Supporting Information

Ru(II)/Ru(IV) Catalyzed C(sp^2)–H Allylation with Alkene Difunctionalization to Access Isochroman-1-imines

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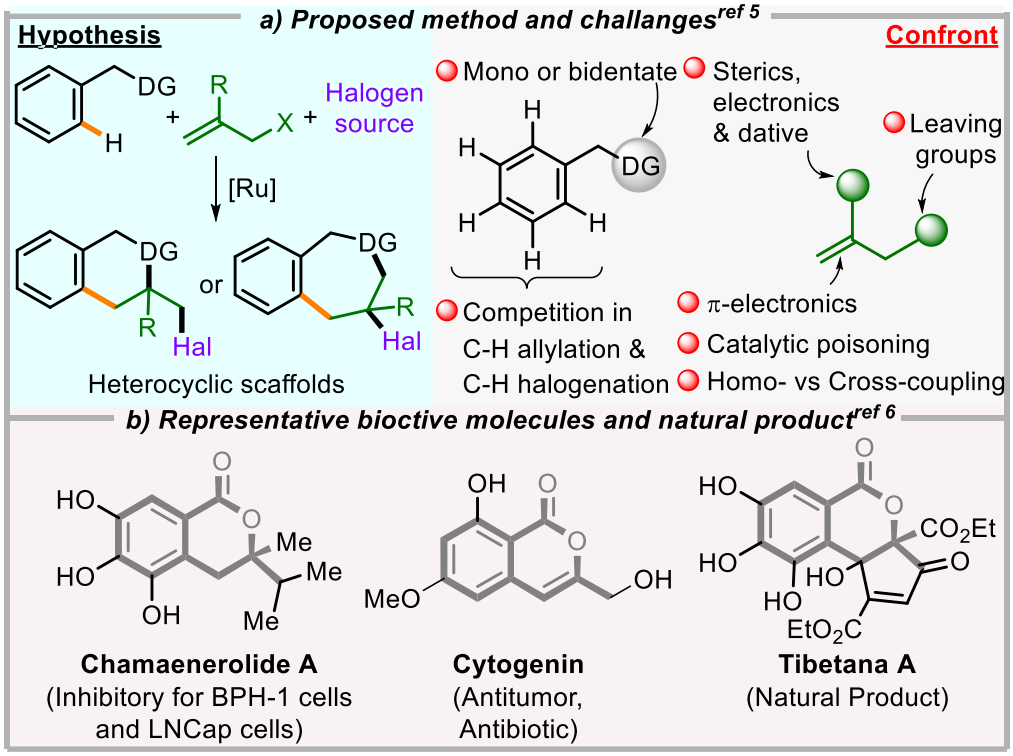
General methods

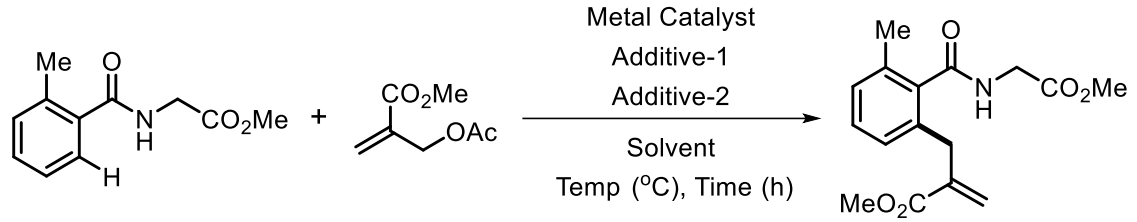
Commercially available reagents were used without additional purification, unless otherwise stated. *N*-benzoyl amino esters **1a**−**1z**,[1, 4] Morita-Baylis-Hillman adducts and other allyl sources[2] and 1-bromopyrrolidin-2-one[3] were prepared according to the reported procedures. Characterization data of known compounds e.g. (**1c**, **1e**, **1f**, **1l**, **1n** and **1o**)[1] and (**1s**, **1v**, and **1z**)[4] and were reported in literature.[1,4] Sealed tubes (13 × 100 mm^2) were purchased from Merck and dried in oven for overnight and cooled at room temperature prior to use. Thin Layer Chromatography (TLC) was carried out using aluminum support silica gel 60 F_{254} (purchased from Merck). Silica gel with 230–400 mesh size was purchased from Finar and used in flash column chromatography for purification of all synthesized compounds. Nuclear Magnetic Resonance (NMR) spectra (^{1}H and ^{13}C NMR) were recorded on Bruker spectrometer at 300, 400 and 500 MHz for ^{1}H and 75, 100, 125 MHz for ^{13}C in $CDCl_3$ solution and chemical shifts are reported as parts per million (ppm). Resonance patterns are reported with the notations s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), ddd (doublet of doublet of doublet), td (triplet of doublet), br s (broad singlet) and m (multiplet). Coupling constants (*J*) are reported in hertz (Hz). IR spectra were recorded on a Bruker ALPHA Infrared spectrophotometer and are reported as cm^{-1}. IR spectra were recorded on a Bruker ALPHA Infrared spectrophotometer and are reported as cm^{-1}. MS-ESI data were collected on waters e2695 separators module (Waters, Milford, MA, USA) mass spectrometer, and High Resolution Mass Spectra (HRMS) were recorded on a Thermo Scientific Orbitrap Exploris 120 spectrometer. Mobile phase was (A) Water + 0.1 % Formic Acid, (B) Acetonitrile + 0.1 % Formic Acid, flow rate: 0.6 mL min^{-1}, Run time: 2 min, injection volume: 10 µL, Scan range: 50-2000 m/z, polarity: positive mode. Melting point was recorded on Digital Melting Point apparatus. Liquid Chromatography-Mass Spectrometry (LC-MS) data were monitored on LCMS–2020 Shimadzu Lab Solutions.

