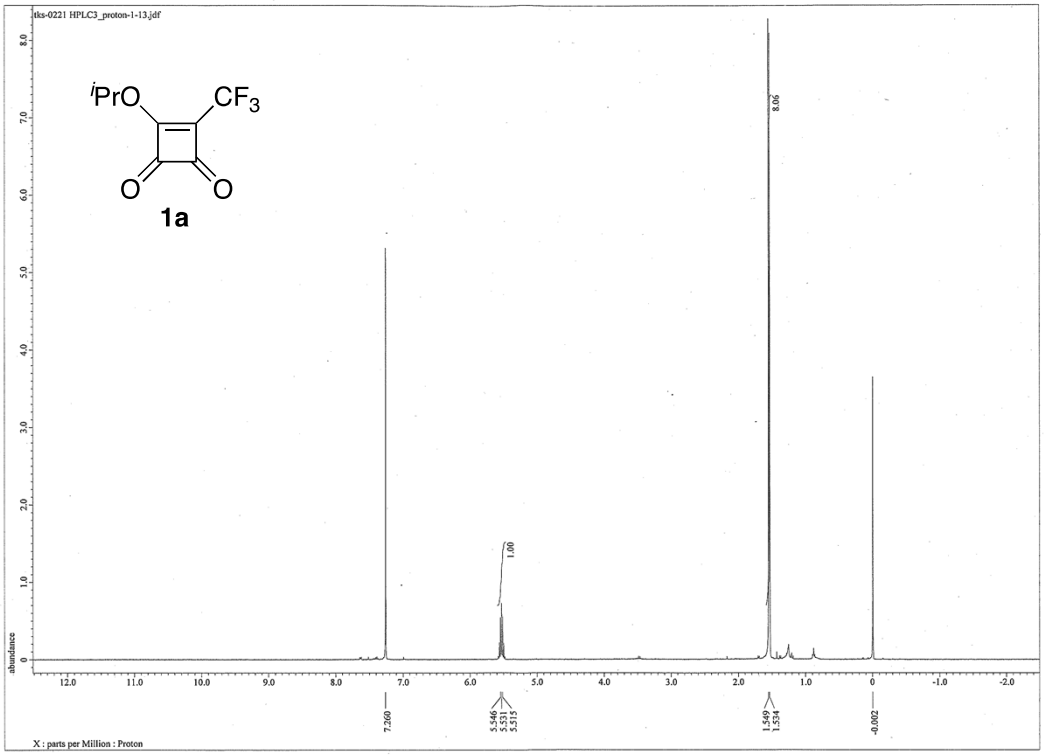
Figure S1. ORTEP drawing of **6m**.

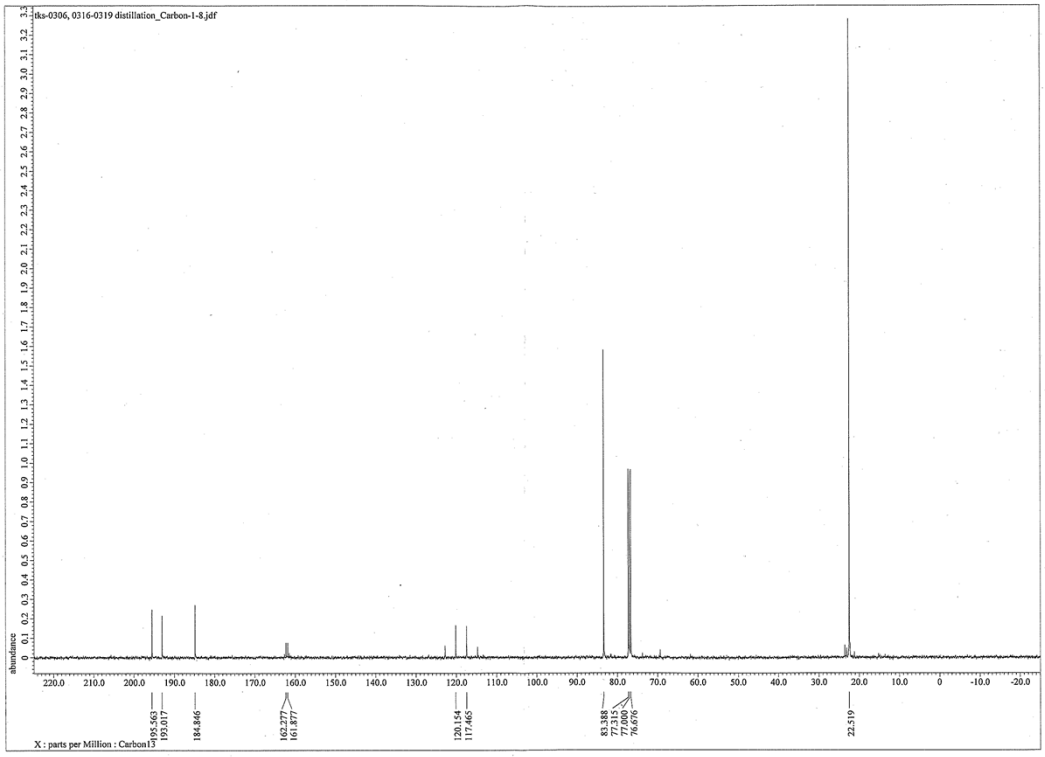
Table S1. Selected Crystallographic data and collection parameters for **6m**.

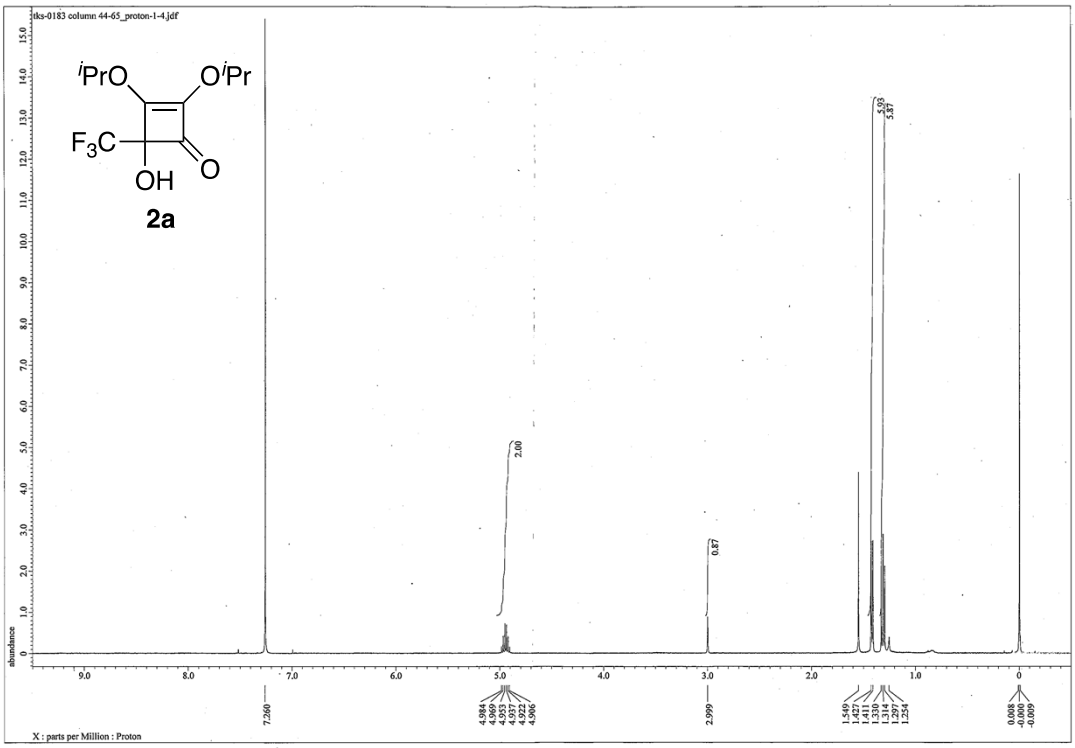
formula	$C_{21}H_{20}F_3NO_5$
fw	423.38
crystal system	monoclinic
space group	P2(1)/c
a , Å	14.1742(13)
b , Å	11.9882(11)
c , Å	11.3206(10)
β, deg	90.796(3)
volume, Å^3	1923.4(3)
Z	4
D (calcd), Mg m^{-3}	1.462
μ, mm^{-1}	0.123
F(000)	880
crystal size, mm	0.5 x 0.4 x 0.2
θ range for data collection, deg	2.23 to 25.07
index ranges	-16≤h≤15, -14≤k≤14, -13≤l≤13
reflections collected	12346
independent reflections [*R*(int)]	3328 [R(int) = 0.0597]
coverage of independent reflections	97.5%
data / restraints / parameters	3328 / 0 / 276
goodness-of-fit on F^2	0.969
R_1 [4730 data; $I > 2\sigma(I)$]	0.0472
wR_2 [4730 data; $I > 2\sigma(I)$]	0.1250
R_1 (all data)	0.0497
wR_2 (all data)	0.1279
largest diff. peak and hole, e Å^{-3}	0.262 and -0.378
R.M.S. deviation from mean, e Å^{-3}	0.074

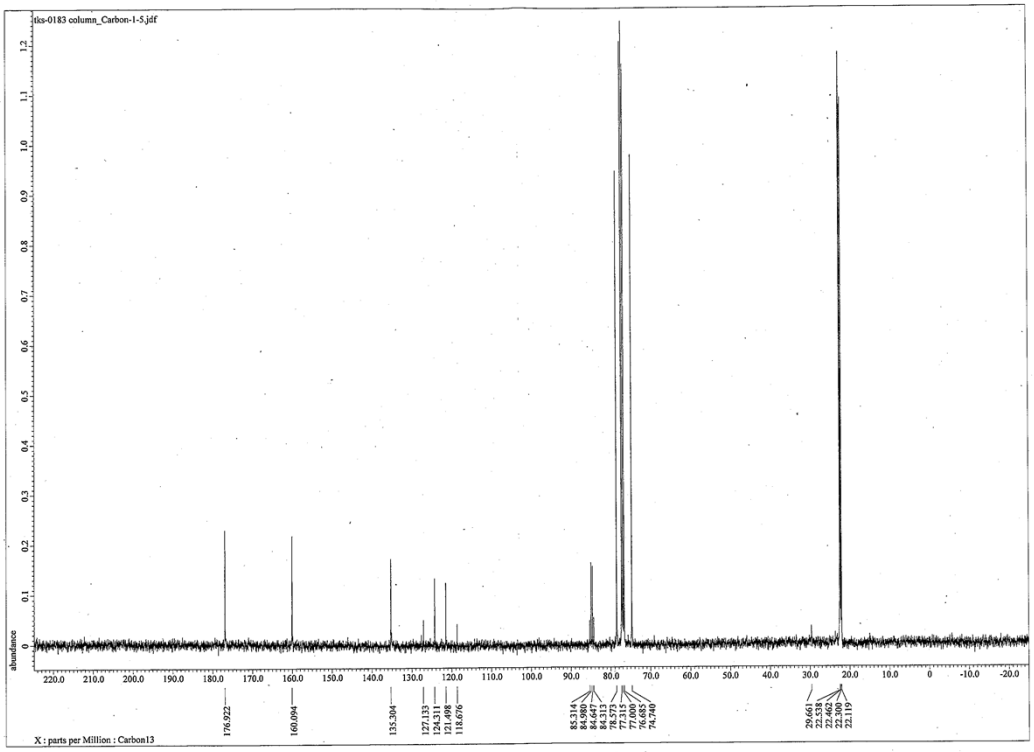
$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $wR_2 = \{\Sigma[(\sigma(F_o^2-F_c^2)^2)]/\Sigma[\sigma(F_o^2)^2]\}^{1/2}$.

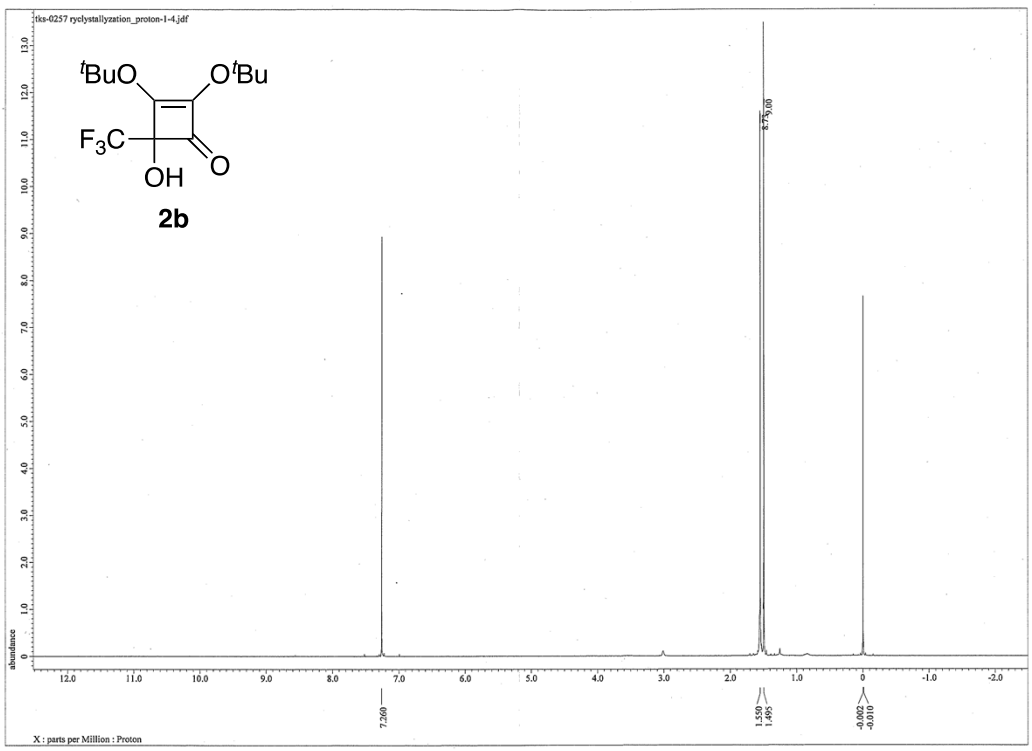
NMR Charts

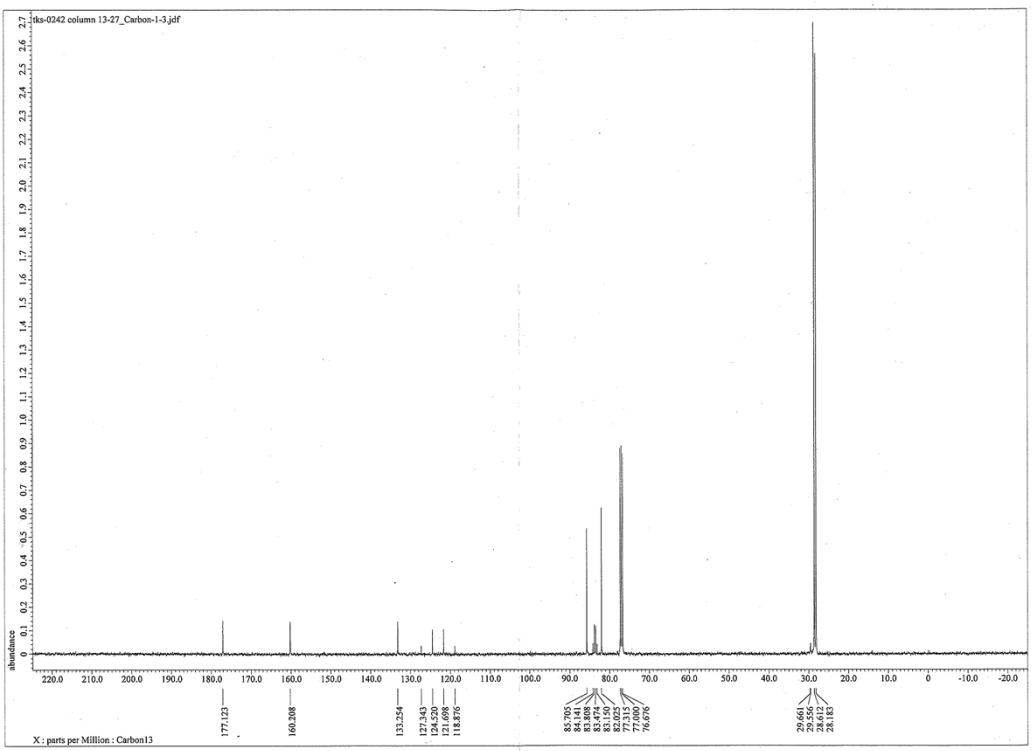

tks-0221 HPLC3_proton-1-13.jdf
iPrO
CF3
O
O
1a
8.06
1.00
7.260
5.546
5.531
5.515
1.549
1.534
-0.002
X : parts per Million : Proton

