Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Benzothiazolines as Radical Transfer Reagents: Hydroalkylation and Hydroacylation of Alkenes by Radical Generation under Photoirradiation Conditions

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1. General Methods

All operations were performed under air unless otherwise noted. NMR spectra for products data (^1H and ^{13}C) were recorded on a Bruker AVANCE-III (400 MHz for ^1H, 125 MHz for ^{13}C) spectrometer using $CDCl_3$ [tetramethylsilane (0 ppm) served as an internal standard in ^1H NMR and $CDCl_3$ (77.0 ppm) in ^{13}C NMR, hexafluorobenzene (–163 ppm) served as an external standard in ^{19}F NMR]. Chemical shifts are expressed in parts per million (ppm). IR spectra were recorded on an FT/IR-4200 (JASCO Co., Ltd.). UV-Vis spectra were recorded on a V-670 UV-VIS-NIR spectrophotometer (JASCO Co., Ltd.). ESI mass analyses were performed on Bruker micrOTOF mass spectrometer. GPC purification was performed on a LC-918R/U (Japan Analytical Industry Co., Ltd.). Cyclic Voltammetry was performed on VersaSTAT 4 (AMETEL Co., Ltd.).

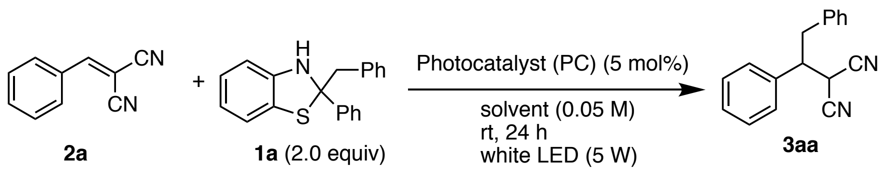
All solvents were distilled according to the usual procedures and stored over molecular sieves unless otherwise noted. All of the substrates were purified by distillation (for liquid) or recrystallization (for solid). Benzalmalononitrile derivatives (**2a, 2c-2l**)[S1], malonate derivatives (**2m,**[S2] **2n,** [S3] **2o,** [S4] **2p** [S5]), methyl α-phenylacrylate (**2x**)[S6] and imines (**4a-4j**)[S7] were synthesized according to the literature procedures. Other chemicals were purchased and used as received.

2. Additional Data

2-1. Screening of detail conditions of hydroalkylation and hydroacylation

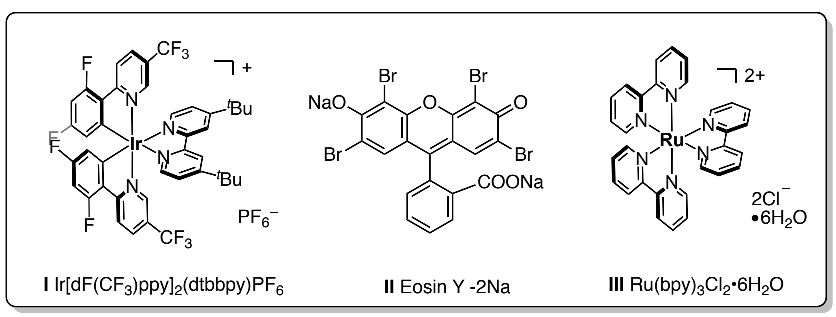
· Hydroalkylation of benzalmalononitrile **2a**.

Table S1. Screening of conditions of hydroalkylation of benzalmalononitrile



entry	PC	solvent	yield[a)]
1	**I**	EtOH (0.2 M)	0%
2	**I**	Toluene (0.2 M)	15%
3	**I**	DCE (0.2 M)	45%
4[b)]	**I**	DCE (0.2 M)	33%
5[b)]	**II**	DCE (0.2 M)	14%
6[b)]	**III**	DCE (0.2 M)	88%
7	**III**	DCE	>95%
8	–	DCE	5%
9[c)]	**III**	DCE	24%

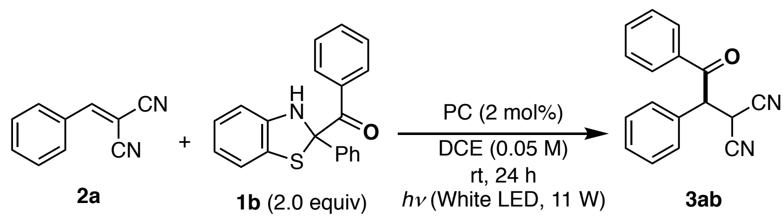
a) NMR Yield (Internal standard substance: 1,1,2-trichloroethane)
b) Using 11 W white LED.
c) No light irradiation condition.



1,2-Dichloroethane (DCE) gave the best result in combination with **I** as a photoredox catalyst (entries 1-3). The most suitable photoredox catalyst was $Ru(bpy)_3Cl_2$ (entries 4-6), and use of stronger light source decreased the yield of the products. The reaction was over in 5 h. But, it was difficult to follow the reaction by TLC because the spot was overlapped with the starting materials.

· Hydroacylation of benzalmalononitrile **2a**.

Table S2. Screening of conditions of hydroacylation of benzalmalononitrile 2a.

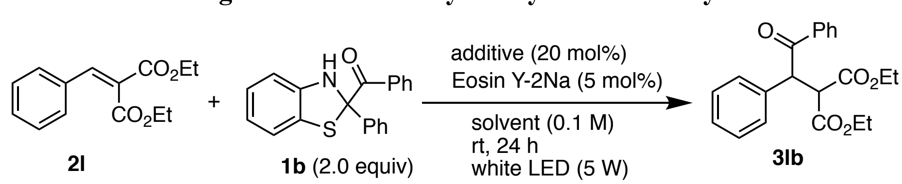


entry	PC	yield[a)]
1	**I**	80%
2	**II**	48%
3	**III**	> 95%
4	–	9%
5[b)]	**III**	0%

a) NMR yield (Internal standard: 1,1,2-trichloroethane)
b) No light irradiation conditions.

· Hydroacylation of benzylidenemalonate **2l**.

Table S3. Screening of conditions of hydroacylation of benzylidenemalonate.



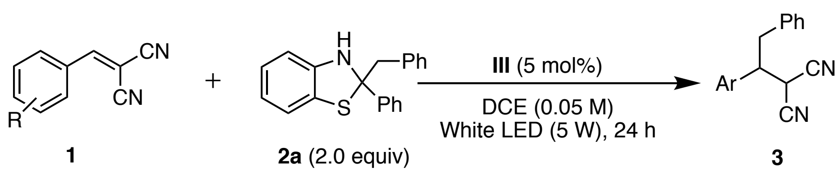
entry	solvent	additive	yield[a)]
1	DCE	$Yb(OTf)_3$	78% (67%)
2	DMF	$Yb(OTf)_3$	10%
3	THF	$Yb(OTf)_3$	25%
4	toluene	$Yb(OTf)_3$	36%
5	DCE	$La(OTf)_3$	58%
6	DCE	$BF_3{\bullet}OEt_2$	24%
7	DCE	$AlCl_3$	> 5%
8	DCE	TsOH	24%

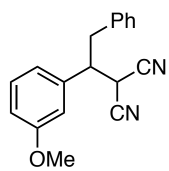
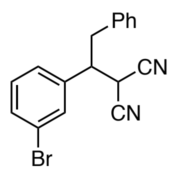
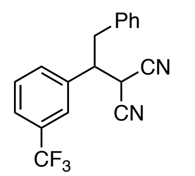
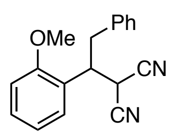
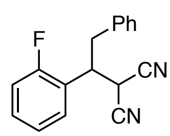
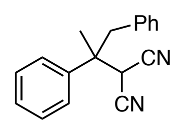
a) NMR Yield (Internal standard substance: 1,1,2-trichloroethane)

Ytterbium triflate was the most effective Lewis acid and **3lb** was obtained in 67% isolated yield.

2-2. Substrate scope of benzalmalononitrile derivatives

Table S4. Substrate scope of benzalmalononitrile derivatives.



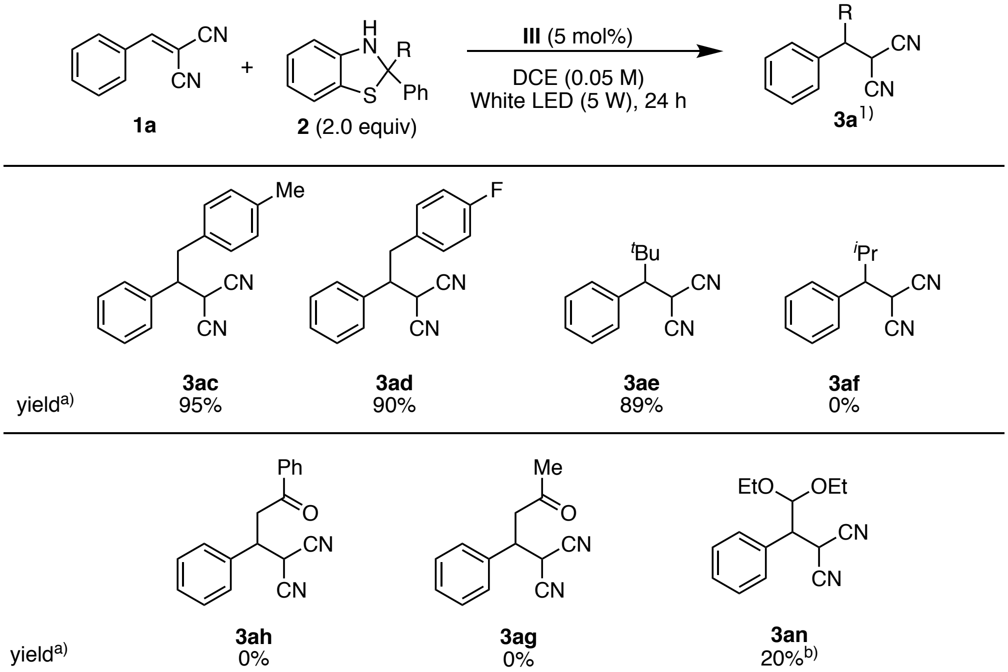
			
yield[a)]	**3xa** >95%	**3ya** 68%	**3za** >95% (85%)
			
yield[a)]	**3αa** 88%	**3βa** >95% (94%)	**3γa** 0%

a) NMR yield (Isolated yield)

Meta- and *ortho-*substituted benzalmalononitriles were also found to be suitable substrates. But, α-methyl benzalmalononitrile did not participate in this reaction due to its steric hindrance.

2-3. Generality of the alkyl and acyl group using benzalmalononitrile

Table S5. Generality of the alkyl and acyl group using benzalmalononitrile.



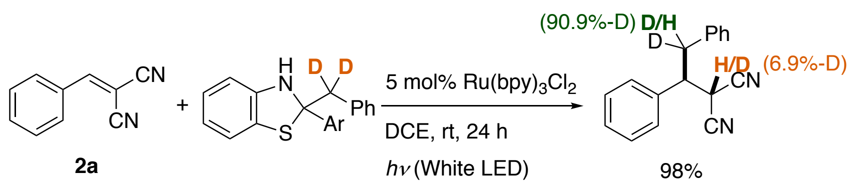
a) NMR yield
b) Reduction product was obtained in 51% yield.

Generality of the alkyl group was investigated for benzalmalononitrile (**1a**). Although substituted benzyl and *tert*-butyl group were transferred efficiently, phenacyl and acetonyl group, which successfully reacted with barbituric acid derivative **1n**, were not transferred. Diethoxymethyl group adduct **3an** was obtained in a low yield and the reduction product **7** was obtained in 51% yield. The mechanism of formation of **7** has not been clarified.

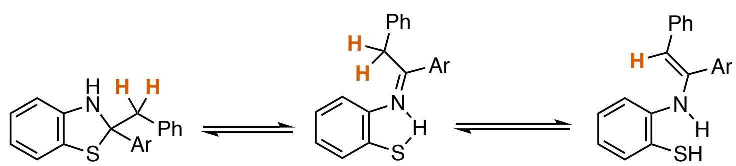
2-4. The reaction of benzothiazoline 1-*d*, deuterated at benzyl position

Deuterated benzyl transfer reaction was performed by mixing **2a** and **1a-*d*** under the standard photoredox conditions (Scheme S1). The reaction proceeded similar to the non-deuterated one, however, the deuteration ratio of benzyl position was decreased in the product (3.6% lack from **1a-*d***). In addition, partial deuteration (6.9%) was observed at β-position of the product. It means that the exchange at benzyl position of benzothiazoline **1a** or protonation of the resulting anion species from imine intermediate (Scheme S2) occurred under the reaction conditions.

Scheme S1. Deuterated benzyl transfer

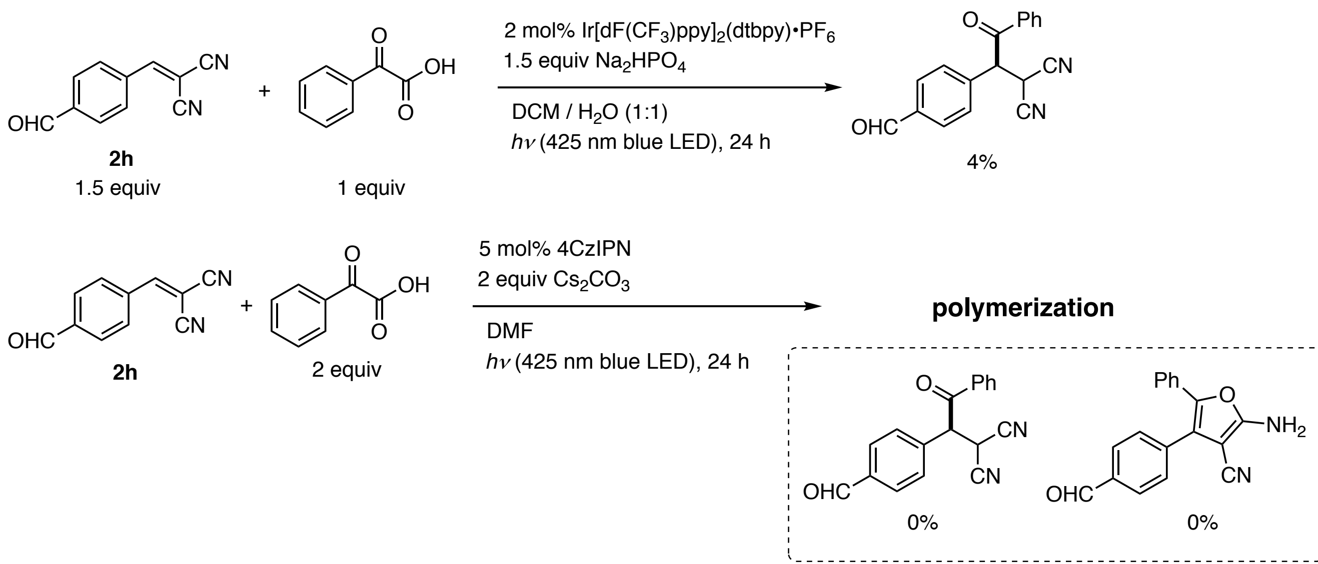


Scheme S2. Proposed mechanism of the isomerization of 2-benzothiazolines



2-5. Comparison with carboxylates

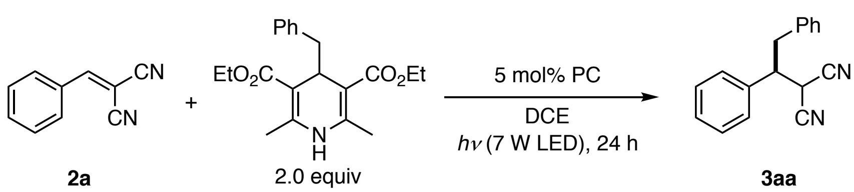
Scheme S3. Hydroacylation of 2h by using carboxylate as an acyl radical precursor.



By use of benzothiazoline, high substituent tolerance was shown, and hydroformylation product of electron deficient alkene bearing formyl group **2h** was selectively obtained in 60% yield (Table 1). In contrast, by use of carboxylate under basic condition, desired hydroalkylation product was not obtained and polymerization proceeded under the basic conditions.

2-6. Comparison with Hantzsch ester

Table S6. Hydrobenzylation of benzalmalononitrile 2a by using Hantzsch ester



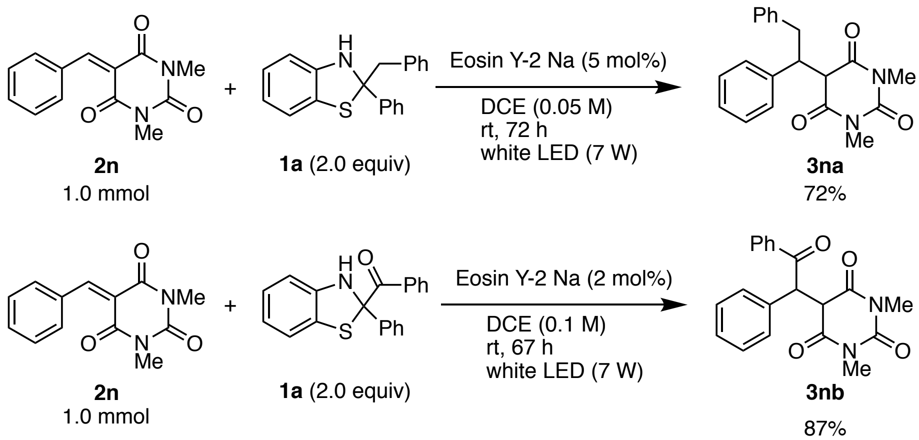
PC	yield[a)]
$Ru(bpy)_3Cl_2•6H_2O$	74%
$Ir[dF(CF_3)ppy]_2(dtbpy)•PF_6$	68%

a) NMR yield.

Use of Hantzsch ester furnished the addition product **3aa** in about 70% yields, which are lower than that using benzothiazoline **1a**.

2-7. Large scale experiments for isolation of product

Scheme S4. Hydroalkylation and hydroacylation of 2n in 1 mmol scale.

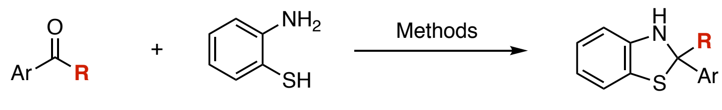


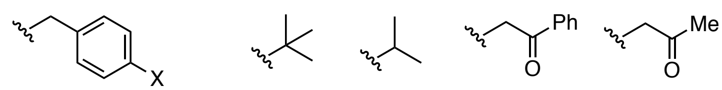
Although the longer reaction time was necessary, both hydrobenzylation and hydrobenzoylation products **3na** and **3nb** were obtained in good yields in 1 mmol scale.

3. Synthetic Procedures and Characterization of New Compounds

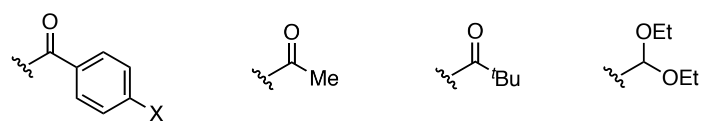
3-1. Synthesis of the benzothiazolines 1, 1' and 1''

Table S7. Synthesis of benzothiazolines

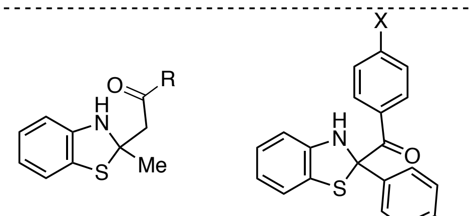




R	1a / 1c / 1d	1e	1f	1'g	1'h
yield (Methods)	**1a** (X = H) 85% (A) **1c** (X = Me) 58% (C) **1d** (X = F) 91% (C)	86% (C)	11% (D)	22% (E)	49% (E)



R	1b / 1''i / 1''j	1k	1l	1m
yield (Methods)	**1b** (X = H) 91% (B) **1''i** (X = Me) 92% (B) **1''j** (X = Br) 88% (B)	17% (F)	69% (G)	69% (H)



1' **1''**

Method A (1a)

Corresponding ketones (10.2 mmol) and 2-aminothiophenol (2.2 mL, 20.7 mmol) were mixed in EtOH (10 mL) under N_2, and heated at 80 ºC for 4 d. The mixture was cooled and the solvent was removed under vacuum. The crude product was purified by recrystallization from a mixture of dichloromethane and hexane followed by silica-gel column chromatography to give benzothiazolines **1**.

Method B (1b, 1''i, 1''j)

Corresponding ketones (24 mmol) and 2-aminothiophenol (3.8 mL, 36 mmol) were mixed in EtOH (20 mL) under N_2. The mixture was stirred for 16 h and then the precipitate was filtered to give benzothiazolines **1b** and **1''** in pure form.

Method C (1c-1e)

Corresponding ketones (54.3 mmol) and 2-aminothiophenol (1.2 mL, 82 mmol) were mixed in benzene (11 mL) under N_2. Then TsOH•H_2O (25.5 mg, 0.136 mmol) was added to the reaction mixture, and refluxed for 30 hours. After the solvent was removed, the crude product was purified by silica gel column chromatography to give the products. If the crude mixture couldn't be purified, the mixture was dissolved in EtOH and 0.5 equiv of $NaBH_4$ was added at 0 ºC, and stirred at room temperature. After the ketone was consumed, acetone was added and solvent was removed. The crude residue was dissolved in dichloromethane and extracted with dichloromethane for 3 times, then combined organic layers were washed with brine and dried by Na_2SO_4. After removed the solvent, the crude product was purified by silica gel column chromatography to give the desired product.

Method D (1f)

Isopropyl phenyl ketone (3 mL, 19.9 mmol) and 2-aminothiophenol (3.3 mL, 29.9 mmol) were mixed with alumina (30 g, 1000 wt%), and were heated at 80 ºC for 48 h. The alumina was filtered out by Celite® and washed with chloroform, followed by purified by silica gel column chromatography. Then the mixture was dissolved in EtOH and 0.5 equiv of $NaBH_4$ was added at 0 ºC, and stirred at room temperature. After the ketone was consumed, acetone was added and removed solvent. The residue was dissolved in dichloromethane and extracted with dichloromethane for 3 times, then combined organic phase was washed with brine and dried by Na_2SO_4. After removed the solvent, the crude product was purified by silica gel column chromatography to give the **1f** in 11% yield.

Method E (1'g, 1'h)

Corresponding ketone (15 mmol) and 2-aminothiophenol (2.1 mL, 19.5 mmol) were mixed (10 mL) under N_2. The mixture was heated at 80 ºC (**1'g**) or 50 ºC (**1'h**) for 3 h and then the crude product was purified by recrystallization from a mixture of dichloromethane and hexane, followed by silica-gel column chromatography, and further recrystallized from a mixture of dichloromethane and hexane to give benzothiazolines **1'**.

Method F (1k)

1-Phenyl-1,2-propanedione (15 mmol) and 2-aminothiophenol (1.6 mL, 15 mmol) were mixed in EtOH 15 mL) under N_2. After the reaction mixture was stirred at 50 ºC for 51 h, generated precipitate was filtered, washed with hexane to give the **1k** (657 mg, 2.57 mmol) in 17% yield.

Method G (1l)

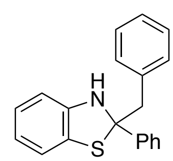
3,3-Dimethyl-1-phenyl-1,2-butanedione (5.5 mmol) and 2-aminothiophenol (1.2 mL, 11 mmol) were mixed in benzene (3.7 mL) under N_2. Then TsOH•H_2O (52.2 mg, 0.274 mmol) was added to the reaction mixture, and stirred at room temperature for 48 h. The solvent was removed and the residue was purified by silica-gel column chromatography, followed by recrystallization from hexane to give product (1.13 g, 3.80 mmol, 69% yield).

Method H (1m)

α,α-Diethoxy acetophenone (2.50 mL, 12.5 mmol) and 2-aminothiophenol (2.0 mL, 19 mmol) were mixed in benzene (25 mL) under N_2. Then TsOH•H_2O (59.3 mg, 0.312 mmol) was added to the reaction mixture, and stirred at room temperature for 26 h. After the solvent was removed, the crude product was purified by silica gel column chromatography and recrystallized with dichloromethane and hexane to give the products.

<u>Data of benzothiazolines</u>

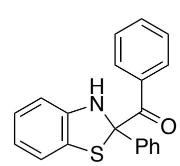
2-Benzyl-2-phenylbenzothiazoline (1a)



1a

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.37 (m, 2H), 7.35-7.30 (m, 2H), 7.30-7.26 (m, 1H), 7.21-7.12 (m, 3H), 7.10-7.06 (m, 1H), 7.01-6.95 (m, 1H), 6.81-6.76 (m, 4H), 4.47 (brs, 1H), 3.65 (d, J = 13.2 Hz, 1H), 3.57 (d, J = 13.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.6, 143.2, 135.2, 120.4, 128.3, 128.2, 127.6, 127.1, 127.0, 126.0, 125.6, 122.2, 120.8, 111.1, 81.7, 49.6 ppm; IR (neat, cm^{-1}): 3352, 3060, 3027, 2922, 1579, 1495, 1471, 1460, 1390, 1256, 742, 699; LRMS (ESI): m/z = 304 [M+H]; HRMS (ESI): Calcd for $C_{20}H_{18}NS$: 304.1154. Found 304.1143.

2-Benzoyl-2-phenylbenzothiazoline (1b)

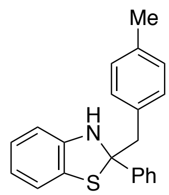


1b

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H), 7.46 (t, J = 8.0 Hz, 1H), 7.44-

7.27 (m, 5H), 7.06 (d, J = 7.6 Hz, 1H), 6.98 (t, J = 7.6 Hz, 1H), 6.78 (t, J = 7.6 Hz, 2H), 5.68 (brs, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.6, 144.9, 140.8, 133.1, 132.9, 130.3, 129.2, 128.8, 128.3, 126.8, 126.2, 125.6, 121.24, 121.19, 111.8, 84.2 ppm.[S8]

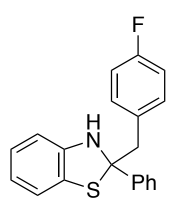
2-(*p*-Methoxybenzyl)-2-phenylbenzothiazoline (1c)



1c

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.37 (m, 2H), 7.36-7.30 (m,2H), 7.30-7.25 (m, 1H), 7.09-7.05 (m, 1H), 7.01-6.94 (m, 3H), 6.80-6.74 (m,2H), 6.67-6.63 (m,2H), 4.48 (brs, 1H), 3.61 (d, J = 13.6 Hz, 1H), 3.54 (d, J = 13.2Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.6, 143.4, 136.7, 132.1, 130.2, 128.9, 128.3, 127.5, 127.0, 126.0, 125.5, 122.2, 120.7, 111.0, 81.6, 49.1, 21.1 ppm; IR (neat, cm^{-1}): 3350, 3023, 2919, 1578, 1513, 1471, 1459, 1390, 741, 697; LRMS (ESI): *m/z* = 318 [M+H]; HRMS (ESI): Calcd for $C_{21}H_{20}NS$: 318.1311. Found 318.1300.

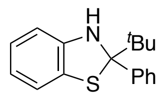
2-(*p*-Fluorobenzyl)-2-phenylbenzothiazoline (1d)



1d

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.26 (m, 5H), 7.10-7.06 (m, 1H), 7.01-6.95 (m, 1H), 6.87-6.71 (m, 6H), 4.41 (brs, 1H), 3.60 (d, J = 13.6 Hz, 1H), 3.52 (d, J = 13.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.0 (d, J = 244 Hz), 145.4, 143.0, 131.8 (d, J = 8.0 Hz), 131.0 (d, J = 3.1 Hz), 128.4, 127.7, 127.2, 126.0, 125.6, 122.2, 121.0, 115.0 (d, J = 20.9 Hz), 111.3, 81.7, 48.9 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ –116.92 - –117.00 (m, 1F) ppm; IR (neat, cm^{-1}): 3356, 3063, 2921, 2362, 1890, 1603, 1579, 1508,1472, 1460, 1222, 759, 742, 698; LRMS (ESI): *m/z* = 322 [M+H]; HRMS (ESI): Calcd for $C_{20}H_{17}FNS$: 322.1060. Found 322.1046.

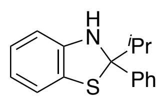
2-*tert*-Butyl-2-phenylbenzothiazoline (1e)



1e

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.52 (m, 2H), 7.30-7.24 (m, 2H), 7.23-7.19 (m, 1H), 7.02-6.98 (m, 1H), 6.89-6.83 (m, 1H), 6.75-6.65 (m, 2H), 4.70 (brs, 1H), 1.08 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.3, 144.3, 128.2, 127.1, 126.9, 124.8, 121.1, 120.7, 111.0, 91.2, 40.2, 26.9 ppm; IR (neat, cm^{-1}): 3398, 3060, 3030, 2969, 2905, 2870, 2361, 1583, 1472, 1391, 741, 700; LRMS (ESI): *m/z* = 292 [M+Na]; HRMS (ESI): Calcd for $C_{17}H_{19}NSNa$: 292.1130. Found 292.1123.

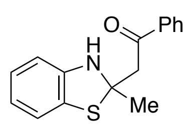
2-Isopropyl-2-phenylbenzothiazoline (1f)



1f

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.49 (m, 2H), 7.35-7.29 (m, 2H), 7.26-7.20 (m, 1H), 7.02-6.98 (m, 1H), 6.93-6.87 (m, 1H), 6.75-6.68 (m, 2H), 4.43 (brs, 1H), 2.52 (sept, J = 6.8 Hz, 1H), 1.06 (d, J = 6.8 Hz, 3H), 0.93 (d, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.2, 145.5, 128.1,127.5, 127.2, 125.9, 124.9, 121.3, 120.7, 110.6, 86.9, 39.6, 18.4, 18.3 ppm.[S9]

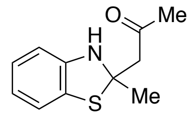
2-Phenacyl-2-methylbenzothiazoline (1’g)



1’g

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (dd, J = 8.2, 1.2 Hz, 2H), 7.61 (dt, J = 7.2, 2.0 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.05 (dd, J = 7.6, 0.8 Hz, 1H), 6.92 (td, J = 7.6, 1.2 Hz, 1H), 6.71 (td, J = 7.6, 1.2 Hz, 1H), 6.62 (dd, J = 7.8, 1.2 Hz, 1H), 5.30 (s, 1H), 3.78 (d, J = 16.0 Hz, 1H), 3.63 (d, J = 16.0 Hz, 1H), 1.89 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.6, 145.9, 136.8, 133.7, 128.8, 128.1, 125.5, 125.1, 122.2, 119.9, 109.9, 75.6, 50.3, 28.5 ppm.[S10]

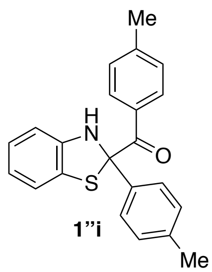
2-Acetonyl-2-methylbenzothiazoline (1’h)



1'h

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.03 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.91 (td, *J* = 7.8, 1.2 Hz, 1H), 6.71 (td, *J* = 7.6, 1.2 Hz, 1H), 6.60 (dd, *J* = 8.0, 0.8 Hz, 1H), 5.06 (s, 1H), 3.30 (d, *J* = 16.0 Hz, 1H), 3.05 (d, *J* = 20.0 Hz, 1H), 2.17 (s, 3H), 1.80 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.5, 145.8, 125.5, 125.2, 122.1, 120.0, 110.0, 74.8, 55.1, 31.3, 28.5 ppm.[S9]

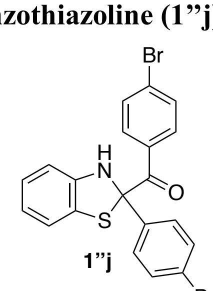
2-(*p*-Methylbenzoyl) -2-(*p*-methylphenyl)benzothiazoline (1''i)



1''i

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.76 (t, *J* = 7.6 Hz, 2H), 5.66 (brs, 1H), 2.34 (s, 3H), 2.33 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.5, 145.0, 144.1, 138.7, 138.2, 130.5, 130.2, 129.8, 129.0, 126.7, 126.0, 125.8, 121.1, 121.0, 111.8, 83.9, 21.7, 21.1 ppm; IR (neat, cm^{-1}): 3337, 3027, 2919, 1673, 1606, 1473, 1259, 1183, 742; LRMS (ESI): *m/z* = 368 [M+Na]; HRMS (ESI): Calcd for $C_{22}H_{19}NNaOS$: 368.1080. Found 368.1098.

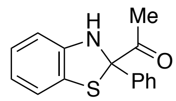
2-(*p*-Bromobenzoyl) -2-(*p*-bromophenyl)benzothiazoline (1''j)



1''j

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61-7.42 (m, 8H), 7.07 (d, *J* = 8.0 Hz, 1H), 7.00 (t, *J* = 8.0 Hz, 1H), 6.86-6.74 (m, 2H), 5.63 (brs, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.2, 144.6, 139.8, 132.4, 131.8, 131.7, 131.3, 128. 8, 128. 6, 126. 5, 125.4, 123.3, 121.7, 121.3, 112.3, 83.4 ppm; IR (neat, cm^{-1}): 3343, 3067, 1678, 1584, 1485, 1472, 1395, 1258, 1239, 1073, 1009, 737; LRMS (ESI): *m/z* - 496 [M+Na]; HRMS (ESI): Calcd for $C_{20}H_{13}Br_2NNaOS$: 495.8977. Found 495.8994.

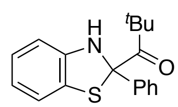
2-Acetyl-2-phenylbenzothiazoline (1k)



1k

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.2 Hz, 2H), 7.48-7.31 (m, 3H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.81 (t, *J* = 6.4 Hz, 2H), 5.53 (brs, 1H), 2.22 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.8, 145.9, 138.8, 129.0, 128.9, 127.0, 126.1, 125.0, 121.7, 121.5, 112.4, 86.3, 24.7 ppm; IR (neat, cm^{-1}): 3339, 1701, 1460, 1177, 753, 697; LRMS (ESI): *m/z* = 278 [M+Na] HRMS (ESI): Calcd for $C_{15}H_{13}NNaOS$: 278.0610. Found 278.0600.

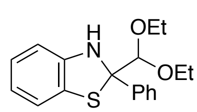
2-Pivaloyl-2-phenylbenzothiazoline (1l)



1l

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 7.6 Hz, 2H), 7.46-7.29 (m, 3H), 7.10 (d, *J* = 7.6 Hz, 1H), 6.95 (t, *J* = 8.0 Hz, 1H), 6.77 (t, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 5.66 (brs, 1H), 1.12 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.6, 145.6, 139.3, 129.0, 128.6, 126.6, 126.0, 125.2, 121.2, 121.1, 111.8, 85.3, 43.8, 29.4 ppm; IR (neat, cm^{-1}): 3344, 2984, 1688, 1580, 1474, 741, 701; LRMS (ESI): *m/z* = 320 [M+Na]; HRMS (ESI): Calcd for $C_{18}H_{19}NNaOS$: 320.1080. Found 320.1071.

2-Diethoxymethyl-2-phenylbenzothiazoline (1m)



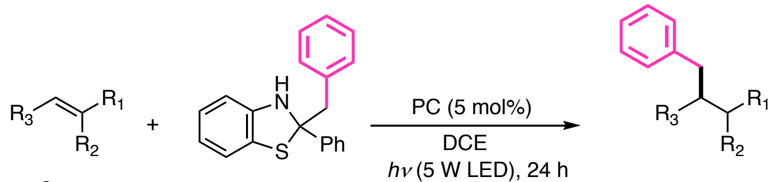
1m

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63-7.59 (m, 2H), 7.35-7.29 (m, 2H), 7.28-7.24 (m, 1H), 7.02-6.98 (m, 1H), 6.93-

6.89 (m, 1H), 6.75-6.68 (m, 2H), 4.87 (s, 1H), 3.87-3.71 (m, 2H), 3.68-3.56 (m, 2H), 1.21-1.12 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.3, 141.8, 127.8, 127.6, 127.2, 126.5, 125.2, 121.3, 120.4, 110.3, 107.5, 83.1, 67.0, 66.1, 15.30, 15.28 ppm; IR (neat, cm^{-1}): 3367, 3062, 2975, 2879, 1581, 1473, 1460, 1446, 1111, 1062, 741, 714, 696; LRMS (ESI): *m/z* = 338 [M+Na]; HRMS (ESI): Calcd for $C_{18}H_{21}NO_2SNa$: 338.1185. Found 338.1192.

3-2. General procedure of hydroalkylation and hydroacylation

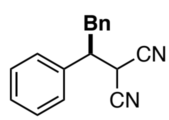
General procedure of alkylation (Procedure I)



Alkenes (0.05 mmol), **1a** (30.4 mg, 0.1 mmol) and $Ru(bpy)_3Cl_2$•$6H_2O$ (1.9 mg, 0.0025 mmol) were dissolved in degassed 1,2-dichloroethane (1.0 mL), if necessary, other additives were added at this point. Then white LED (5 W) was irradiated at room temperature for 24 h. The solvent was evaporated and 1,1,2-trichloroethane was added as an internal standard and ^1H NMR was measured in $CDCl_3$ for the calculation of the NMR yield. Then crude products were purified by preparative TLC to give **3**.

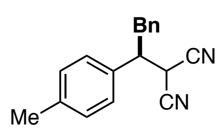
Other hydroalkylation reactions in Table 4 were performed based on this Procedure I.

Data of products



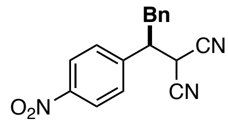
3aa

^1H NMR (400 MHz, $CDCl_3$): δ 7.45-7.37 (m, 5 H), 7.34-7.27 (m, 3H), 7.21-7.17 (m, 2H), 3.85 (d, J = 4.8 Hz, 1H), 3.50-3.42 (m, 1H), 3.27-3.21 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.6, 136.4, 129.23, 129.19, 129.1, 128.9, 128.0, 127.6, 112.1, 111.4, 48.3, 38.5, 28.5 ppm.[S11]



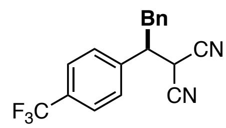
3ba

^1H NMR (400 MHz, $CDCl_3$): δ 7.35-7.27 (m, 5H), 7.24-7.18 (m, 4H), 3.82 (d, J = 4.8 Hz, 1H), 3.50-3.40 (m, 1H), 3.31-3.18 (m, 2H), 2.37 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.0, 136.8, 133.4, 129.9, 129.2, 128.9, 127.8, 127.6, 112.2, 111.5, 48.0, 38.5, 28.7, 21.2 ppm; IR (neat, cm^{-1}) 3445, 3062, 3029, 2922, 2862, 2360, 2254, 1905, 1604, 1515, 1496, 1455, 702; LRMS (ESI): m/z = 283 [M+Na]; HRMS (ESI): Calcd for $C_{18}H_{16}N_2Na$: 283.1206. Found 283.1217.



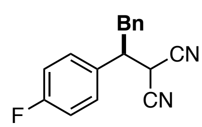
3ca

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32-8.28 (m, 2H), 7.62-7.58 (m, 2H), 7.37-7.30 (m, 3H), 7.21-7.17 (m, 2H), 3.92 (d, *J* = 2.4 Hz, 1H), 3.64-3.57 (m, 1H), 3.36-3.23 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 143.3. 135.9, 129.5, 129.3, 128.8, 128.1, 124.4, 111.5, 110.8, 47.7, 38.3, 28.0 ppm; IR (neat, cm^{-1}): 3085, 3028, 2906, 2850, 2360, 2255, 1605, 1516, 1350, 701; LRMS (ESI): *m/z* = 314 [M+Na]; HRMS (ESI): Calcd for $C_{17}H_{13}N_3O_2Na$: 314.0900. Found 314.0894.



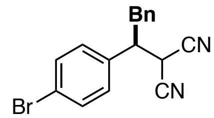
3da

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.39-7.29 (m, 3H), 7.14-7.10 (m, 2H), 3.88 (d, *J* = 5.2 Hz, 1H), 3.57-3.50 (m, 1H), 3.34-3.21 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.2, 135.9, 131.4 (q, *J* = 32 Hz), 129.4, 129.0, 128.9, 128.6, 127.9,126.2 (q, *J* = 3.7 Hz), 123.6 (q, *J* = 271 Hz), 111.2, 111.1, 48.0, 38.3, 28.2 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ –64.29 (s, 3F) ppm; IR (neat, cm^{-1}): 3065, 3031, 2903, 2365, 2256, 1924, 1620, 1422, 1327, 1169, 1126, 1070, 701; LRMS (ESI): *m/z* = 337 [M+Na]; HRMS (ESI): Calcd for $C_{18}H_{13}F_3N_2Na$: 337.0923. Found 337.0939.



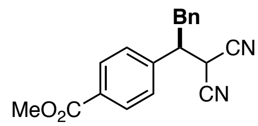
3ea

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.34 (m, 2H), 7.34-7.26 (m, 3H), 7.20-7.16 (m, 2H), 7.14-7.08 (m, 2H), 3.84 (d, *J* = 5.2 Hz, 1H), 3.57-3.42 (m, 1H), 3.29-3.17 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.0 (d, *J* = 247 Hz), 136.4, 132.2 (d, *J* = 3.4 Hz), 129.94, 129.87, 129.3, 128.9, 127.7, 116.4, 116.2, 112.0, 111.3, 47.6, 38.6, 28.6 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ 113.65 - –113.72 (m, 1F) ppm; IR (neat, cm^{-1}): 3064, 3030, 2903, 2863, 2255, 2230, 1955, 1894, 1682, 1605, 1512, 1497, 1455, 1231, 1162, 841, 757, 701; LRMS (ESI): *m/z* = 287 [M+Na]; HRMS (ESI) Calcd for $C_{17}H_{13}FN_2Na$: 287.0955. Found 287.0942.



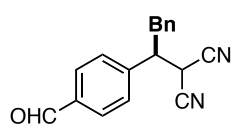
3fa

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.38-7.25 (m, 5H), 7.18 (d, *J* = 6.8 Hz, 2H), 3.83 (d, *J* = 4.8 Hz, 1H), 3.47-3.40 (m, 1H), 3.29-3.18 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.2, 135.3, 132.4, 129.7, 129.3, 127.8, 123.3, 111.8, 111.2, 47.8, 38.4, 28.3 ppm; IR (neat, cm^{-1}): 3064, 3029, 2900, 2255, 2230, 1902, 1592, 1490, 1455, 1409, 1075, 1011, 759, 701; LRMS (ESI): *m/z* = 347 [M+Na]; HRMS (ESI): Calcd for $C_{17}H_{13}BrN_2Na$: 347.0213. Found 347.0165.



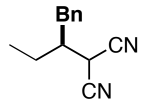
3ga

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11-8.07 (m, 2H), 7.49-7.45 (m, 2H), 7.34-7.27 (m, 3H), 7.20-7.16 (m, 2H), 3.93 (s, 3H), 3.89 (d, *J* = 5.2 Hz, 1H), 3.55-3.51 (m, 1H), 3.51-3.25 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 141.2, 136.1, 120.9, 120.4, 129.3, 128.9, 128.2, 127.8, 111.8, 111.2, 52.3, 48.2, 38.4, 28.2 ppm; IR (neat, cm^{-1}) :3422, 3063, 3029, 2952, 2902, 2360, 2255, 1942, 1720, 1285, 1114, 708, 419; LRMS (ESI): *m/z* = 327 [M+Na]; HRMS (ESI): Calcd for $C_{19}H_{16}N_2O_2Na$: 327.1104. Found 283.1111.



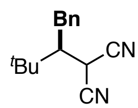
3ha

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.04 (s, 1H), 7.97-7.92 (m, 2H), 7.60-7.56 (m, 2H), 7.34 (m, 3H), 7.21-7.17 (m, 2H), 3.92 (d, *J* = 5.2 Hz, 1H), 3.60-3.53 (m, 1H), 3.36-3.23 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.5, 142.8, 136.8, 135.9, 130.4, 129.3, 128.90, 128.88, 127.9, 111.7,111.1, 48.3, 38.4, 28.1 ppm; IR (neat, cm^{-1}): 3379, 3064, 3029, 2903, 2850, 2747, 2255, 1955, 1814, 1703, 1608, 1215, 757; LRMS (ESI): *m/z* = 297 [M+Na]; HRMS (ESI): Calcd for $C_{18}H_{14}N_2ONa$: 297.0998. Found 297.1013.



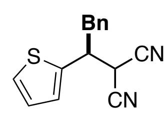
3ia

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.39-7.33 (m, 2H), 7.33-7.27 (m, 1H), 7.21-7.17 (m, 2H), 3.61 (d, *J* = 4.0 Hz, 1H), 3.04 (dd, *J* = 14.2, 6.0 Hz, 1H), 2.65 (dd, *J* = 14.2, 9.6 Hz, 1H), 2.25-2.15 (m, 1H), 1.91-1.78 (m, 1H), 1.74-1.61 (m, 1H), 1.13 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ 137.0, 129.2, 128.9, 127.5, 112.5, 111.5, 44.4, 37.1, 26.4, 24.4, 11.3 ppm; IR (neat, cm^{-1}): 3087, 3064, 3029, 2969, 2930, 2881, 2254, 19551812, 1718, 1655, 1604, 1584, 1496, 1456, 737, 701; LRMS (ESI): *m/z* = 199 [M+H]; HRMS (ESI): Calcd for $C_{13}H_{15}N_2$: 199.1230. Found 199.1228.



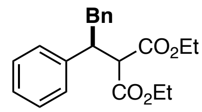
3ja

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.40-7.27 (m, 5H), 3.87 (d, *J* = 2.0 Hz, 1H), 3.20 (dd, *J* =14.2, 4.0 Hz, 1H), 2.73 (dd, *J* = 14.4, 11.2 Hz, 1H), 2.19-2.15 (m, 1H), 1.91-1.78 (m, 1H), 1.74-1.61 (m, 1H), 1.13 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ 137.8, 129.22, 129.18, 127.6, 113.1, 112.2, 53.0, 34.6, 34.5, 28.2, 22.3 ppm; IR (neat, cm^{-1}): 3087, 3064, 3030, 2967, 2873, 2251, 1604, 1585, 1496, 1478, 1456, 1373, 1227, 742, 700; LRMS (ESI): *m/z* = 249 [M+Na]; HRMS (ESI) Calcd for $C_{15}H_{18}N_2Na$: 249.1362. Found 249.1371.



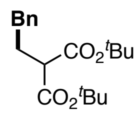
3ka

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.38-7.27 (m, 5H), 7.25-7.22 (m, 2H), 7.22-7.15 (m, 1H), 7.11-7.04 (m, 1H), 3.86-3.77 (m, 2H), 3.38-3.20 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ 138.6, 136.2, 129.3, 129.1, 28.8, 128.4, 128.2, 127.8, 127.4, 127.0, 126.0, 111.9, 111.1, 44.1, 40.0, 29.3 ppm; IR (neat, cm^{-1}): 3445, 3108, 3064, 3030, 2900, 2855, 2255, 2224, 1603, 1571, 1496, 1455, 701; LRMS (ESI): *m/z* = 275 [M+Na]; HRMS (ESI) Calcd for $C_{15}H_{12}N_2SNa$: 275.0613. Found 275.0601.



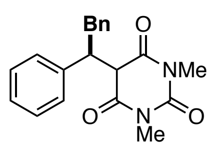
3la

^1H NMR (400 MHz, $CDCl_3$): δ 7.19-7.03 (m, 8H), 6.94-6.90 (m, 2H), 4.25 (q, J = 6.8 Hz, 2H), 3.88 (q, J = 7.2 Hz, 2H), 3.79 (d, J = 10.8 Hz, 1H), 3.71-3.62 (m, 1H), 3.10 (dd, J = 13.2 Hz, 4.0 Hz, 1H), 2.83 (dd, J = 13.2 Hz, 10.4 Hz, 1H), 1.31 (t, J = 7.2 Hz, 3H), 0.92 (t, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5, 167.7. 140.0, 139.0, 129.3, 128.5, 128.1, 128.0, 126.9, 126.1, 61.7, 61.2, 58.0, 47.7, 40.8, 14.2, 13.7 ppm.[S12]



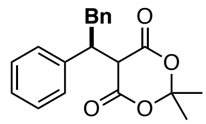
3ma

^1H NMR (400 MHz, $CDCl_3$): δ 7.32-7.26 (m, 2H), 7.22-7.17 (m, 3H), 3.14 (t, J = 7.6 Hz, 1H), 2.65 (t, J = 7.6 Hz, 2H), 2.16-2.08 (m, 2H), 1.49 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.8, 141.1, 128.6, 128.4, 126.1, 81.4, 53.2, 33.3, 30.4, 28.0 ppm; IR (neat, cm^{-1}): 3449, 3087, 3063, 3028, 3004, 2978, 2931, 2865, 1743, 1727, 1368, 1287, 1254, 1138, 849, 700; LRMS (ESI): m/z = 343 [M+Na]; HRMS (ESI): Calcd for $C_{19}H_{28}O_4Na$: 343.1880. Found 343.1880.



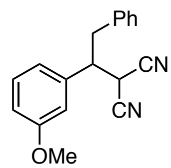
3na

^1H NMR (400 MHz, $CDCl_3$): δ 7.40-7.37 (m, 2H), 7.34-7.19 (m, 6H), 7.10-7.04 (m, 2H), 3.88-3.82 (m, 1H), 3.61-3.52 (m, 2H), 3.21-3.04 (m, 1H), 3.04 (s, 3H), 3.01 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0, 167.3, 150.9, 138.8, 138.2, 129.6, 128.9, 128.64, 128.59, 128.4, 127.3, 126.7, 52.3, 52.3, 37.6, 28.1, 27.9 ppm; IR (neat, cm^{-1}): 3062, 3029, 2923, 2852, 1746, 1681, 1453, 1421, 1380, 754, 703; LRMS (ESI): m/z = 359 [M+Na]; HRMS (ESI): Calcd for $C_{20}H_{20}N_2O_3Na$: 359.1366. Found 359.1383.



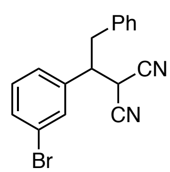
3oa

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.23 (m, 10H), 4.11-4.04 (m, 1H), 3.72 (dd, *J* = 14.0, 11.2 Hz, 1H), 3.54 (d, *J* = 2.8 Hz, 1H), 3.25 (dd, *J* = 13.6, 5.6 Hz, 1H), 1.57 (s, 3H), 1.54 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 164.7, 139.6, 139.2, 129.4, 129.0, 128.8, 127.9, 126.9, 105.4, 48.5, 47.8, 38.3, 28.2, 28.1 ppm.[S13]



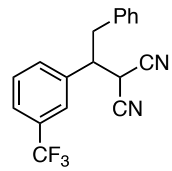
3xa

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.27 (m, 4H), 7.22-7.18 (m, 2H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.94-6.90 (m, 2H), 3.84 (d, *J* = 5.2 Hz, 1H), 3.81 (s, 3H), 3.46-3.39 (m, 1H), 3.25 (d, *J* = 8.0 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 137.9, 136.6, 130.3, 129.2, 128.9, 127.6, 120.2, 114.3, 113.9, 112.1, 111.5, 55.3, 48.3, 38.5, 28.5 ppm; IR (neat, cm^{-1}): 3649, 3381, 3062, 3029, 2923, 2853, 2838, 2360, 2254, 1954, 1682, 1602, 1585, 1494, 1455, 1438, 1264, 1051, 702; LRMS (ESI): *m/z* = 299 [M+Na]; HRMS (ESI): Calcd for $C_{18}H_{16}N_2ONa$: 299.1155. Found 299.1155.



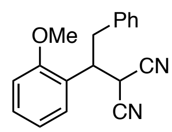
3ya

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.52 (m, 2H), 7.38-7.27 (m, 5H), 7.21-7.17 (m, 2H), 3.85 (d, *J* = 5.2 Hz, 1H), 3.46-3.39 (m, 1H), 3.30-3.20 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.6, 136.1, 132.4, 131.2, 130.8, 129.3, 128.9, 127.8, 127.0, 123.2, 111.7, 111.1, 47.9, 38.4, 28.3 ppm; IR (neat, cm^{-1}): 3551, 3063, 3029, 2917, 2850, 2255, 1952, 1878, 1718, 1569, 1476, 704; LRMS (ESI): *m/z* = 347 [M+Na]; HRMS (ESI): Calcd for $C_{17}H_{13}BrN_2Na$: 347.0213. Found 347.0204.



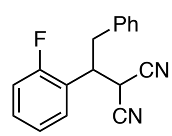
3za

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.69-7.53 (m, 4H), 7.38-7.27 (m, 3H), 7.21-7.17 (m, 2H), 3.88 (d, J = 5.2 Hz, 1H), 3.58-3.51 (m, 1H), 3.34-3.21 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ 137.4, 135.9, 131.6 (q, J = 32.8 Hz), 131.1, 129.8, 129.1, 128.9, 127.9, 126.1 (q, J = 3.7 Hz), 125.0 (q, J = 3.8 Hz), 123.7 (q, J = 271 Hz), 111.7, 111.1, 48.1, 38.4, 28.2 ppm;^{19}F NMR (376 MHz, CDCl$_3$): δ –64.09 (s, 3F) ppm; IR (neat, cm^{-1}): 3066, 3031, 2903, 2360, 1691, 1672, 1603, 1496, 1454, 1330, 1168, 1128, 1076, 704; LRMS (ESI): *m/z* = 337 [M+Na]; HRMS (ESI) Calcd for $C_{18}H_{13}F_3N_2Na$: 337.0923. Found 337.0936.



3αa

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.34-7.19 (m, 5H), 7.16-7.12 (m, 2H), 6.97-6.90 (m, 2H), 4.15 (d, J = 6.4 Hz, 1H), 4.03-3.95 (m, 1H), 3.86 (s, 3H), 3.33-3.21 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ 156.9, 137.2, 129.9, 129.0, 128.84, 128.78, 127.2, 124.3, 121.1, 112.3, 112.2, 111.0, 55.5, 42.2, 37.0, 27.3 ppm; IR (neat, cm^{-1}) 3566, 3064, 3029, 2922, 2841, 2254, 2044, 1952, 1904, 1682, 1603, 1587, 1495, 1248, 1027, 755, 700; LRMS (ESI): *m/z* = 299 [M+Na]; HRMS (ESI): Calcd for $C_{18}H_{16}N_2ONa$: 299.1155. Found 299.1157.

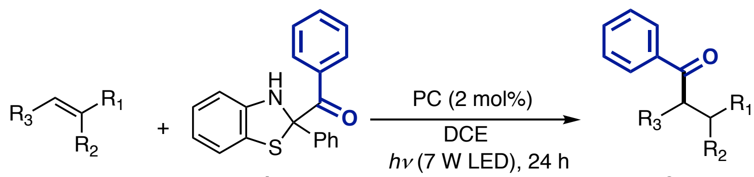


3βa

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.42-7.23 (m, 5H), 7.22-7.09 (m, 4H), 3.98 (d, J = 6.4 Hz, 1H), 3.95-3.88 (m, 1H), 3.37-3.28 (m, 1H), 3.27-3.18 (m, 1H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ 160.1 (d, J = 245 Hz), 136.3, 130.7 (d, J = 8.6 Hz), 129.1, 128.92, 128.88, 127.6, 124.9 (d, J = 3.5 Hz), 123.5 (d, J = 13.4 Hz), 116.2 (d, J = 22.4 Hz), 111.8, 111.5, 41.4, 37.8, 27.6, 27.6 ppm; IR (neat, cm^{-1}): 3566, 3087, 3065, 3030, 2905, 2666, 2256, 1956, 1806, 1616, 1603, 1585, 1493, 1456, 760, 700; ^{19}F NMR (376 MHz, CDCl$_3$): δ –117.95- –118.01 (m, 1F) ppm; LRMS

(ESI): *m/z* = 287 [M+Na]; HRMS (ESI): Calcd for $C_{17}H_{13}N_2FNa$: 287.0955. Found 287.0961.

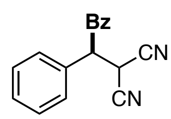
General procedure of acylation (Procedure II)



2 1b 3

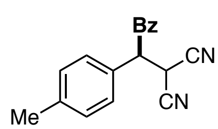
Alkenes (0.10 mmol), **1b** (63.4 mg, 0.20 mmol) and Eosin Y-2Na (1.4 mg, 0.0020 mmol) was dissolved in degassed 1,2-dichloroethane (1.0 mL), if necessary, other additives were added at this point. Then irradiation of white LED (7 W) at room temperature. After 24 h, the solvent was evaporated and the 1,1,2-trichloroethane as an internal standard was added and ^{1}H NMR was measured in $CDCl_3$ for the calculation of the NMR yield. Then crude products were purified by preparative TLC to give **3**.

Other acylation reactions in Table 4 were performed based on this Procedure II.