Figure S1: Hypothesis of methodology and related natural products and bioactive molecules



Optimization of reaction conditions:

Table S1: Reaction conditions for C(sp^2)–H allylated intermediate formation (3a)[a]

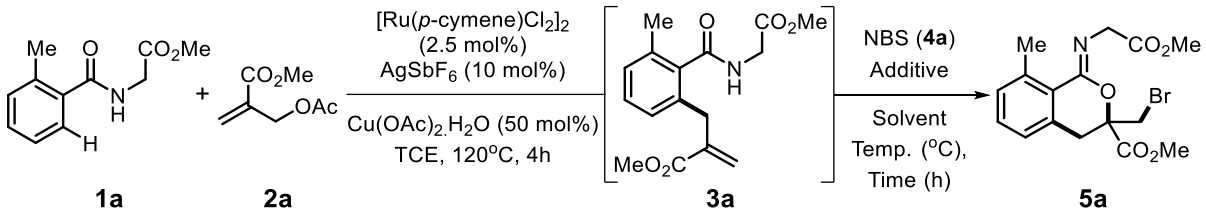


1a **2a** **3a**

Entry	Metal Catalyst (mol%)	Additive-1 (mol%)	Additive-2 (mol%)	Solvent	Temp. (°C)	Time (h)	Yield[a] (%)
1	[Ru(*p*-cymene)Cl_2]$_2$ (2.5)	$AgSbF_6$ (10)	$Cu(OAc)_2.H_2O$ (50)	DCE	120	4 h	82
2	[Ru(*p*-cymene)Cl_2]$_2$ (2.5)	$AgSbF_6$ (10)	$Cu(OAc)_2.H_2O$ (30)	DCE	120	4 h	65
3	[Ru(*p*-cymene)Cl_2]$_2$ (2.5)	$AgSbF_6$ (10)	Li_2CO_3 (50)	DCE	120	4 h	41
4	[Ru(*p*-cymene)Cl_2]$_2$ (2.5)	$AgSbF_6$ (10)	Na_2CO_3 (50)	DCE	120	4 h	75
5	[Ru(*p*-cymene)Cl_2]$_2$ (2.5)	$AgSbF_6$ (10)	K_2CO_3 (50)	DCE	120	4 h	72
6	[Ru(*p*-cymene)Cl_2]$_2$ (2.5)	$AgSbF_6$ (10)	Cs_2CO_3 (50)	DCE	120	4 h	<5
7	[Ru(*p*-cymene)Cl_2]$_2$ (2.5)	$AgSbF_6$ (10)	Ag_2CO_3 (50)	DCE	120	4 h	49
8	[Ru(*p*-cymene)Cl_2]$_2$ (2.5)	$AgSbF_6$ (10)	$Cu(OAc)_2.H_2O$ (50)	1,4-Dioxane	120	4 h	59
9	[Ru(*p*-cymene)Cl_2]$_2$ (2.5)	$AgSbF_6$ (10)	$Cu(OAc)_2.H_2O$ (50)	THF	120	4 h	57
10	[Ru(*p*-cymene)Cl_2]$_2$ (2.5)	$AgSbF_6$ (10)	$Cu(OAc)_2.H_2O$ (50)	Toluene	120	4 h	8
11	[Ru(*p*-cymene)Cl_2]$_2$ (2.5)	$AgSbF_6$ (10)	$Cu(OAc)_2.H_2O$ (50)	MeOH	120	4 h	<5
12	[Ru(*p*-cymene)Cl_2]$_2$ (2.5)	$AgSbF_6$ (10)	$Cu(OAc)_2.H_2O$ (50)	DMF	120	4 h	NR
13	**[Ru(*p*-cymene)Cl_2]$_2$ (2.5)**	**$AgSbF_6$ (10)**	**$Cu(OAc)_2.H_2O$ (50)**	**TCE**	**120**	**4 h**	**83**
14	[Ru(benzene)Cl_2]$_2$ (2.5)	$AgSbF_6$ (10)	$Cu(OAc)_2.H_2O$ (50)	DCE	120	4 h	78
15	[Ru(mesitylene)Cl_2]$_2$ (2.5)	$AgSbF_6$ (10)	$Cu(OAc)_2.H_2O$ (50)	DCE	120	4 h	49
16	[Ru(*p*-cymene)I_2]$_2$ (2.5)	$AgSbF_6$ (10)	$Cu(OAc)_2.H_2O$ (50)	DCE	120	4 h	49
17	[IrCp*Cl_2]$_2$ (2.5)	$AgSbF_6$ (10)	$Cu(OAc)_2.H_2O$ (50)	DCE	120	4 h	66
18	[RhCp*Cl_2]$_2$ (2.5)	$AgSbF_6$ (10)	$Cu(OAc)_2.H_2O$ (50)	DCE	120	4 h	NR
19	[Ru(*p*-cymene)Cl_2]$_2$ (2.5)	$AgSbF_6$ (10)	-	DCE	120	4 h	41
20	[Ru(*p*-cymene)Cl_2]$_2$ (2.5)	-	$Cu(OAc)_2.H_2O$ (50)	DMF	120	4 h	NR
21	-	$AgSbF_6$ (10)	$Cu(OAc)_2.H_2O$ (50)	DMF	120	4 h	NR