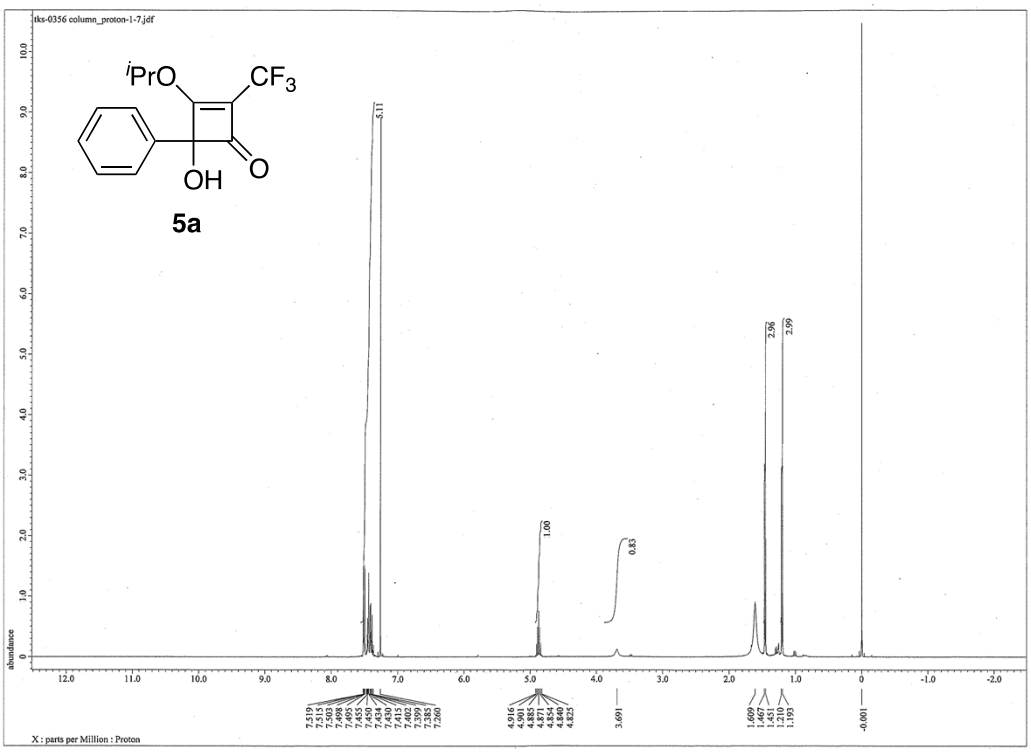

tks-0306, 0316-0319 distillation_Carbon-1-8.jdf
195.563
193.017
184.846
162.277
161.897
120.154
117.465
83.388
77.315
77.000
76.676
22.519
X : parts per Million : Carbon13

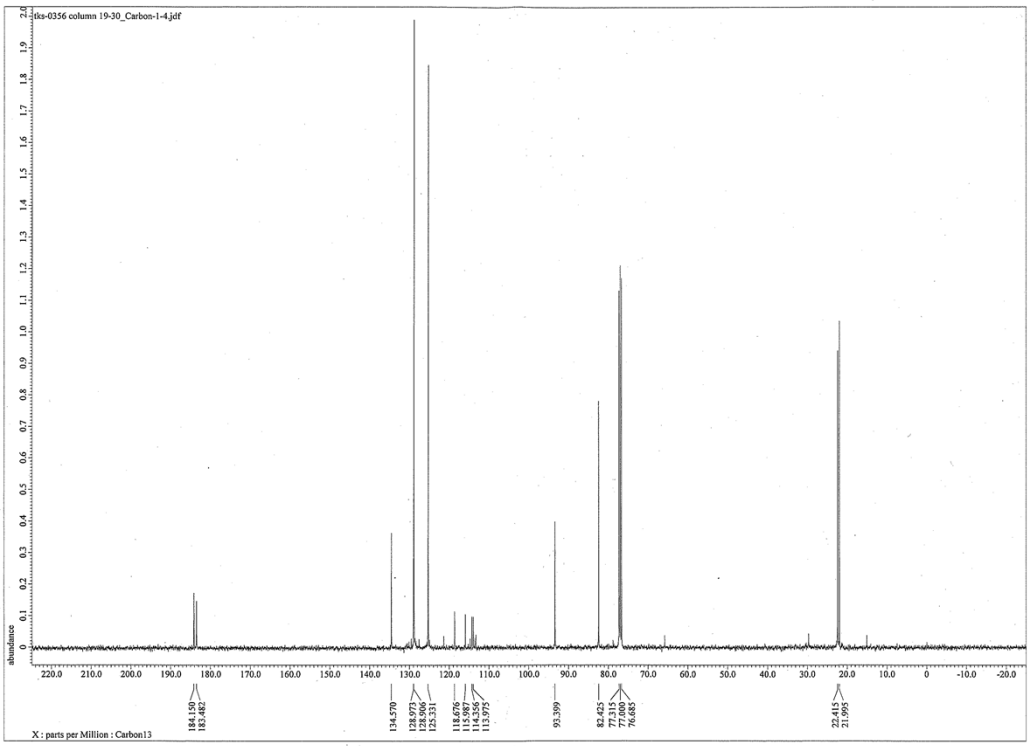

tks-0183 column 44-65_proton-1-4.jdf
iPrO
OiPr
F3C
OH
O
2a
abundance
X : parts per Million : Proton

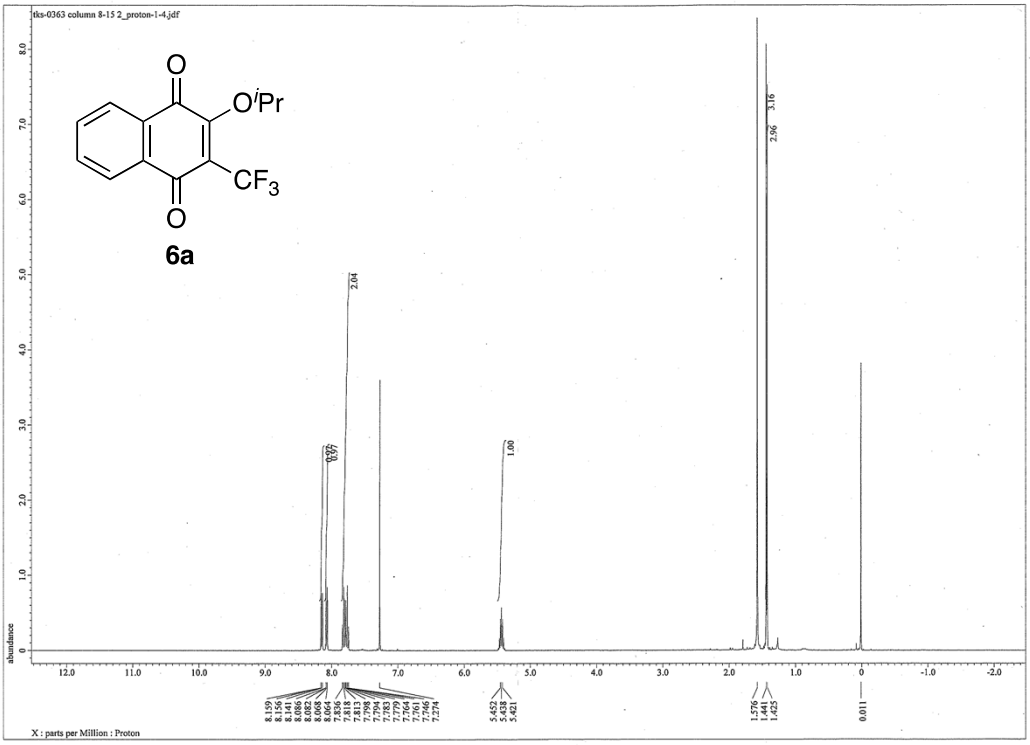

tks-0183 column_Carbon-1-5.jdf
abundance
X : parts per Million : Carbon13

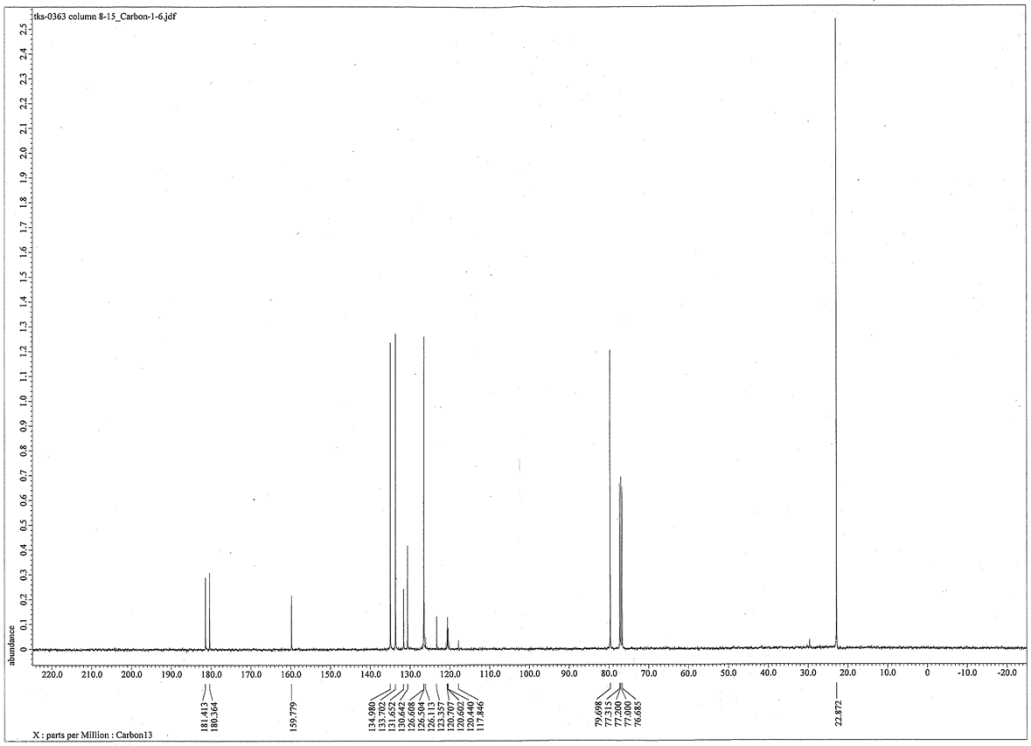

tks-0257 ryclystallyzation_proton-1-4.jdf
tBuO
OtBu
F3C
OH
O
2b
abundance
X : parts per Million : Proton
7.260
1.550
1.495
0.002
-0.010

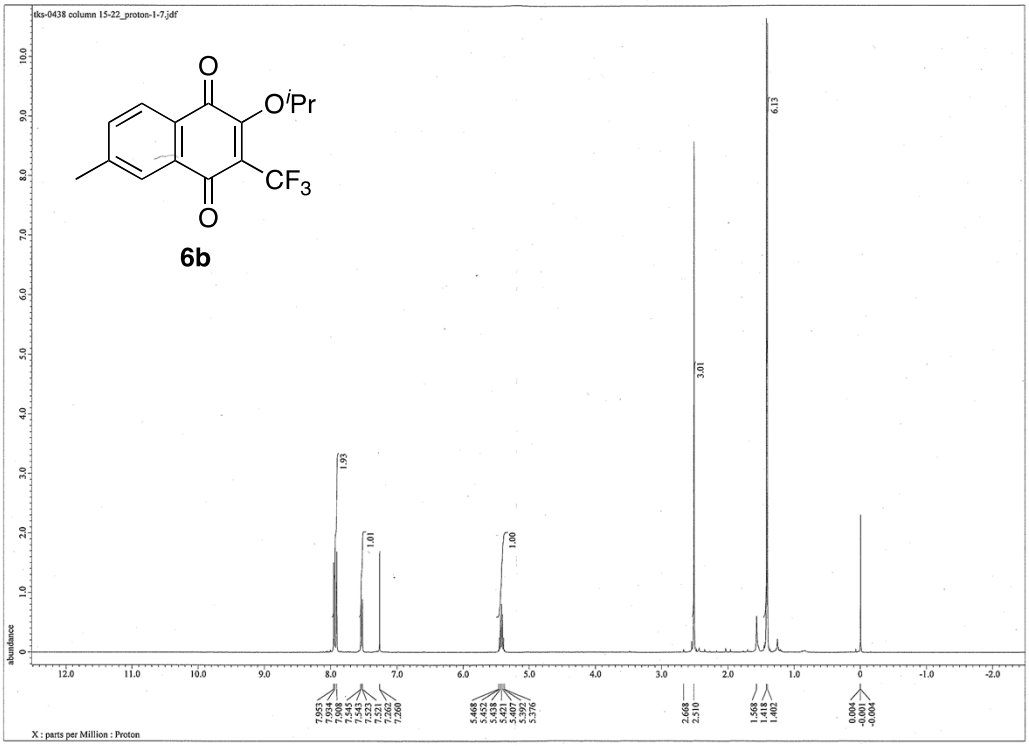

tks-0242 column 13-27_Carbon-1-3.jdf
abundance
X : parts per Million : Carbon13
177.123
160.208
133.254
127.343
124.520
121.698
118.876
85.705
84.141
83.808
83.474
83.150
82.025
77.315
77.000
76.676
29.661
29.556
29.451
28.183

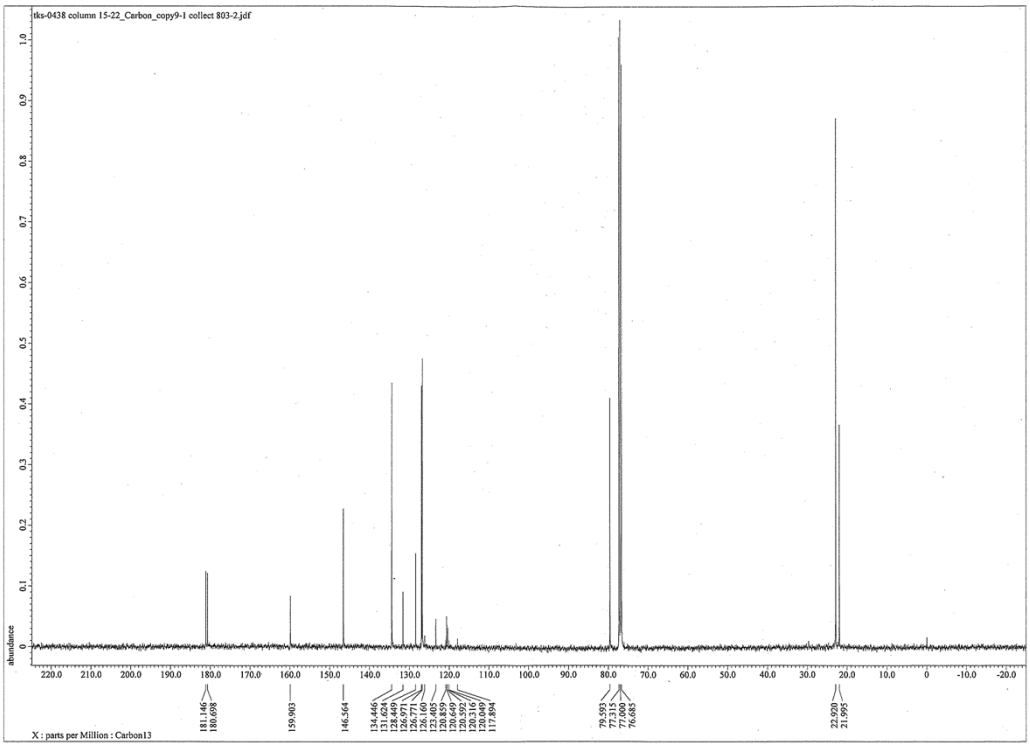

tks-0356 column_proton-1-7.jdf
iPrO
CF3
OH
O
5a
5.11
1.00
0.83
2.96
2.99
abundance
X : parts per Million : Proton

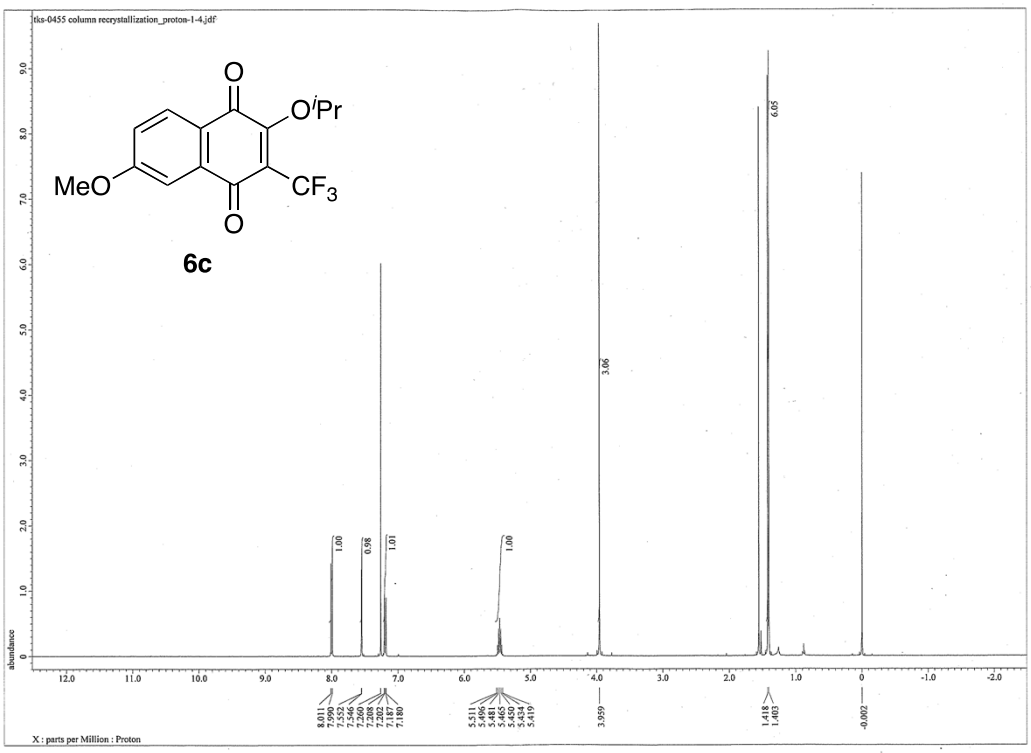

tks-0356 column 19-30_Carbon-1-4.jdf
abundance
X : parts per Million : Carbon13

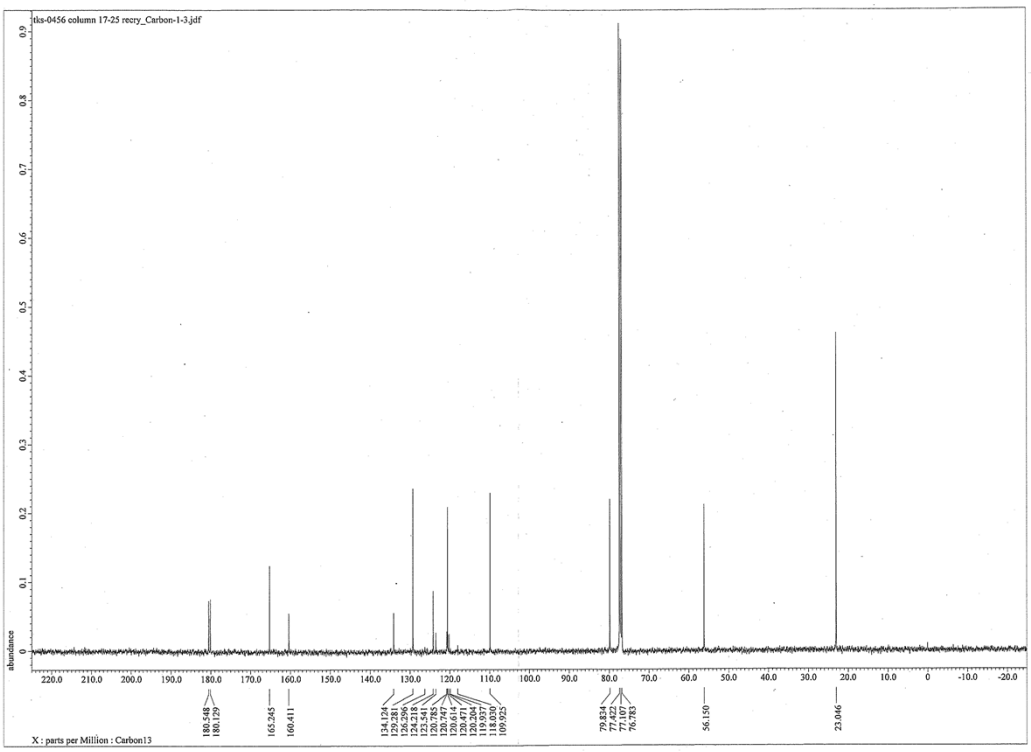

tks-0363 column 8-15 2_proton-1-4.jdf
O
O^{i}Pr
CF$_3$
O
6a
2.04
1.00
3.16
2.96
X : parts per Million : Proton