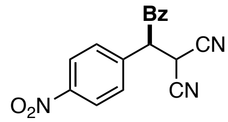
3ab

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 7.2 Hz, 2H), 7.55 (t, J = 7.6 Hz, 1H), 7.46-7.30 (m, 7H), 5.11 (d, J = 8.4 Hz, 1H), 4.54 (d, J = 8.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.0, 134.4, 133.9, 132.1, 130.1, 129.9, 129.3, 129.0, 128.6, 112.1, 111.6, 54.8, 26.8 ppm.[S11]



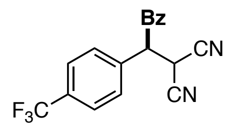
3bb

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92-7.88 (m, 2H), 7.57-7.51 (m, 1H), 7.44-7.38 (m, 2H), 7.26-7.19 (m, 4H), 5.07 (d, J = 8.4 Hz, 1H), 4.51 (d, J = 8.4 Hz), 2.32 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.1, 140.1, 134.4, 133.9, 130.8, 129.3, 129.0, 128.9, 128.4, 112.2, 111.7, 54.6, 26.9, 21.2 ppm; IR (neat, cm^{-1}): 3350, 3059, 3027, 2921, 2360, 2257, 2209, 1968, 1910, 1811, 1772, 1682, 1256, 1223, 755, 688; LRMS (ESI): *m/z* 275 [M+H] HRMS (ESI) Calcd for $C_{18}H_{15}N_2O$: 275.1179. Found 275.1179.



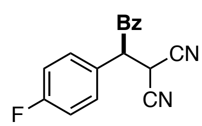
3cb

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.0 Hz, 2H), 7.87 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.62-7.57 (m, 3H), 7.45 (t, *J* = 8.0 Hz, 2H), 5.23 (d, *J* = 8.0 Hz, 1H), 4.60 (d, *J* = 7.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.0, 148.8, 138.6, 135.1, 133.3, 129.9, 129.3, 129.2, 125.2, 111.4, 110.9, 54.0, 26.5 ppm; IR (KBr, cm^{-1}) 3354, 3082, 3025, 2919, 2258, 2211, 1931, 1683, 1597, 1524, 1449, 1350, 1260, 1224, 1112, 843, 755, 706; ESI-MS (*m*/*z*): $[M]^+$ calcd. for $C_{17}H_{11}N_3NaO_3$, 328.0700; found, 328.0693.



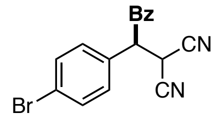
3db

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90-7.86 (m, 2H), 7.72-7.66 (m, 2H), 7.62-7.56 (m, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.47-7.40 (m, 2H), 5.19 (d, *J* = 8.0 Hz, 1H), 4.57 (d, *J* = 8.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.4, 135.8, 134.9, 133.4, 132.3 (q, *J* = 2.9 Hz), 129.24, 129.17, 127.14, 127.10, 127.07, 127.0, 123.1 (q, *J* = 271 Hz), 111.7, 111.1, 54.2 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ –64.35 (s, 3F) ppm; IR (neat, cm^{-1}): 3066, 3028, 2920, 2360, 2258, 1927, 1684, 1619, 1597, 1580, 1326, 1171, 1130, 1069, 758, 699; LRMS (ESI): *m/z* = 351 [M+Na]; HRMS (ESI): Calcd for $C_{18}H_{11}F_3N_2ONa$: 351.0716. Found 351.0726.



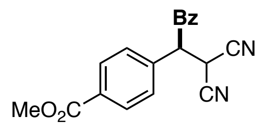
3eb

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (dd, *J* = 8.4, 0.4 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.37-7.33 (m, 2H), 7.12 (t, *J* = 8.4 Hz, 2H), 5.10 (d, *J* = 8.0 Hz, 1H), 4.52 (d, *J* = 8.0, 1H) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ –111.54 (m, 1F); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.9, 164.7, 162.2, 134.6, 133.7, 130.6 (d, *J* = 8.6 Hz), 129.2 (d, *J* = 19.8 Hz), 127.9 (d, *J* = 3.3 Hz), 117.3 (d, *J* = 21.9 Hz), 112.0, 111.5, 53.9, 26.9 ppm; IR (KBr, cm^{-1}) 3071, 3027, 2918, 2258, 1902, 1682, 1598, 1510, 1449, 1239, 1162, 816, 758, 689; ESI-MS (*m*/*z*): $[M]^+$ calcd. for $C_{17}H_{11}FN_2NaO$, 301.0753; found, 301.0748.



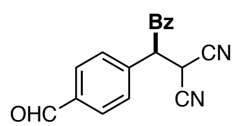
3fb

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89-7.85 (m, 2H), 7.60-7.53 (m, 3H), 7.46-7.40 (m, 2H), 7.26-7.22 (m, 2H), 5.08 (d, J = 8.0 Hz, 1H), 4.52 (d, J = 8.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.6, 134.7, 133.6, 122.4, 131.0, 130.2, 129.2, 129.1, 124.5, 111.9, 111.3, 54.1, 26.6 ppm; IR (neat, cm^{-1}): 3026, 2916, 2360, 2257, 1908, 1682, 1596, 1579, 1489, 1258, 1222, 1074, 1011, 761; LRMS (ESI): *m/z* = 360 [M+Na]; HRMS (ESI): Calcd for $C_{17}H_{11}BrN_2ONa$: 360.9947. Found 360.9960.



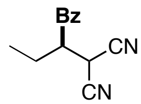
3gb

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11-8.07 (m, 2H), 7.90-7.85 (m, 2H), 7.60-7.54 (m, 1H), 7.47-7.39 (m, 4H), 5.16 (d, J = 8.4 Hz, 1H), 4.57 (d, J = 8.0 Hz, 1H), 3.91 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.5, 165.9, 136.6, 134.7, 133.6, 131.7, 131.2, 129.2, 129.1, 128.8, 111.8, 111.2, 54.6, 52.4, 26.5 ppm; IR (neat, cm^{-1}): 3348, 3064, 3025, 2953, 2917, 2846, 2258, 1938, 1816, 1717, 1683, 1286, 1114, 759, 706; LRMS (ESI): *m/z* = 341 [M+Na]; HRMS (ESI): Calcd for $C_{19}H_{14}N_2O_3Na$: 341.0897. Found 341.0911.



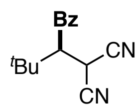
3hb

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.01 (s, 1H), 7.97-7.93 (m, 2H), 7.91-7.86 (m, 2H), 7.61-7.54 (m, 3H), 7.46-7.40 (m, 2H), 5.20 (d, J = 8.4 Hz, 1H), 4.60 (d, J = 8.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.3, 190.9, 138.0, 137.2, 134.9, 133.5, 131.1, 129.5, 129.2, 129.2, 111.7, 111.1, 54.6, 26.5 ppm; IR (neat, cm^{-1}): 3354, 3063, 3025, 2917, 2838, 2743, 2363, 2258, 1931, 1703, 1684, 1607, 1213, 1174, 759, 696; LRMS (ESI): *m/z* = 311 [M+Na]; HRMS (ESI) Calcd for $C_{18}H_{12}N_2O_3Na$: 311.0791. Found 348.0803.



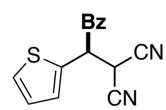
3ib

[1]H NMR (400 MHz, $CDCl_3$): δ 7.98-7.93 (m, 2H), 7.71-7.65 (m, 1H), 7.58-7.52 (m, 2H), 4.32 (d, J = 8.8 Hz, 1H), 4.14-4.09 (m, 1H), 2.20-1.98 (m, 2H), 0.94 (t, J = 7.6 Hz, 3H) ppm; [13]C NMR (100 MHz, $CDCl_3$): δ 196.4, 134.7, 134.5, 129.2, 128.6, 112.2, 111.9, 48.3, 24.0, 23.1, 9.7 ppm; IR (neat, cm^{-1}): 3064, 2973, 2916, 2359, 2256, 1682, 1597, 1579, 1449, 697; LRMS (ESI): m/z = 235 [M+Na]; HRMS (ESI): Calcd for $C_{13}H_{12}N_2ONa$: 235.0842. Found 235.0843.



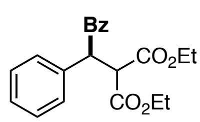
3jb

[1]H NMR (400 MHz, $CDCl_3$): δ 7.96 (dd, J = 10.0, 4.0 Hz, 2H), 7.66 (td, J = 8.0, 1.2 Hz, 1H), 7.53 (t, J = 8.0 Hz, 2H), 4.28 (d, J = 8.0 Hz, 1H), 4.07 (d, J = 8.0 Hz, 1H), 1.14 (s, 9H) ppm; [13]C NMR (100 MHz, $CDCl_3$): δ = 198.2, 137.4, 134.4, 129.1, 128.6, 113.2, 112.5, 54.1, 34.8, 28.6, 22.3 ppm; IR (KBr, cm^{-1}) 3382, 3063, 2969, 2925, 2255, 1675, 1597, 1579, 1477, 1448, 1374, 1303, 1247, 1219, 756, 690; ESI-MS (m/z): $[M]^+$ calcd. for $C_{15}H_{16}N_2NaO$, 263.1165; Found, 263.1155.



3kb

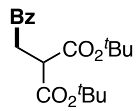
[1]H NMR (400 MHz, $CDCl_3$): δ 7.98-7.93 (m, 2H), 7.63-7.57 (m, 1H), 7.49-7.43 (m, 2H), 7.40-7.37 (m, 1H), 7.14-7.11 (m, 1H), 7.05-7.01 (m, 1H), 5.41 (d, J = 8.4 Hz, 1H), 4.59 (dd, J = 8.4, 0.8 Hz, 1H) ppm; [13]C NMR (100 MHz, $CDCl_3$): δ 191.7, 134.7, 133.6, 132.8, 129.3, 129.2, 129.1, 128.4, 128.3, 111.7, 111.4, 49.5, 27.4 ppm; IR (neat, cm^{-1}): 3110, 2918, 2360, 2257, 1683, 1449, 1247, 754, 707, 687; LRMS (ESI): m/z = 289 [M+Na]; HRMS (ESI): Calcd for $C_{15}H_{10}N_2OSNa$: 289.0406. Found 289.0408.



3lb

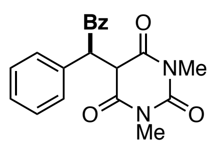
[1]H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 7.2 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.35-

7.16 (m, 5H), 5.32 (d, *J* = 11.2 Hz, 1H), 4.44 (d, *J* = 11.2 Hz, 1H), 4.23-4.11 (m, 2H), 3.94 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H), 0.96 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.3, 168.2, 168.1, 135.9, 134.5, 133.2, 129.02, 128.97, 128.91, 128.6, 128.0, 61.9, 61.4, 56.0, 52.9, 14.0, 13.8 ppm; IR (neat, cm^{-1}): 3456, 3344, 3063, 3030, 2982, 2938, 2905, 1966, 1902, 1730, 1682, 1597, 1449, 756, 699, 604, 548; LRMS (ESI): *m/z* 377 [M+Na]; HRMS (ESI): Calcd for $C_{21}H_{22}NaO_5$: 377.1359. Found 377.1375.



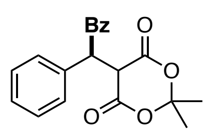
3mb

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 6.8 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 3.89 (t, *J* = 7.2 Hz, 1H), 3.52 (d, *J* = 7.2 Hz, 2H), 1.48 (s, 18H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.9, 168.4, 136.4, 133.3, 128.6, 128.1, 81.8, 49.2, 37.8, 27.9 ppm; IR (neat, cm^{-1}): 3447, 2978, 1730, 1692, 1368, 1256, 1142, 849, 768, 691; LRMS (ESI): *m/z* = 357 [M+Na]; HRMS (ESI): Calcd for $C_{19}H_{26}NaO_5$: 357.1672. Found 357.1681.



3nb

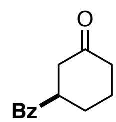
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.37-7.20 (m, 7H), 5.82 (d, *J* = 3.2 Hz, 1H), 3.83 (d, *J* = 3.2 Hz, 1H), 3.33 (s, 3H), 3.30 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.1, 167.7, 167.1, 151.5, 137.0, 134.9, 133.6, 130.2, 129.4, 128.59, 128.58, 127.7, 56.7, 51.4, 28.9, 28.6 ppm; IR (neat, cm^{-1}): 3429, 3063, 2959, 1968, 1908, 1682, 1597, 1580, 1455, 1109, 938, 864, 751, 701, 629, 562; LRMS (ESI): *m/z* = 373 [M+Na]; HRMS (ESI): Calcd for $C_{20}H_{18}N_2NaO_4$: 373.1159. Found 373.1152.



3ob

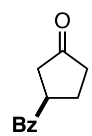
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.40-7.20 (m, 7H), 5.59 (d, *J* = 4.8 Hz, 1H), 4.20 (d, *J* = 4.8 Hz, 1H), 1.84 (s, 3H), 1.82 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.9, 164.7, 164.3, 136.1, 135.0, 133.4, 130.3, 129.3, 128.7, 128.5, 127.8, 105.2, 53.7, 49.5, 28.4, 27.0 ppm; IR (neat, cm^{-1}) 3063, 3003, 2924, 1748, 1680, 1318, 1266, 1225, 737, 718, 699; LRMS (ESI): *m/z* = 361 [M+Na]; HRMS (ESI)

Calcd for $C_{20}H_{18}NaO_5$: 361.1046. Found 361.1062.



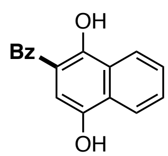
3qb

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 7.6 Hz, 2H), 7.60 (t, J = 7.2 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 3.90-3.75 (m, 1H), 2.73 (dd, J = 14.4, 11.0 Hz, 1H), 2.54-2.30 (m, 3H), 2.20-2.05 (m, 2H), 1.95-1.78 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.2, 200.4, 135.4, 133.5, 128.9, 128.4, 45.2, 43.2, 41.0, 28.4, 24.8 ppm.[S16]



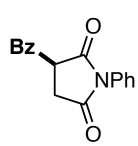
3rb

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 7.2 Hz, 2H), 7.62 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 7.4 Hz, 2H), 4.20-4.08 (m, 1H), 2.72 (dd, J = 18.4, 7.8 Hz, 1H), 2.51-2.10 (m, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 216.8, 200.2, 135.6, 133.6, 128.9, 128.5, 43.0, 41.0, 37.3, 27.0 ppm.[S16]



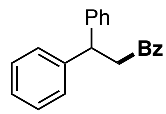
3sb

^{1}H NMR (400 MHz, $CDCl_3$): δ 13.56 (s, 1H), 8.52 (d, J = 8.0 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.77-7.40 (m, 7H), 6.86 (s, 1H), 5.10 (brs, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.9, 158.8, 142.6, 138.2, 131.6, 130.1, 129.4, 128.9, 128.4, 126.6, 126.1, 124.7, 121.7, 111.5, 108.0 ppm.[S17]



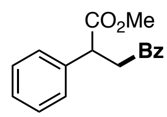
3ub

Mixture of keto and enol. The data of keto form: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19-8.13 (m, 2H), 7.79-7.27 (m, 8H), 5.02 (dd, 9.2, 4.0 Hz, 1H), 3.57 (dd, J = 18.4, 4.4 Hz, 1H), 3.06 (dd, J = 18.0, 8.8 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.7, 171.8, 135.3, 134.4, 131.6, 131.4, 129.9, 129.2, 128.9, 128.8, 128.7, 127.7, 126.5, 126.4, 48.6, 33.8, 31.9 ppm.



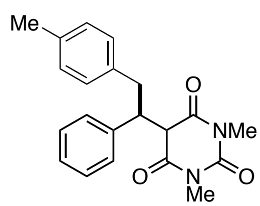
3vb

[1]H NMR (400 MHz, $CDCl_3$): δ 7.96-7.90 (m, 2H), 7.58-7.52 (m, 1H), 7.47-7.41 (m, 2H), 7.28-7.23 (m, 7H), 7.21-7.14 (m, 2H), 4.83 (t, 7.4 Hz, 1H), 3.74 (d, *J* = 7.2 Hz, 2H) ppm; [13]C NMR (100 MHz, $CDCl_3$): δ 198.0, 144.2, 137.1, 133.1, 128.61, 128.58, 128.1, 127.9, 126.4, 45.9, 44.7 ppm.[S18]



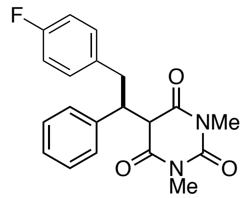
3wb

[1]H NMR (400 MHz, $CDCl_3$): δ 8.00-7.96 (m, 2H), 7.60-7.54 (m, 1H), 7.49-7.42 (m, 2H), 7.39-7.27 (m, 5H), 4.30 (dd, *J* = 10.4, 4.0 Hz, 1H), 3.96 (dd, *J* = 18.0, 10.4 Hz, 1H), 3.70 (s, 3H), 3.28 (dd, *J* = 18.0, 4.0 Hz, 1H) ppm; [13]C NMR (100 MHz, $CDCl_3$): δ 197.6, 173.9, 138.3, 136.4, 133.3, 128.9, 128.6, 128.1, 127.8, 127.6, 52.4, 46.3, 42.8 ppm.[S19]



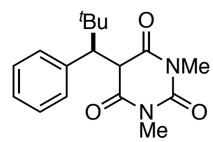
3nc

[1]H NMR (400 MHz, $CDCl_3$): δ 7.29-7.22 (m, 5H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.10-7.04 (m, 2H), 3.85-3.79 (m, 1H), 3.60 (d, *J* = 3.2 Hz, 1H), 3.51 (dd, *J* = 14.0, 10.4 Hz, 1H), 3.13 (dd, *J* = 14.0, 6.0 Hz, 1H), 3.041 (s, 3H), 3.035 (s, 3H), 2.31 (s, 3H) ppm; [13]C NMR (100 MHz, $CDCl_3$): δ 169.1, 167.3, 150.9, 138.3, 136.2, 135.7, 129.4, 129.3, 128.6, 128.3, 127.4, 52.4, 52.3, 37.2, 28.1, 27.9, 21.1 ppm; IR (neat, cm^{-1}): 3413, 3028, 2955, 2922, 2863, 1903, 1746, 1682, 1451, 1422, 1380, 754, 703; LRMS (ESI): *m/z* = 373 [M+Na]; HRMS (ESI): Calcd for $C_{21}H_{22}N_2O_3Na$: 373.1523. Found 373.1527.



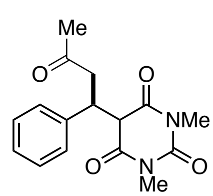
3nd

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.32 (m, 2H), 7.29-7.24 (m, 3H), 7.07-6.96 (m, 4H), 3.81-3.74 (m, 1H), 3.56 (d, J = 3.2 Hz, 1H), 3.55-3.49 (m, 1H), 3.14 (dd, J = 14.0, 6.0 Hz, 1H), 3.06 (s, 3H), 3.03 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0, 167.3, 161.7 (d, J = 243 Hz), 150.8, 137.8, 134.5 (d, J = 3.1 Hz), 131.0 (d, J = 7.9 Hz), 128.6, 128.5, 127.3, 115.5 (d, J = 21 Hz), 52.4, 52.2, 36.8, 28.1, 27.9 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ–117.60- –117.67 (m, 1F) ppm; IR (neat, cm^{-1}): 3415, 3031, 2958, 2922, 1894, 1746, 1682, 1509, 1453, 1423, 1381, 755, 704 ppm; LRMS (ESI): *m/z* = 377 [M+Na]; HRMS (ESI): Calcd for $C_{20}H_{19}FN_2O_3Na$: 377.1272. Found 377.1256.



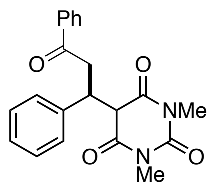
3ne

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.21 (m, 3H), 7.03-6.97 (m, 2H), 4.05 (d, J = 2.8 Hz, 1H), 3.13 (d, J = 2.8 Hz, 1H), 3.07 (s, 3H), 2.97 (s, 3H), 1.15 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3, 168.7, 151.0, 137.1, 129.4, 128.2, 128.0, 63.3, 52.4, 35.8, 29.1, 28.2 ppm; IR (neat, cm^{-1}): 3412, 3031, 2957, 1745, 1677, 1452, 1423, 1378, 753, 713; LRMS (ESI): *m/z* = 325 [M+Na]; HRMS (ESI): Calcd for $C_{17}H_{22}N_2O_3Na$: 325.1523. Found 325.1534.



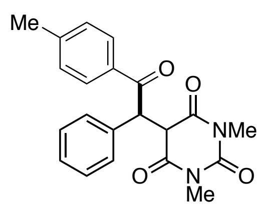
3ng

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.23 (m, 3H), 7.01-6.97 (m, 2H), 4.16-4.08 (m, 1H), 3.89 (d, J = 4.4 Hz, 1H), 3.50 (dd, J = 9.6 Hz, 18.4 Hz, 1H), 3.11 (s, 3H), 3.01 (s, 3H), 2.97 (dd, J = 6.0 Hz, 18.2 Hz, 1H), 2.22 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.3, 168.2, 167.6, 150.9, 137.7, 128.7, 128.4, 127.3, 52.7, 45.0, 44.1, 30.5, 28.1, 28.0 ppm; IR (neat, cm^{-1}): 3413, 3030, 2957, 2924, 2851, 2363, 1746, 1715, 1678, 1379, 756; LRMS (ESI): *m/z* = 303 [M+H]; HRMS (ESI): Calcd for $C_{16}H_{19}N_2O_4$: 303.1339. Found 303.1349.



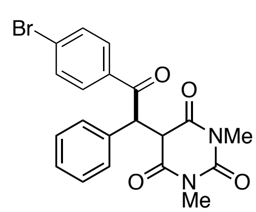
3nh

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06-8.00 (m, 2H), 7.61-7.55 (m, 1H), 7.51-7.45 (m, 2H), 7.31-7.25 (m, 3H), 7.13-7.08 (m, 2H), 4.36-4.33 (m, 1H), 4.09 (dd, *J* = 18.2, 9.2 Hz, 1H), 3.99 (d, *J* = 4.0 Hz, 1H), 3.53 (dd, *J* = 18.2, 6.0 Hz, 1H), 3.11 (s, 3H), 3.05 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 168.3, 167.8, 151.0, 138.2, 136.8, 133.4, 1128.7, 128.4, 128.1, 127.4, 53.0, 44.5, 40.4, 28.2, 28.0 ppm; IR (neat, cm^{-1}): 3361, 3062, 3030, 2956, 2924, 2852, 2360, 1746, 1682, 1449, 1379, 752; LRMS (ESI): *m/z* = 387 [M+Na]; HRMS (ESI) Calcd for $C_{21}H_{20}N_2O_4Na$: 387.1315. Found 387.1333.



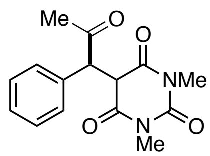
3ni

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.38-7.22 (m, 5H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.80 (d, *J* = 3.2 Hz, 1H), 3.80 (d, *J* = 3.2 Hz, 1H), 3.33 (s, 3H), 3.30 (s, 3H), 2.33 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.6, 167.7, 167.2, 151.6, 144.6, 137.3, 132.3, 130.1, 129.5, 129.3, 128.6, 127.7, 56.7, 51.4, 28.9, 28.6, 21.7 ppm; IR (neat, cm^{-1}) 2957, 2924, 1682, 1605, 1455, 1379, 1275, 741, 701. LRMS (ESI) *m/z* 387 [M+Na] HRMS (ESI) Calcd for $C_{21}H_{20}N_2NaO_4$: 387.1315. Found 387.1329.



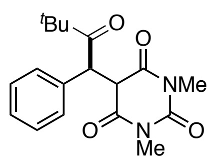
3nj

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.36-7.20 (m, 5H), 5.74 (d, *J* = 2.4 Hz, 1H), 3.84 (d, *J* = 2.4 Hz, 1H), 3.32 (s, 3H), 3.30 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.1, 167.5, 167.0, 151.5, 136.6, 133.6, 131.9, 130.8, 130.1, 128.9, 128.7, 127.9, 56.6, 51.3, 28.9, 28.6 ppm; IR (neat, cm^{-1}): 3437, 3061, 2957, 1682, 1584, 751; LRMS (ESI): *m/z* = 451 [M+Na]; HRMS (ESI): Calcd for $C_{20}H_{17}BrN_2NaO_4$: 451.0264. Found 451.0256.



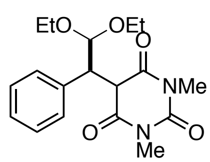
3nk

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.31 (m, 5H), 4.87 (d, *J* = 2.4 Hz, 1H), 3.88 (d, *J* = 2.8 Hz, 1H), 3.29 (s, 3H), 3.27 (s, 3H), 2.17 (s, 3H) ppm.; ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.3, 167.24, 167.22, 151.3, 135.8, 130.5, 128.8, 128.2, 60.5, 51.3, 28.9, 28.6, 28.5 ppm; IR (neat, cm^{-1}) 3061, 2924, 1682, 1455, 1422, 1379, 756, 702. LRMS (ESI) *m/z* 311 [M+Na] HRMS (ESI) Calcd for $C_{15}H_{16}N_2NaO_4$: 311.1002. Found 311.1017.



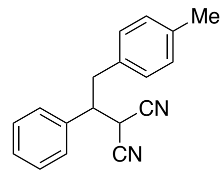
3nl

The pivaloyl adduct **3nl** was obtained too low yield to isolate. The ^{1}H NMR data from crude product, see: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.15 (m, 5H), 5.27 (d, *J* = 4.4 Hz, 1H), 3.62 (d, *J* = 4.0 Hz, 1H), 3.31 (s, 3H), 3.26 (s, 3H), 1.02 (s, 9H) ppm.



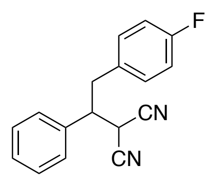
3nm

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.24 (m, 3H), 7.20-7.16 (m, 2H), 5.28 (d, *J* = 8.8 Hz, 1H), 4.01 (d, *J* = 2.8 Hz, 1H), 3.94-3.89 (m, 1H), 3.88-3.82 (m, 1H), 3.67-3.60 (m, 1H), 3.51-3.38 (m, 2H), 3.16 (s, 3H), 3.15 (s, 3H), 1.23 (t, *J* = 7.0 Hz, 3H), 0.95 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 167.9, 151.2, 136.4, 128.52, 128.49, 127.9, 101.8, 63.2, 61.5, 52.0, 51.7, 28.3, 28.2, 15.21, 15.18 ppm; IR (neat, cm^{-1}): 3418, 3032, 2976, 2930, 1747, 1678, 1453, 1422, 1379, 1124, 1061, 757, 704; LRMS (ESI): *m/z* 371 [M+Na]; HRMS (ESI) Calcd for $C_{18}H_{24}N_2O_5Na$: 371.1577. Found 371.1571.



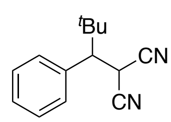
3ac

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.36 (m, 5H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 3.84 (d, *J* = 5.2 Hz, 1H), 3.46-3.39 (m, 1H), 3.21 (d, *J* = 14.4 Hz, 2H), 2.33 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.3, 136.5, 133.5, 129.9, 129.1, 129.2, 128.8, 128.1, 112.1, 111.5, 48.4, 38.1, 28.4, 21.1 ppm; IR (neat, cm^{-1}): 3090, 3031, 2922, 2862, 2366, 2255, 1955, 1906, 1515, 1497, 1455, 812, 758, 701; LRMS (ESI): *m/z* 283 [M+Na]; HRMS (ESI): Calcd for $C_{18}H_{16}N_2Na$: 283.1206. Found 283.1194.



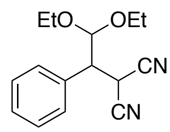
3ad

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.38 (m, 3H), 7.37-7.33 (m, 2H), 7.15-7.09 (m, 2H), 7.03-6.96 (m, 2H), 3.86 (d, *J* = 5.2 Hz, 1H), 3.47-3.39 (m, 1H), 3.33-3.18 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.1 (d, *J* = 245 Hz), 136.1, 132.3 (d, *J* = 3.3 Hz), 130.54, 130.46, 129.3, 129.2, 128.0, 116.0 (d, *J* = 21.4 Hz), 111.9, 114.4, 48.4, 37.8, 28.7 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ –116.00- –116.07 (m, 1F) ppm; IR (neat, cm^{-1}): 3034, 2904, 2359, 2256, 1889, 1603, 1510, 1455, 1224,1510, 834, 760, 701; LRMS (ESI): *m/z* 287 [M+Na]; HRMS (ESI): Calcd for $C_{17}H_{13}FN_2Na$: 287.0955. Found 287.0950.



3ae

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (s, 5H), 4.22 (d, *J* = 5.6 Hz, 1H), 3.01 (d, *J* = 5.6 Hz, 1H), 1.11 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.2, 129.3, 128.7, 128.6, 56.8, 35.0, 28.5, 25.1 ppm; IR (neat, cm^{-1}): 3064, 3033, 2968, 2913, 2253, 1604, 1497, 1479, 1455, 1371, 1216, 714; LRMS (ESI): *m/z* 235 [M+Na]; HRMS (ESI): Calcd for $C_{14}H_{16}N_2Na$: 235.1206. Found 236.1200.



3am

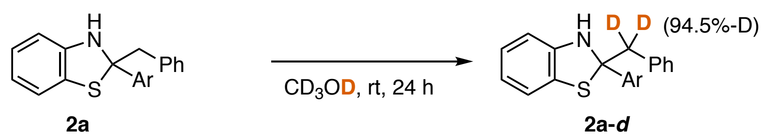
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.38 (m, 5H), 4.90 (d, J = 6.4 Hz, 1H), 4.39 (d, J = 5.6 Hz, 1H), 3.91-3.81 (m, 1H), 3.67-3.53 (m, 2H), 3.45-3.34 (m, 2H), 1.29 (t, J = 7.0 Hz, 3H), 1.06 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.8, 129.1, 128.8, 112.1, 112.0, 102.4, 64.7, 64.0, 50.0, 25.7, 15.10, 15.07 ppm; IR (neat, cm^{-1}): 3065, 3034, 2979, 2924, 2377, 2255, 1719, 1456, 1118, 1067, 702; LRMS (ESI): *m/z* 281 [M+Na]; HRMS (ESI): Calcd for $C_{15}H_{18}N_2O_2Na$: 281.1260. Found 281.1274.

3-3. Other experimental methods

Synthesis of deuterated benzalmalononitrile 2a-*d*

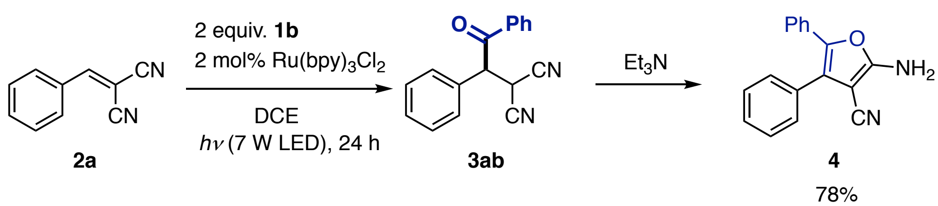
Deuterated benzaldehyde (0.30 mL, 2.54 mmol) and piperidine (25 μL, 0.254 mmol) were mixed in EtOH, then malononitrile (169 mg, 2.54 mmol) was added to the mixture. After about 10 min, the product was generated as a precipitate. The mixture was stirred overnight, the precipitate was filtered and washed with EtOH. The crude product was recrystallized by dichloromethane and hexane to give **2a-*d*** (223 mg, 1.32 mmol, 52%).

Deuteration of benzylic position of 1a



2a (251.4 mg, 0.829 mmol) was dissolved in mixture of methanol-d_4 (2.0 mL) and dichloromethane (3.0 mL). After the mixture was stirred for 24 h, the solvent was removed to give **2a-*d*** (94.5 % deuterated).

Synthesis of 2-aminofuran derivative

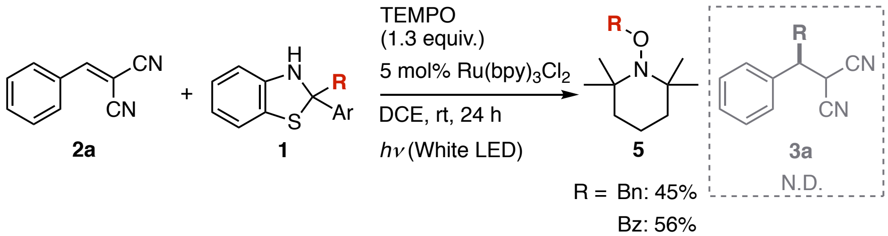


Triethylamine (50 μL) was added to the resulting mixture of **3a**, which was obtained by the Procedure II. Then, the reaction mixture was stirred for 1 h, and the solvent was removed, and the residue was purified by PTLC to give 2-aminofuran derivative **4** in 78% yield.

Data of **4**:

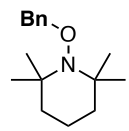
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.34 (m, 7H), 7.26-7.19 (m, 3H), 4.97 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2, 139.7, 135.3, 131.7, 131.0, 129.5, 129.0, 128.5, 128.4, 127.4, 115.0, 73.6 ppm.[S20]

Radical scavenging experiments



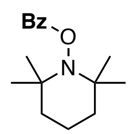
According to the general procedure of alkylation and acylation. TEMPO (19.8 mg, 0.127 mmol) was added to the solution. Then crude products were purified by preparative TLC (hexane: AcOEt = 10:1) to give **5**.

Data of **5**:



5a

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38-7.32 (m, 4H), 7.28 (d, *J*=6.4 Hz, 1H), 4.83 (s, 2H), 1.63-1.32 (m, 6H), 1.26 (s, 6H), 1.15 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.3, 128.2, 127.5, 127.3, 78.7, 60.0, 39.7, 33.1, 20.3, 17.1 ppm.[S21]



5b

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 1.85-1.53 (m, 4H), 1.50-1.41 (m, 1H), 1.28 (s, 6H), 1.12 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 132.9, 129.8, 129.6, 128.5, 60.4, 39.1, 32.0, 20.9, 17.0 ppm.[S22]

The products from maleic anhydride (**3t**) were decomposed by any purification methods and they couldn't be separated and collected data.

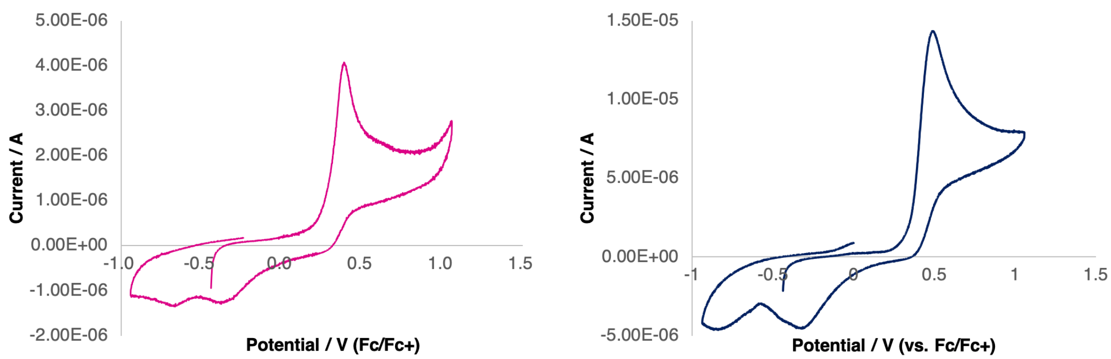
4. Mechanistic studies

4-1. Cyclic Voltammetry

All voltammograms were measured at room temperature using Ag/$AgNO_3$ reference electrode, a platinum (Pt) counter and working electrode. The conditions of the experiments were as follows: a CH_3CN solution of 100 mM tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) and a scan rate of 50 mV/s. The potentials of 1,3-dimethyl-5-benzylidene barbituric acid **2o** and benzylidenemeldrum's acid **2p** were taken at half-wave potential ($E_{1/2}$) since the oxidation was reversible. The potentials of benzothiazolines were taken at half-height of the peak ($E_{p/2}$) since the oxidations were non-reversible.

To convert the potentials from Ag/$AgNO_3$ to Fc/Fc^+ reference, ferrocene was measured under the above conditions in a CH_3CN solution, and –0.44 V was subtracted from the measured values. To convert the potentials from Fc/Fc^+ to SCE reference, +0.38 V was added from the values according to the literature.[S23)]

According to Figure S1, the oxidation potential of **1e** and **1f** was almost same value (**1e**: $E_{p/2}$ = 0.69 V vs. SCE, **1f**: $E_{p/2}$ = 0.70 V vs. SCE) and both of them could be oxidized by photoredox catalysts ($Ru(bpy)_3^{2+}$, Eosin Y-2Na). Hence, the reason why isopropyl transfer didn't proceed is C-C bond cleavage of **1f** couldn't be occurred from the cation radical species.



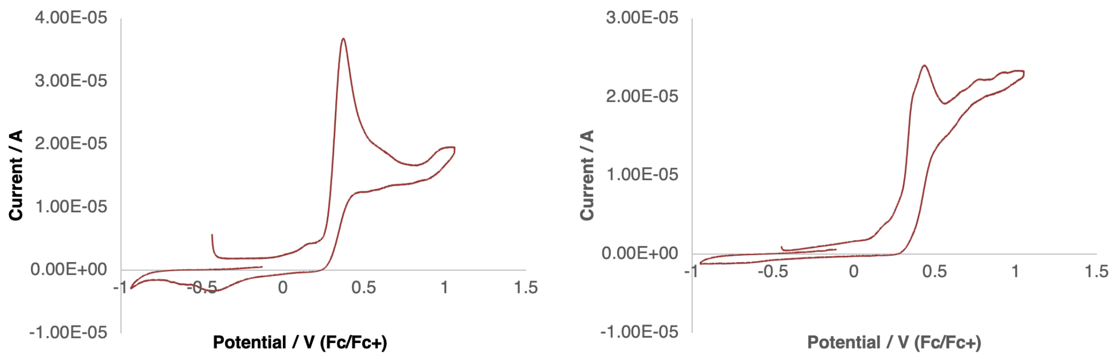
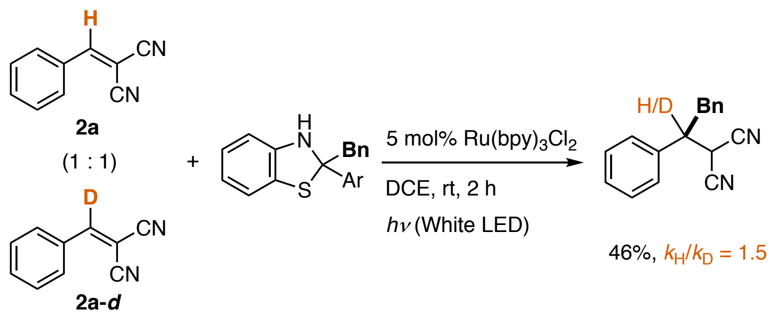


Figure S1. Cyclic voltammograms of benzothiazoline derivatives. Upper left: 2-benzyl-2-phenylbenzothiazoline (**1a**), Upper right: 2-benzoyl-2-phenylbenzothiazoline (**1b**), Lower left: 2-*tert*-butyl-2-phenylbenzothiazoline (**1e**), Lower right: 2-isopropyl-2-phenylbenzothiazoline (**1f**).

4-2. KIE study

The procedure of KIE study using deuterated benzalmalononitrile (Scheme 4B)

Scheme S5. KIE determined experiment from an intermolecular competition of benzalmalononitrile.



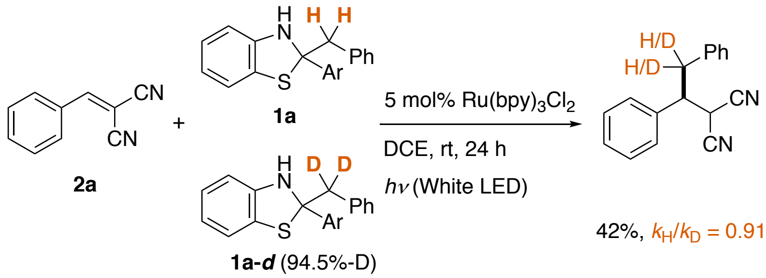
The 1:1 mixture of **2a** (11.6 mg, 0.075 mmol) and α-deuterated **2a** (**2a-*d***, 11.6 mg, 0.075 mmol), and benzothiazoline **1a** (91.3 mg, 0.3 mmol), photoredox catalyst ($Ru(bpy)_3Cl_2$) (5.8 mg, 0.0077 mmol) was dissolved in degassed 1,2-dichloroethane (3.0 mL). Then irradiation of white LED (5 W) at room temperature. After 2 h, the solvent was evaporated and 1,1,2,2-tetrachloroethane was added as an internal standard and ^{1}H NMR was measured in $CDCl_3$ for the calculation of the NMR yield.

The procedure of KIE study using deuterated benzothiazoline derivative (Scheme 4C)

According to the Scheme S1, the hydrogen-exchange of benzothiazoline **2a** was not fast (7% exchange for 24 h), and the KIE study was performed for a few hours (2 h). Thus, we defined the hydrogen-exchange could be almost negligible under the KIE conditions.

Then, the KIE measurement of the C-C bond cleavage of **1a** was performed by using 1:1 mixture of **1a** and **1a-*d*$_2$** in the same vessel under the standard condition. After 2 h, the negative secondary KIE was observed ($k_H/k_D = 0.91$). This result suggested that the C-C bond cleavage of the benzothiazoline **1a** was not the rate-determined step but the radical addition to alkenes was the rate-determined step of this reaction.

Scheme S6. KIE determination experiment from an intermolecular competition of benzothiazoline 1a.



2a (7.7 mg, 0.05 mmol) and 1:1 mixture of benzothiazoline **1a** (15.2 mg, 0.05 mmol) and deuterated benzothiazoline **1a-*d*** (15.3 mg, 0.05 mmol), photoredox catalyst ($Ru(bpy)_3Cl_2•6H_2O$) (2.0 mg, 0.0025 mmol) were dissolved in degassed 1,2-dichloroethane (1.0 mL). Then white LED (5 W) was irradiated at room temperature for 2 h. After evaporation of the solvent, 1,1,2,2-tetrachloroethane was added as an internal standard, and ^{1}H NMR was measured in $CDCl_3$ for the calculation of the NMR yield.

Calculation method of KIE: **1a-*d*** was containing 5.5% of ^{1}H, the k_H/k_D could not be estimated by simply comparison of these yields. Since the deuterated product was underestimated, the correction of the KIE value was conducted. We calculated the simple simultaneous equations as follows:

$k_H/k_D = n_H/n_D$ ($n_{H/D}$: the amounts of the products)

$n_H(obs) = n_H + 0.055n_D$

$n_D(obs) = 0.945n_D$

($n_{H/D}(obs)$: observed the amounts of products)

The rate of mono-deuterated benzyl one, which contained in **1a-*d*** at a rate of 5.5%, was approximated as almost same value with the rate of **1a-*d***.

4-3. Proposed Mechanism.

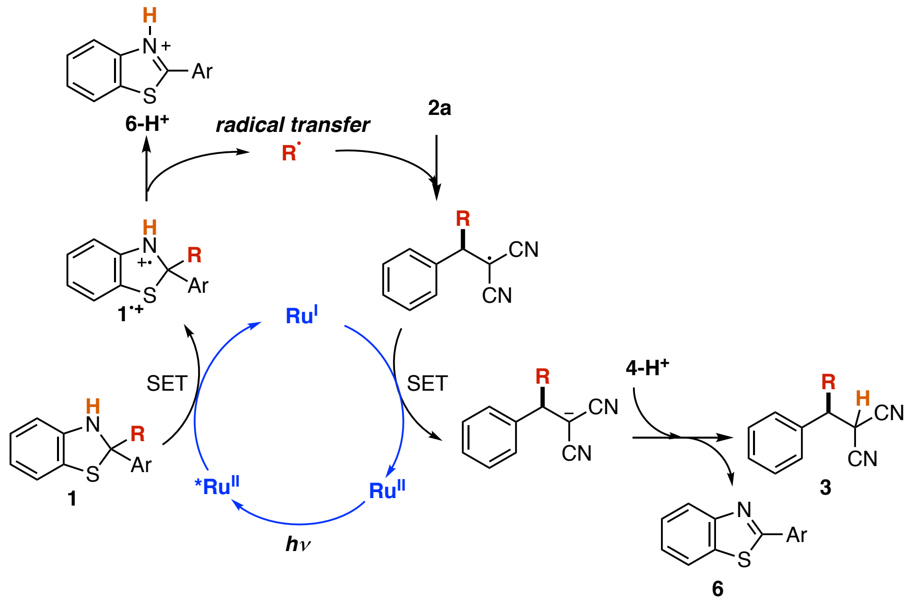


Figure S2. Proposed mechanism

Benzothiazoline **1** is oxidized by an excited photoredox catalyst via single-electron transfer (SET), and the generated cation radical species ($\mathbf{1}^{\cdot+}$) releases radical species (R•). The radical species adds to substrate **2a**, followed by a reduction via SET with a photoredox catalyst. The generated carbanion is protonated by **6-H**$^+$ to give product **3**.

5. References

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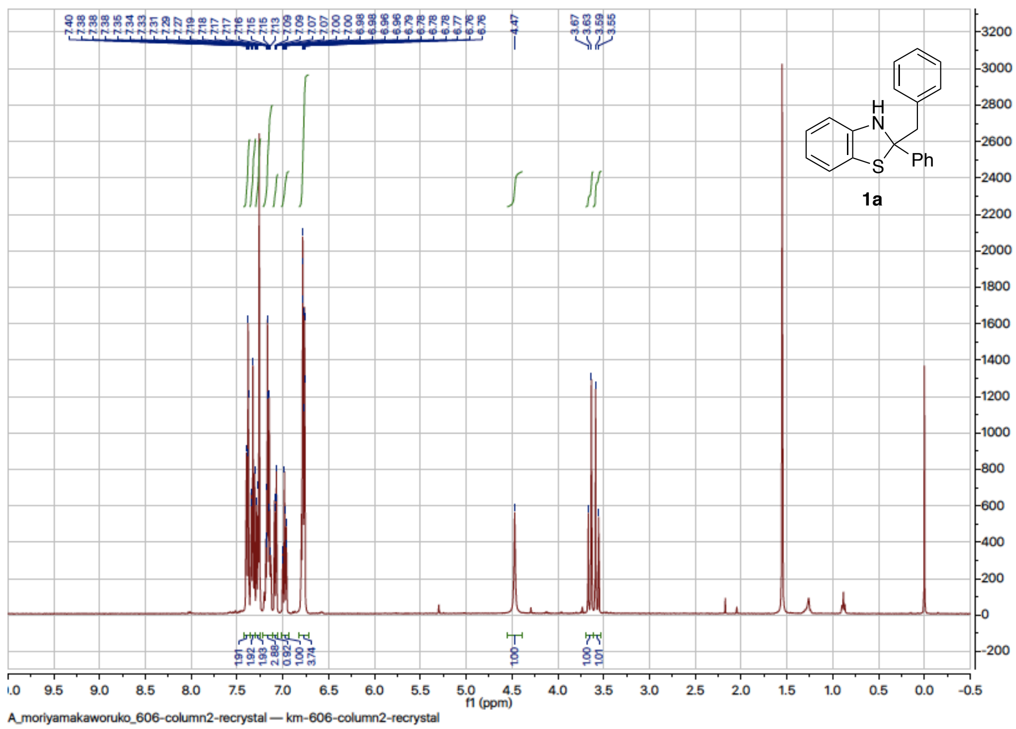
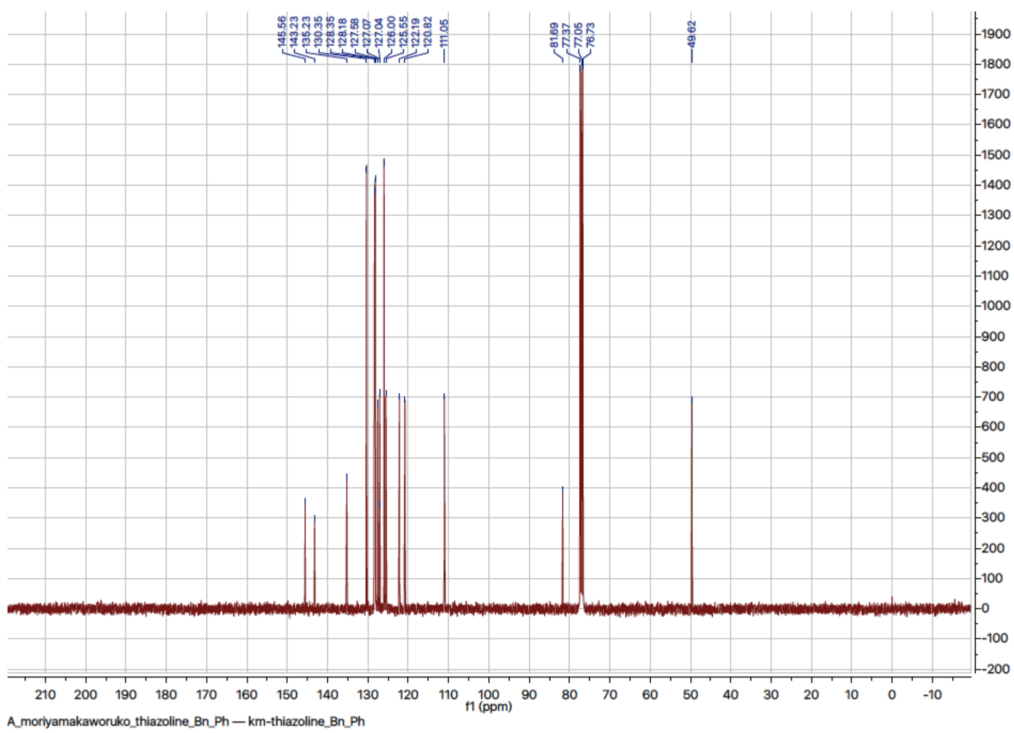
6. Spectral data

1a





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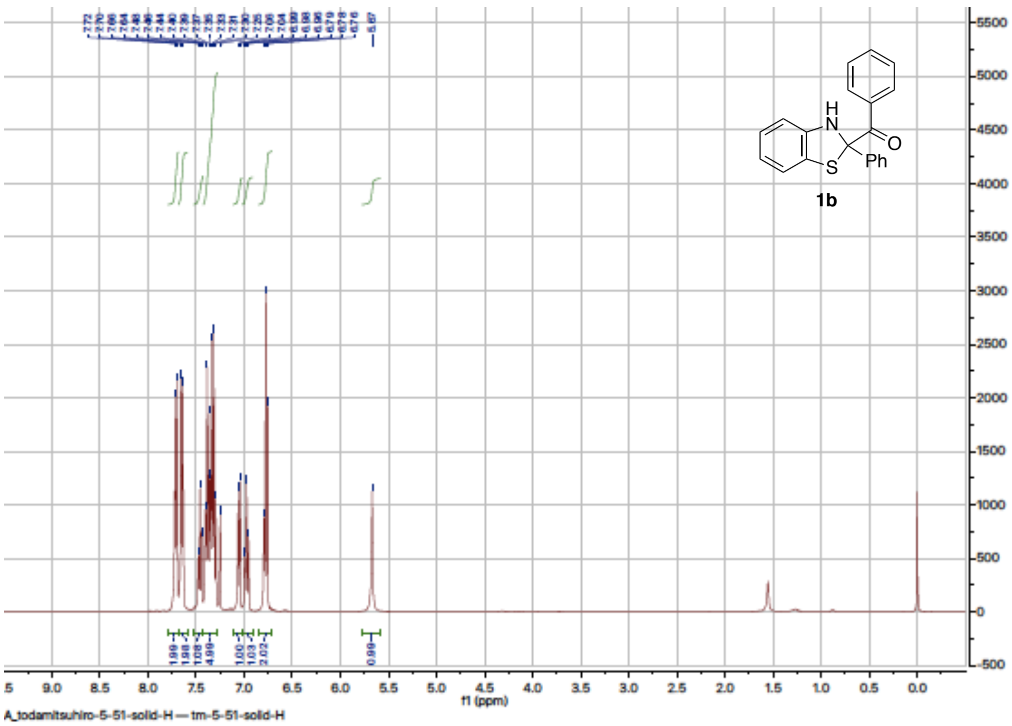
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7.30
7.25
7.06
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6.96
6.79
6.78
6.76
5.67
1b
Ph
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1.98
1.08
4.99
1.00
1.03
2.02
0.99
f1 (ppm)
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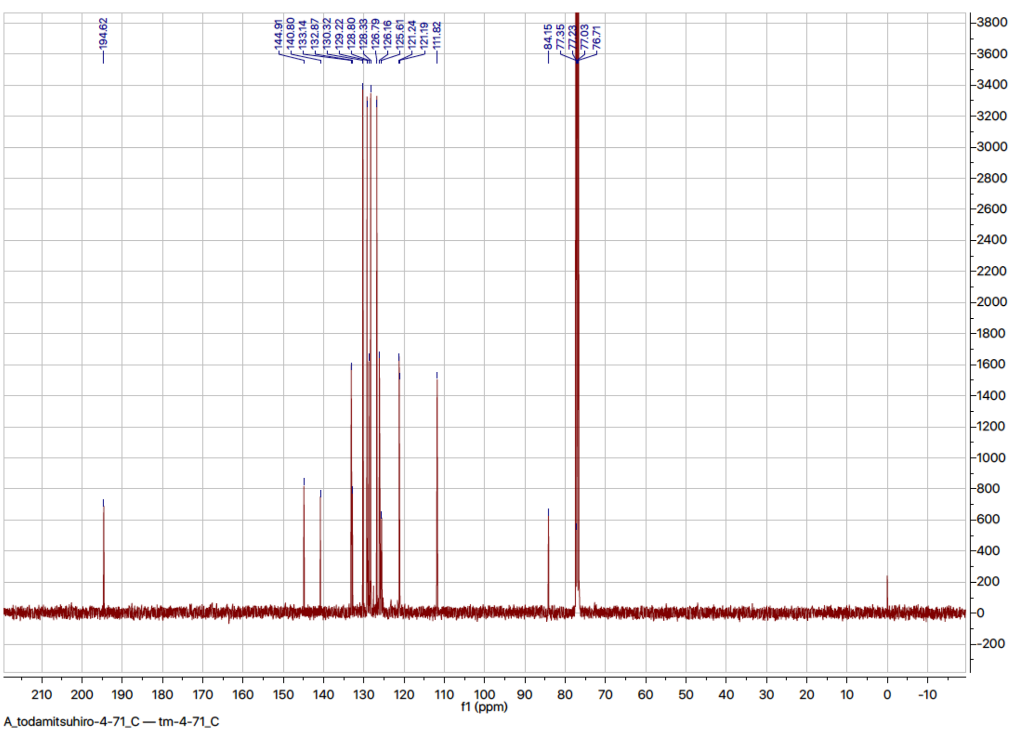
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121.24
121.19
111.82
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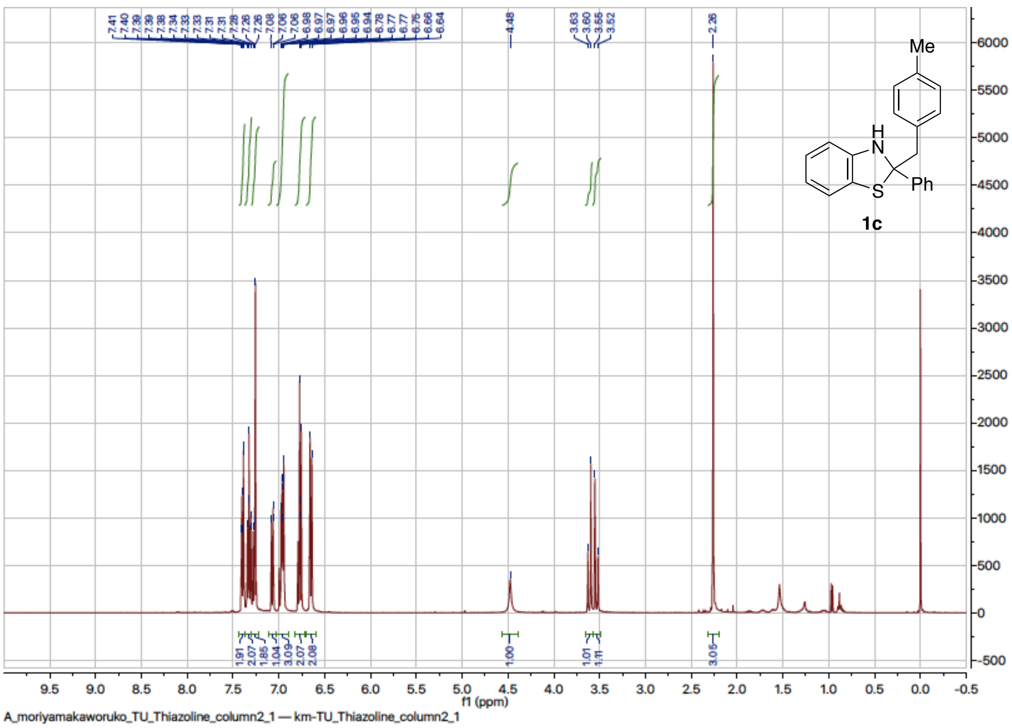
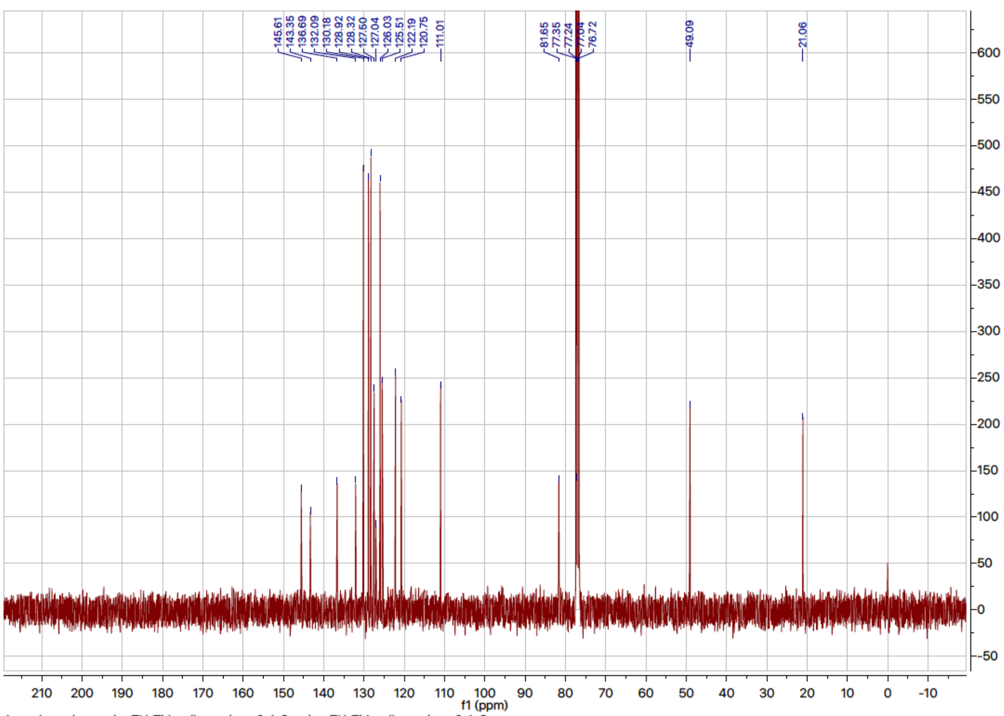
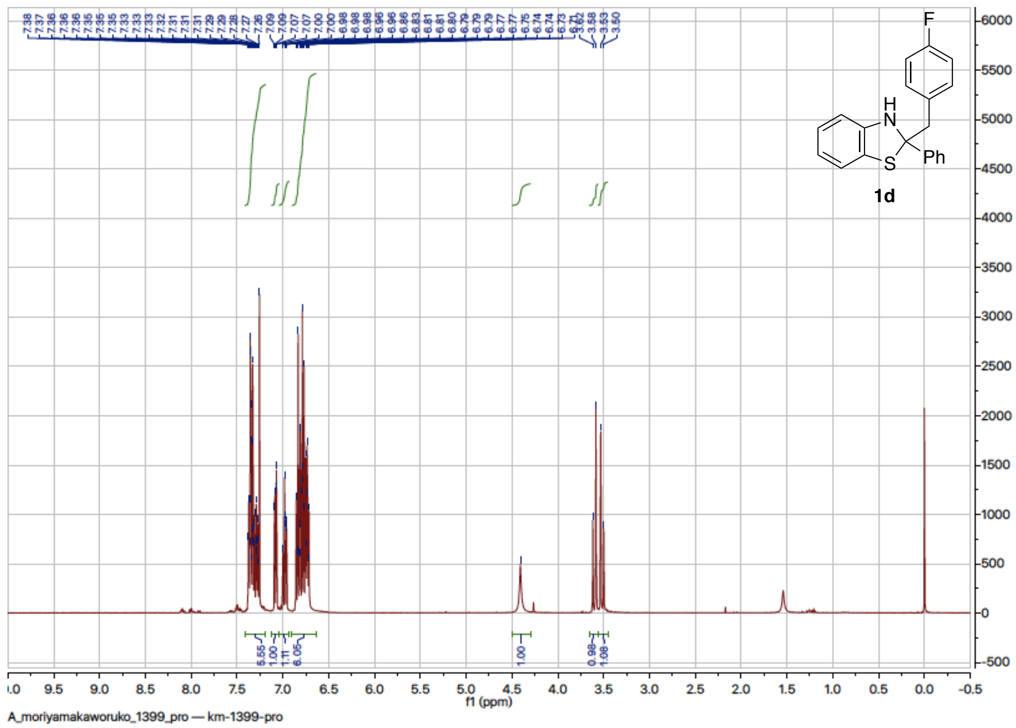
77.35
77.23
77.03
76.71
f1 (ppm)
A_todamitsuhiro-4-71_C — tm-4-71_C