[a] Reaction condition: **1a** (0.2 mmol), **2a** (0.4 mmol), solvent (1 mL) in pressure tube. Isolated yield by flash column chromatography. DCE = 1, 2-dichloroethane, TCE = 1, 1, 2, 2-tetrachloroethane, THF = tetrahydrofuran, DMF = *N*, *N*-dimethyl formamide, NR = no reaction.

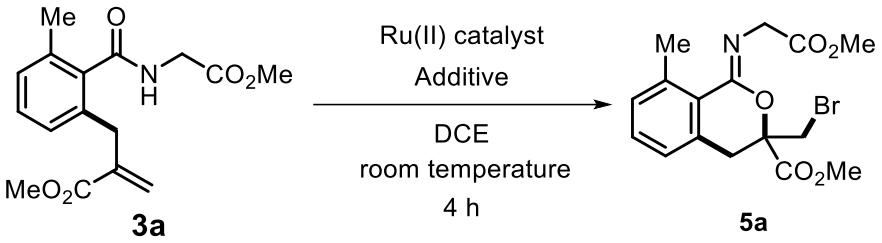
Table S2: Reaction conditions for isochroman-1-imine formation (5a)[a]



Entry	NBS[a] (mol%)	Additive (mol%)	Solvent	Temp. (°C)	Time (h)	Yield (%)[b]
1	NBS (200)	-	DCE	rt	4 h	61
2	NBS (300)	-	DCE	rt	4 h	47
3	NBS (200)	-	DCE	rt	8 h	49
4	NBS (200)	-	DCE	-10	4 h	<5
5	NBS (200)	-	DCE	60	4 h	27
6	NBS (200)	-	DCE	120	4 h	NR
7	NBS (200)	$ZnCl_2$ (10)	DCE	rt	4 h	45
9	NBS (200)	$SnCl_2$ (10)	DCE	rt	4 h	43
11	NBS (200)	NiF_2 (10)	DCE	rt	4 h	43
12	NBS (200)	$NiCl_2$ (10)	DCE	rt	4 h	47
13	NBS (200)	$NiBr_2$ (10)	DCE	rt	4 h	48
14	NBS (200)	NiI_2 (10)	DCE	rt	4 h	44
15	NBS (200)	$NiCO_3$ (10)	DCE	rt	4 h	50
16	NBS (200)	$Ni(OTf)_2$ (10)	DCE	rt	4 h	50
17	NBS (200)	$Cu(OTf)_2$ (10)	DCE	rt	4 h	49
18	NBS (200)	Ru(*p*-cymene)Cl_2 (2.5)	DCE	rt	4 h	65
19	NBS (200)	Ru(*p*-cymene)Cl_2 (5)	DCE	rt	4 h	70
20	NBS (200)	$AgSbF_6$ (10)	DCE	rt	4 h	46
21	**NBS (200)**	**-**	**TCE**	**rt**	**4 h**	**75**
22	NBS (200)	-	CH_3CN	rt	4 h	41
23	NBS (200)	-	THF	rt	4 h	26
24	NBS (200)	-	CH_2Cl_2	rt	4 h	46
25	NBS (200)	-	CCl_4	rt	4 h	26
26	NBS (200)	-	$PhCF_3$	rt	4 h	33
27	NBS (200)	-	PhCl	rt	4 h	36