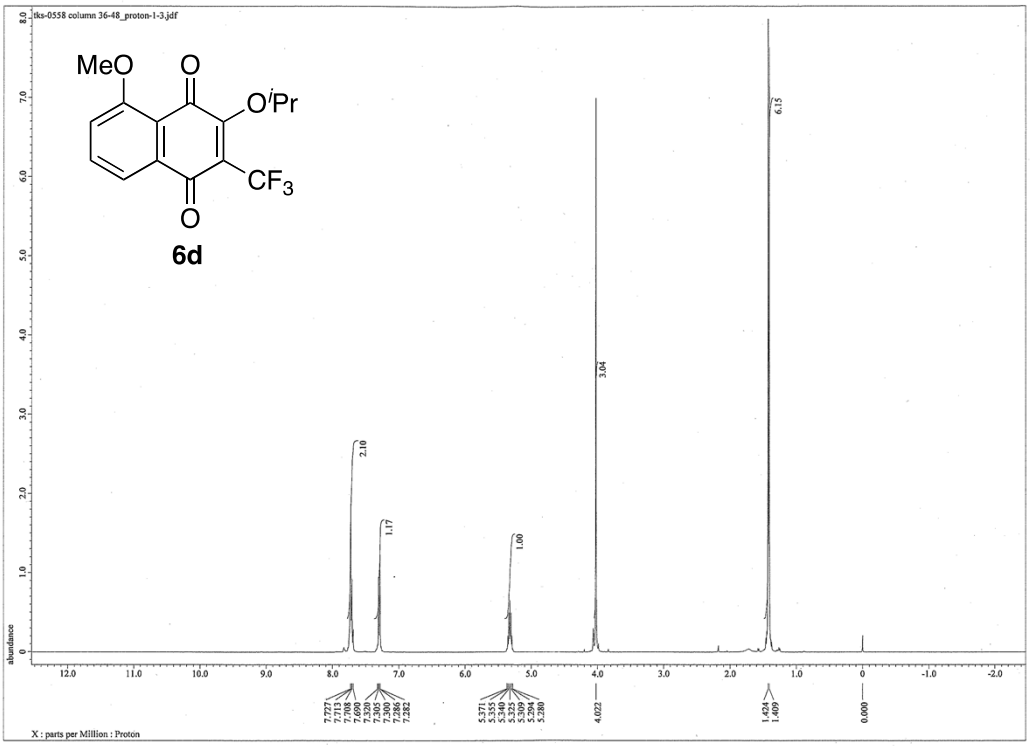

tks-0363 column 8-15_Carbon-1-6.jdf
X : parts per Million : Carbon13

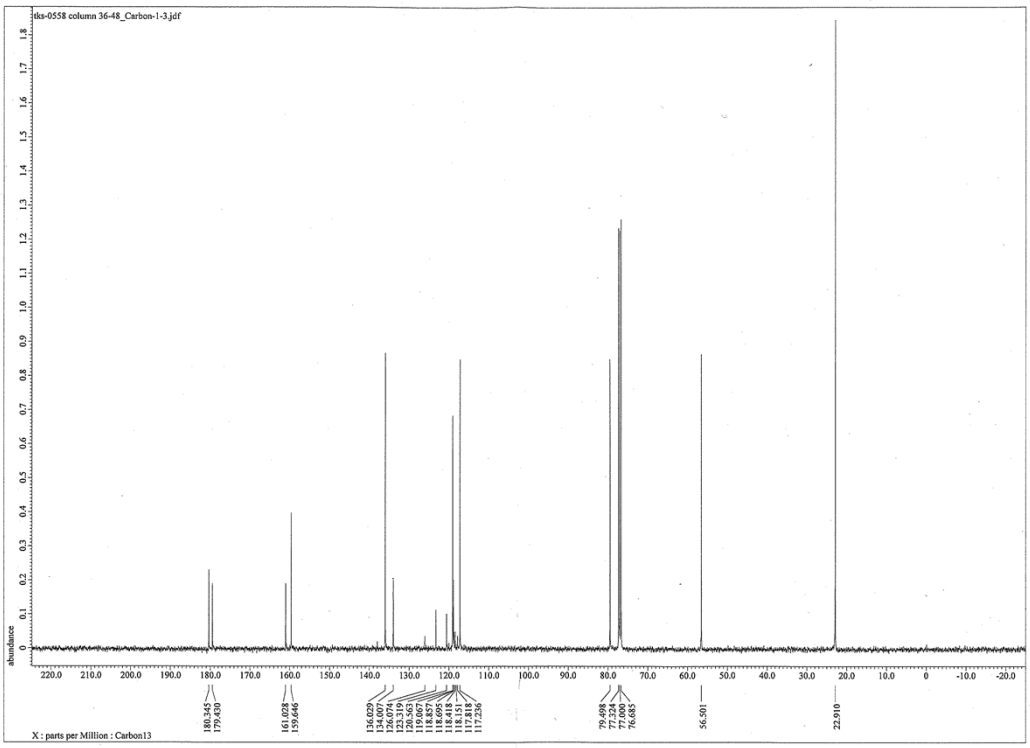

tks-0438 column 15-22_proton-1-7.jdf
O
O^{i}Pr
CF$_3$
O
6b
X : parts per Million : Proton


tks-0438 column 15-22_Carbon_copy9-1 collect 803-2.jdf
X : parts per Million : Carbon13


tks-0455 column recrystallization_proton-1-4.jdf
O
O^{i}Pr
MeO
CF$_3$
O
6c
abundance
X : parts per Million : Proton


tks-0456 column 17-25 recry_Carbon-1-3.jdf
abundance
X : parts per Million : Carbon13


tks-0558 column 36-48_proton-1-3.jdf
MeO
O
O^{i}Pr
CF$_3$
O
6d
2.10
1.17
1.00
3.04
6.15
abundance
X : parts per Million : Proton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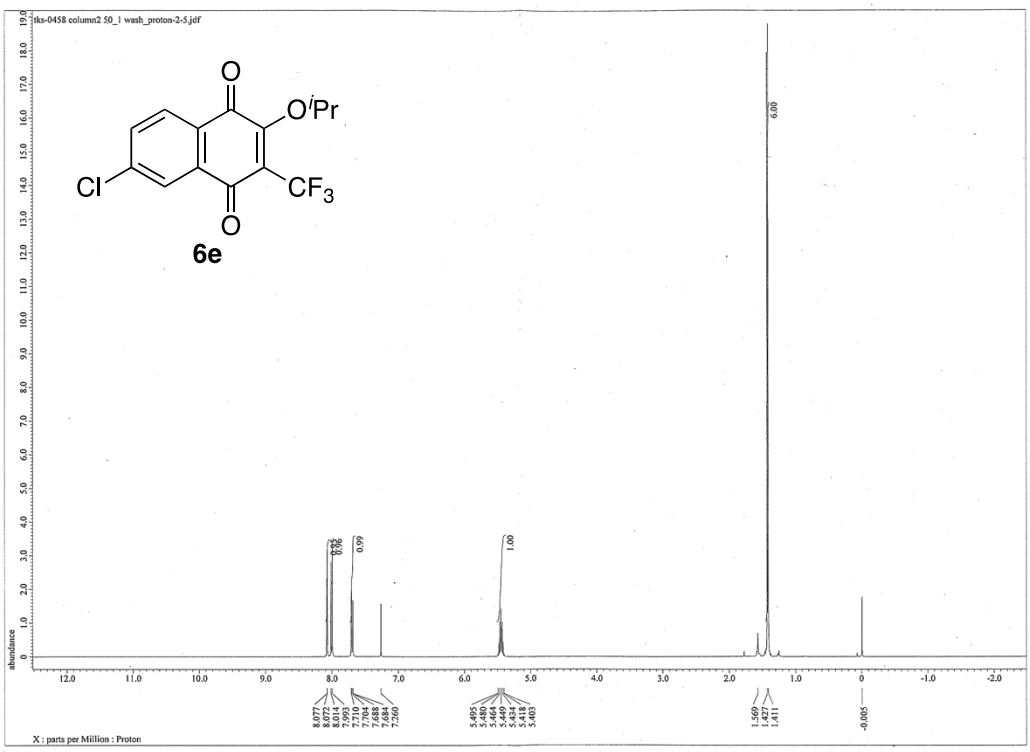
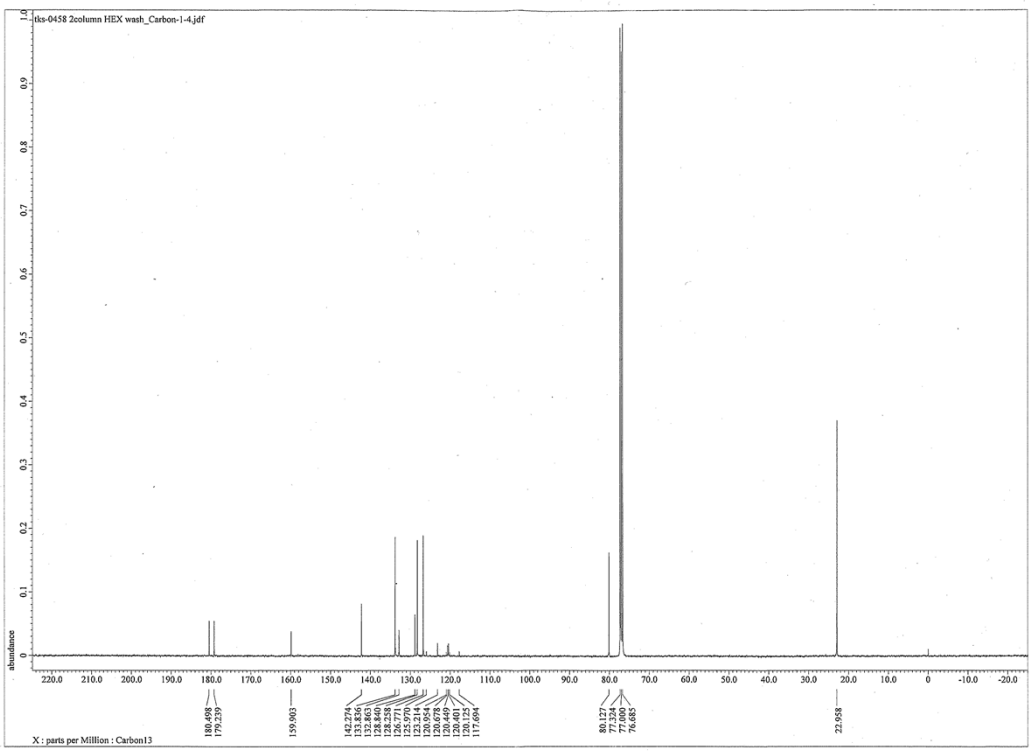
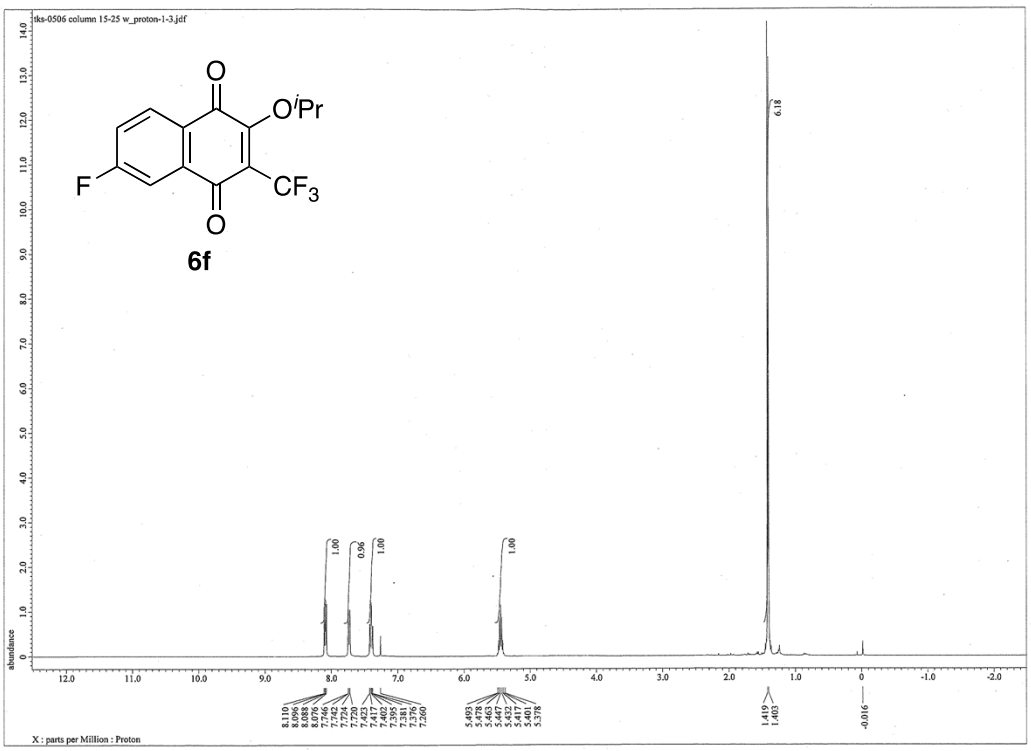
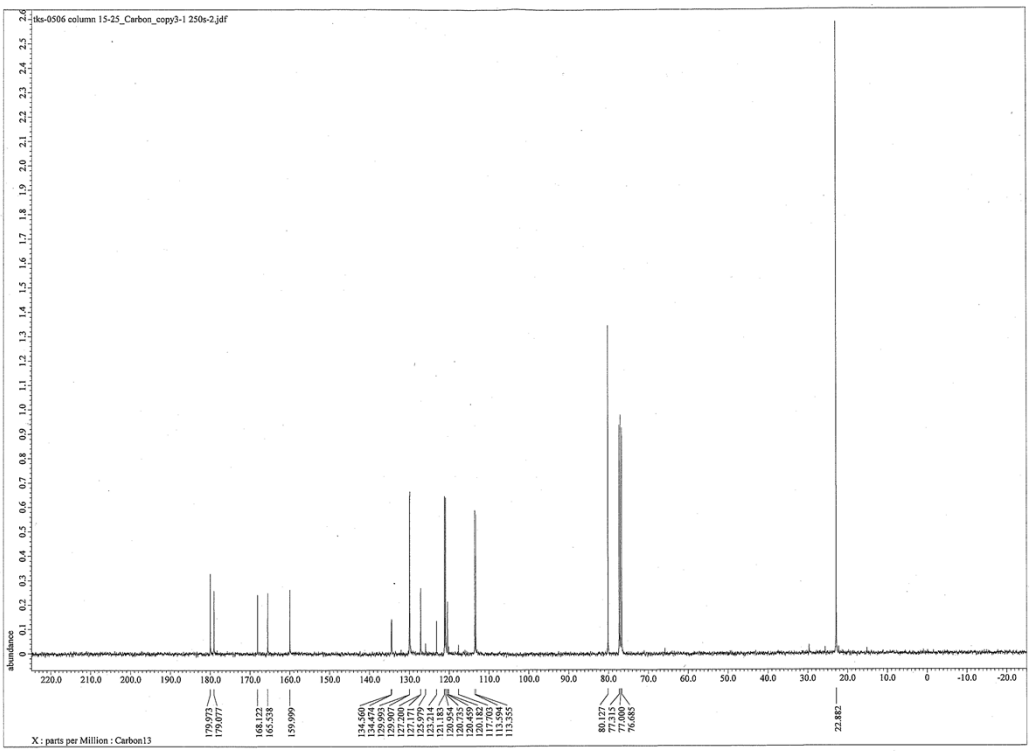
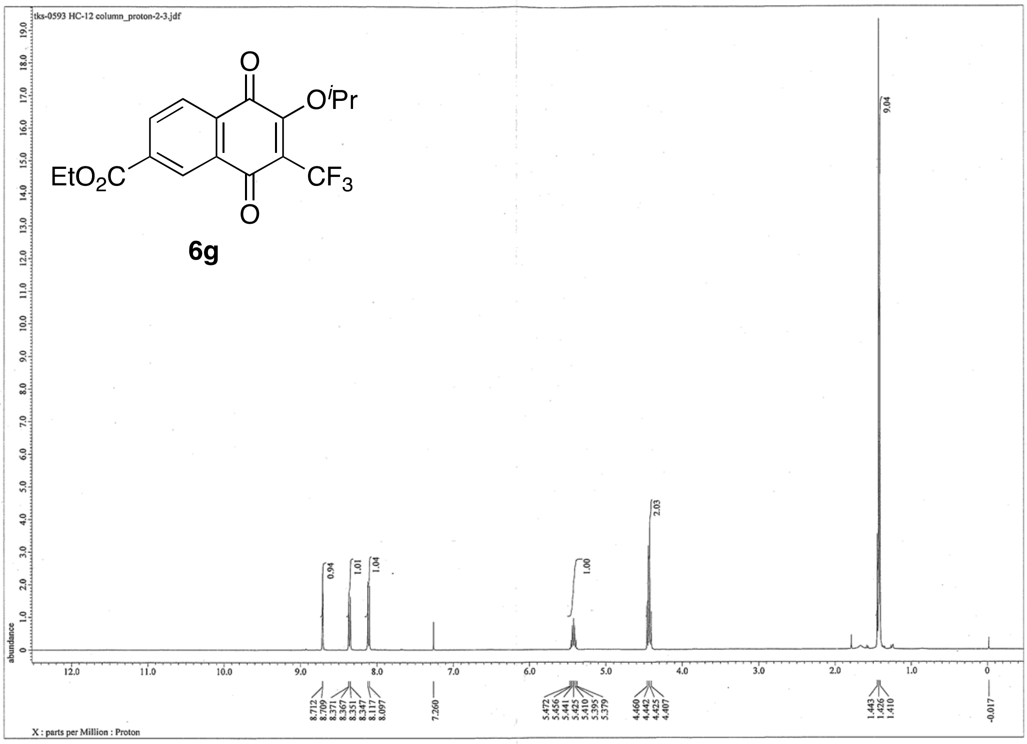
abundance
X : parts per Million : Carbon13


tks-0458 column2 50_1 wash_proton-2-5.jdf
O
O
O
Cl
CF3
6e
6.00
1.00
0.99
X : parts per Million : Proton

