Supporting Information

Solid-state [2+2] photodimerization of eniminium salts: stereoselective synthesis of 1,3-diacetylcyclobutanes

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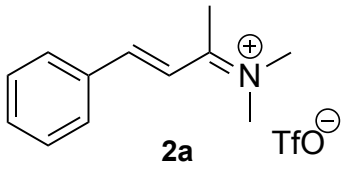
1. General Information.

Unless otherwise noted, reagents and starting materials were purchased from traditional suppliers and were used without further purification. Column chromatography was carried out using silica gel 60 N. TLC was carried out on silica gel 60 PF_{254}. IR spectra were recorded as KBr pellets or neat films between NaCl plates, or using an ATR attachment. ^{1}H NMR spectra were obtained at 400, 500 or 600 MHz as dilute solution in $CDCl_3$ and CD_3CN. The chemical shifts were reported relative to internal TMS. ^{13}C NMR spectra were obtained at 100 or 150 MHz as dilute solution in $CDCl_3$ and CD_3CN, and the chemical shifts were reported relative to internal TMS. The measurement of the distances between the coupled peaks with a scale gave the J values within the error of ±0.02 Hz. High- and low- resolution mass spectra were recorded on LC−MS using ESI ionization mode. X-ray measurements at 123 K were carried out using an imaging plate area detector with graphite monochromated Cu−Kα radiation. All calculations were performed using the CrystalStructure crystallographic software package except for refinement, which was performed using SHELXL-2013. The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm. All structures were solved by a combination of direct methods and difference Fourier syntheses, and refined by full- matrix least-squares on F^2, by using the SHELXTL software package.

2. General procedure for synthesis of eniminium salts and spectral data for 2a and 3a-3h

2.1 Synthesis of (*E*)-*N*-(1-methyl-3-phenyl-2-propen-1-ylidene)-*N*-methylmethanaminium trifluoromethanesulfonate 2a

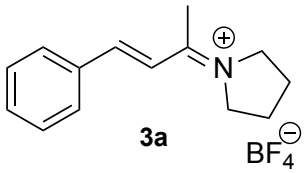
To a solution of (*E*)-4-phenylbut-3-en-2-one (222.1 mg, 1.5 mmol) and *N*-trimethylsilyl dimethylamine (248 μL, 1.6 mmol) in dry diethyl ether (4.5 mL) was added dropwise trimethylsilyl trifluoromethanesulfonate (286 μL, 1.6 mmol). After stirred for 5h at room temperature, the precipitate was filtered and the solid was washed with diethyl ether. Recrystallization of the solid from dichloromethane/diethyl ether gave **2a** in 30% yield (148.4 mg, 0.45 mmol). Colorless crystal. mp 119.5-121.0 ℃. IR (ATR) 1618, 1595, 355, 1262, 1223, 1190, 1180, 1141, 1079, 1032, 965, 766, 692, 634, 619, 572, 517, 477 cm^{-1}. ^{1}H NMR (500MHz, CD_3CN) δ 2.57 (s, 3H), 3.54 (s, 3H), 3.62 (s, 3H), 7.26 (d, *J* = 15.8 Hz, 1H), 7.50-7.56 (m, 3H), 7.81 (d, *J* = 7.2 Hz, 2H), 7.94 (d, *J* = 15.8 Hz, 1H). ^{13}C NMR (150 MHz, CD_3CN) δ 18.9, 45.2, 46.1, 119.5, 122.0 (*J* = 320 Hz), 130.2, 130.5, 133.5, 134.8, 153.4, 178.8. HRMS (ESI-QTOF): calcd for $C_{12}H_{16}N$ [M^+]: 174.1277, found 174.1279.



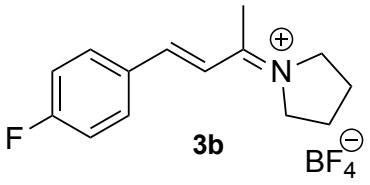
2.2 General procedure for synthesis of (*E*)-1-(4-Aryl-3-buten-2-ylidene) pyrrolidine tetrafluoroborates 3a-3h.

To a solution of pyrrolidine tetrafluoroborate (345 mg, 2.17 mmol) and (*E*)-4-phenyl-3-buten-2-one (268 mg, 1.84 mmol) in ethanol (1.0 mL) was added triethylamine (25μL, 0.18 mmol). After stirring the solution for 18h at rt, the precipitate was filtered and washed with ethanol. The solid was recrystallized from dichloromethane or acetonitrile/ethanol to give **3a** (228 mg, 0.79 mmol) in 43% yield.

Eniminium salt **3a**[1,2]: Colorless crystal, 43% yield. ^{1}H NMR (600MHz, CD_3CN) δ 2.09-2.14 (m, 4H), 2.56 (s, 3H), 3.92 (t, *J* = 6.3 Hz, 2H), 4.04 (t, *J* = 6.3 Hz, 2H), 7.15 (d, *J* = 15.6 Hz, 1H), 7.50-7.53 (m, 2H), 7.55-7.80 (m, 1H), 7.81 (d, *J* = 7.2 Hz, 2H), 7.93 (d, *J* = 15.6 Hz, 1H). X-ray crystallographic analysis evidenced the structure (ESI, p.S33).

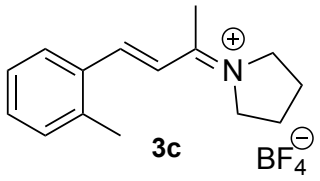


Eniminium salt **3b**: Yellow crystal, 27 % yield. mp 180.1-181.2 ℃. IR (ATR) 1624 1593 1510 1441 1325 1235 1163 1096 1047 1034 978 955 928 833 513 cm^{-1}. ^{1}H NMR (600MHz, CD_3CN) δ 2.11-2.13 (m, 4H), 2.55 (s, 3H), 3.92 (t, *J* = 6.6 Hz, 2H), 4.03-4.05 (m, 2H), 7.09 (d, *J* = 16.2 1H), 7.27 (t, *J* = 8.7

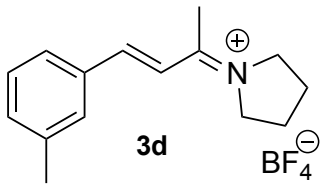


Hz, 2H), 7.86-7.89 (m, 2H) 7.91 (d, *J* = 16.2 Hz, 1H). ^{13}C NMR (150 MHz, CD_3CN) δ 19.3, 24.9 25.2, 54.6, 55.5, 117.3 (*J* = 22.5 Hz), 120.2, 131.3, 133.0 (*J* = 10.5 Hz), 151.2, 166.0 (*J* = 251 Hz), 174.8. HRMS (EIS-QTOF) calcd for $C_{14}H_{17}FN$ [M^+]: 218,1340 found 218.1343.

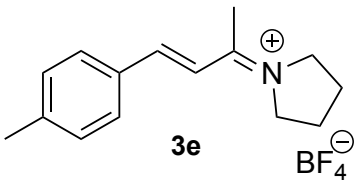
Eniminium salt **3c**: Colorless crystal, 33% yield. mp 175.3-176.3 ℃. IR (ATR) 1614 1595 1445 1387 1327 1047 1034 959 930 839 777 520 cm^{-1}. ^{1}H NMR (600MHz, CD_3CN) δ 2.12-2.13 (m, 4H), 2.51 (s, 3H), 2.59 (s, 3H), 3.94 (t, *J* = 6.3 Hz, 2H), 4.04-4.06 (m, 2H), 7.08 (d, *J* = 15.6 Hz, 1H), 7.32-7.34 (m, 2H), 7.43-7.45 (m, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 8.13 (d, *J* = 15.6 Hz, 1H). ^{13}C NMR (150 MHz, CD_3CN) δ 19.5, 19.7, 24.9, 25.2, 54.7, 55.6, 121.3, 127.6, 128.4, 132.1, 133.2, 133.6, 140.6, 149.8, 175.0. HRMS (EIS-QTOF) calcd for $C_{15}H_{20}N$ [M^+]: 214.1590, found 214.1593.



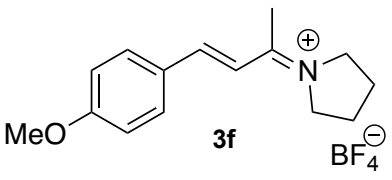
Eniminium salt **3d**: Colorless crystal, 39% yield. mp 166.9-168.3 ℃. IR (ATR) 1622 1332 1090 1049 1035 972 791 694 518 cm^{-1}. ^{1}H NMR (600MHz, CD_3CN) δ 2.10-2.13 (m, 4H), 2.40 (s, 3H), 2.56 (s, 3H), 3.92 (t, *J* = 6.3 Hz, 2H), 4.04 (t, *J* = 6.3 Hz, 3H), 7.15 (d, *J* = 15.6 Hz, 1H), 7.38-7.42(m, 2H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.67 (s, 1H), 7.90 (d, *J* = 15.6 Hz, 1H). ^{13}C NMR (150 MHz, CD_3CN) δ 19.3, 21.1, 24.9, 25.2, 54.6, 55.5, 120.2, 128.0, 130.1, 130.7, 134.3, 134.8, 140.2, 152.8, 174.9. HRMS (EIS-QTOF) calcd for $C_{15}H_{20}N$ [M^+]: 214.1590, found 214.1594.



Eniminium salt **3e**: Colorless crystal, 30% yield. mp 187.1-188.4℃. IR (ATR) 2359 2342 1622 1599 1441 1329 1188 1093 1049 1033 976 957 925 816 495 cm^{-1}. ^{1}H NMR (600MHz, CD_3CN) δ 2.10-2.13 (m, 4H), 2.41 (s, 3H), 2.54 (s, 3H), 3.91 (t, *J* = 6.6 Hz, 2H), 4.02 (t, *J* = 6.6 Hz, 3H), 7.10 (d, *J* = 15.6 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.91 (d, *J* = 15.6 Hz, 1H). ^{13}C NMR (150 MHz, CD_3CN) δ 19.2, 21.6, 24.9, 25.2, 54.5, 55.4, 119.2, 130.6, 130.9, 132.1, 144.9, 152.8, 174.8. HRMS (ESI-QTOF): calcd for $C_{15}H_{20}N$ [M^+]: 214.1590, found 214.1593.

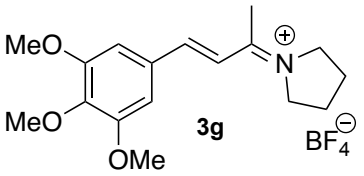


Eniminium salt **3f**: Yellow crystal, 34 % yield. mp 156.1-156.9 ℃. IR (ATR) 1584 1568 1514 1464 1427 1321 1252 1179 1092 1049 1017 1004 982 943 831 816 598 556 521 cm^{-1}. ^{1}H NMR (400MHz, CD_3CN) δ 2.09-2.11 (m, 4H), 2.52 (s, 3H), 3.86 (s, 3H), 3.89 (t, *J* = 4.3 Hz, 2H), 3.99 (t, *J* = 4.3 Hz,

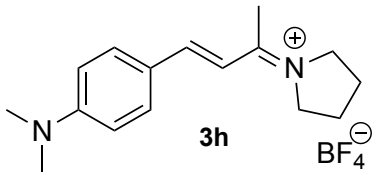


2H), 6.99 (d, *J* = 15.6 Hz, 1H), 7.05 (d, *J* = 8.8 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 15.6 Hz, 1H). ^{13}C NMR (150 MHz, CD_3CN) δ 19.1, 25.0, 25.3, 54.3, 55.2, 56.4, 115.8, 117.6, 127.5, 132.9, 152.7 164.5, 174.5. HRMS (EIS-QTOF) calcd for $C_{15}H_{20}NO$ [M^+]: 230.1539, found 230.1545.

Eniminium salt **3g**: Yellow crystal, 78 % yield. mp 193.8-194.7 ℃. IR (ATR) 1620 1603 1580 1503 1458 1423 1316 1285 1254 1161 1121 1045 1024 997 972 922 874 835 787 664 594 512 428 cm^{-1}. ^{1}H NMR (400MHz, CD_3CN) δ 2.28-2.34 (m, 4H), 2.52 (s, 3H), 3.80 (s, 3H), 3.88 (s, 6H), 4.11 (t, *J* = 6.4 Hz, 2H), 4.24 (t, *J* = 6.4 Hz, 2H), 7.02 (d, *J* = 15.6 Hz, 1H), 7.27 (s, 2H), 7.79 (d, *J* = 15.6 Hz, 1H). ^{13}C NMR (150 MHz, CD_3CN) δ 19.3, 25.0, 25.3, 54.6, 55.5, 57.0, 61.1, 108.2, 119.4, 130.3, 143.0, 152.9, 154.6, 1774.7. HRMS (EIS-QTOF) calcd for $C_{17}H_{24}NO_3$ [M^+]: 290.1751, found 290.1755.



Eniminium salt **3h**: Red crystal, 44 % yield. mp 184.0-185.4℃. IR (ATR) 3626 3557 2915 1566 1530 1441 1368 1310 1294 1188 1167 1101 1057 1026 988 943 916 828 814 760 702 515 cm^{-1}. ^{1}H NMR (600MHz, CD_3CN) δ 2.06-2.08 (m, 4H), 2.47 (s, 3H), 3.09 (s, 6H), 3.84 (t, *J* = 6.6 Hz, 2H), 3.91 (t, *J* = 6.6 Hz, 2H), 6.78 (m, 3H), 7.67 (d, *J* = 9.0 Hz, 1H), 7.82 (d, *J* = 15.6 Hz, 1H). ^{13}C NMR (150 MHz, CD_3CN) δ 18.4, 25.0, 25.2, 40.3, 53.3, 54.3, 112.8, 112.9 122.1, 133.4, 153.8, 154.9, 172.7. HRMS (EIS-QTOF) calcd for $C_{16}H_{23}N_2$ [M^+]: 243.1858, found 243.1858.



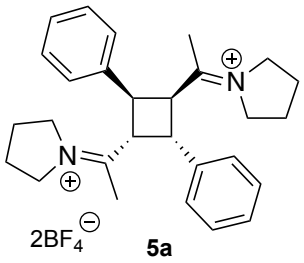
References

1. The following paper does not contain data for **3a**. H. Guan, M. Iimura, M. P. Magee, J. R. Norton, *G. Zhu, J. Am. Chem. Soc*., 2005, **127**, 7805-7814.
2. The following papers contain data for the ClO_4^- salt of **3a**. (a) N. J. Leonard and J. V. Paukstelis, *J.Org. Chem.*, 1963, **28**, 3021-3024. (b) M. Yamaguchi, T. Shiraishi and M. Hirama, *J.Org. Chem*., 1996, **61**, 3520-3530.

3. General procedure for irradiation of iminium salts in the solid-state

The powdered crystals of eniminium salt were placed between two glass plates and were irradiated with a 250 W high-pressure mercury lamp for 3-6 h. The crude products **4** and **5** were collected, and the product ratio was determined by ^{1}H NMR. As the products **4** and **5** were unstable in open atmosphere, it was hydrolyzed to diacetyl ketones as described below. To confirm the structure of dimer **5**, ^{1}H NMR, ^{13}C NMR and X-ray crystallographic analyses for dimer **5a** were achieved.

Dimer **5a:** Irradiation of iminium **3a** gave dimer **5a**, which was obtained as a white solid. Fortunately, recrystallization of crude **5a** from CH_3CN/CH_2Cl_2 gave crystals suitable for X-ray crystallographic analysis (p.S49).



5a

^{1}H NMR (600MHz, CD_3CN) δ 1.76-1.83 (m, 4H), 1.93-2.31 (m, 4H), 2.31 (s, 6H), 3.41 (m, 2H), 3.72 (m, 4H), 3.89 (m, 2H), 4.49 (t, J = 9.6 Hz, 2H), 4.92 (t, J = 9.6 Hz, 2H), 7.40-7.48(m, 10H). ^{13}C NMR (150 MHz, CD_3CN) δ 23.3, 24.1, 24.8, 44.0, 49.0, 55.7, 56.0, 127.8, 129.2, 130.0, 136.4, 186.

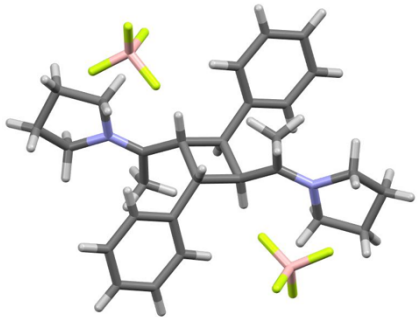
Crystal structure of **5a** (see, ESI, S49)

Monoclinic, $P2_1$, V = 1345.71(8) Å^3

a = 7.1302(3) Å, b = 14.6918(5) Å, c = 13.1044(4) Å

β = 101.392(2) °

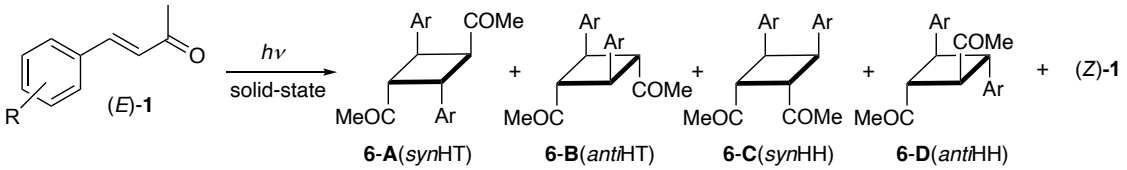
R1 = 0.0448, wR2 = 0.1348.



4. Control experiments of irradiation of α,β-unsaturated ketones

As control experiments, direct photodimerization of conjugated ketones **1a**, **1f**, **1g** and **1h** was investigated. Of the compounds **1a**-**1h**, **1b**-**1e** could not be used in this study because **1b**-**1e** is liquid at rt.

Table S1 Solid-state irradiation of (*E*)-**1**



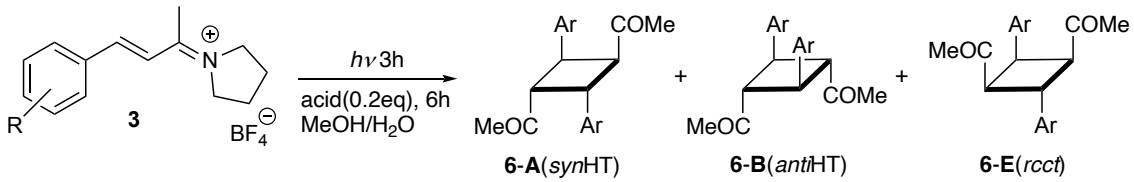
(*E*)-**1**	Time(h)	Conv(%)	yield(%)				
			6-**A**(*syn*HT)	**6**-**B**(*anti*HT)	**6**-**C**(*syn*HH)	**6**-**D**(*anti*HH)	(*Z*)-**1**
1a	3	84	36	4	13	28	19
1f	18	79	6	7	53	34	0
1g	3	99	15	4	53	28	0
1h	3	0	-	-	-	-	-

a) Determined by ^{1}H NMR spectra.

5. Attempt on hydrolysis of photodimers to diacetylcyclobutanes

A survey of various hydrolysis conditions revealed that acetic acid and citric acid induced considerable isomerization of **6-A** (synHT) to **6-C** (rcct-dimer), while PPTS is effective in hydrolysis without isomerization.

Table S2 Hydrolysis of intermediate photodimers after irradiation of **3a** and **3b**



Substrate	Acid (0.2 eq)	yield(%)[a]		
		6-A(*syn*HT)	**6-B**(*anti*HT)	**6-E**(*rcct*)
3a (R = H)	acetic acid	68	8	24
3a (R = H)	citric acid	55	9	36
3a (R = H)	PPTS	88	6	5
3b (R = F)	PPTS	95	0	5

a) Determined by ^{1}H NMR.

6. General procedure of hydrolysis of photodimers and spectral data for 6a-6h

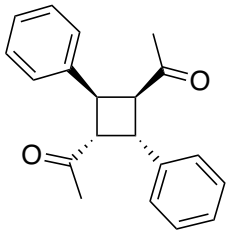
6.1 Hydrolysis of dimers of iminium salt 2a

To a solution of 1.0 M HCl was added the photoproduct obtained from iminium salt **2a**. The mixture was stirred for 18h, and the crude product was extracted with dichloromethane. The organic layer was separated and dried over anhydrous magnesium sulfate. The solution was then filtered, and the solvent was removed under reduced pressure. The product ratio was determined by ^{1}H NMR spectroscopy and separated by PTLC.

6.2 General procedure for hydrolysis of dimers of iminium salts 3

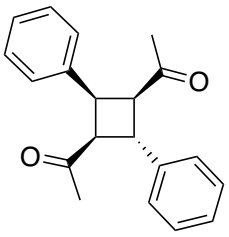
To a solution of pyridinium *p*-toluenesulfonate (PPTS) (0.2 eq) in a 1:3 mixture of H_2O and MeOH (0.5 mL/1.5 mL) was added the photoproduct obtained from iminium salt **3**. The mixture was stirred for 6-18 h and the crude product was extracted with dichloromethane. The organic layer was washed with brine and dried over anhydrous magnesium sulfate. The solution was filtered, and the solvent was removed under reduced pressure. The product ratio was determined by ^{1}H NMR spectroscopy and separated by PTLC.

6a-A(*syn*HT): Colorless solid. ^{1}H NMR (500MHz, $CDCl_3$) δ 1.63 (s, 6H), 3.90 (dd, *J* = 11.0, 7.3 Hz, 2H), 4.61 (dd, *J* = 11.0, 7.3 Hz, 2H), 7.23-7.35 (m, 10H).
The ^{1}H NMR chemical shifts are consistent with those reported.[1)] For further structural confirmation, the X-ray crystal structure is shown in SI(p.S51).



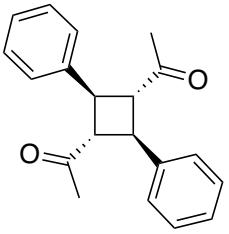
6a-A

6a-E(*r-cct*): Colorless solid. mp 153~154.5 °C.^{1}H NMR (400MHz, $CDCl_3$) δ 1.69 (s, 6H), 3.71 (t, *J* = 10.0 Hz, 2H), 4.38 (t, *J* = 10.0 Hz, 1H), 4.81 (t, *J* = 10.0 Hz, 1H), 7.18 (m, 10H). 1703, 1494, 1356, 1182, 169, 700 cm^{-1}.
The ^{1}H NMR chemical shifts and IR data are consistent with those reported.[2)]



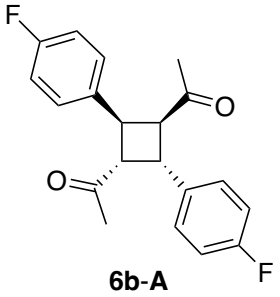
6a-E

6a-B(*anti*HT): Colorless crystalline solid. mp 100~102°C. IR (KBr) 2926, 1708, 1602, 1495, 1455, 1358, 1261, 1180, 1031, 800, 745, 696 cm^{-1}. ^{1}H NMR (500MHz, $CDCl_3$) δ 1.98 (s, 6H), 3.38 (t, *J* = 9.6 Hz, 2H), 3.37 (t, *J* = 9.6 Hz, 2H), 7.28-7.31 (m, 2H), 7.37-7.41 (m, 8H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 28.8, 42.2, 56.5, 127.3, 127.5, 129.1, 141.1, 206.7. HRMS (ESI-QTOF) calcd for $C_{20}H_{20}NaO_2$ $[M+Na]^+$ 315.1356, found 315.1358. The X-ray crystal structure was shown in ESI(p.S53).



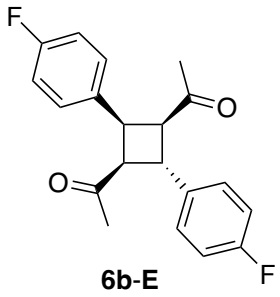
6a-B

6b-A(*syn*HT): Colorless crystalline solid. mp 172~174 °C. IR (KBr) 1700, 1608, 1513, 1355, 1233, 1178, 834, 816, 559, 522 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$) δ 1.66 (s, 6H), 3.85 (dd, *J* = 10.8, 7.1 Hz, 2H), 4.57 (dd, *J* = 10.8, 7.1 Hz, 2H), 6.99-7.05 (m, 4H), 7.24 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 29.9, 40.0, 54.9, 115.8 (*J* = 18 Hz), 129.6 (*J* = 9 Hz), 134.7 (*J* = 4.5 Hz), 162.2 (*J* = 245 Hz), 206.8. HRMS (ESI-QTOF) calcd for $C_{20}H_{18}NaO_2$ $[M+Na]^+$ 351.1167, found 351.1169.



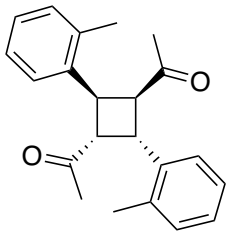
6b-A

6b-E(*r-cct*): Colorless crystalline solid. mp 159~161 °C. IR (KBr) 1705, 1604, 1510, 1351, 1225, 1168, 847, 810, 680, 582, 551, 523 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$) δ 1.69 (s, 3H), 3.66 (t, *J* = 10.3 Hz, 2H), 4.38 (t, *J* = 10.3 Hz, 1H), 4.75 (t, *J* = 10.3 Hz, 1H), 6.97-7.02 (m, 4H), 7.15-7.21 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 28.7, 38.8, 44.2, 54.4, 115.4 (*J* = 21 Hz), 116.2 (*J* = 21 Hz), 128.2 (*J* = 7.5 Hz), 130.1 (*J* = 7.5 Hz), 132.7 (*J* = 3 Hz), 138.1 (*J* = 3 Hz), 161.2 (*J* = 78 Hz), 162.8 (*J* = 8.1), 206.1. HRMS (ESI-QTOF) calcd for $C_{20}H_{18}NaO_2$ $[M+Na]^+$ 351.1167, found 351.1171.