[a] Reaction condition: **1a** (0.2 mmol), **2a** (0.4 mmol), solvent (1 mL) in pressure tube. NBS = *N*-bromosuccinamide, [b]Isolated yield by flash column chromatography, DCE = 1, 2-dichloroethane, TCE = 1, 1, 2, 2-tetrachloroethane, THF = tetrahydrofuran, rt = room temperature.

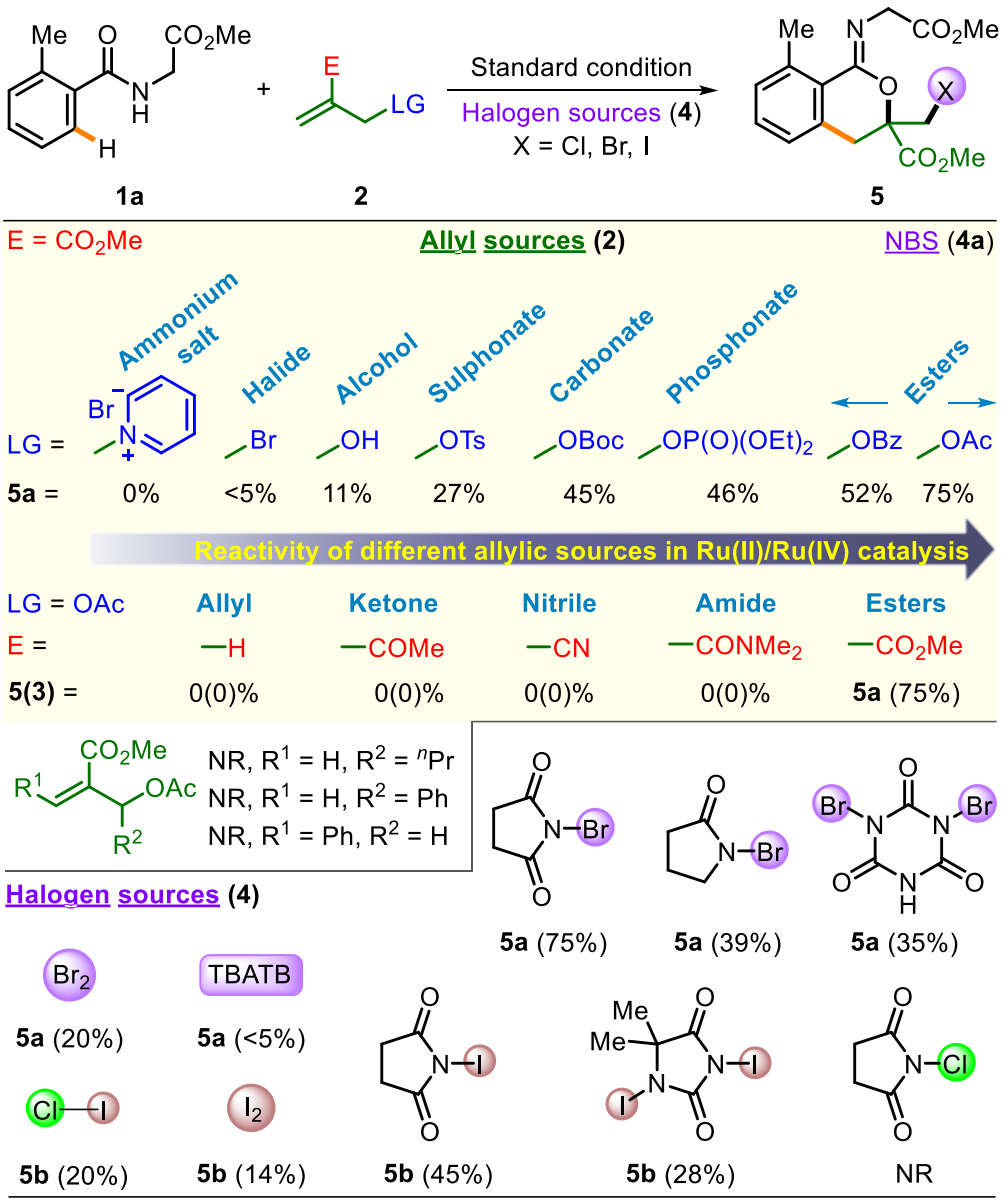
Table S3: Effect of [Ru(*p*-cymene)Cl$_2$]$_2$ catalyst and other additives on alkene difunctionalization of allylated intermediate (3a)[a]