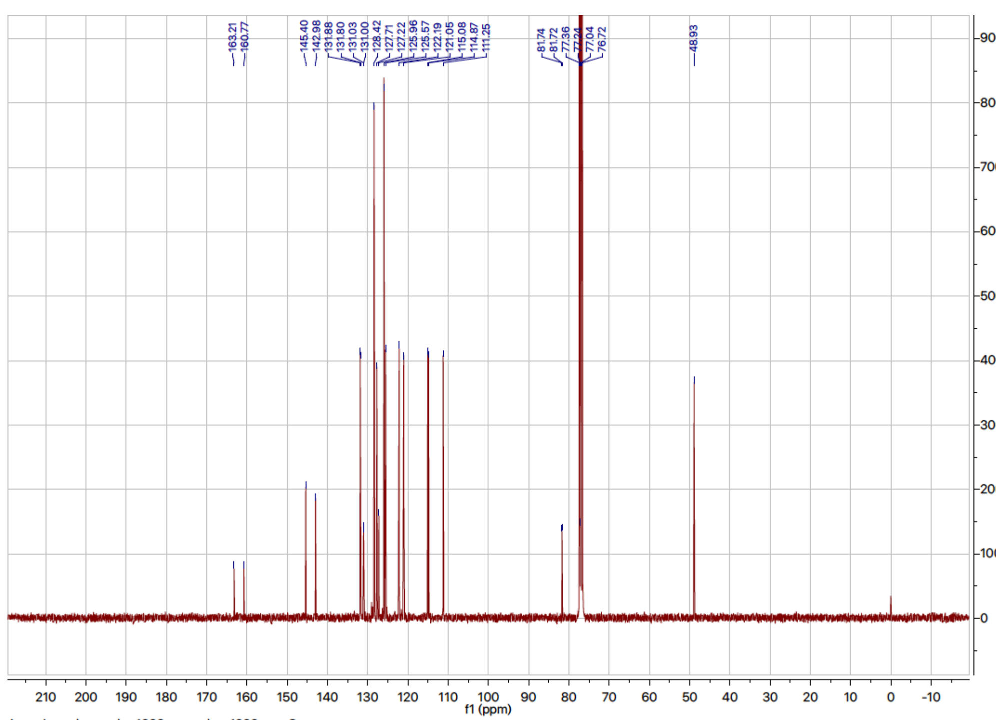
1c



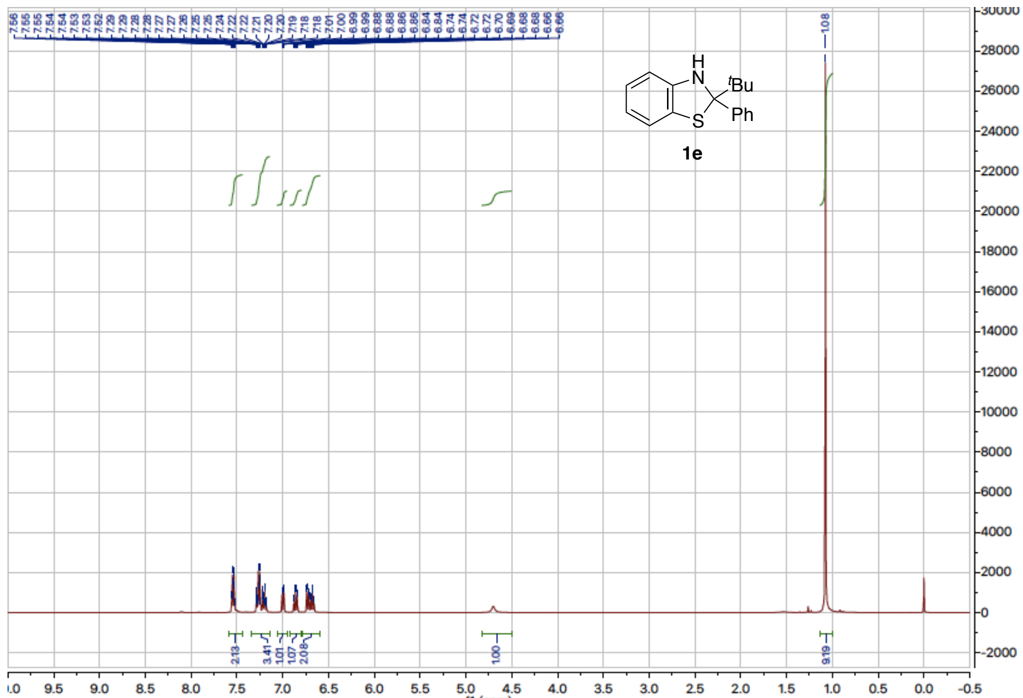


1d





1e



1e
f1 (ppm)
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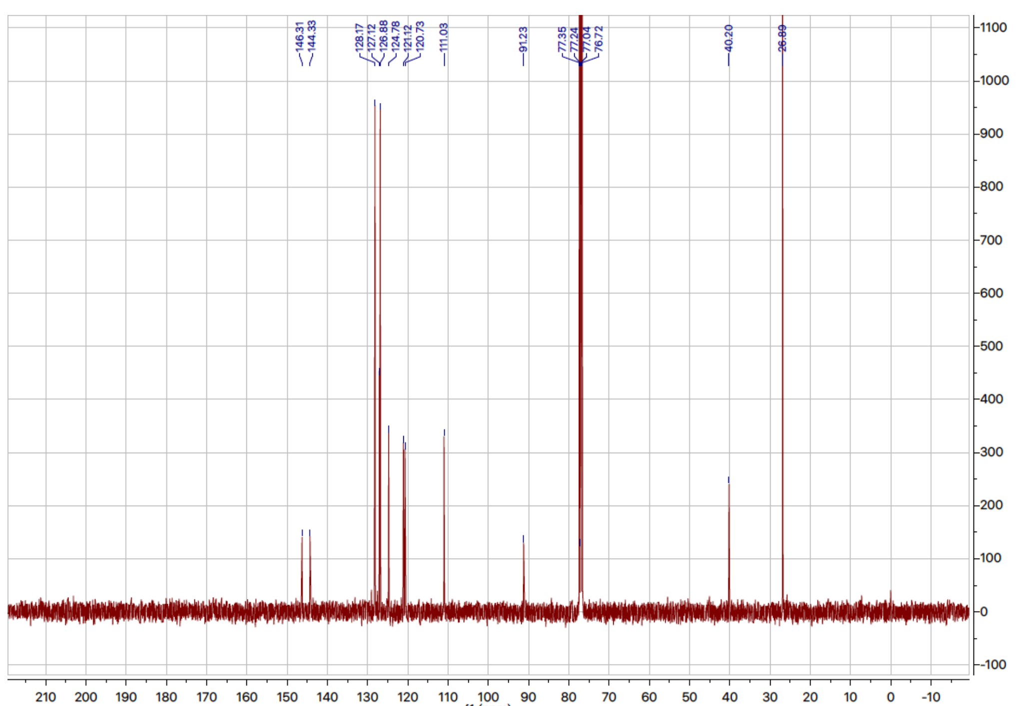

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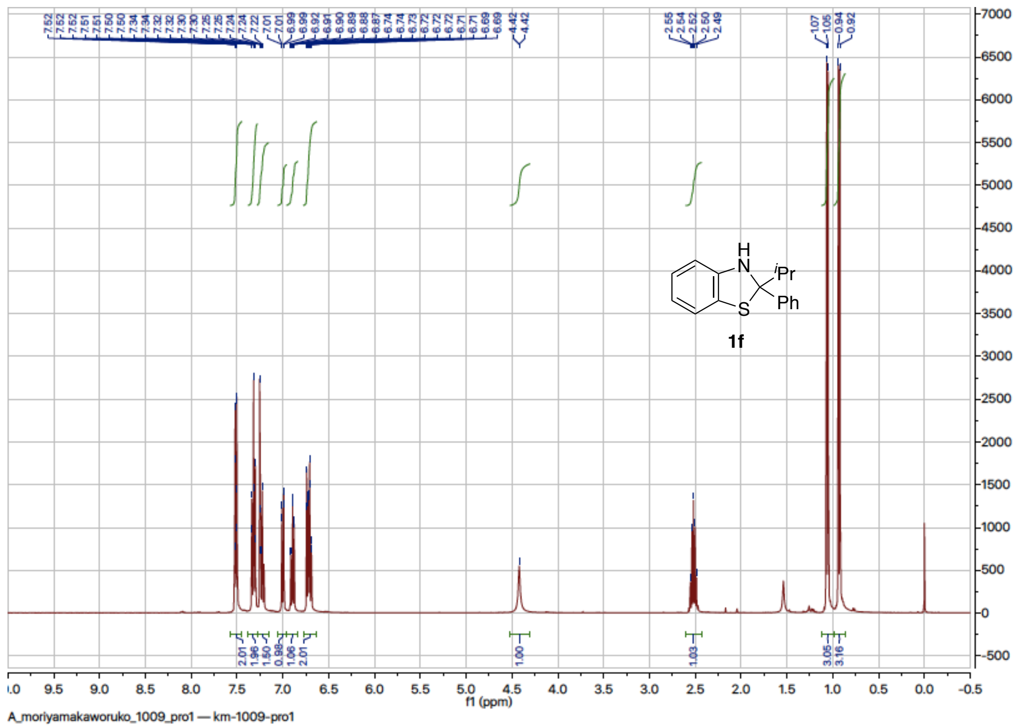
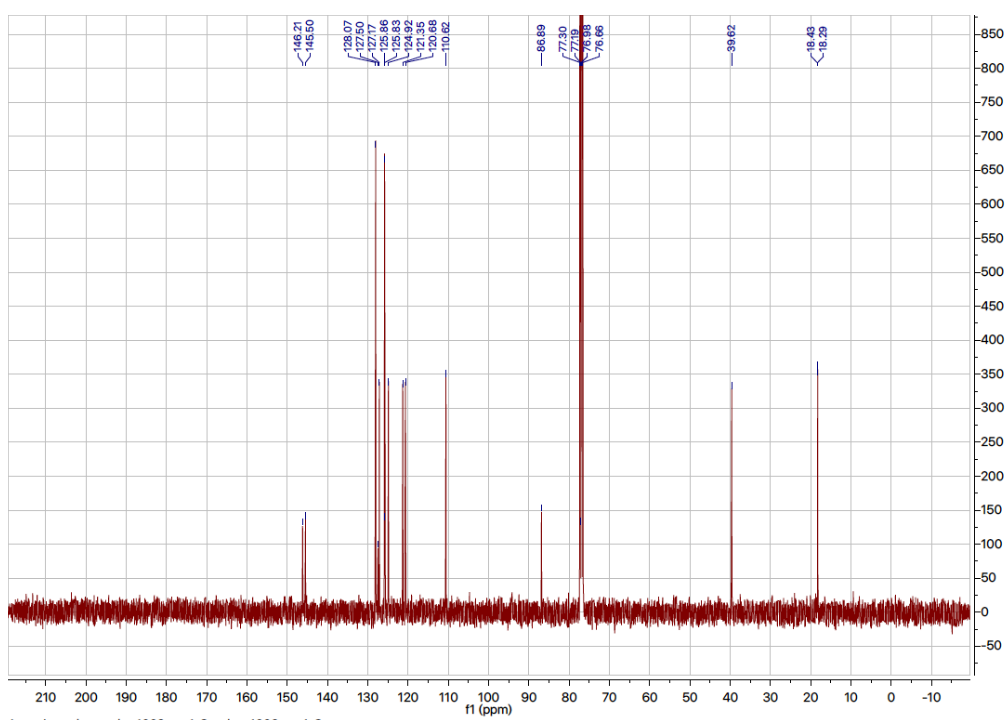
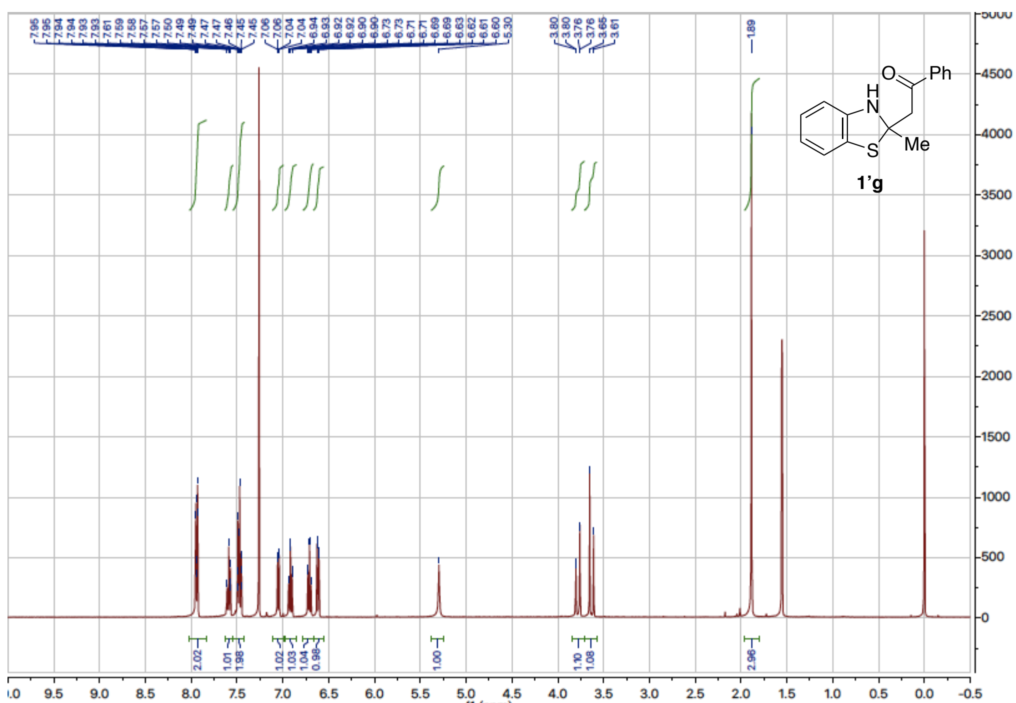
76.72
40.20
26.89
f1 (ppm)
A_moriyamakaworuko_752_pro — km-752-pro-C

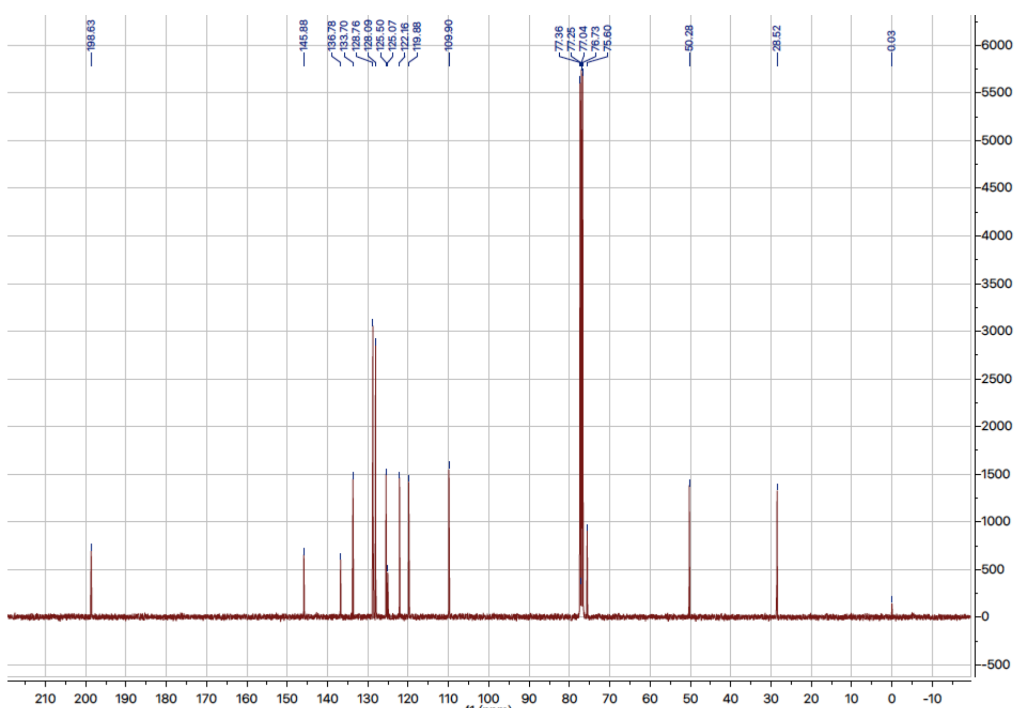
1f



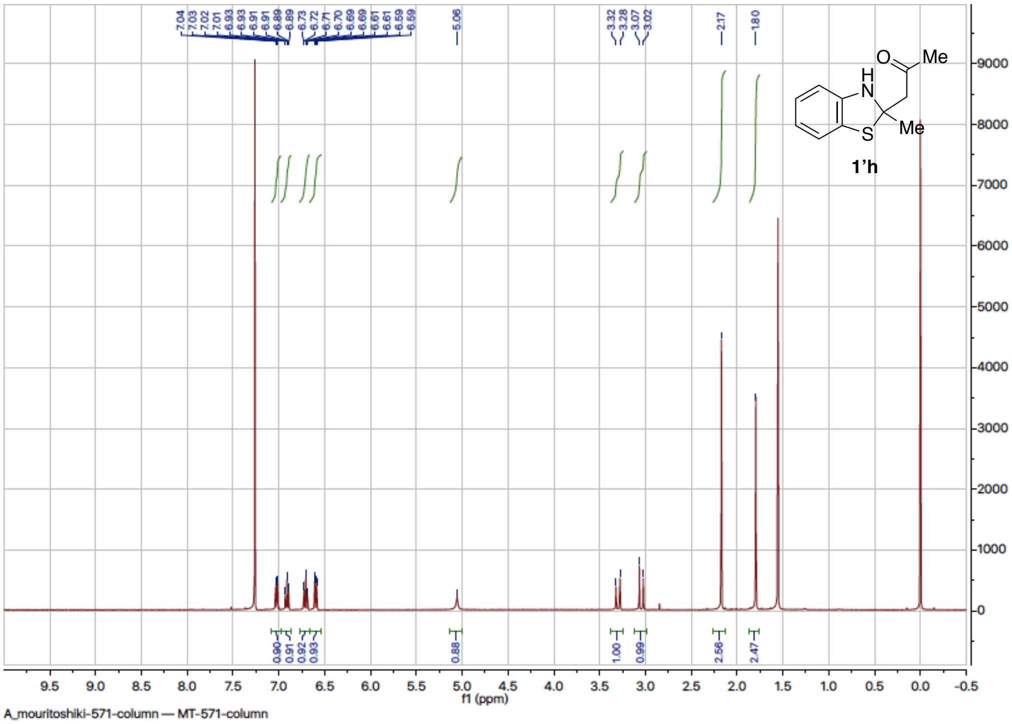


1’g

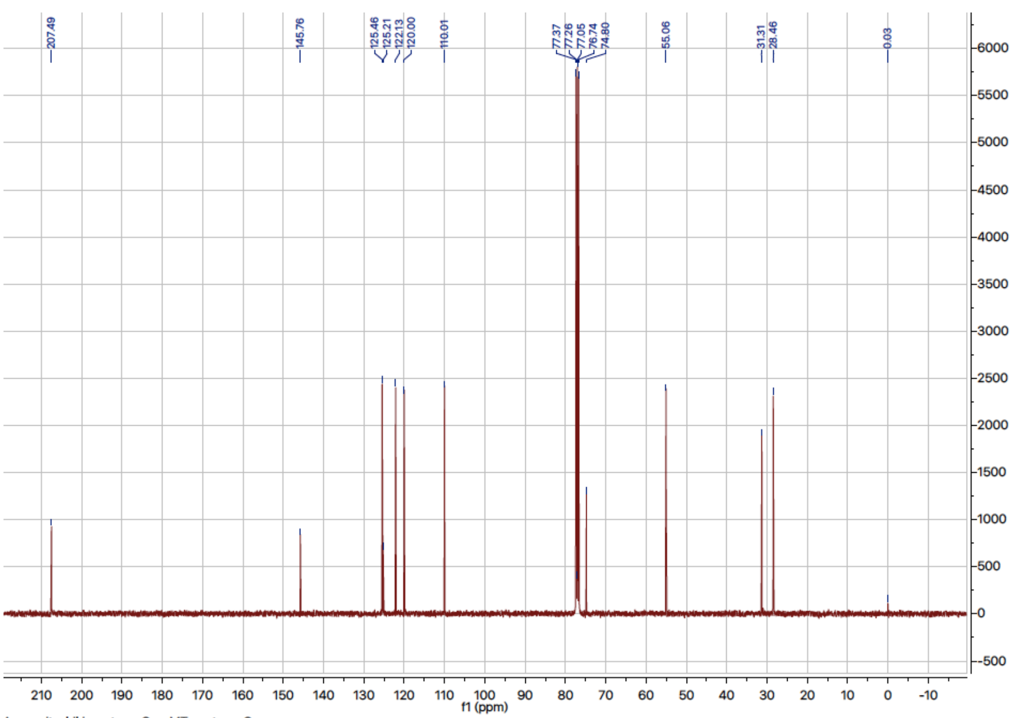

1’g
f1 (ppm)
A_mouritoshiki-637-pro — MT-637-pro


f1 (ppm)
A-mouritoshiki-acetophen-C — MT-acetophen-C

1'h

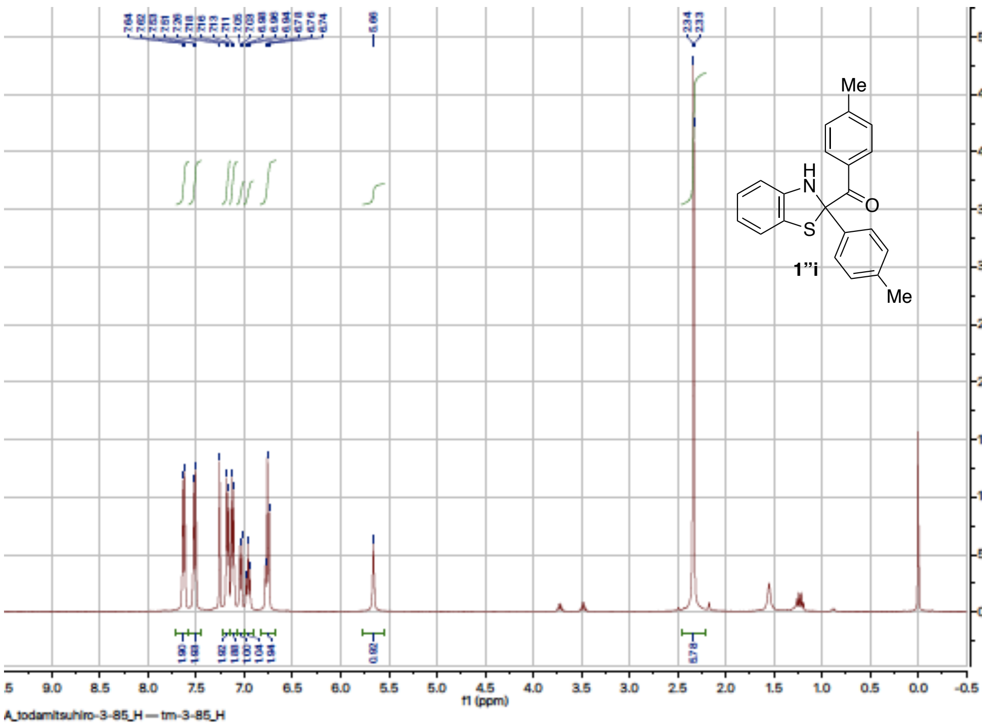


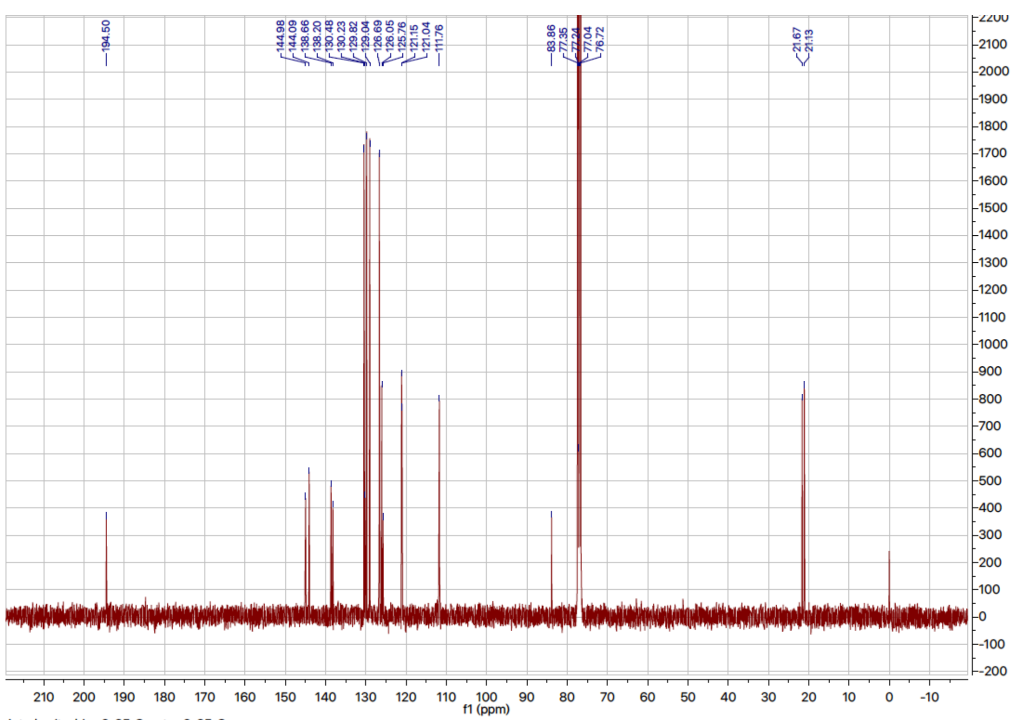
7.04
7.03
7.02
7.01
6.93
6.93
6.91
6.91
6.89
6.89
6.73
6.72
6.71
6.70
6.69
6.69
6.61
6.61
6.59
6.59
5.06
3.32
3.28
3.07
3.02
2.17
1.80
1'h
0.90
0.91
0.92
0.93
0.88
1.00
0.99
2.56
2.47
f1 (ppm)
A_mouritoshiki-571-column — MT-571-column



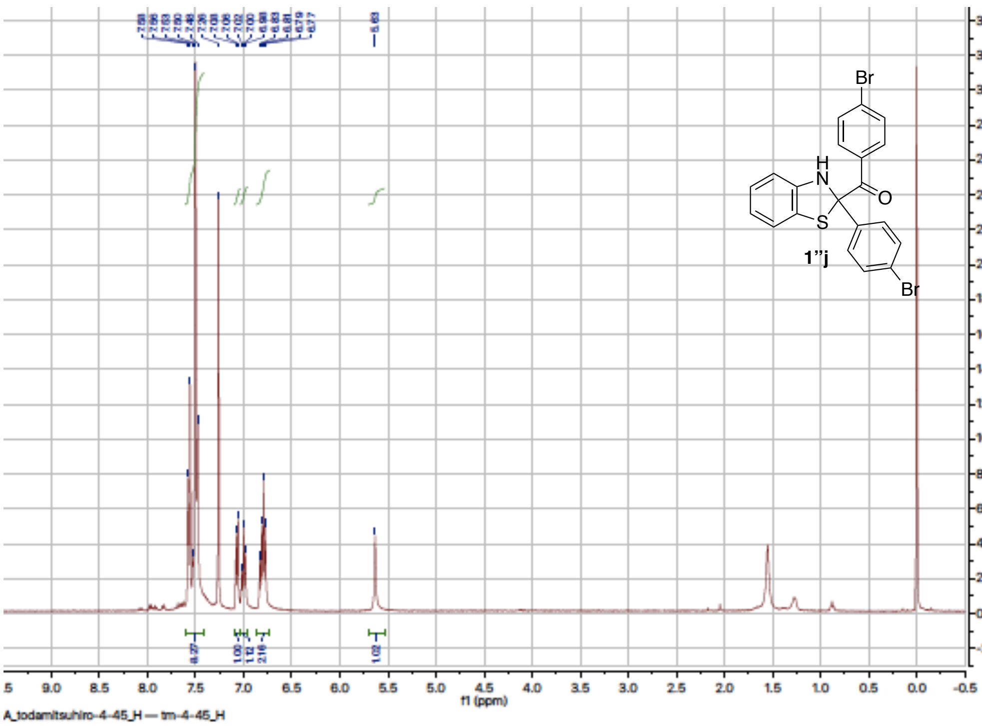
207.49
145.76
125.46
125.21
122.13
120.00
110.01
77.37
77.26
77.05
76.74
74.80
55.06
31.31
28.46
0.03
f1 (ppm)
A-mouritoshiki-acetone-C — MT-acetone-C

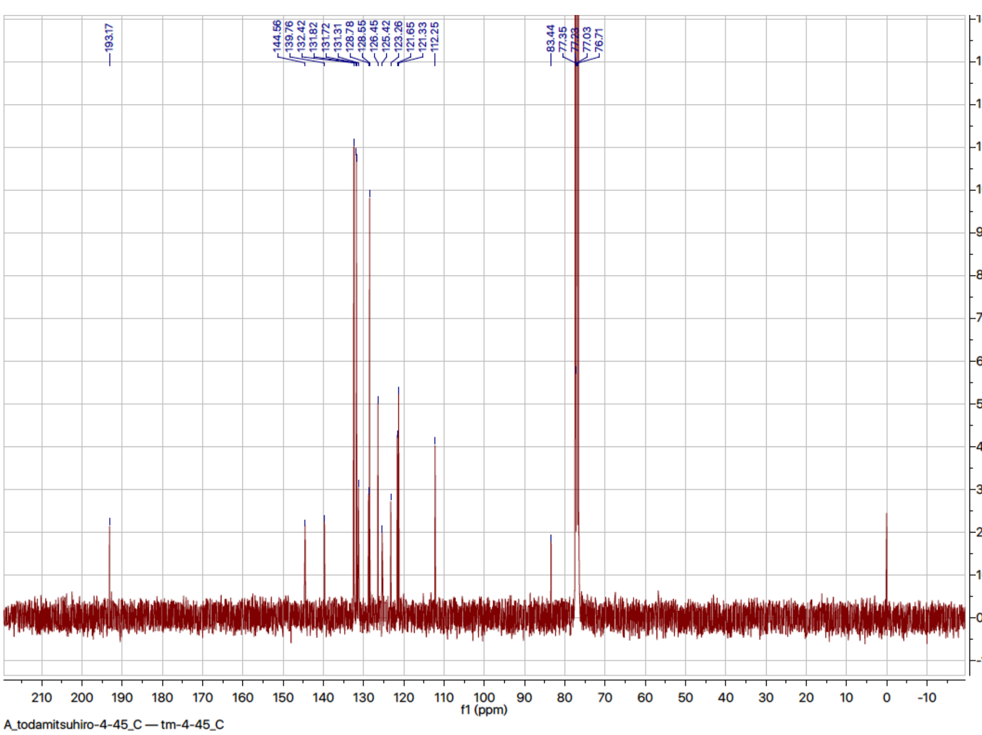
1''i



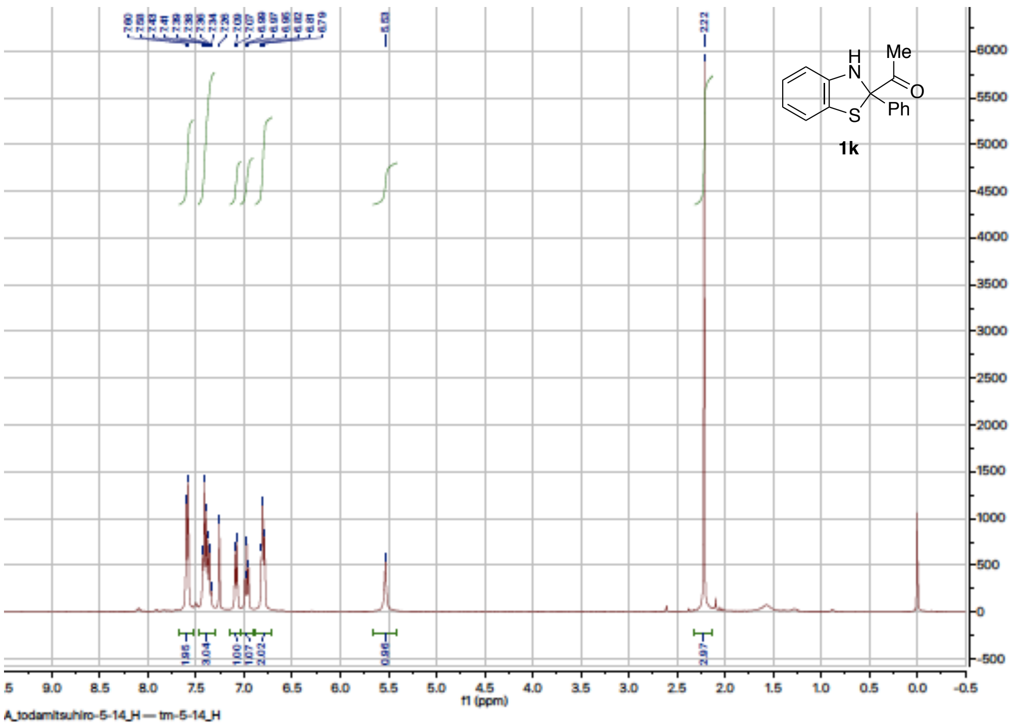


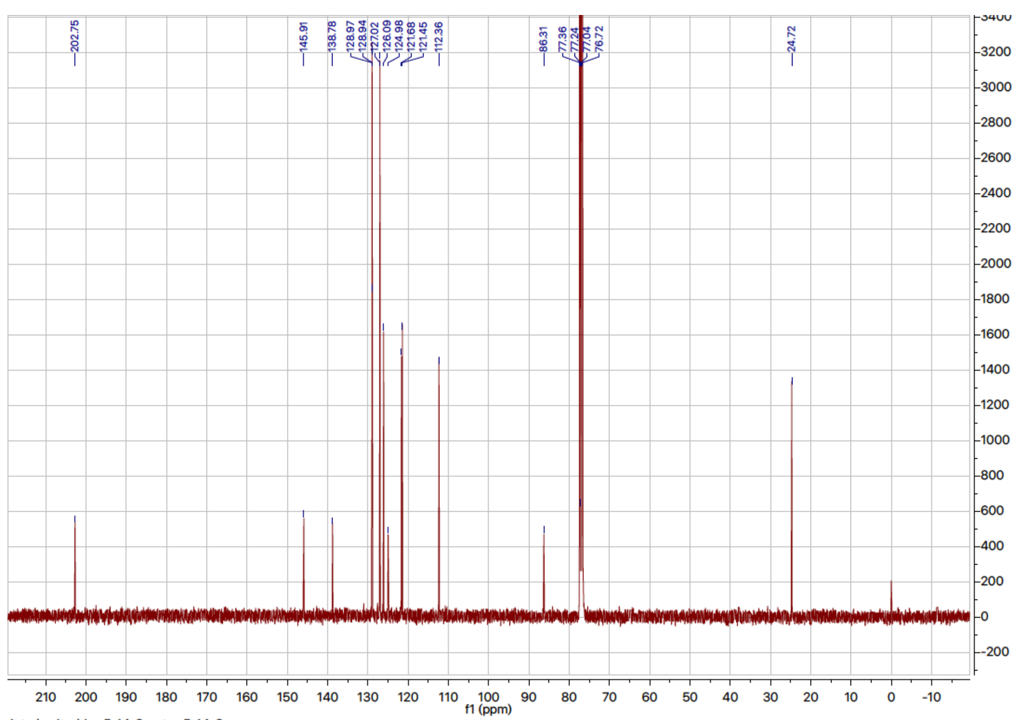
1”j


Br
H
N
O
S
1”j
Br
f1 (ppm)
A_todamitsuhiro-4-45_H — tm-4-45_H

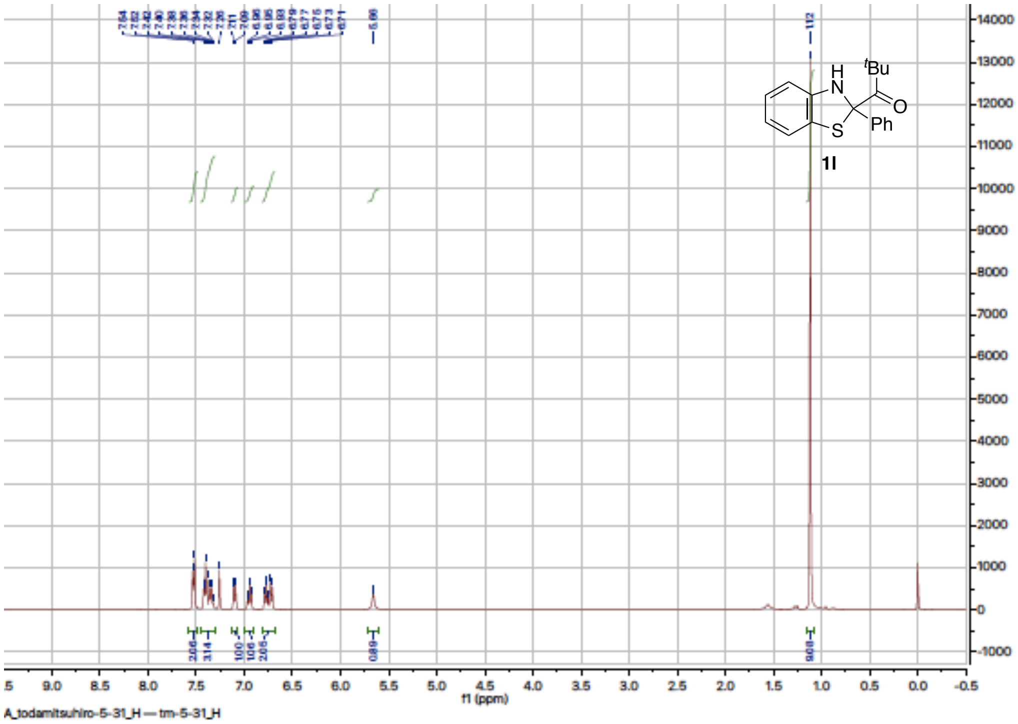

f1 (ppm)
A_todamitsuhiro-4-45_C — tm-4-45_C

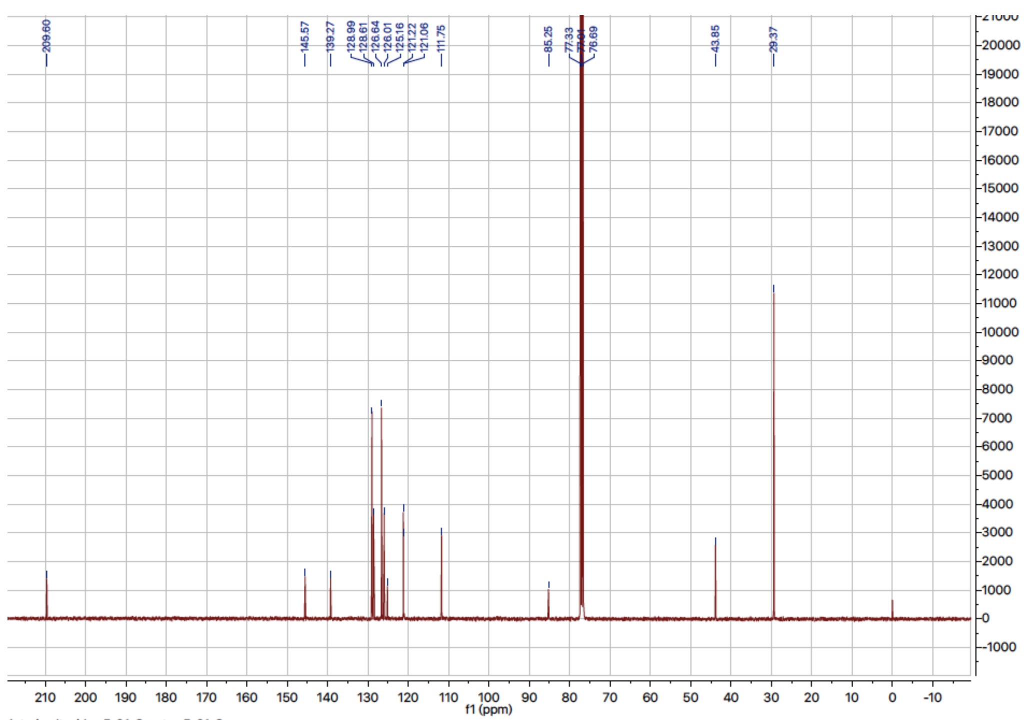
1k


1k
Me
H
N
O
S
Ph
f1 (ppm)
A_todamitsuhiro-5-14_H — tm-5-14_H

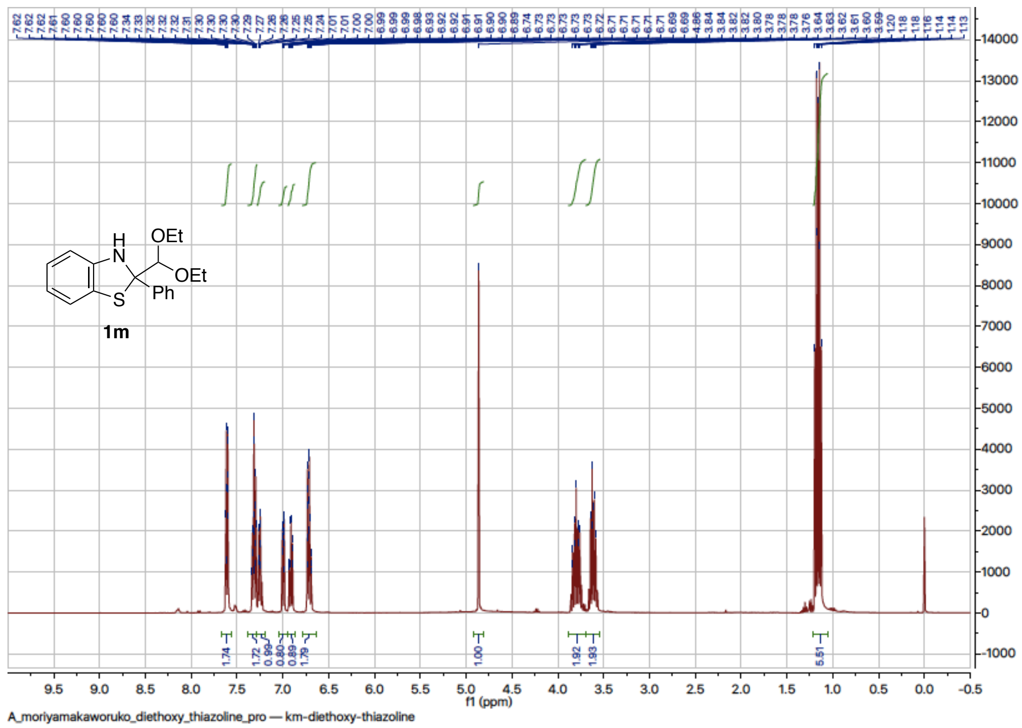

f1 (ppm)
A_todamitsuhiro-5-14_C — tm-5-14_C

1l

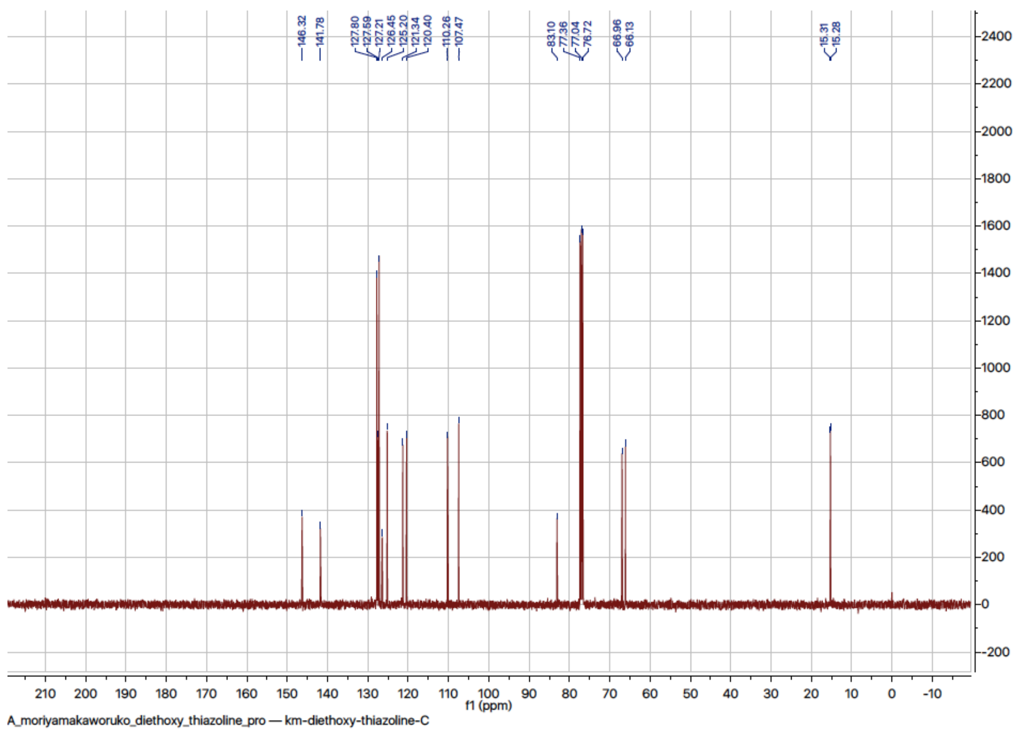




1m

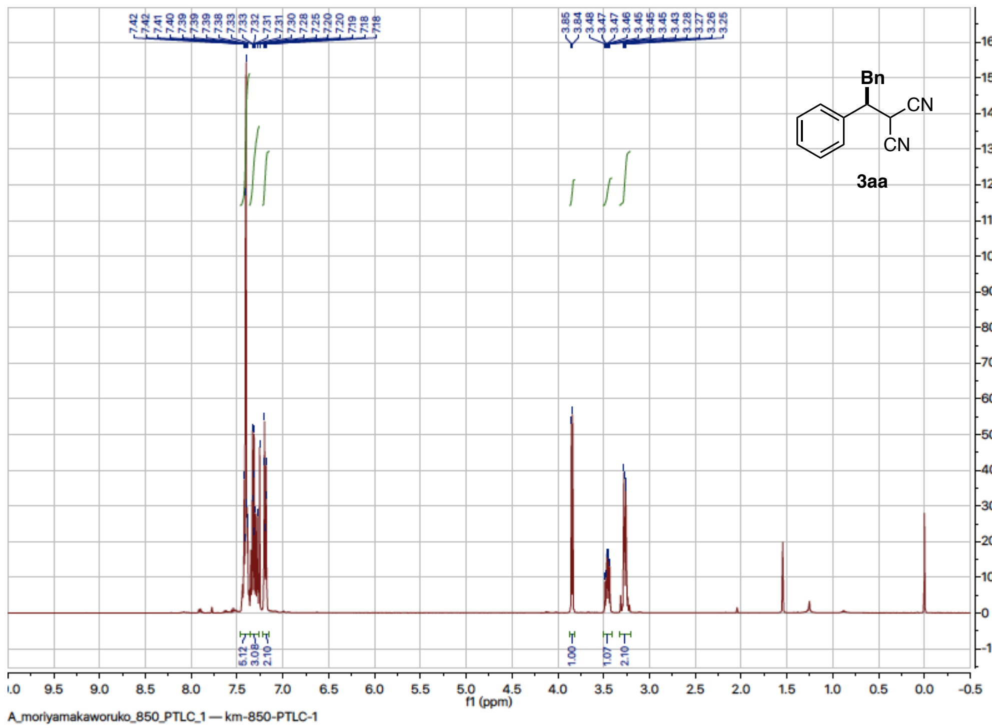


OEt
H
N
OEt
S
Ph
1m
1.74
1.72
0.99
0.80
0.89
1.79
1.00
1.92
1.93
5.51
f1 (ppm)
A_moriyamakaworuko_diethoxy_thiazoline_pro — km-diethoxy-thiazoline

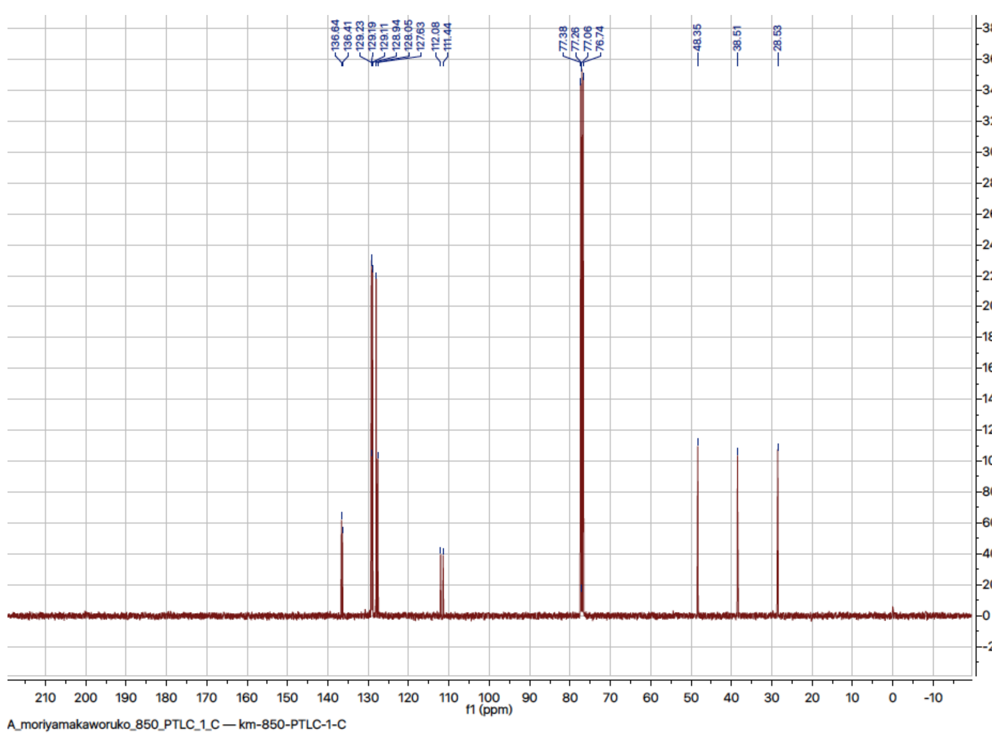


146.32
141.78
127.80
127.59
127.21
126.45
125.20
121.34
120.40
110.26
107.47
83.10
77.36
77.04
76.72
66.96
66.13
15.31
15.28
f1 (ppm)
A_moriyamakaworuko_diethoxy_thiazoline_pro — km-diethoxy-thiazoline-C