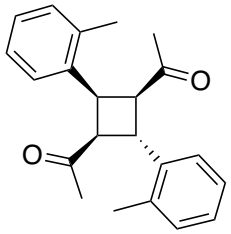
6b-E

6c-A(*syn*HT): Colorless crystalline solid. mp 143~145 °C. IR (KBr) 3057,2971, 1697, 1496, 1463, 1349, 1306, 1219, 1195, 1172, 769, 731, 569 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$) δ 1.63 (s, 6H), 2.47 (s, 6H), 3.94, (dd, *J* = 11.0, 7.3 Hz, 2H), 4.83 (dd, *J* = 11.0, 7.3 Hz, 2H), 7.15-7.22 (m, 8H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.3, 29.3, 36.9, 53.3, 126.3, 126.7, 127.3, 130.6, 136.3, 137.1, 207.2. HRMS (ESI-QTOF) calcd for $C_{22}H_{24}NaO_2$ $[M+Na]^+$ 343.1669, found 343.1670.



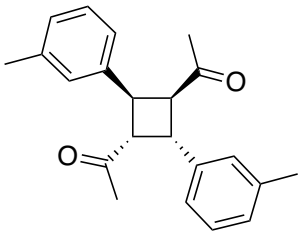
6c-A

6c-E(*r-cct*): Colorless crystalline solid. mp 184~186 °C. IR (KBr) 1699, 1559, 1490, 1355, 1187, 766, 731, 541 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$) δ 1.58 (s, 6H), 2.46 (s, 3H), 2.69 (s, 3H), 3.74 (t, *J* = 10.3 Hz, 2H), 4.82 (t, *J* = 10.3 Hz, 1H), 4.96 (t, *J* = 10.3 Hz, 1H), 7.08-7.24 (m, 7H), 7.35 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.3, 20.8, 28.2, 35.7, 38.4, 55.8, 125.9, 126.2, 126.7, 127.0, 127.0, 127.5, 130.6, 130.9, 135.3, 135.8, 137.3, 140.9, 206.0. HRMS (ESI-QTOF) calcd for $C_{22}H_{24}NaO_2$ $[M+Na]^+$ 343.1669, found 343.1674.



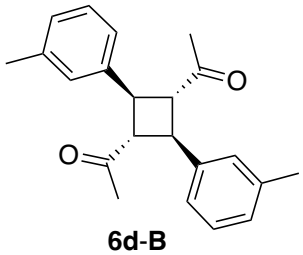
6c-E

6d-A(*syn*HT): Colorless crystalline solid. mp 108~110°C. IR (KBr) 2930, 1699, 1607, 1349, 1182, 1127, 784, 702 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$) δ 1.64 (s, 6H), 2.34 (s, 6H), 3.87 (dd, *J* = 11.2, 7.1 Hz, 2H), 4.56 (dd, *J* = 11.2, 7.1 Hz, 2H), 7.04-7.09 (m, 6H), 7.19-7.23 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.6, 29.9, 40.9, 54.7, 125.0, 128.2, 128.8, 128.8, 138.5, 139.1, 207.1. HRMS (ESI-QTOF) calcd for $C_{22}H_{24}NaO_2$ $[M+Na]^+$ 343.1669, found 343.1669.



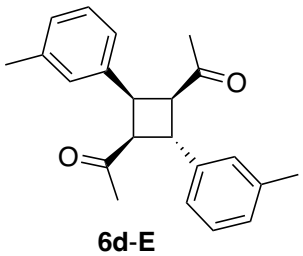
6d-A

6d-B(*anti*HT): Colorless oil. IR (neat) 2921, 1710, 1607, 1489, 1357, 1071, 774, 698 cm-1. ^1H NMR (400MHz, $CDCl_3$) δ 1.98 (s, 6H), 2.38 (s, 6H), 3.36 (t, *J* = 9.6 Hz, 2H), 3.68 (t, *J* = 9.6 Hz, 2H), 7.10 (d, *J* = 7.3 Hz, 2H), 7.16-7.18 (m, 4H), 7.26-7.30 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.5 28.8 42.0 56.4 124.1 128.0 128.2 128.8 138.6 141.0 206.8. HRMS (ESI-QTOF) calcd for $C_{22}H_{24}NaO_2$ $[M+Na]^+$ 343.1669, found 343.1673.



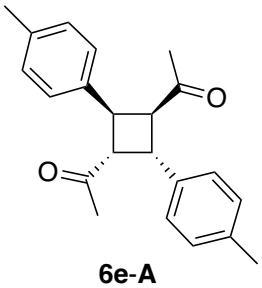
6d-B

6d-E(*r-cct*): Colorless crystalline solid. mp 135~137 °C. IR (KBr) 1700, 1355, 1177, 782, 706 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$) δ 1.67 (s, 6H), 2.31 (s, 3H), 2.33 (s, 3H), 3.68 (t, *J* = 10.3 Hz, 2H), 4.32 (t, *J* = 10.3 Hz, 1H), 4.76 (t, *J* = 10.3 Hz, 1H), 7.00-7.07 (m, 6H), 7.15-7.22 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.6, 28.6, 39.6, 45.0, 54.4, 123.6, 125.4, 127.4, 127.5, 128.5, 128.6, 129.0, 129.2, 137.2, 138.3, 138.7,142.8, 206.9. HRMS (ESI-QTOF) calcd for $C_{22}H_{25}O_2$ $[M+H]^+$ 321.1849, found 321.1853.



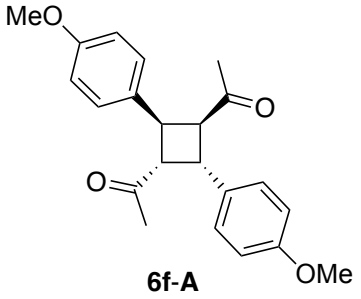
6d-E

6e-A(*syn*HT): Colorless crystalline solid. mp 179~181°C. IR (KBr) 2922, 1699, 1515, 1353, 1316, 1254, 1222, 1175, 1118, 1025, 818, 729, 559 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$) δ1.64 (s, 6H), 2.31 (s, 6H), 3.85 (dd, *J* = 11.0, 7.3 Hz, 2H), 4.55 (dd, *J* = 11.0, 7.3 Hz, 2H), 7.11-7.18 (m, 8H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.2, 30.0, 40.6, 54.9, 127.9, 129.6, 136.1, 137.1, 207.3. HRMS (ESI-QTOF) calcd for $C_{22}H_{24}NaO_2$ $[M+Na]^+$ 343.1669, found 343.1672.



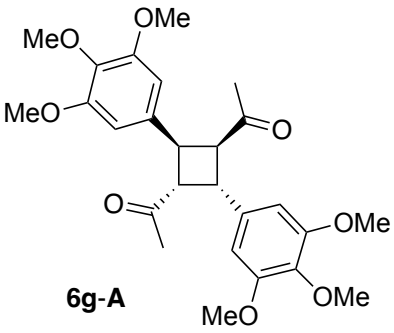
6e-A

6f-A(*syn*HT): Colorless crystalline solid. mp 152~154 °C. IR (KBr) 3001, 2964, 1700, 1613, 1517, 1458, 1318, 1250, 1179, 1038, 844, 814, 562 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$) δ 1.64 (s, 6H), 3.79-3.85 (m, 8H), 4.53 (dd, *J* = 11.0, 7.3 Hz, 2H), 6.84-6.87 (m, 4H), 7.18-7.21 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 30.0, 40.1, 55.2, 55.4, 114.2, 129.1, 131.2 158.8, 207.4. HRMS (ESI-QTOF) calcd for $C_{22}H_{24}NaO_4$ $[M+Na]^+$ 375.1567, found 375.1576.



6f-A

6g-A(*syn*HT): Colorless crystalline solid. mp 168~170 °C. IR (KBr) 3002, 1697, 1587, 1507, 1457, 1429, 1330, 1248, 1122, 999, 834 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$) δ 1.70 (s, 6H), 3.78-3.82 (m, 8H), 3.89 (s, 12H), 4.54 (dd, *J* = 11.2, 7.1 Hz, 2H), 6.48 (s, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 29.9, 41.3, 55.4, 56.3, 61.1, 104.9, 135.0, 137.2, 153.4, 207.3. HRMS (ESI-QTOF) calcd for $C_{26}H_{32}NaO_8$ $[M+Na]^+$ 495.1989, found 495.1992.



6g-A

References

1. G. Montaudo and S. Caccamese, *J. Org.Chem.,* 1973, **38***,* 710-716.
2. J. Dekker and T. G. Dekker, *J. Org. Chem*., 1968, **33**, 2604-2605.

7. Details of computational methods

All calculations on geometries and energies were performed with the Mac SPARTAN[1-3] Pro 20' program package. The geometries for compounds **3a**, **3h**, **5b** and **6b** were fully optimized by DFT calculations at the B3LYP/6-31G(d) level.

7.1 Comparison of the electrostatic charge between 3a and 3h

The electrostatic potential maps for **3a** and **3h** were obtained for their optimized geometries.

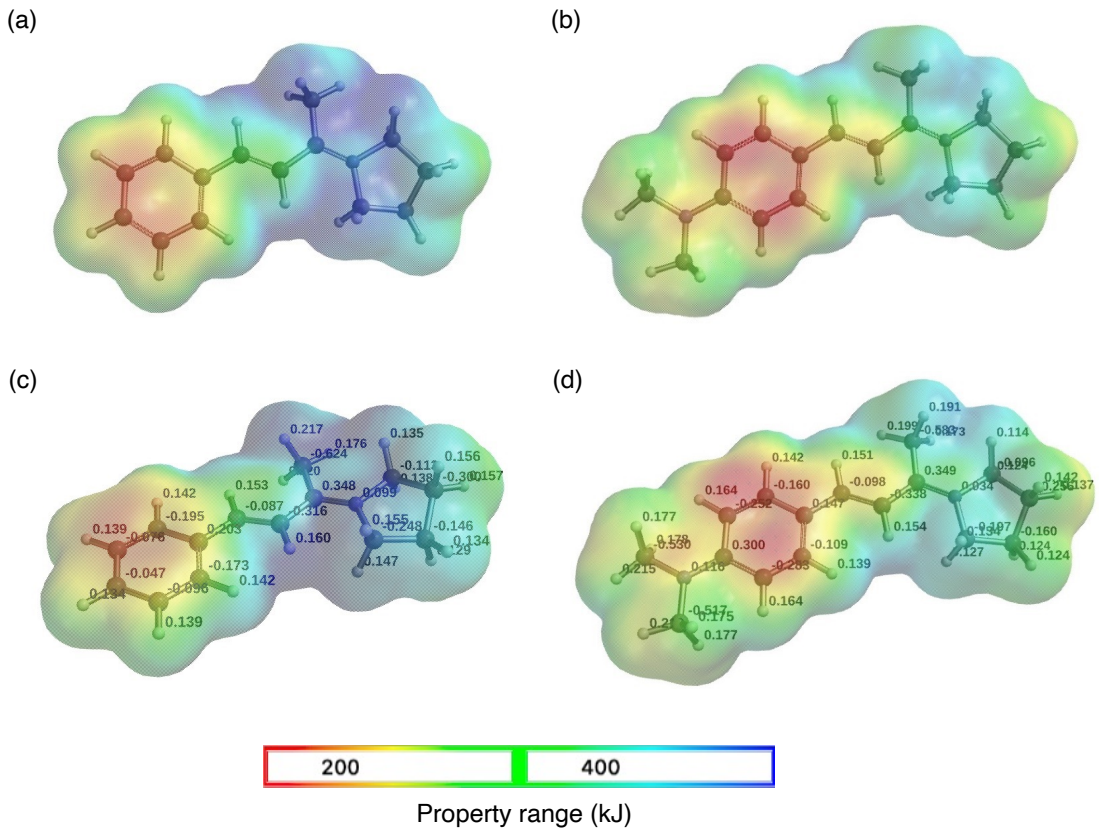


Fig. S1 The electrostatic potential maps for **3a** (a) and **3h (b)**, and electrostatic charge for **3a** (c) and **3h** (d).

7.2 Comparison of energies of stable conformers of compound 5b.

Structure optimization of **5b** gave two conformers **A** and **B**, which were shown in Fig S2. The conformer **A** is much more stable than conformer **B**. The reduction with DIBAL-H seems to occur from conformer **A** as shown in Fig S2

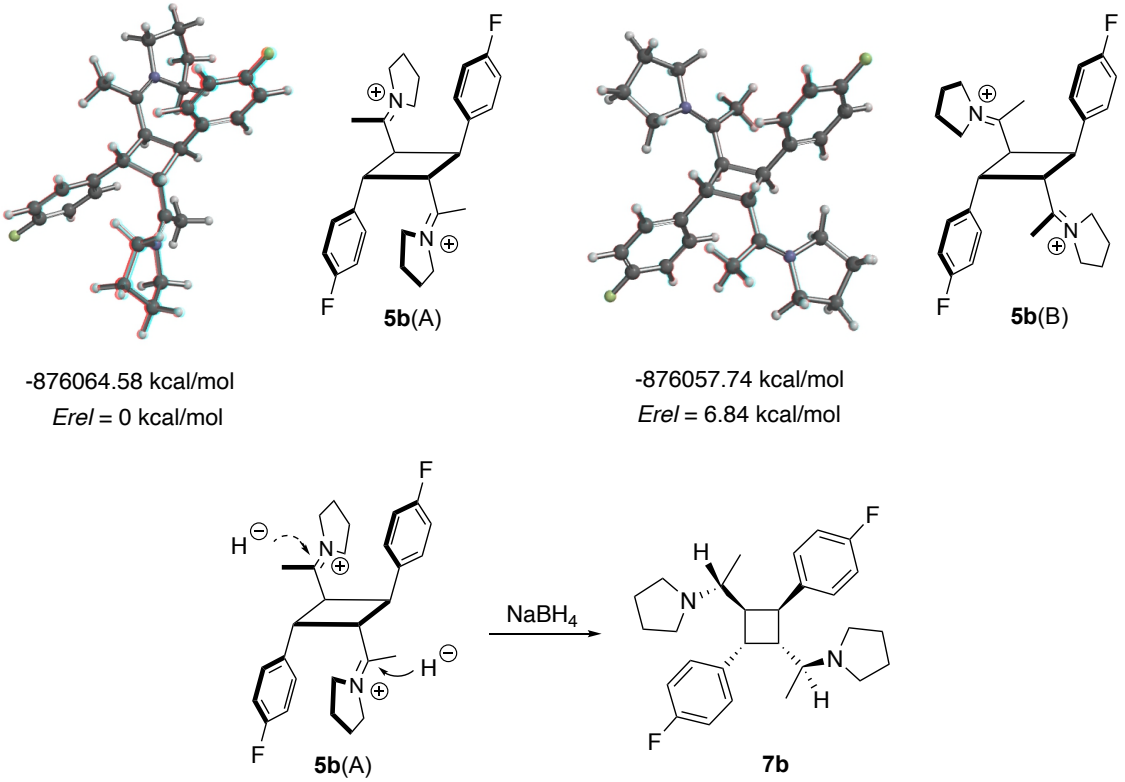


Fig. S2 Two optimized conformers **5b**(A) and **5b**(B), and plausible reduction pathway

7.3 Structure optimization of 6b

The structure optimization of **6b** gave only one conformer, which is shown in Fig S3. This was close to that of crystal structure.

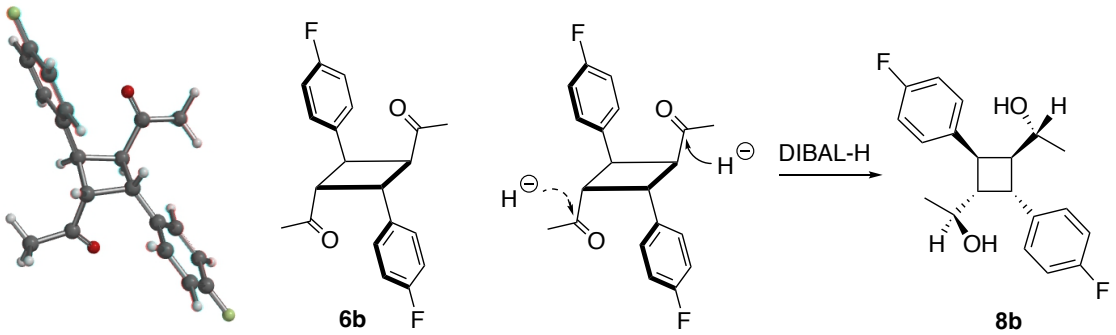
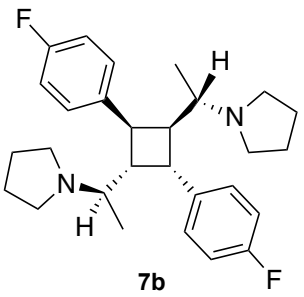


Fig. S3 Optimized geometry of **6b**, and plausible reduction pathway

8. Synthesis of dimer derivatives

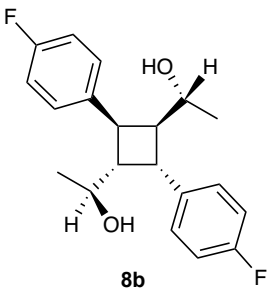
8.1 Synthesis of 7b



7b

The powdered crystal of iminium salt **3b** (99.8 mg, 0.33mmol) was spread thinly in a circular shape about 10 cm in diameter and sandwiched between two glass plates, which was irradiated with a 365 nm 18W LED lamp for 3h. The reaction mixture was dissolved in dry MeOH (4 mL), and $NaBH_4$ (6.2 mg) was added to the solution. After stirring for overnight at rt, saturated NH_4Cl solution was added and the reaction mixture was extracted with dichloromethane. The organic layer was washed with brine, and dried over anhydrous magnesium sulfate. The solution was filtered, and the solvent was removed under reduced pressure to give crude **7b**. This was recrystallized from CH2Cl2/ether to give white crystals (57.3 mg, 80% from **3b**). Colorless crystal. mp 170~172 °C. IR (KBr) 2962, 2805, 1602, 1507, 1458, 1369, 1219, 1162, 1139, 855, 817 cm^{-1}. ^1H NMR (600MHz, $CDCl_3$) δ 0.35 (d, *J* = 6.6 Hz, 6H), 1.33-1.40 (m, 4H), 1.43-1.47 (m, 4H), 2.14-2.17 (m, 4H)、2.24-2.17 (m, 4H), 2.63-2.68 (m, 2H), 2.72-2.77 (m, 2H), 3.78 (dd, *J* = 10.2, 7.2 Hz, 2H), 7.00 (t, *J* = 9,0 Hz, 4H), 7.26-7.32 (m, 4H).^{13}C NMR (150 MHz, $CDCl_3$) δ 10.3, 23.5, 43.0, 47.7, 48.6, 54.9, 114.9 (*J* = 21 Hz), 130.2 (*J* = 7.5 Hz), 138.7, 161.3 (*J* = 243 Hz). HRMS (ESI-QTOF) calcd for $C_{28}H_{37}N_2F_2$ $[M+H]^+$ 439.2919, found 439.2930.

8.2 Synthesis of 8b from 3b



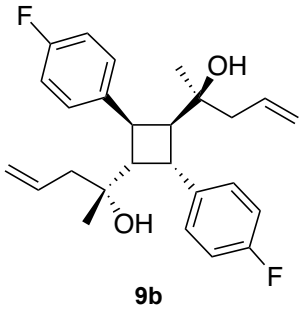
8b

The powdered crystal of iminium salt **3b** (57.2 mg, 0.18 mmol) was spread thinly in a circular shape about 10 cm in diameter and sandwiched between two glass plates, which was irradiated with a 365 nm 18W LED lamp for 3h. The photoproduct was hydrolized to diketone **6b** with PPTS as described above. To a solution of the diketone **6b** in dry CH_2Cl_2 (2mL) was added 1.0M DIBAL-H in hexane (0.3 ml) at -30°C. After stirring for 2h, saturated NH_4Cl solution was added and the reaction mixture was extracted with dichloromethane. The organic layer was washed with brine, and dried over anhydrous magnesium sulfate. The solution was filtered, and the solvent was removed under reduced pressure to give white solid (17 mg, 59% from **3b**). Colorless crystal. mp 177~179 °C. IR (KBr) 3545, 3446, 2975, 2923, 1603, 1507, 1374, 1225, 1158, 1127, 1071, 986, 909, 886, 842, 751, 623, 542 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$) δ 0.91 (d, *J* = 6.4 Hz, 6H), 1.02 (br s, 2H), 2.82 (dd, *J* = 16.9, 9.6 Hz, 2H), 3.42 (dd, *J* = 9.6, 7.6 Hz, 2H), 3.77 (t, *J* = 7.6 Hz, 2H), 7.08-7,13 (m, 4H), 7.38-7.42 (m, 4H). ^{13}C NMR

(150 MHz, $CDCl_3$) δ 20.0, 41.7, 49.1, 68.2, 116.1 (*J* = 21 Hz), 129.9 (*J* = 7.5 Hz), 135.8 (*J* = 3 Hz), 162.0 (*J* = 245 Hz). HRMS (ESI-QTOF) calcd for $C_{20}H_{22}F_2NaO_2$ $[M+Na]^+$ 355.1480, found 355.1484.

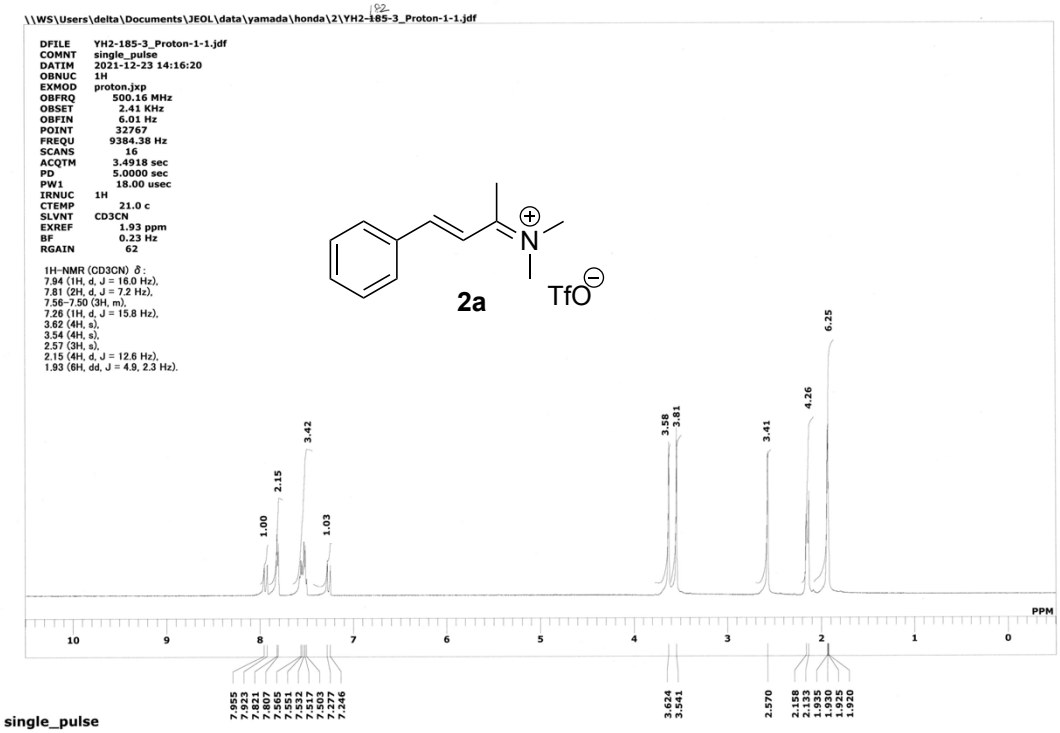
8.3 Synthesis of 9b from 3b

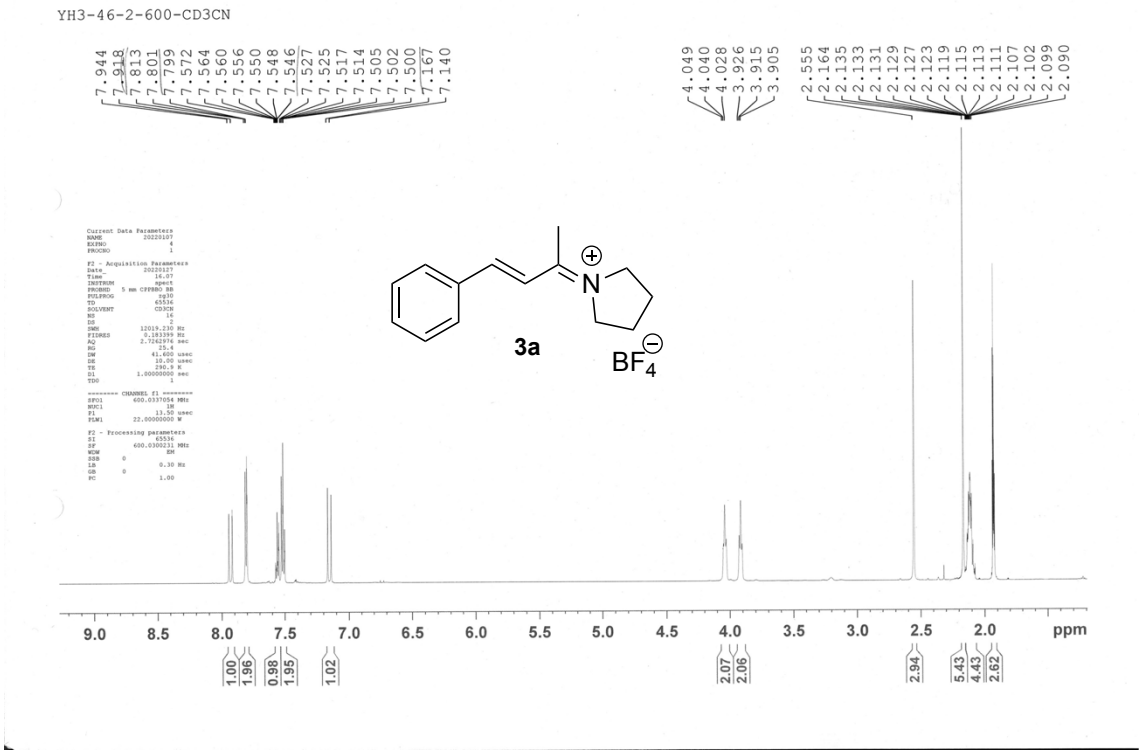
The powdered crystal of iminium salt **3b** (70 mg, 0.23 mmol) was spread thinly in a circular shape about 10 cm in diameter and sandwiched between two glass plates, which was irradiated with a 365 nm 18W LED lamp for 3h. The photoproduct was hydrolized to diketone **6b** with PPTS as described above. To a solution of the crude diketone **6b** (36.5 mg) in dry THF (2mL) was added 1.0 M allyl magnesium chloride in THF (0.4 ml) at 0°C. After stirring for 48h at rt, saturated NH_4Cl solution was added and the reaction mixture was extracted with dichloromethane. The organic layer was washed with brine, and dried over anhydrous magnesium sulfate. The solution was filtered, and the solvent was removed under reduced pressure to give crude product. This was subjected to PTLC in a 3:1 mixture of Hexane/EtOAc to give an 89:11 diastereomeric mixture of **9b** as white solid (37.6 mg, 79.3% yield). IR (KBr) 3580, 3456, 1639, 1603, 1508, 1223, 1159, 1096, 916, 815, 529 cm^{-1}. ^1H NMR (500MHz, $CDCl_3$) δ 0.84 (s, 6H), 1.16 (br s, 2H), 1.26 (t, *J* = 7.5 Hz, 2H), 1.81 (dd, *J* = 7.0, 14.0 Hz, 2H), 1.91 (dd, *J* = 7.0, 14.0 Hz, 2H), 3.02-3.07 (m, 2H), 4.10-4.14 (m, 2H), 4.78 (dd, *J* = 2.0, 17.0 Hz, 2H), 4.95 (dd, *J* = 2.0, 10.0 Hz), 5.54-5.61 (m, 2H), 7.01-7.06 (m, 4H), 7.45-7.51 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 25.1, 41.1, 45.6, 50.7, 74.6, 115.3 (*J* = 21 Hz), 118.8 (*J* = 4.5 Hz), 131.3 (*J* = 7.5 Hz), 133.5, 137.6, 161.6 (*J* = 243 Hz). HRMS (ESI-QTOF) calcd for $C_{26}H_{29}F_2O_2$ $[M-1]^+$ 411.2142, found 411.2141.