Entry	[Ru(*p*-cymene)Cl$_2$]$_2$ (mol%)	Additive (mol%)	Yield[b] (%)
1	-	-	35
2	[Ru(*p*-cymene)Cl$_2$] (2.5)	-	55
3	[Ru(*p*-cymene)Cl$_2$] (2.5)	$AgSbF_6$ (10)	46
4	[Ru(*p*-cymene)Cl$_2$] (2.5)	$Cu(OAc)_2 \cdot H_2O$ (50)	37
5	-	$AgSbF_6$ (10)	60
6	-	$AgSbF_6$ (20)	53
7	-	$Cu(OAc)_2 \cdot H_2O$ (50)	36
8	[Ru(*p*-cymene)Cl$_2$] (5)	-	63
9	[Ru(*p*-cymene)Cl$_2$] (10)	-	59

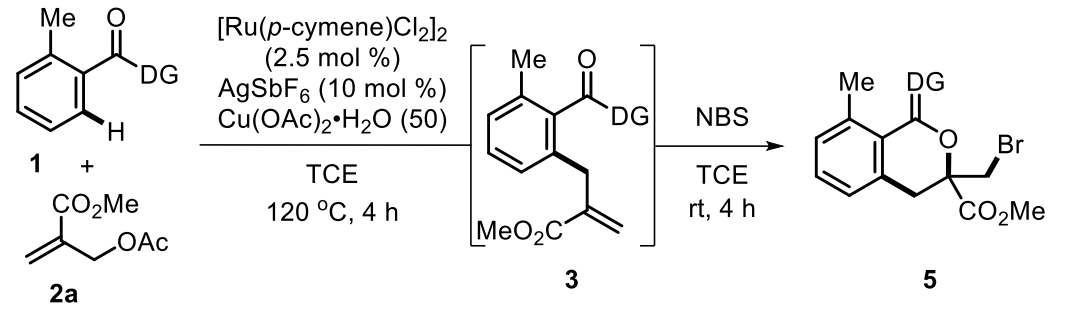
[a]Isolated yield by flash column chromatography, DCE = 1, 2-dichloroethane

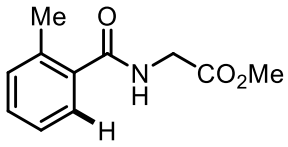
Table S4: Scope of allylic and halonium sources[a]



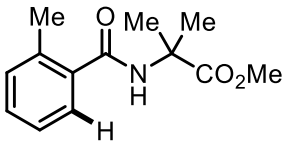
[a] Standard condition: **1a** (0.2 mmol), **2** (0.4 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (2.5 mol %), $AgSbF_5$ (10 mol %), $Cu(OAc)_2 \cdot H_2O$ (50 mol %), TCE (1 mL) at 120 °C for 4 h in pressure tube, celite filter after **3a** formation then **4** and additional TCE (0.5 mL) at rt for 4 h in pressure tube, isolated yield of **3** and **5**. TBATB = *n*-tetrabutylammonium tribromide.

Table S5: Effect of different directing groups on C(sp^2)–H allylated intermediate (3a) formation and isochroman-1-imine formation (5a)[a]

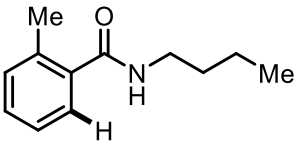




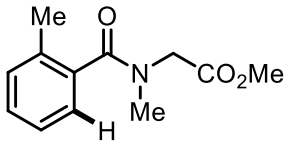
5a(3a) = 75(83%)



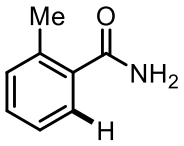
5x(3x) = 65(70%)



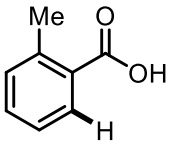
5z(3z) = 38(57%)