3aa

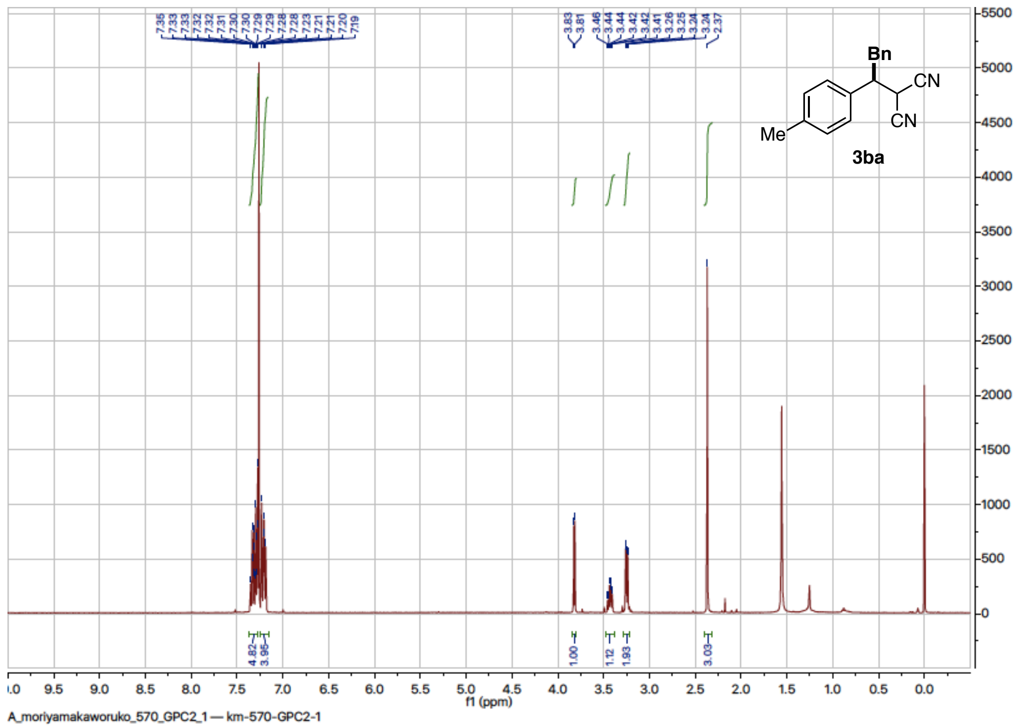


Bn
CN
CN
3aa
f1 (ppm)
A_moriyamakaworuko_850_PTLC_1 — km-850-PTLC-1

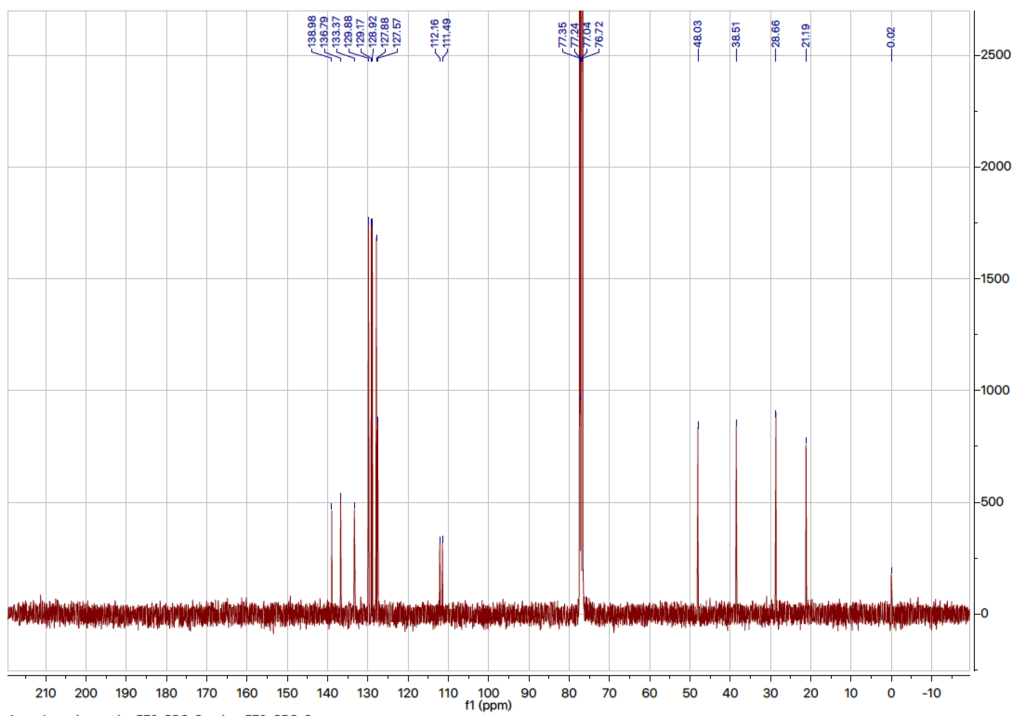


f1 (ppm)
A_moriyamakaworuko_850_PTLC_1_C — km-850-PTLC-1-C

3ba

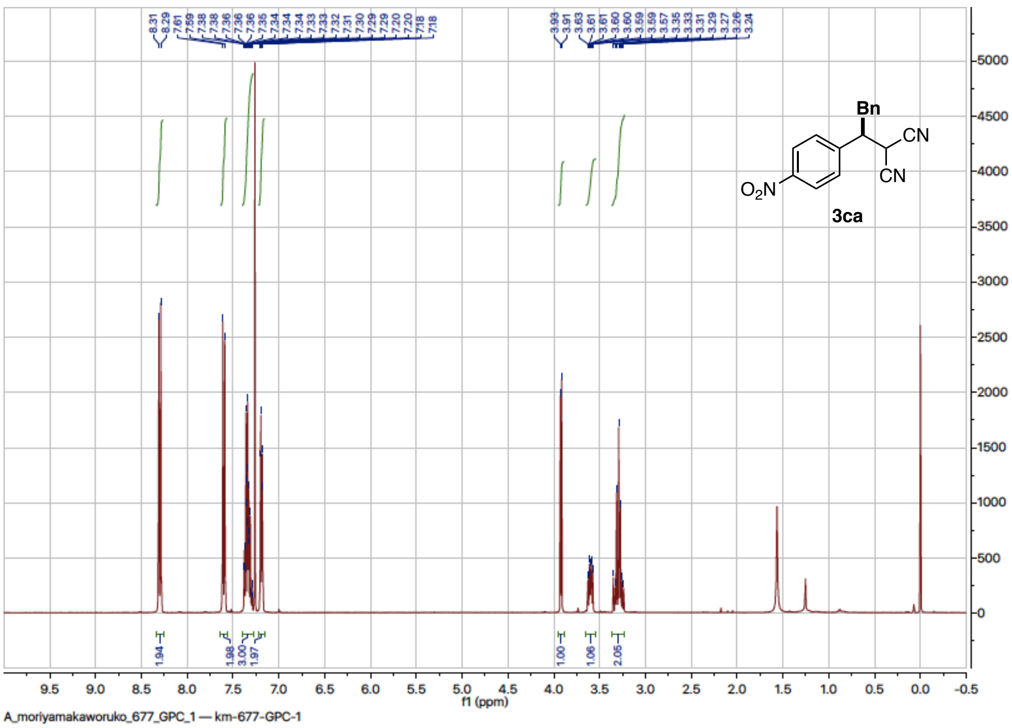


7.35
7.33
7.33
7.32
7.32
7.31
7.30
7.30
7.29
7.29
7.29
7.28
7.28
7.23
7.21
7.21
7.20
7.19
3.83
3.81
3.46
3.44
3.44
3.44
3.42
3.42
3.41
3.26
3.25
3.24
3.24
2.37
Bn
CN
CN
Me
3ba
4.82
3.96
1.00
1.12
1.93
3.03
f1 (ppm)
A_moriyamakaworuko_570_GPC2_1 — km-570-GPC2-1

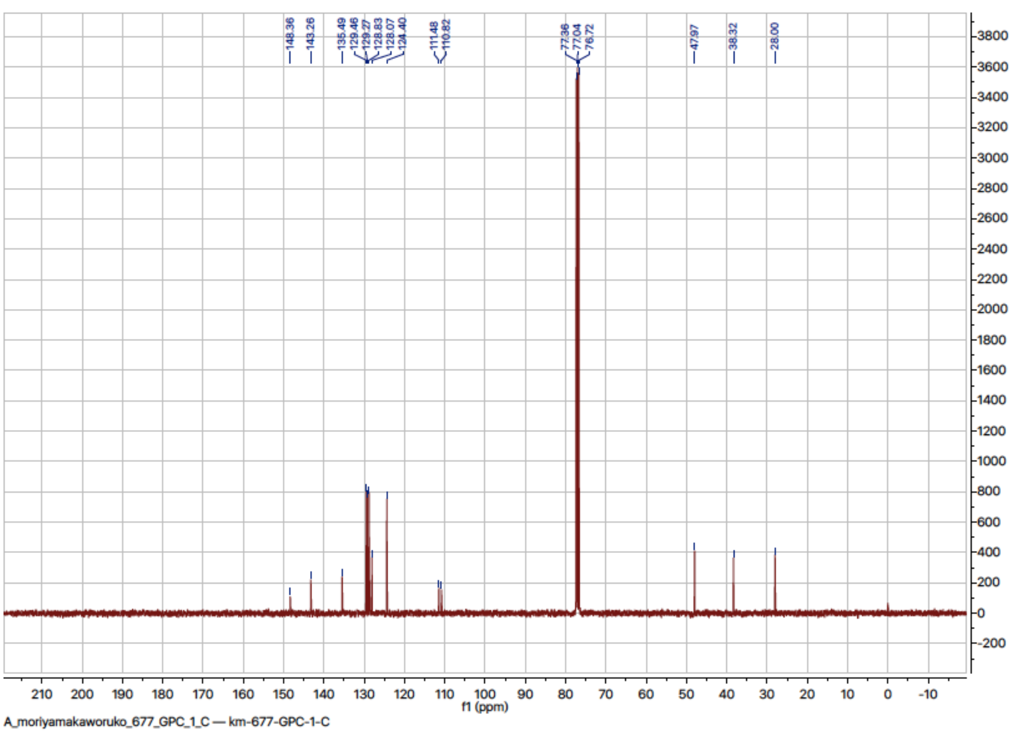


138.98
136.79
133.37
129.88
129.17
128.92
127.88
127.57
112.16
111.49
77.35
77.24
77.04
76.72
48.03
38.51
28.66
21.19
0.02
f1 (ppm)
A_moriyamakaworuko_570_GPC_C — km-570-GPC-C

3ca

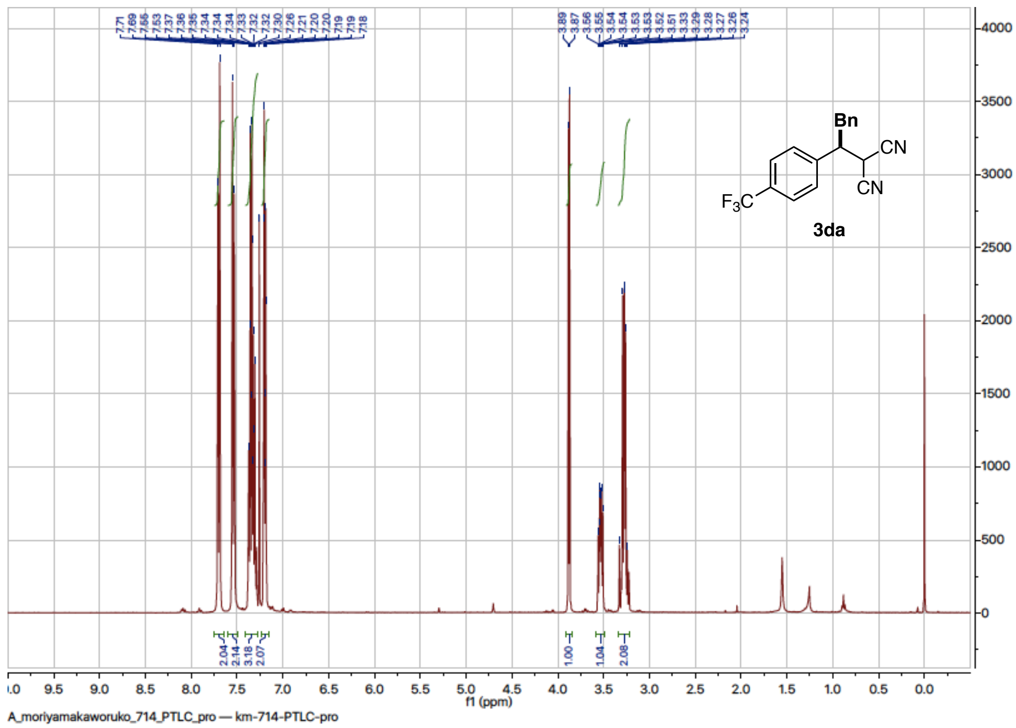


Bn
CN
CN
O2N
3ca
f1 (ppm)
A_moriyamakaworuko_677_GPC_1 — km-677-GPC-1

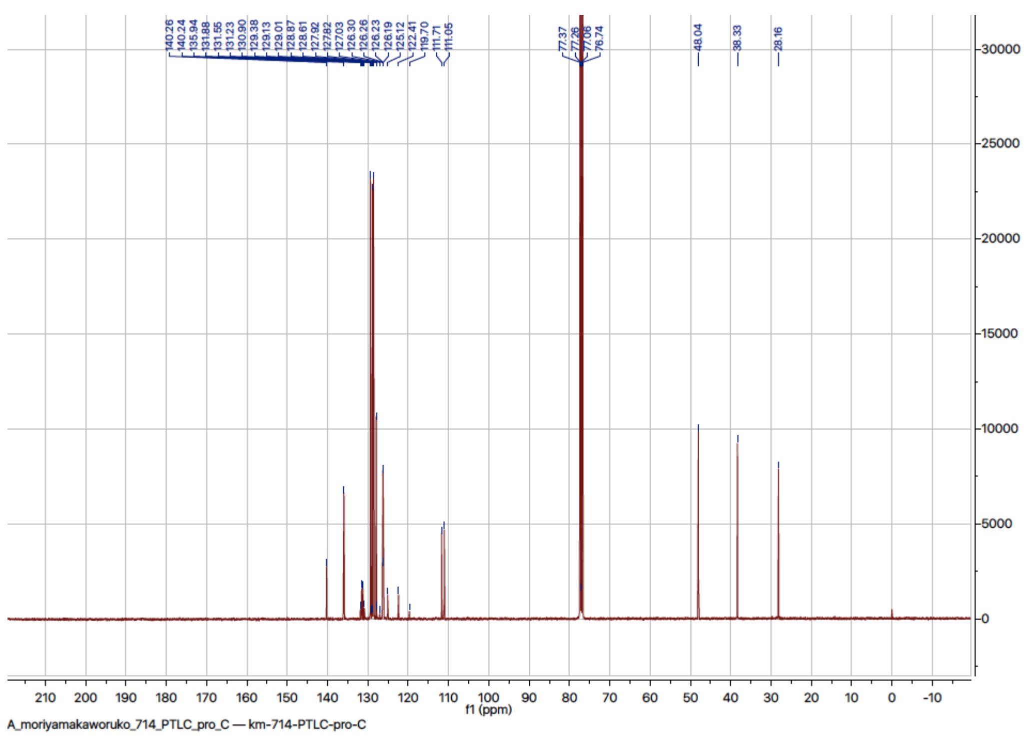


f1 (ppm)
A_moriyamakaworuko_677_GPC_1_C — km-677-GPC-1-C

3da

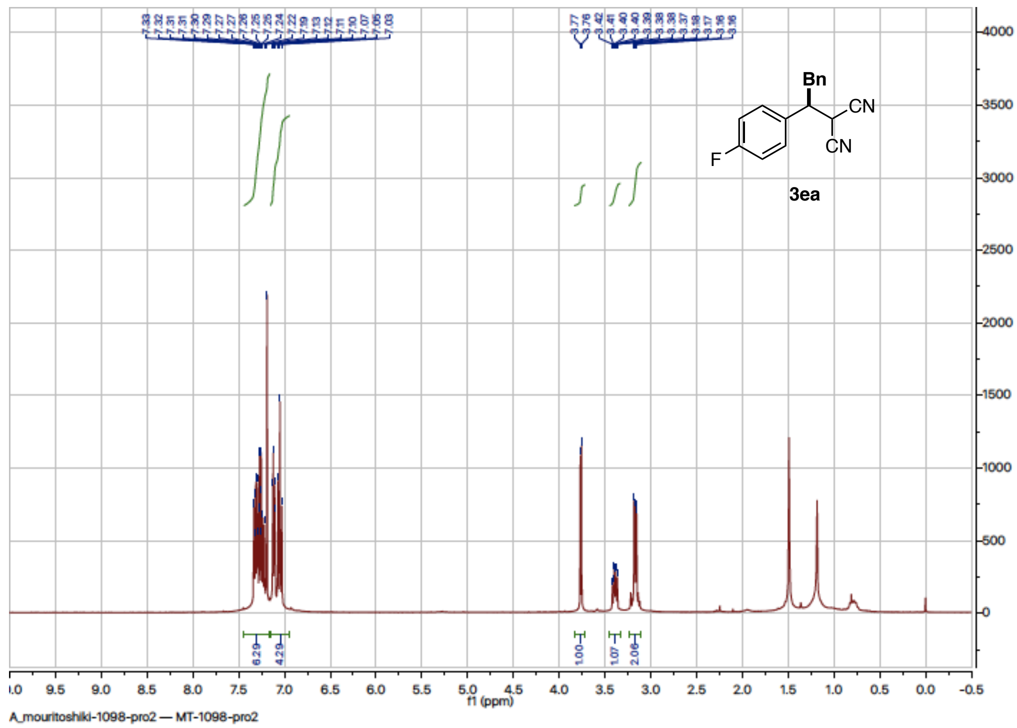


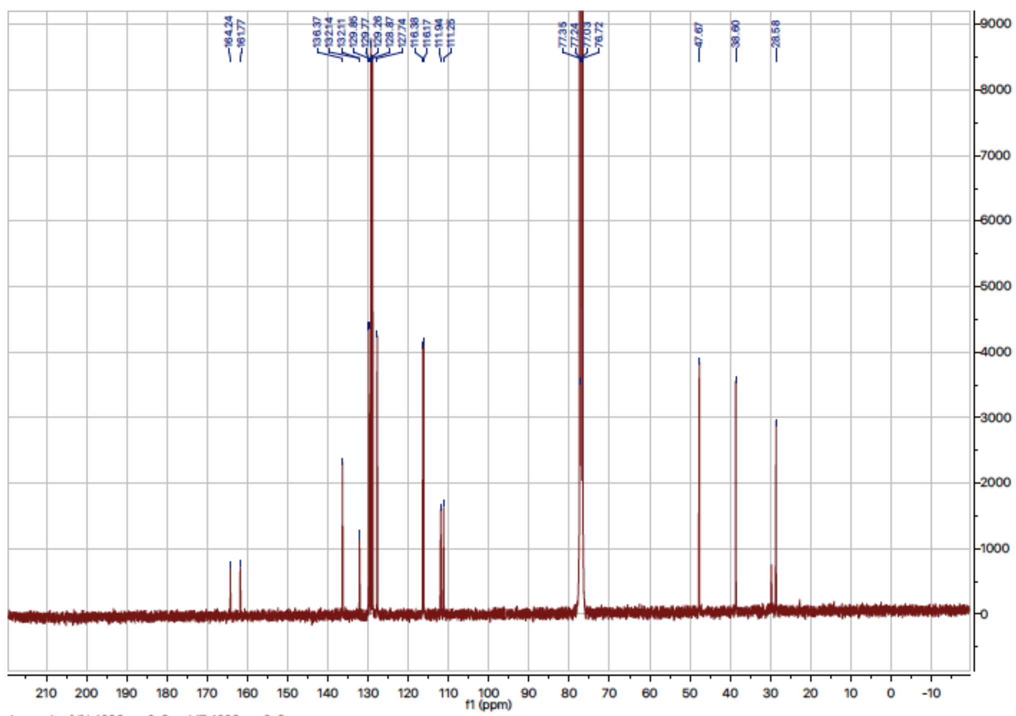
Bn
CN
CN
F3C
3da
f1 (ppm)
A_moriyamakaworuko_714_PTLC_pro — km-714-PTLC-pro



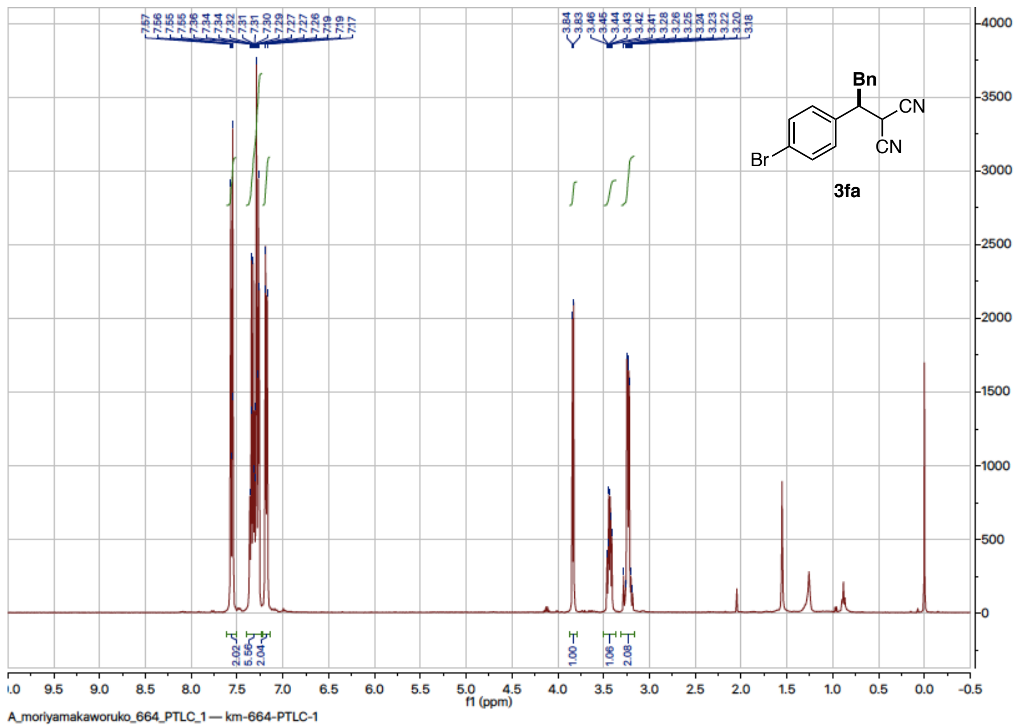
f1 (ppm)
A_moriyamakaworuko_714_PTLC_pro_C — km-714-PTLC-pro-C

3ea

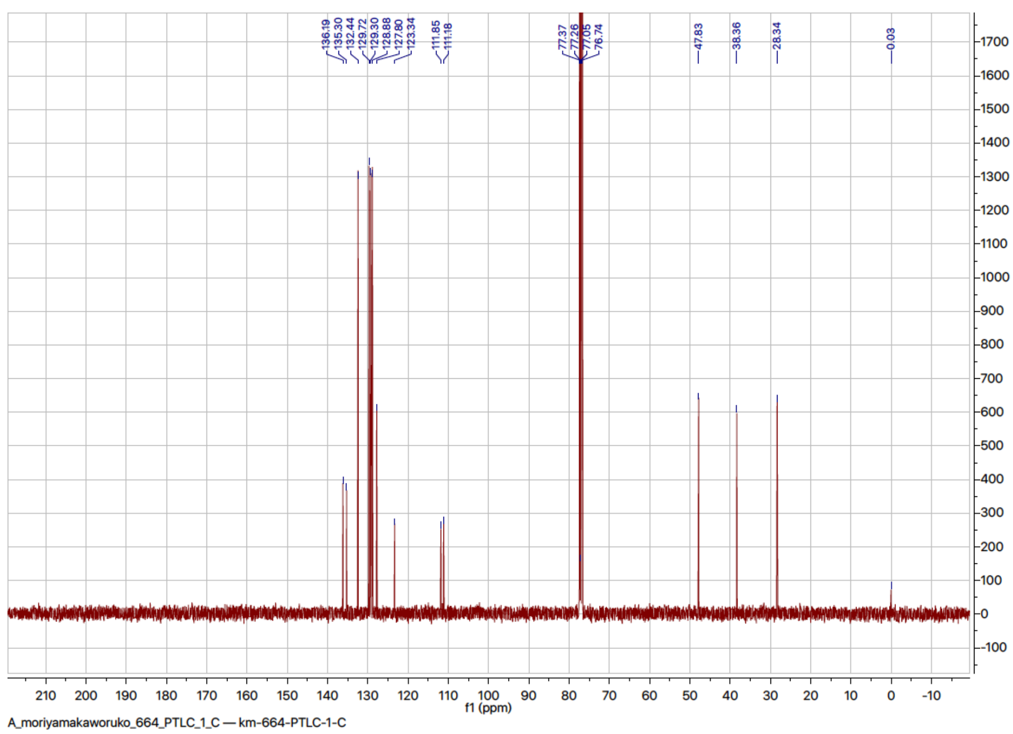




3fa

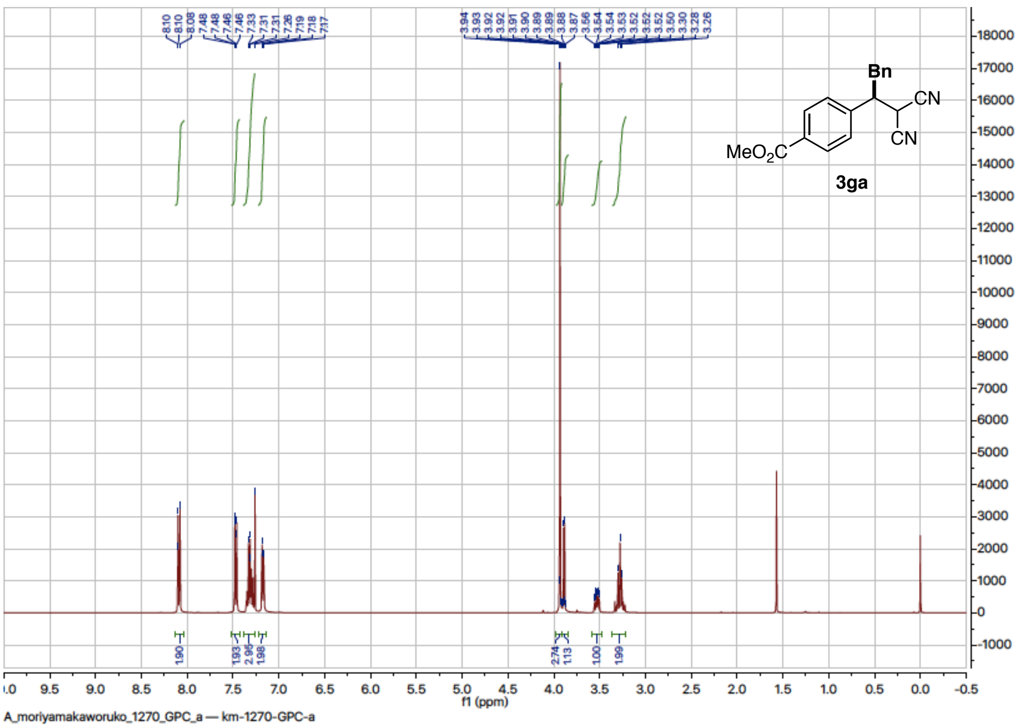


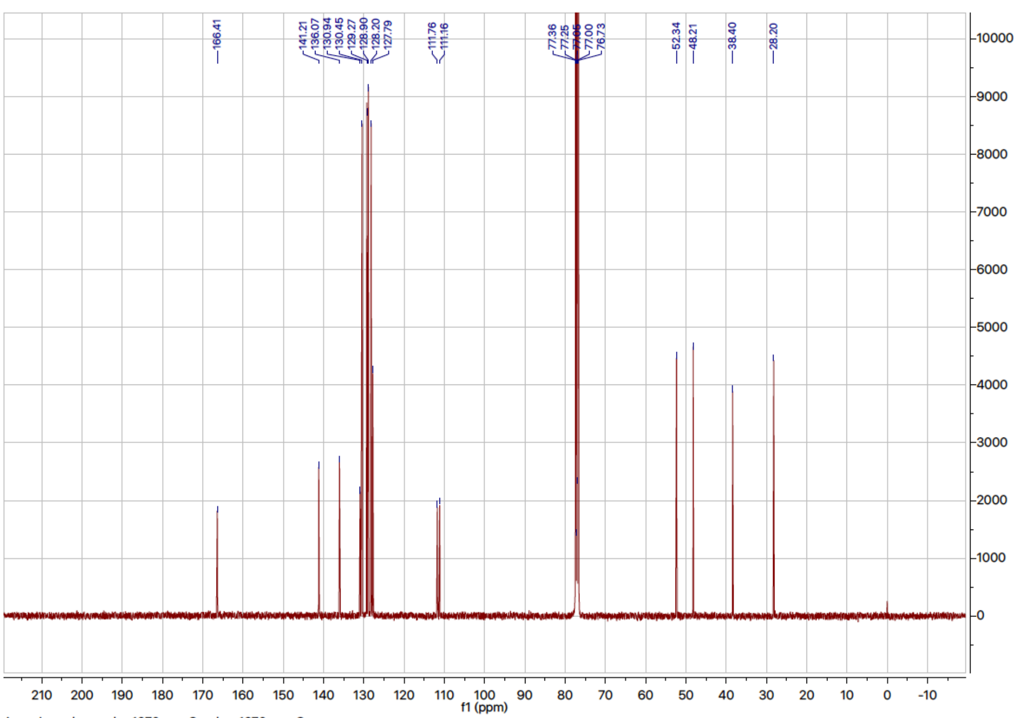
Bn
CN
CN
Br
3fa
f1 (ppm)
A_moriyamakaworuko_664_PTLC_1 — km-664-PTLC-1



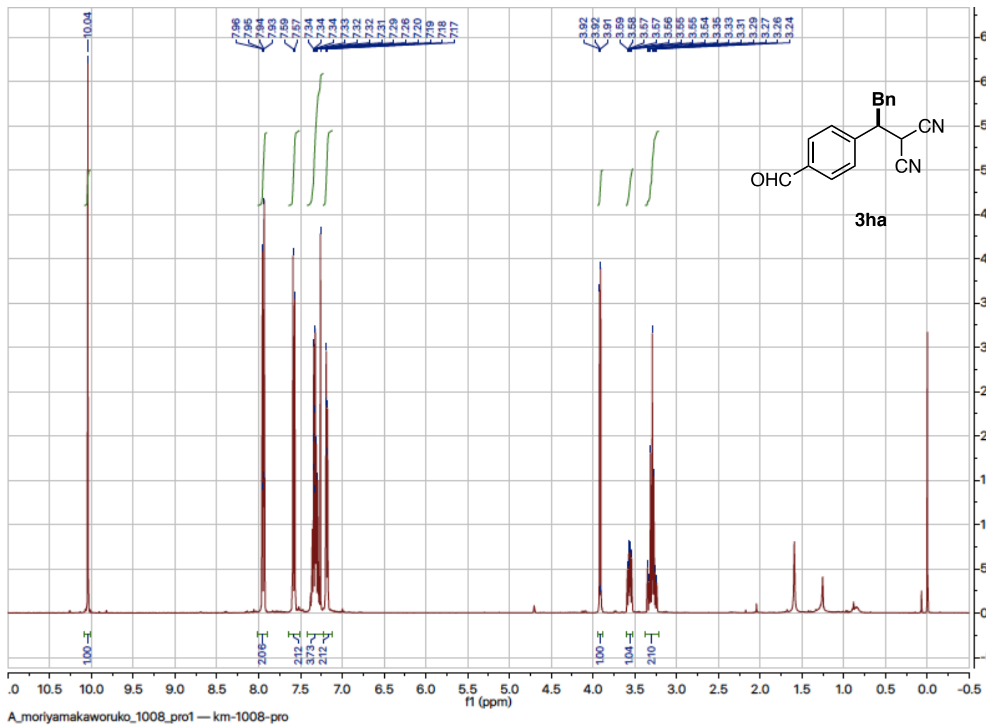
136.19
135.30
132.44
129.72
129.30
128.88
127.80
123.34
111.85
111.18
77.37
77.26
77.05
76.74
47.83
38.36
28.34
0.03
f1 (ppm)
A_moriyamakaworuko_664_PTLC_1_C — km-664-PTLC-1-C

3ga

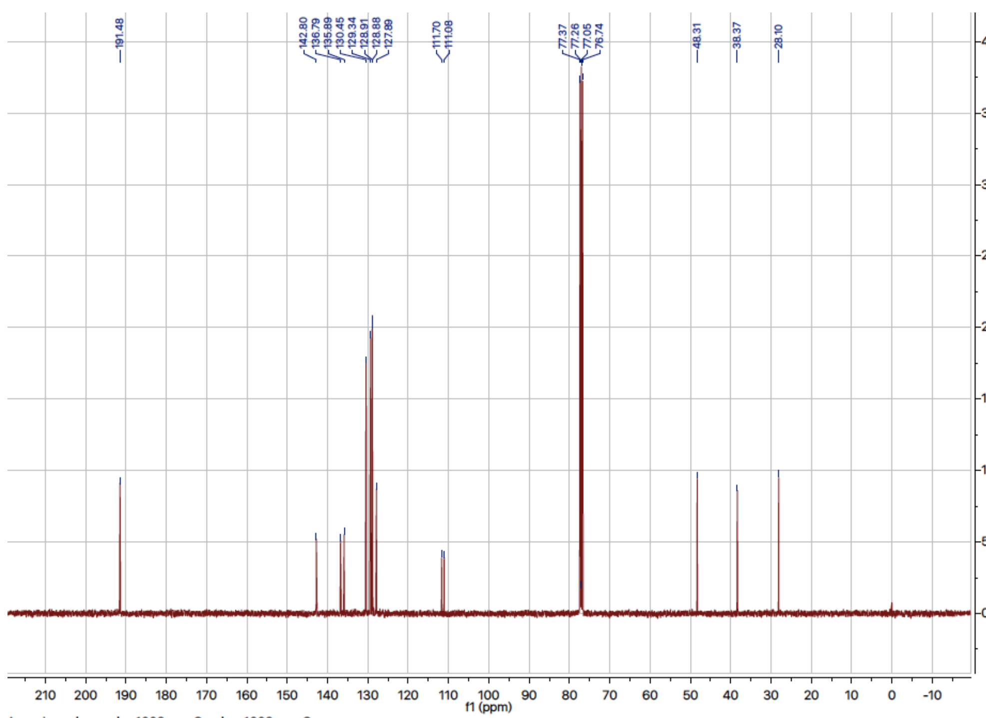

Bn
CN
CN
MeO2C
3ga
f1 (ppm)
A_moriyamakaworuko_1270_GPC_a — km-1270-GPC-a


166.41
141.21
136.07
130.94
130.45
129.27
128.90
128.20
127.79
111.76
111.16
77.36
77.25
77.05
77.00
76.73
52.34
48.21
38.40
28.20
f1 (ppm)
A_moriyamakaworuko_1270_pro_C — km-1270-pro-C

3ha

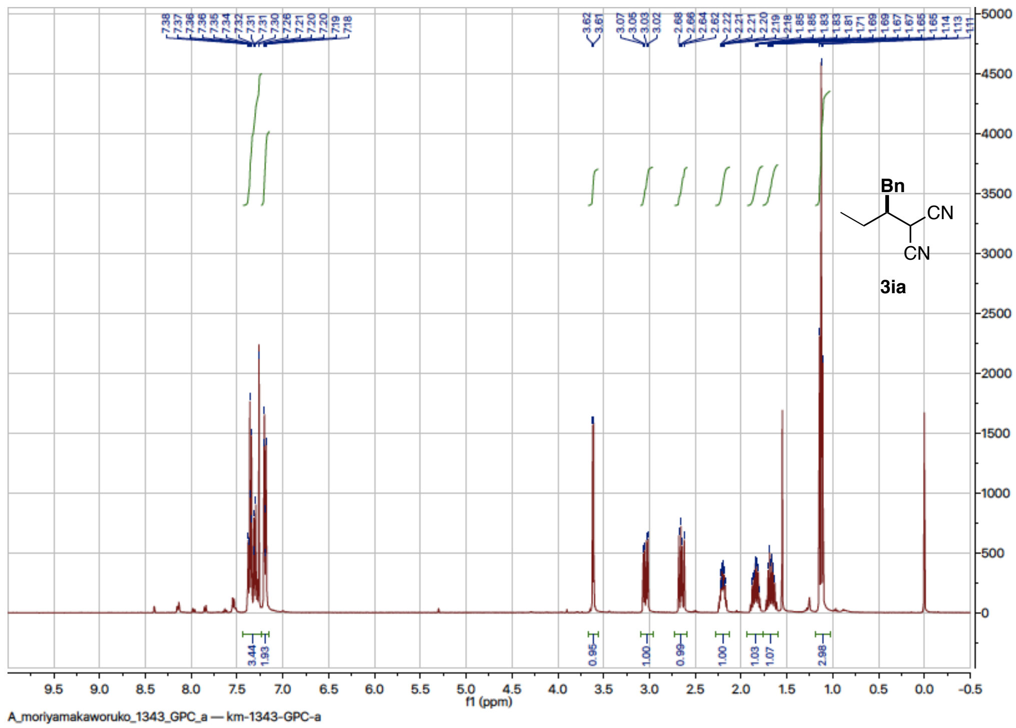


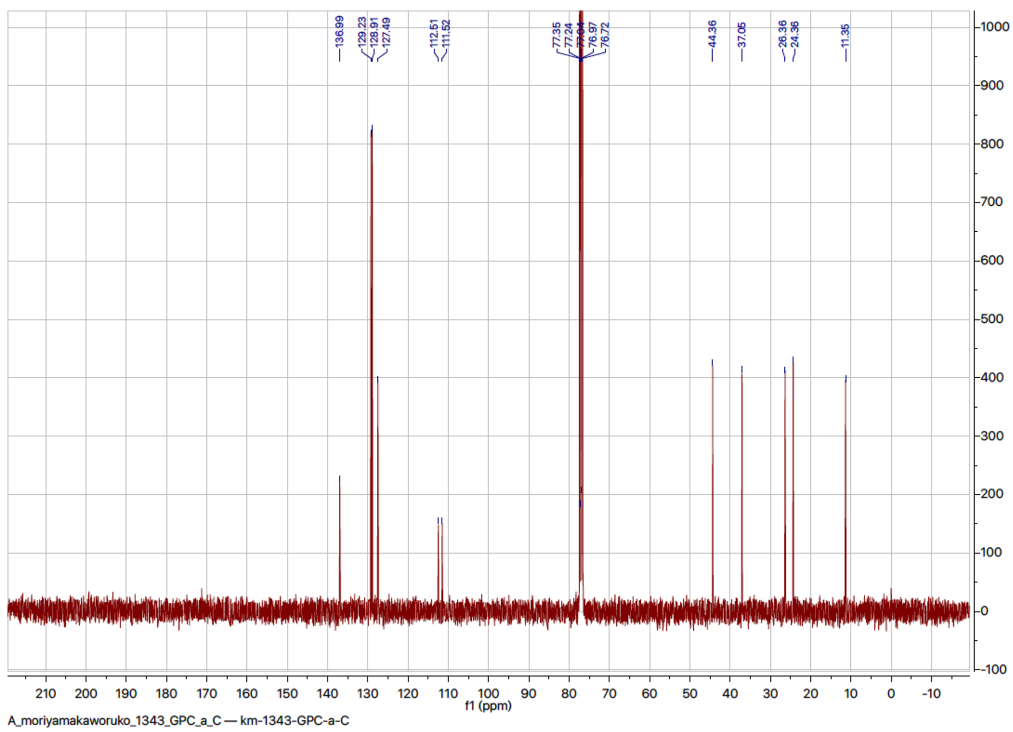
Bn
CN
CN
OHC
3ha
f1 (ppm)
A_moriyamakaworuko_1008_pro1 — km-1008-pro



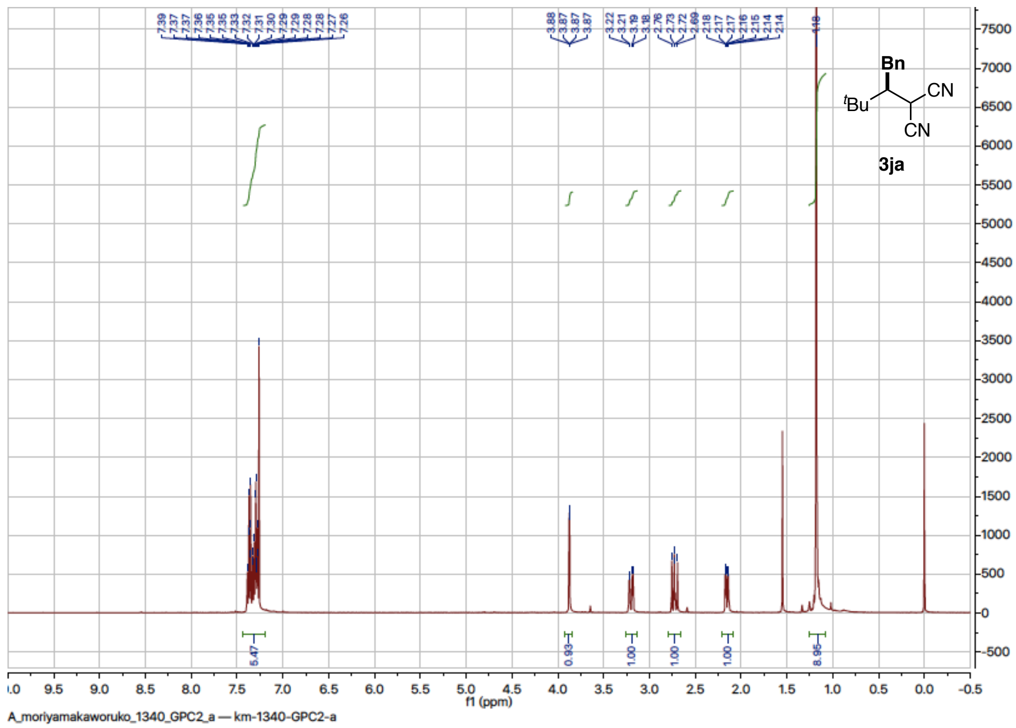
f1 (ppm)
A_moriyamakaworuko_1008_pro_C — km-1008-pro-C

3ia

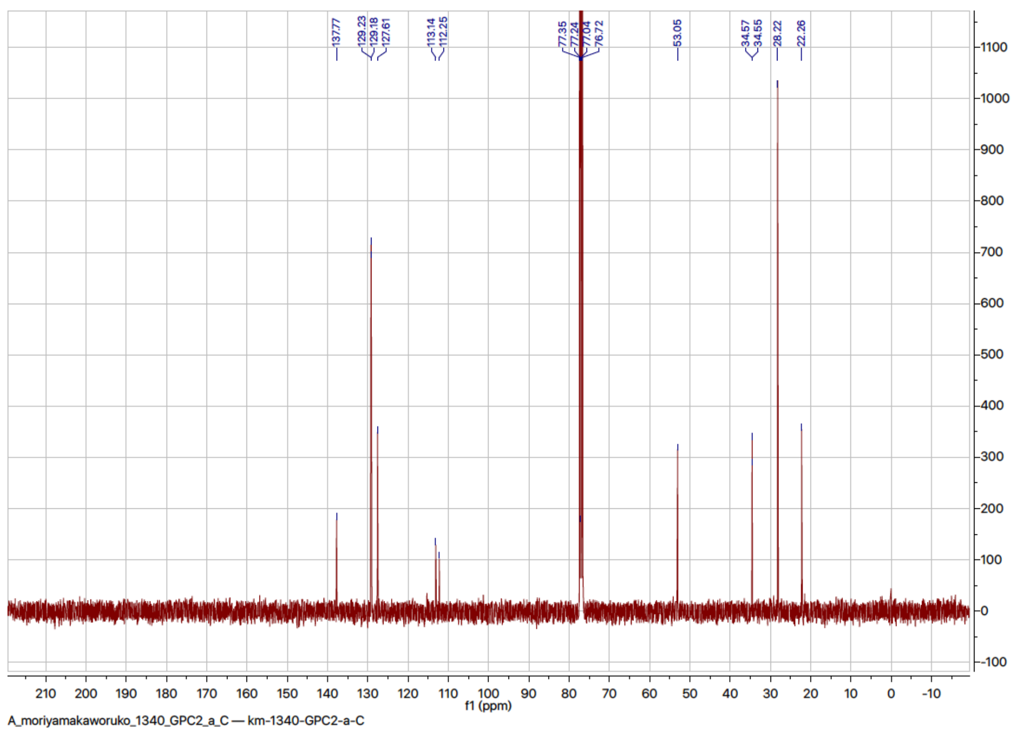




3ja

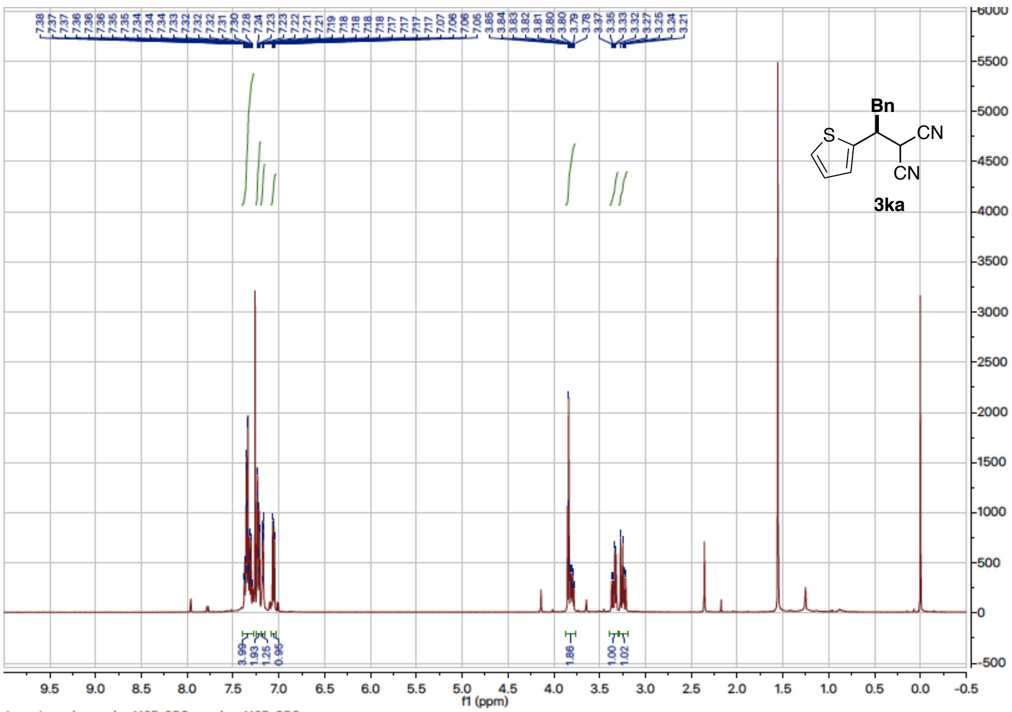


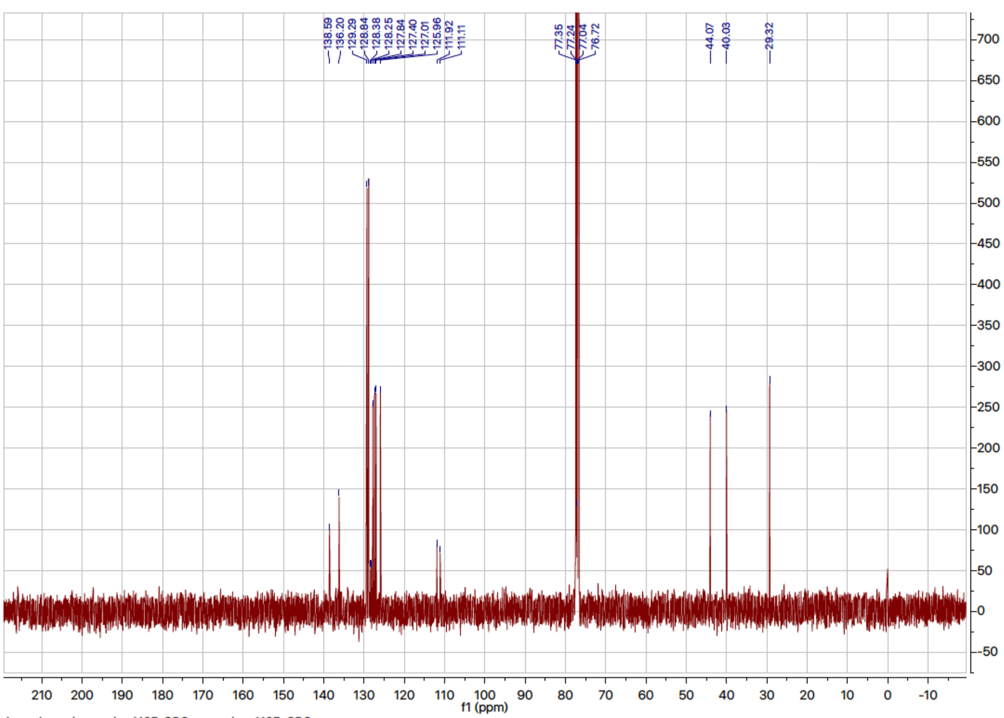
A_moriyamakaworuko_1340_GPC2_a — km-1340-GPC2-a
f1 (ppm)
Bn
tBu
CN
CN
3ja



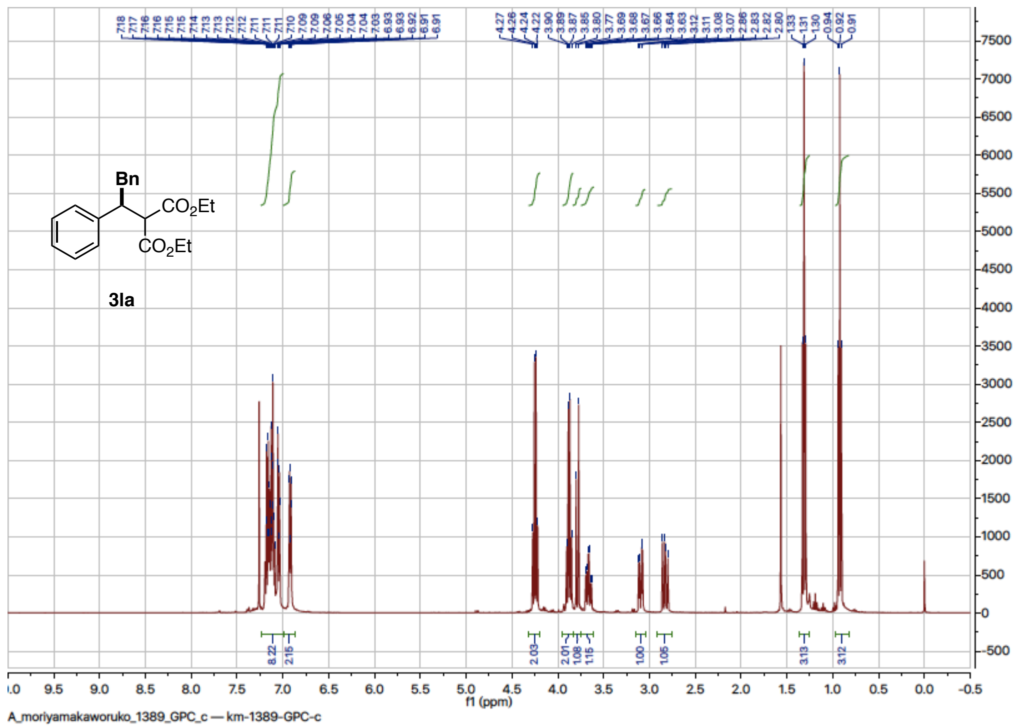
A_moriyamakaworuko_1340_GPC2_a_C — km-1340-GPC2-a-C
f1 (ppm)

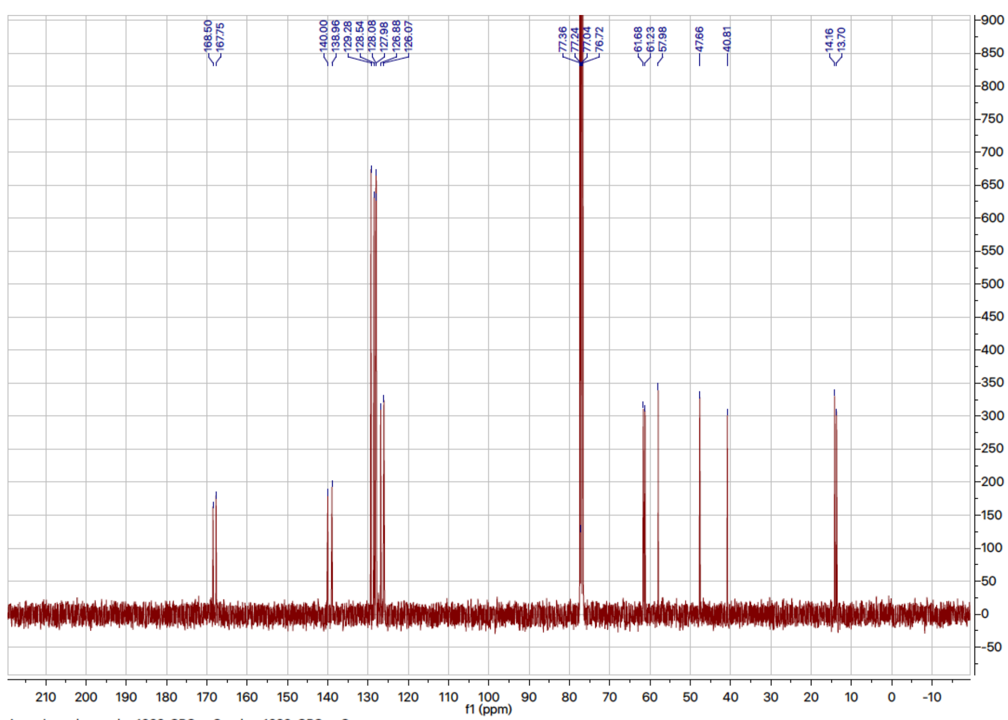
3ka


3ka
A_moriyamakaworuko_1125_GPC_a — km-1125-GPC-a

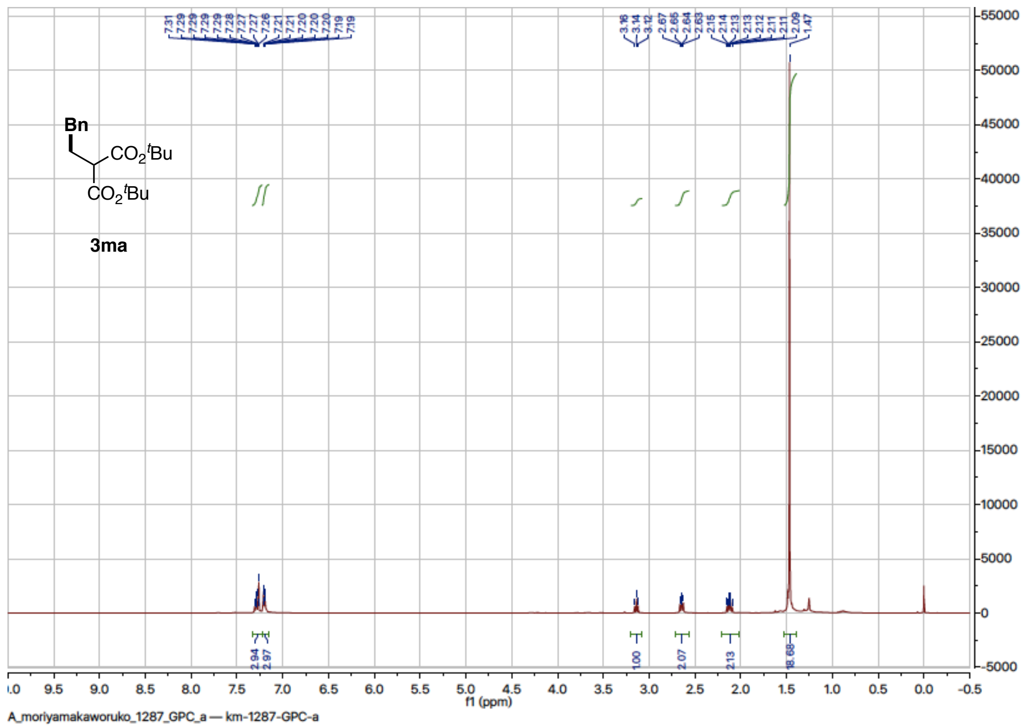

A_moriyamakaworuko_1125_GPC_pro — km-1125-GPC-pro

3la

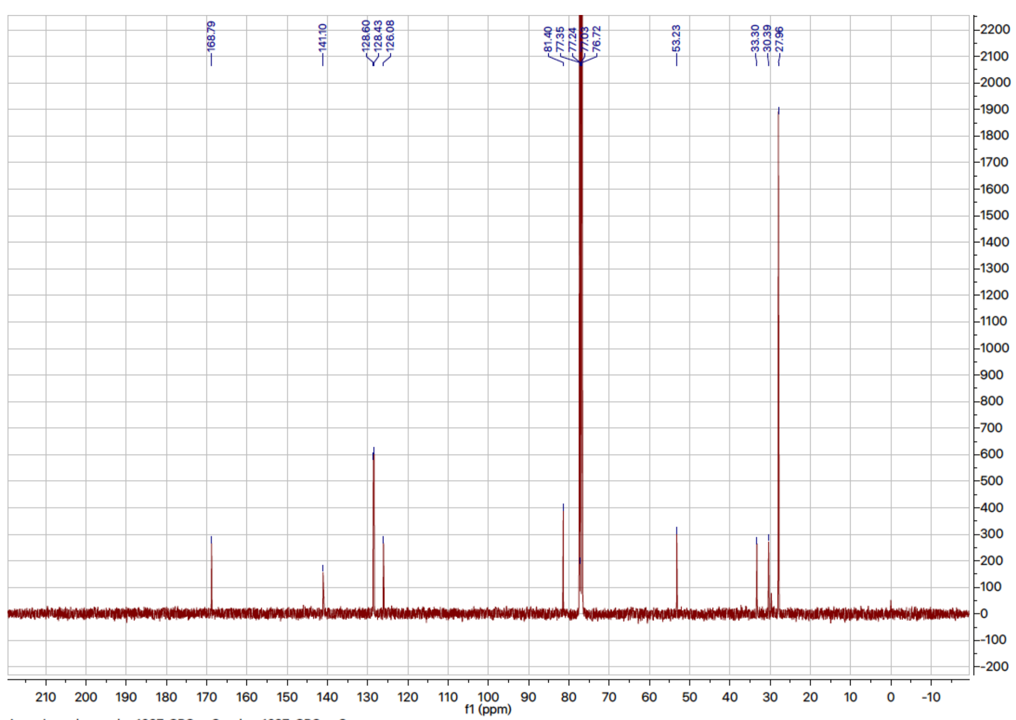

Bn
CO2Et
CO2Et
3la
8.22
2.16
2.03
2.01
1.08
1.15
1.00
1.05
3.13
3.12
f1 (ppm)
A_moriyamakaworuko_1389_GPC_c — km-1389-GPC-c