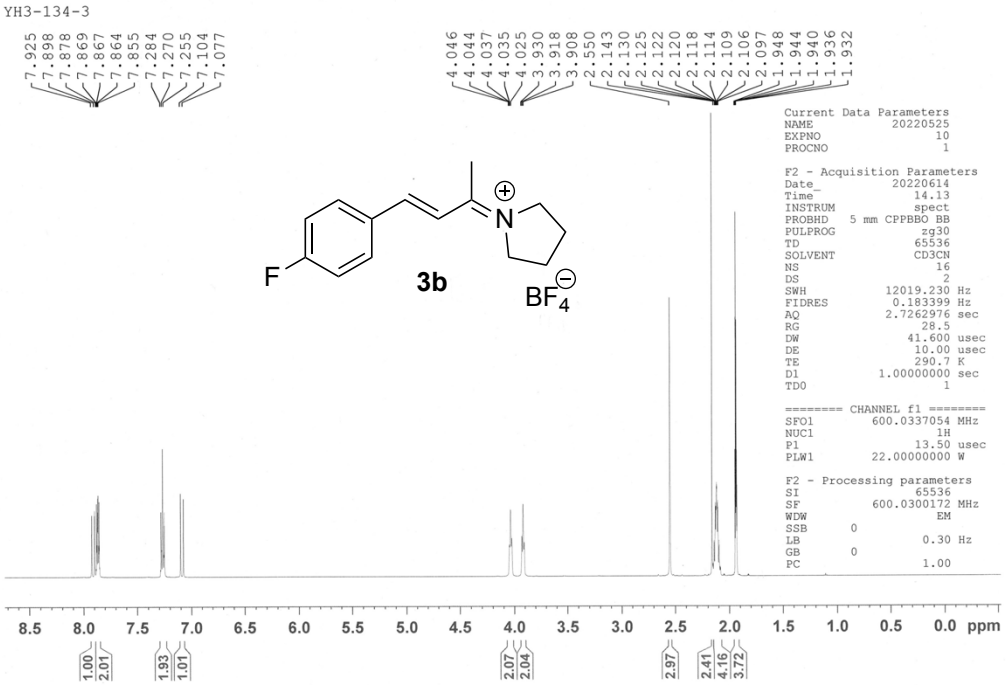


9b

9. ^{1}H NMR spectra for 2a, 3a-3h, 5b and 6a-6h



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7.284
7.270
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7.104
7.077
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4.044
4.037
4.035
4.025
3.930
3.918
3.908
2.550
2.143
2.130
2.125
2.122
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Time 14.13
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DS 2
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DW 41.600 usec
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1.01
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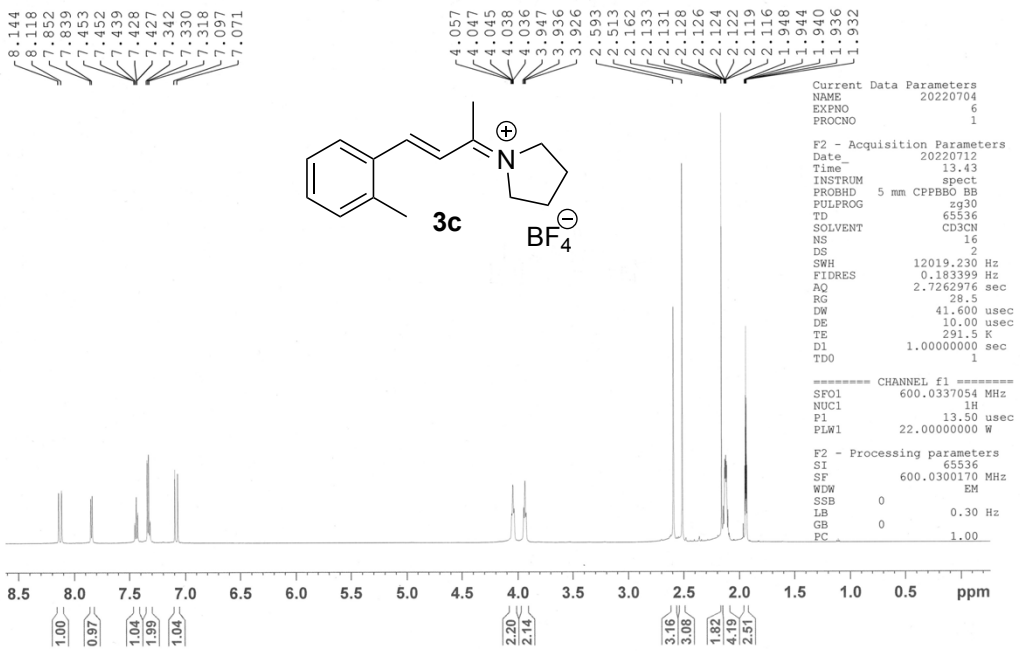
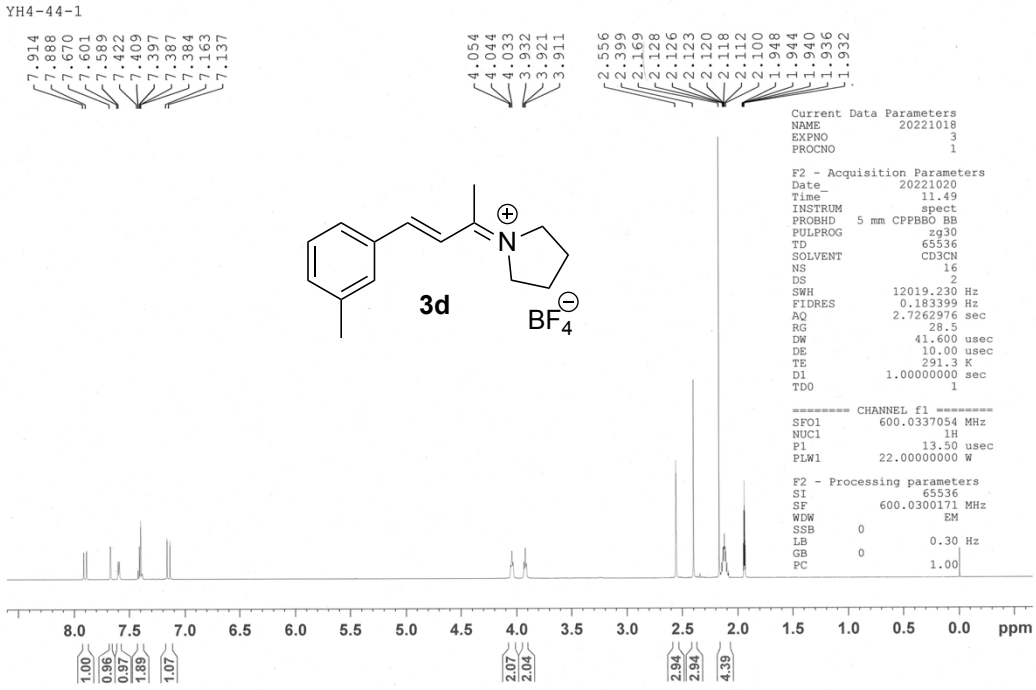
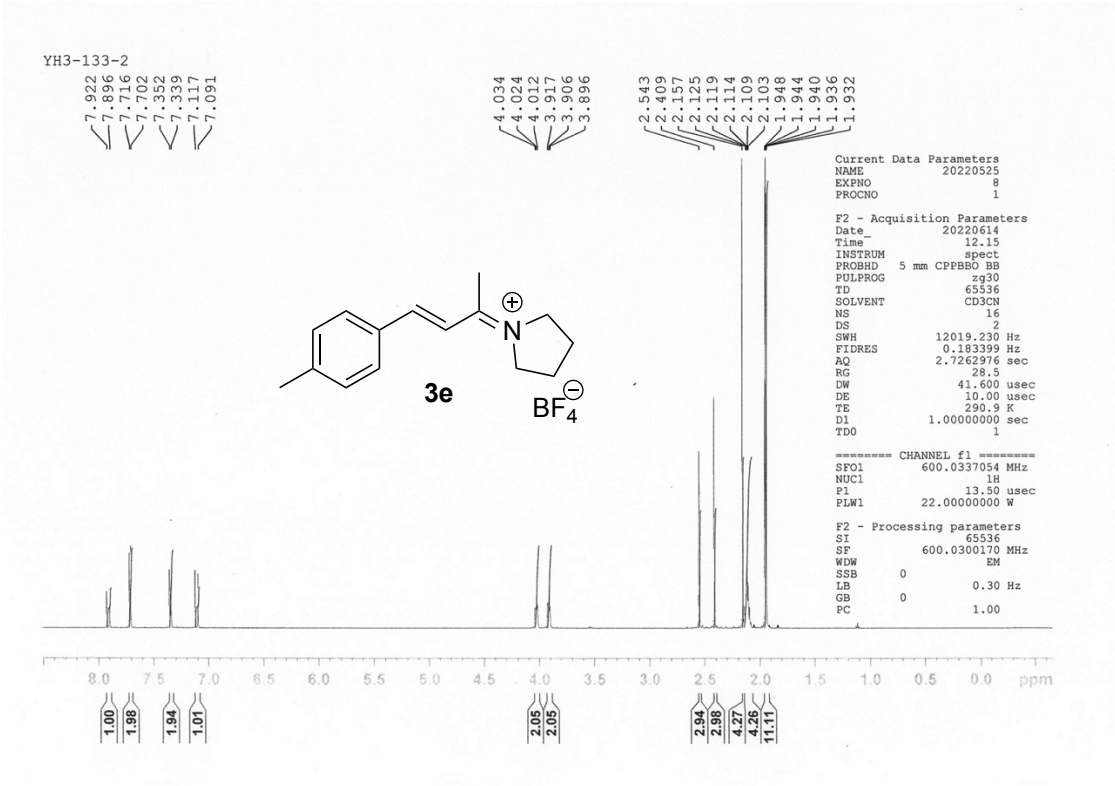
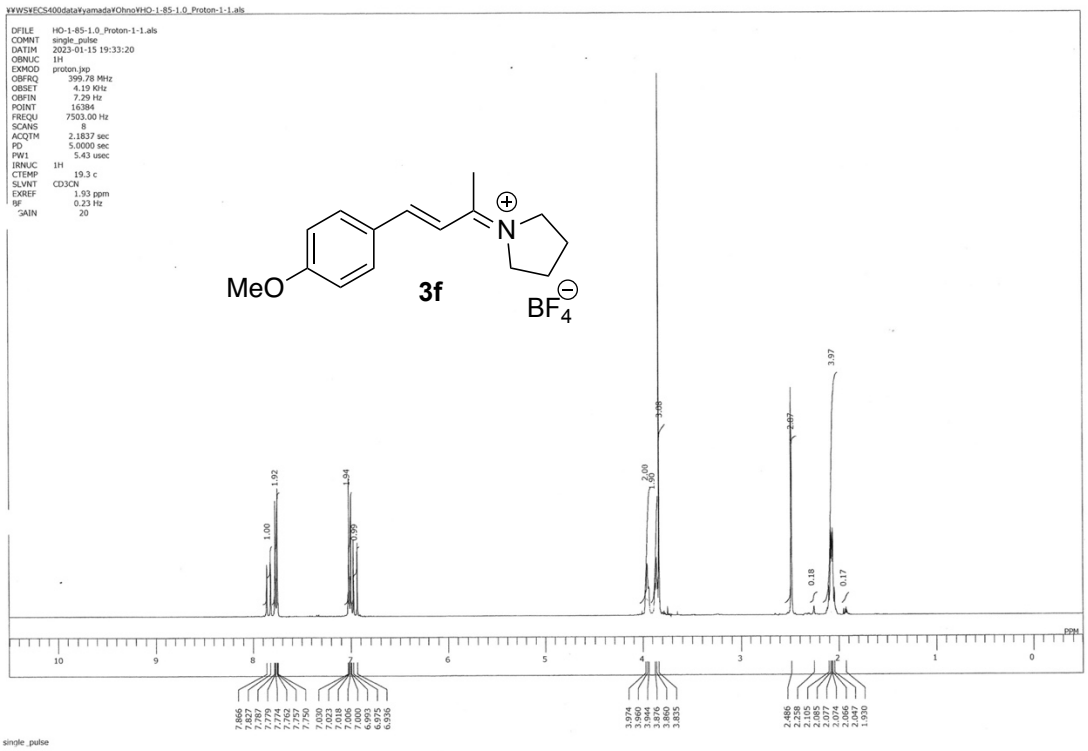
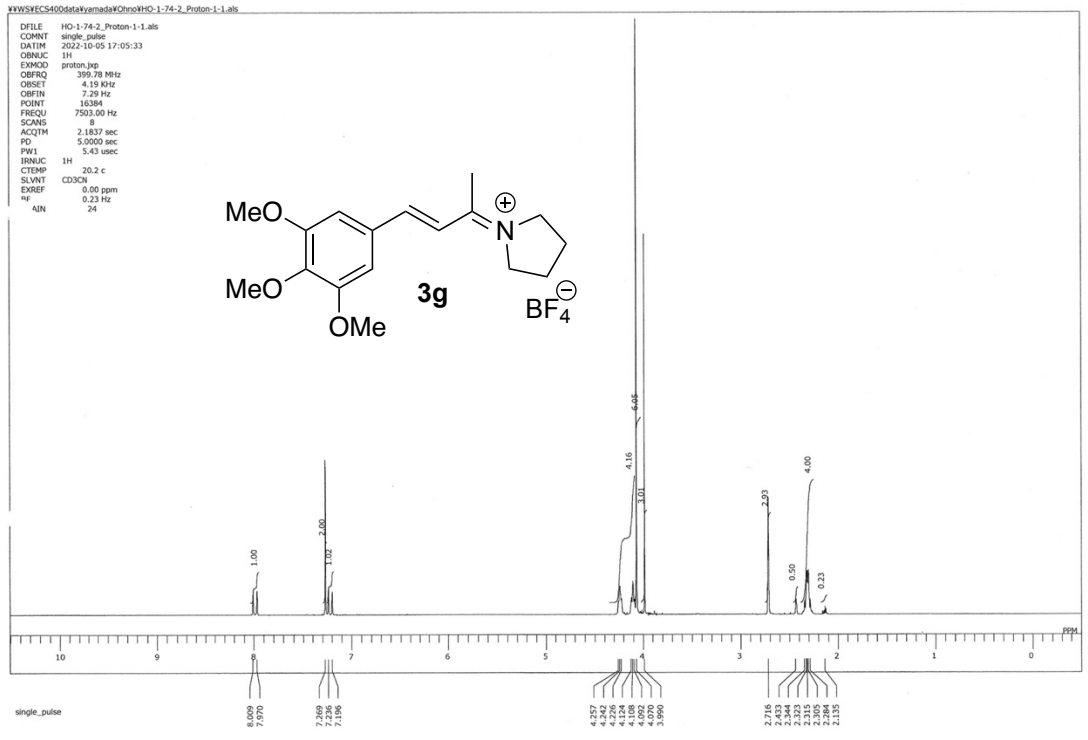


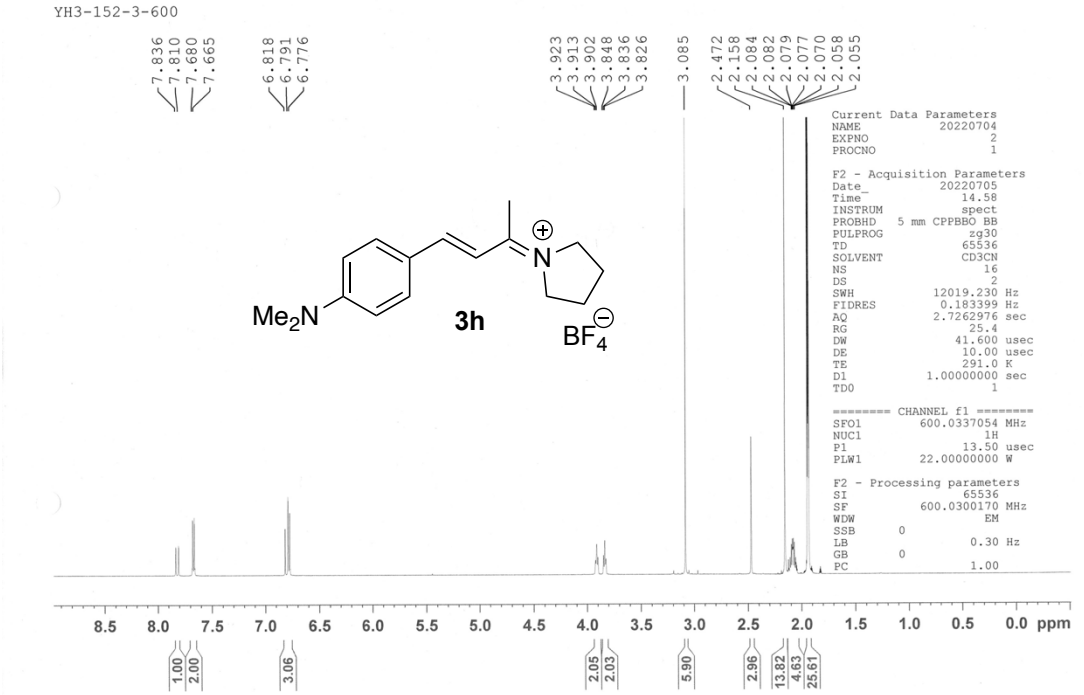
YH4-44-1

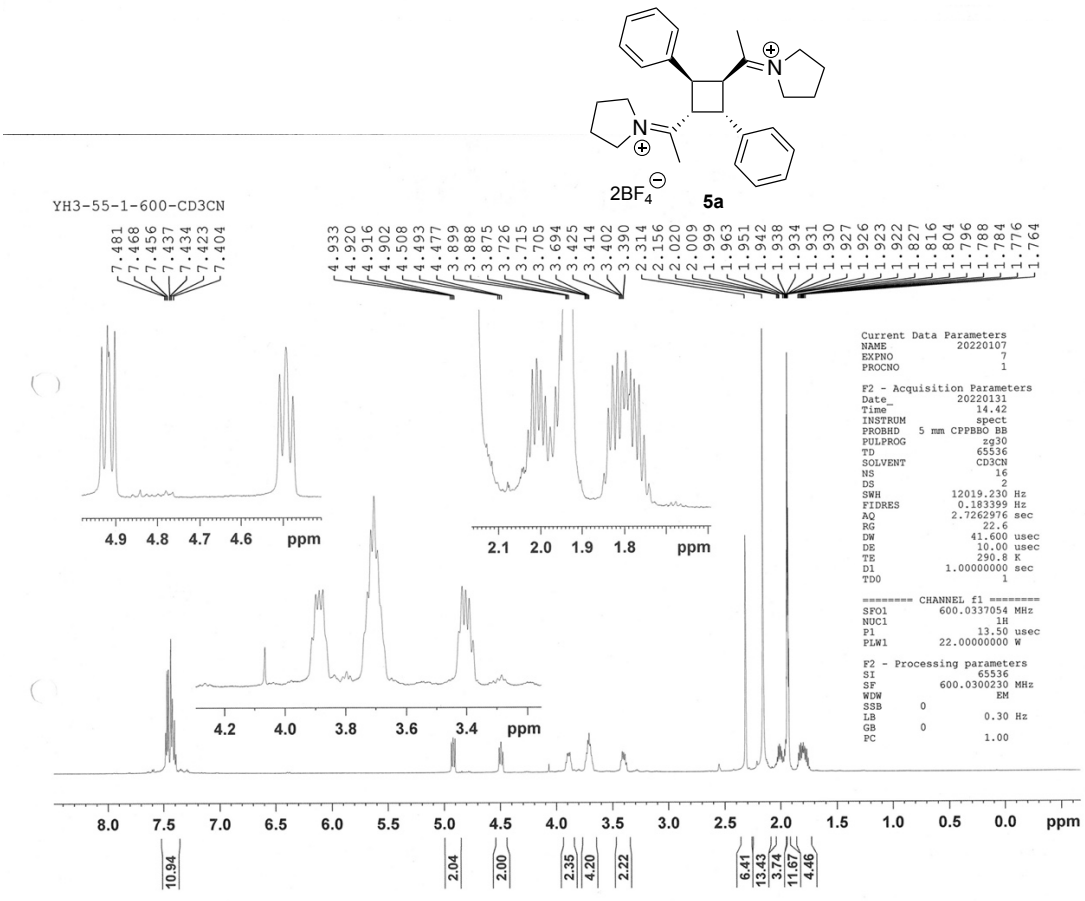


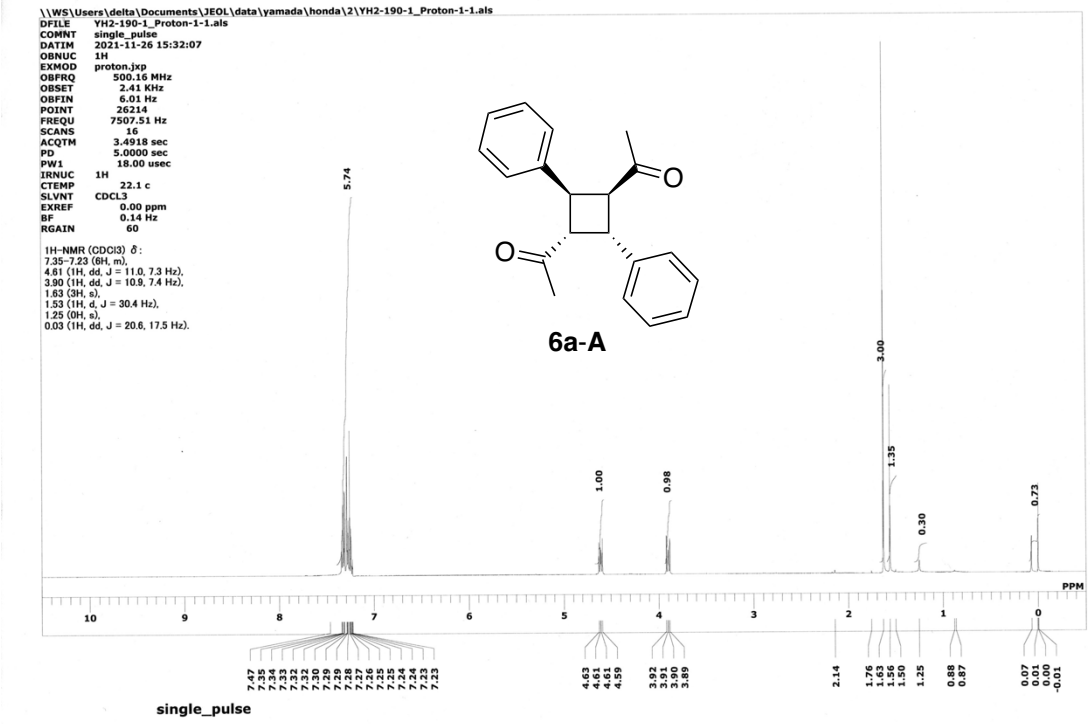

YH3-133-2
7.922
7.896
7.716
7.702
7.352
7.339
7.117
7.091
4.034
4.024
4.012
3.917
3.906
3.896
2.543
2.409
2.157
2.125
2.119
2.114
2.109
2.103
1.948
1.944
1.940
1.936
1.932
3e
BF4
Current Data Parameters
NAME 20220525
EXPNO 8
PROCNO 1
F2 - Acquisition Parameters
Date_ 20220614
Time 12.15
INSTRUM spect
PROBHD 5 mm CPPBBO BB
PULPROG zg30
TD 65536
SOLVENT CD3CN
NS 16
DS 2
SWH 12019.230 Hz
FIDRES 0.183399 Hz
AQ 2.7262976 sec
RG 28.5
DW 41.600 usec
DE 10.00 usec
TE 290.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 600.0337054 MHz
NUC1 1H
P1 13.50 usec
PLW1 22.00000000 W
F2 - Processing parameters
SI 65536
SF 600.0300170 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.98
1.94
1.01
2.05
2.05
2.94
2.98
4.27
4.26
11.11