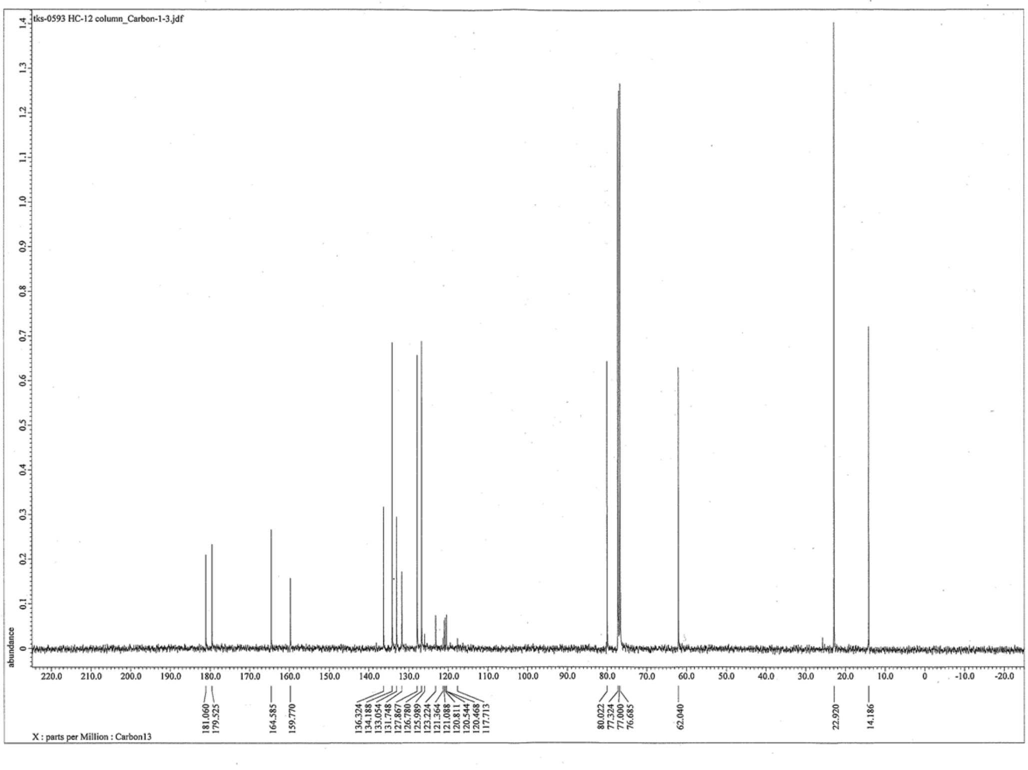

tks-0458 2column HEX wash_Carbon-1-4.jdf
X : parts per Million : Carbon13


tks-0506 column 15-25 w_proton-1-3.jdf
O
O
O
F
CF3
6f
6.18
1.00
0.96
1.00
1.00
X : parts per Million : Proton

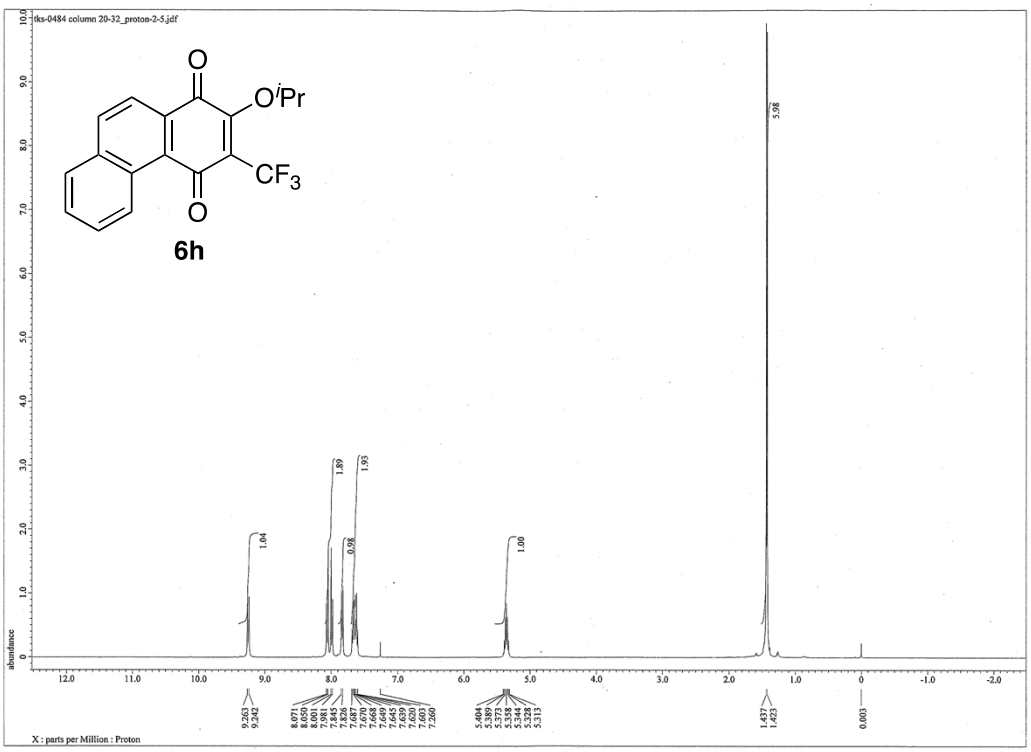

tks-0506 column 15-25_Carbon_copy3-1 250s-2.jdf
X : parts per Million : Carbon13

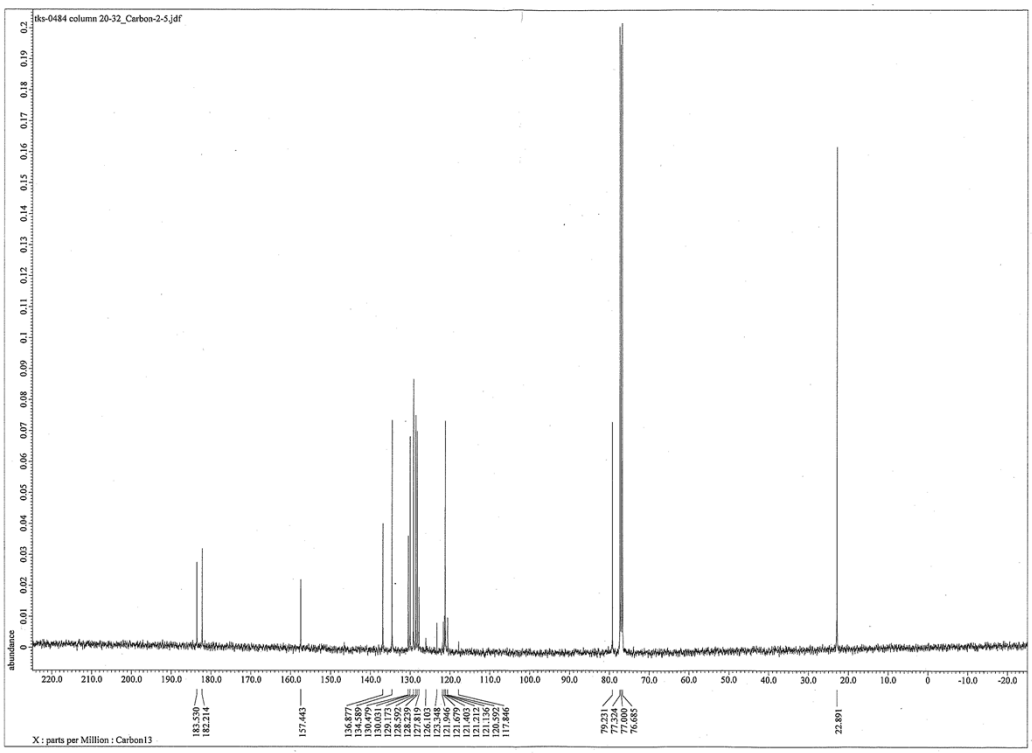


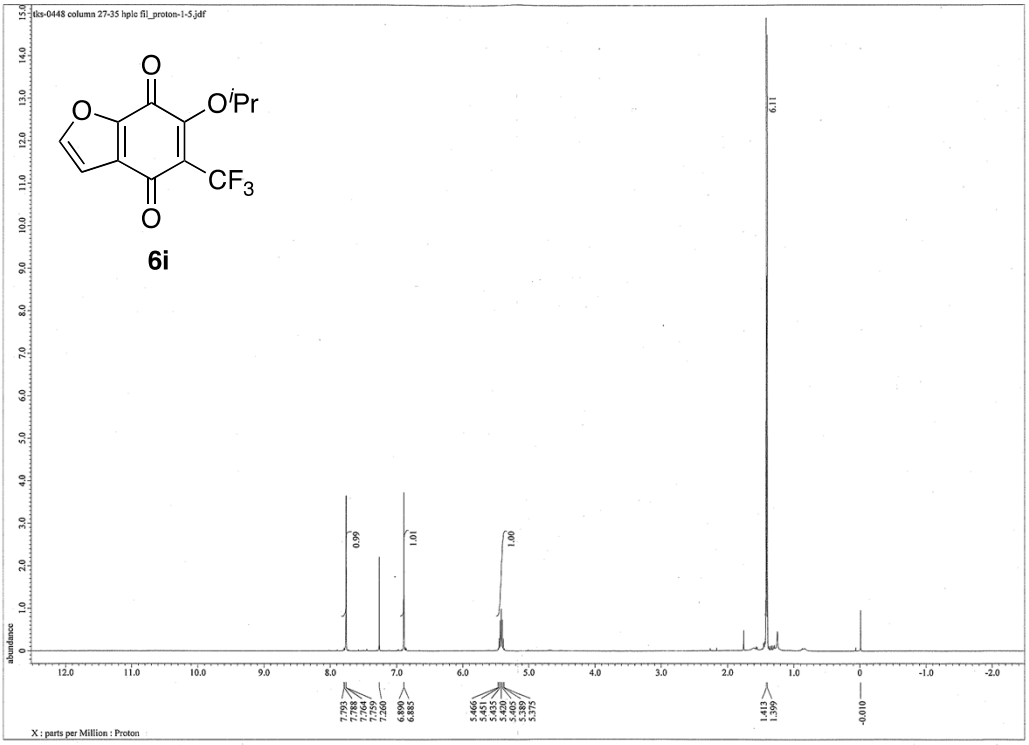
tks-0593 HC-12 column_proton-2-3.jdf
EtO2C
OiPr
CF3
6g
0.94
1.01
1.04
1.00
2.03
9.04
8.712 8.709 8.371 8.367 8.351 8.347 8.117 8.097
7.260
5.472 5.456 5.441 5.425 5.410 5.395 5.379
4.460 4.442 4.425 4.407
1.443 1.426 1.410
-0.017
X : parts per Million : Proton

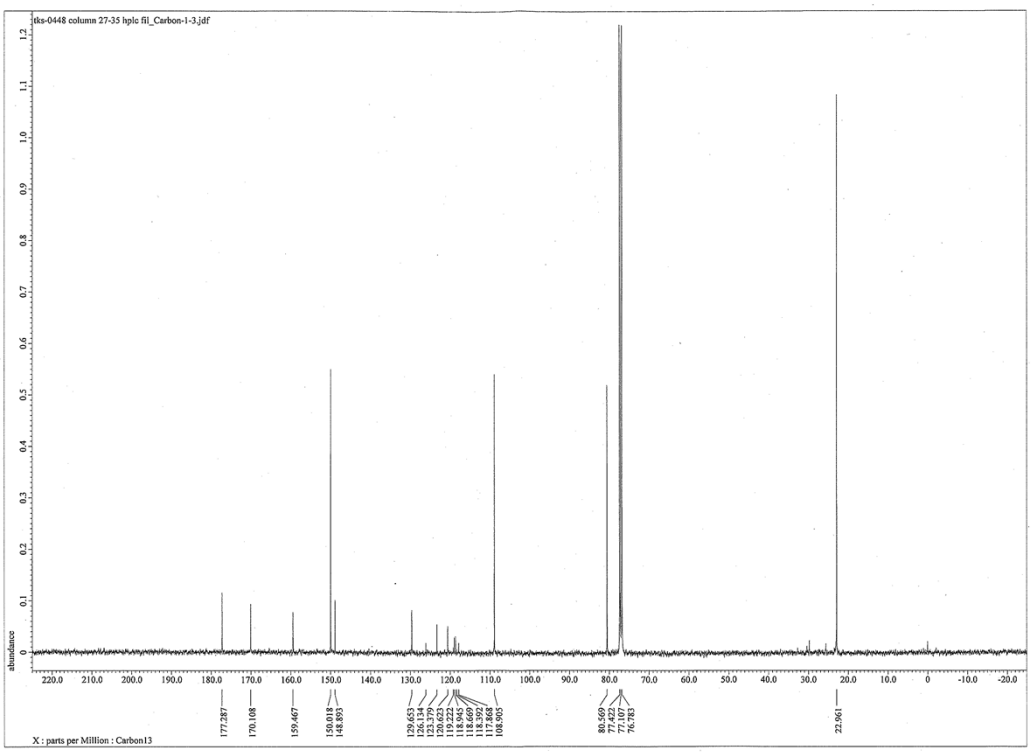


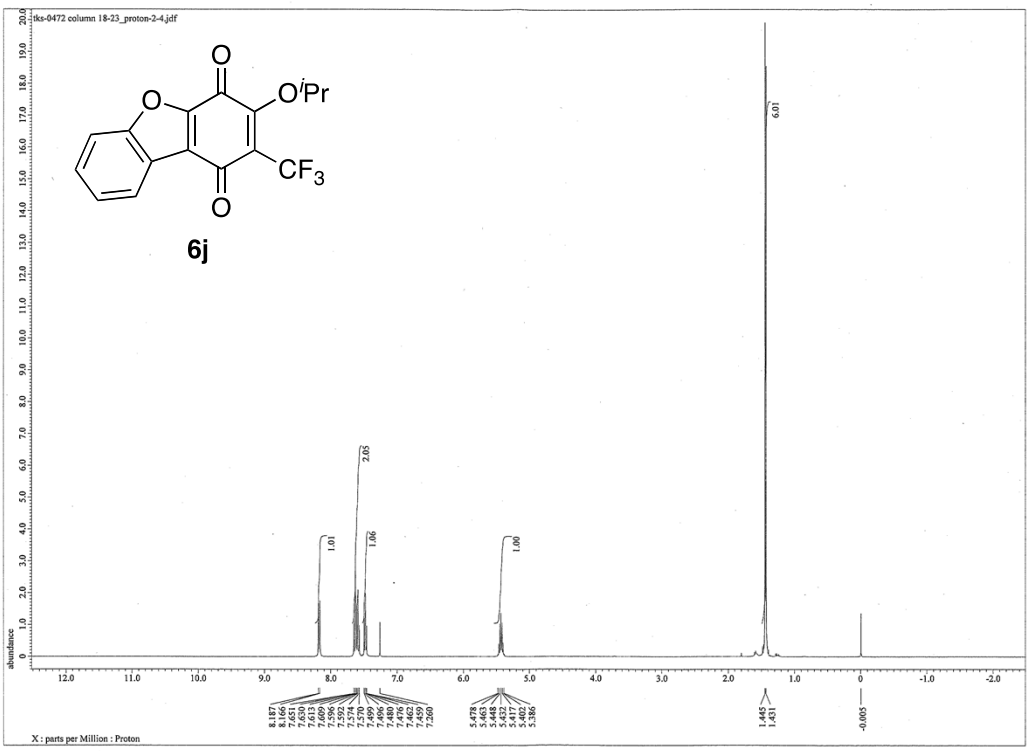
tks-0593 HC-12 column_Carbon-1-3.jdf
181.060 179.525
164.585
159.770
136.324 134.188 133.054 131.748 127.867 126.780 125.989 123.224 121.364 121.088 120.811 120.544 120.468 117.713
80.022 77.324 77.000 76.683
62.040
22.920
14.186
X : parts per Million : Carbon13