NR



NR

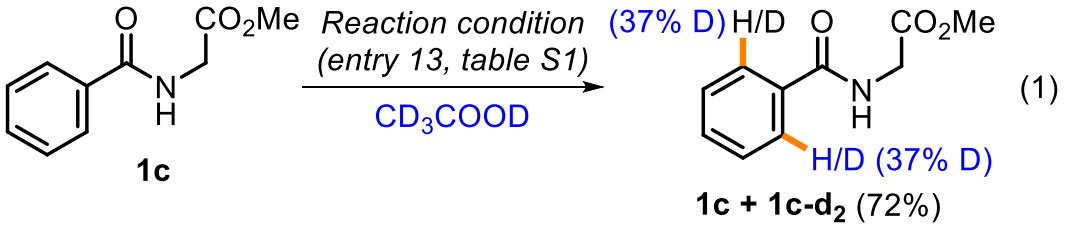


NR

[a]Standard condition: **1** (0.2 mmol), **2a** (0.4 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (2.5 mol %), $AgSbF_5$ (10 mol %), $Cu(OAc)_2$•H_2O (50 mol %), TCE (1 mL) at 120 °C for 4 h in pressure tube, celite filter after **3** formation then **4** and additional TCE (0.5 mL) at rt for 4 h in pressure tube, isolated yield by flash column chromatography, NR = no reaction, TCE = 1, 1, 2, 2-tetrachloroethane.

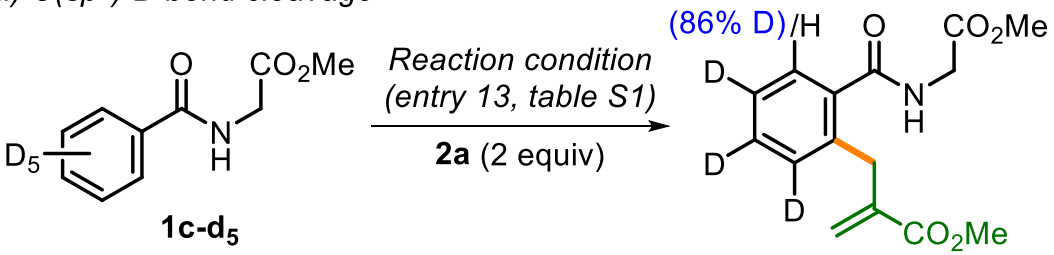
Scheme S1. Deuterium-labeling and Kinetic Isotope Effect (KIE) experiments

(i) H/D exchange experiment



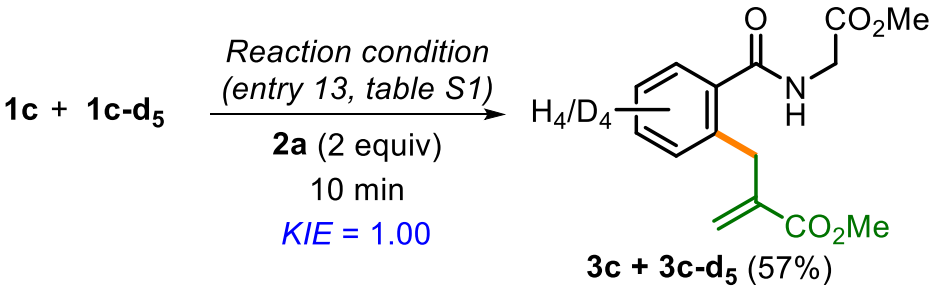
(1)

(ii) C(sp^2)-D bond cleavage



(2)

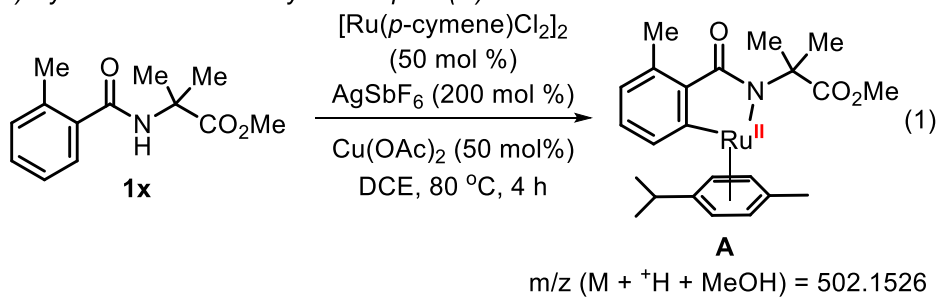
(iii) Intermolecular competition experiment