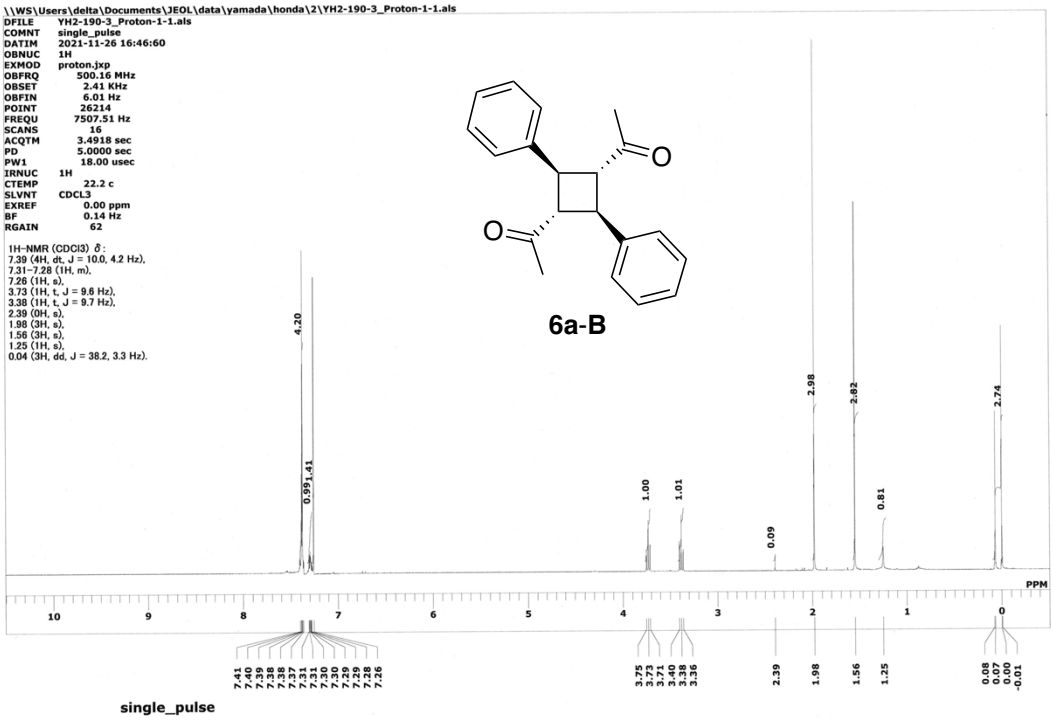

¥¥WS¥ECS400data¥yamada¥Ohno¥HO-1-85-1.0_Proton-1-1.als
DFILE HO-1-85-1.0_Proton-1-1.als
COMNT single_pulse
DATIM 2023-01-15 19:33:20
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 16384
FREQU 7503.00 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.43 usec
IRNUC 1H
CTEMP 19.3 c
SLVNT CD3CN
EXREF 1.93 ppm
BF 0.23 Hz
SAIN 20
MeO
3f
BF4
single_pulse

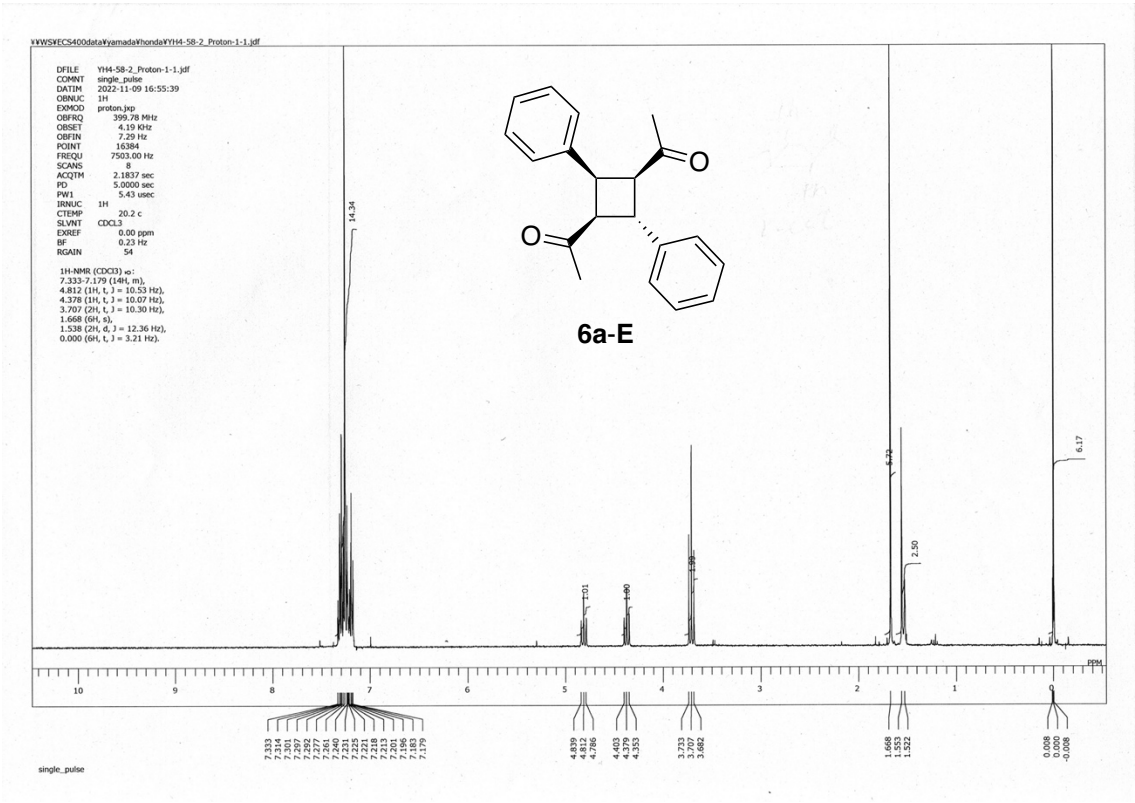

¥¥WS¥ECS400data¥yamada¥Ohno¥HO-1-74-2_Proton-1-1.als
DFILE HO-1-74-2_Proton-1-1.als
COMNT single_pulse
DATIM 2022-10-05 17:05:33
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 16384
FREQU 7503.00 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.43 usec
IRNUC 1H
CTEMP 20.2 c
SLVNT CD3CN
EXREF 0.00 ppm
BF 0.23 Hz
SAIN 24
MeO
MeO
OMe
3g
BF4
single_pulse

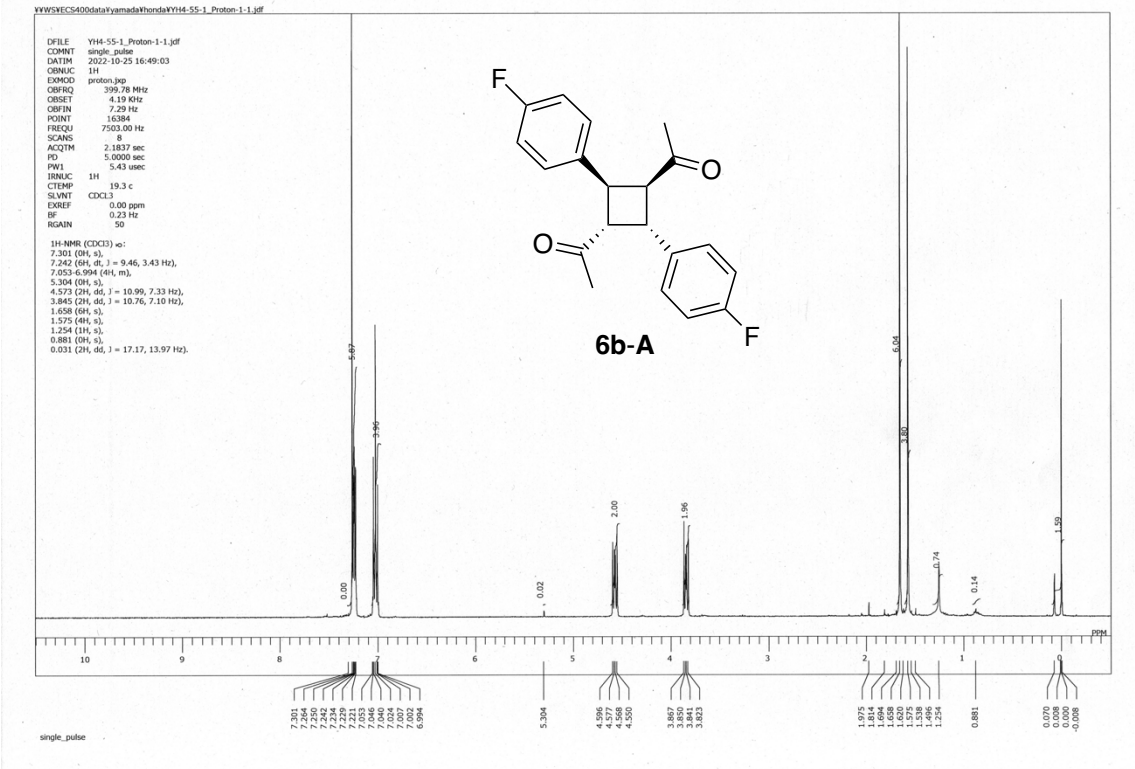

YH3-152-3-600
7.836
7.810
7.680
7.665
6.818
6.791
6.776
3.923
3.913
3.902
3.848
3.836
3.826
3.085
2.472
2.158
2.084
2.082
2.079
2.077
2.070
2.058
2.055
Me2N
3h
BF4
Current Data Parameters
NAME 20220704
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20220705
Time 14.58
INSTRUM spect
PROBHD 5 mm CPPBBO BB
PULPROG zg30
TD 65536
SOLVENT CD3CN
NS 16
DS 2
SWH 12019.230 Hz
FIDRES 0.183399 Hz
AQ 2.7262976 sec
RG 25.4
DW 41.600 usec
DE 10.00 usec
TE 291.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 600.0337054 MHz
NUC1 1H
P1 13.50 usec
PLW1 22.00000000 W
F2 - Processing parameters
SI 65536
SF 600.0300170 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
2.00
3.06
2.05
2.03
5.90
2.96
13.82
4.63
25.61

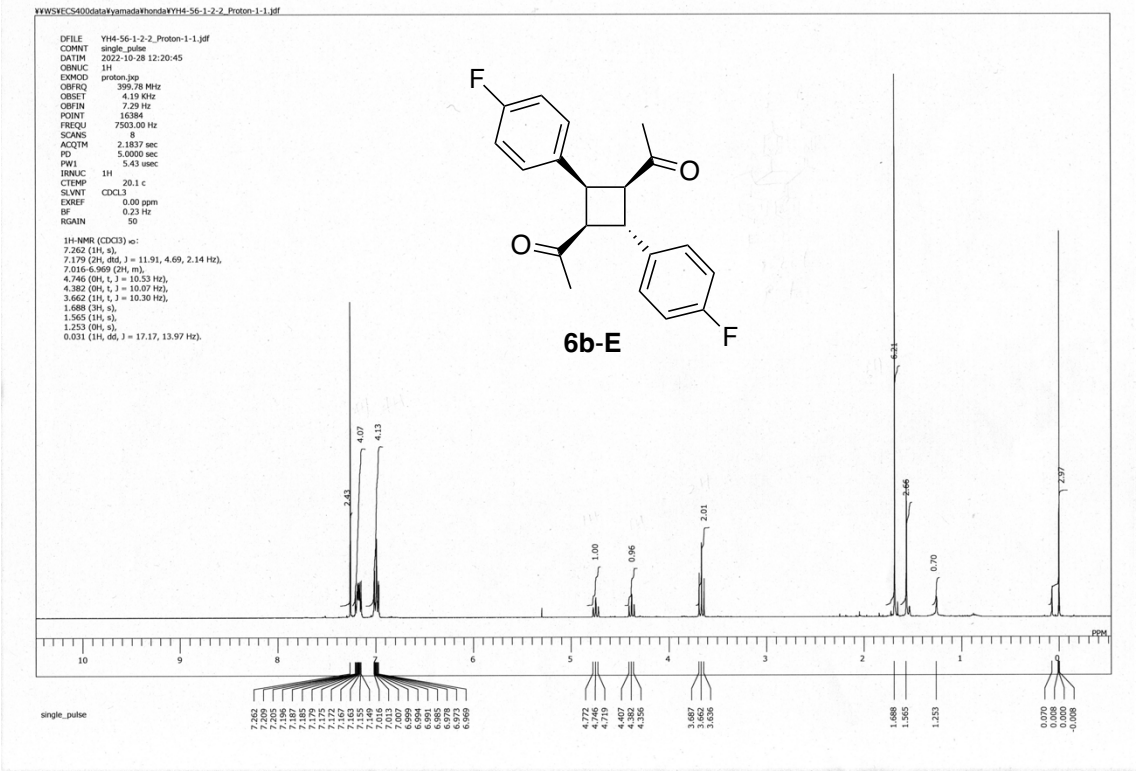

2BF4
5a
YH3-55-1-600-CD3CN
7.481
7.468
7.456
7.437
7.434
7.423
7.404
4.933
4.920
4.916
4.902
4.508
4.493
4.477
3.899
3.888
3.875
3.726
3.715
3.705
3.694
3.425
3.414
3.402
3.390
2.314
2.156
2.020
2.009
1.999
1.963
1.951
1.942
1.938
1.934
1.931
1.930
1.927
1.926
1.923
1.922
1.827
1.816
1.804
1.796
1.788
1.784
1.776
1.764
4.9 4.8 4.7 4.6 ppm
2.1 2.0 1.9 1.8 ppm
4.2 4.0 3.8 3.6 3.4 ppm
Current Data Parameters
NAME 20220107
EXPNO 7
PROCNO 1
F2 - Acquisition Parameters
Date_ 20220131
Time 14.42
INSTRUM spect
PROBHD 5 mm CPPBBO BB
PULPROG zg30
TD 65536
SOLVENT CD3CN
NS 16
DS 2
SWH 12019.230 Hz
FIDRES 0.183399 Hz
AQ 2.7262976 sec
RG 22.6
DW 41.600 usec
DE 10.00 usec
TE 290.8 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 600.0337054 MHz
NUC1 1H
P1 13.50 usec
PLW1 22.00000000 W
F2 - Processing parameters
SI 65536
SF 600.0300230 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
10.94
2.04
2.00
2.35
4.20
2.22
6.41
13.43
3.74
11.67
4.46

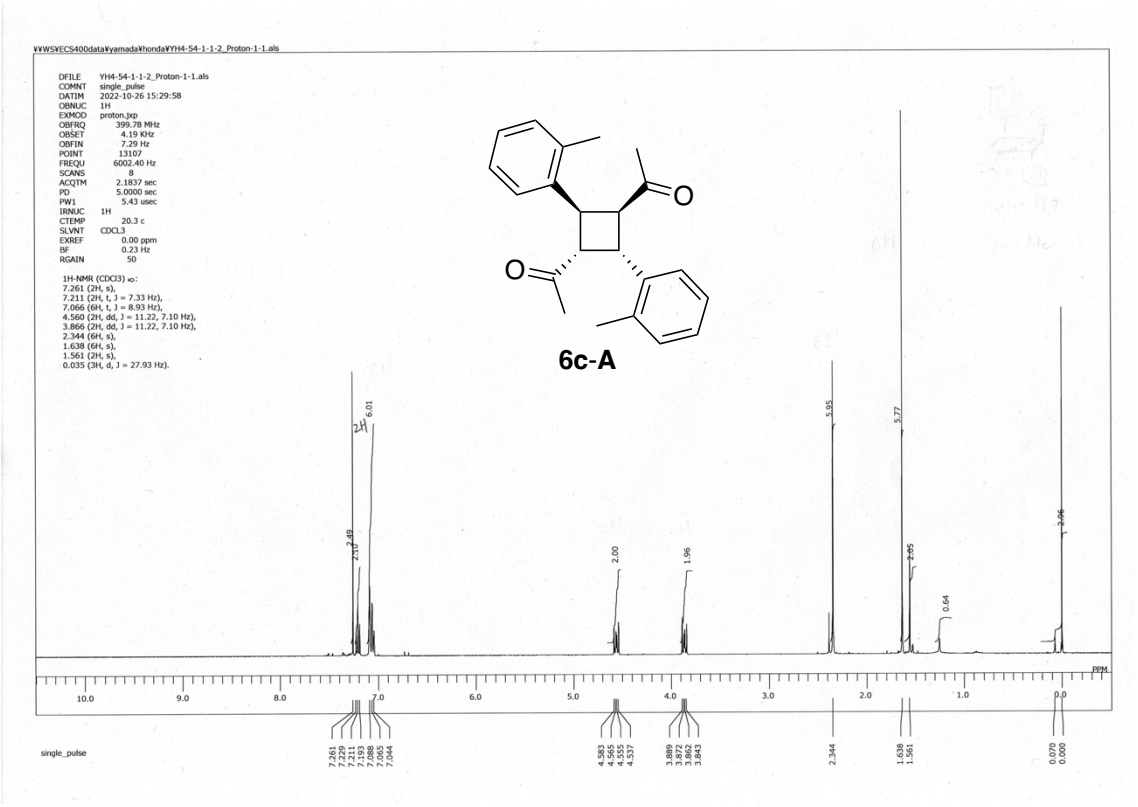

\\WS\Users\delta\Documents\JEOL\data\yamada\honda\2\YH2-190-1_Proton-1-1.als
DFILE YH2-190-1_Proton-1-1.als
COMNT single_pulse
DATIM 2021-11-26 15:32:07
OBNUC 1H
EXMOD proton.jxp
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 26214
FREQU 7507.51 Hz
SCANS 16
ACQTM 3.4918 sec
PD 5.0000 sec
PW1 18.00 usec
IRNUC 1H
CTEMP 22.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.14 Hz
RGAIN 60
1H-NMR (CDCl3) δ :
7.35–7.23 (6H, m),
4.61 (1H, dd, J = 11.0, 7.3 Hz),
3.90 (1H, dd, J = 10.9, 7.4 Hz),
1.63 (3H, s),
1.53 (1H, d, J = 30.4 Hz),
1.25 (0H, s),
0.03 (1H, dd, J = 20.6, 17.5 Hz).
6a-A
single_pulse
PPM

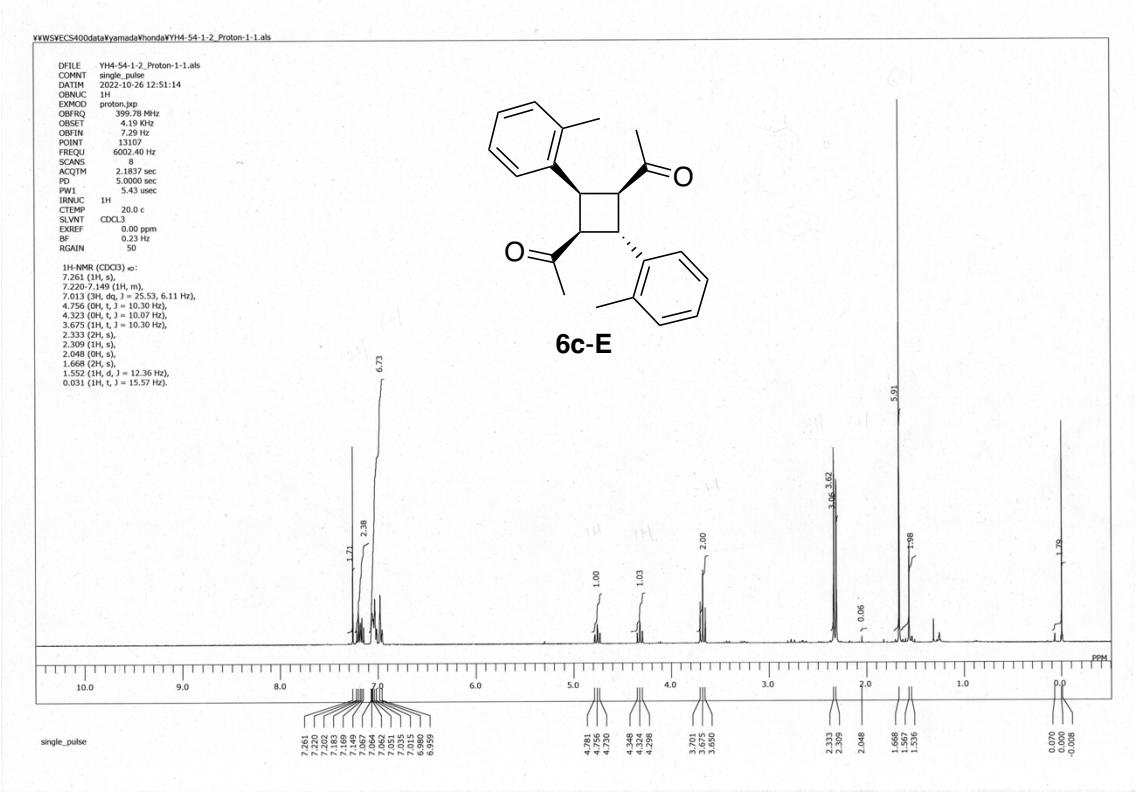

\\WS\Users\delta\Documents\JEOL\data\yamada\honda\2\YH2-190-3_Proton-1-1.als
DFILE YH2-190-3_Proton-1-1.als
COMNT single_pulse
DATIM 2021-11-26 16:46:60
OBNUC 1H
EXMOD proton.jxp
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 26214
FREQU 7507.51 Hz
SCANS 16
ACQTM 3.4918 sec
PD 5.0000 sec
PW1 18.00 usec
IRNUC 1H
CTEMP 22.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.14 Hz
RGAIN 62
1H-NMR (CDCl3) δ :
7.39 (4H, dt, J = 10.0, 4.2 Hz),
7.31–7.28 (1H, m),
7.26 (1H, s),
3.73 (1H, t, J = 9.6 Hz),
3.38 (1H, t, J = 9.7 Hz),
2.39 (0H, s),
1.98 (3H, s),
1.56 (3H, s),
1.25 (1H, s),
0.04 (3H, dd, J = 38.2, 3.3 Hz).
6a-B
single_pulse
PPM

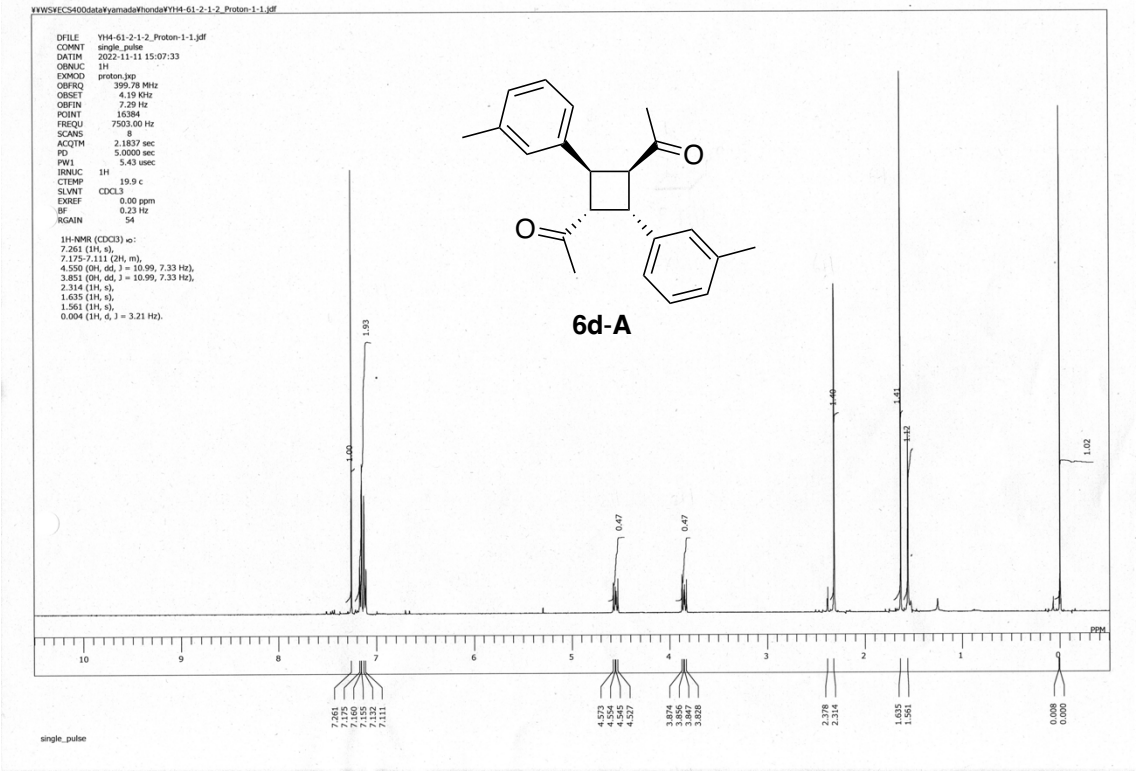

¥¥WS¥ECS400data¥yamada¥honda¥YH4-58-2_Proton-1-1.jdf
DFILE YH4-58-2_Proton-1-1.jdf
COMNT single_pulse
DATIM 2022-11-09 16:55:39
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 16384
FREQU 7503.00 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.43 usec
IRNUC 1H
CTEMP 20.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.23 Hz
RGAIN 54
1H-NMR (CDCl3) ¤o:
7.333-7.179 (14H, m),
4.812 (1H, t, J = 10.53 Hz),
4.378 (1H, t, J = 10.07 Hz),
3.707 (2H, t, J = 10.30 Hz),
1.668 (6H, s),
1.538 (2H, d, J = 12.36 Hz),
0.000 (6H, t, J = 3.21 Hz).
O
O
6a-E
single_pulse
PPM