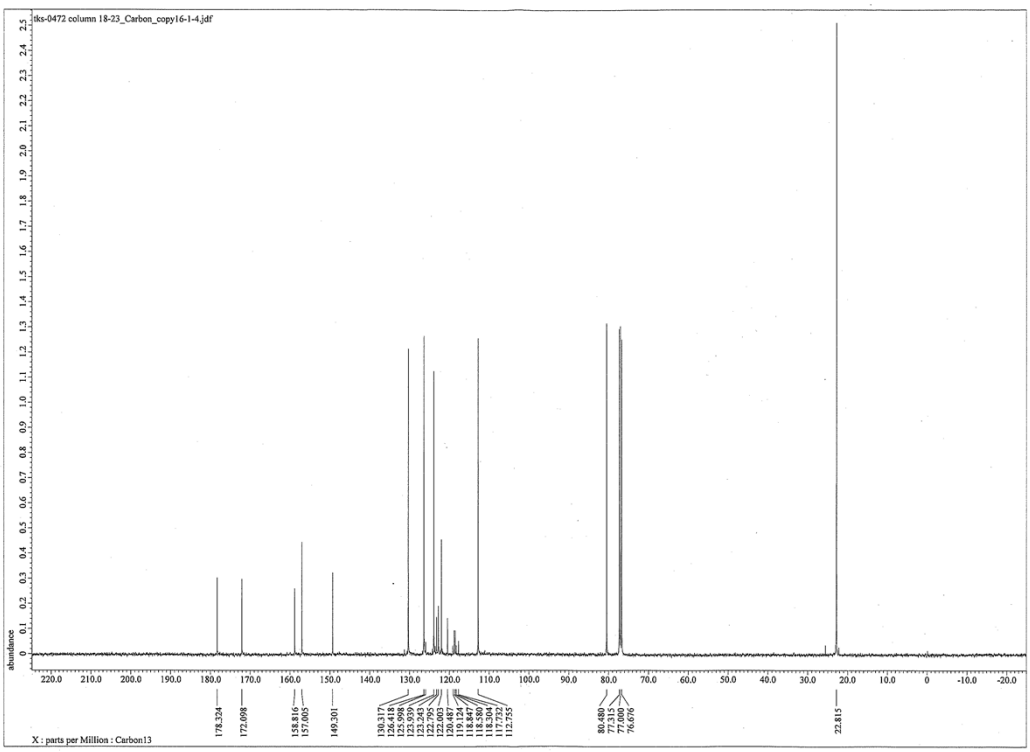

tks-0484 column 20-32_proton-2-5.jdf
O
O^{i}Pr
CF$_3$
O
6h
X : parts per Million : Proton

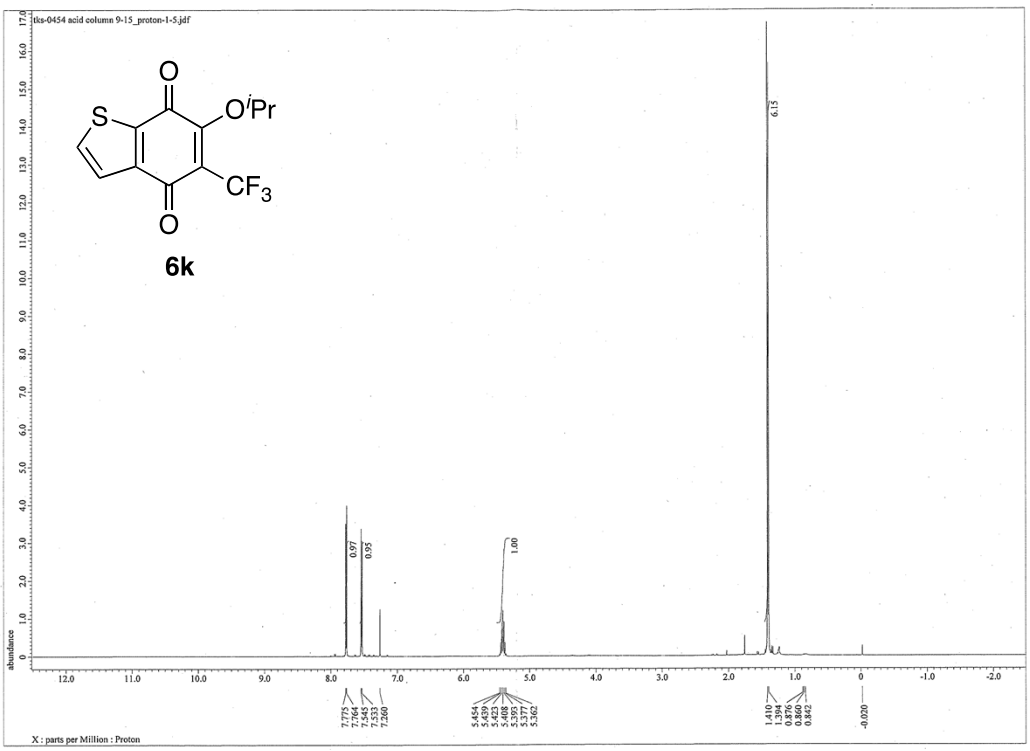

tks-0484 column 20-32_Carbon-2-5.jdf
X : parts per Million : Carbon13

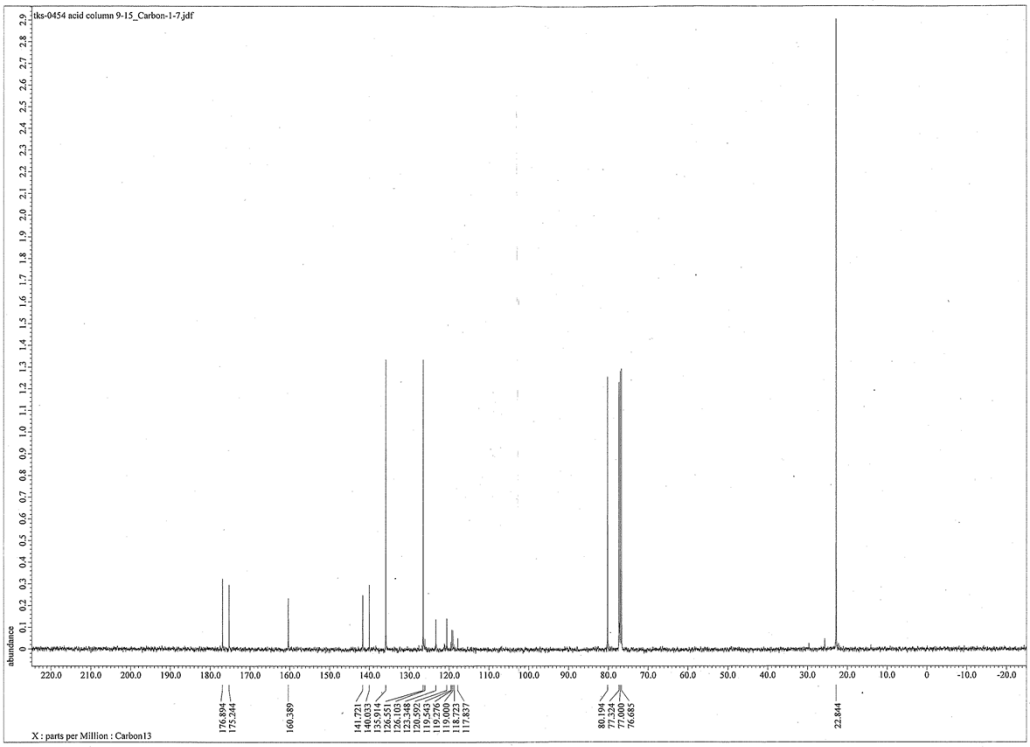

tks-0448 column 27-35 hplc fil_proton-1-5.jdf
O
O
O
O^{i}Pr
CF$_3$
6i
6.11
0.99
1.01
1.00
7.793
7.788
7.764
7.759
7.260
6.899
6.883
5.466
5.451
5.435
5.420
5.405
5.389
5.375
1.413
1.399
-0.010
abundance
X : parts per Million : Proton

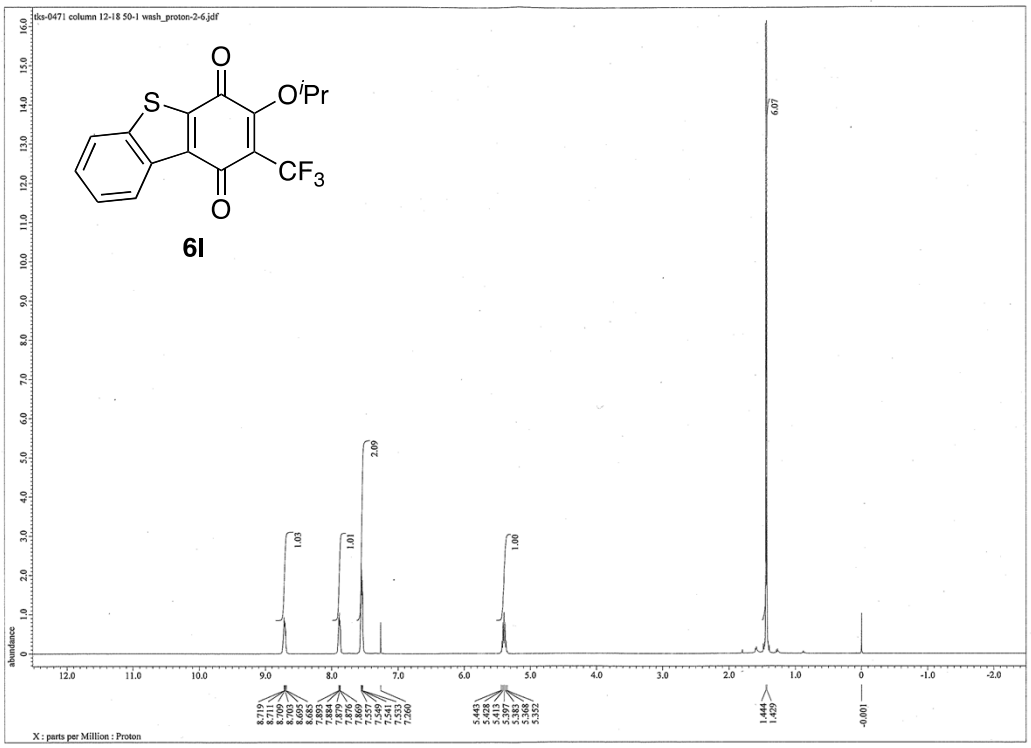

tks-0448 column 27-35 hplc fil_Carbon-1-3.jdf
177.287
170.108
159.467
150.018
148.893
129.653
126.134
123.379
120.223
118.945
118.669
118.392
117.868
108.905
80.569
77.423
77.107
76.783
22.961
abundance
X : parts per Million : Carbon13

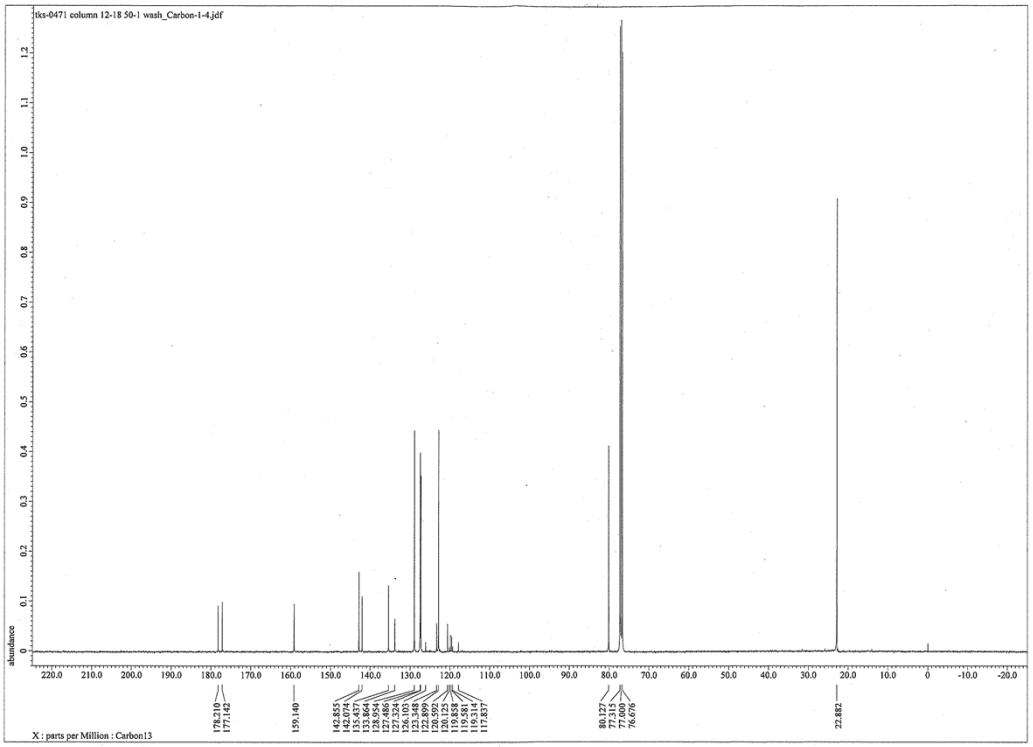

tks-0472 column 18-23_proton-2-4.jdf
O
O
O^{i}Pr
CF$_3$
O
6j
6.01
2.05
1.01
1.06
1.00
1.445
1.431
-0.005
X : parts per Million : Proton

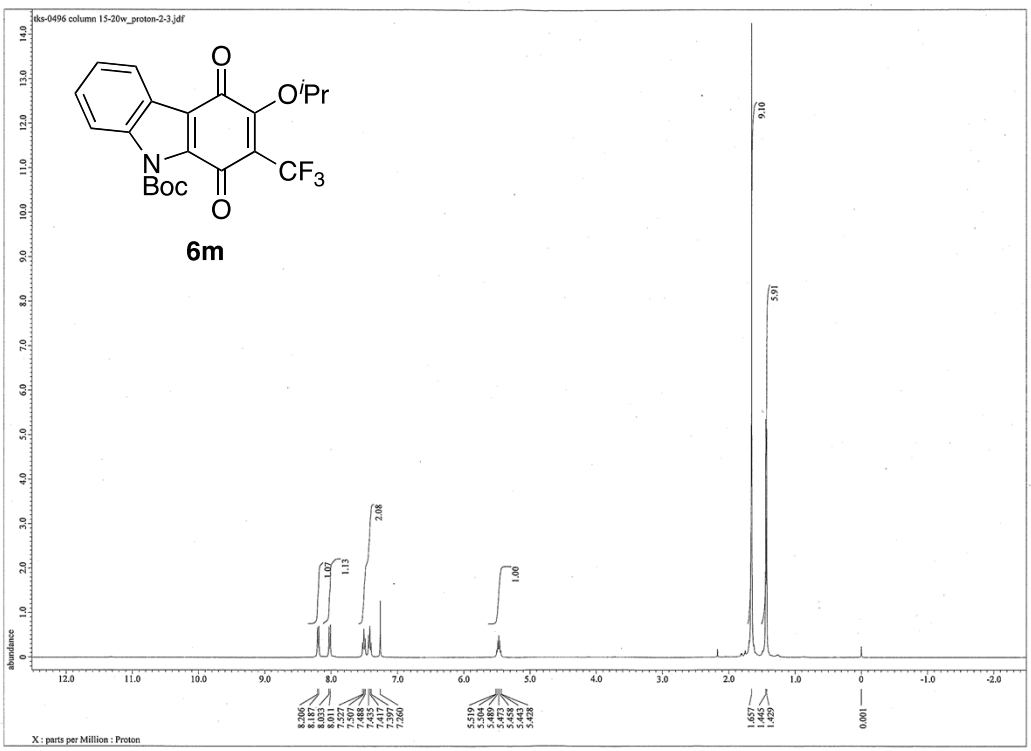

tks-0472 column 18-23_Carbon_copy16-1-4.jdf
178.334
172.098
158.816
157.605
149.301
130.317
126.418
125.998
123.939
123.353
122.795
122.003
120.447
119.124
118.847
118.390
118.304
117.732
112.755
80.480
77.315
77.000
76.696
22.815
X : parts per Million : Carbon13

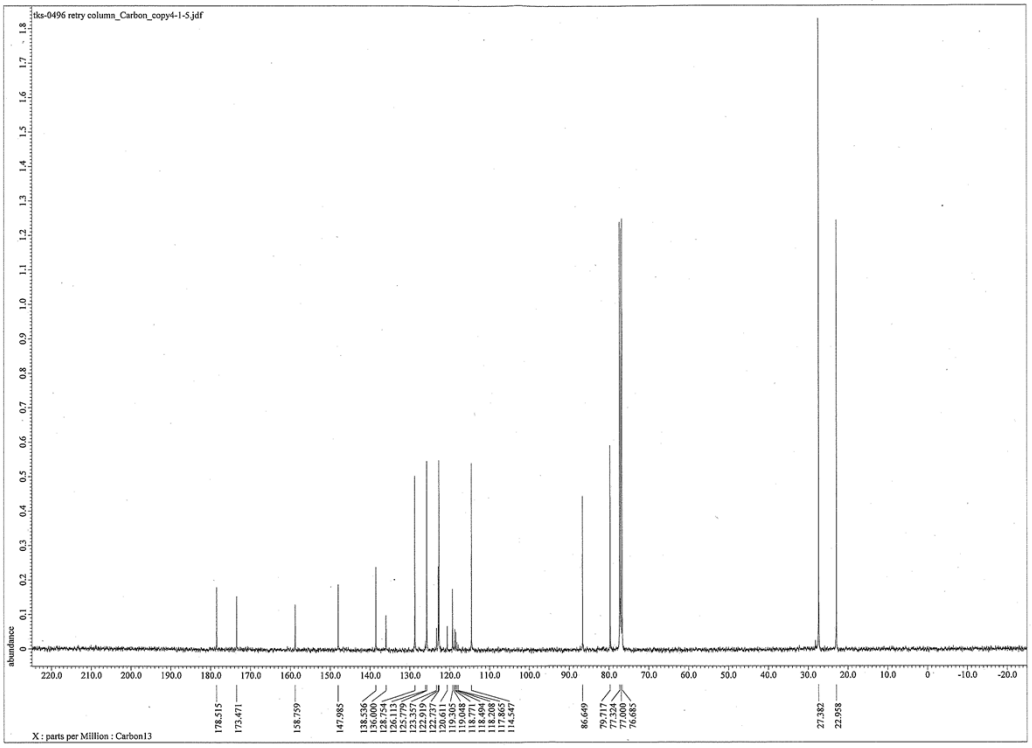

tks-0454 acid column 9-15_proton-1-5.jdf
O
S
O^{i}Pr
CF$_3$
O
6k
6.15
0.97
0.95
1.00
7.775
7.764
7.545
7.533
7.260
5.454
5.439
5.415
5.408
5.393
5.377
5.362
1.410
1.394
1.376
0.860
0.842
-0.020
X : parts per Million : Proton