(3)

Scheme S2. Complex characterization and controlled reactions study

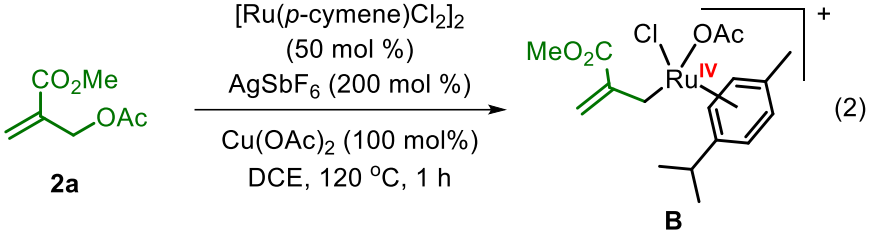
*(a) Synthesis of ruthanacycle complex (**A**)*



(1)

m/z (M + $^{+}$H + MeOH) = 502.1526

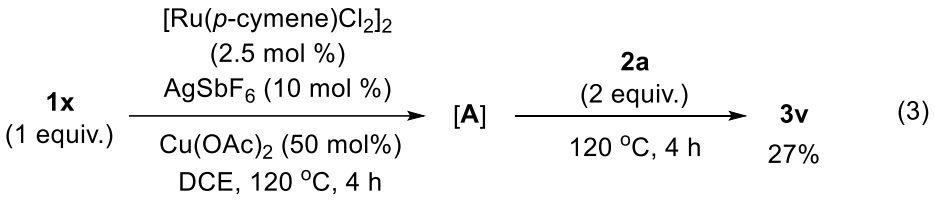
*(b) Synthesis of Ru(IV)allyl complex (**B**)*



(2)

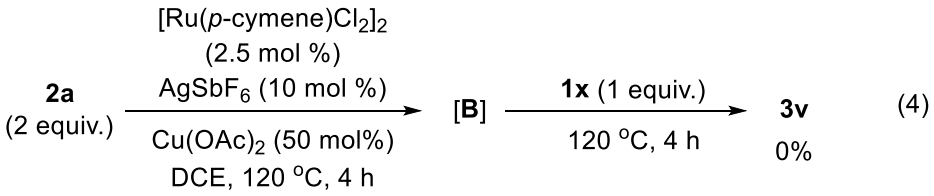
m/z (M + $^{+}$NH$_4$) = 447.0723

*(c) Reactivity of complex **A** in C(sp^2)–H allylation with **2a***



(3)

*(d) Reactivity of complex **B** in C(sp^2)–H allylation with **1x***



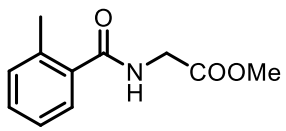
(4)

General procedure for the synthesis and characterization of starting materials 1a, 1d, 1h to 1k, 1m, 1q, 1r, 1t, 1u, 1w and 1x

Step 1: In an oven-dried screw cap sealed tube containing a magnetic stir bar, benzoic acid derivative (4 mmol, 100 mol %) was dissolved in toluene (4.5 mL) and thionyl chloride (20 mmol, 500 mol %) and DMF (150 µL) were added to the reaction mixture at room temperature. The reaction mixture was allowed to stir at 115 °C for 5 h. The reaction mixture was cooled to room temperature and resulting reaction mixture was concentrated in rotary evaporation. The residue was directly used in the next step 2.

Step 2: Glycine methyl ester hydrochloride (4.8 mmol, 120 mol %) and a magnetic bead were added to the crude mixture of step 1 in open atmosphere. Mouth of round bottom flask was closed with a septum and degassed with N_2 gas balloon followed by addition of dry DCM (10 mL). The reaction mixture is transferred to ice bath followed by dropwise addition of triethylamine (8 mmol, 200 mol %) to the mixture. Ice bath was removed and the reaction mixture was stirred at room temperature. Reaction progress was monitored on TLC. After the completion of the reaction, the reaction mixture was diluted with DCM (20 mL) and the combined organic layer was washed with saturated $NaHCO_3$ (10 mL). Organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (EtOAc/*n*-hexane = 1:1) using silica gel (230-400 MS) to afford the desired starting material **1**.