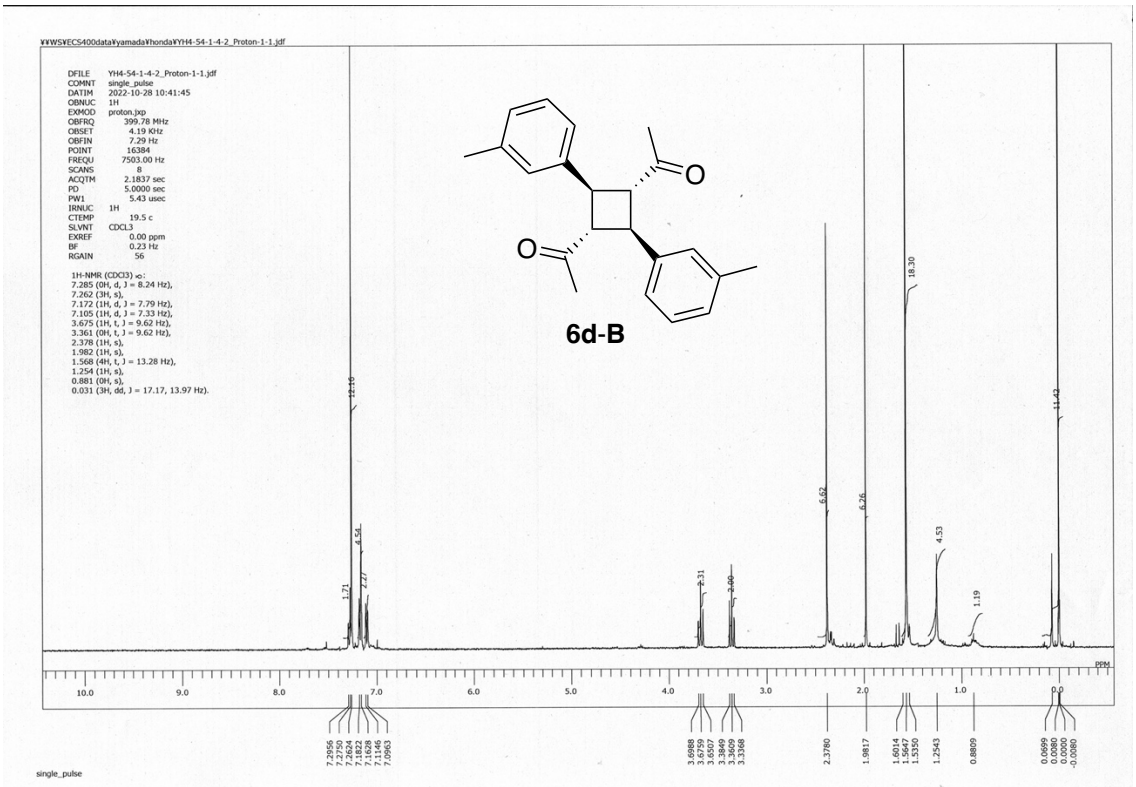

¥¥WS¥ECS400data¥yamada¥honda¥YH4-55-1_Proton-1-1.jdf
DFILE YH4-55-1_Proton-1-1.jdf
COMNT single_pulse
DATIM 2022-10-25 16:49:03
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 16384
FREQU 7503.00 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.43 usec
IRNUC 1H
CTEMP 19.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.23 Hz
RGAIN 50
1H-NMR (CDCl3) ¤o:
7.301 (0H, s),
7.242 (6H, dt, J = 9.46, 3.43 Hz),
7.053-6.994 (4H, m),
5.304 (0H, s),
4.573 (2H, dd, J = 10.99, 7.33 Hz),
3.845 (2H, dd, J = 10.76, 7.10 Hz),
1.658 (6H, s),
1.575 (4H, s),
1.254 (1H, s),
0.881 (0H, s),
0.031 (2H, dd, J = 17.17, 13.97 Hz).
F
O
O
F
6b-A
single_pulse
PPM

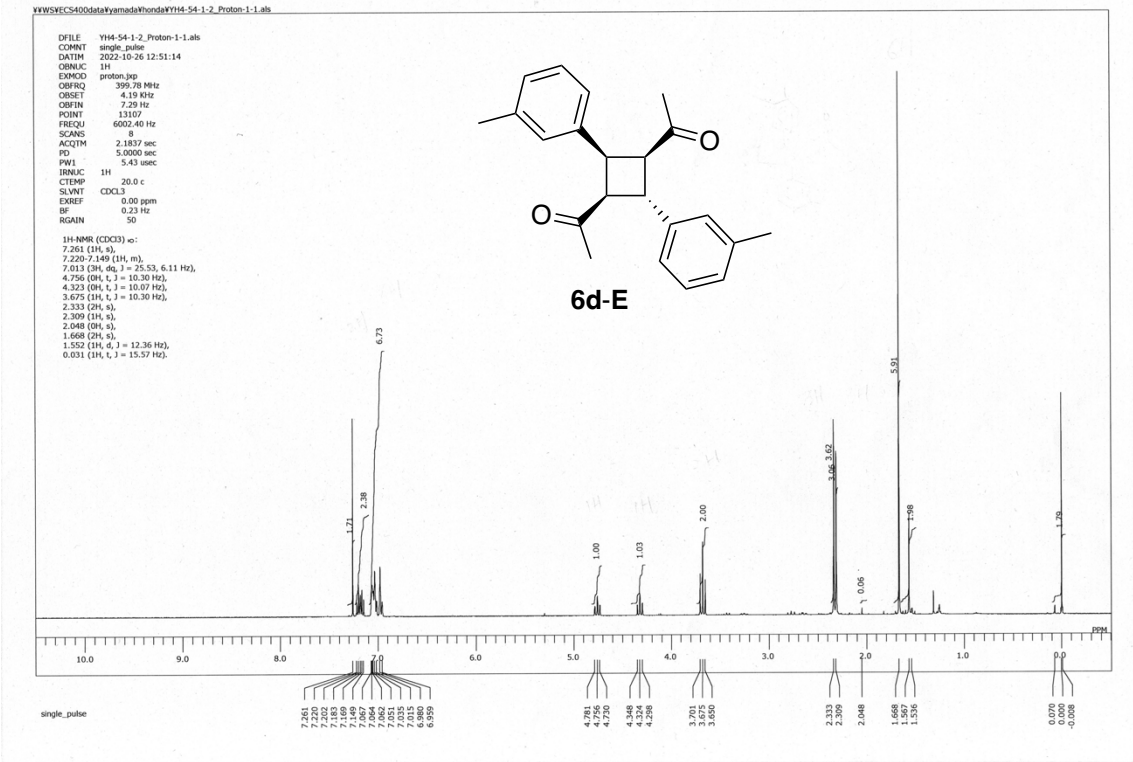

¥¥WS¥ECS400data¥yamada¥honda¥YH4-56-1-2-2_Proton-1-1.jdf
DFILE YH4-56-1-2-2_Proton-1-1.jdf
COMNT single_pulse
DATIM 2022-10-28 12:20:45
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 16384
FREQU 7503.00 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.43 usec
IRNUC 1H
CTEMP 20.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.23 Hz
RGAIN 50
1H-NMR (CDCl3) ω:
7.262 (1H, s),
7.179 (2H, dtd, J = 11.91, 4.69, 2.14 Hz),
7.016-6.969 (2H, m),
4.746 (0H, t, J = 10.53 Hz),
4.382 (0H, t, J = 10.07 Hz),
3.662 (1H, t, J = 10.30 Hz),
1.688 (3H, s),
1.565 (1H, s),
1.253 (0H, s),
0.031 (1H, dd, J = 17.17, 13.97 Hz).
F
O
O
F
6b-E
2.83
4.07
4.13
1.00
0.96
2.01
6.21
2.66
0.70
2.97
PPM
single_pulse

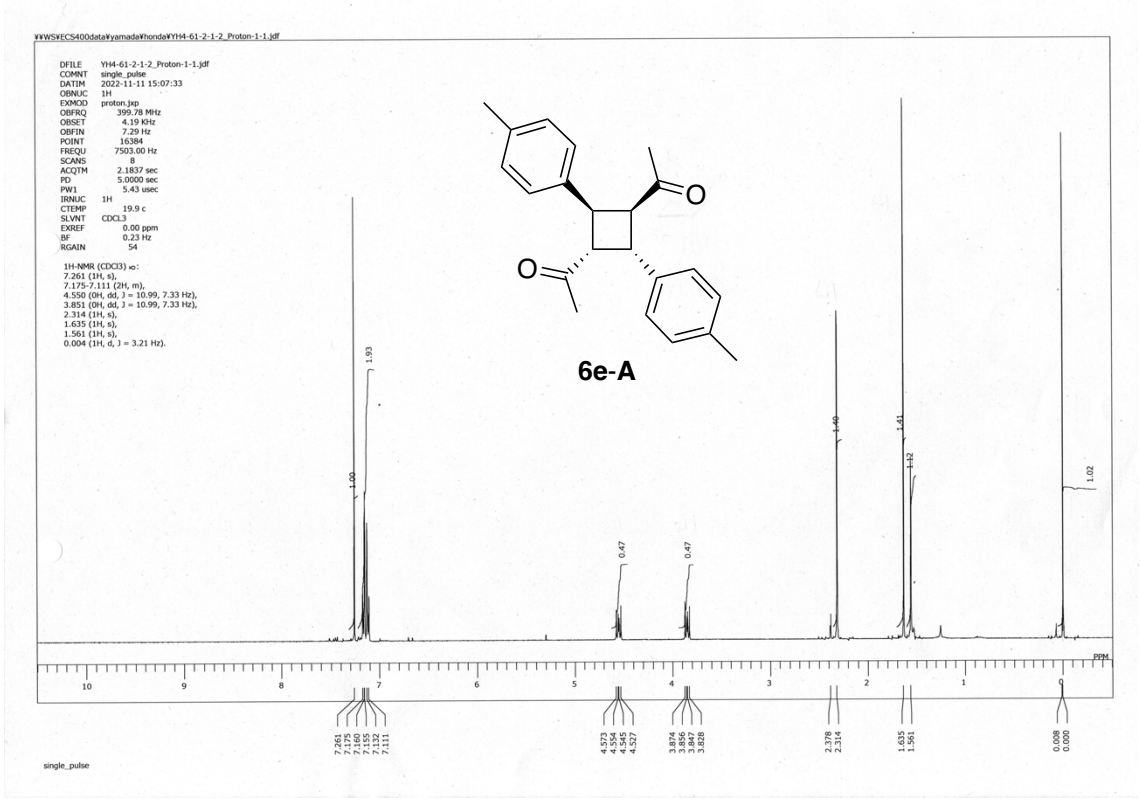

¥¥WS¥ECS400data¥yamada¥honda¥YH4-54-1-1-2_Proton-1-1.als
DFILE YH4-54-1-1-2_Proton-1-1.als
COMNT single_pulse
DATIM 2022-10-26 15:29:58
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.43 usec
IRNUC 1H
CTEMP 20.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.23 Hz
RGAIN 50
1H-NMR (CDCl3) ω:
7.261 (2H, s),
7.211 (2H, t, J = 7.33 Hz),
7.066 (6H, t, J = 8.93 Hz),
4.560 (2H, dd, J = 11.22, 7.10 Hz),
3.866 (2H, dd, J = 11.22, 7.10 Hz),
2.344 (6H, s),
1.638 (6H, s),
1.561 (2H, s),
0.035 (3H, d, J = 27.93 Hz).
O
O
6c-A
2H
6.01
2.49
2.00
1.96
5.95
5.77
0.64
2.06
PPM
single_pulse

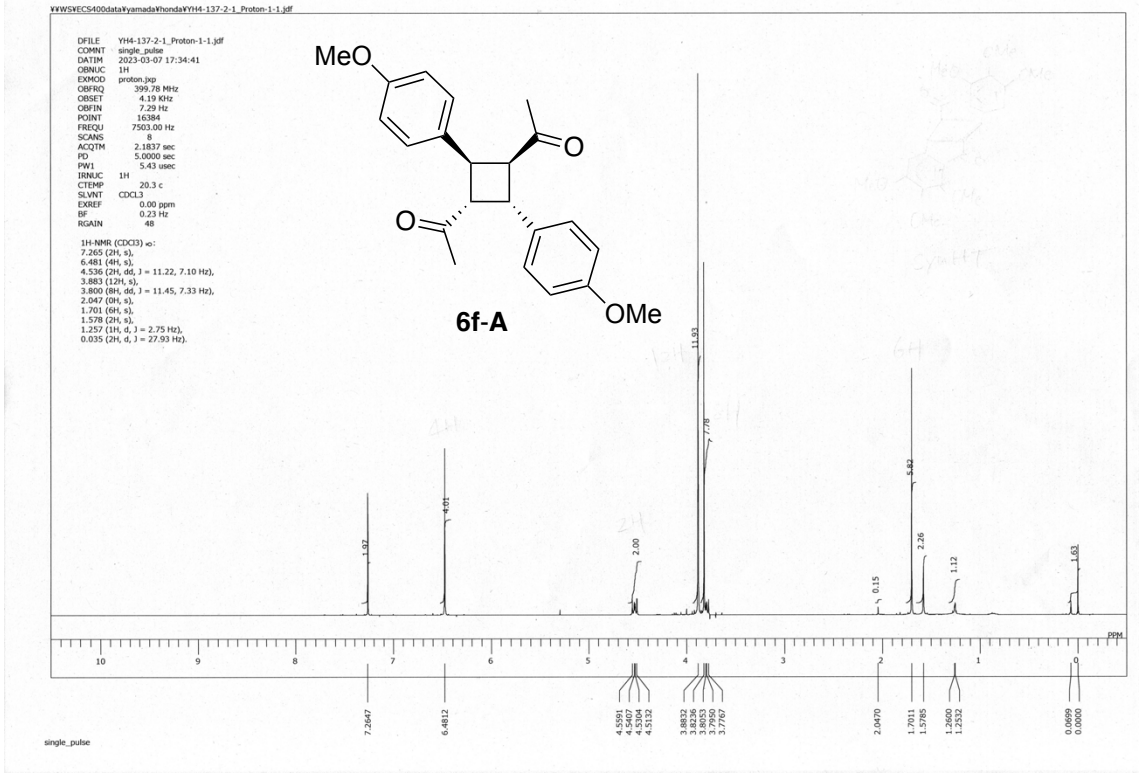

¥¥WS¥ECS400data¥yamada¥honda¥YH4-54-1-2_Proton-1-1.als
DFILE YH4-54-1-2_Proton-1-1.als
COMNT single_pulse
DATIM 2022-10-26 12:51:14
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.43 usec
IRNUC 1H
CTEMP 20.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.23 Hz
RGAIN 50
1H-NMR (CDCl3) ∞:
7.261 (1H, s),
7.220-7.149 (1H, m),
7.013 (3H, dq, J = 25.53, 6.11 Hz),
4.756 (0H, t, J = 10.30 Hz),
4.323 (0H, t, J = 10.07 Hz),
3.675 (1H, t, J = 10.30 Hz),
2.333 (2H, s),
2.309 (1H, s),
2.048 (0H, s),
1.668 (2H, s),
1.552 (1H, d, J = 12.36 Hz),
0.031 (1H, t, J = 15.57 Hz).
O
O
6c-E
6.73
1.71
2.38
1.00
1.03
2.00
3.06
3.62
0.06
5.91
1.98
1.79
ppm
single_pulse

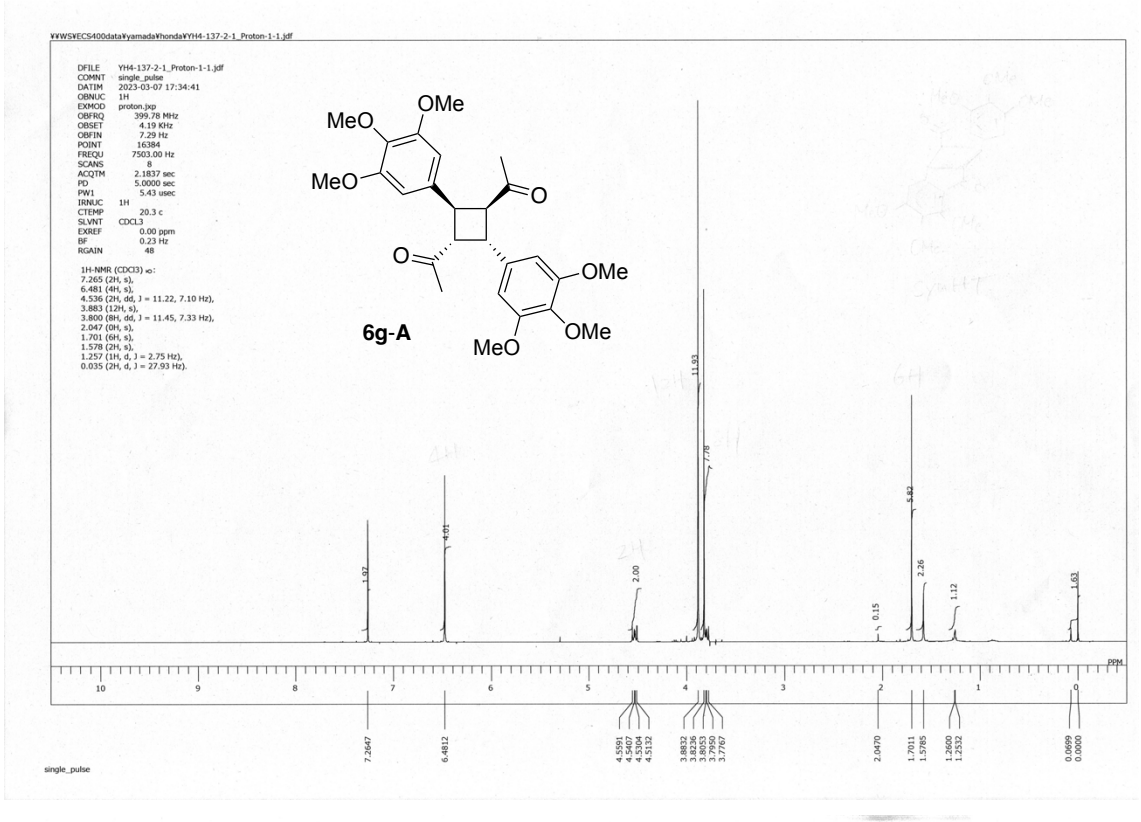

¥¥WS¥ECS400data¥yamada¥honda¥YH4-61-2-1-2_Proton-1-1.jdf
DFILE YH4-61-2-1-2_Proton-1-1.jdf
COMNT single_pulse
DATIM 2022-11-11 15:07:33
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 16384
FREQU 7503.00 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.43 usec
IRNUC 1H
CTEMP 19.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.23 Hz
RGAIN 54
1H-NMR (CDCl3) ∞:
7.261 (1H, s),
7.175-7.111 (2H, m),
4.550 (0H, dd, J = 10.99, 7.33 Hz),
3.851 (0H, dd, J = 10.99, 7.33 Hz),
2.314 (1H, s),
1.635 (1H, s),
1.561 (1H, s),
0.004 (1H, d, J = 3.21 Hz).
O
O
6d-A
1.93
1.00
0.47
0.47
1.40
1.61
1.12
1.02
ppm
single_pulse

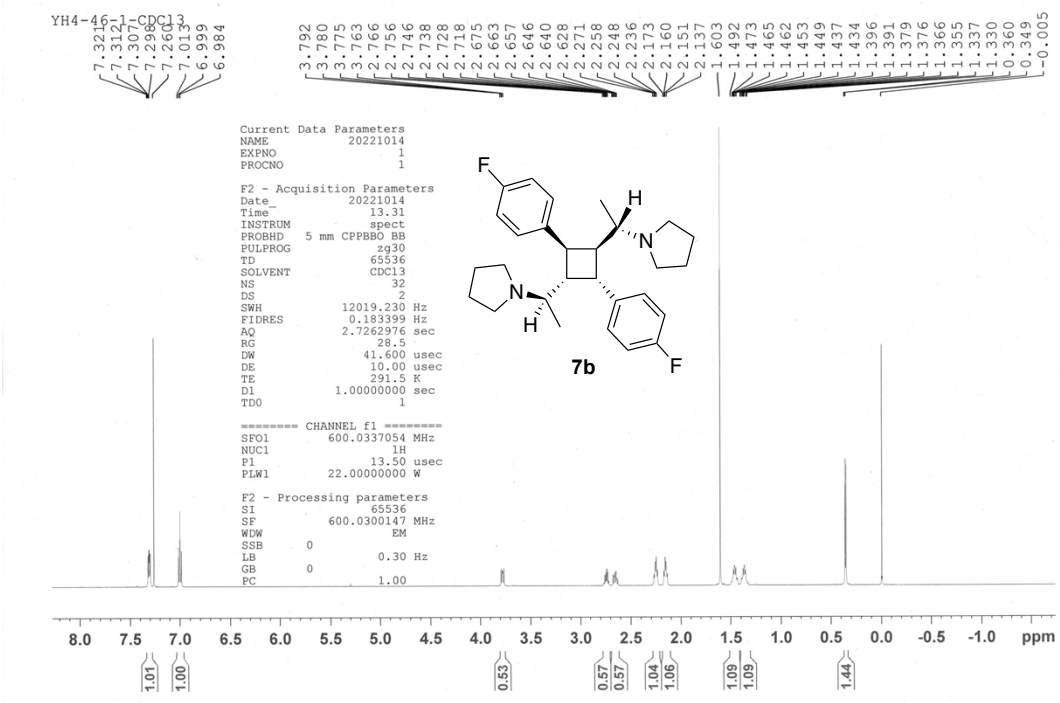

¥¥WS¥ECS400data¥yamada¥honda¥YH4-54-1-4-2_Proton-1-1.jdf
DFILE YH4-54-1-4-2_Proton-1-1.jdf
COMNT single_pulse
DATIM 2022-10-28 10:41:45
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 16384
FREQU 7503.00 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.43 usec
IRNUC 1H
CTEMP 19.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.23 Hz
RGAIN 56
1H-NMR (CDCl3) ω:
7.285 (0H, d, J = 8.24 Hz),
7.262 (3H, s),
7.172 (1H, d, J = 7.79 Hz),
7.105 (1H, d, J = 7.33 Hz),
3.675 (1H, t, J = 9.62 Hz),
3.361 (0H, t, J = 9.62 Hz),
2.378 (1H, s),
1.982 (1H, s),
1.568 (4H, t, J = 13.28 Hz),
1.254 (1H, s),
0.881 (0H, s),
0.031 (3H, dd, J = 17.17, 13.97 Hz).
6d-B
single_pulse
ppm