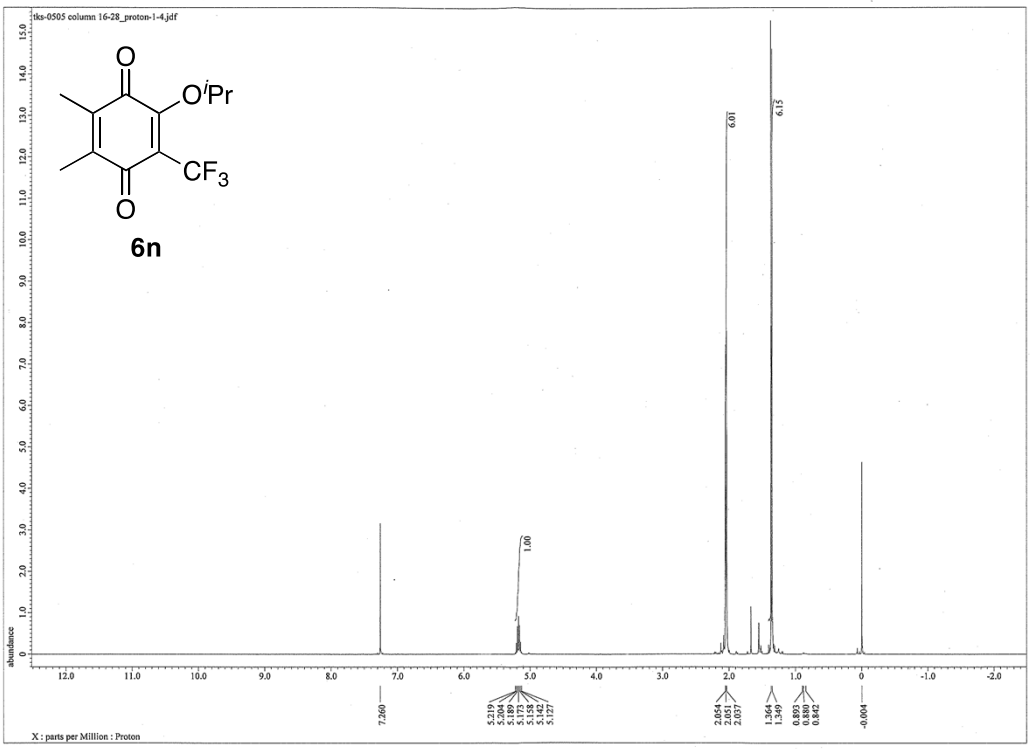

tks-0454 acid column 9-15_Carbon-1-7.jdf
176.894
175.244
160.389
141.731
140.153
135.914
126.551
126.103
123.348
120.592
119.543
119.295
119.000
118.723
117.857
80.194
77.324
77.000
76.685
22.844
X : parts per Million : Carbon13

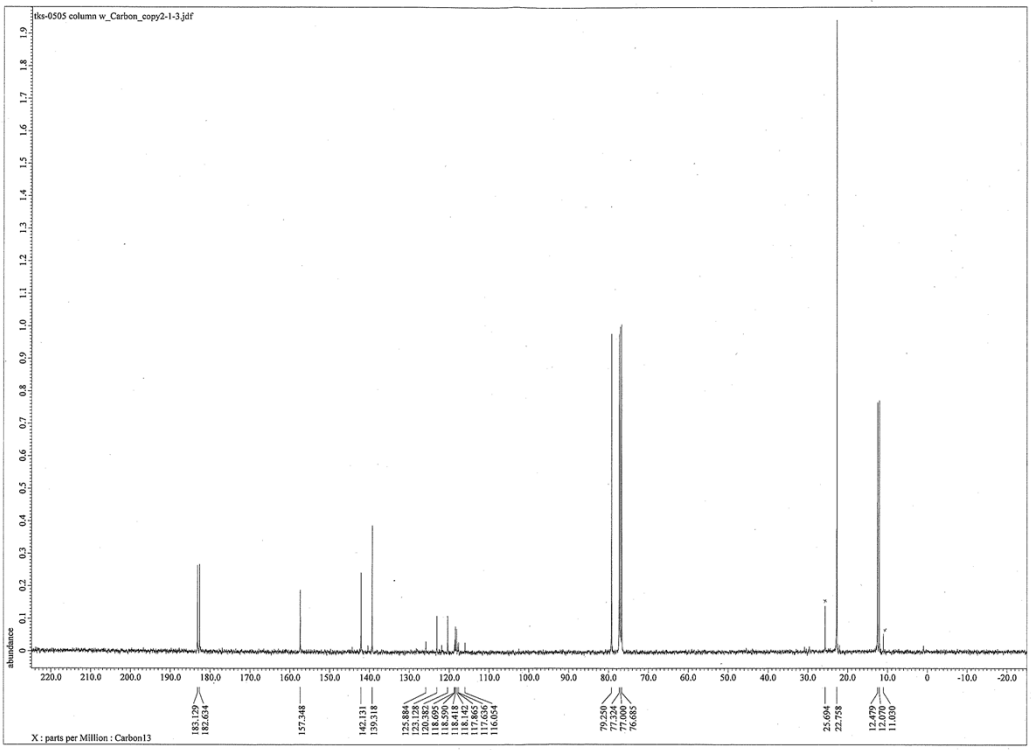

tks-0471 column 12-18 50-1 wash_proton-2-6.jdf
O
S
O^{i}Pr
CF$_3$
O
6l
6.07
2.69
1.03
1.01
1.00
abundance
X : parts per Million : Proton

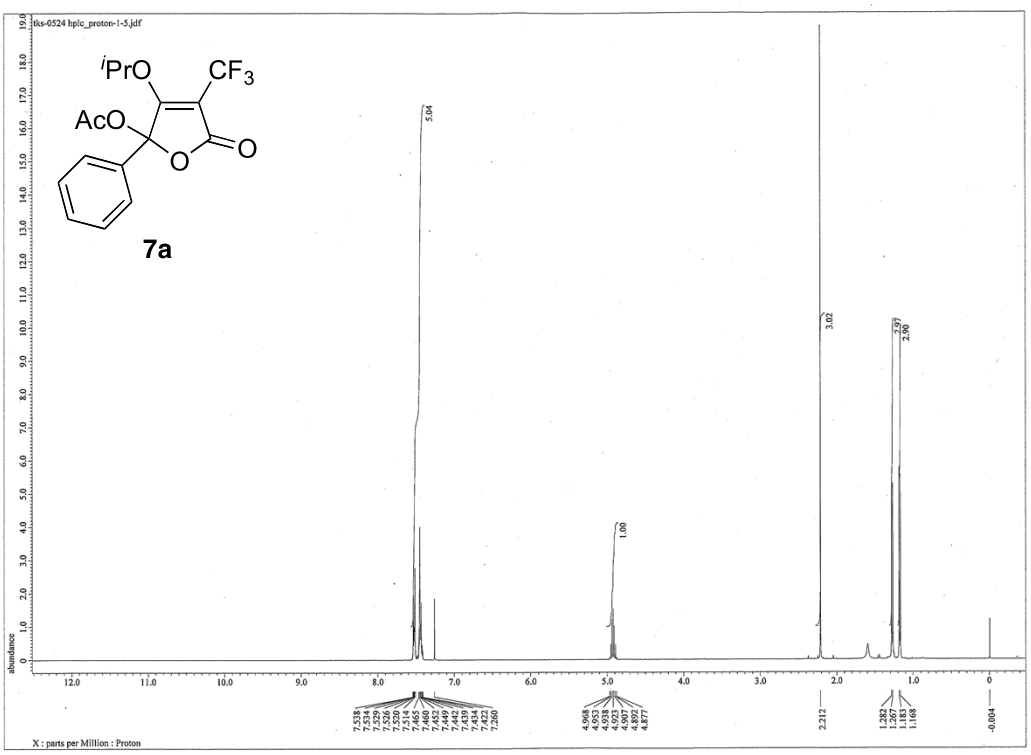

tks-0471 column 12-18 50-1 wash_Carbon-1-4.jdf
abundance
X : parts per Million : Carbon13

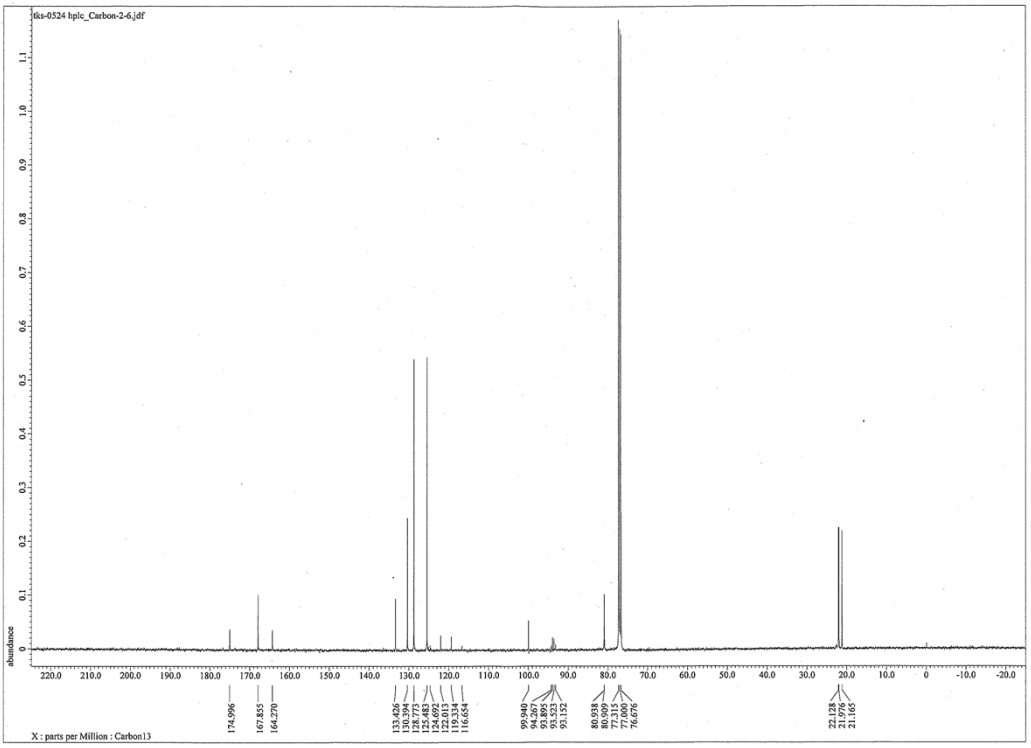

tks-0496 column 15-20w_proton-2-3.jdf
O
O^{i}Pr
N
Boc
CF$_3$
O
6m
9.10
5.91
2.08
1.07
1.13
1.00
abundance
X : parts per Million : Proton

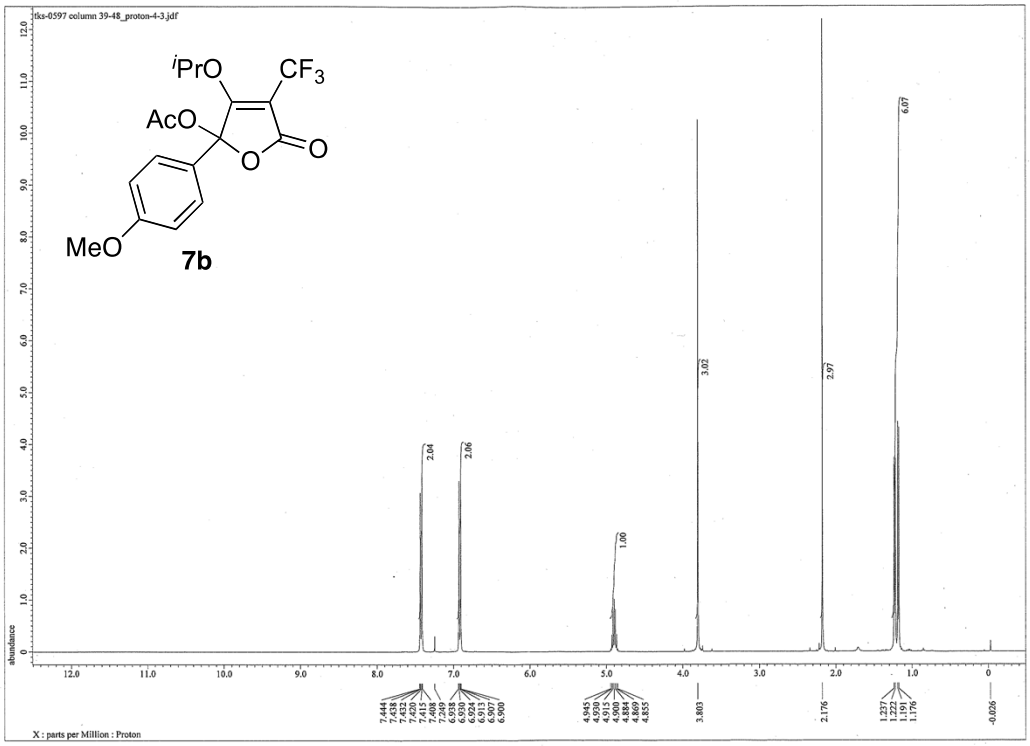

tks-0496 retry column_Carbon_copy4-1-5.jdf
abundance
X : parts per Million : Carbon13

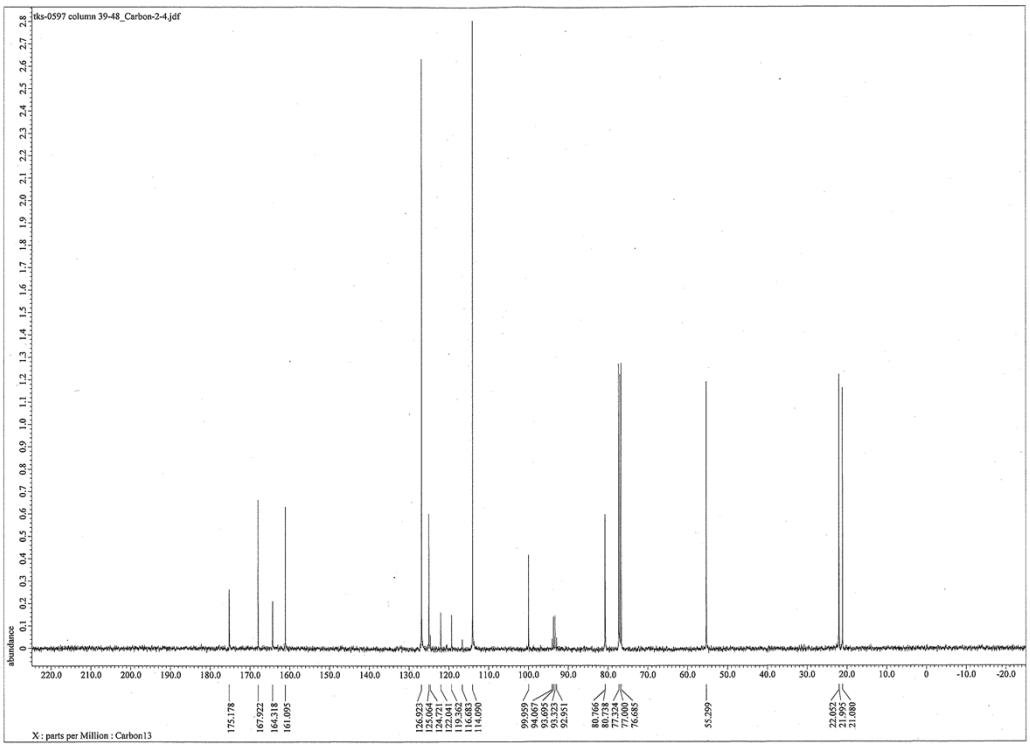

tks-0505 column 16-28_proton-1-4.jdf
O
O^{i}Pr
CF$_3$
O
6n
6.91
6.15
1.00
7.260
5.219
5.204
5.189
5.173
5.158
5.142
5.127
2.054
2.051
2.037
1.364
1.349
0.893
0.880
0.842
-0.004
abundance
X : parts per Million : Proton