168.50
167.75
140.00
138.96
129.28
128.54
128.08
127.98
126.88
126.07
77.36
77.24
77.04
76.72
61.68
61.23
57.98
47.66
40.81
14.16
13.70
f1 (ppm)
A_moriyamakaworuko_1389_GPC_c_C — km-1389-GPC-c-C

3ma

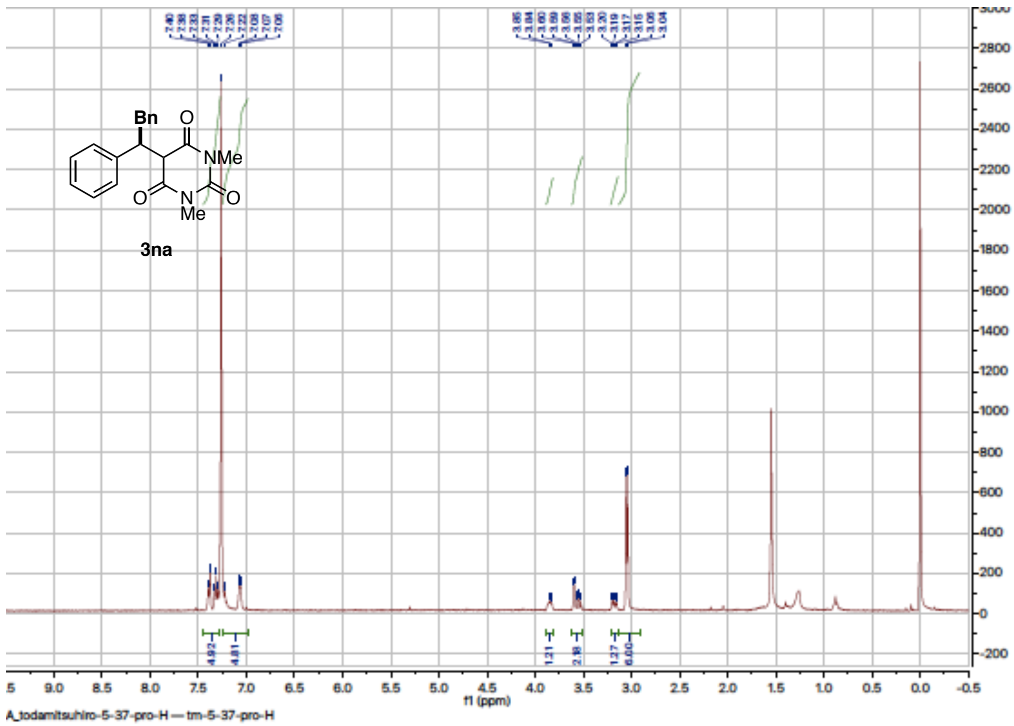


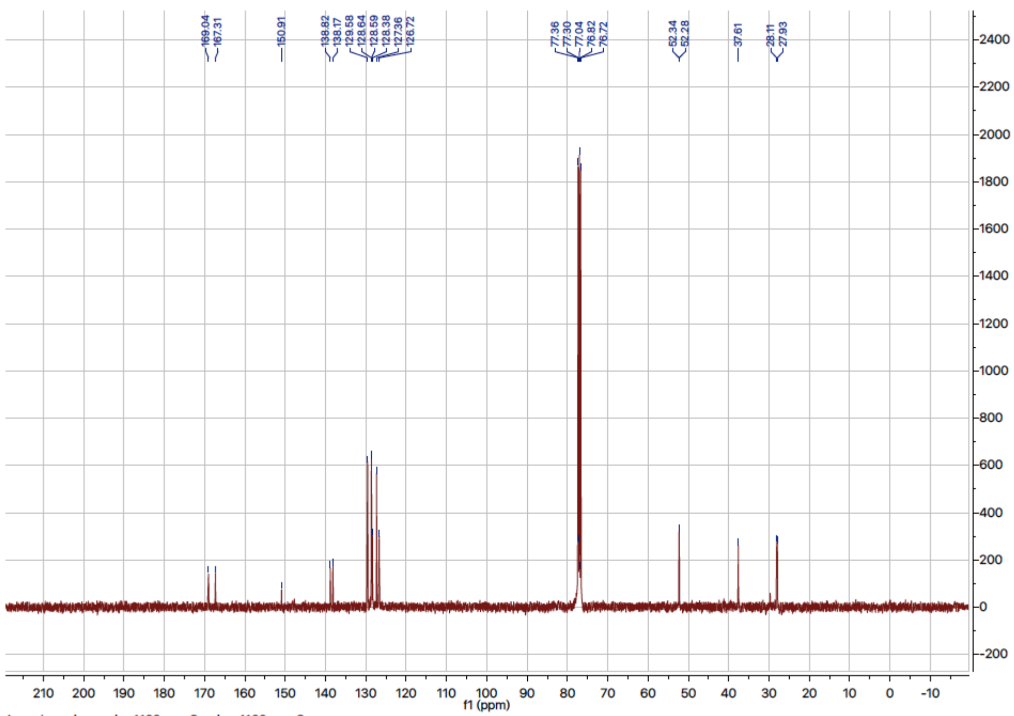
3ma
A_moriyamakaworuko_1287_GPC_a — km-1287-GPC-a
f1 (ppm)



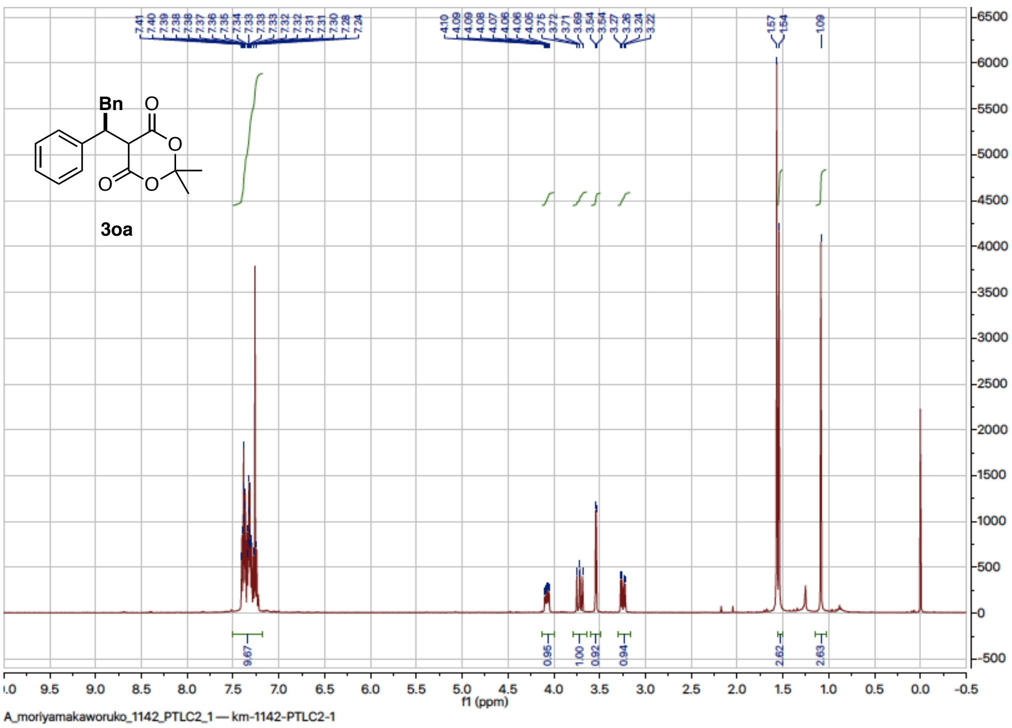
A_moriyamakaworuko_1287_GPC_a_C — km-1287-GPC-a-C
f1 (ppm)

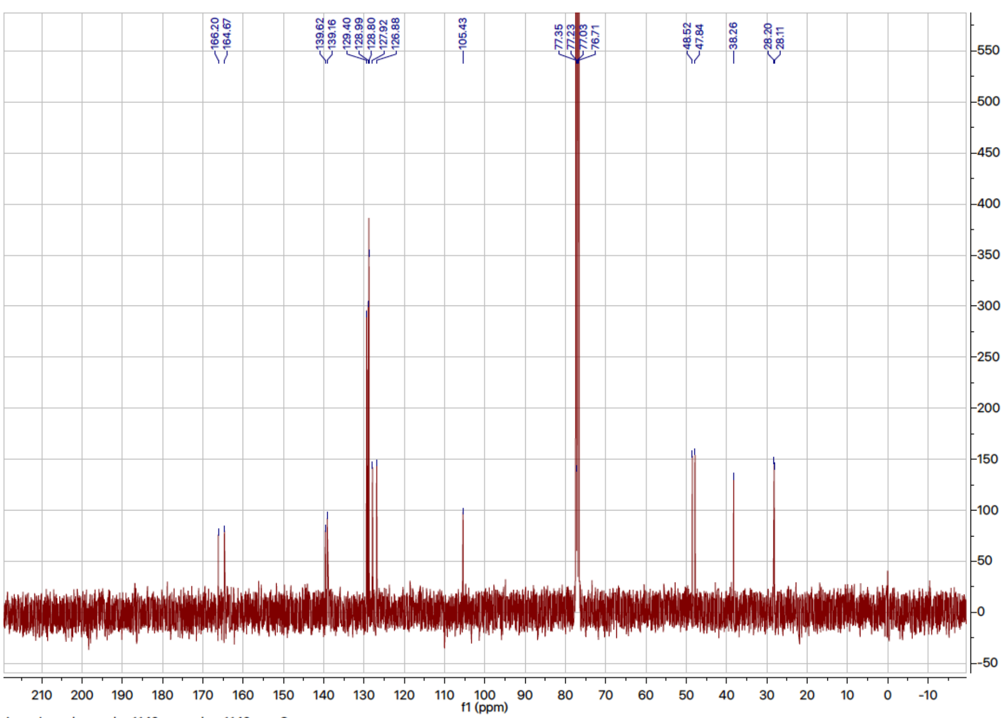
3na



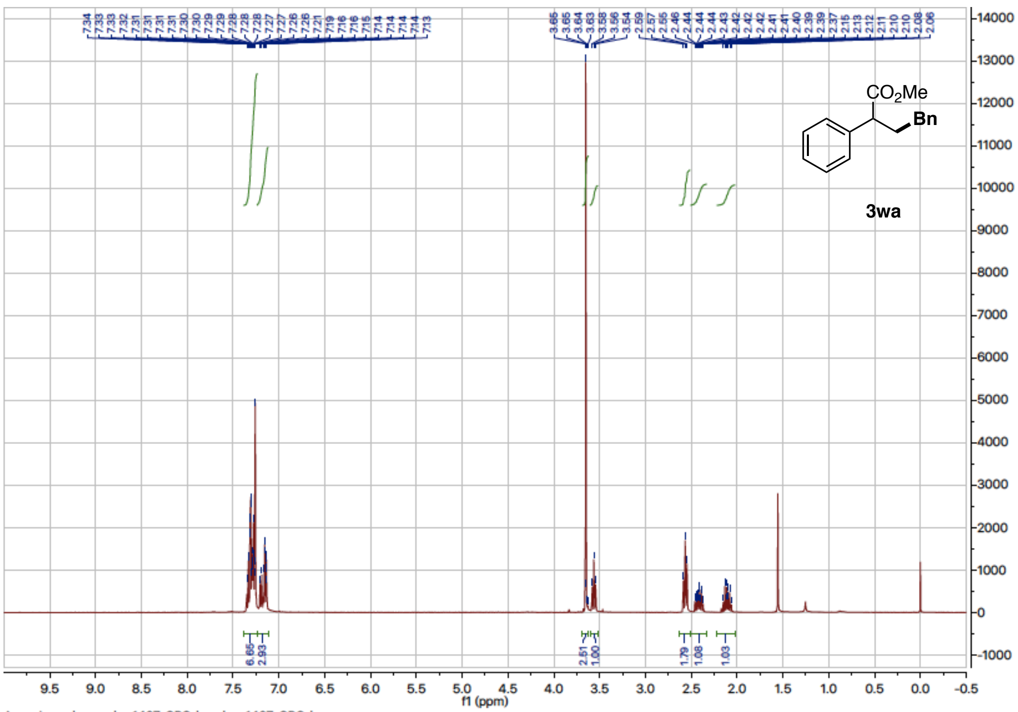


3oa

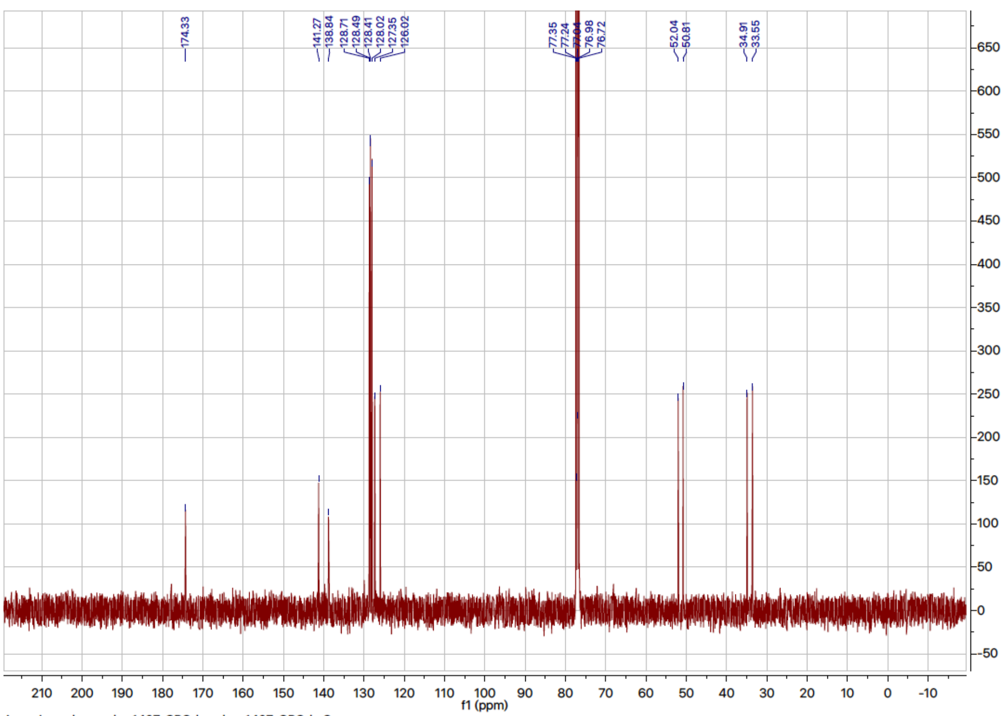

7.41
7.40
7.39
7.38
7.38
7.37
7.36
7.35
7.34
7.33
7.33
7.33
7.32
7.32
7.31
7.31
7.30
7.28
7.24
4.10
4.09
4.09
4.08
4.07
4.06
4.06
4.05
3.75
3.72
3.71
3.69
3.54
3.54
3.27
3.26
3.24
3.22
1.57
1.54
1.09
Bn
3oa
9.67
0.95
1.00
0.92
0.94
2.62
2.63
f1 (ppm)
A_moriyamakaworuko_1142_PTLC2_1 — km-1142-PTLC2-1


166.20
164.67
139.62
139.16
129.40
128.99
128.80
127.92
126.88
105.43
77.35
77.23
77.03
76.71
48.52
47.84
38.26
28.20
28.11
f1 (ppm)
A_moriyamakaworuko_1142_pro — km-1142-pro-C

3wa

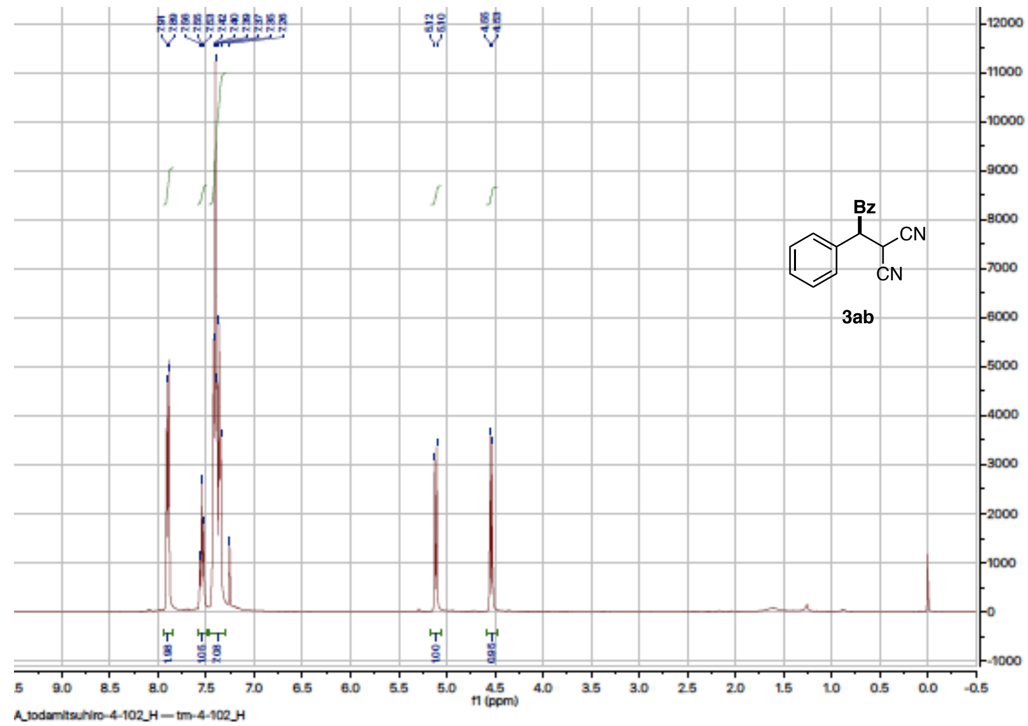


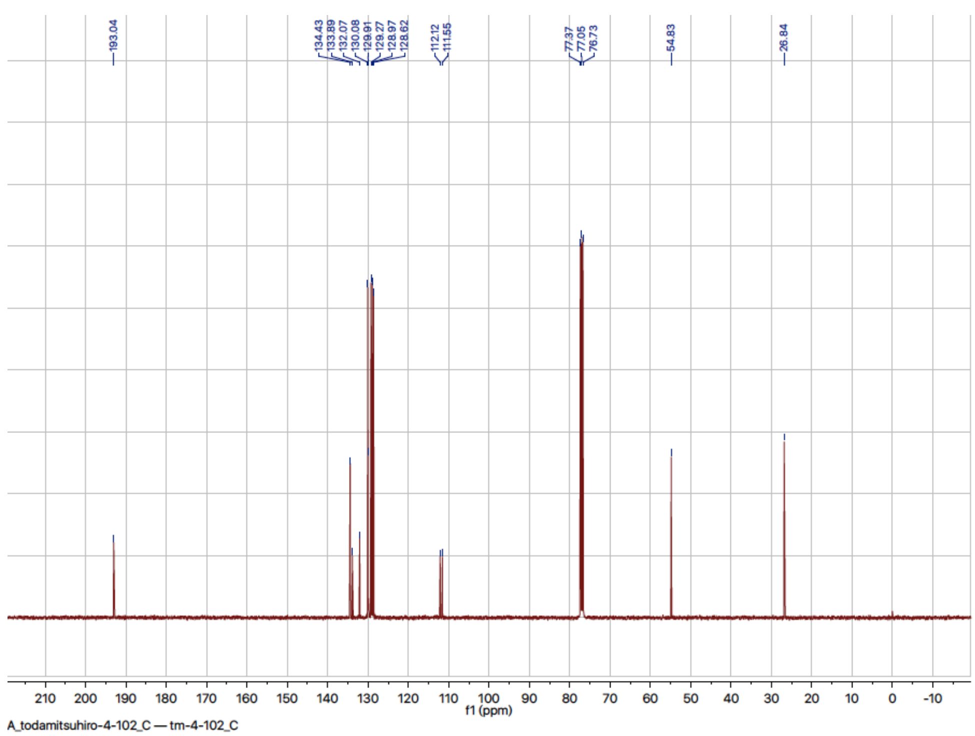
A_moriyamakaworuko_1407_GPC_b — km-1407-GPC-b



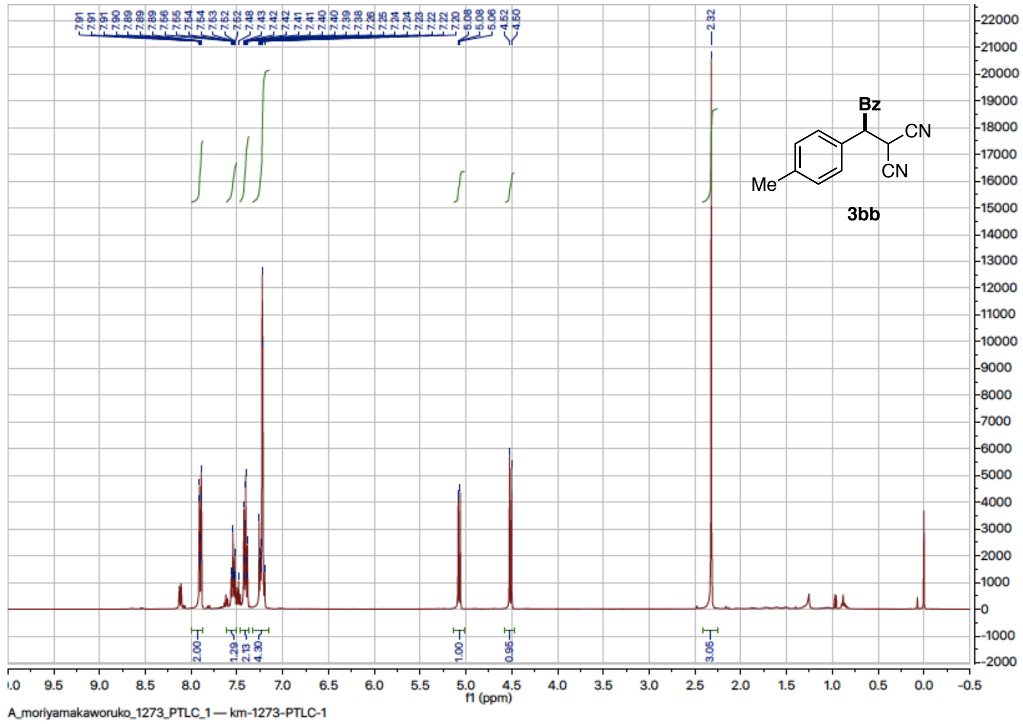
A_moriyamakaworuko_1407_GPC_b — km-1407-GPC-b-C

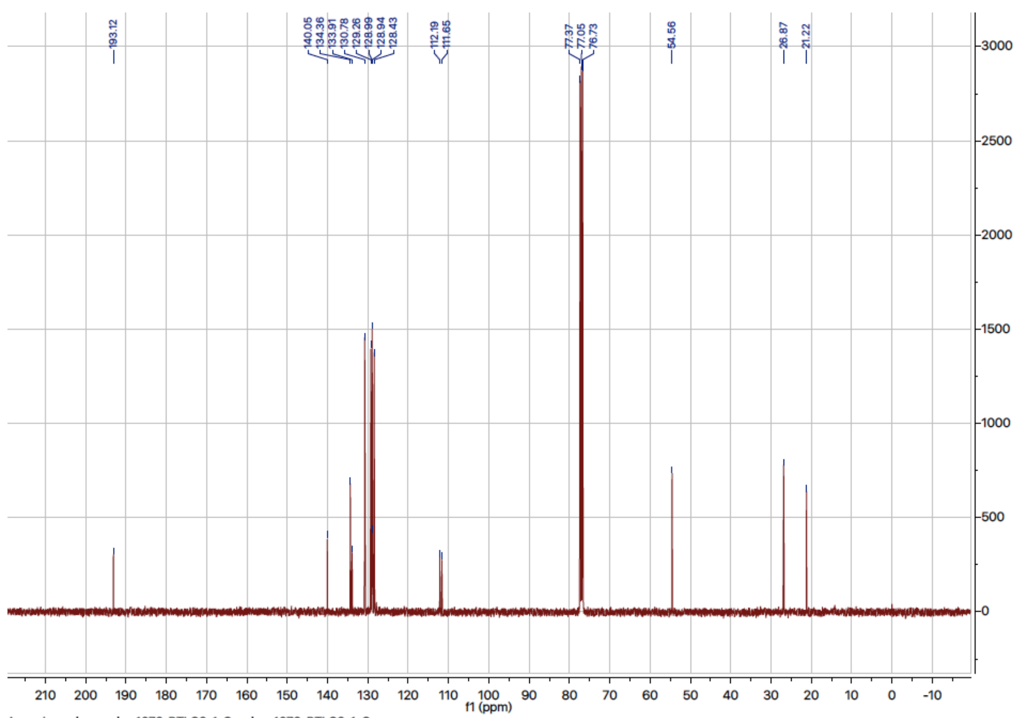
3ab


Bz
CN
CN
3ab
f1 (ppm)
A_todamitsuhiro-4-102_H — tm-4-102_H

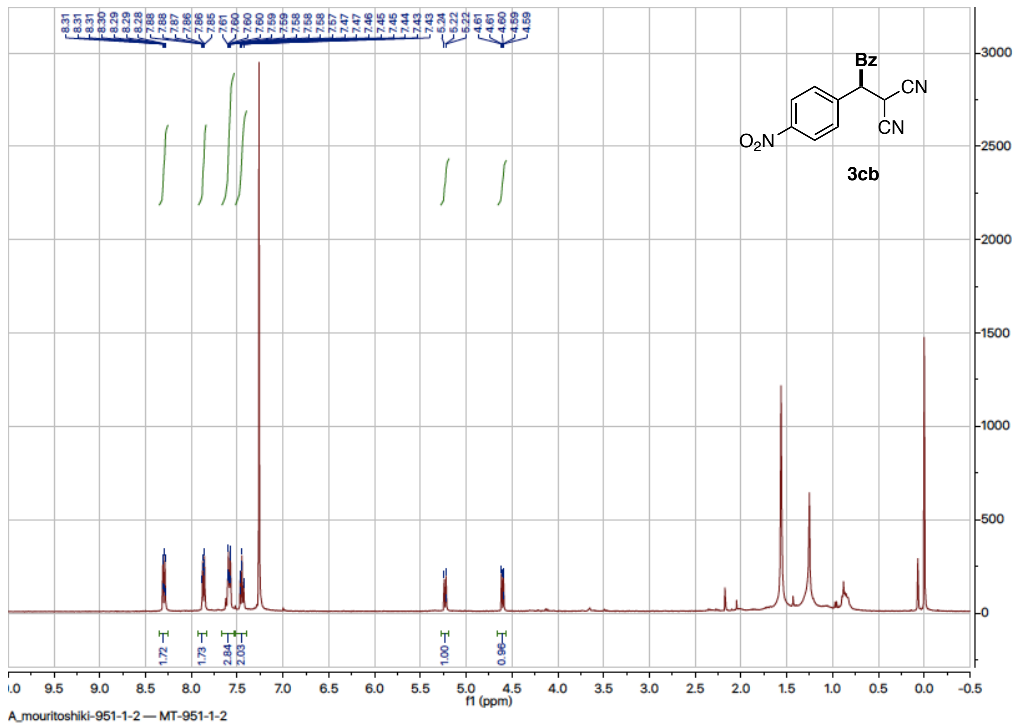

193.04
134.43
133.89
132.07
130.08
129.91
129.27
128.97
128.62
112.12
111.55
77.37
77.05
76.73
54.83
26.84
f1 (ppm)
A_todamitsuhiro-4-102_C — tm-4-102_C

3bb

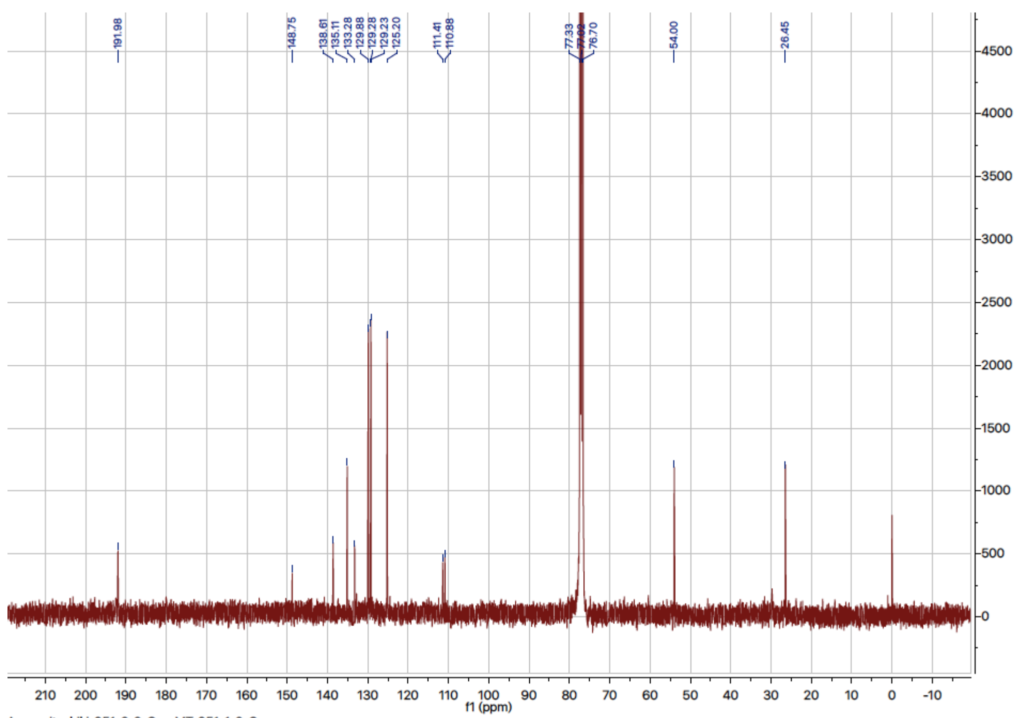

Bz
CN
CN
Me
3bb
2.32
5.08
5.06
4.52
4.50
2.00
1.29
2.13
4.30
1.00
0.95
3.05
f1 (ppm)
A_moriyamakaworuko_1273_PTLC_1 — km-1273-PTLC-1


193.12
140.05
134.36
133.91
130.78
129.26
128.99
128.94
128.43
112.19
111.65
77.37
77.05
76.73
54.56
26.87
21.22
f1 (ppm)
A_moriyamakaworuko_1273_PTLC3_1_C — km-1273-PTLC3-1-C

3cb

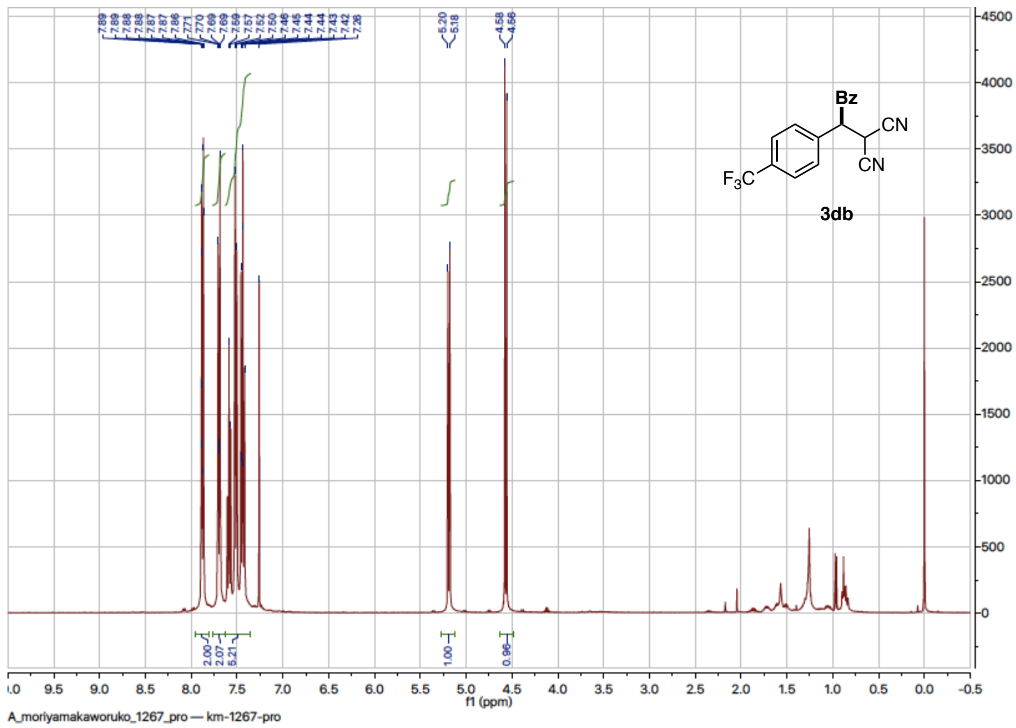


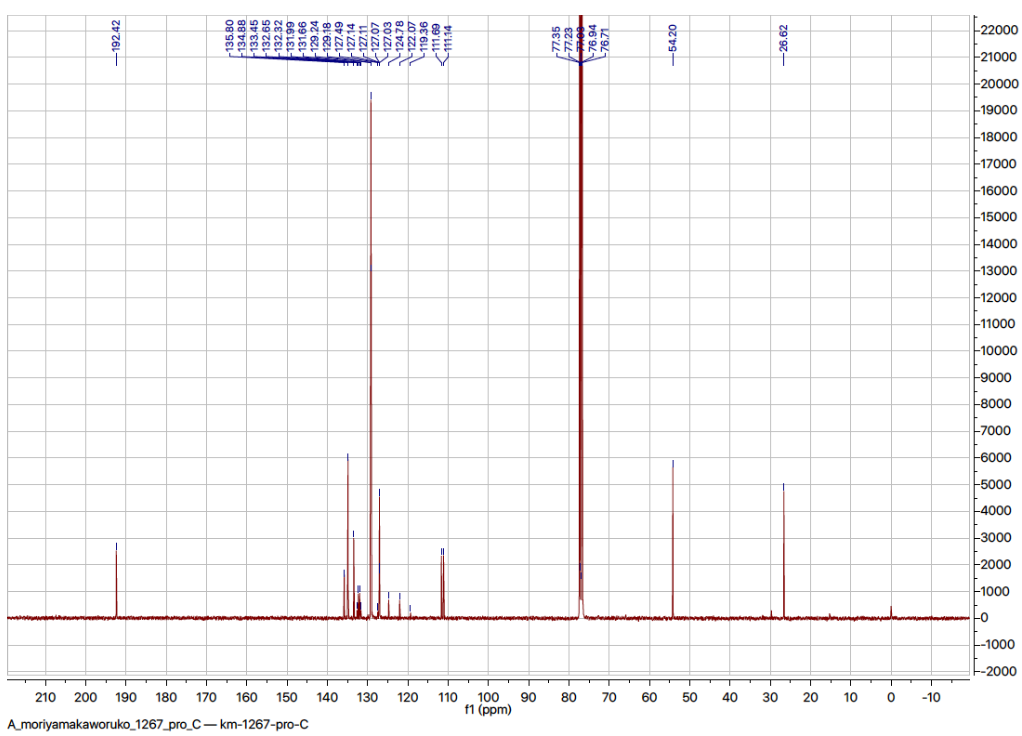
Bz
CN
CN
O_2N
3cb
f1 (ppm)
A_mouritoshiki-951-1-2 — MT-951-1-2



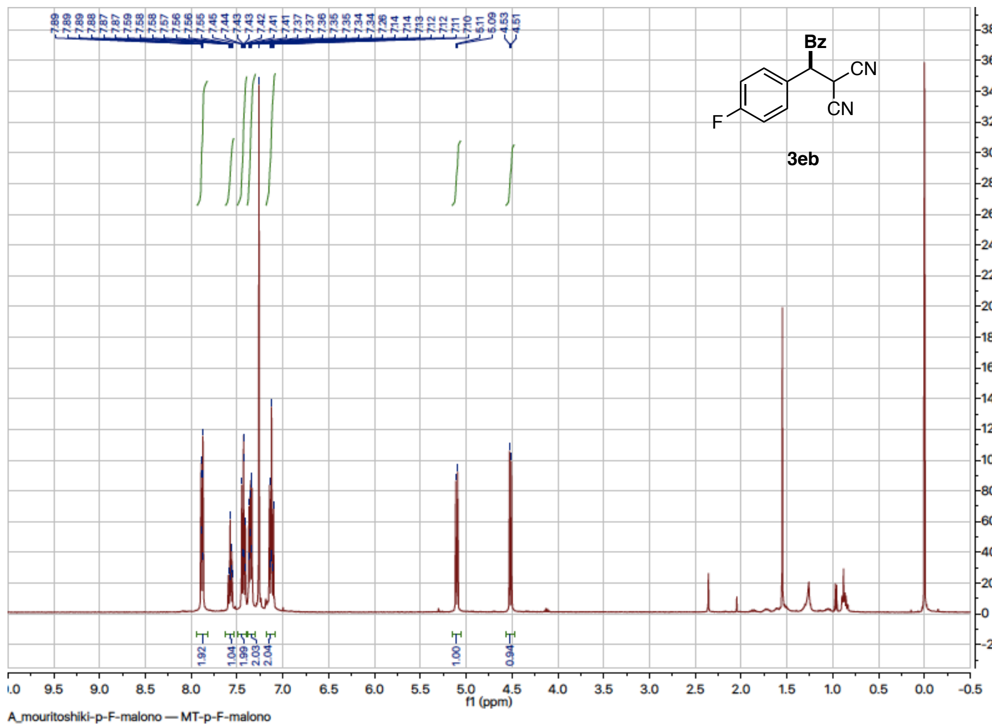
191.98
148.75
138.61
135.11
133.28
129.88
129.28
129.23
125.20
111.41
110.88
77.33
76.70
54.00
26.45
f1 (ppm)
A_mouritoshiki-951-2-2-C — MT-951-1-2-C

3db

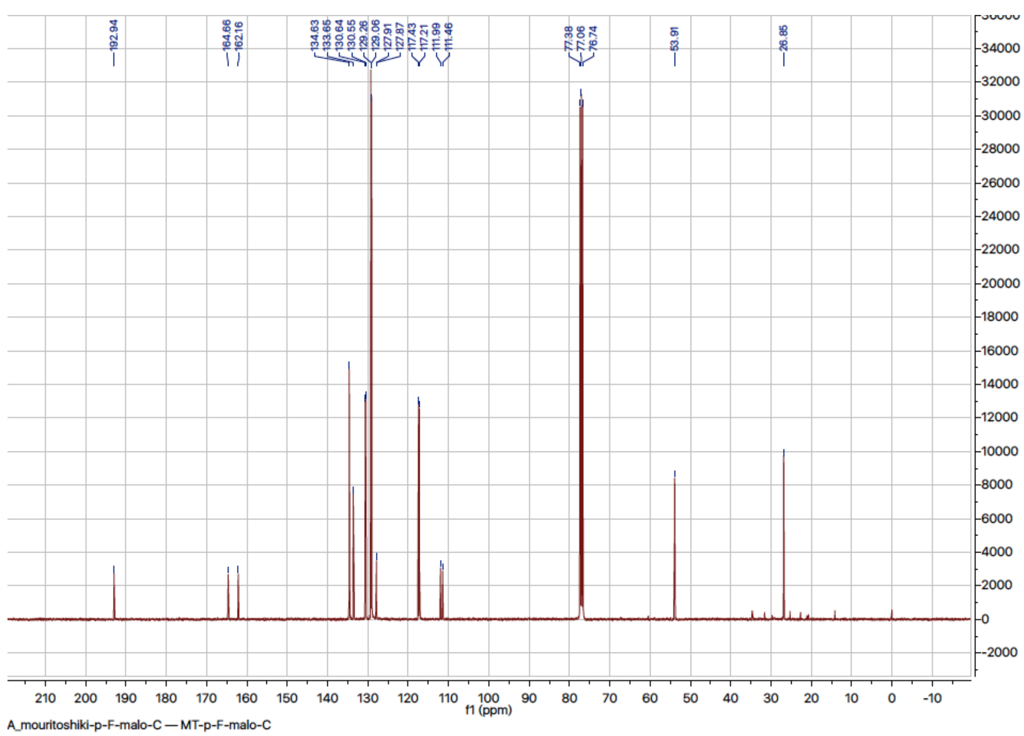

Bz
CN
CN
F3C
3db
f1 (ppm)
A_moriyamakaworuko_1267_pro — km-1267-pro


f1 (ppm)
A_moriyamakaworuko_1267_pro_C — km-1267-pro-C

3eb

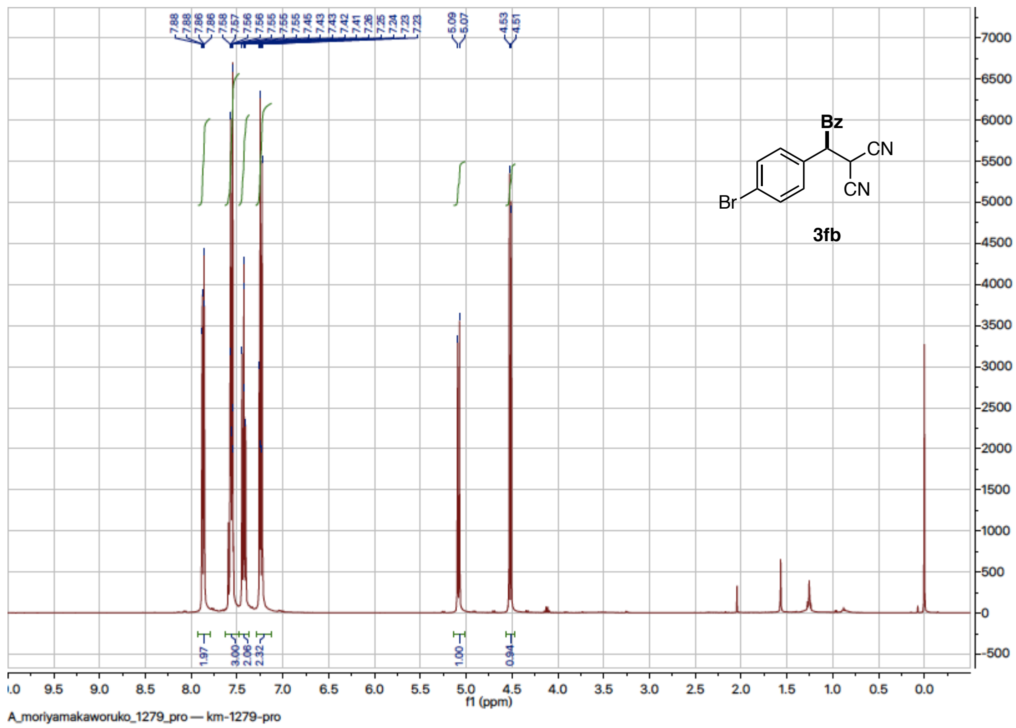


Bz
CN
CN
F
3eb
f1 (ppm)
A_mouritoshiki-p-F-malono — MT-p-F-malono

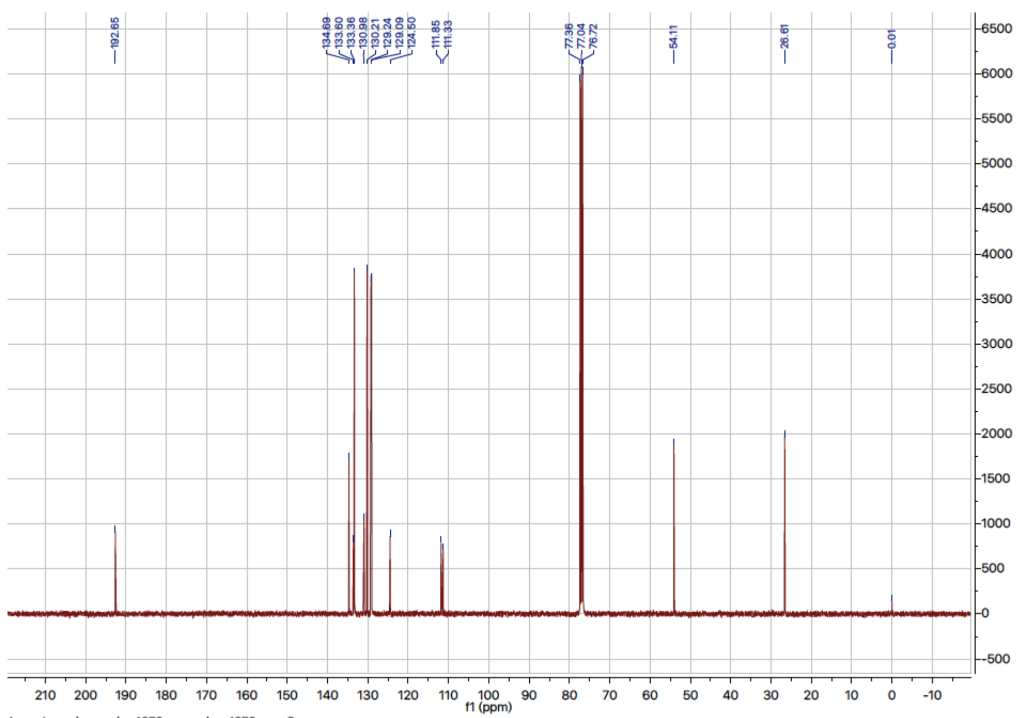


192.94
164.66
162.16
134.63
133.65
130.64
130.55
129.26
129.06
127.91
127.87
117.43
117.21
111.99
111.46
77.38
77.06
76.74
53.91
26.85
f1 (ppm)
A_mouritoshiki-p-F-malo-C — MT-p-F-malo-C

3fb

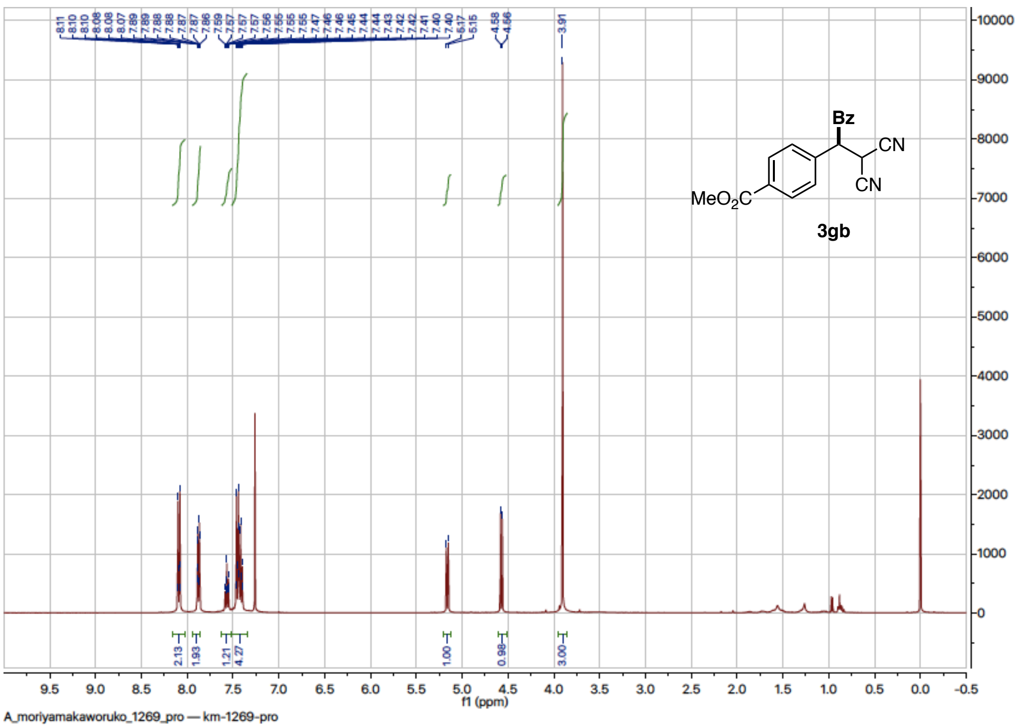


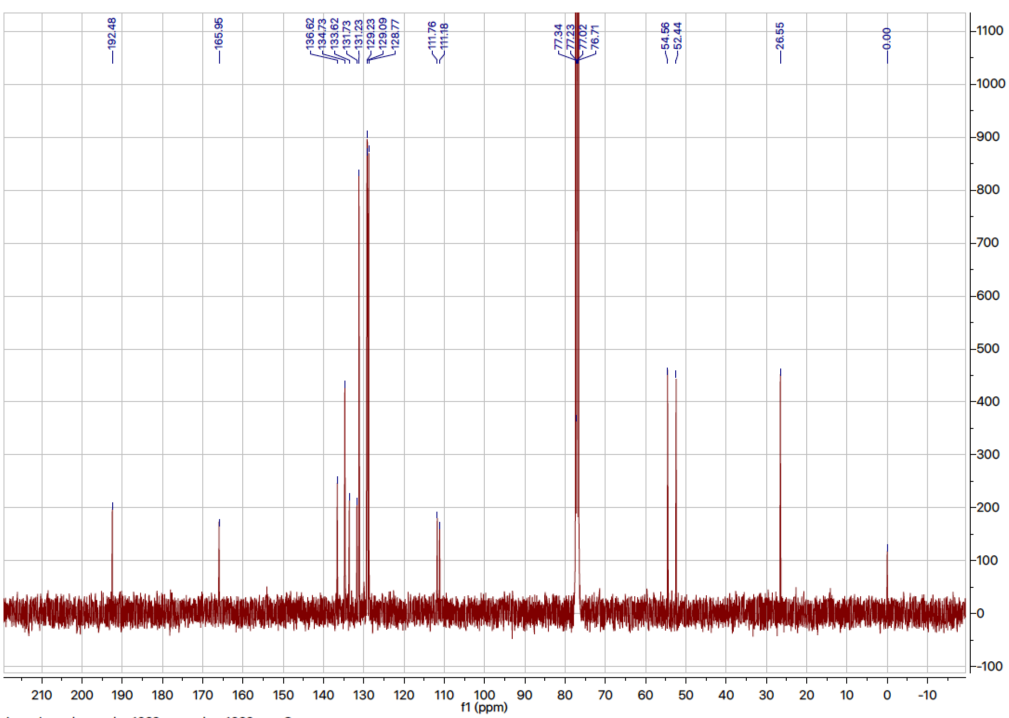
Bz
CN
CN
Br
3fb
f1 (ppm)
A_moriyamakaworuko_1279_pro — km-1279-pro



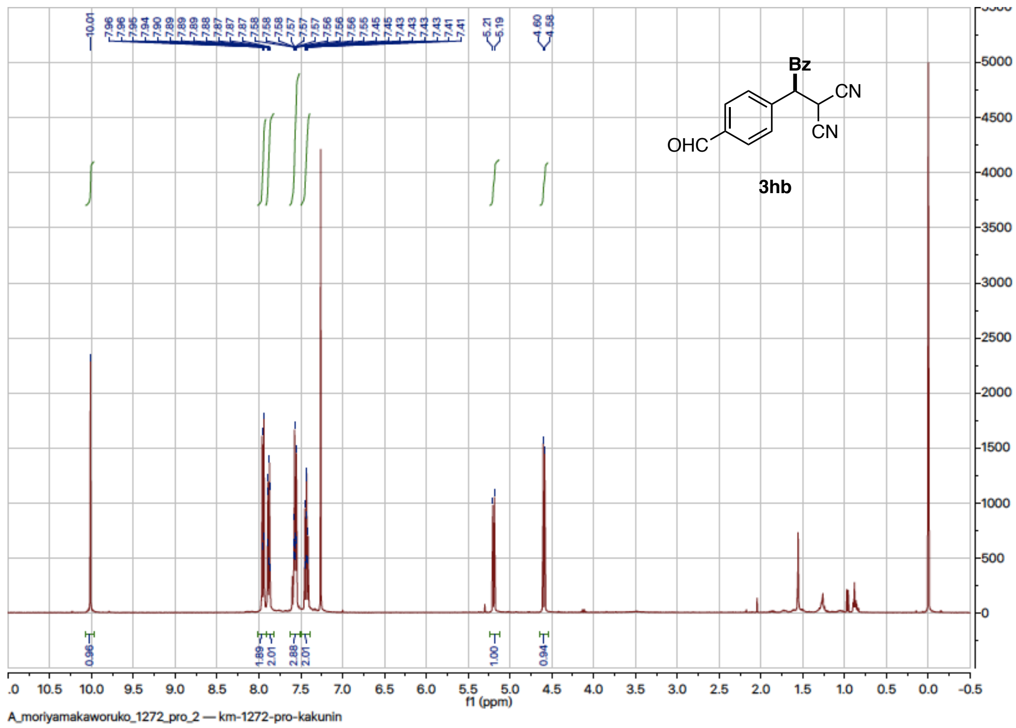
192.65
134.69
133.60
133.36
130.98
130.21
129.24
129.09
124.50
111.85
111.33
77.36
77.04
76.72
54.11
26.61
0.01
f1 (ppm)
A_moriyamakaworuko_1279_pro — km-1279-pro-C

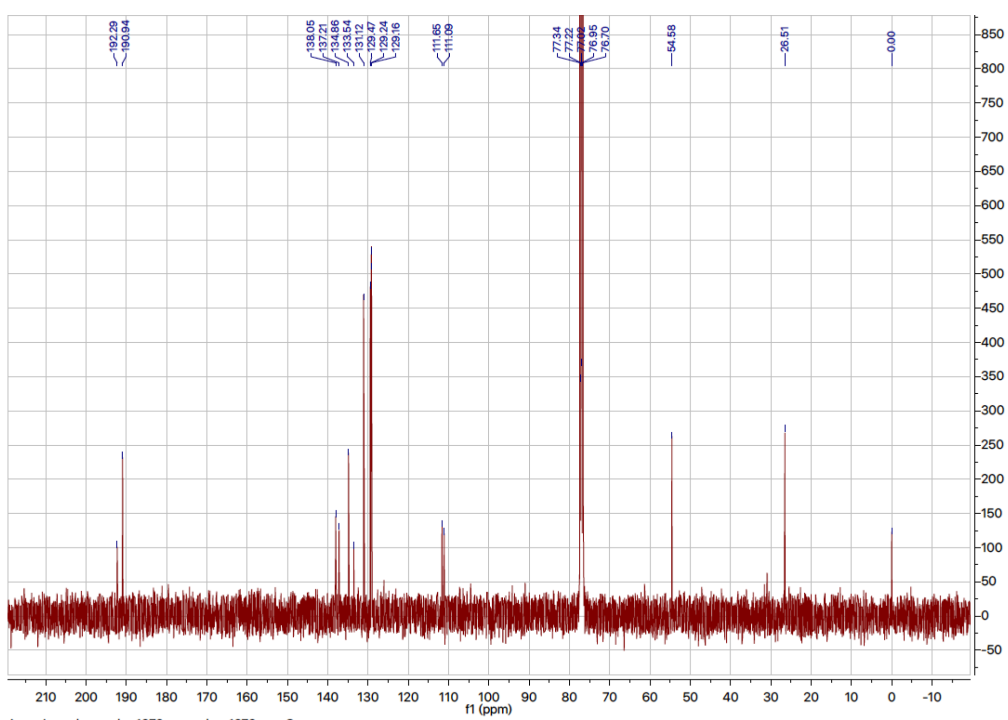
3gb


3gb
MeO2C
Bz
CN
CN
f1 (ppm)
A_moriyamakaworuko_1269_pro — km-1269-pro

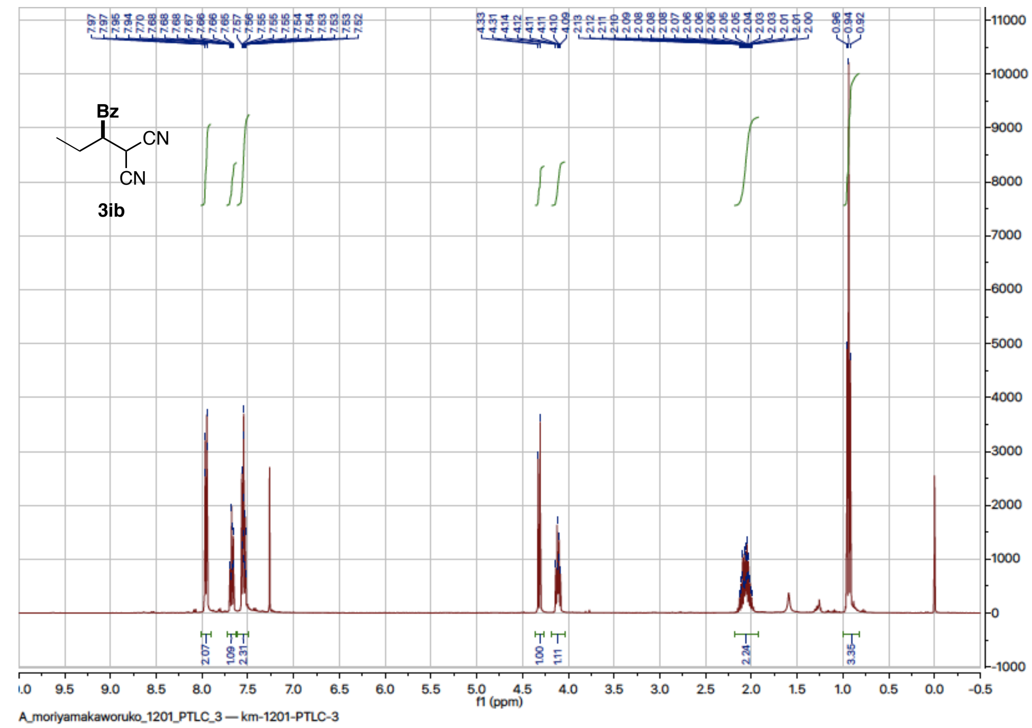

f1 (ppm)
A_moriyamakaworuko_1269_pro — km-1269-pro-C

3hb

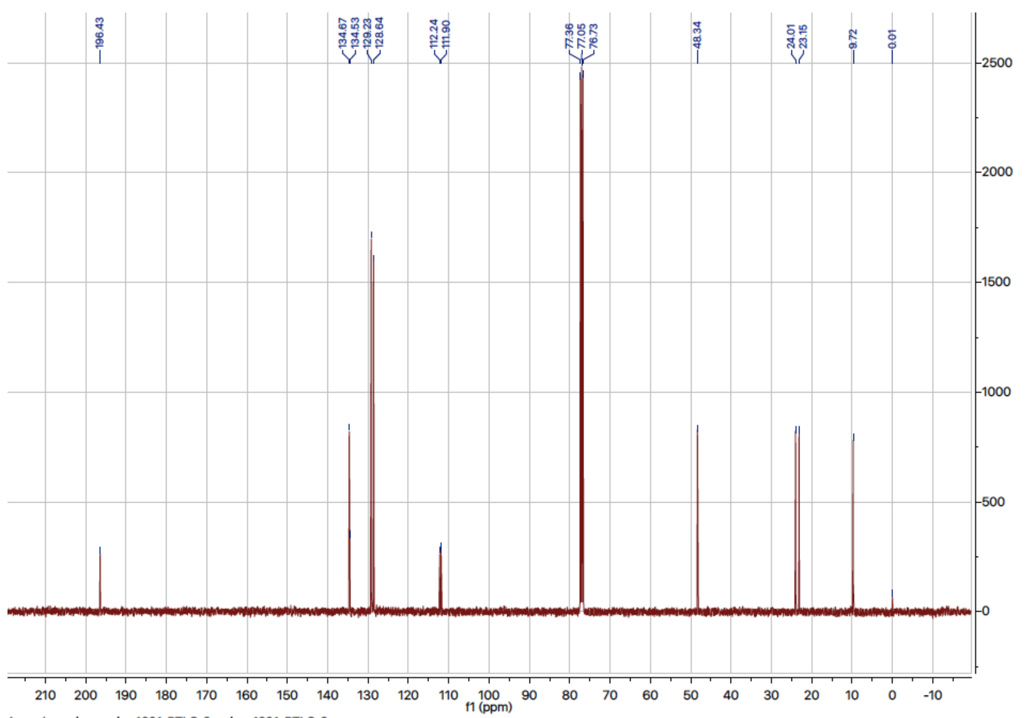

10.01
7.96 7.96 7.95 7.94 7.90 7.89 7.89 7.88 7.87 7.87 7.87 7.58 7.58 7.58 7.57 7.57 7.57 7.56 7.56 7.55 7.45 7.45 7.43 7.43 7.43 7.41 7.41
5.21 5.19
4.60 4.58
Bz
CN
CN
OHC
3hb
0.96 1.89 2.01 2.88 2.01 1.00 0.94
f1 (ppm)
A_moriyamakaworuko_1272_pro_2 — km-1272-pro-kakunin