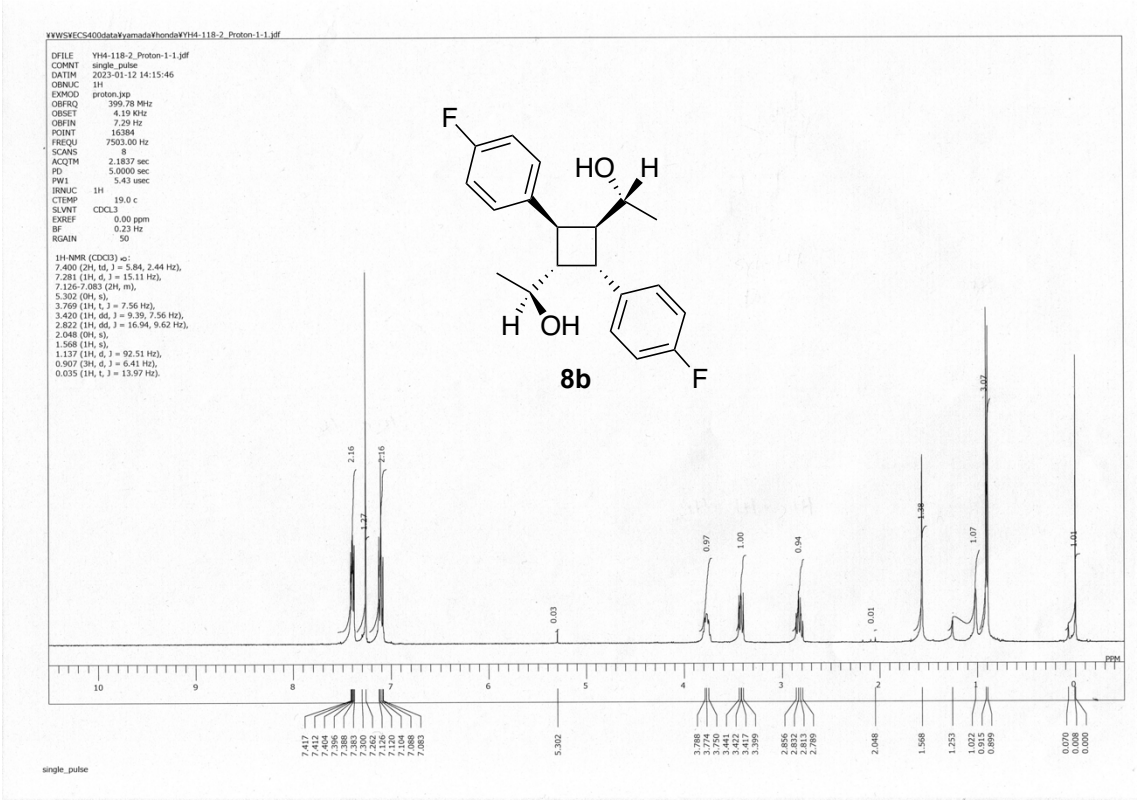

¥¥WS¥ECS400data¥yamada¥honda¥YH4-54-1-2_Proton-1-1.als
DFILE YH4-54-1-2_Proton-1-1.als
COMNT single_pulse
DATIM 2022-10-26 12:51:14
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.43 usec
IRNUC 1H
CTEMP 20.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.23 Hz
RGAIN 50
1H-NMR (CDCl3) ω:
7.261 (1H, s),
7.220-7.149 (1H, m),
7.013 (3H, dq, J = 25.53, 6.11 Hz),
4.756 (0H, t, J = 10.30 Hz),
4.323 (0H, t, J = 10.07 Hz),
3.675 (1H, t, J = 10.30 Hz),
2.333 (2H, s),
2.309 (1H, s),
2.048 (0H, s),
1.668 (2H, s),
1.552 (1H, d, J = 12.36 Hz),
0.031 (1H, t, J = 15.57 Hz).
6d-E
single_pulse
ppm

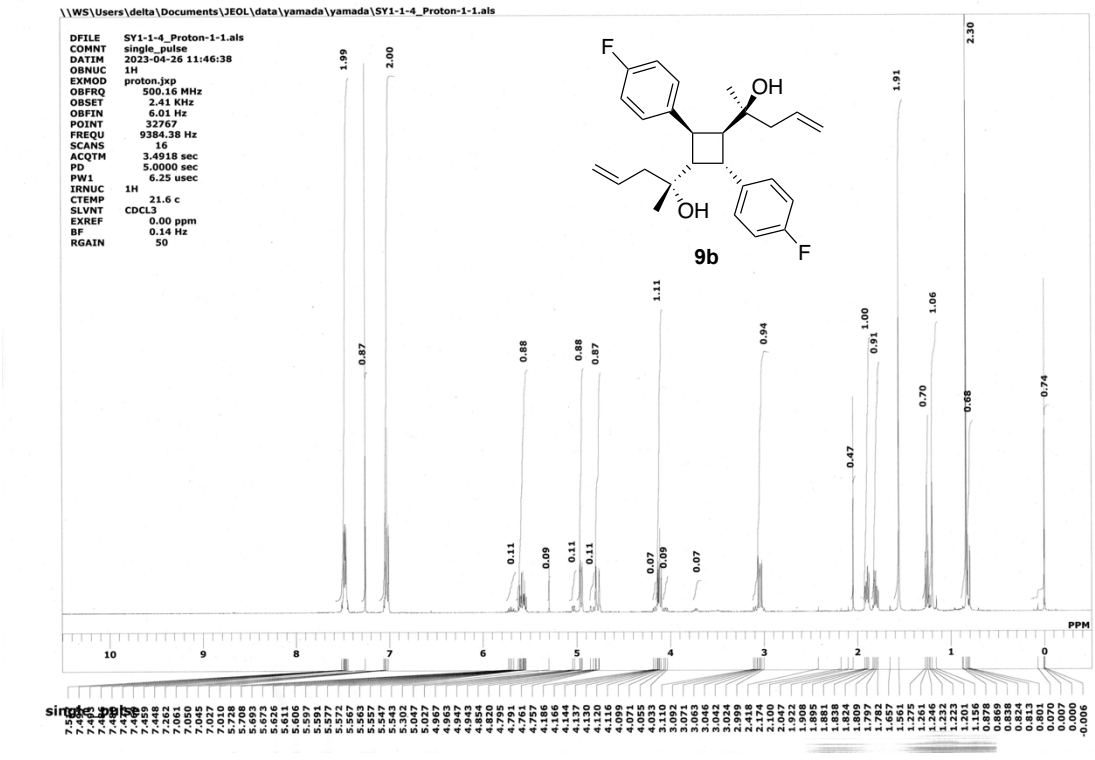

¥¥WS¥ECS400data¥yamada¥honda¥YH4-61-2-1-2_Proton-1-1.jdf
DFILE YH4-61-2-1-2_Proton-1-1.jdf
COMNT single_pulse
DATIM 2022-11-11 15:07:33
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 16384
FREQU 7503.00 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.43 usec
IRNUC 1H
CTEMP 19.9 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 0.23 Hz
RGAIN 54
1H-NMR (CDCl3) ∞:
7.261 (1H, s),
7.175-7.111 (2H, m),
4.550 (0H, dd, J = 10.99, 7.33 Hz),
3.851 (0H, dd, J = 10.99, 7.33 Hz),
2.314 (1H, s),
1.635 (1H, s),
1.561 (1H, s),
0.004 (1H, d, J = 3.21 Hz).
O
O
6e-A
1.93
1.00
0.47
0.47
1.40
1.41
1.12
1.02
PPM
10
9
8
7
6
5
4
3
2
1
0
7.261
7.175
7.160
7.155
7.132
7.111
4.573
4.564
4.545
4.527
3.874
3.866
3.847
3.828
2.378
2.314
1.635
1.561
0.008
0.000
single_pulse


¥¥WS¥ECS400data¥yamada¥honda¥YH4-137-2-1_Proton-1-1.jdf
DFILE YH4-137-2-1_Proton-1-1.jdf
COMNT single_pulse
DATIM 2023-03-07 17:34:41
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 16384
FREQU 7503.00 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.43 usec
IRNUC 1H
CTEMP 20.3 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 0.23 Hz
RGAIN 48
1H-NMR (CDCl3) ∞:
7.265 (2H, s),
6.481 (4H, s),
4.536 (2H, dd, J = 11.22, 7.10 Hz),
3.883 (12H, s),
3.800 (8H, dd, J = 11.45, 7.33 Hz),
2.047 (0H, s),
1.701 (6H, s),
1.578 (2H, s),
1.257 (1H, d, J = 2.75 Hz),
0.035 (2H, d, J = 27.93 Hz).
MeO
O
O
OMe
6f-A
11.93
7.78
4.01
1.92
2.00
5.82
2.26
1.12
0.15
1.63
PPM
10
9
8
7
6
5
4
3
2
1
0
7.2647
6.4812
4.5591
4.5467
4.5304
4.5132
3.8832
3.8236
3.8053
3.7859
3.7767
2.0470
1.7011
1.5765
1.2600
1.2332
0.0699
0.0000
single_pulse


¥¥WS¥ECS400data¥yamada¥honda¥YH4-137-2-1_Proton-1-1.jdf
DFILE YH4-137-2-1_Proton-1-1.jdf
COMNT single_pulse
DATIM 2023-03-07 17:34:41
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 16384
FREQU 7503.00 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.43 usec
IRNUC 1H
CTEMP 20.3 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 0.23 Hz
RGAIN 48
1H-NMR (CDCl3) δ:
7.265 (2H, s),
6.481 (4H, s),
4.536 (2H, dd, J = 11.22, 7.10 Hz),
3.883 (12H, s),
3.800 (8H, dd, J = 11.45, 7.33 Hz),
2.047 (6H, s),
1.701 (6H, s),
1.578 (2H, s),
1.257 (1H, d, J = 2.75 Hz),
0.035 (2H, d, J = 27.93 Hz).
MeO
OMe
MeO
O
O
OMe
OMe
MeO
6g-A
PPM
single_pulse


YH4-46-1-CDCl3
Current Data Parameters
NAME 20221014
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20221014
Time 13.31
INSTRUM spect
PROBHD 5 mm CPPBBO BB
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 12019.230 Hz
FIDRES 0.183399 Hz
AQ 2.7262976 sec
RG 28.5
DW 41.600 usec
DE 10.00 usec
TE 291.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 600.0337054 MHz
NUC1 1H
P1 13.50 usec
PLW1 22.00000000 W
F2 - Processing parameters
SI 65536
SF 600.0300147 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
F
H
N
N
H
F
7b
ppm


¥¥WS¥ECS400data¥yamada¥honda¥YH4-118-2_Proton-1-1.jdf
DFILE YH4-118-2_Proton-1-1.jdf
COMNT single_pulse
DATIM 2023-01-12 14:15:46
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 16384
FREQU 7503.00 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.43 usec
IRNUC 1H
CTEMP 19.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.23 Hz
RGAIN 50
1H-NMR (CDCl3) δ:
7.400 (2H, td, J = 5.84, 2.44 Hz),
7.281 (1H, d, J = 15.11 Hz),
7.126-7.083 (2H, m),
5.302 (0H, s),
3.769 (1H, t, J = 7.56 Hz),
3.420 (1H, dd, J = 9.39, 7.56 Hz),
2.822 (1H, dd, J = 16.94, 9.62 Hz),
2.048 (0H, s),
1.568 (1H, s),
1.137 (1H, d, J = 92.51 Hz),
0.907 (3H, d, J = 6.41 Hz),
0.035 (1H, t, J = 13.97 Hz).
F
HO
H
H
OH
F
8b
2.16
1.27
2.16
0.03
0.97
1.00
0.94
0.01
1.38
1.07
3.07
1.01
PPM
10
9
8
7
6
5
4
3
2
1
0
7.417
7.412
7.404
7.396
7.388
7.383
7.380
7.262
7.126
7.119
7.104
7.088
7.083
5.302
3.788
3.774
3.750
3.744
3.422
3.417
3.399
2.856
2.832
2.813
2.789
2.048
1.568
1.253
1.022
0.915
0.899
0.070
0.063
0.000
single_pulse


\\WS\Users\delta\Documents\JEOL\data\yamada\yamada\SY1-1-4_Proton-1-1.als
DFILE SY1-1-4_Proton-1-1.als
COMNT single_pulse
DATIM 2023-04-26 11:46:38
OBNUC 1H
EXMOD proton.jxp
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 32767
FREQU 9384.38 Hz
SCANS 16
ACQTM 3.4918 sec
PD 5.0000 sec
PW1 6.25 usec
IRNUC 1H
CTEMP 21.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.14 Hz
RGAIN 50
F
OH
OH
F
9b
1.99
2.00
0.87
0.88
0.88
0.87
1.11
0.94
1.91
2.30
1.00
0.91
1.06
0.70
0.68
0.74
0.47
0.11
0.09
0.11
0.11
0.07
0.09
0.07
PPM
10
9
8
7
6
5
4
3
2
1
0
single_pulse

10. X-ray crystallographic data for 2a, 3a-3h and 6a-6h, and their crystal packing diagrams

Summary for **2a**

Formula: C13 H16 O3 N1 F3 S1

******* Unit Cell Parameters *******	
a:	7.1898(2)
b:	10.2610(3)
c:	10.7376(3)
alpha:	82.873(2)
beta:	81.112(2)
gamma:	73.186(2)
volume:	746.55(4)

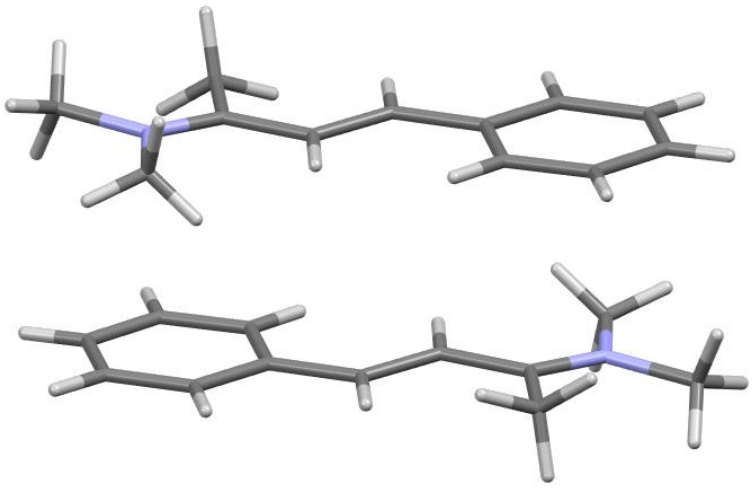
********* Model Refinement *********	
R1 factor[I>2.0sigma(I)]:	0.0463
R factor[all data]:	0.0580
wR factor[all data]:	0.1566
goodness of fit:	1.120
# of observations:	2670
# of variables:	193
refl/para ratio:	13.8
maximum shift/error:	0.00
Refinement program:	SHELXL 2014/7
Refinement mode:	Single

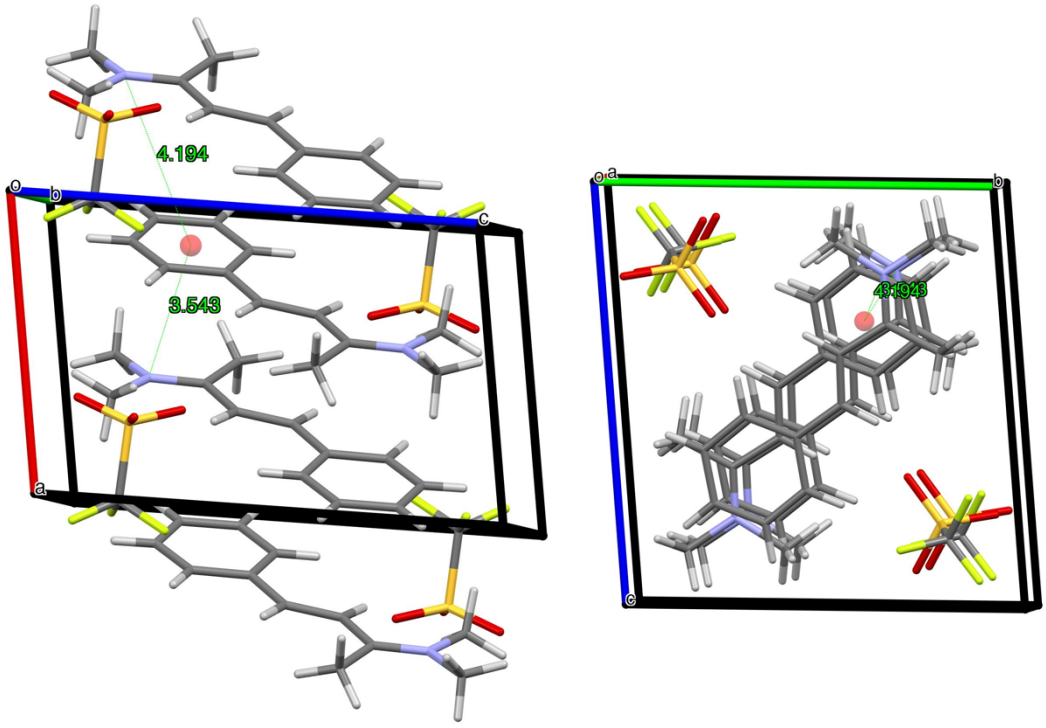
****** Space Group Information *****	
symbol:	P-1
number:	2
centricity:	centric
Z value:	2
formula weight:	323.33
calculated density:	1.438
mu (cm-1):	23.391
crystal system:	triclinic
laue group:	-1
lattice type:	P

****** Reflection Corrections ******	
absorption applied:	Yes
abs. type:	SYM
abs. range:	0.778-1.000
decay applied:	No
decay (%):	0.00
redundants averaged:	Yes

******* Reflection Processing ******	
total # processed:	8508
total # unique:	2670
R merge (%):	5.31
Wilson B:	2.29

***** Experimental Information ****	
radiation:	Cu
wavelength:	1.54187
max. 2theta:	136.5
sin(theta)/lambda:	0.6024
temperature (C):	-150.0





Side view Top view

Summary for **3a**

Formula: C14 H18 N1 B1 F4

******* Unit Cell Parameters *******	
a:	8.57365(16)
b:	16.3060(3)
c:	9.96321(18)
alpha:	90.000
beta:	90.6392(10)
gamma:	90.000
volume:	1392.79(4)

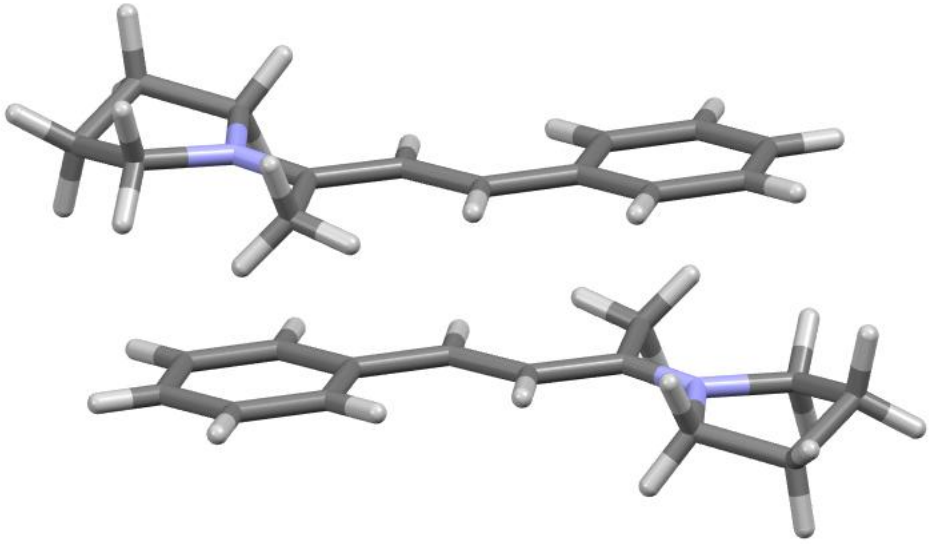
********* Model Refinement *********	
R1 factor[I>2.0sigma(I)]:	0.0512
R factor[all data]:	0.0769
wR factor[all data]:	0.1417
goodness of fit:	1.123
# of observations:	2500
# of variables:	183
refl/para ratio:	13.7
maximum shift/error:	0.00
Refinement program:	SHELXL 2014/7
Refinement mode:	Single

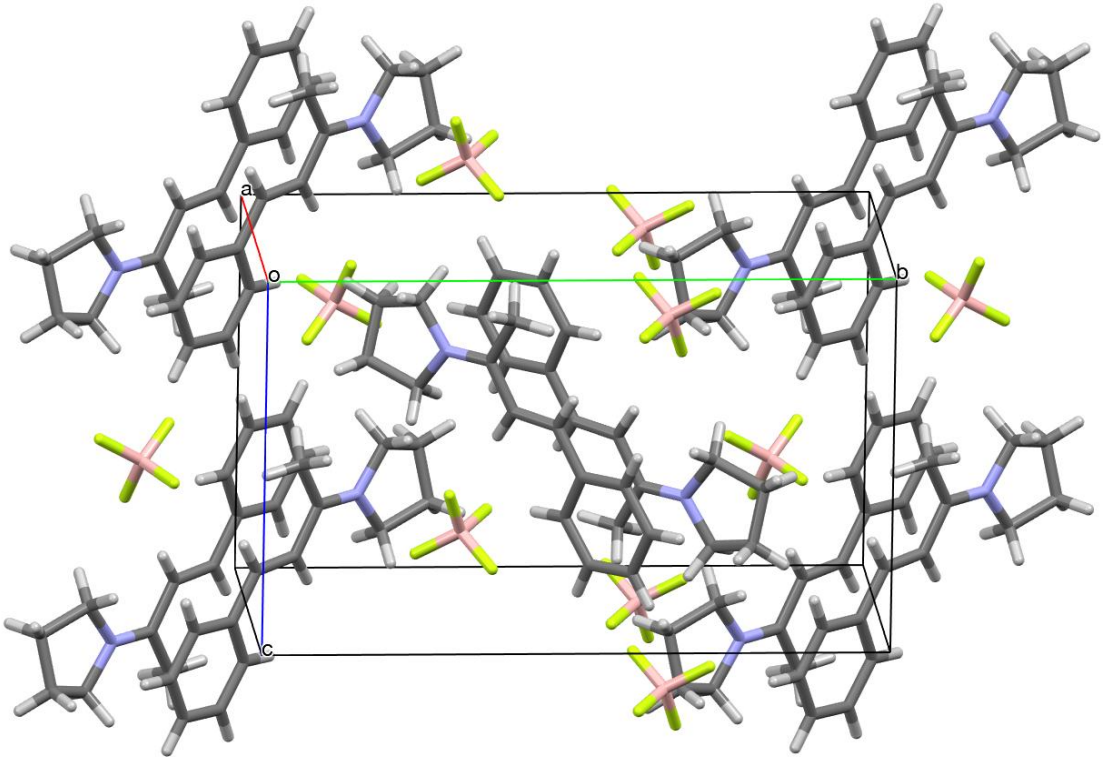
****** Space Group Information *****	
symbol:	P21/n
number:	14
centricity:	centric
Z value:	4
formula weight:	287.11
calculated density:	1.369
mu (cm-1):	9.992
crystal system:	monoclinic
laue group:	2/m
lattice type:	P

****** Reflection Corrections ******	
absorption applied:	Yes
abs. type:	SYM
abs. range:	0.896-1.000
decay applied:	No
decay (%):	0.00
redundants averaged:	Yes

******* Reflection Processing ******	
total # processed:	22881
total # unique:	2500
R merge (%):	3.80
Wilson B:	3.02

***** Experimental Information ****	
radiation:	Cu
wavelength:	1.54187
max. 2theta:	136.5
sin(theta)/lambda:	0.6023
temperature (C):	-150.0




a
o
b
c

Summary for **3b**

Formula: C14 H17 N1 B1 F5

******* Unit Cell Parameters *******	
a:	8.51495(19)
b:	16.4158(4)
c:	10.0399(3)
alpha:	90.000
beta:	90.7420(15)
gamma:	90.000
volume:	1403.26(6)

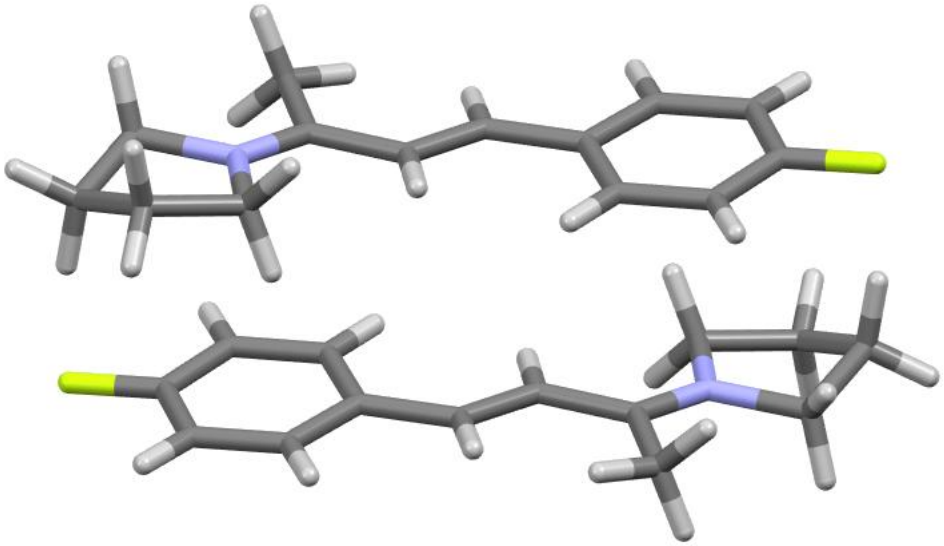
********* Model Refinement *********	
R1 factor[I>2.0sigma(I)]:	0.0435
R factor[all data]:	0.0642
wR factor[all data]:	0.1119
goodness of fit:	1.142
# of observations:	2566
# of variables:	191
refl/pararatio:	13.4
maximum shift/error:	0.00
Refinement program:	SHELXL 2014/7
Refinement mode:	Single