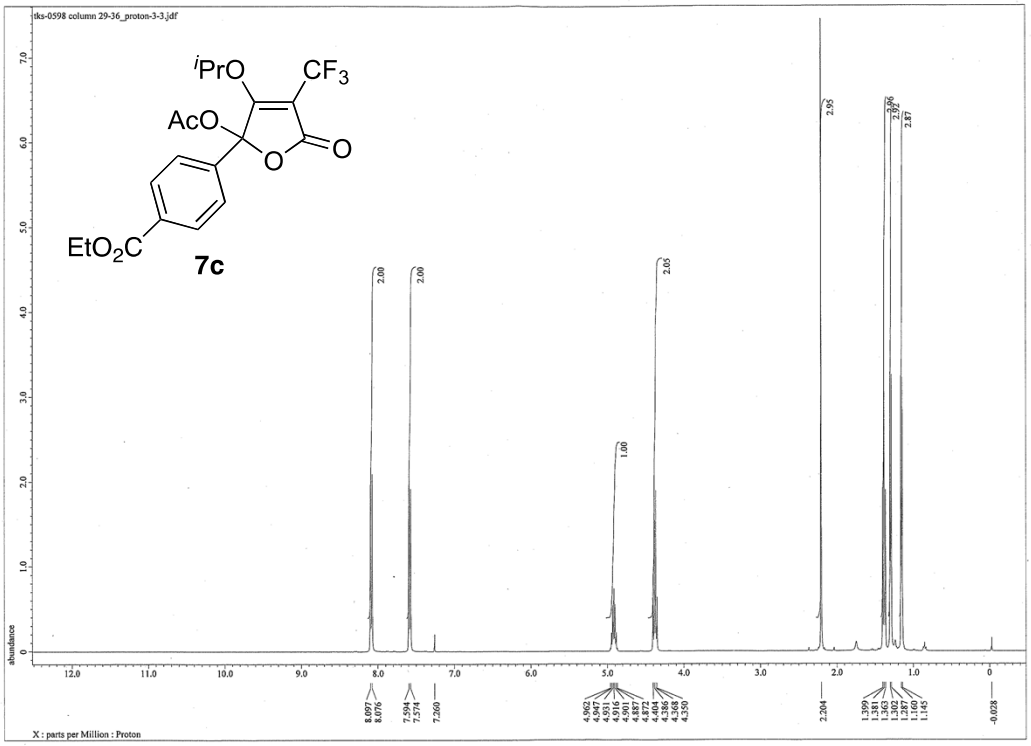

tks-0505 column w_Carbon_copy2-1-3.jdf
183.129
182.634
157.348
142.131
139.318
125.884
123.128
120.985
118.590
118.418
118.167
117.865
117.056
116.054
79.259
77.324
77.000
76.685
25.694
22.758
12.479
12.070
11.030
abundance
X : parts per Million : Carbon13

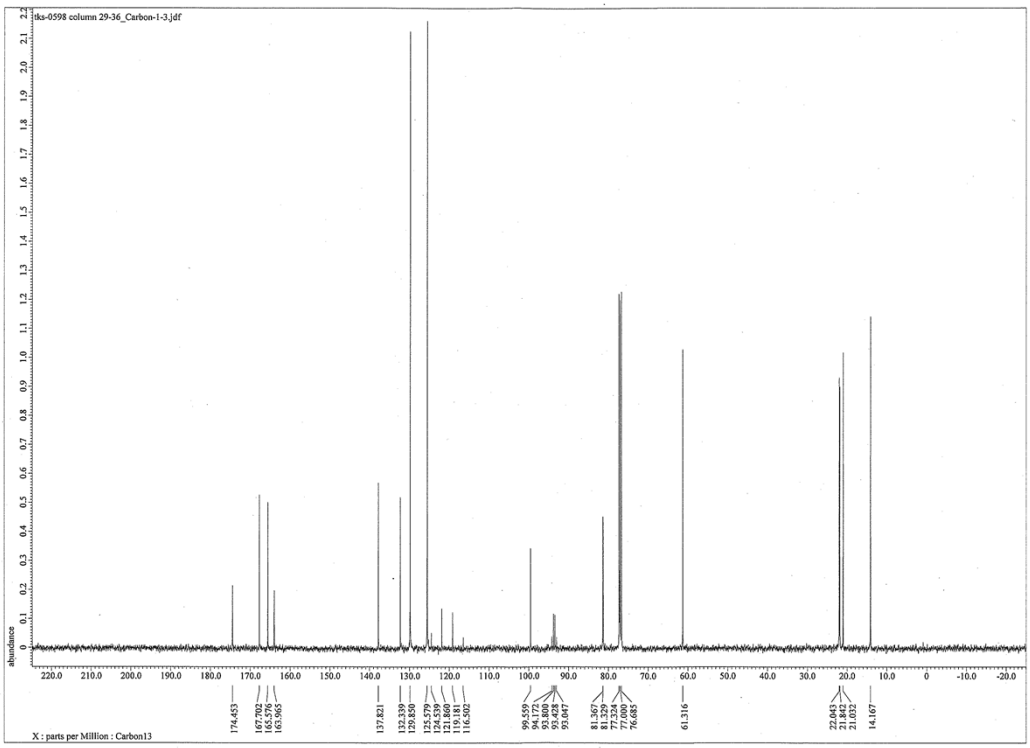

tks-0524 hplc_proton-1-5.jdf
iPrO
CF3
AcO
O
O
7a
5.04
3.02
2.97
2.90
1.00
abundance
X : parts per Million : Proton

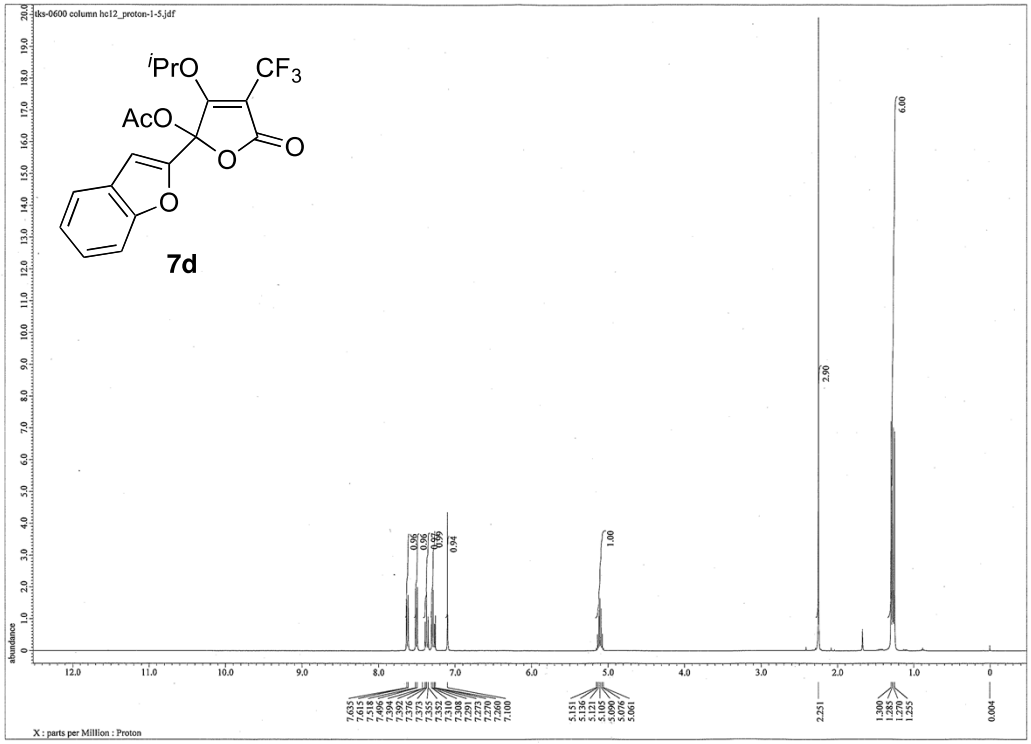

tks-0524 hplc_Carbon-2-6.jdf
abundance
X : parts per Million : Carbon13

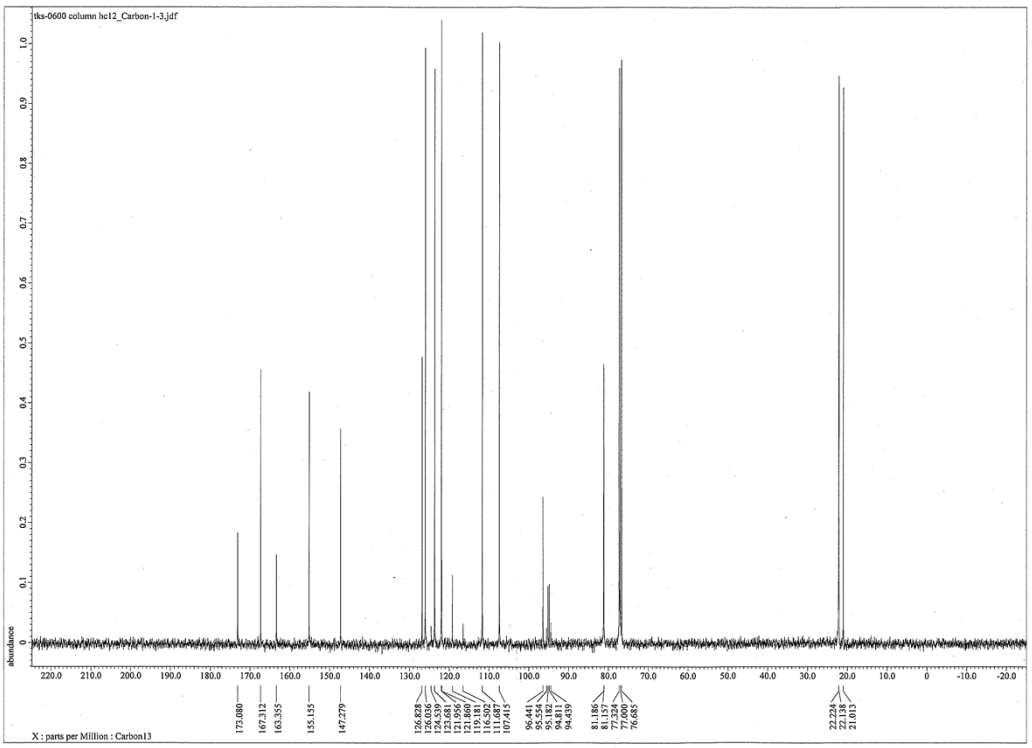

tks-0597 column 39-48_proton-4-3.jdf
iPrO
CF3
AcO
O
O
MeO
7b
X : parts per Million : Proton

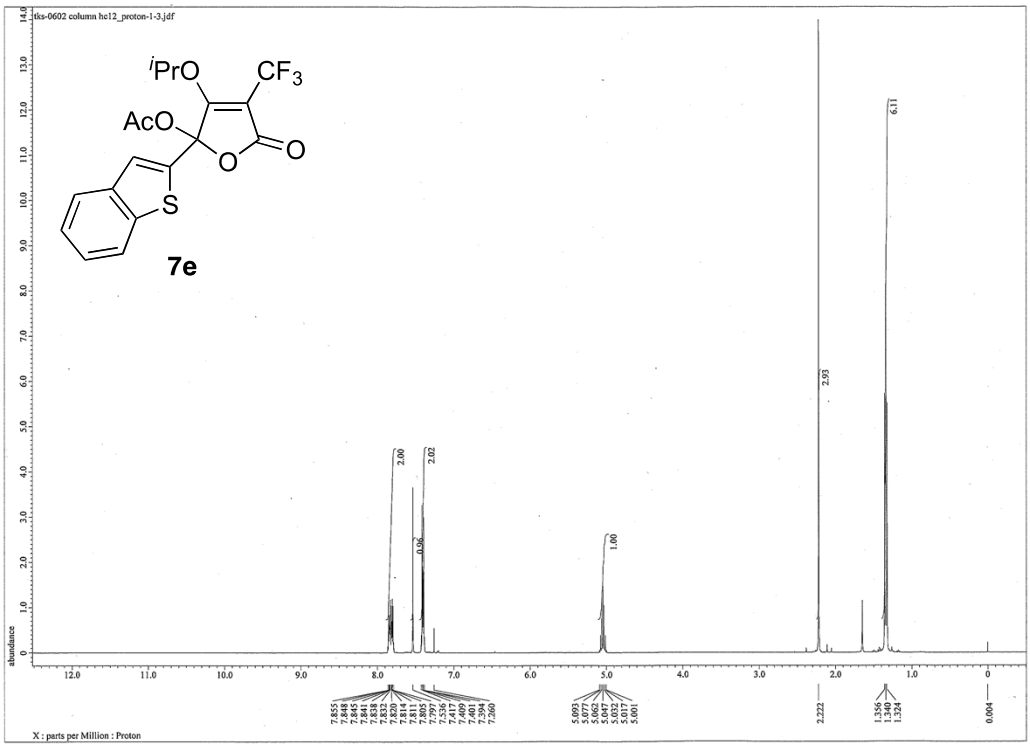

tks-0597 column 39-48_Carbon-2-4.jdf
X : parts per Million : Carbon13

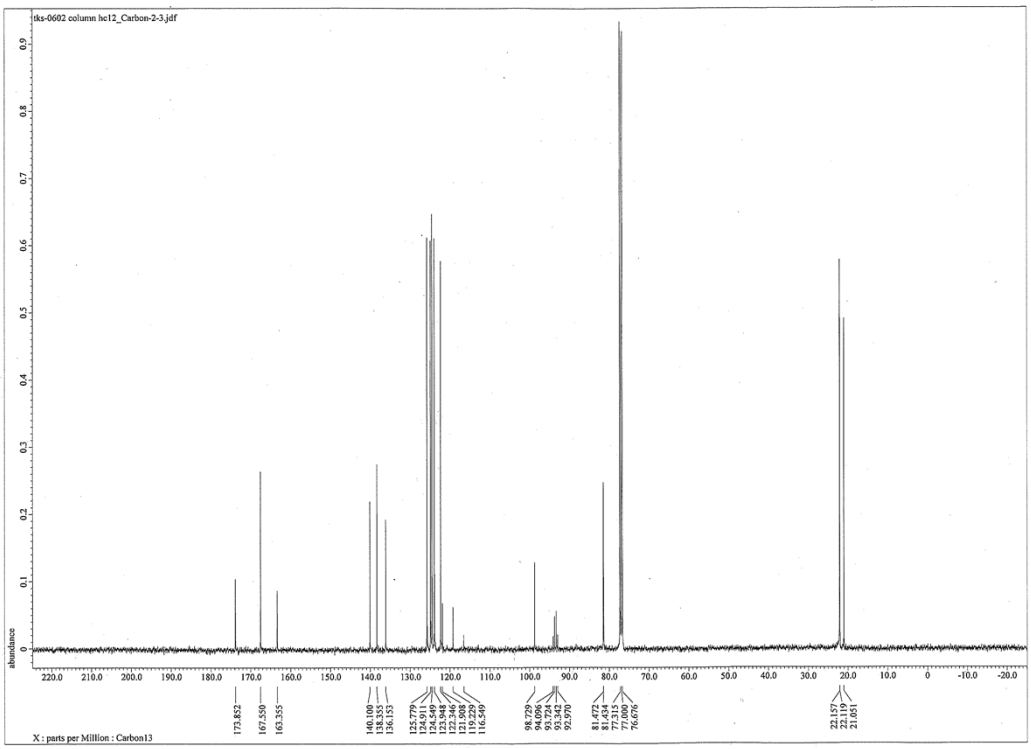

tks-0598 column 29-36_proton-3-3.jdf
iPrO
CF3
AcO
O
O
EtO2C
7c
X : parts per Million : Proton

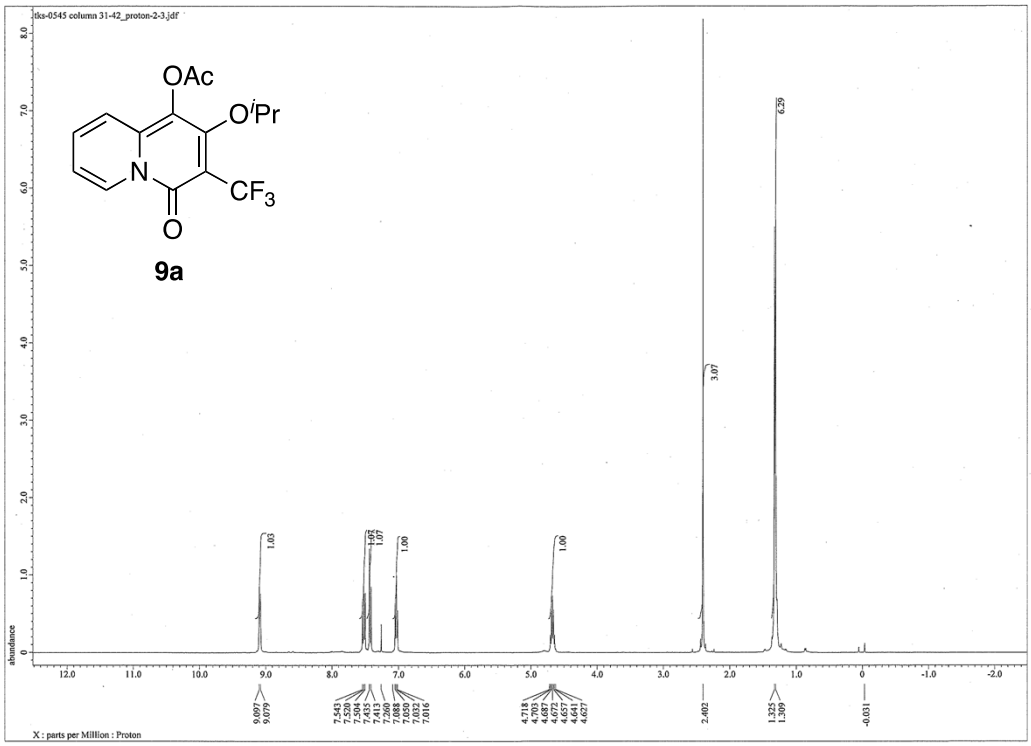

tks-0598 column 29-36_Carbon-1-3.jdf
X : parts per Million : Carbon13

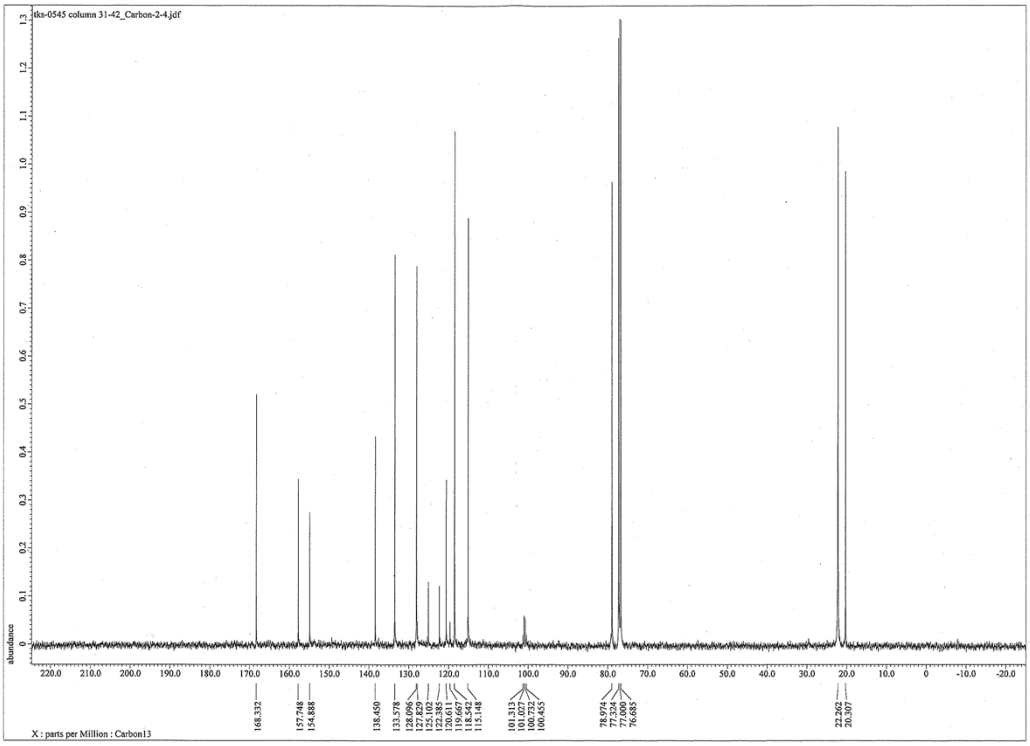

tks-0600 column hc12_proton-1-5.jdf
iPrO
CF3
AcO
O
O
O
7d
2.90
6.00
1.00
0.96
0.92
0.99
0.94
X : parts per Million : Proton