192.29 190.94
138.05 137.21 134.86 133.54 131.12 129.47 129.24 129.16
111.65 111.09
77.34 77.22 77.02 76.95 76.70
54.58
26.51
0.00
f1 (ppm)
A_moriyamakaworuko_1272_pro — km-1272-pro-C

3ib

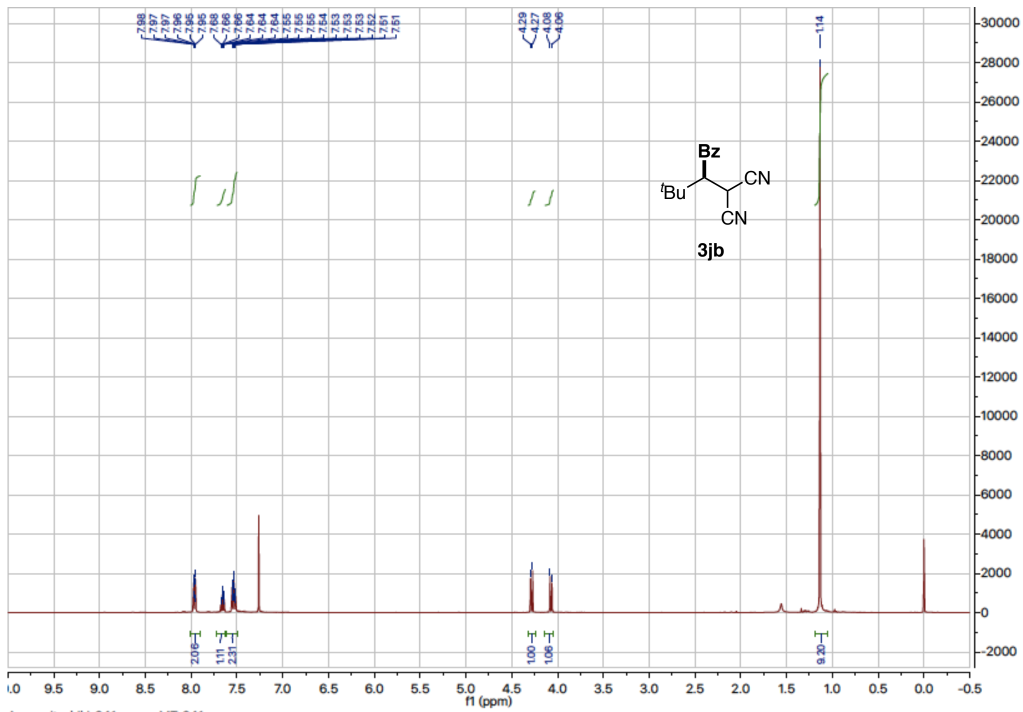


Bz
CN
CN
3ib
7.97 7.97 7.95 7.94 7.70 7.68 7.68 7.68 7.67 7.66 7.66 7.65 7.57 7.56 7.55 7.55 7.55 7.54 7.53 7.53 7.53 7.52
4.33 4.31 4.14 4.12 4.11 4.11 4.10 4.09
0.96 0.94 0.92
2.07 1.09 2.31 1.00 1.11 2.24 3.35
f1 (ppm)
A_moriyamakaworuko_1201_PTLC_3 — km-1201-PTLC-3

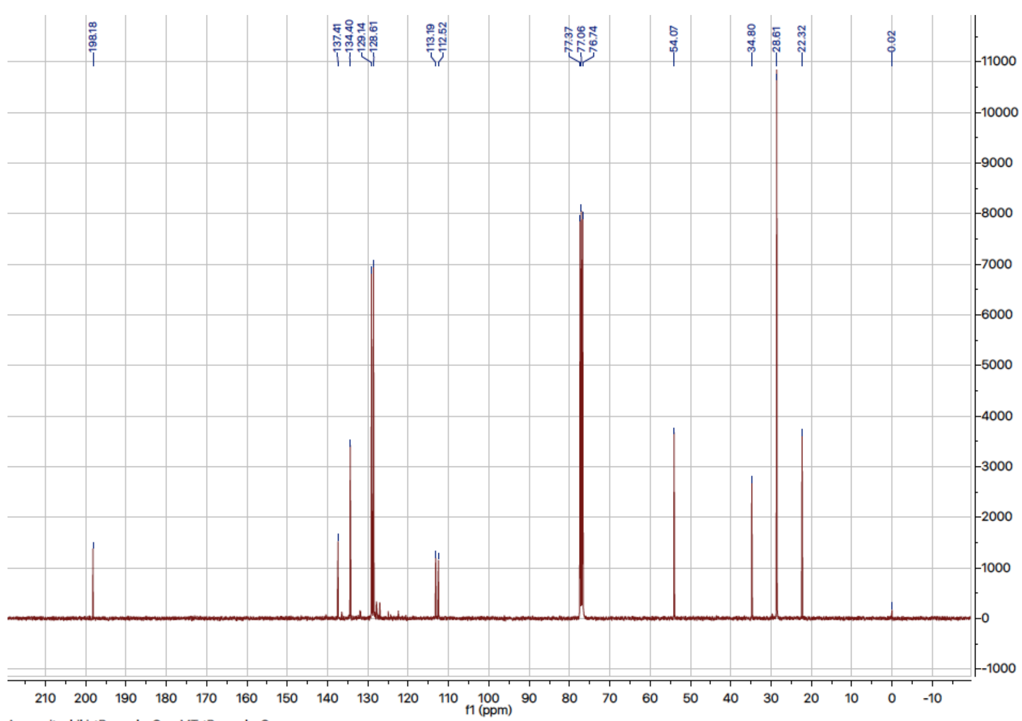


196.43
134.67 134.53 129.23 128.64
112.24 111.90
77.36 77.05 76.73
48.34
24.01 23.15
9.72
0.01
f1 (ppm)
A_moriyamakaworuko_1201_PTLC_3 — km-1201-PTLC-3

3jb

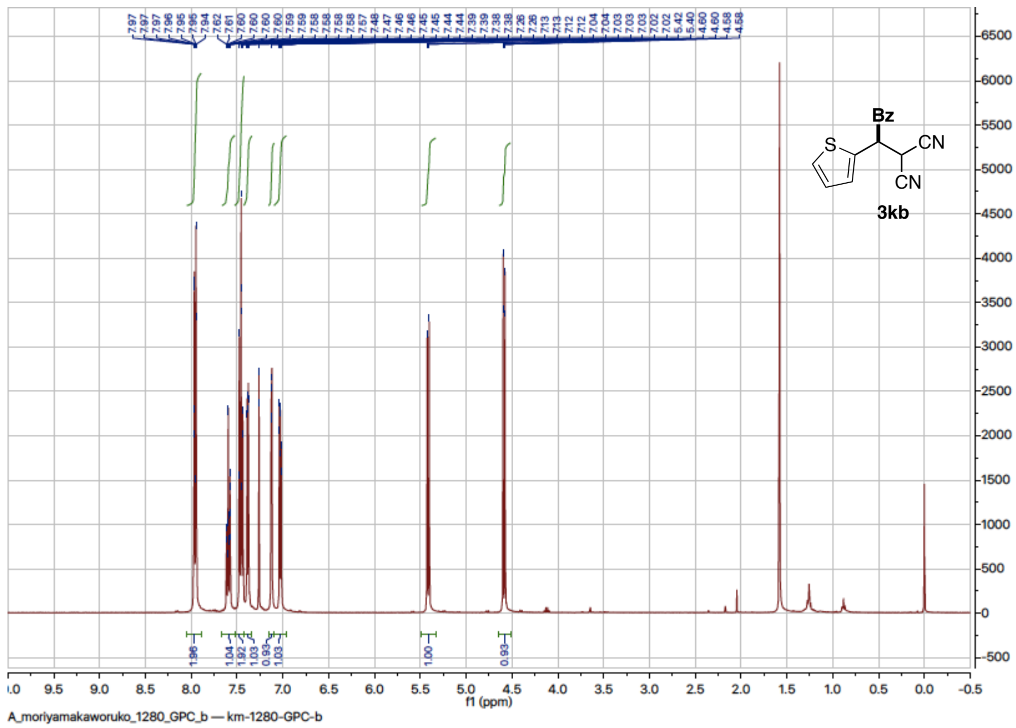


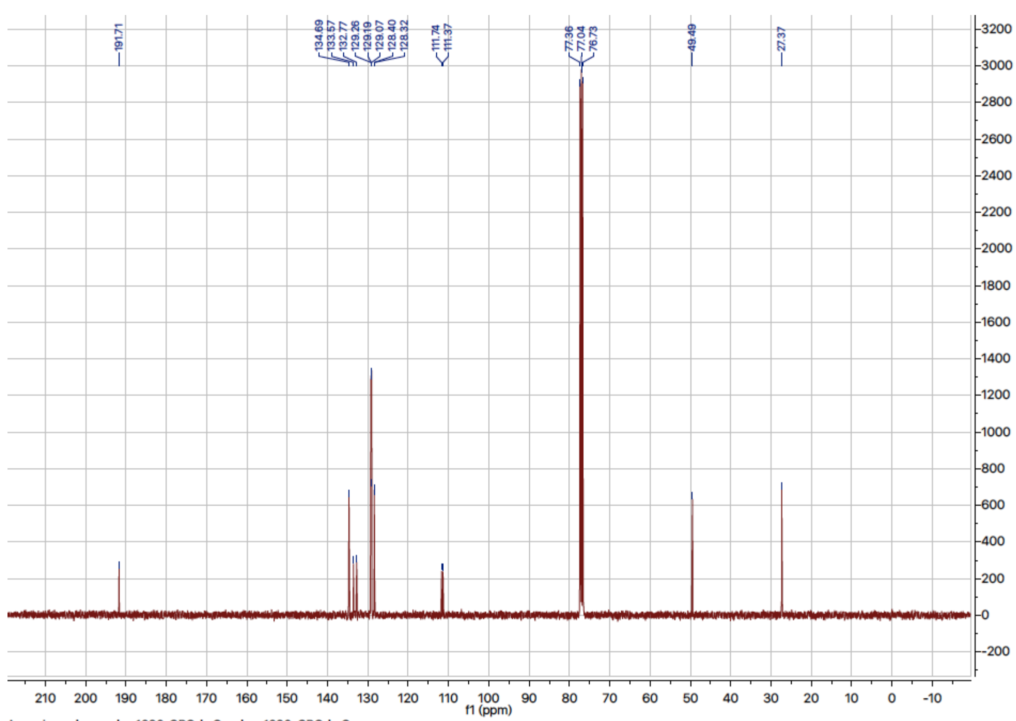
Bz
CN
ᵗBu
CN
3jb
f1 (ppm)
A_mouritoshiki-941-pro — MT-941-pro



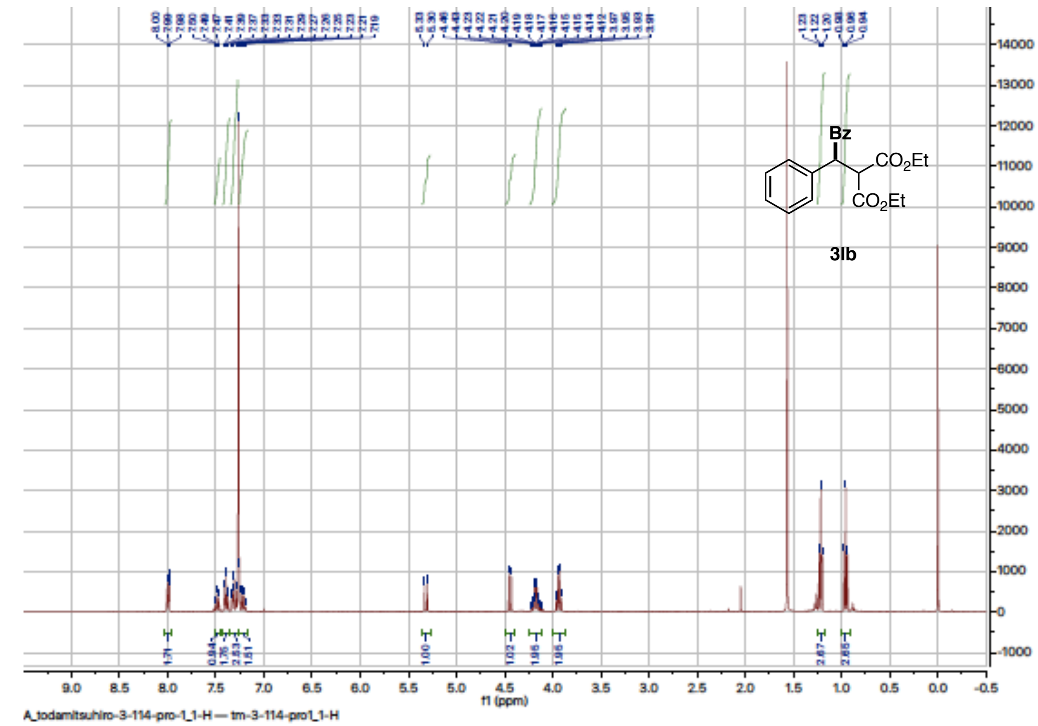
f1 (ppm)
A_mouritoshiki-tBu-malo-C — MT-tBu-malo-C

3kb

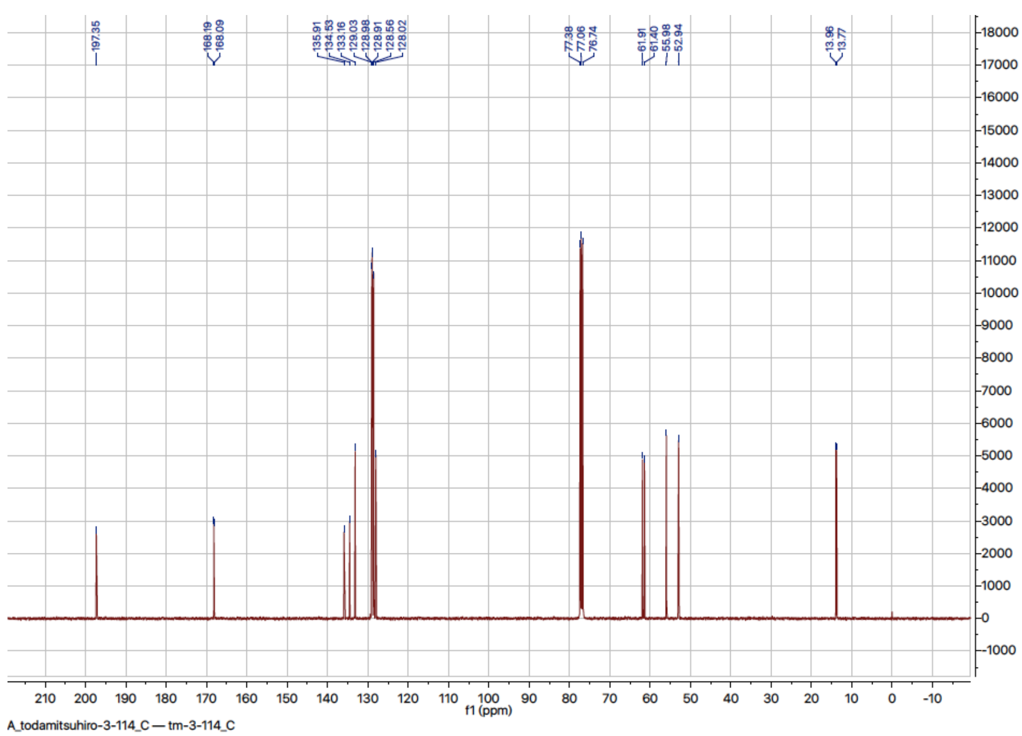

Bz
CN
CN
S
3kb
f1 (ppm)
A_moriyamakaworuko_1280_GPC_b — km-1280-GPC-b


f1 (ppm)
A_moriyamakaworuko_1280_GPC_b_C — km-1280-GPC-b-C

3lb

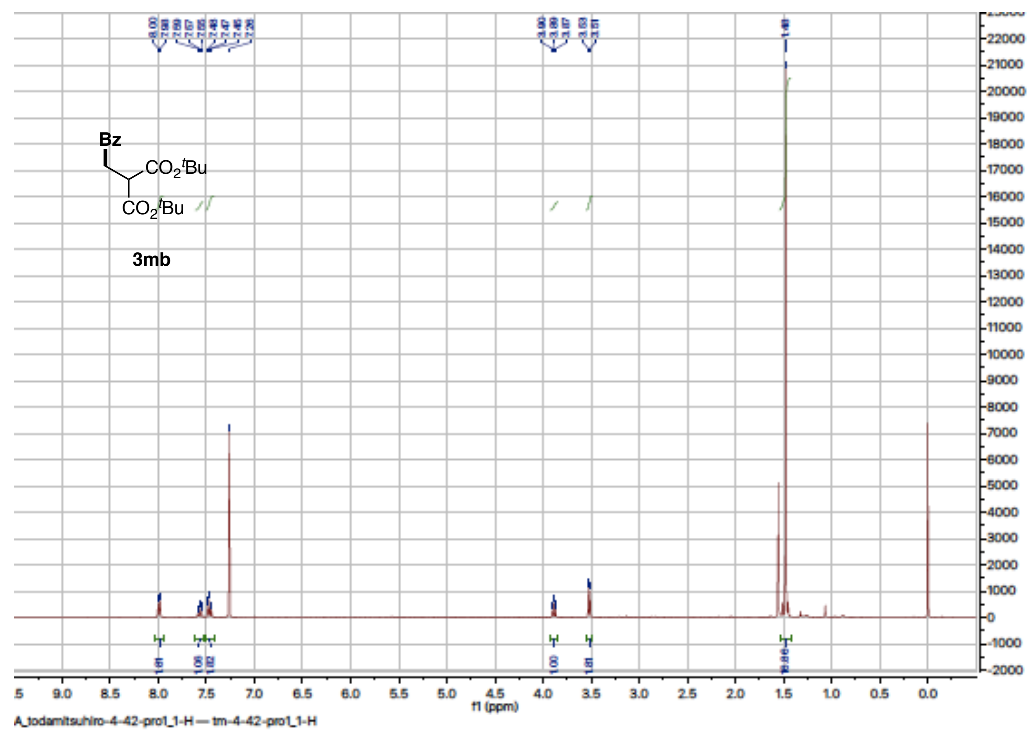


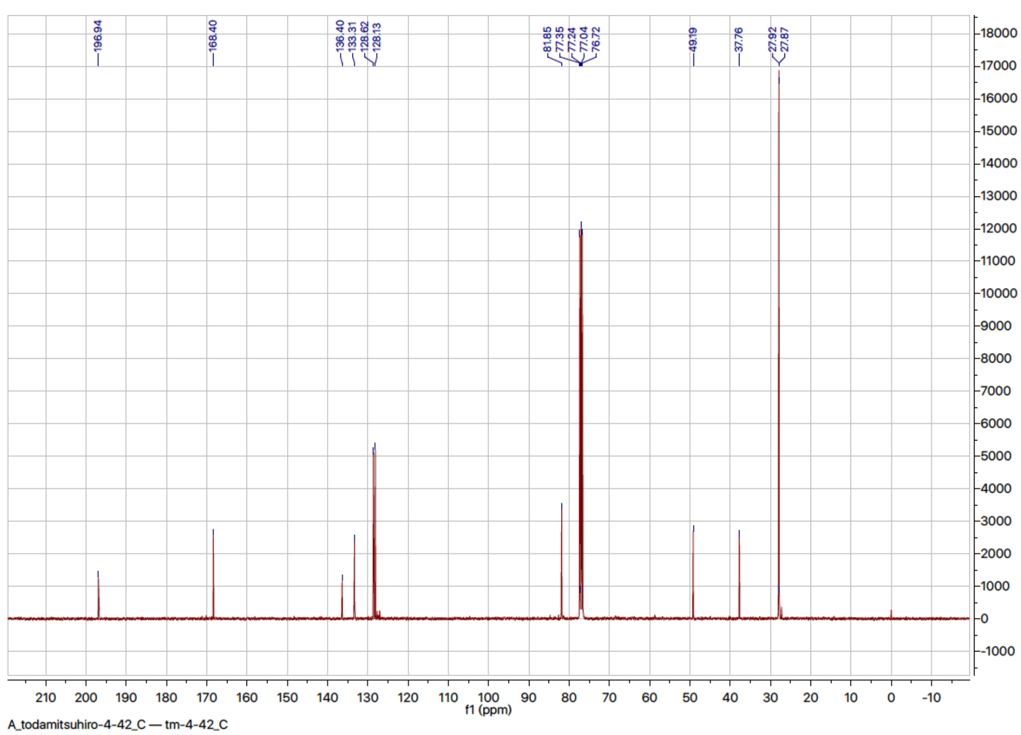
8.00
7.99
7.98
7.50
7.49
7.47
7.41
7.39
7.37
7.33
7.31
7.29
7.27
7.26
7.25
7.23
7.21
7.19
5.33
5.30
4.46
4.43
4.23
4.22
4.21
4.20
4.19
4.18
4.17
4.16
4.15
4.15
4.14
4.12
3.97
3.95
3.93
3.91
1.23
1.22
1.20
0.98
0.96
0.94
Bz
CO2Et
CO2Et
3lb
1.71
0.94
1.76
2.83
1.81
1.00
1.02
1.95
1.95
2.67
2.65
f1 (ppm)
A_todamitsuhiro-3-114-pro-1_1-H — tm-3-114-pro1_1-H



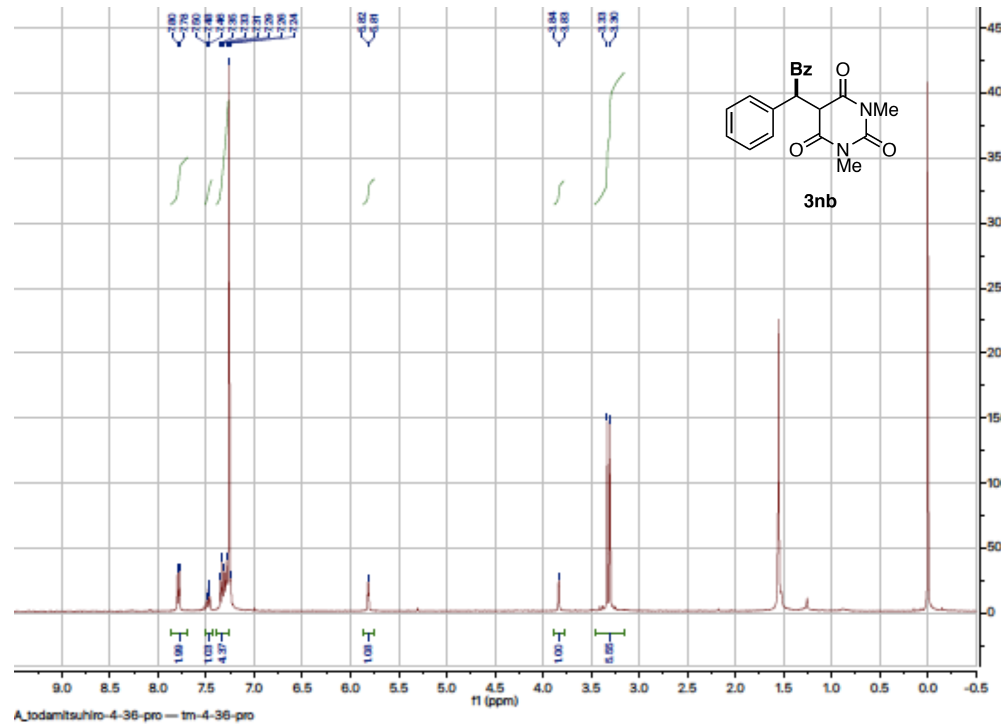
197.35
168.19
168.09
135.91
134.53
133.16
129.03
128.98
128.91
128.56
128.02
77.38
77.06
76.74
61.91
61.40
55.98
52.94
13.96
13.77
f1 (ppm)
A_todamitsuhiro-3-114_C — tm-3-114_C

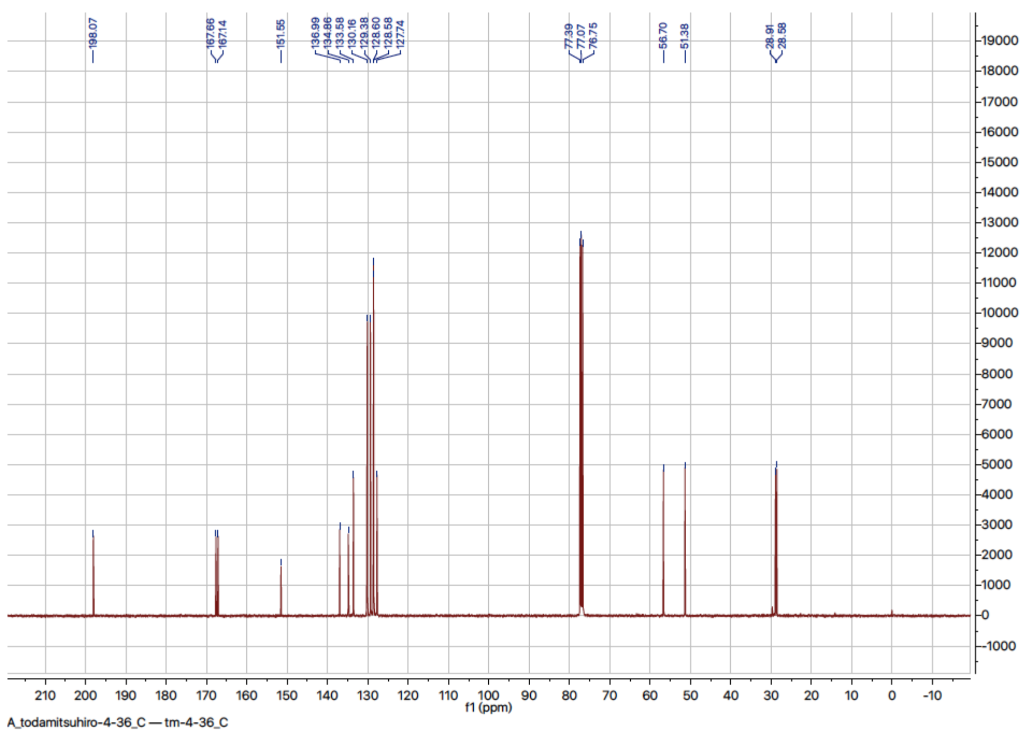
3mb



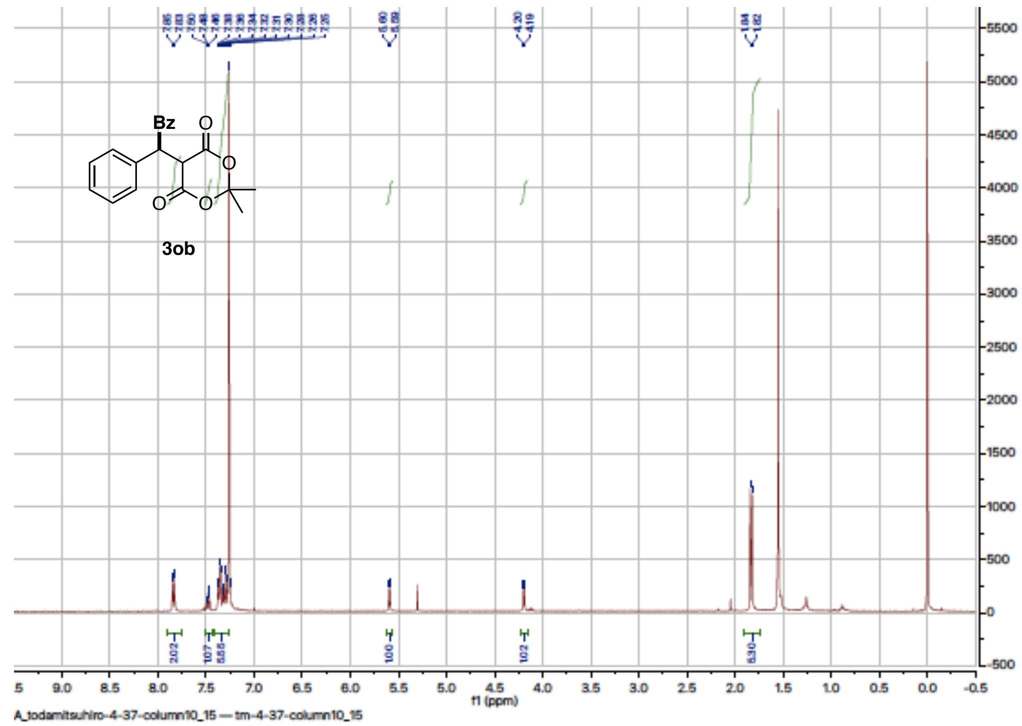


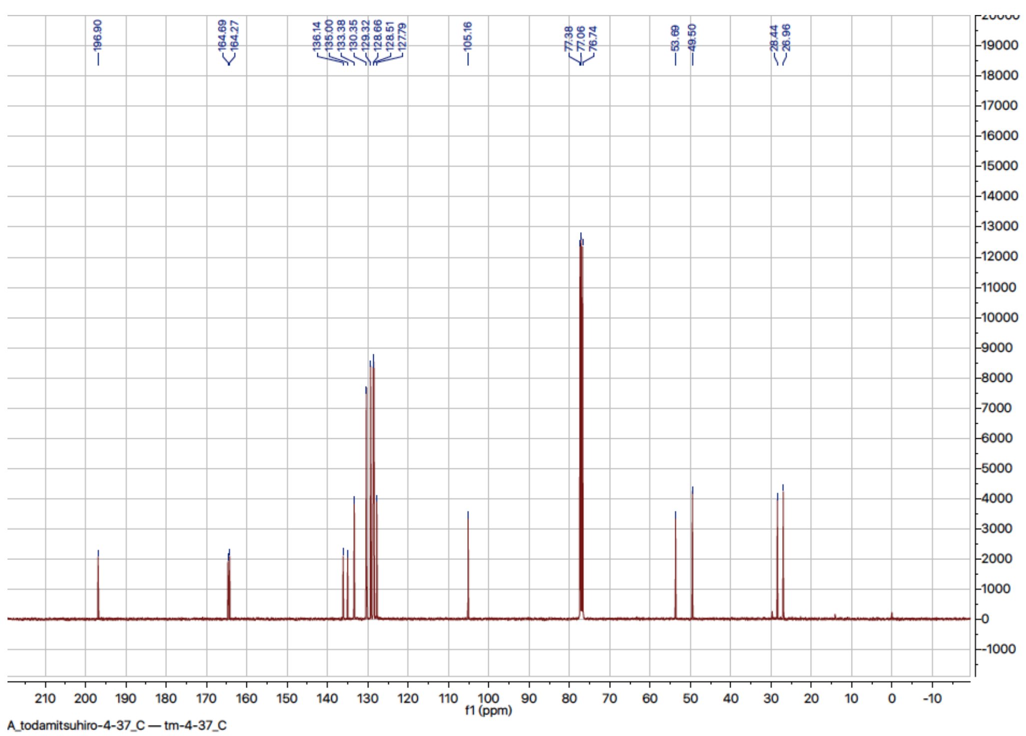
3nb



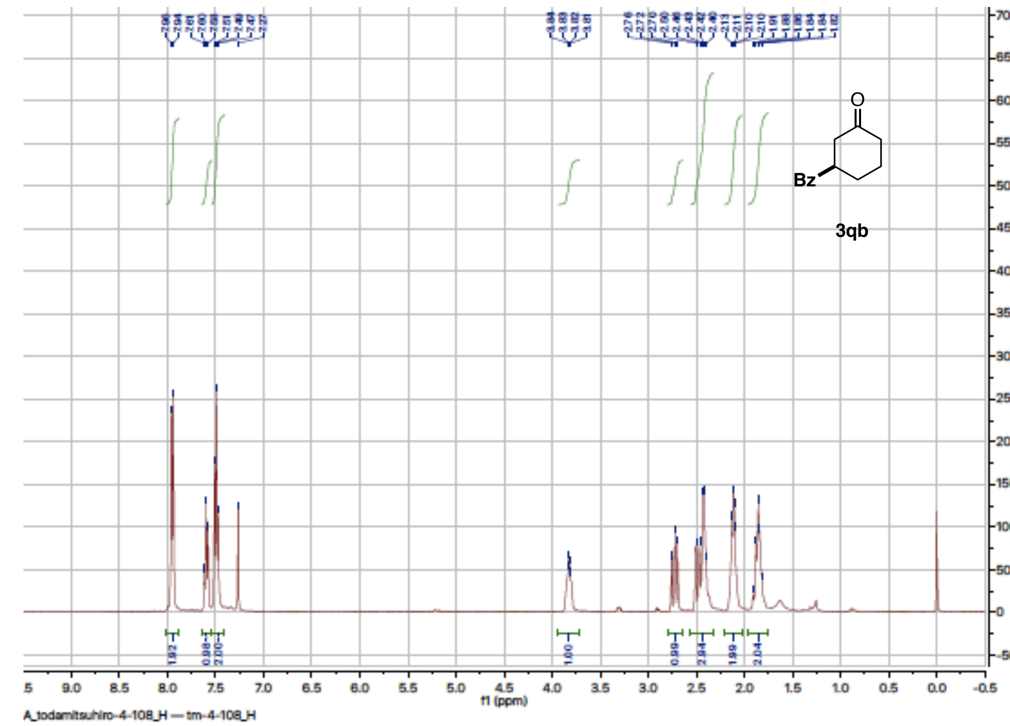


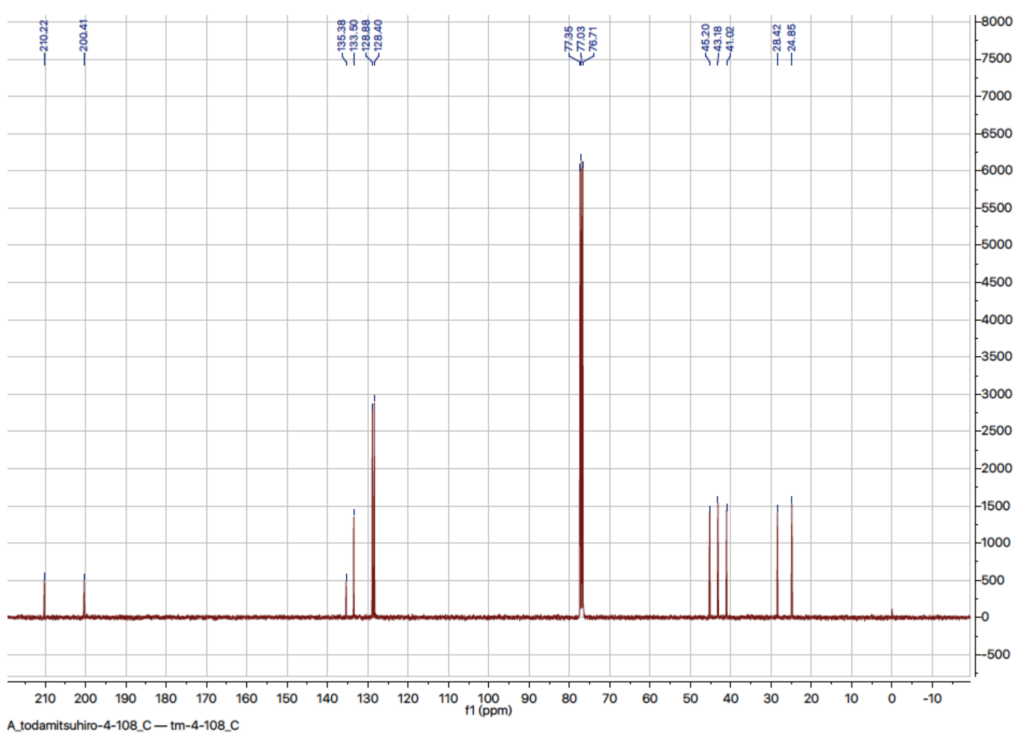
3ob



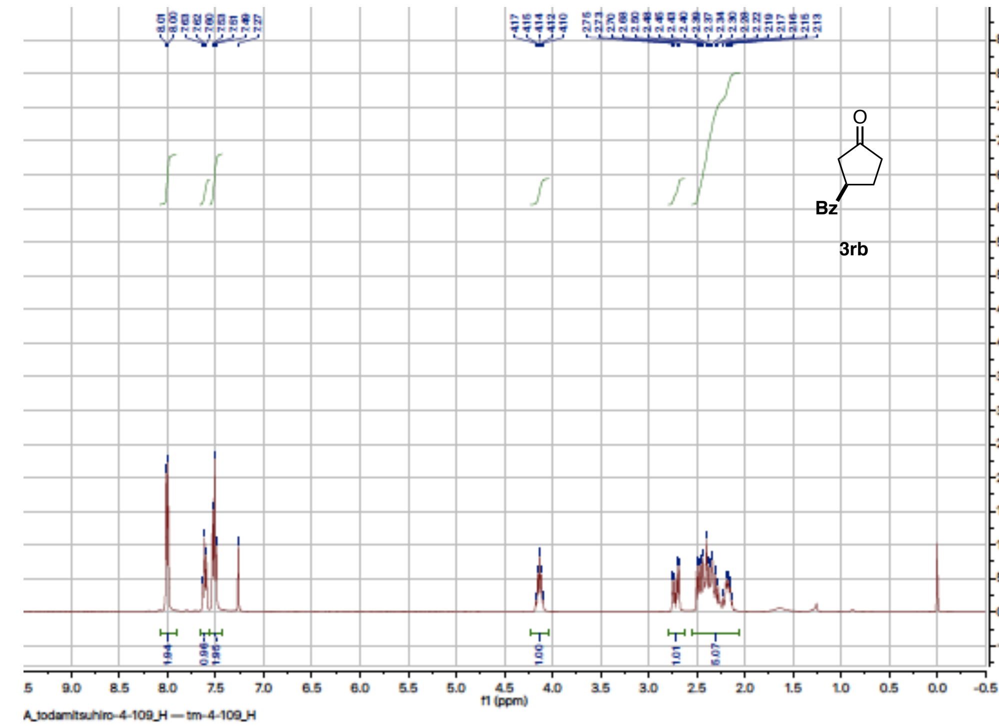


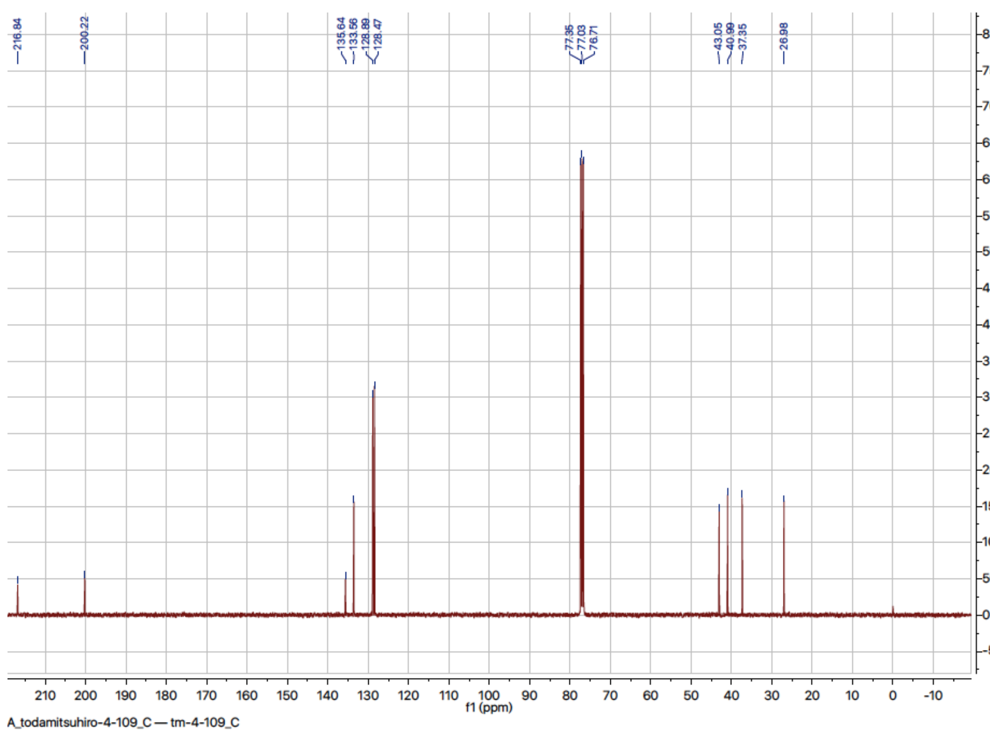
3qb


Bz
3qb
f1 (ppm)
A_todamitsuhiro-4-108_H — tm-4-108_H

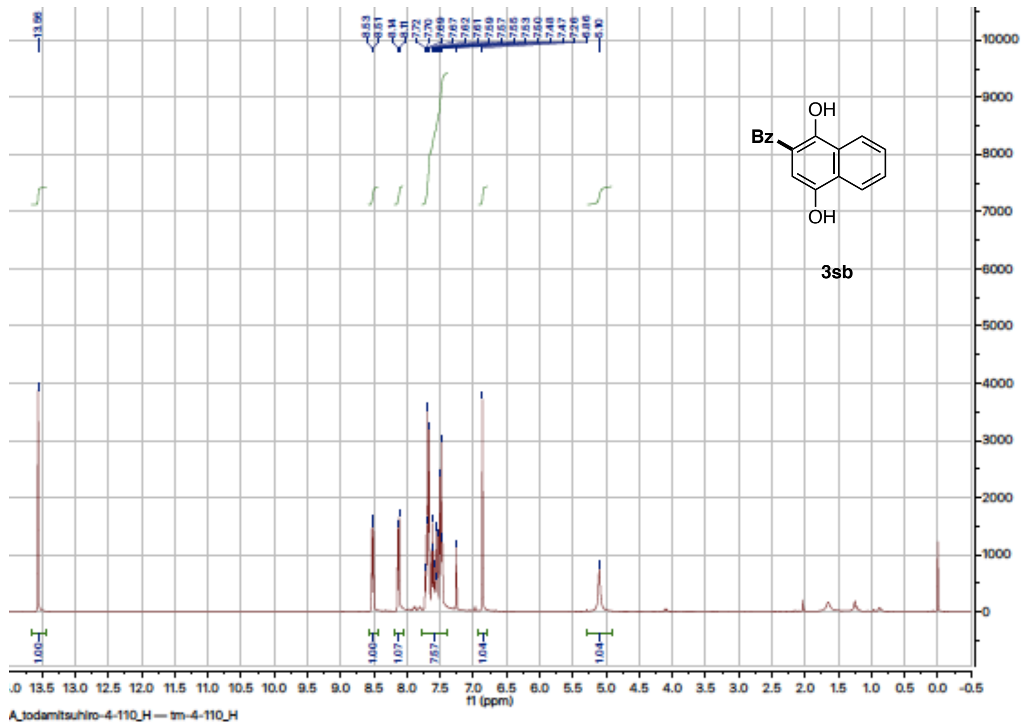

210.22
200.41
135.38
133.50
128.88
128.40
77.35
77.03
76.71
45.20
43.18
41.02
28.42
24.85
f1 (ppm)
A_todamitsuhiro-4-108_C — tm-4-108_C

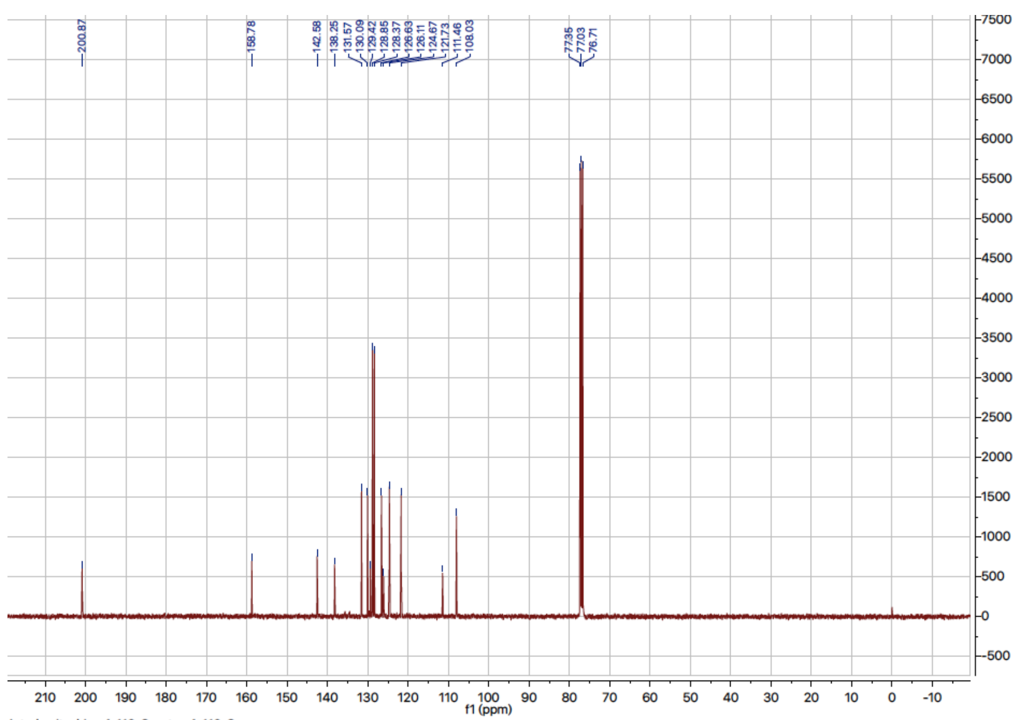
3rb


8.01
8.00
7.63
7.62
7.60
7.53
7.51
7.49
7.27
4.17
4.15
4.14
4.12
4.10
2.76
2.73
2.70
2.68
2.50
2.48
2.45
2.43
2.40
2.39
2.37
2.34
2.30
2.28
2.22
2.19
2.17
2.16
2.15
2.13
O
Bz
3rb
1.94
0.96
1.95
1.00
1.01
6.07
f1 (ppm)
A_todamitsuhiro-4-109_H — tm-4-109_H

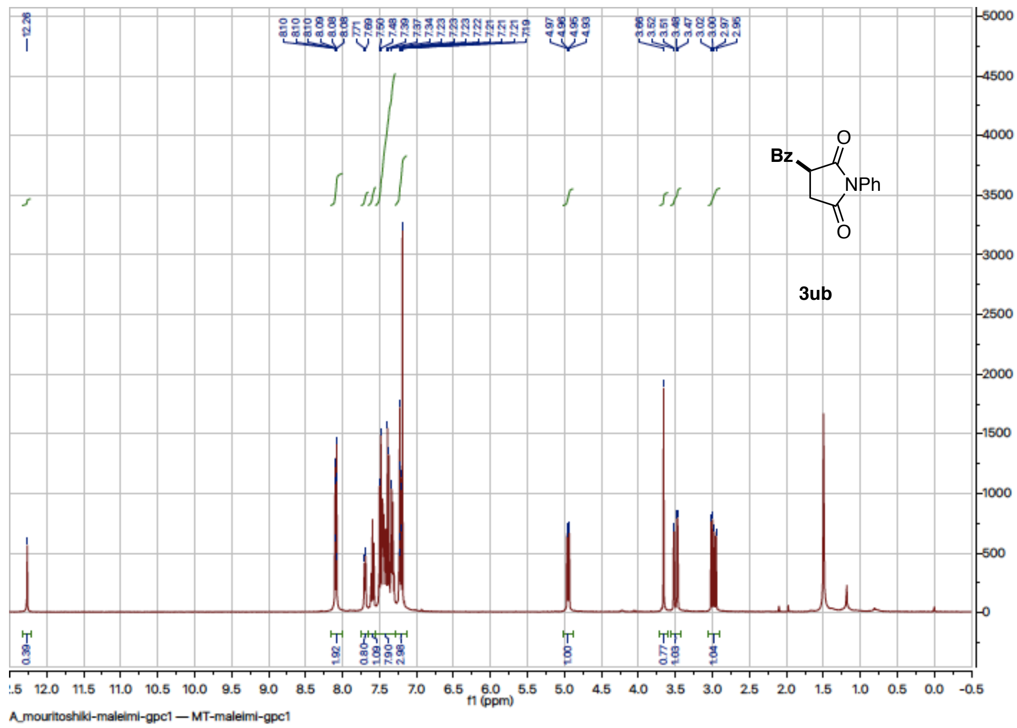

216.84
200.22
135.64
133.56
128.89
128.47
77.35
77.03
76.71
43.05
40.99
37.35
26.98
f1 (ppm)
A_todamitsuhiro-4-109_C — tm-4-109_C