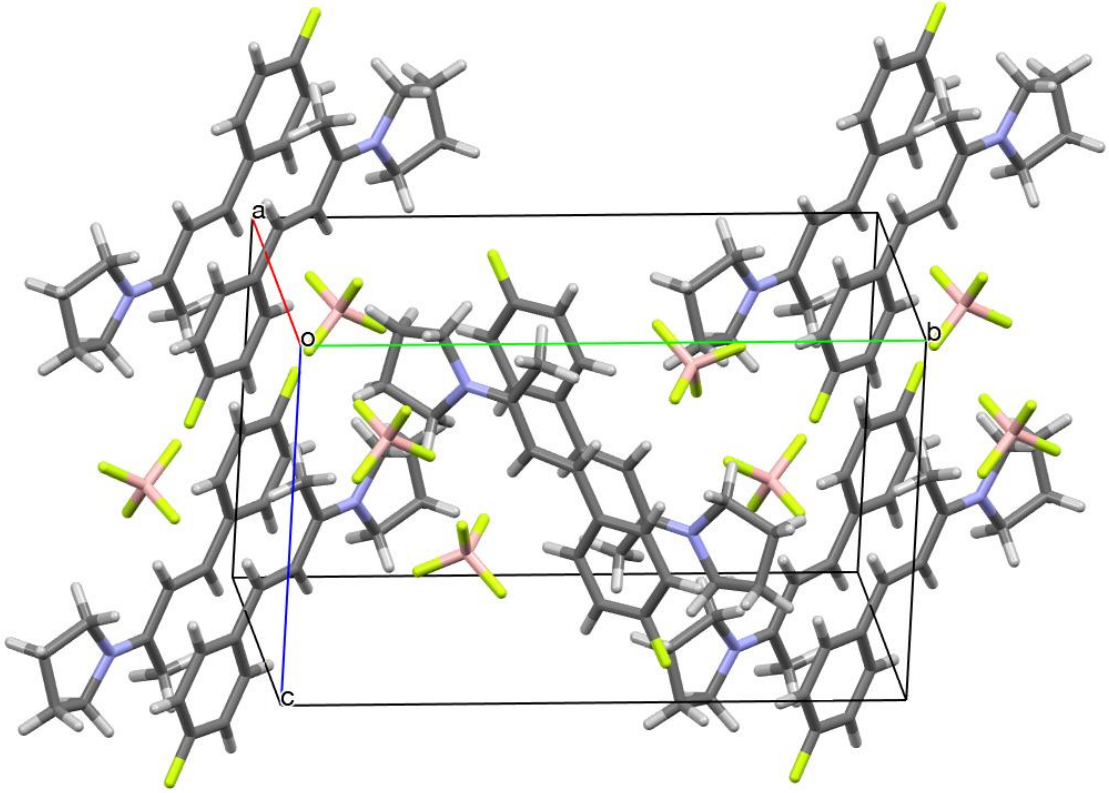
****** Space Group Information *****	
symbol:	P21/n
number:	14
centricity:	centric
Z value:	4
formula weight:	305.10
calculated density:	1.444
mu (cm-1):	11.336
crystal system:	monoclinic
laue group:	2/m
lattice type:	P

****** Reflection Corrections ******	
absorption applied:	Yes
abs. type:	SYM
abs. range:	0.714-1.000
decay applied:	No
decay (%):	0.00
redundants averaged:	Yes

******* Reflection Processing ******	
total # processed:	15309
total # unique:	2566
R merge (%):	5.19
Wilson B:	2.09

***** Experimental Information ****	
radiation:	Cu
wavelength:	1.54187
max. 2theta:	136.4
sin(theta)/lambda:	0.6022
temperature (C):	-150.0




a
o
b
c

Summary for **3c**

Formula: C15 H20 N1 B1 F4

******* Unit Cell Parameters *******	
a:	7.5602(3)
b:	15.2074(5)
c:	12.6685(5)
alpha:	90.000
beta:	95.164(2)
gamma:	90.000
volume:	1450.60(9)

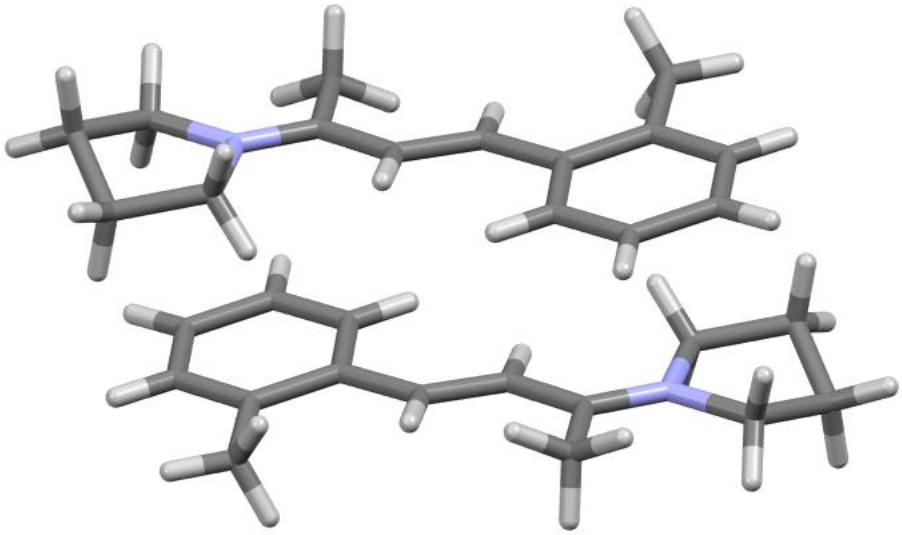
********* Model Refinement *********	
R1 factor[I>2.0sigma(I)]:	0.0734
R factor[all data]:	0.0998
wR factor[all data]:	0.2621
goodness of fit:	1.198
# of observations:	2641
# of variables:	192
refl/para ratio:	13.8
maximum shift/error:	0.00
Refinement program:	SHELXL 2014/7
Refinement mode:	Single

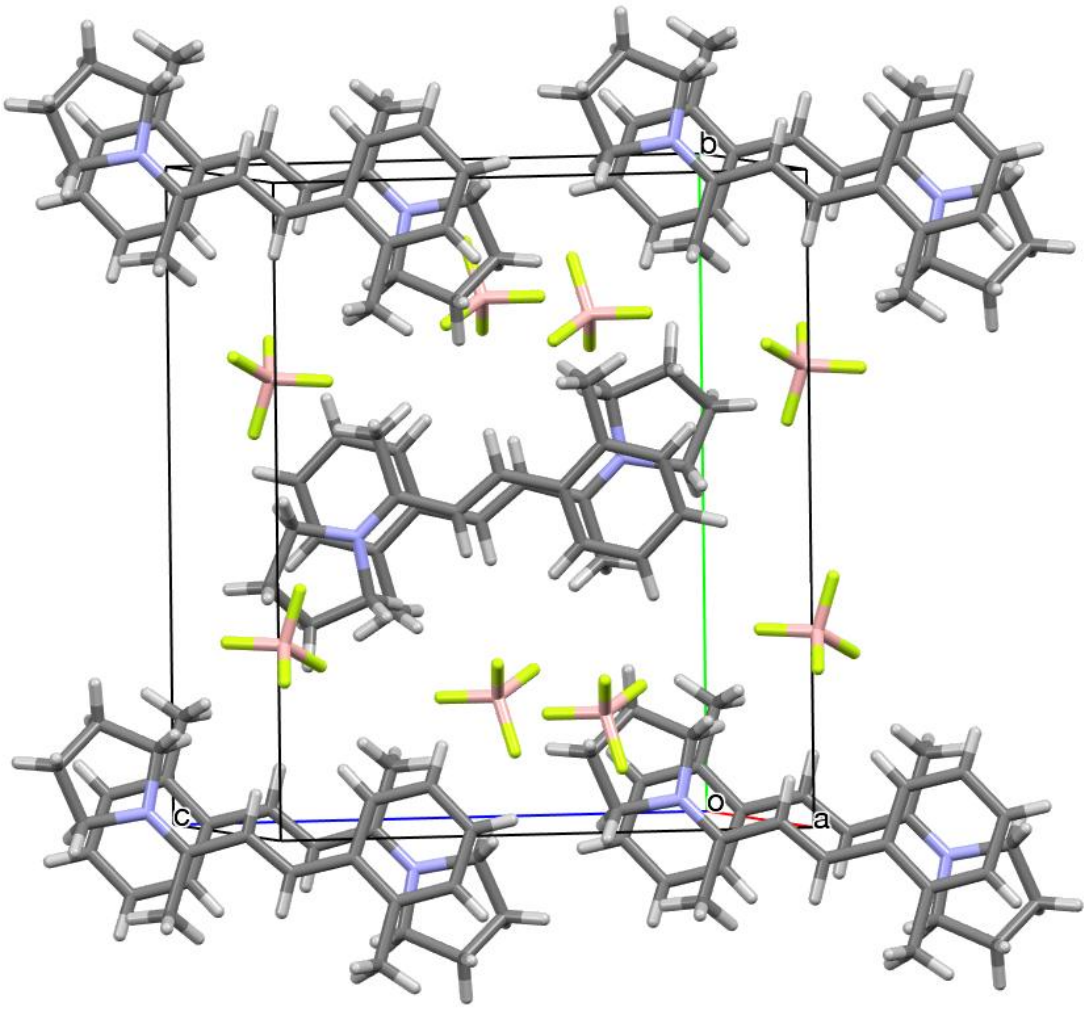
****** Space Group Information *****	
symbol:	P21/n
number:	14
centricity:	centric
Z value:	4
formula weight:	301.13
calculated density:	1.379
mu (cm-1):	9.845
crystal system:	monoclinic
laue group:	2/m
lattice type:	P

****** Reflection Corrections ******	
absorption applied:	Yes
abs. type:	SYM
abs. range:	0.850-1.000
decay applied:	No
decay (%):	0.00
redundants averaged:	Yes

******* Reflection Processing ******	
total # processed:	16580
total # unique:	2641
R merge (%):	5.78
Wilson B:	3.51

***** Experimental Information ****	
radiation:	Cu
wavelength:	1.54187
max. 2theta:	136.5
sin(theta)/lambda:	0.6024
temperature (C):	-150.0




b
c
o
a

Summary for **3d**

Formula: C15 H20 N1 B1 F4

******* Unit Cell Parameters *******	
a:	10.0997(3)
b:	8.3125(2)
c:	17.8495(6)
alpha:	90.000
beta:	96.1210(19)
gamma:	90.000
volume:	1489.99(7)

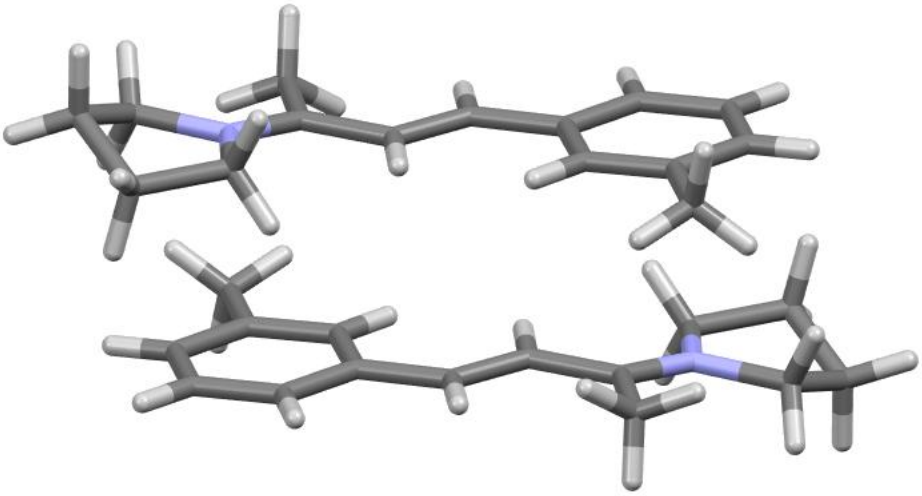
********* Model Refinement *********	
R1 factor[I>2.0sigma(I)]:	0.0771
R factor[all data]:	0.0969
wR factor[all data]:	0.2424
goodness of fit:	1.103
# of observations:	2438
# of variables:	192
refl/para ratio:	12.7
maximum shift/error:	0.00
Refinement program:	SHELXL 2014/7
Refinement mode:	Single

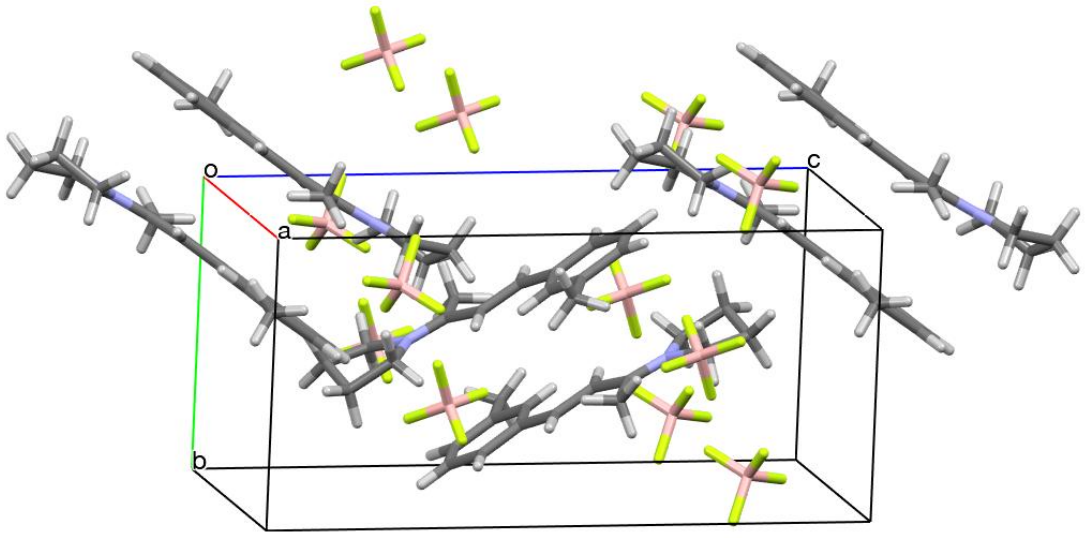
****** Space Group Information *****	
symbol:	P21/c
number:	14
centricity:	centric
Z value:	4
formula weight:	301.13
calculated density:	1.342
mu (cm-1):	9.585
crystal system:	monoclinic
laue group:	2/m
lattice type:	P

****** Reflection Corrections ******	
absorption applied:	Yes
abs. type:	SYM
abs.range:	0.538-1.000
decay applied:	No
decay (%):	0.00
redundants averaged:	Yes

******* Reflection Processing ******	
total # processed:	8976
total # unique:	2438
R merge (%):	7.48
Wilson B:	3.27

***** Experimental Information ****	
radiation:	Cu
wavelength:	1.54187
max. 2theta:	136.5
sin(theta)/lambda:	0.6023
temperature (C):	-150.0




o
a
c
b

Summary for **3e**

Formula: C15 H20 N1 B1 F4

******* Unit Cell Parameters *******	
a:	10.1100(2)
b:	8.7342(2)
c:	16.7607(4)
alpha:	90.000
beta:	90.8200(15)
gamma:	90.000
volume:	1479.87(6)

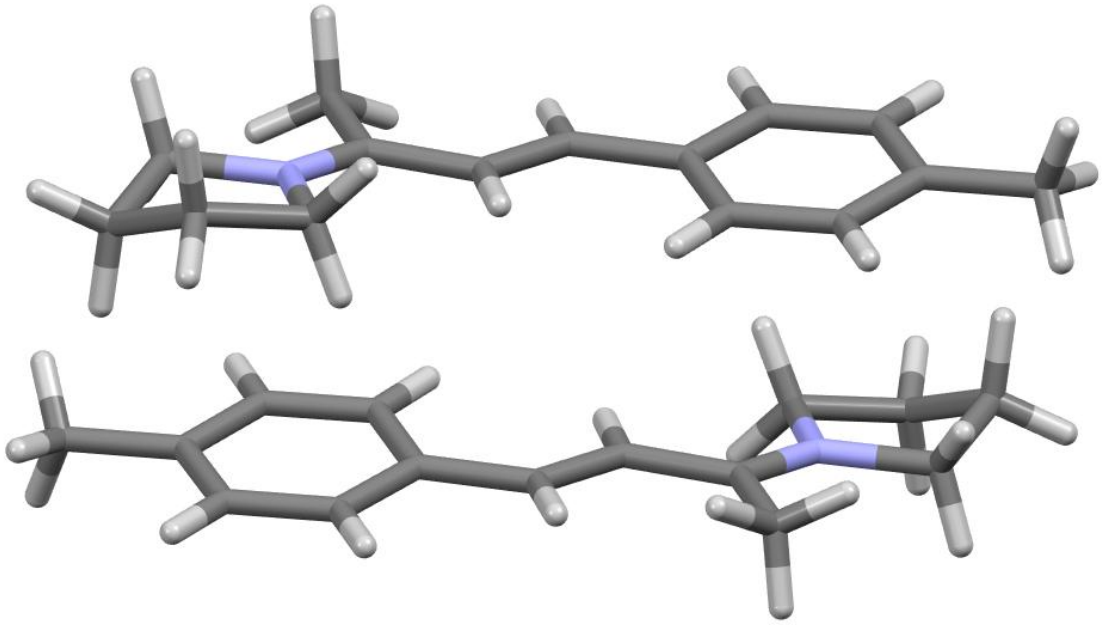
********* Model Refinement *********	
R1 factor[I>2.0sigma(I)]:	0.0685
R factor[all data]:	0.0833
wR factor[all data]:	0.1933
goodness of fit:	1.156
# of observations:	2692
# of variables:	192
refl/para ratio:	14.0
maximum shift/error:	0.00
Refinement program:	SHELXL 2014/7
Refinement mode:	Single

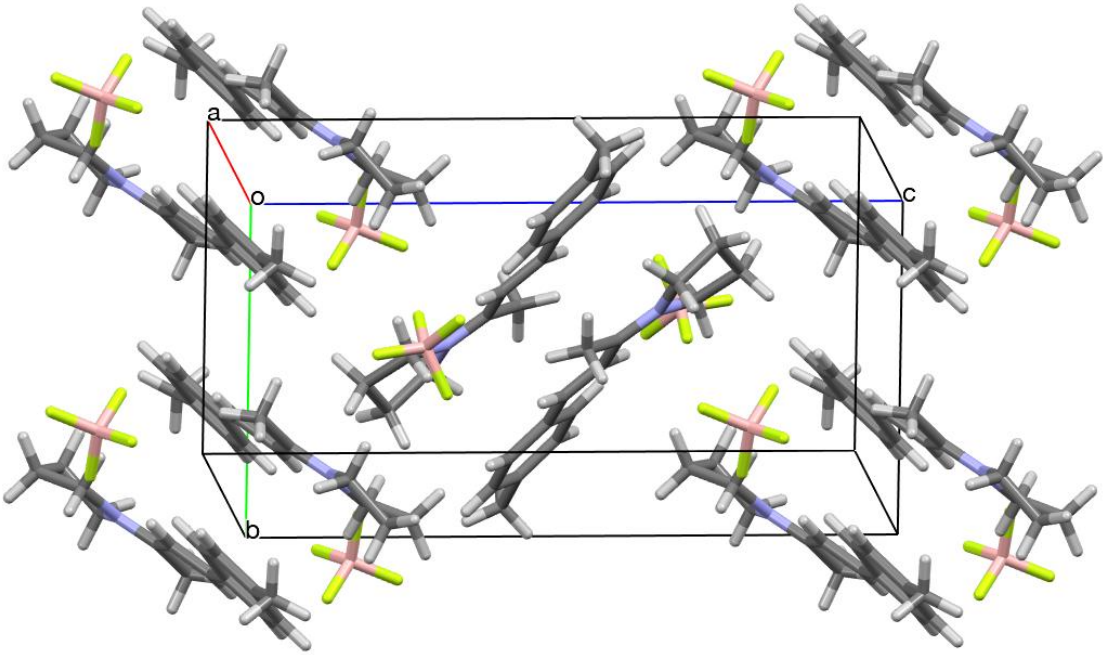
****** Space Group Information *****	
symbol:	P21/c
number:	14
centricity:	centric
Z value:	4
formula weight:	301.13
calculated density:	1.351
mu (cm-1):	9.651
crystal system:	monoclinic
laue group:	2/m
lattice type:	P

****** Reflection Corrections ******	
absorption applied:	Yes
abs.type:	SYM
abs. range:	0.897-1.000
decay applied:	No
decay (%):	0.00
redundants averaged:	Yes

******* Reflection Processing ******	
total # processed:	16192
total # unique:	2692
R merge (%):	4.61
Wilson B:	2.47

***** Experimental Information ****	
radiation:	Cu
wavelength:	1.54187
max. 2theta:	136.4
sin(theta)/lambda:	0.6022
temperature (C):	-150.0




a
o
c
b

Summary for **3f**

Formula: C15 H20 O1 N1 B1 F4

******* Unit Cell Parameters *******	
a:	7.63744(14)
b:	19.6800(4)
c:	10.11448(18)
alpha:	90.000
beta:	100.7280(10)
gamma:	90.000
volume:	1493.69(5)

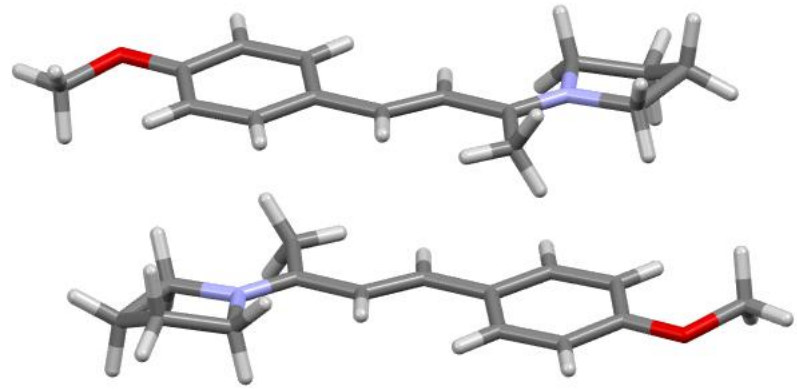
********* Model Refinement *********	
R1 factor[I>2.0sigma(I)]:	0.0386
R factor[all data]:	0.0445
wR factor[all data]:	0.1043
goodness of fit:	1.078
# of observations:	2723
# of variables:	200
refl/para ratio:	13.6
maximum shift/error:	0.00
Refinement program:	SHELXL 2014/7
Refinement mode:	Single

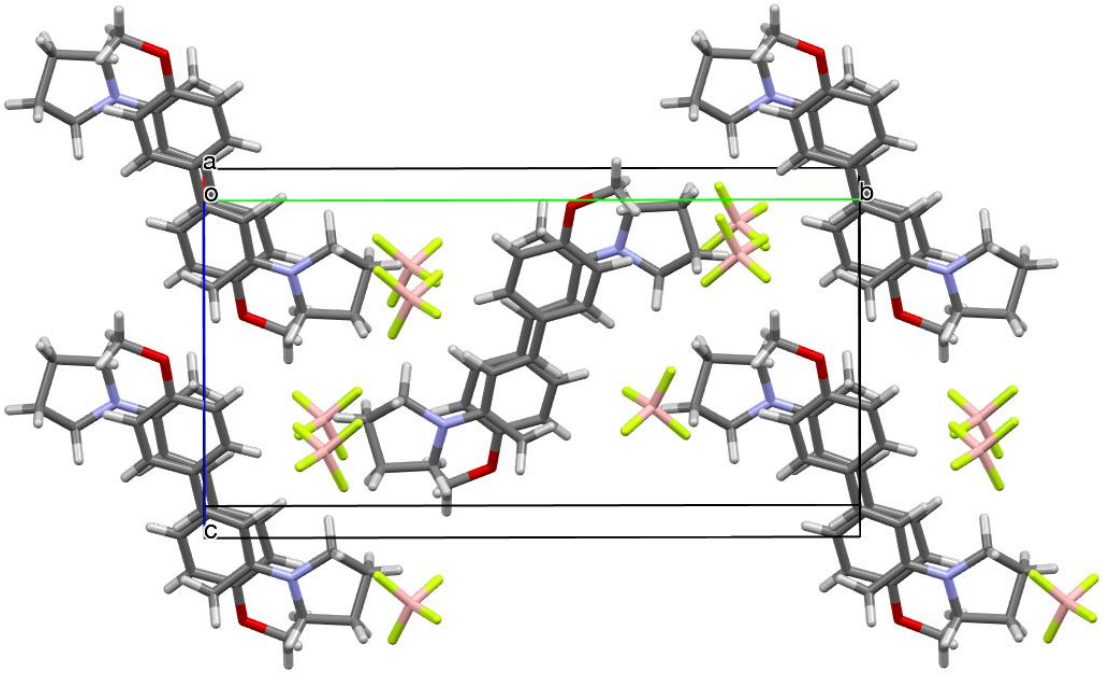
****** Space Group Information *****	
symbol:	P21/n
number:	14
centricity:	centric
Z value:	4
formula weight:	317.13
calculated density:	1.410
mu (cm-1):	10.379
crystal system:	monoclinic
laue group:	2/m
lattice type:	P

****** Reflection Corrections ******	
absorption applied:	Yes
abs. type:	SYM
abs.range:	0.882-1.000
decay applied:	No
decay (%):	0.00
redundants averaged:	Yes

******* Reflection Processing ******	
total # processed:	16393
total # unique:	2723
R merge (%):	3.72
Wilson B:	2.07

***** Experimental Information ****	
radiation:	Cu
wavelength:	1.54187
max. 2theta:	136.5
sin(theta)/lambda:	0.6023
temperature (C):	-150.0




a
o
b
c

Summary for **3g**

Formula: C17 H24 B1 F4 N1 O3

******* Unit Cell Parameters *******	
a:	7.6902(3)
b:	9.9674(3)
c:	12.0352(4)
alpha:	94.287(2)
beta:	96.2441(19)
gamma:	96.7987(19)
volume:	906.99(5)