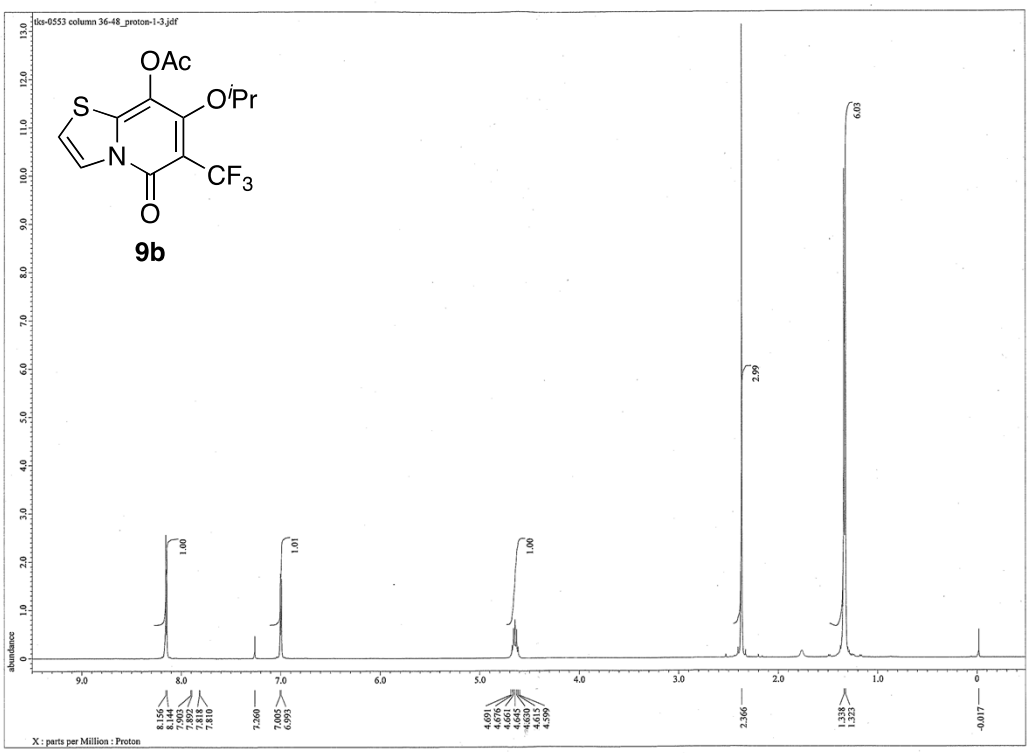

tks-0600 column hc12_Carbon-1-3.jdf
X : parts per Million : Carbon13

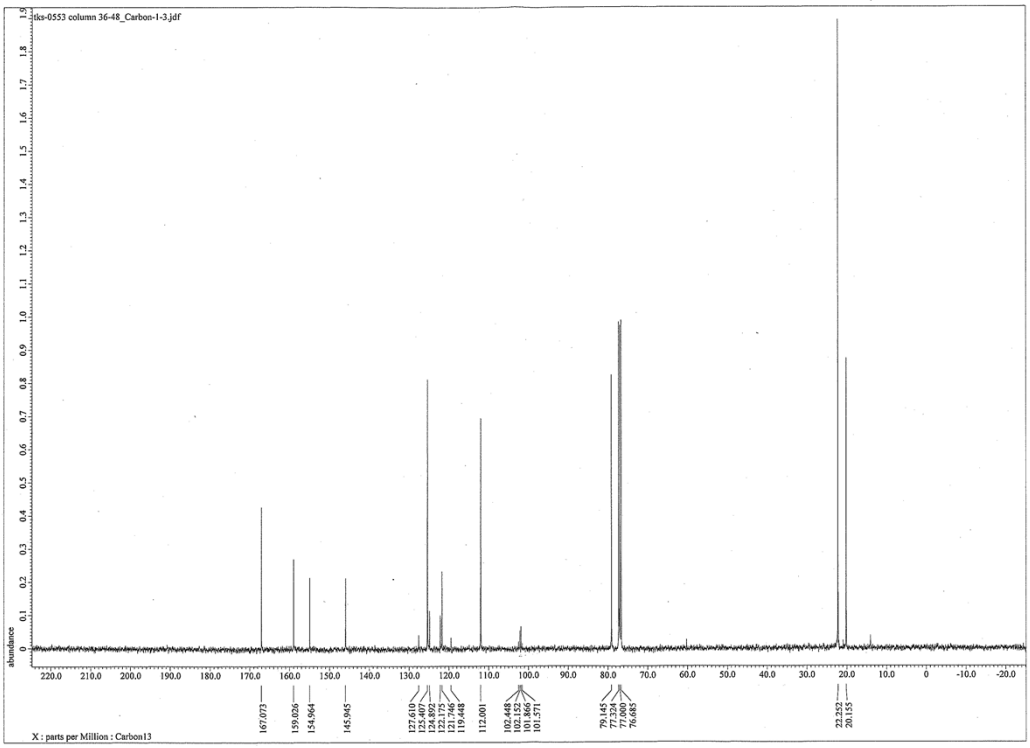

tks-0602 column hc12_proton-1-3.jdf
iPrO
CF3
AcO
O
O
S
7e
2.00
2.02
0.96
1.00
2.93
6.11
X : parts per Million : Proton

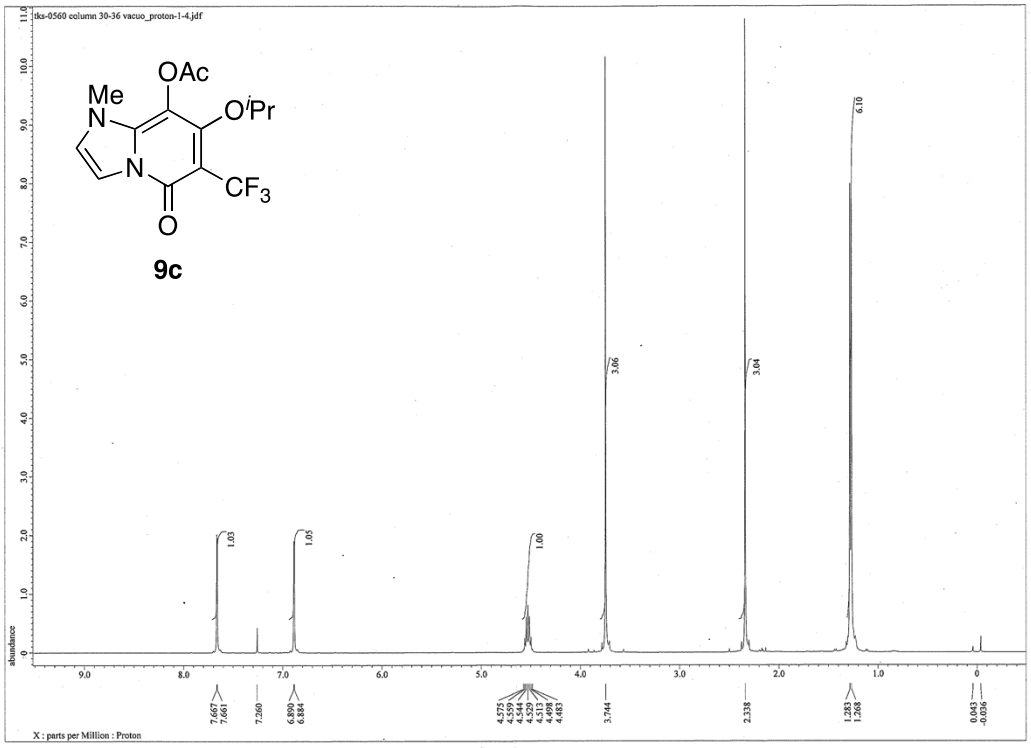

tks-0602 column hc12_Carbon-2-3.jdf
X : parts per Million : Carbon13

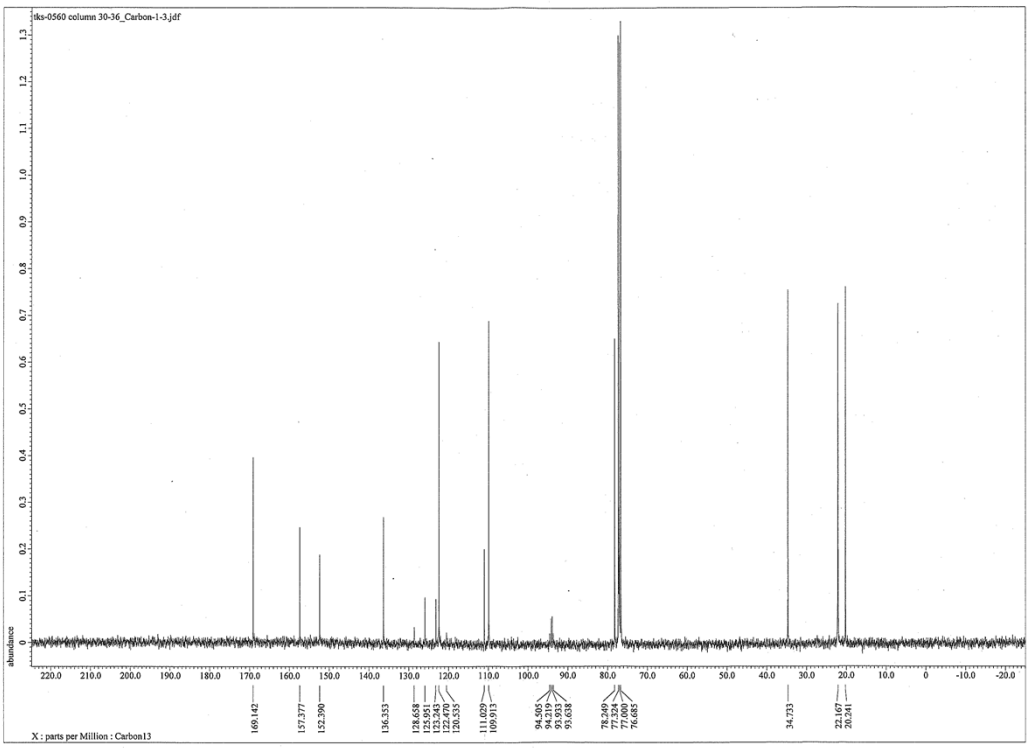

tks-0545 column 31-42_proton-2-3.jdf
OAc
O^{i}Pr
N
CF$_3$
O
9a
X : parts per Million : Proton

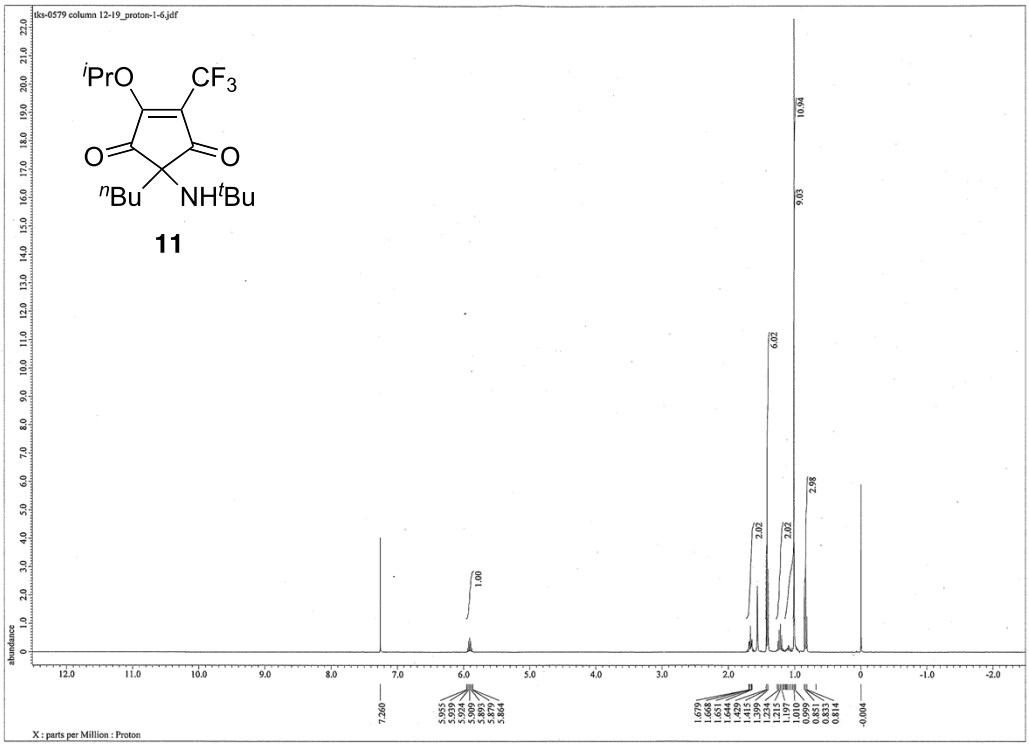

tks-0545 column 31-42_Carbon-2-4.jdf
X : parts per Million : Carbon13

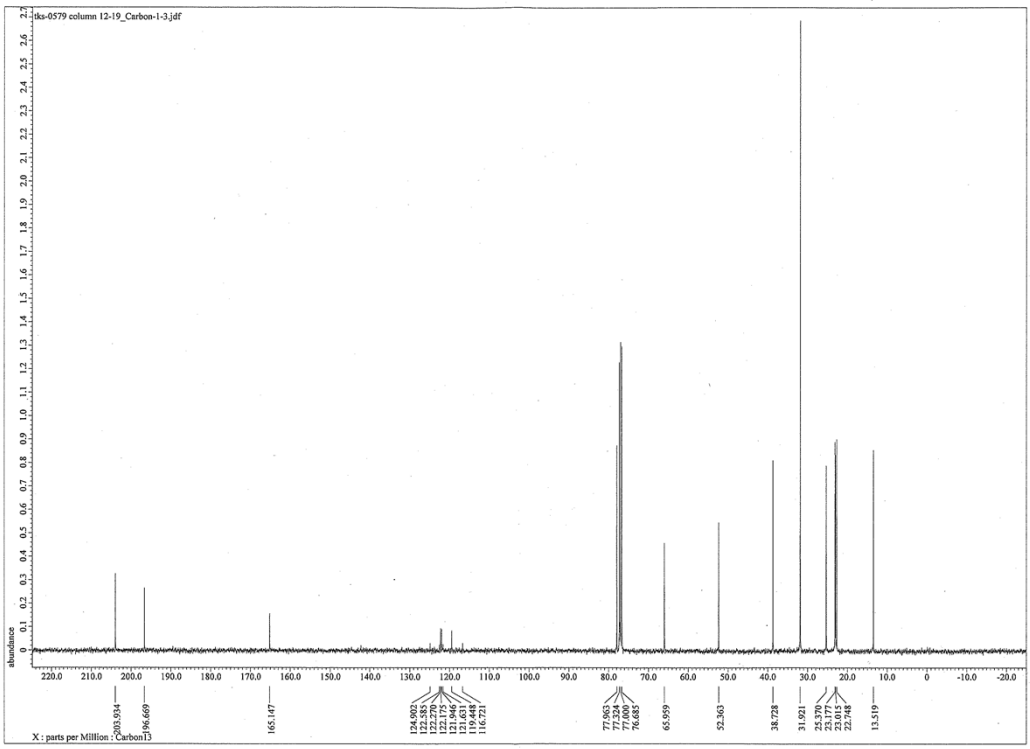

tks-0553 column 36-48_proton-1-3.jdf
OAc
O^{i}Pr
S
N
CF$_3$
O
9b
X : parts per Million : Proton


tks-0553 column 36-48_Carbon-1-3.jdf
X : parts per Million : Carbon13


tks-0560 column 30-36 vacuo_proton-1-4.jdf
OAc
Me
N
O^{i}Pr
N
CF$_3$
O
9c
1.03
1.05
1.00
3.06
3.04
6.10
7.667
7.661
7.360
6.890
6.884
4.575
4.559
4.544
4.529
4.513
4.498
4.483
3.744
2.338
1.283
1.268
0.043
-0.036
X : parts per Million : Proton


tks-0560 column 30-36_Carbon-1-3.jdf
169.142
157.377
152.290
136.353
128.658
125.951
123.145
122.470
120.535
111.029
109.913
94.505
94.139
93.933
93.638
78.349
77.324
77.000
76.685
34.733
22.167
20.241
X : parts per Million : Carbon13


tks-0579 column 12-19_proton-1-6.jdf
iPrO
CF3
O
O
nBu
NHtBu
11
X : parts per Million : Proton


tks-0579 column 12-19_Carbon-1-3.jdf
X : parts per Million : Carbon13