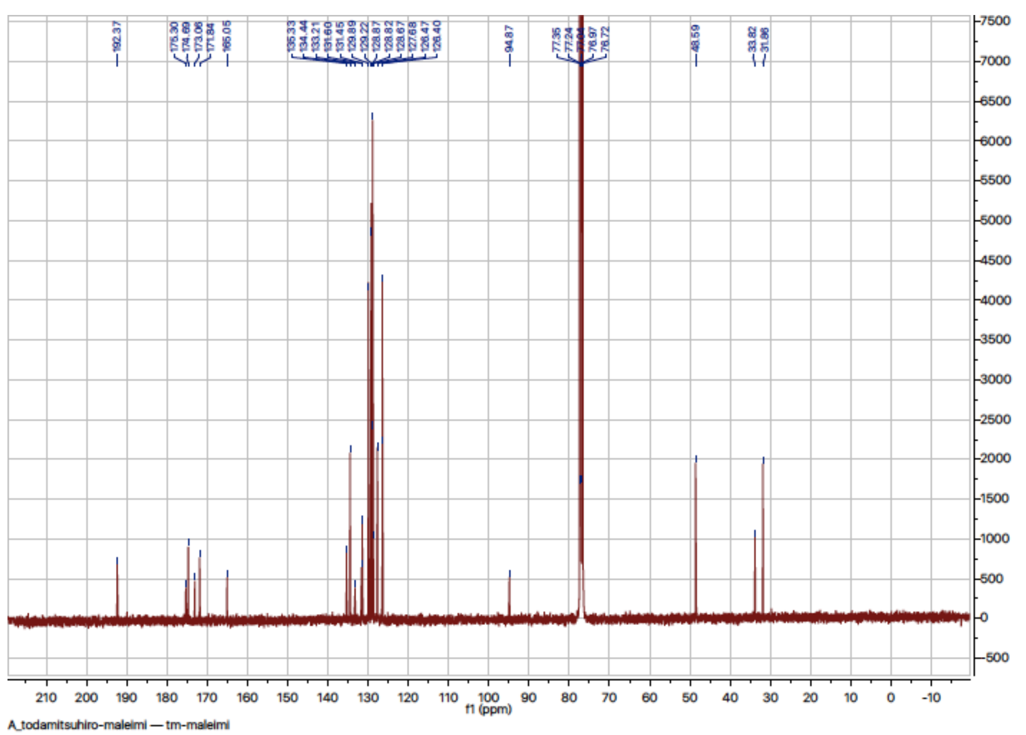
3sb



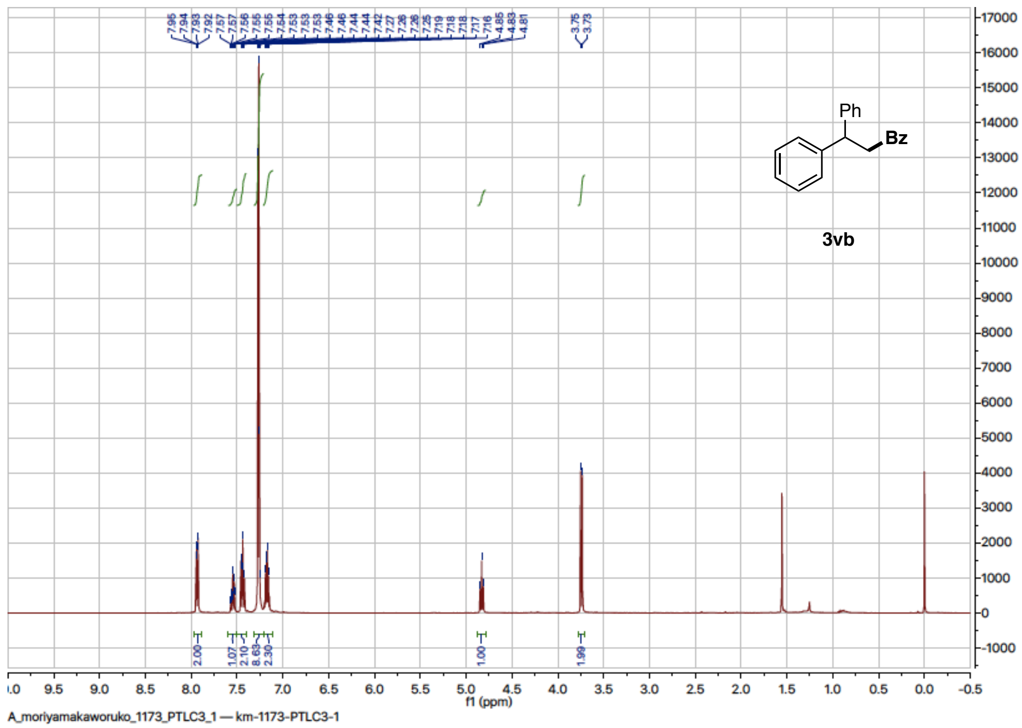


3ub

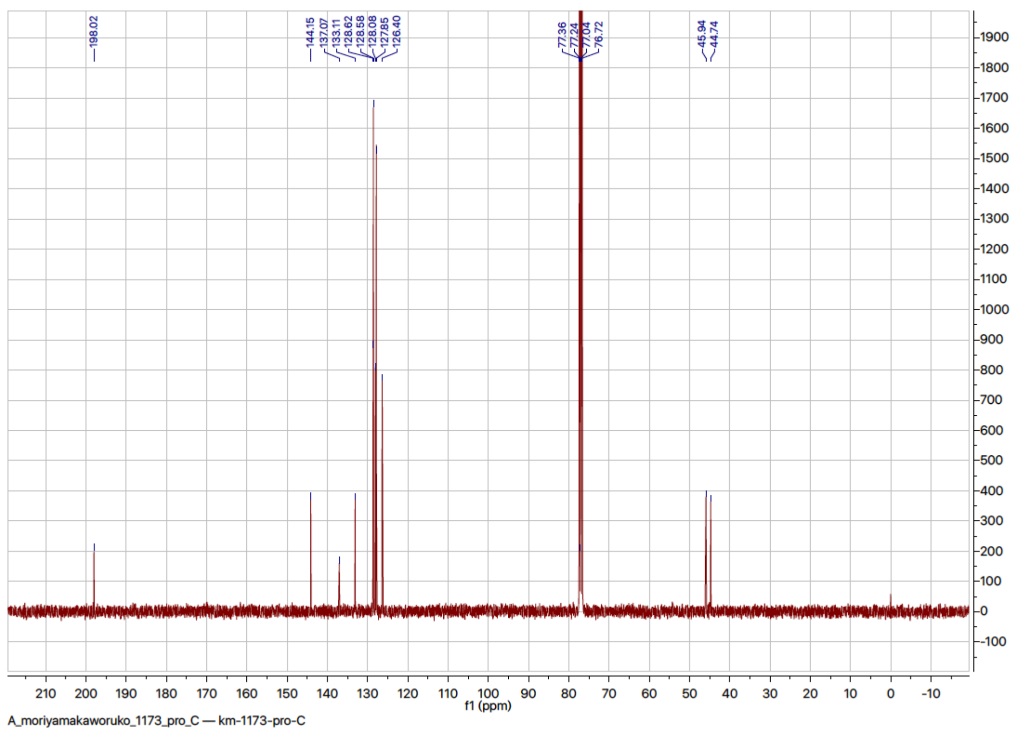




3vb

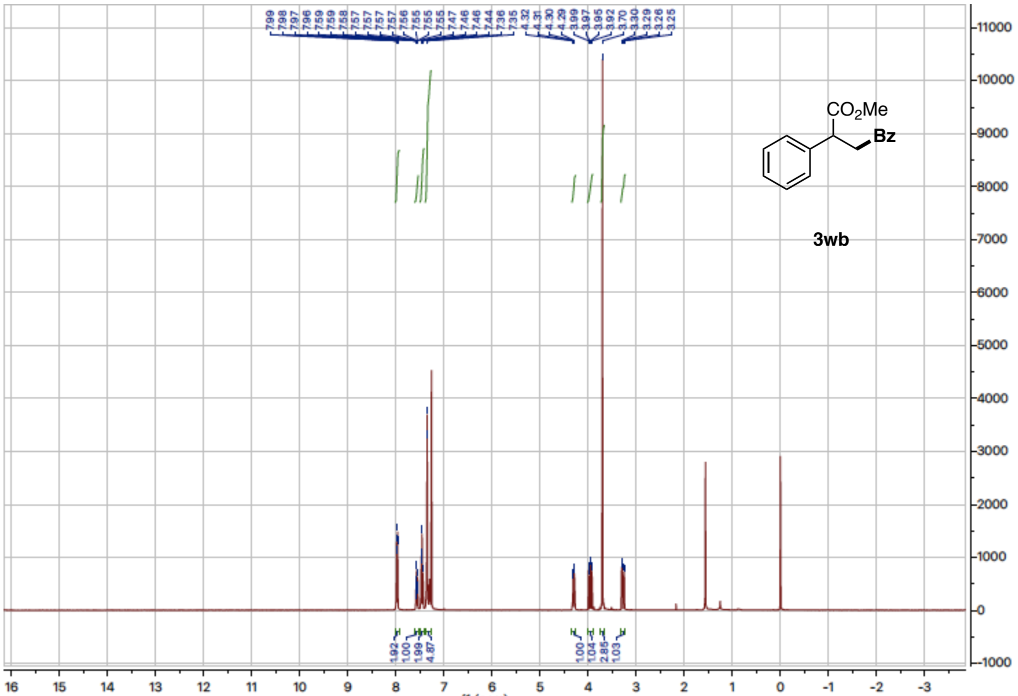


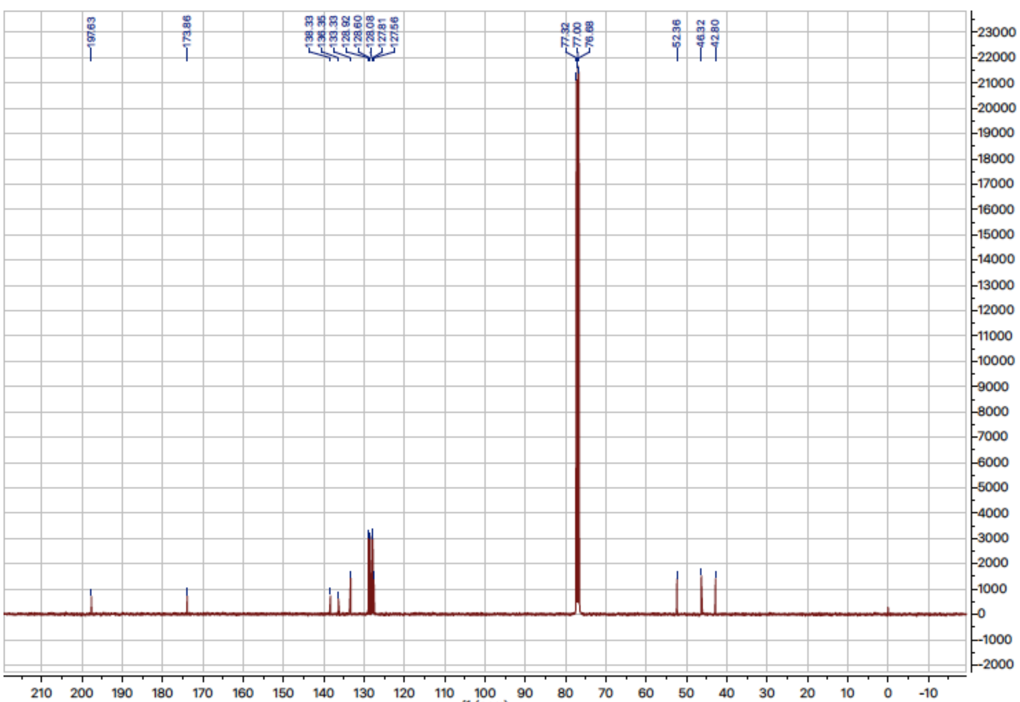
Ph
Bz
3vb
f1 (ppm)
A_moriyamakaworuko_1173_PTLC3_1 — km-1173-PTLC3-1



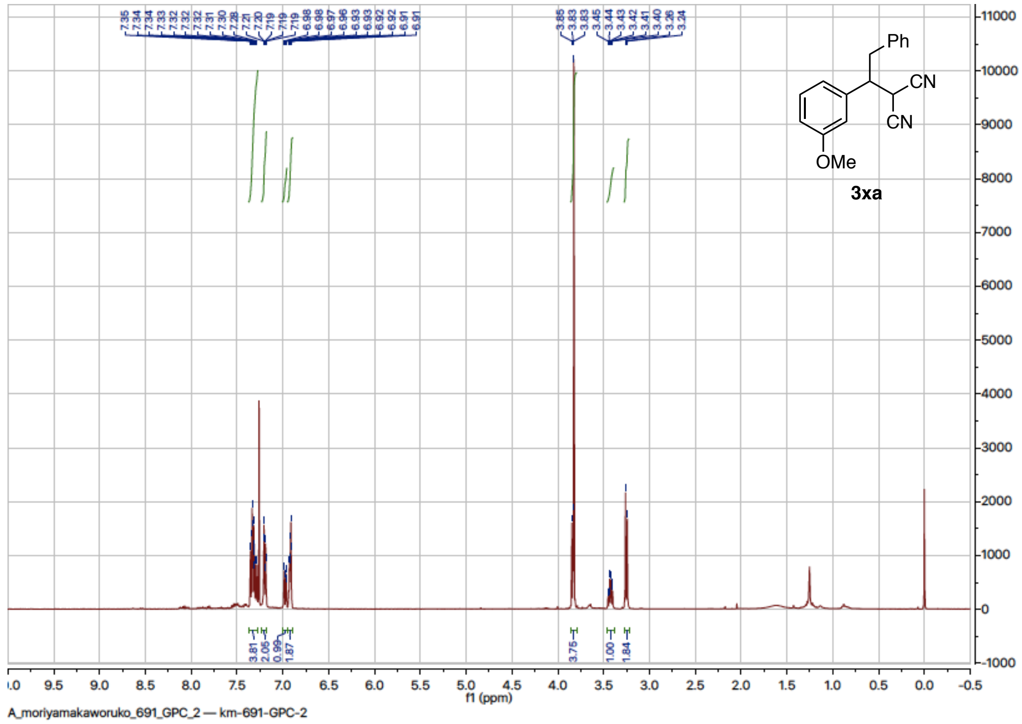
198.02
144.15
137.07
133.11
128.62
128.58
128.08
127.85
126.40
77.36
77.24
77.04
76.72
45.94
44.74
f1 (ppm)
A_moriyamakaworuko_1173_pro_C — km-1173-pro-C

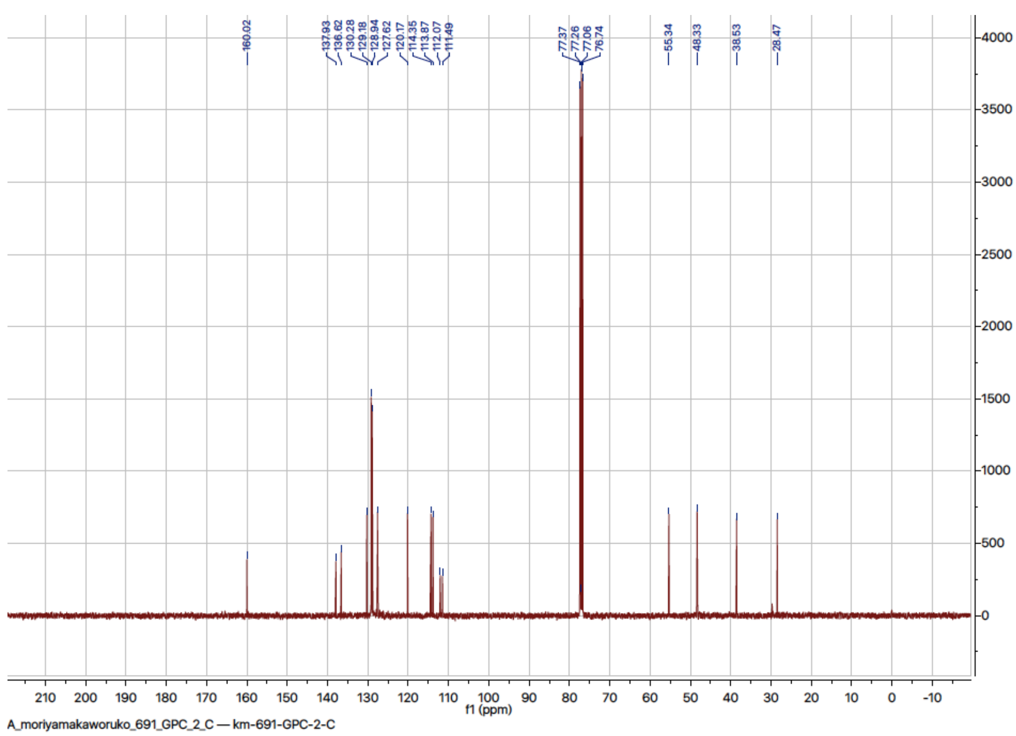
3wb


CO2Me
Bz
3wb
f1 (ppm)
A_uchikura_data_TU_612_GPC — TU_612_GPC

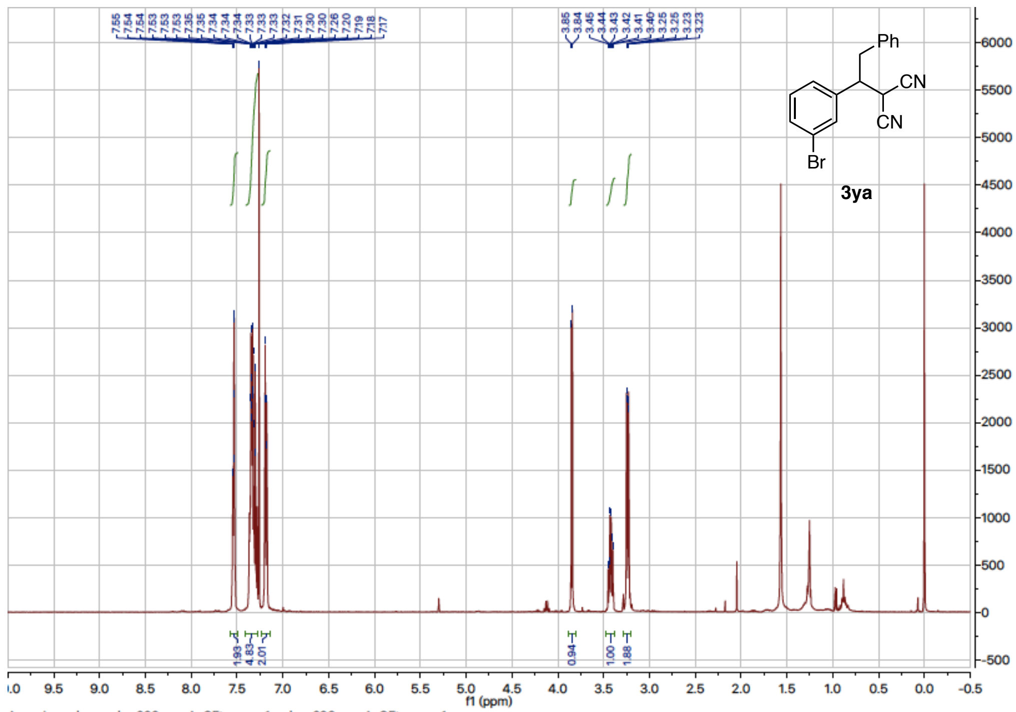

197.63
173.86
138.33
136.35
133.33
128.92
128.60
128.08
127.81
127.56
77.32
77.00
76.68
52.36
46.32
42.80
f1 (ppm)
A_uchikura_data_TU_612_GPC — TU_612_GPC

3xa

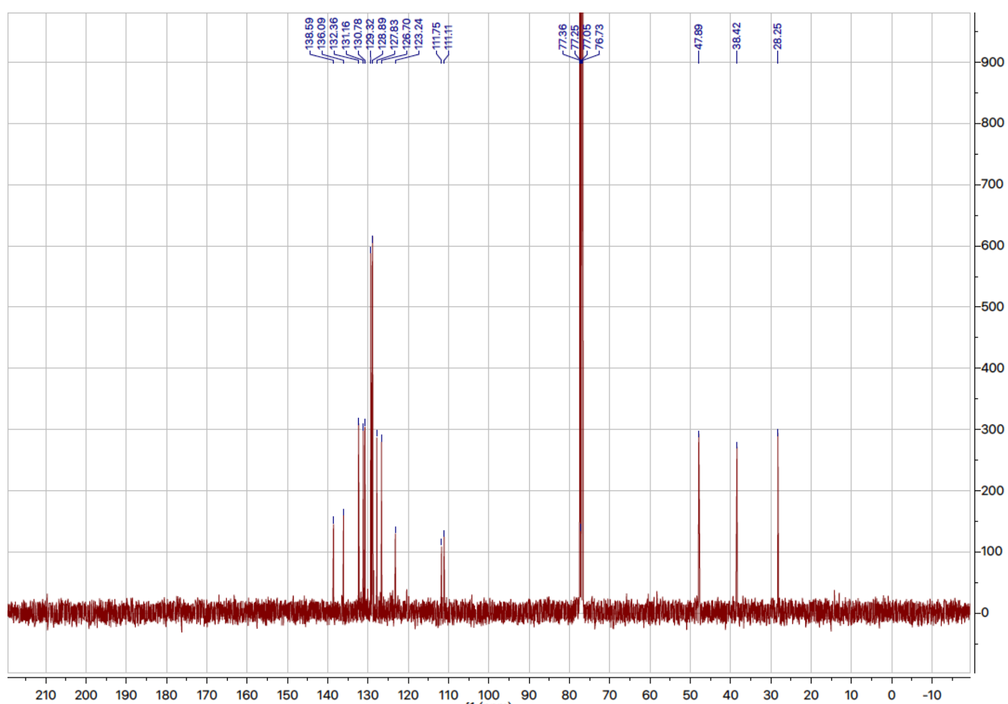

Ph
CN
CN
OMe
3xa
f1 (ppm)
A_moriyamakaworuko_691_GPC_2 — km-691-GPC-2


160.02
137.93
136.62
130.28
129.18
128.94
127.62
120.17
114.35
113.87
112.07
111.49
77.37
77.26
77.06
76.74
55.34
48.33
38.53
28.47
f1 (ppm)
A_moriyamakaworuko_691_GPC_2_C — km-691-GPC-2-C

3ya

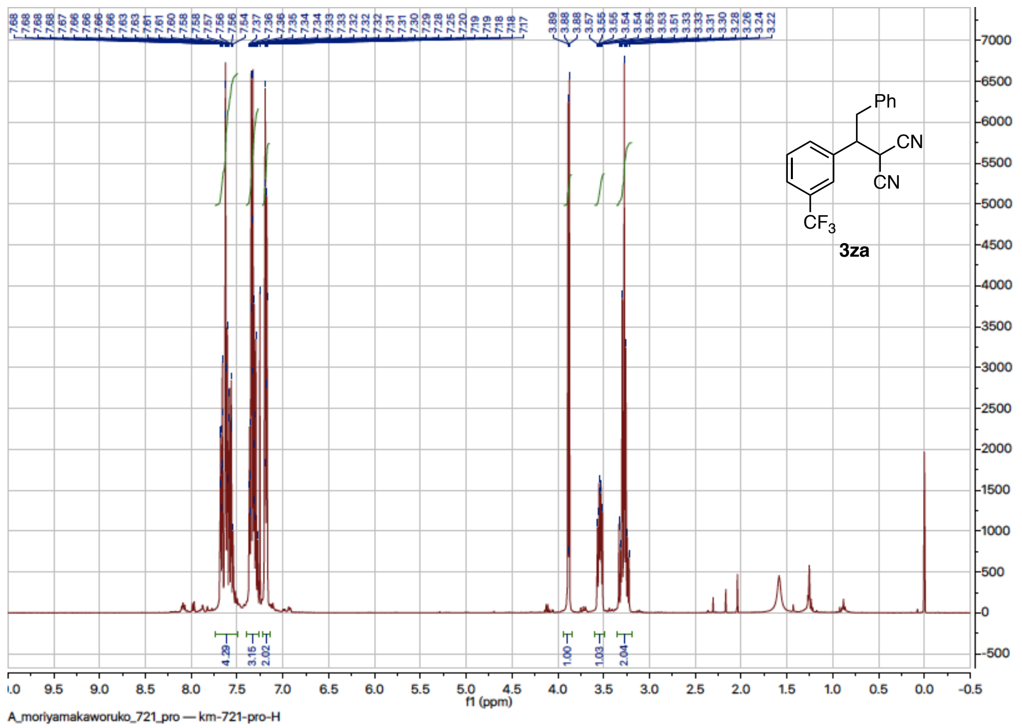


A_moriyamakaworuko_698_pro_AcOEtremove1 — km-698_pro_AcOEtremove1

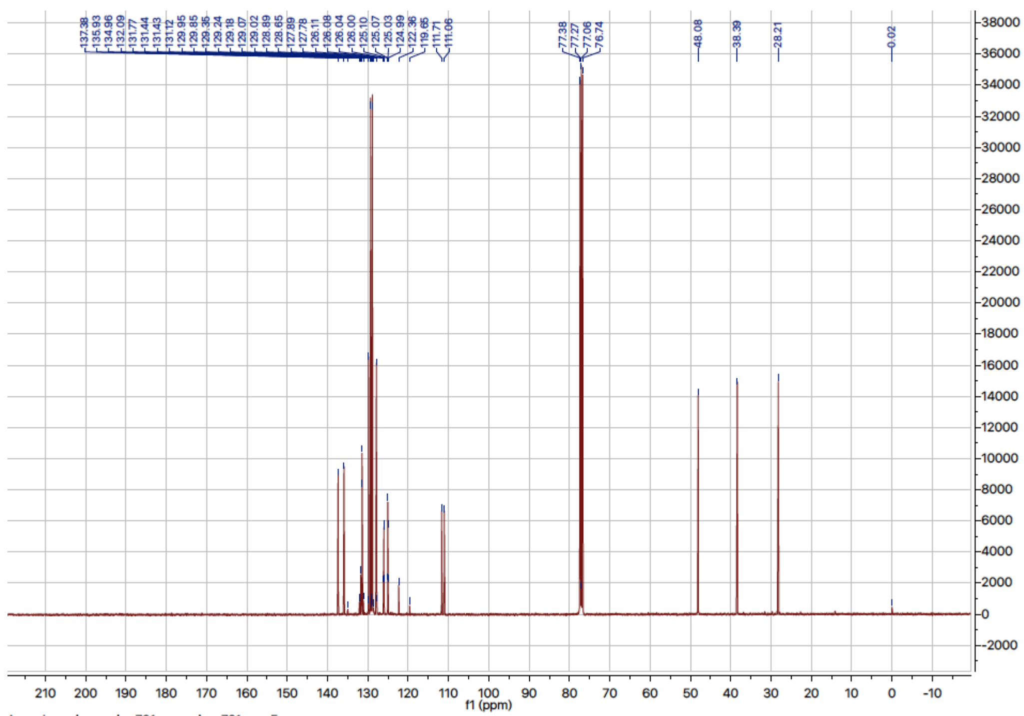


A_moriyamakaworuko_698_C — km-A_698-PTLC-pro-C

3za

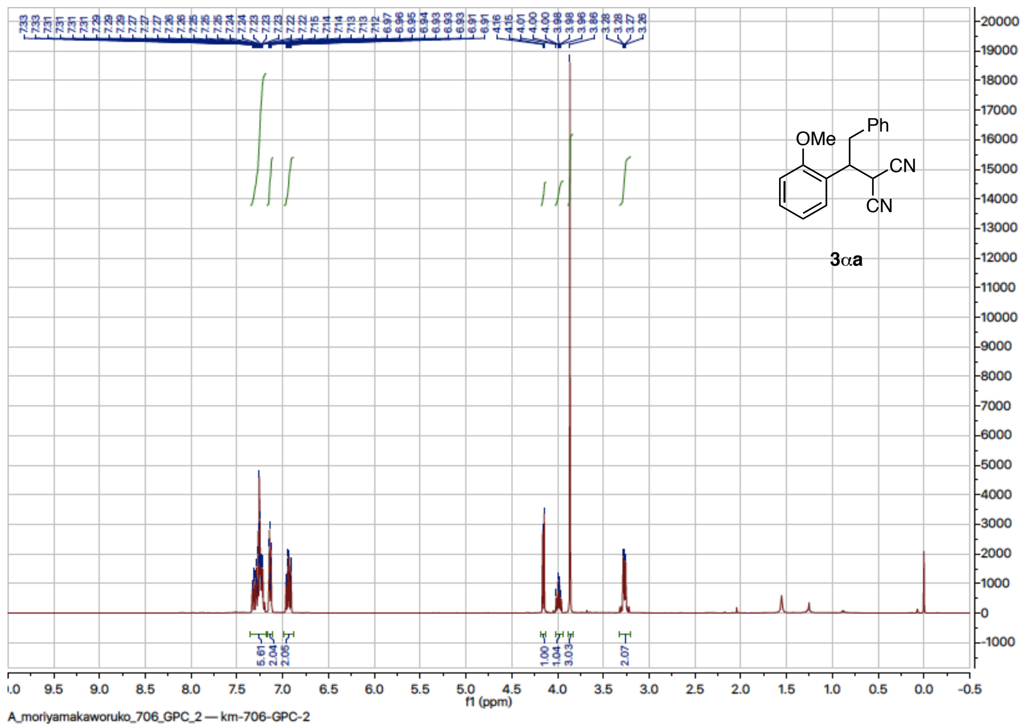


Ph
CN
CN
CF3
3za
f1 (ppm)
A_moriyamakaworuko_721_pro — km-721-pro-H

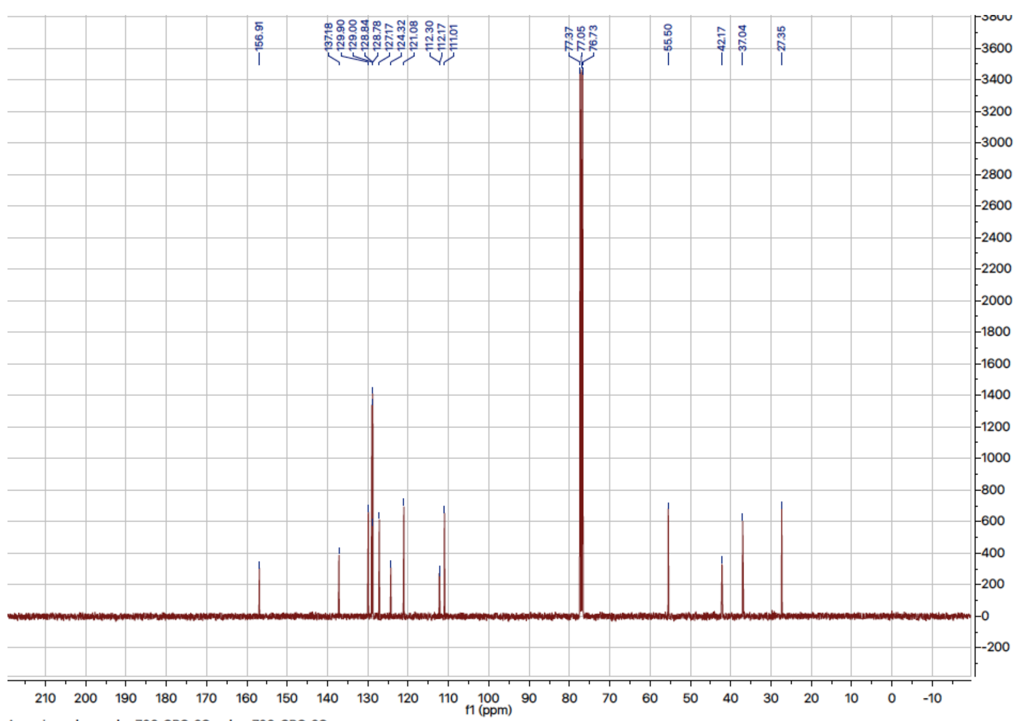


f1 (ppm)
A_moriyamakaworuko_721_pro — km-721-pro-F

3αa

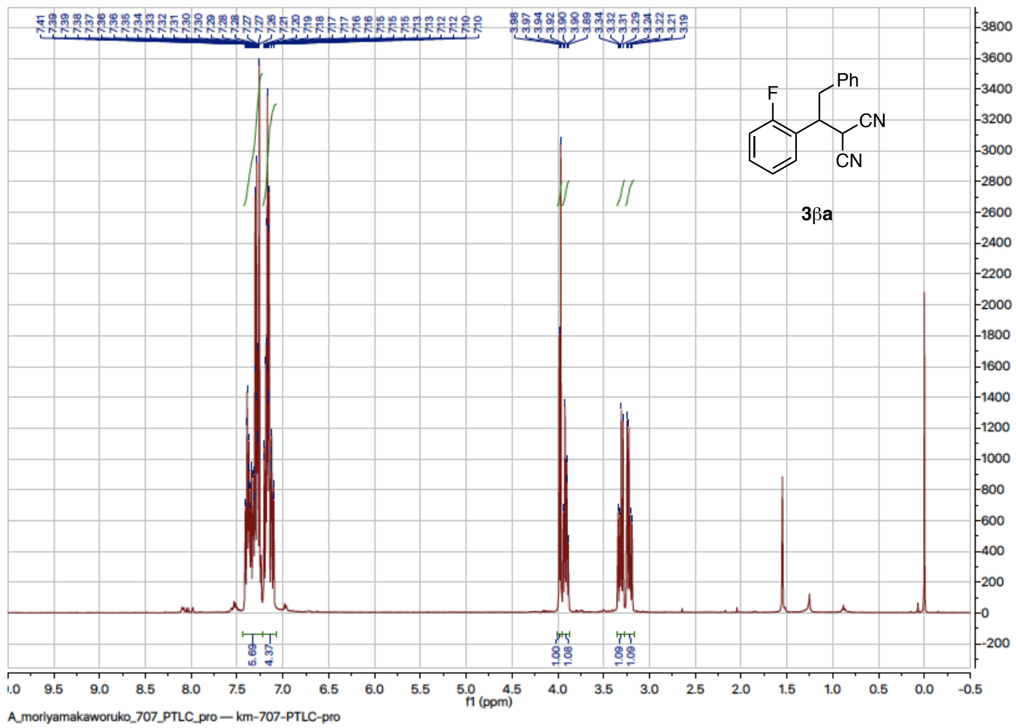


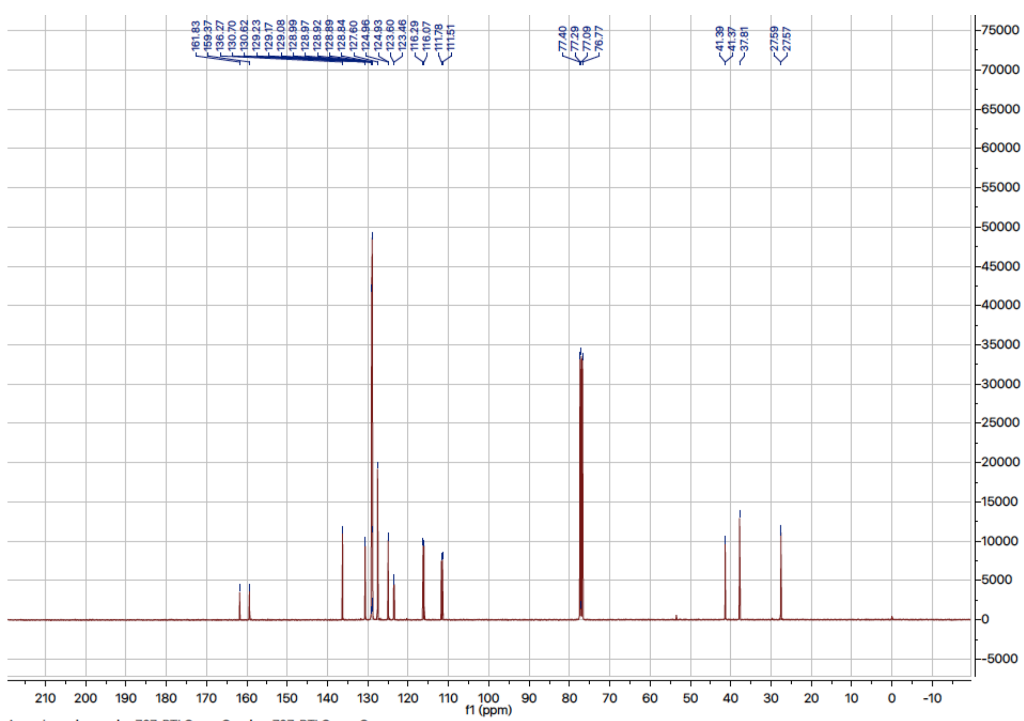
OMe
Ph
CN
CN
3αa
f1 (ppm)
A_moriyamakaworuko_706_GPC_2 — km-706-GPC-2



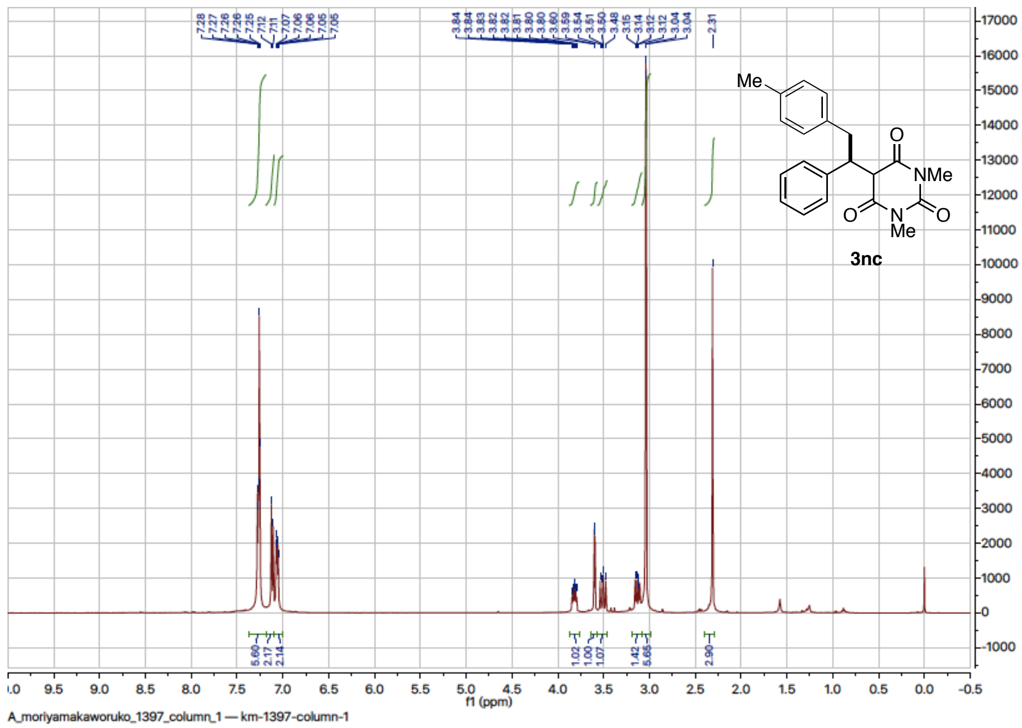
f1 (ppm)
A_moriyamakaworuko_706_GPC_2C — km-706-GPC-2C

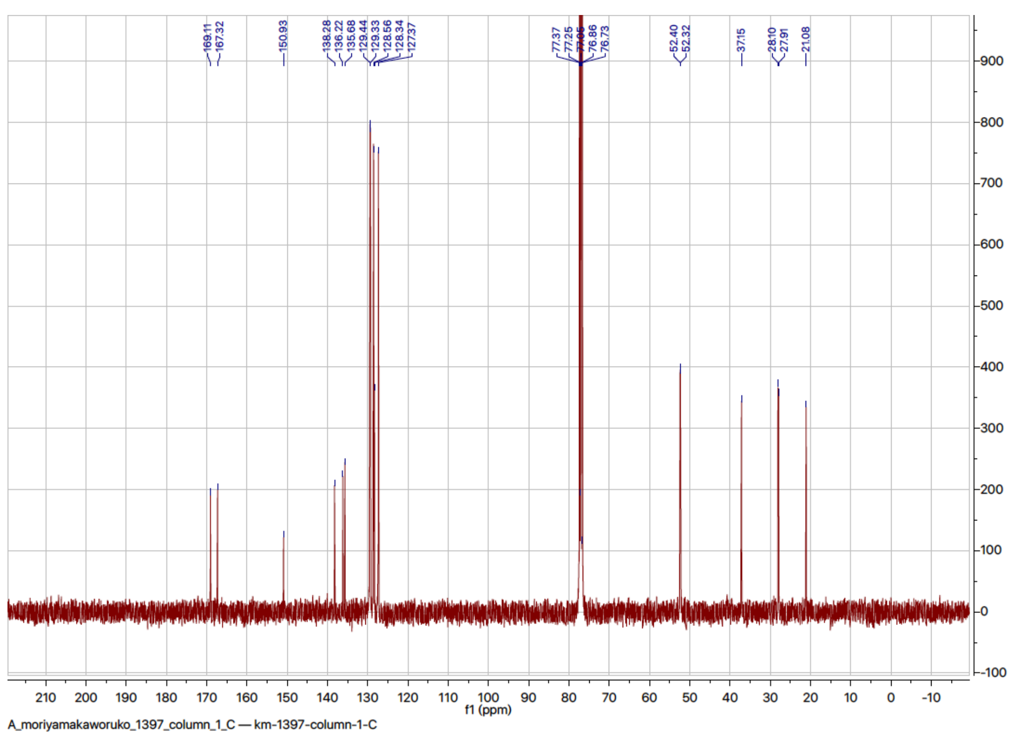
3βa



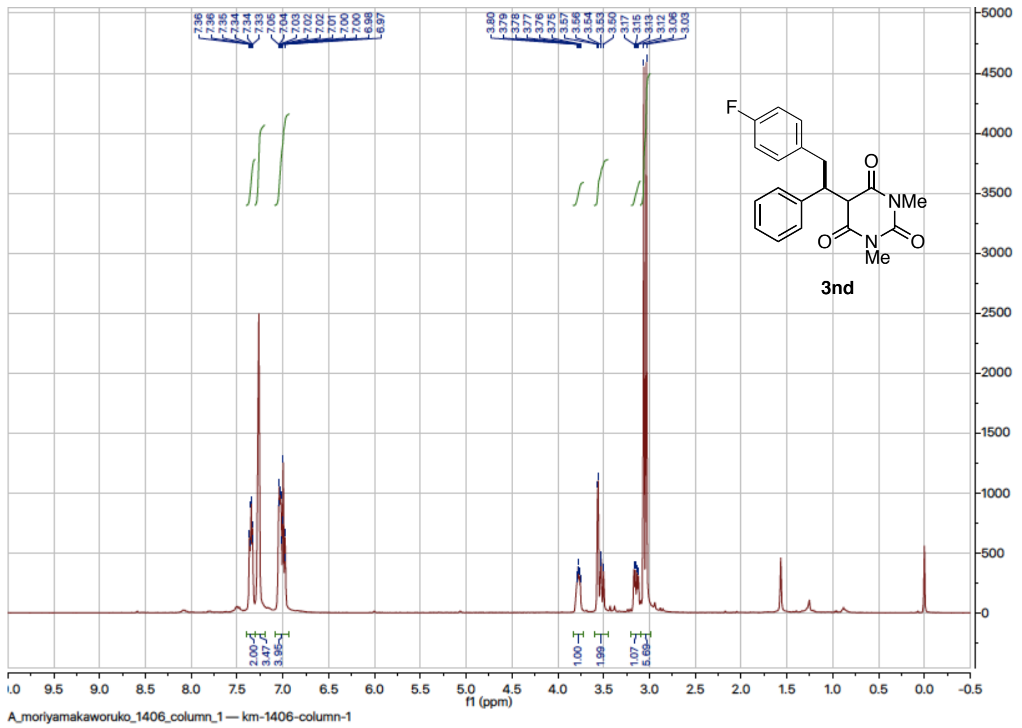


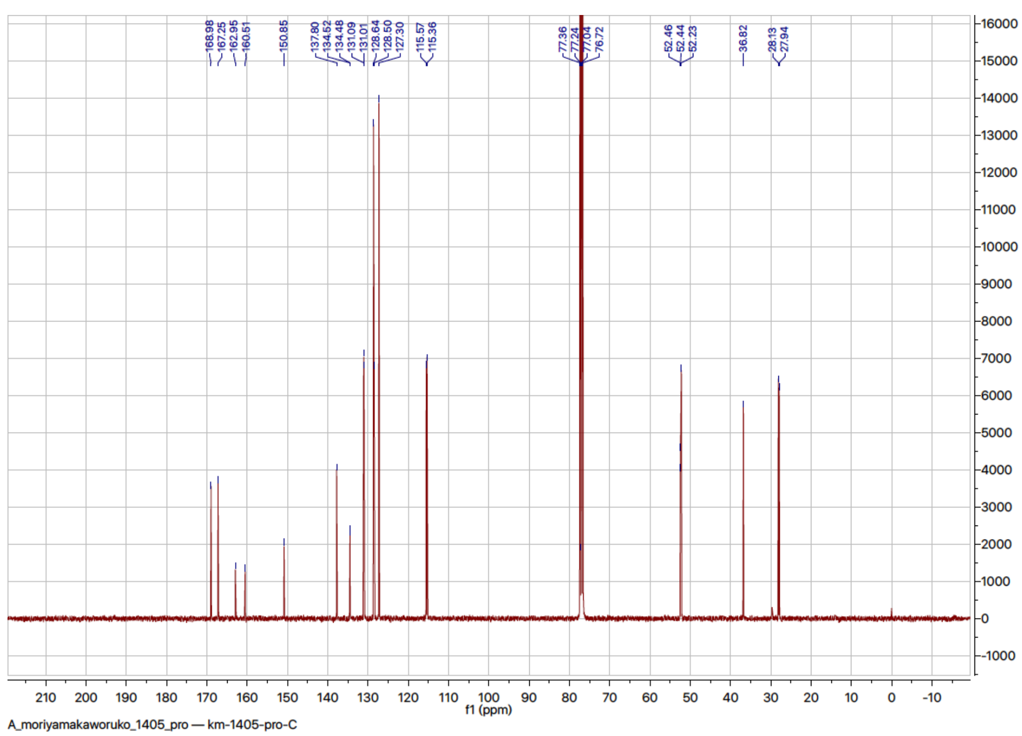
3nc


7.28
7.27
7.26
7.26
7.25
7.12
7.11
7.07
7.06
7.06
7.05
7.05
3.84
3.84
3.83
3.82
3.82
3.81
3.80
3.80
3.60
3.59
3.54
3.51
3.50
3.48
3.15
3.14
3.12
3.12
3.04
3.04
2.31
Me
NMe
Me
O
O
O
3nc
5.60
2.17
2.14
1.02
1.00
1.07
1.42
5.65
2.90
f1 (ppm)
A_moriyamakaworuko_1397_column_1 — km-1397-column-1

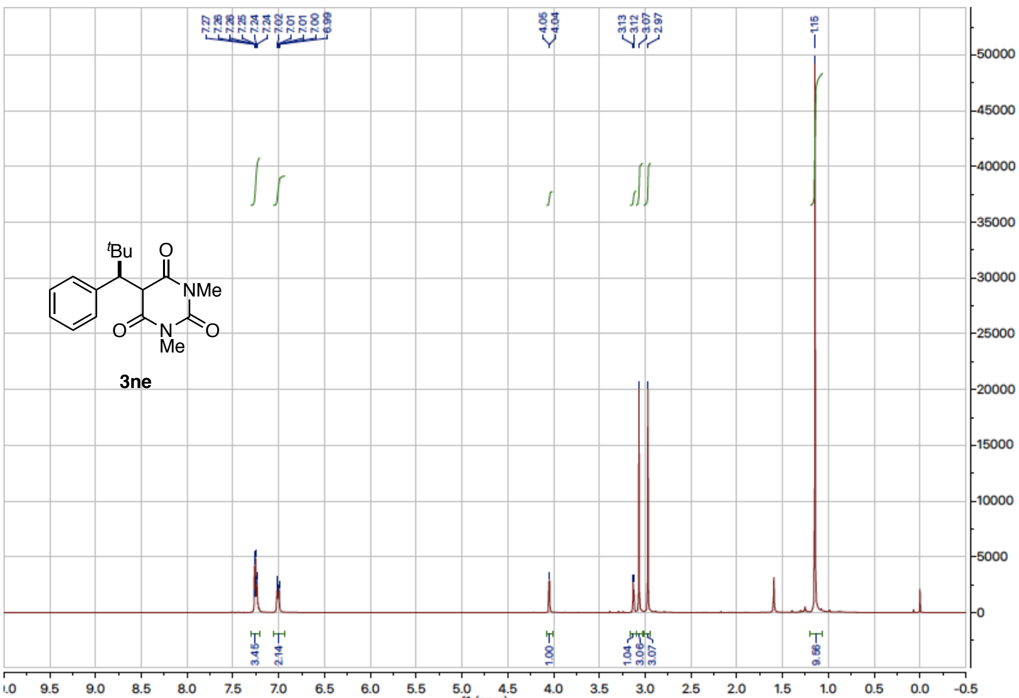

169.11
167.32
150.93
138.28
136.22
135.68
129.44
129.33
128.56
128.34
127.37
77.37
77.25
77.05
76.86
76.73
52.40
52.32
37.15
28.10
27.91
21.08
f1 (ppm)
A_moriyamakaworuko_1397_column_1_C — km-1397-column-1-C

3nd

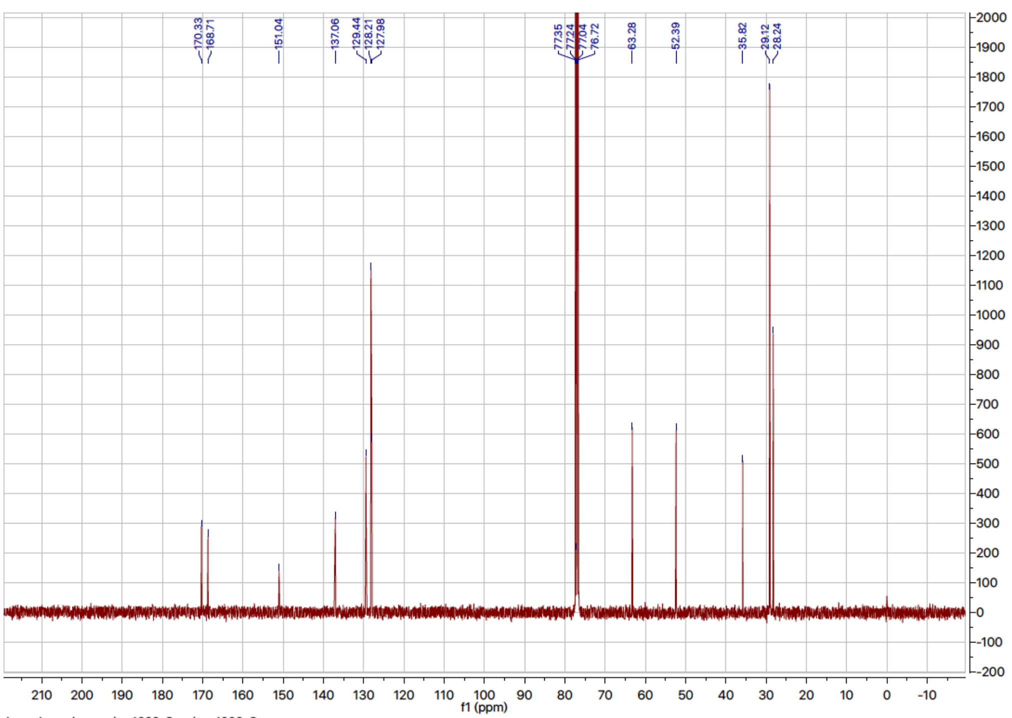




3ne

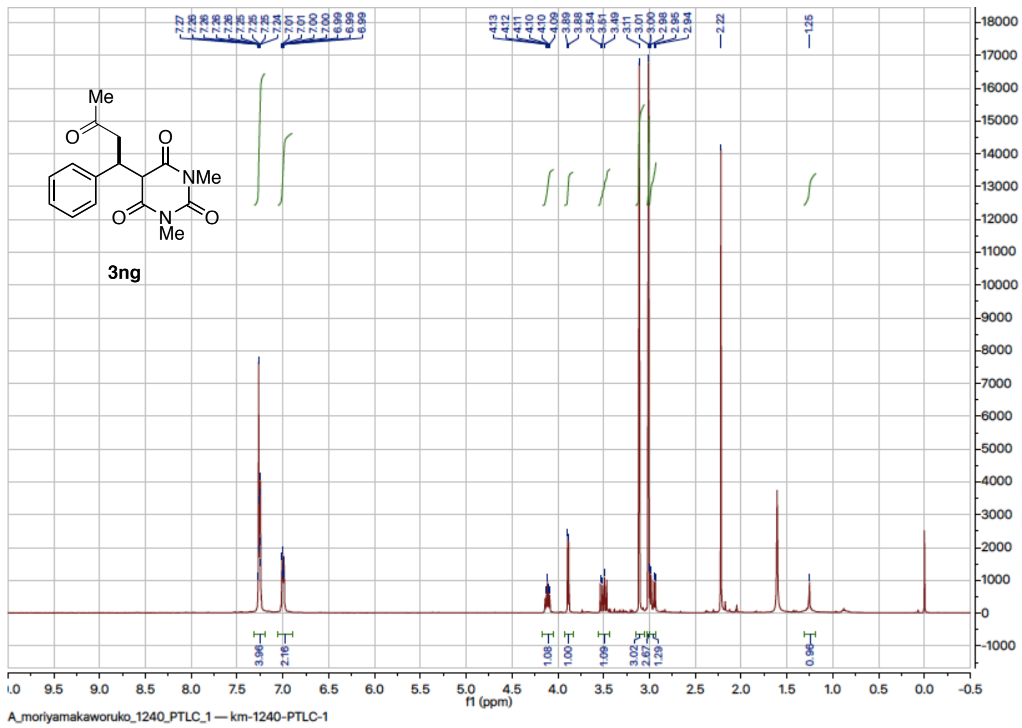


7.27
7.26
7.25
7.25
7.24
7.24
7.02
7.01
7.01
7.00
6.99
4.05
4.04
3.13
3.12
3.07
2.97
1.15
3.45
2.14
1.00
1.04
3.06
3.07
9.56
tBu
O
NMe
O
N
O
Me
3ne
f1 (ppm)
A_moriyamakaworuko_1223_column_1 — km-1223-column-1

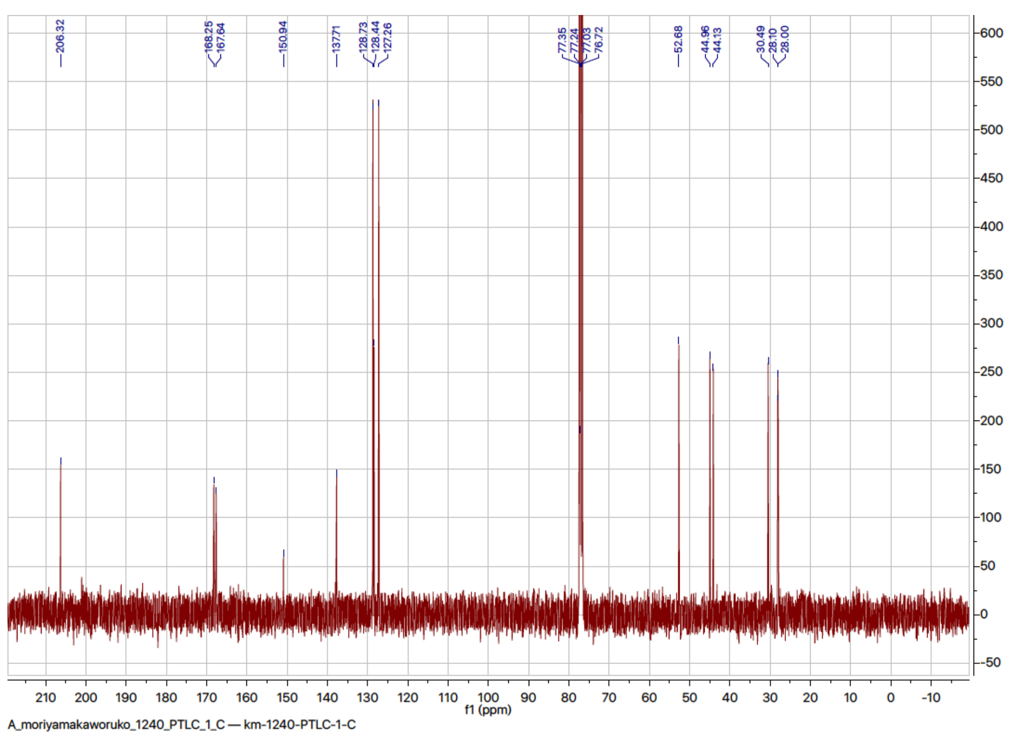


170.33
168.71
151.04
137.06
129.44
128.21
127.98
77.35
77.24
77.04
76.72
63.28
52.39
35.82
29.12
28.24
f1 (ppm)
A_moriyamakaworuko_1223_C — km-1223-C

3ng

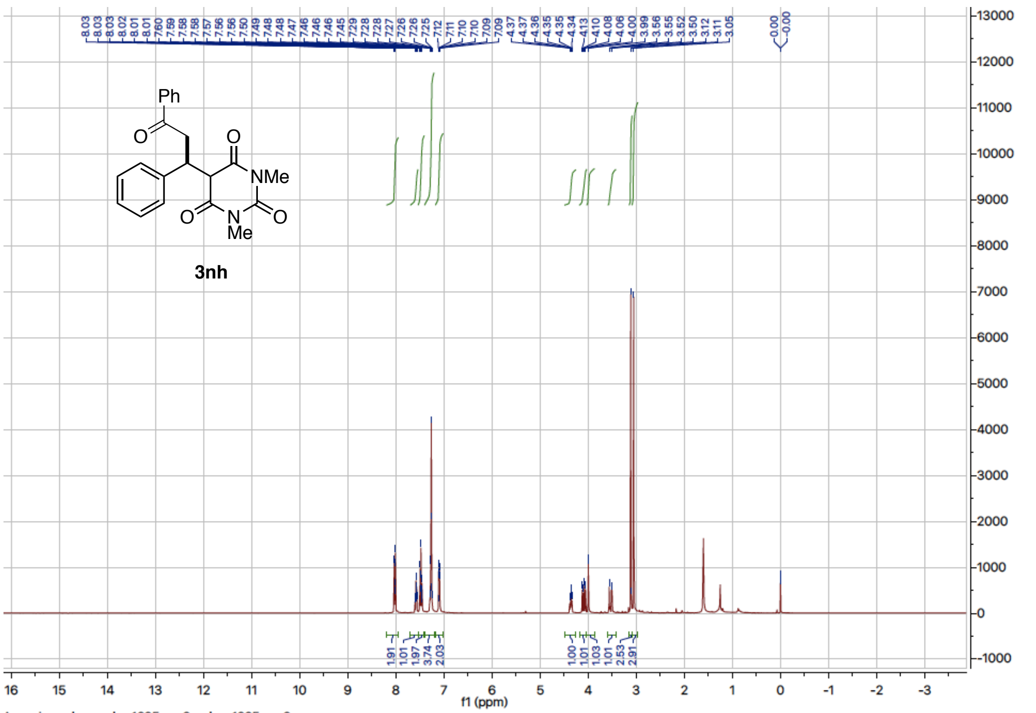


A_moriyamakaworuko_1240_PTLC_1 — km-1240-PTLC-1

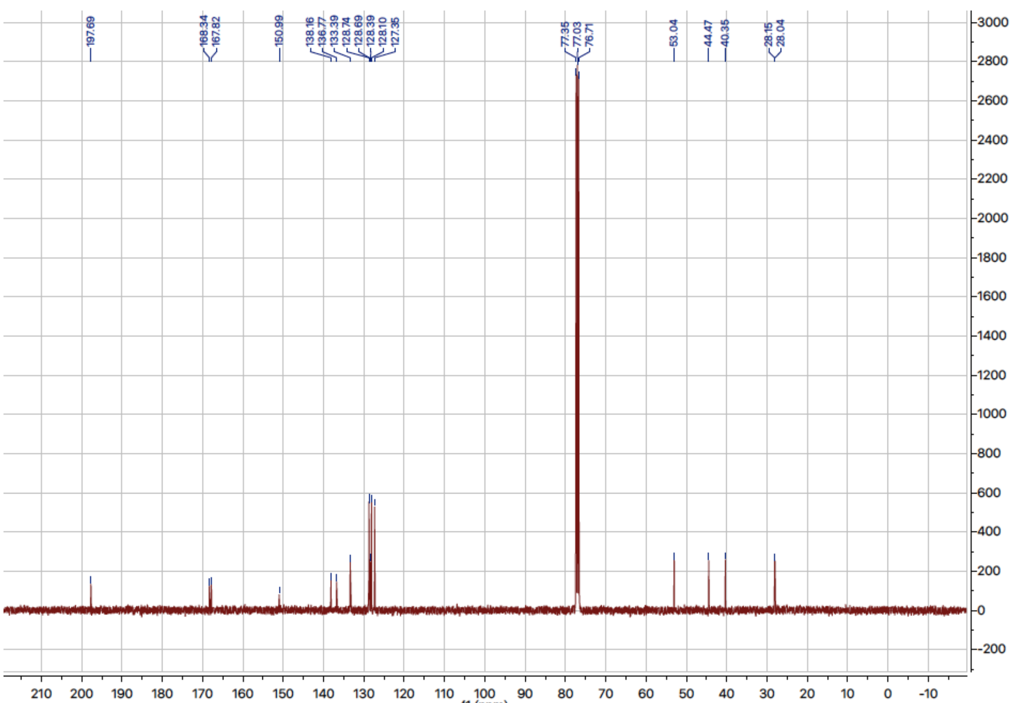


A_moriyamakaworuko_1240_PTLC_1_C — km-1240-PTLC-1-C

3nh

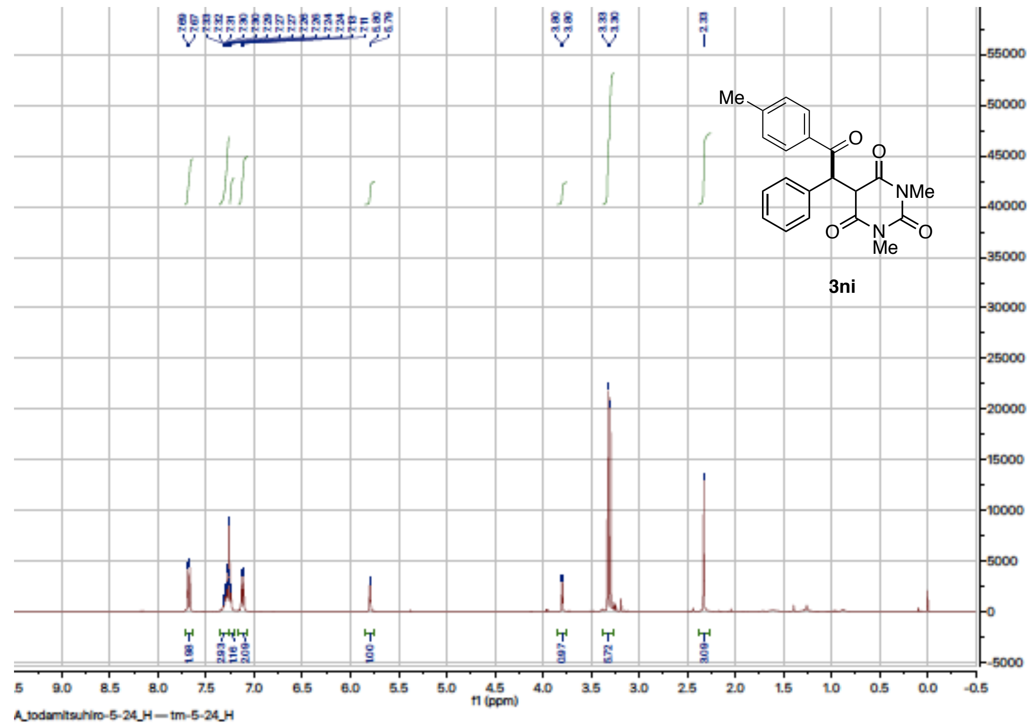


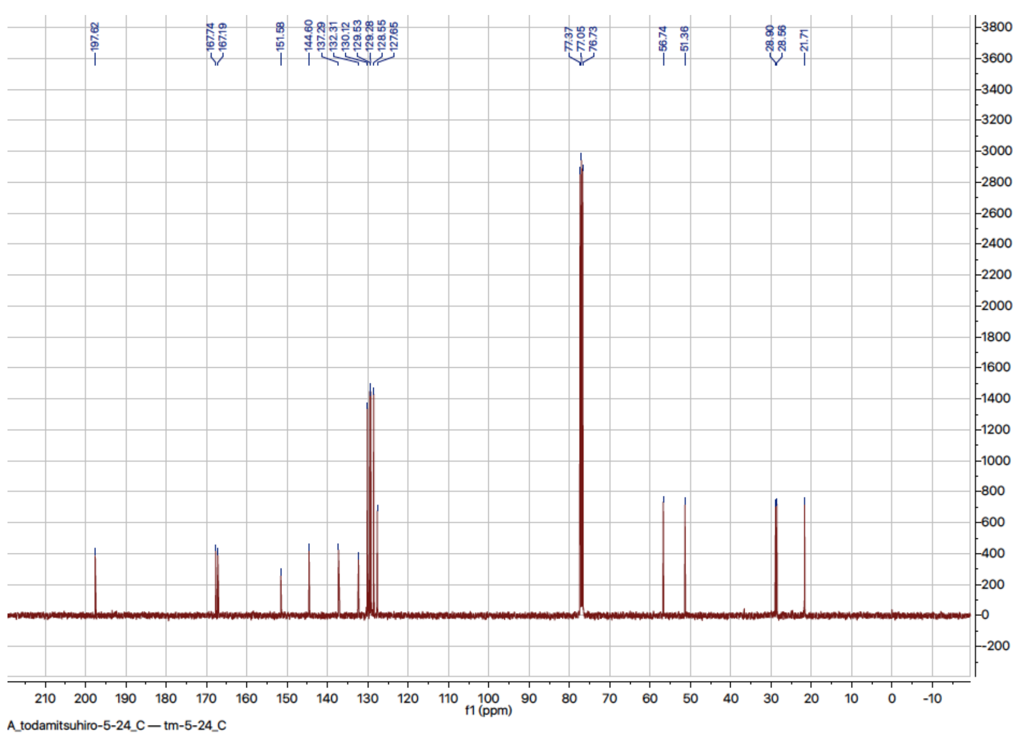
A_moriyamakaworuko_1225_pro2 — km-1225-pro2