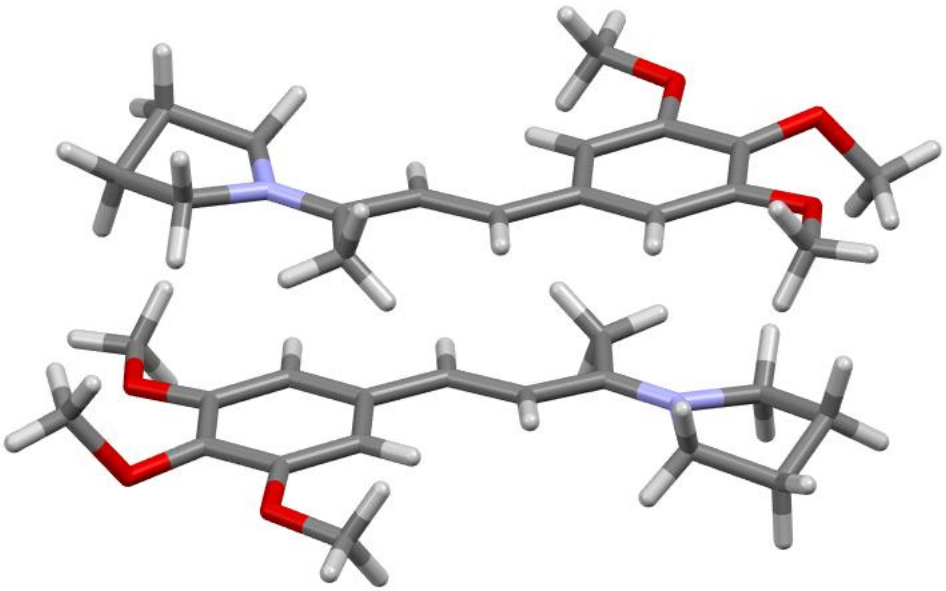
********* Model Refinement *********	
R1 factor[I>2.0sigma(I)]:	0.0593
R factor[all data]:	0.0925
wR factor[all data]:	0.1591
goodness of fit:	1.094
# of observations:	3237
# of variables:	239
refl/para ratio:	13.5
maximum shift/error:	0.00
Refinement program:	SHELXL 2014/7
Refinement mode:	Single

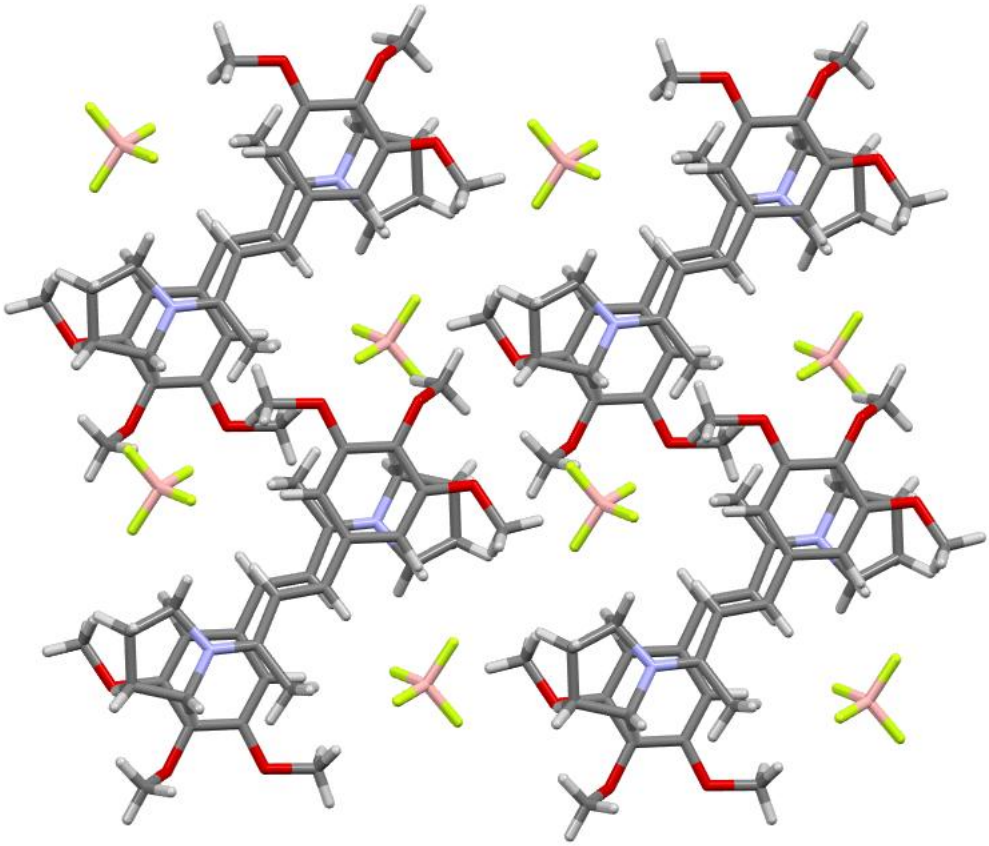
****** Space Group Information *****	
symbol:	P-1
number:	2
centricity:	centric
Z value:	2
formula weight:	377.19
calculated density:	1.381
mu (cm-1):	10.296
crystal system:	triclinic
laue group:	-1
lattice type:	P

****** Reflection Corrections ******	
absorption applied:	Yes
abs. type:	SYM
abs. range:	0.847-1.000
decay applied:	No
decay (%):	0.00
redundants averaged:	Yes

******* Reflection Processing ******	
total # processed:	9485
total # unique:	3237
R merge (%):	5.77
Wilson B:	2.65

***** Experimental Information ****	
radiation:	Cu
wavelength:	1.54187
max. 2theta:	136.4
sin(theta)/lambda:	0.6022
temperature (C):	-150.0





Summary for **3h**

Formula: C16 H25 N2 B1 F4 O1

******* Unit Cell Parameters *******	
a:	6.7623
b:	19.1113
c:	13.5883
alpha:	90.000
beta:	99.365
gamma:	90.000
volume:	1732.694

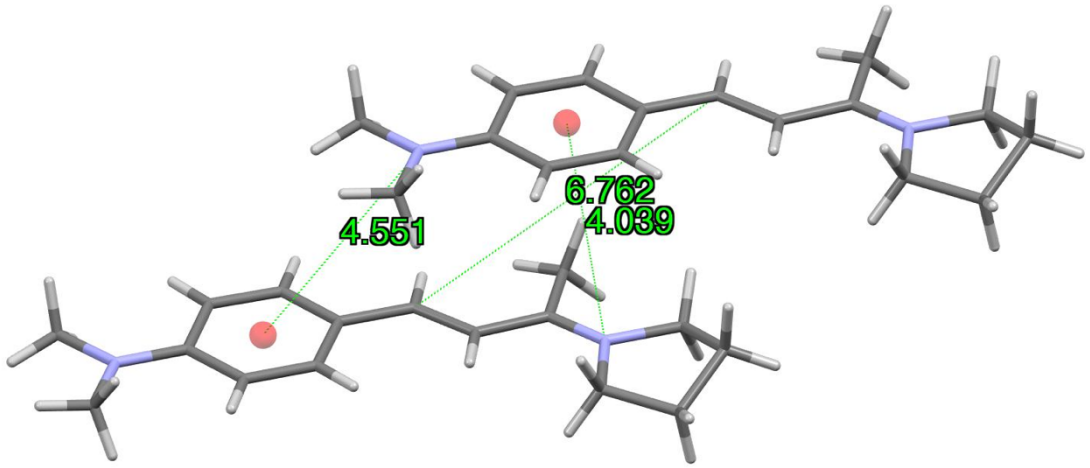
********* Model Refinement *********	
R1 factor[I>2.0sigma(I)]:	0.0779
R factor[all data]:	0.0950
wR factor[alldata]:	0.2548
goodness of fit:	1.143
# of observations:	3119
# of variables:	220
refl/para ratio:	14.2
maximum shift/error:	0.00
Refinement program:	SHELXL 2014/7
Refinement mode:	Single

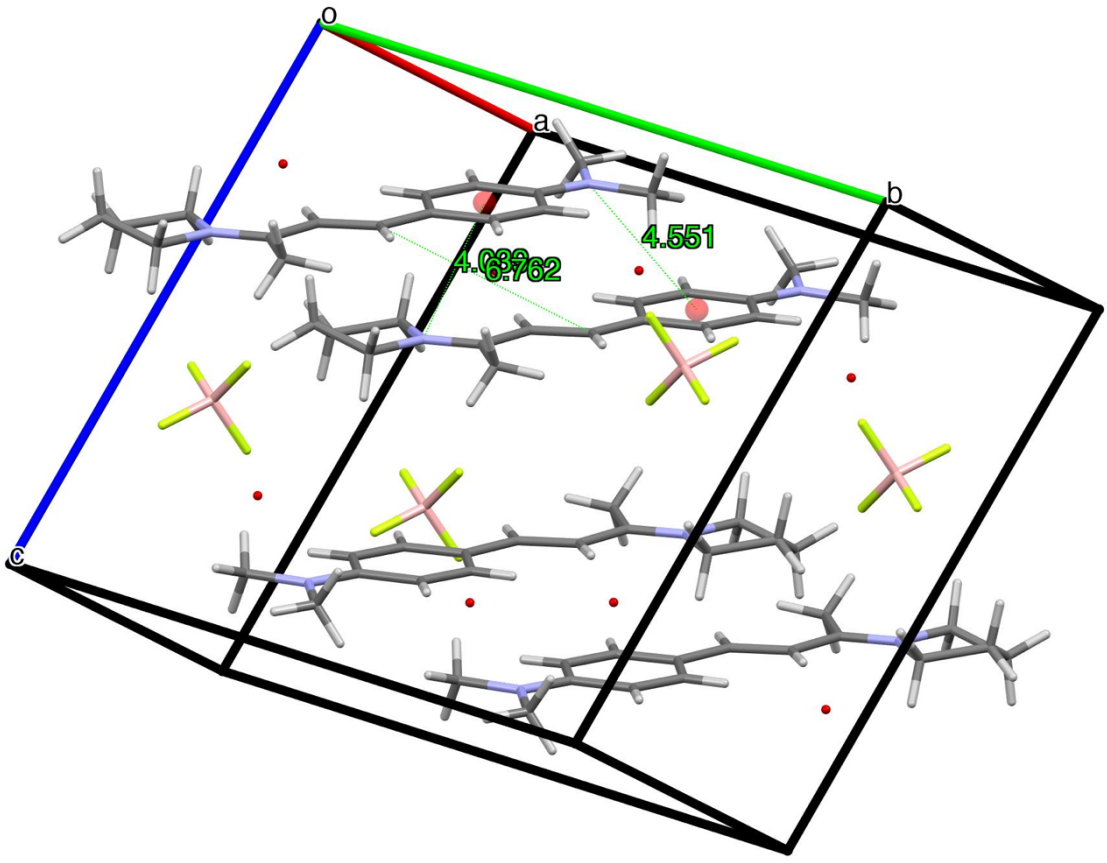
****** Space Group Information *****	
symbol:	P21/n
number:	14
centricity:	centric
Z value:	4
formula weight:	348.19
calculated density:	1.335
mu (cm-1):	9.562
crystal system:	monoclinic
laue group:	2/m
lattice type:	P

****** Reflection Corrections ******	
absorption applied:	Yes
abs. type:	SYM
abs. range:	0.863-1.000
decay applied:	No
decay (%):	0.00
redundants averaged:	Yes

******* Reflection Processing ******	
total # processed:	19286
total # unique:	3119
R merge (%):	5.01
Wilson B:	3.51

***** Experimental Information ****	
radiation:	Cu
wavelength:	1.54187
max. 2theta:	136.5
sin(theta)/lambda:	0.6023
temperature (C):	-150.0


6.762
4.039
4.551


o
a
b
c
4.551
4.039
6.762

Summary for **5a**

Formula: C28 H36 N2 B2 F8

******* Unit Cell Parameters *******	
a:	7.1302(3)
b:	14.6918(5)
c:	13.1044(4)
alpha:	90.000
beta:	101.392(2)
gamma:	90.000
volume:	1345.71(8)

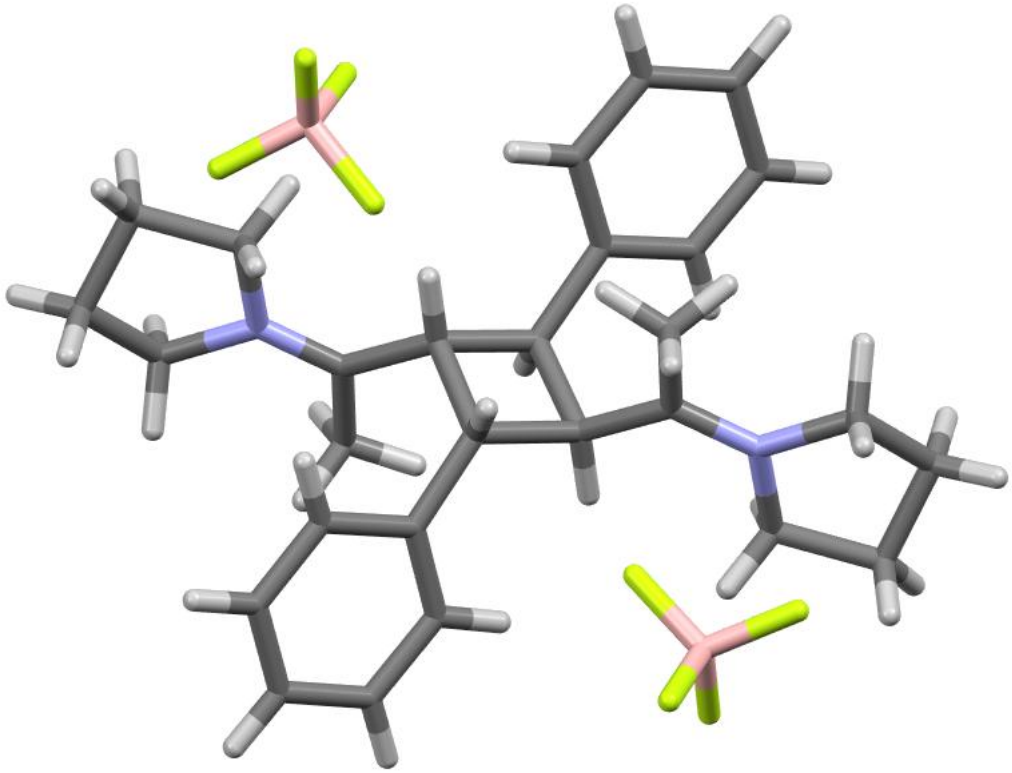
********* Model Refinement *********	
R1 factor[I>2.0sigma(I)]:	0.0448
R factor[all data]:	0.0579
wR factor[all data]:	0.1348
goodness of fit:	1.117
# of observations:	4732
# of variables:	363
refl/para ratio:	13.0
maximum shift/error:	0.00
Refinement program:	SHELXL 2014/7
Refinement mode:	Single
Flack Parameter:	0.48(19)

****** Space Group Information *****	
symbol:	P21
number:	4
centricity:	acentric
Z value:	2
formula weight:	574.21
calculated density:	1.417
mu (cm-1):	10.341
crystal system:	monoclinic
laue group:	2/m
lattice type:	P

****** Reflection Corrections ******	
absorption applied:	Yes
abs. type:	SYM
abs. range:	0.864-1.000
decay applied:	No
decay(%):	0.00
redundants averaged:	Yes

******* Reflection Processing ******	
total # processed:	15256
total # unique:	4732
R merge (%):	2.95
Wilson B:	3.07

***** Experimental Information ****	
radiation:	Cu
wavelength:	1.54187
max. 2theta:	136.5
sin(theta)/lambda:	0.6023
temperature (C):	-150.0



Summary for **syn-6a**

Formula: C20 H20 O2

******* Unit Cell Parameters *******	
a:	9.0741(4)
b:	13.3976(5)
c:	9.2157(3)
alpha:	90.000
beta:	115.370(3)
gamma:	90.000
volume:	1012.31(7)

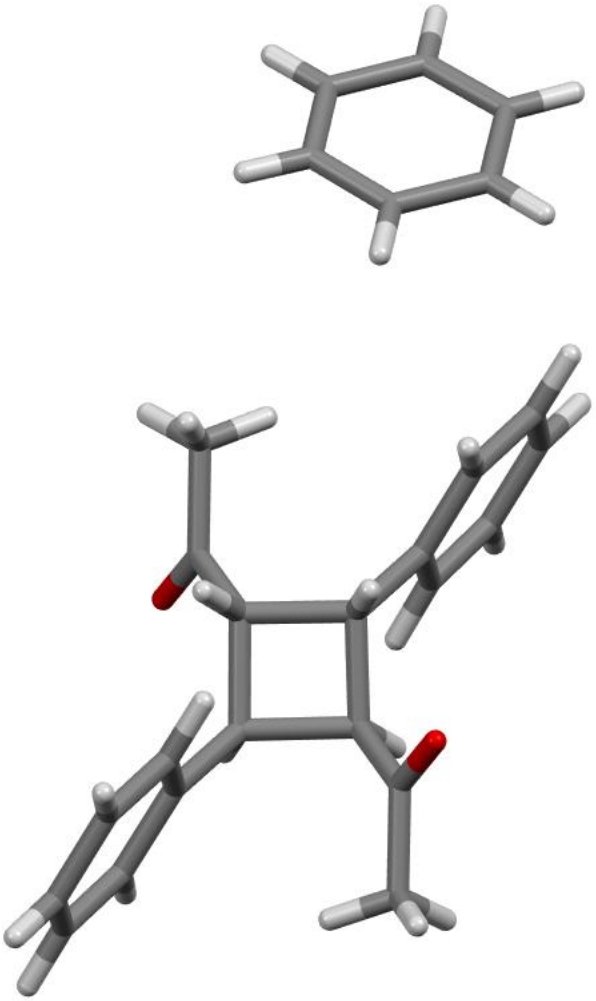
********* Model Refinement *********	
R1 factor[I>2.0sigma(I)]:	0.0423
R factor[all data]:	0.0561
wR factor[all data]:	0.1003
goodness of fit:	1.100
# of observations:	3514
# of variables:	256
refl/para ratio:	13.7
maximum shift/error:	0.19
Refinement program:	SHELXL 2014/7
Refinement mode:	Single
Flack Parameter:	0.0(7)

****** Space Group Information *****	
symbol:	P21
number:	4
centricity:	acentric
Z value:	2
formula weight:	292.38
calculated density:	0.959
mu (cm-1):	4.787
crystal system:	monoclinic
laue group:	2/m
lattice type:	P

****** Reflection Corrections ******	
absorption applied:	Yes
abs. type:	SYM
abs. range:	0.897-1.000
decay applied:	No
decay (%):	0.00
redundants averaged:	Yes

******* Reflection Processing ******	
total # processed:	10456
total # unique:	3514
R merge (%):	4.12
Wilson B:	1.81

***** Experimental Information ****	
radiation:	Cu
wavelength:	1.54187
max. 2theta:	136.5
sin(theta)/lambda:	0.6024
temperature (C):	-150.0



Summary for **anti-6a**

Formula: C20 H20 O2

******* Unit Cell Parameters *******	
a:	9.64367(19)
b:	16.3794(4)
c:	11.2234(3)
alpha:	90.000
beta:	115.7517(13)
gamma:	90.000
volume:	1596.75(6)

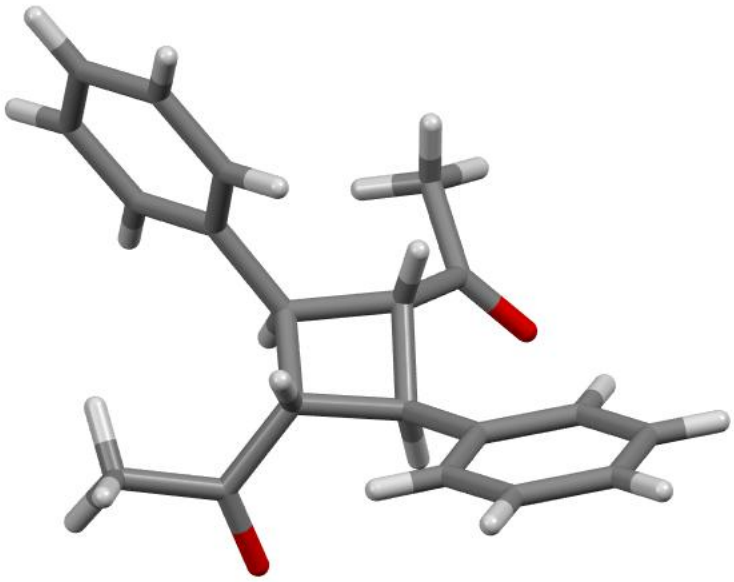
********* Model Refinement *********	
R1 factor[I>2.0sigma(I)]:	0.0401
R factor[all data]:	0.0506
wR factor[all data]:	0.1362
goodness of fit:	1.166
# of observations:	2807
# of variables:	202
refl/para ratio:	13.9
maximum shift/error:	0.00
Refinement program:	SHELXL 2014/7
Refinement mode:	Single

****** Space Group Information *****	
symbol:	P21/n
number:	14
centricity:	centric
Z value:	4
formula weight:	292.38
calculated density:	1.216
mu (cm-1):	6.070
crystal system:	monoclinic
laue group:	2/m
lattice type:	P

****** Reflection Corrections ******	
absorption applied:	Yes
abs. type:	SYM
abs. range:	0.824-1.000
decay applied:	No
decay (%):	0.00
redundants averaged:	Yes

******* Reflection Processing ******	
total # processed:	9890
total # unique:	2807
R merge (%):	3.67
Wilson B:	1.80

***** Experimental Information ****	
radiation:	Cu
wavelength:	1.54187
max. 2theta:	136.5
sin(theta)/lambda:	0.6023
temperature (C):	-150.0



Summary for **7b**

Formula: C28 H36 N2 F2

******* Unit Cell Parameters *******	
a:	9.36553(17)
b:	10.40596(19)
c:	12.2778(2)
alpha:	90.000
beta:	99.9106(11)
gamma:	90.000
volume:	1178.71(4)

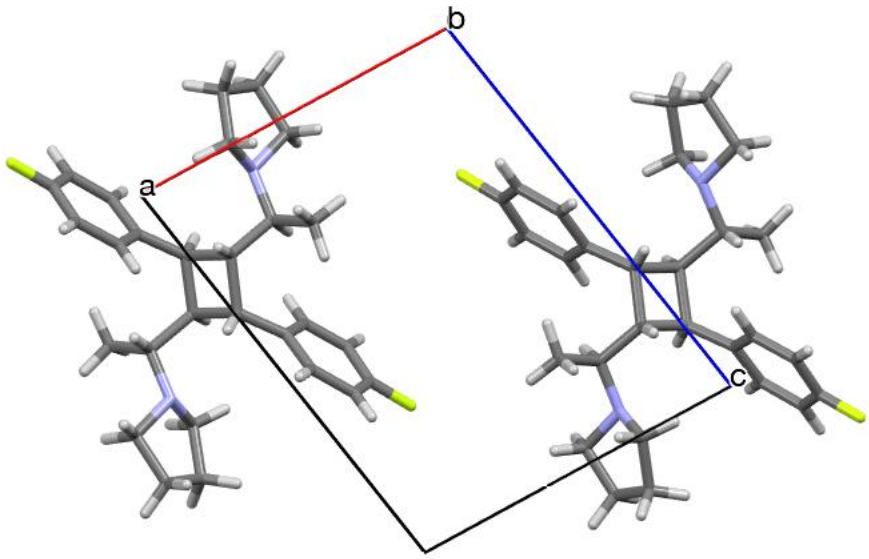
********* Model Refinement *********	
R1 factor[I>2.0sigma(I)]:	0.0355
R factor[all data]:	0.0437
wR factor[all data]:	0.1017
goodness of fit:	1.121
# of observations:	4206
# of variables:	292
refl/para ratio:	14.4
maximum shift/error:	0.00
Refinement program:	SHELXL 2014/7
Refinement mode:	Single
Flack Parameter:	0.42(19)

****** Space Group Information *****	
symbol:	P21
number:	4
centricity:	acentric
Z value:	2
formula weight:	438.60
calculated density:	1.236
mu (cm-1):	6.592
crystal system:	monoclinic
laue group:	2/m
lattice type:	P

****** Reflection Corrections ******	
absorption applied:	Yes
abs. type:	SYM
abs. range:	0.907-1.000
decay applied:	No
decay (%):	0.00
redundants averaged:	Yes

******* Reflection Processing ******	
total # processed:	13488
total # unique:	4206
R merge (%):	3.16
Wilson B:	1.60

***** Experimental Information ****	
radiation:	Cu
wavelength:	1.54187
max. 2theta:	136.5
sin(theta)/lambda:	0.6023
temperature (C):	-150.0


b
a
c

Summary for **8b**

Formula: C20 H22 O2 F2

******* Unit Cell Parameters *******	
a:	15.5432
b:	10.8346
c:	20.4290
alpha:	90.000
beta:	98.712
gamma:	90.000
volume:	3400.656

********* Model Refinement *********	
R1 factor[I>2.0sigma(I)]:	0.0991
R factor[all data]:	0.1892
wR factor[all data]:	0.4346
goodness of fit:	1.068
# of observations:	6221
# of variables:	442
refl/para ratio:	14.1
maximum shift/error:	0.11
Refinement program:	SHELXL 2014/7
Refinement mode:	Single

****** Space Group Information *****	
symbol:	P2/c
number:	13
centricity:	centric
Z value:	8
formula weight:	332.39
calculated density:	1.298
mu (cm-1):	8.048
crystal system:	monoclinic
laue group:	2/m
lattice type:	P

****** Reflection Corrections ******	
absorption applied:	Yes
abs. type:	SYM
abs. range:	0.917-1.000
decay applied:	No
decay (%):	0.00
redundants averaged:	Yes

******* Reflection Processing ******	
total # processed:	36895
total # unique:	6221
R merge (%):	3.93
Wilson B:	2.71

***** Experimental Information ****	
radiation:	Cu
wavelength:	1.54187
max. 2theta:	136.5
sin(theta)/lambda:	0.6024
temperature (C):	-150.0