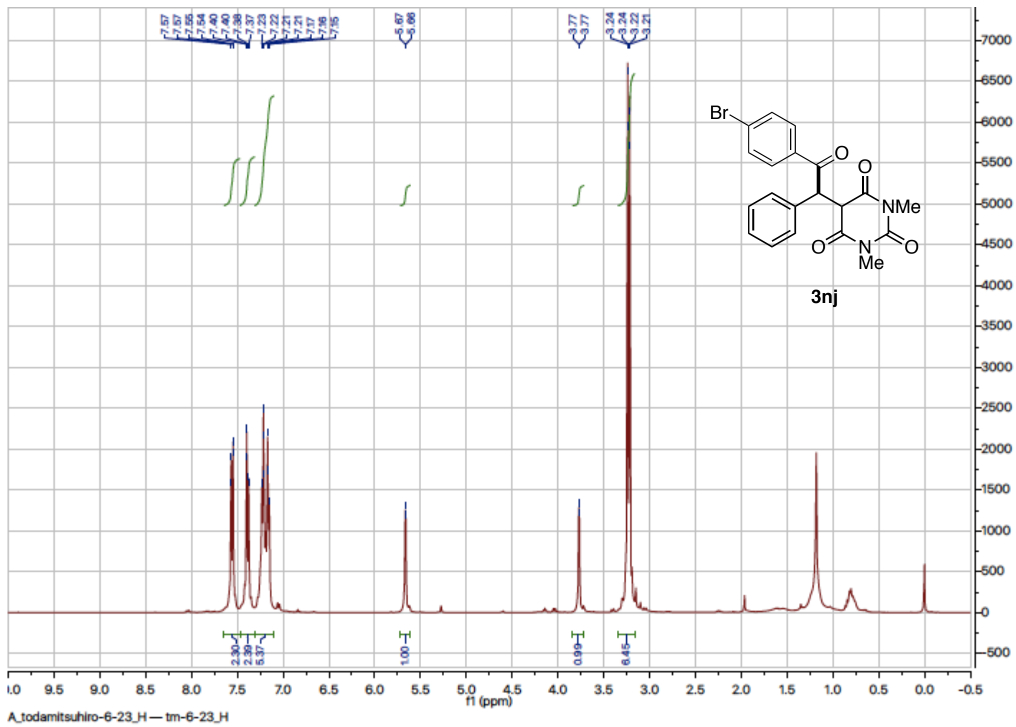
A_moriyamakaworuko_1225_pro2_C — km-1225-pro2-C

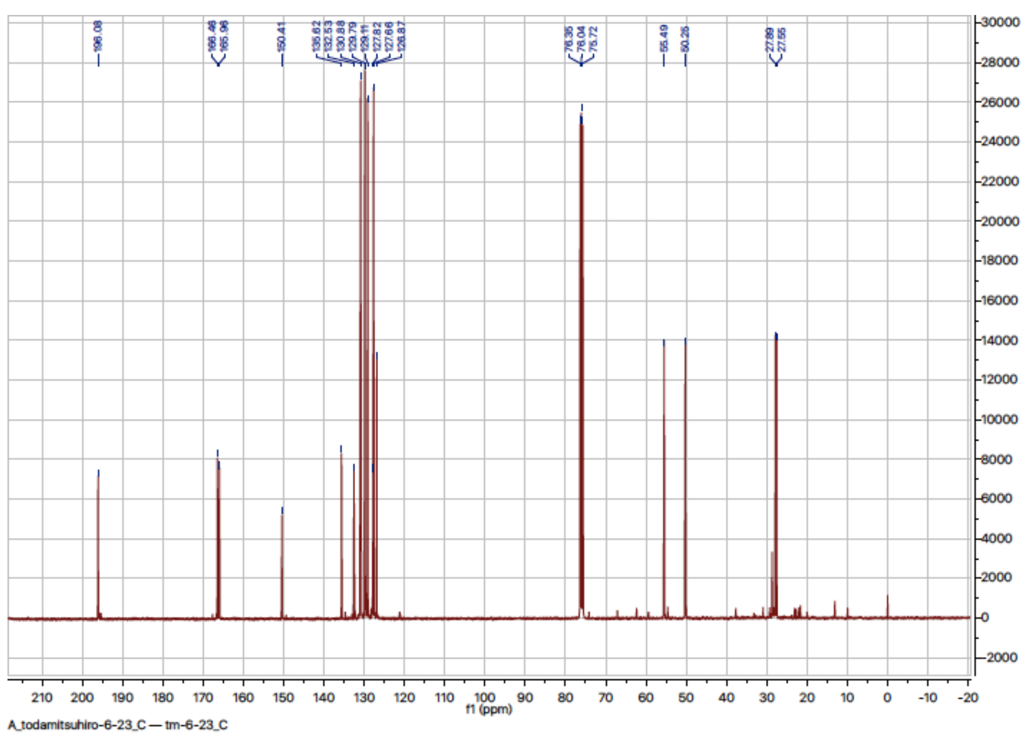
3ni



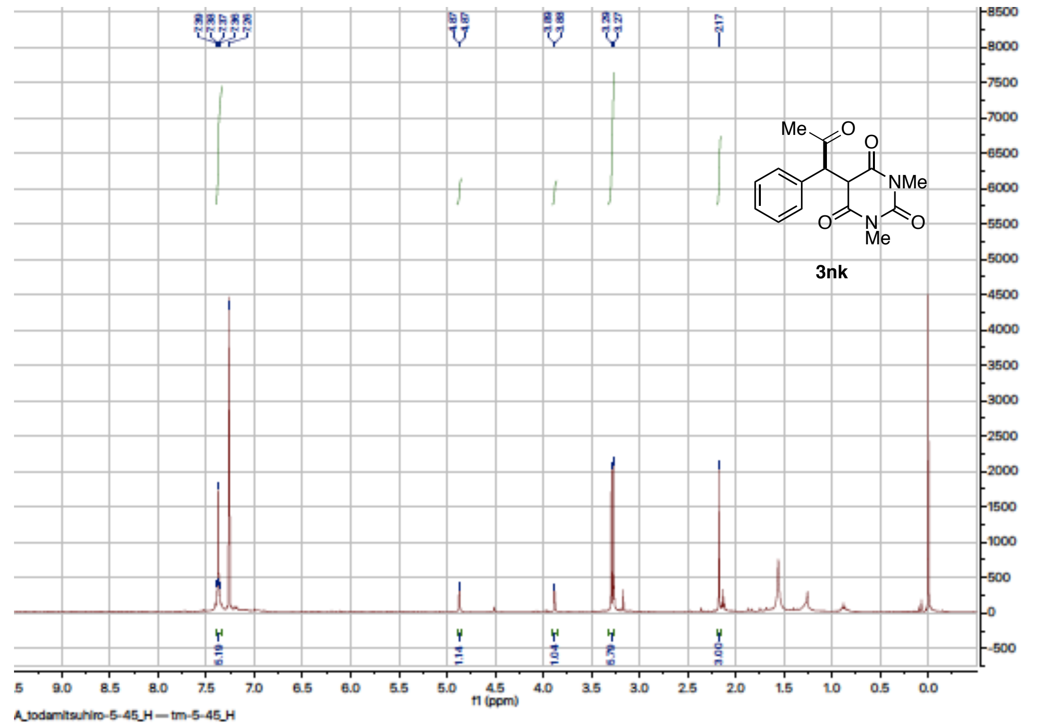


3nj

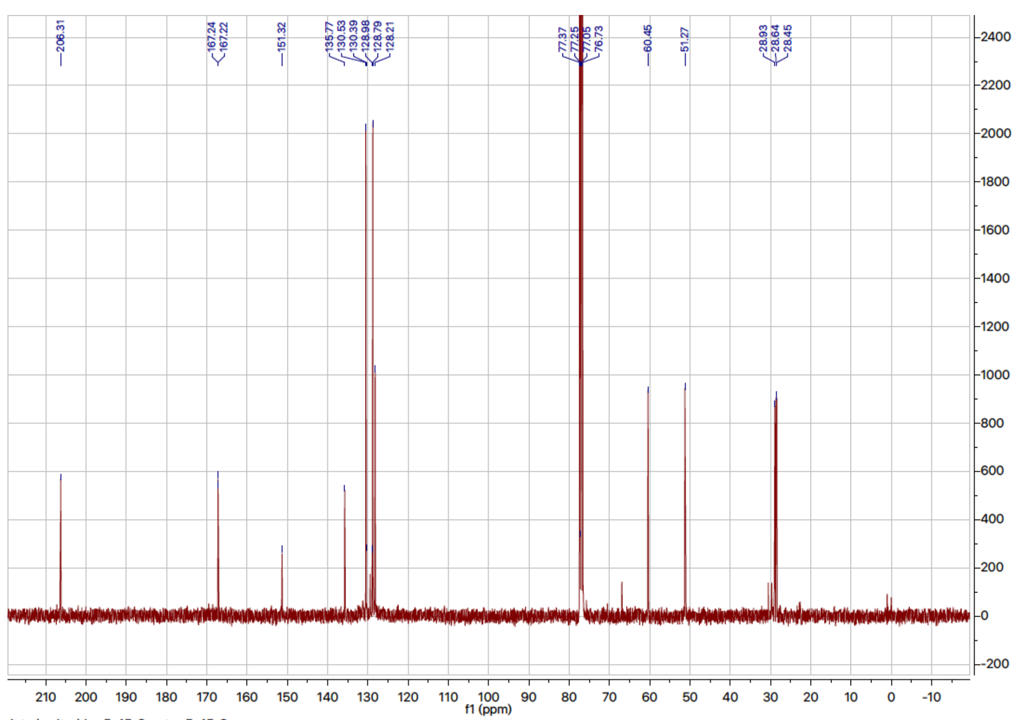

7.57
7.57
7.55
7.54
7.40
7.40
7.38
7.37
7.23
7.22
7.22
7.21
7.21
7.17
7.16
7.15
5.67
5.66
3.77
3.77
3.24
3.24
3.22
3.21
Br
O
O
NMe
O
N
O
Me
3nj
2.30
2.39
5.37
1.00
0.99
6.45
f1 (ppm)
A_todamitsuhiro-6-23_H — tm-6-23_H


196.08
166.46
165.96
150.41
135.62
132.53
130.88
129.79
129.11
127.82
127.66
126.87
76.35
76.04
75.72
55.49
50.25
27.89
27.55
f1 (ppm)
A_todamitsuhiro-6-23_C — tm-6-23_C

3nk

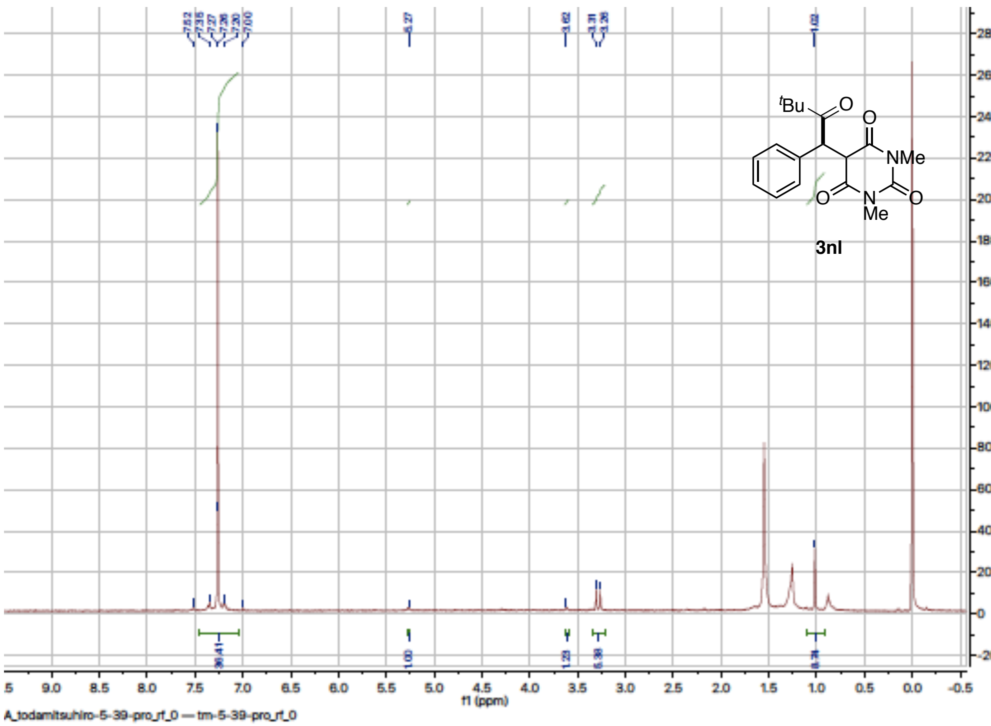


Me
O
O
NMe
O
N
O
Me
3nk
5.19
1.14
1.04
5.79
3.00
f1 (ppm)
A_todamitsuhiro-5-45_H — tm-5-45_H



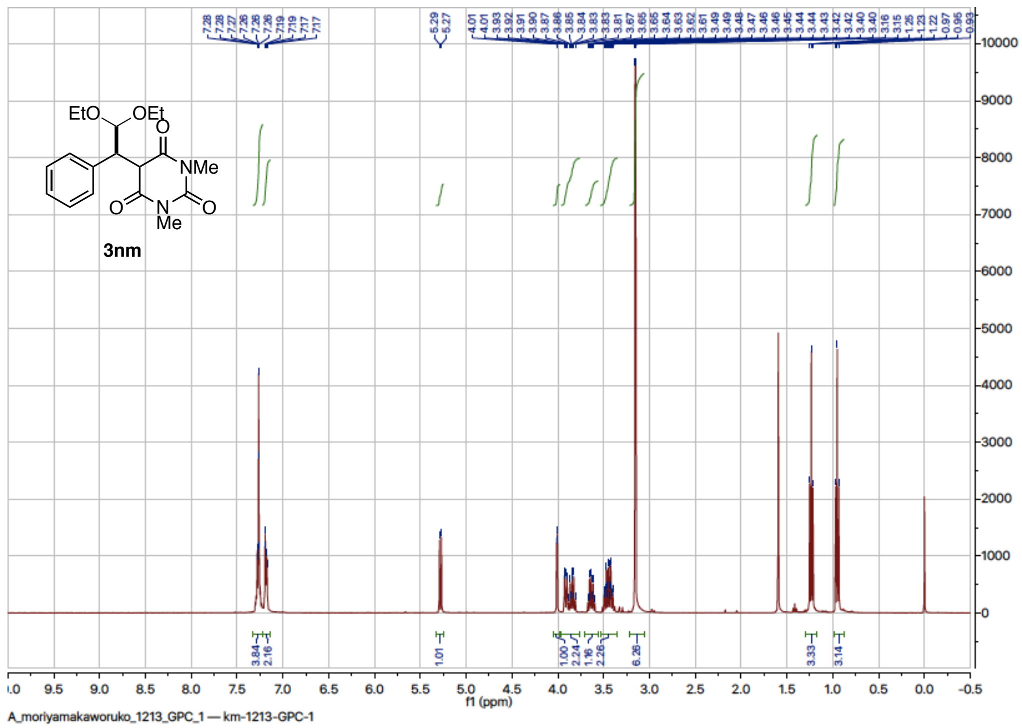
206.31
167.24
167.22
151.32
135.77
130.53
130.39
128.98
128.79
128.21
77.37
77.25
77.05
76.73
60.45
51.27
28.93
28.64
28.45
f1 (ppm)
A_todamitsuhiro-5-45_C — tm-5-45_C

3nl

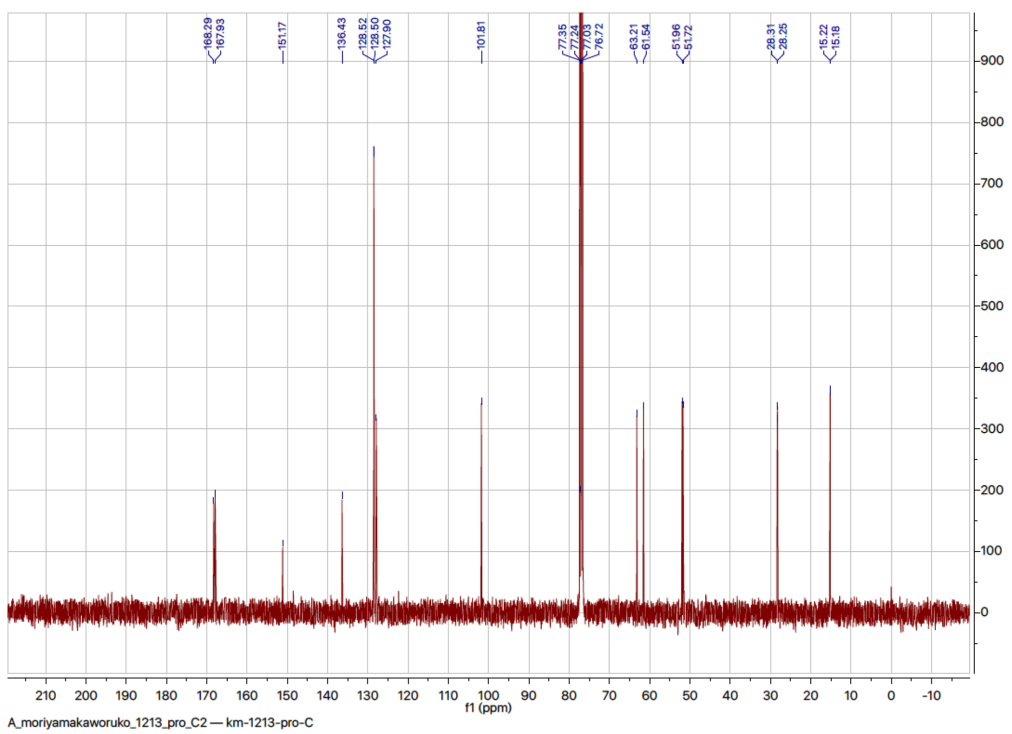


7.52
7.35
7.27
7.26
7.20
7.00
5.27
3.62
3.31
3.28
1.02
^{t}Bu
O
O
NMe
O
N
O
Me
3nl
36.41
1.00
1.23
6.38
8.76
f1 (ppm)
A_todamitsuhiro-5-39-pro_rf_0 — tm-5-39-pro_rf_0

3nm

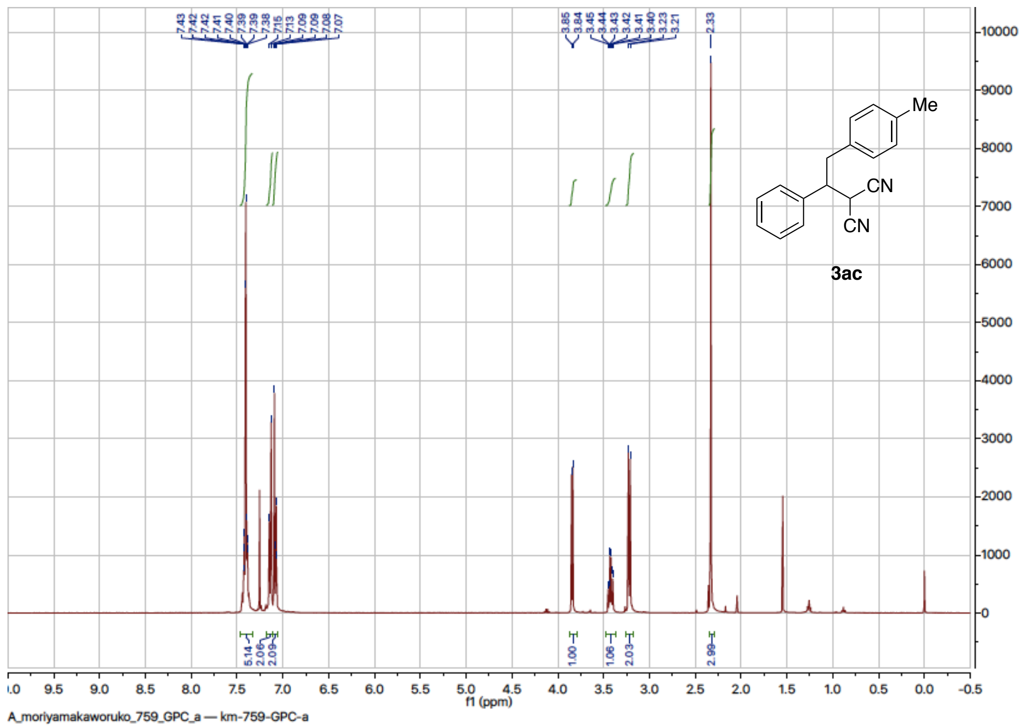


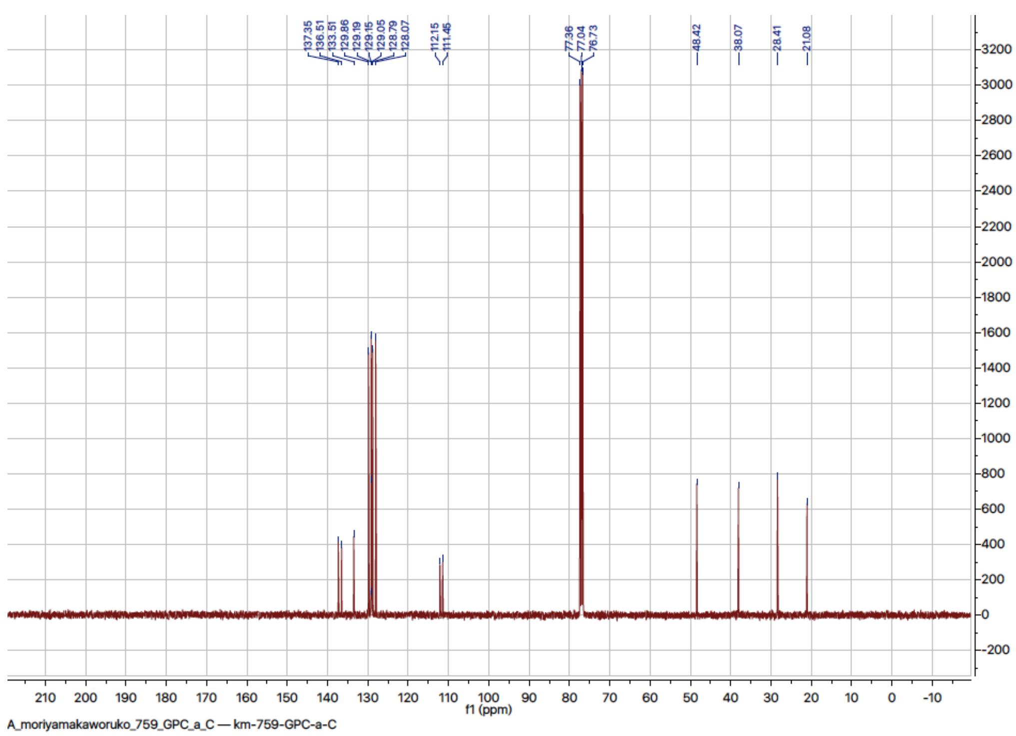
EtO
OEt
O
NMe
O
N
O
Me
3nm
f1 (ppm)
A_moriyamakaworuko_1213_GPC_1 — km-1213-GPC-1



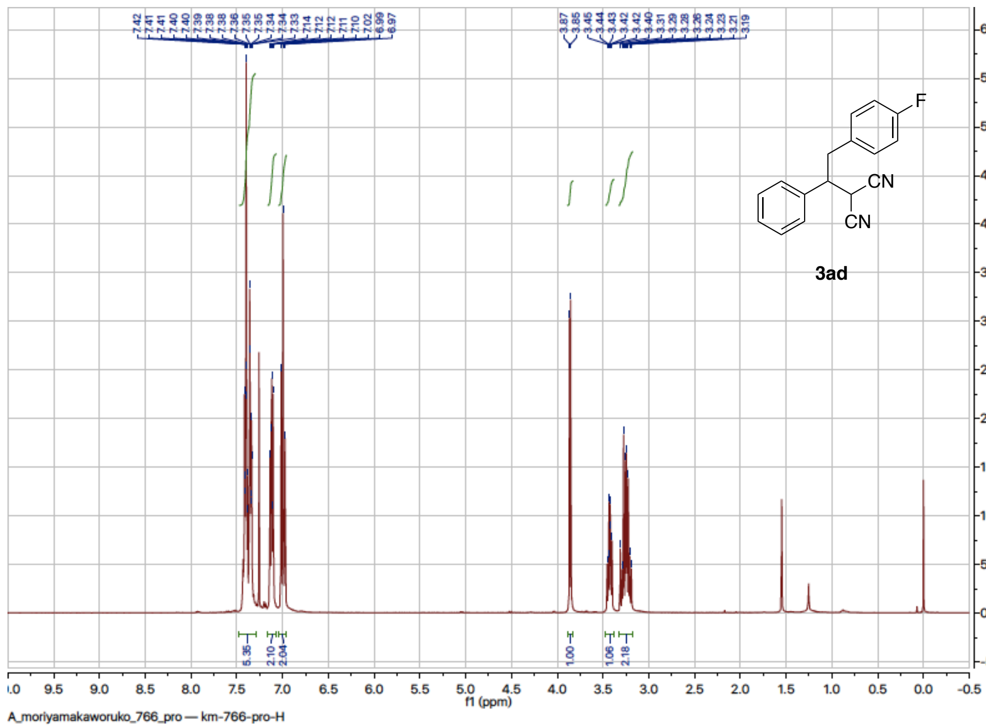
f1 (ppm)
A_moriyamakaworuko_1213_pro_C2 — km-1213-pro-C

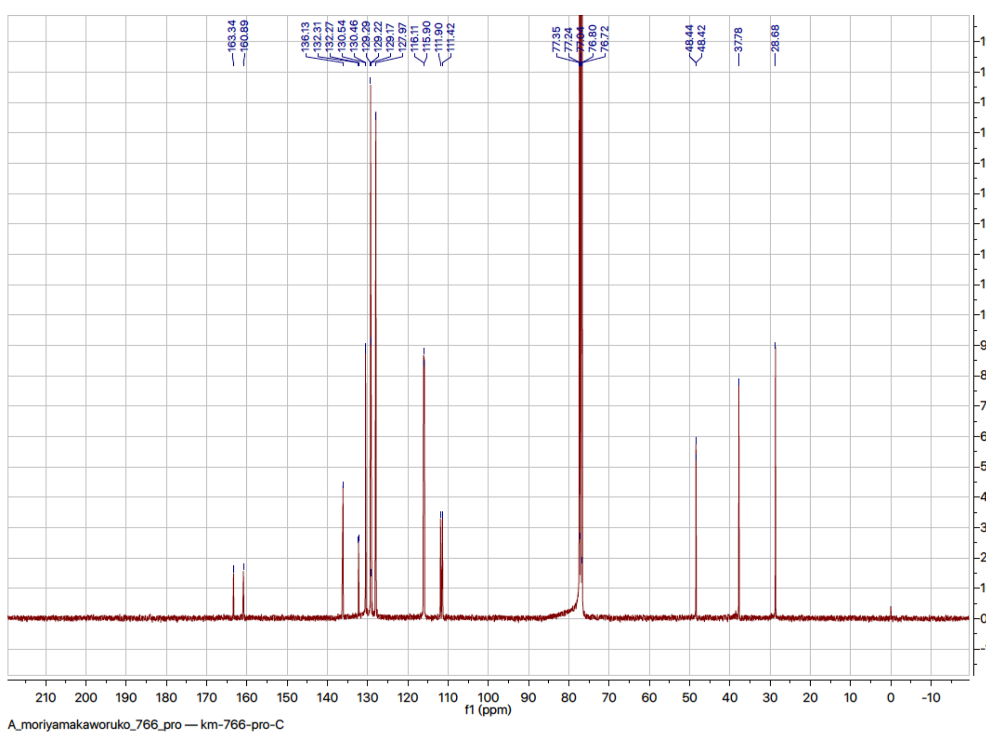
3ac



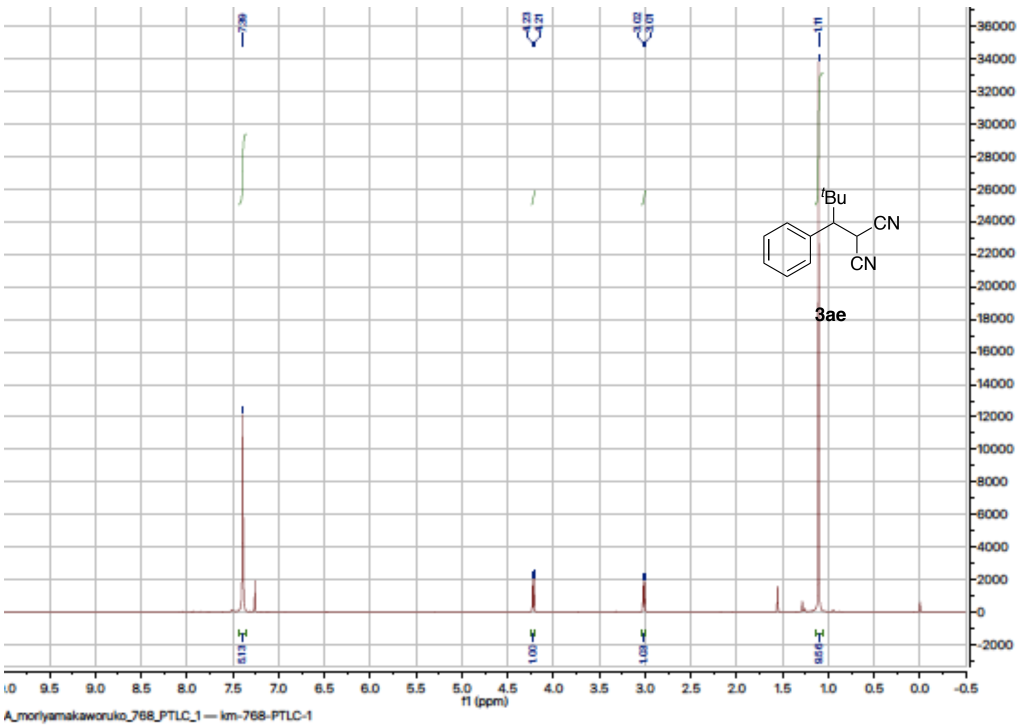


3ad

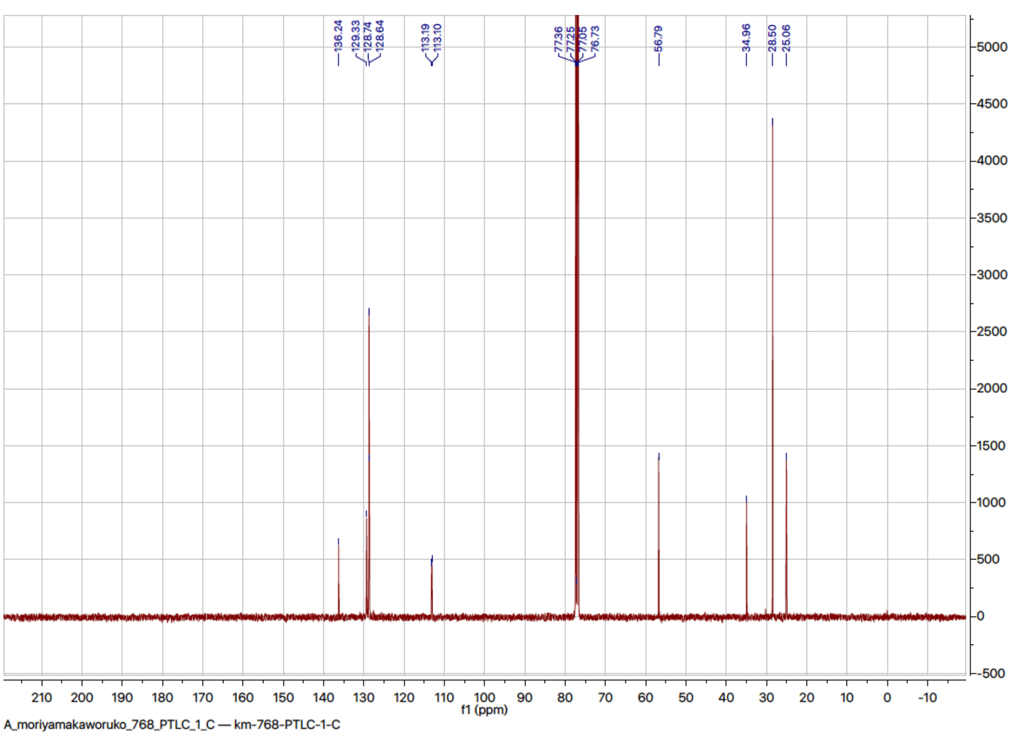




3ae

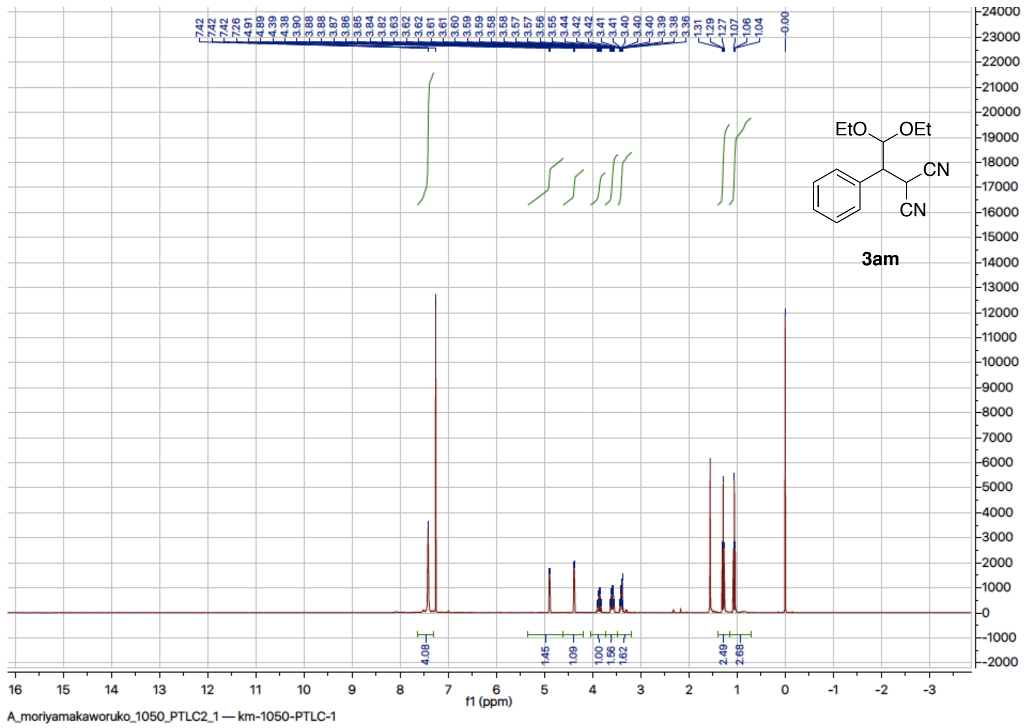


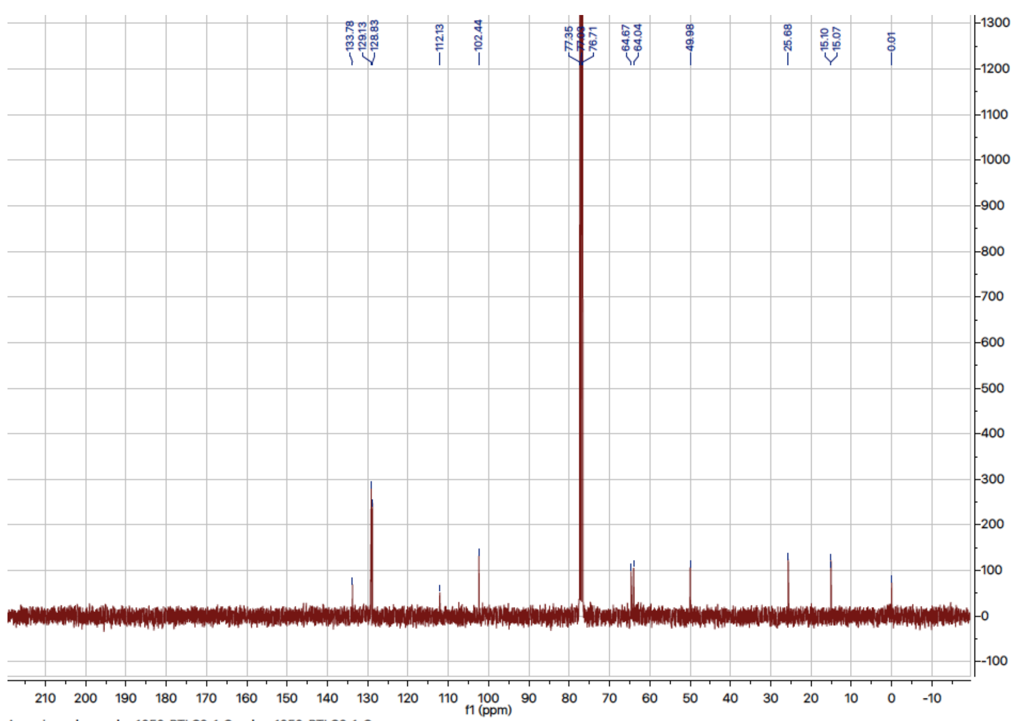
7.39
4.23
4.21
3.02
3.01
1.11
tBu
CN
CN
3ae
5.13
1.00
1.03
9.56
f1 (ppm)
A_moriyamakaworuko_768_PTLC_1 — km-768-PTLC-1



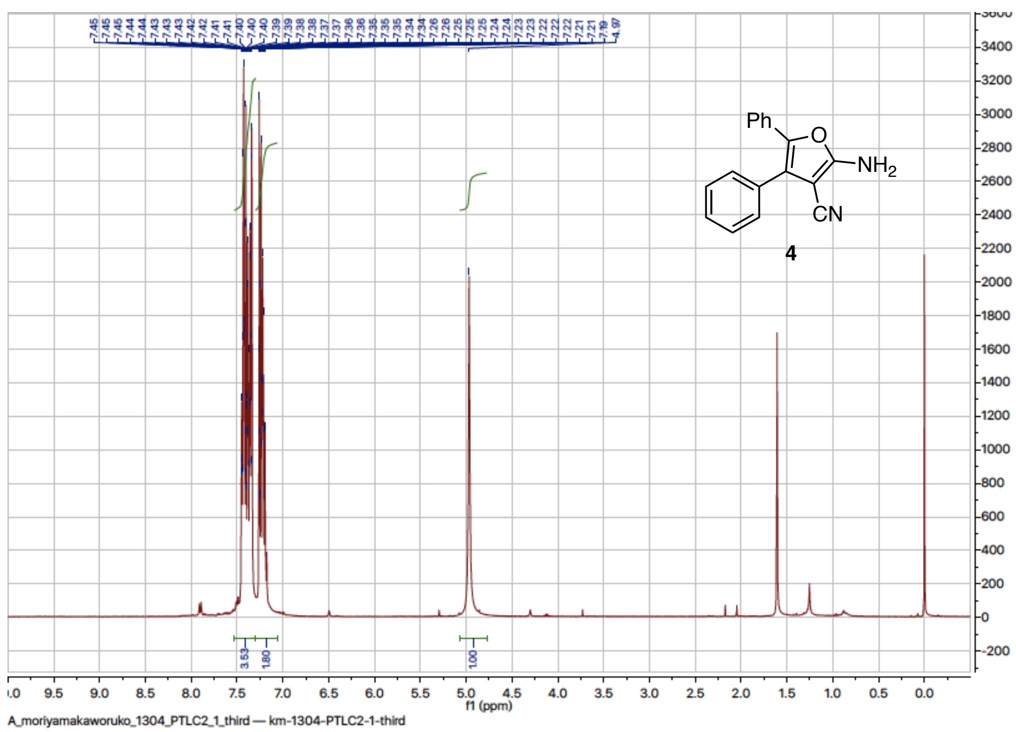
136.24
129.33
128.74
128.64
113.19
113.10
77.36
77.25
77.05
76.73
56.79
34.96
28.50
25.06
f1 (ppm)
A_moriyamakaworuko_768_PTLC_1_C — km-768-PTLC-1-C

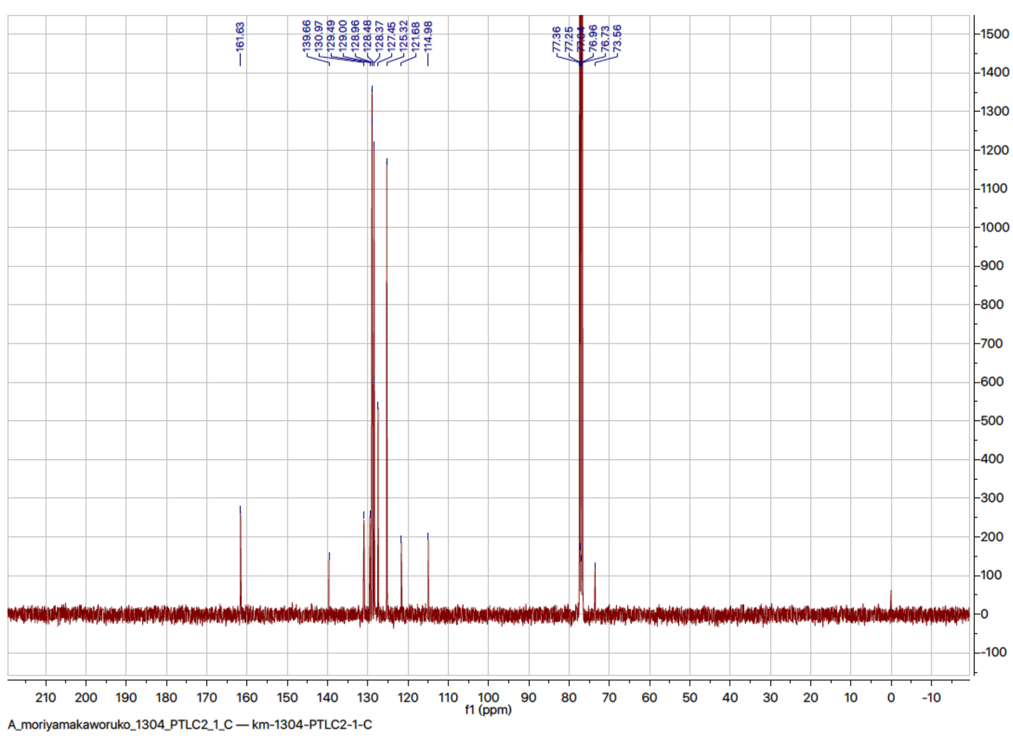
3am


EtO
OEt
CN
CN
3am
f1 (ppm)
A_moriyamakaworuko_1050_PTLC2_1 — km-1050-PTLC-1

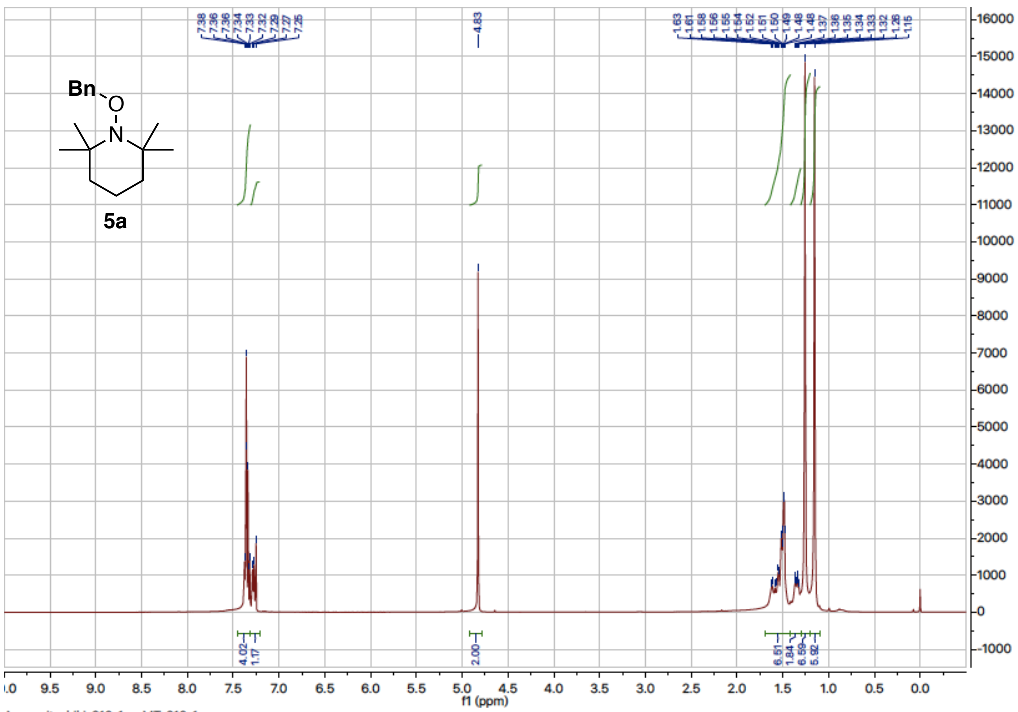

133.78
129.13
128.83
112.13
102.44
77.35
76.71
64.67
64.04
49.98
25.68
15.10
15.07
0.01
f1 (ppm)
A_moriyamakaworuko_1050_PTLC2_1_C — km-1050-PTLC2-1-C

4

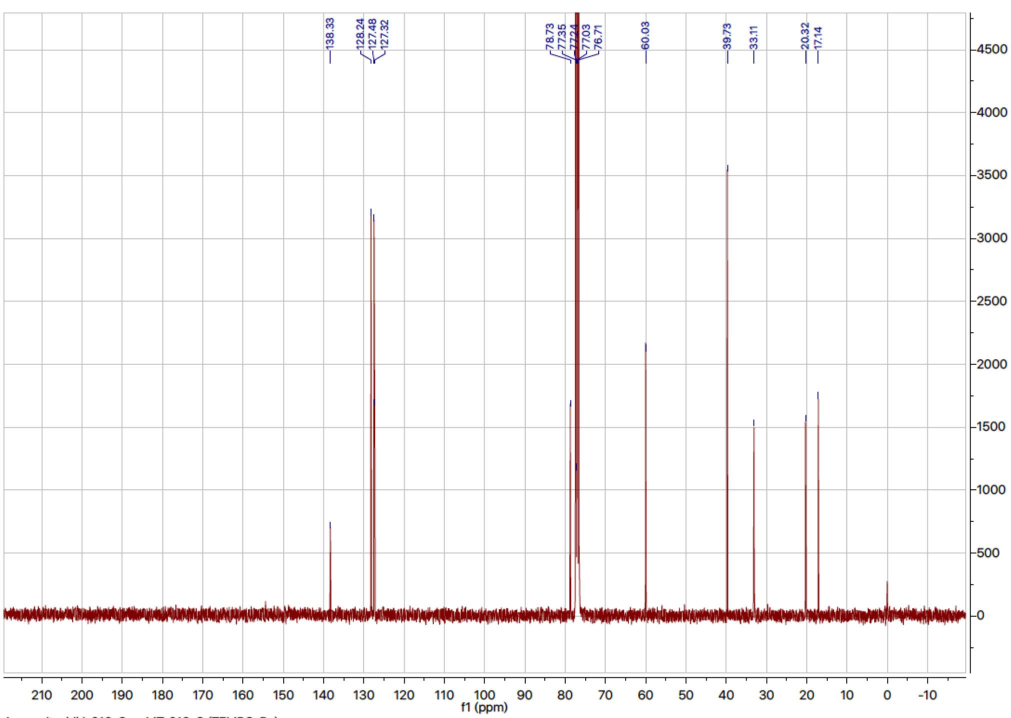




5a

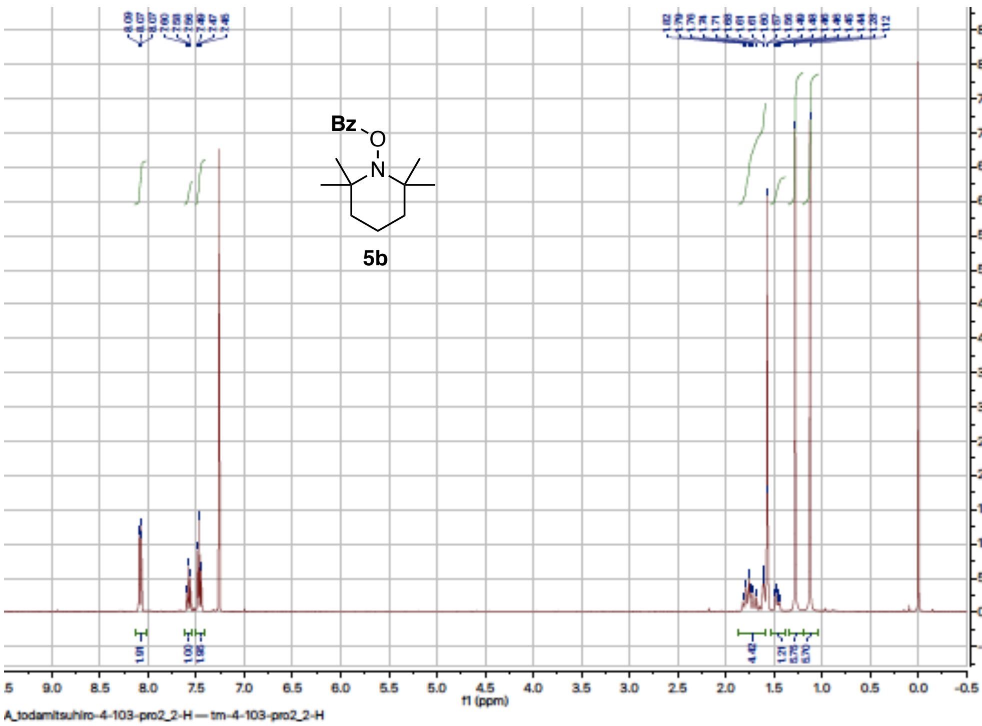


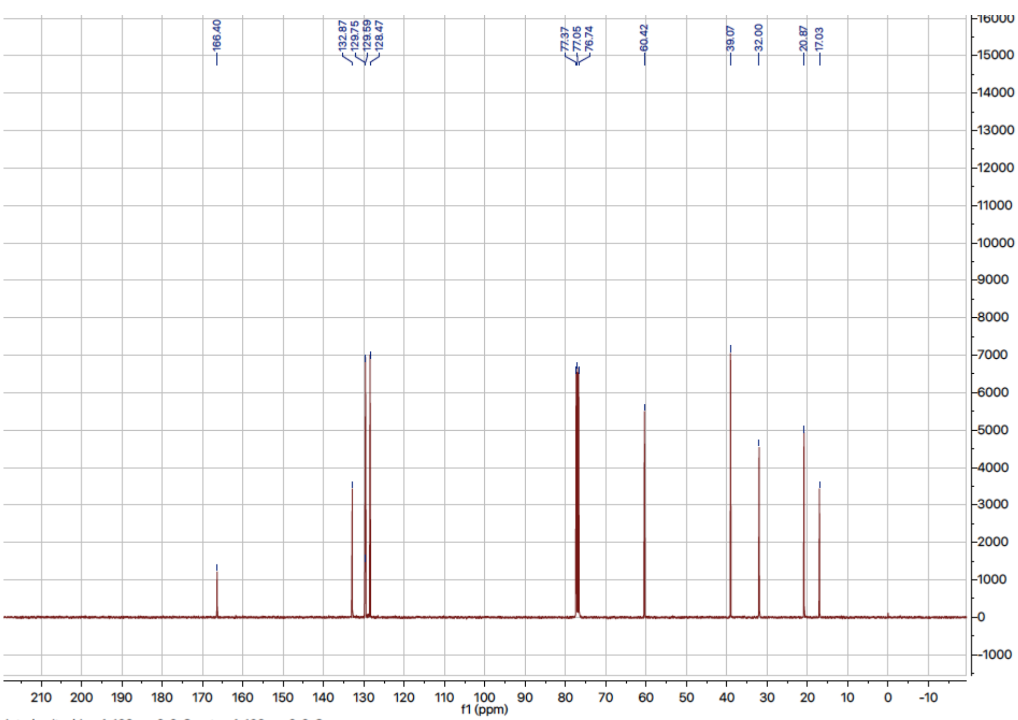
Bn
O
N
5a
7.38
7.36
7.36
7.34
7.33
7.32
7.29
7.27
7.25
4.83
1.63
1.61
1.58
1.56
1.55
1.54
1.52
1.51
1.50
1.49
1.48
1.37
1.36
1.35
1.34
1.33
1.32
1.26
1.15
4.02
1.17
2.00
6.51
1.84
6.59
5.92
f1 (ppm)
A_mouritoshiki-610-1 — MT-610-1



138.33
128.24
127.48
127.32
78.73
77.35
77.24
77.03
76.71
60.03
39.73
33.11
20.32
17.14
f1 (ppm)
A_mouritoshiki-618-C — MT-618-C (TEMPO-Bn)

5b


Bz
O
N
5b
f1 (ppm)
A_todamitsuhiro-4-103-pro2_2-H — tm-4-103-pro2_2-H


166.40
132.87
129.75
129.59
128.47
77.37
77.05
76.74
60.42
39.07
32.00
20.87
17.03
f1 (ppm)
A_todamitsuhiro-4-103-pro2_2-C — tm-4-103-pro2_2-C