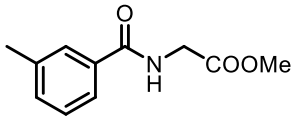
Methyl (2-methylbenzoyl)glycinate (1a)



1a

678 mg (82%); Sticky liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.4 Hz, 1H), 7.33 – 7.27 (m, 1H), 7.22 – 7.14 (m, 2H), 6.48 (s, 1H), 4.20 – 4.12 (m, 2H), 3.75 (d, *J* = 1.4 Hz, 3H), 2.42 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.4, 170.2, 136.4, 135.5, 131.1, 130.2, 127.0, 125.8, 52.4, 41.5, 19.8; **IR** (KBr) υ 3278, 2956, 2856, 1750, 1643, 1203, 976 cm^{-1}; **HRMS** (ESI) $C_{11}H_{14}NO_3$ $[M+H]^+$ calcd for 208.0974, found 208.0968.

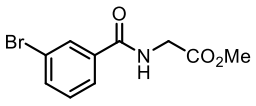
Methyl (3-methylbenzoyl)glycinate (1d)



1d

521 mg (63%); Sticky liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.58 (t, *J* = 4.3 Hz, 1H), 7.30 (dd, *J* = 3.4, 1.8 Hz, 2H), 4.22 (d, *J* = 5.0 Hz, 2H), 3.77 (s, 3H), 2.37 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.6, 167.8, 138.4, 133.6, 132.5, 128.4, 127.8, 124.1, 52.3, 41.7, 21.3; **IR** (KBr) υ 3333, 3017, 1747, 1649, 1213, 743 cm^{-1}; **HRMS** (ESI) $C_{11}H_{14}NO_3$ $[M+H]^+$ calcd for 208.0974, found 208.0968.

Methyl (3-bromobenzoyl)glycinate (1h)

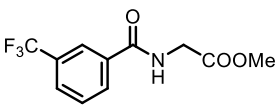


1h

964 mg (89%); sticky colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95 (t, *J* = 1.8 Hz, 1H), 7.72 (ddd, *J* = 7.8, 1.5, 1.1 Hz, 1H), 7.63 (ddd, *J* = 8.0, 1.9, 1.0 Hz, 1H), 7.31 (t, *J* = 7.9 Hz, 1H), 6.75 (br, s, 1H), 4.23 (d, *J* = 5.1 Hz, 2H), 3.80 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.4, 166.2, 135.5, 134.7, 130.4, 130.1, 125.7, 122.7, 52.5, 41.8; **IR** υ 3321, 1745, 1647, 1535, 1209, 1008, 750, 680 cm^{-1}; **HRMS** (ESI) calcd for $C_{10}H_{11}BrNO_3$ $[M+H]^+$ 271.9922, found 271.9918.

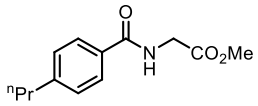
Methyl (3-(trifluoromethyl)benzoyl)glycinate (1i)

459 mg (44%); White solid; mp =89 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 6.93 (s, 1H), 4.24 (d, *J* = 5.2 Hz, 2H), 3.80 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.5, 166.2, 134.5, 131.3 (q, *J* = 32.9 Hz), 130.4, 129.3, 128.5 (d, *J* = 3.3 Hz), 124.3 (d, *J* = 3.6 Hz), 123.7 (q, J_{C-F} = 272.6 Hz), 52.7, 41.9; **IR** (KBr) υ 3328, 2953, 1736, 1645, 1112, 759 cm^{-1}; **HRMS** (ESI) $C_{11}H_{11}F_3NO_3$ $[M+H]^+$ calcd for 262.0691, found 262.0686.



1i

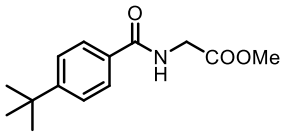
Methyl (4-propylbenzoyl)glycinate (1j)



1j

620 mg (66%); sticky colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 6.95 (br, s, 1H), 4.19 (d, *J* = 5.1 Hz, 2H), 3.74 (s, 3H), 2.90 – 2.47 (m, 2H), 1.75 – 1.41 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 170.7, 167.6, 147.0, 131.1, 128.7, 127.2, 52.5, 41.8, 37.9, 24.4, 13.8; **IR** υ 3018, 1746, 1652, 1500, 1214, 979, 743, 666 cm^{-1}; **HRMS** (ESI) calcd for $C_{13}H_{18}NO_3$ $[M+H]^+$ 236.1287, found 236.1281.

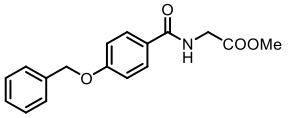
Methyl (4-(tert-butyl)benzoyl)glycinate (1k)



1k

916 mg (92%); White solid; mp =92 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77 – 7.72 (m, 2H), 7.47 – 7.42 (m, 2H), 6.69 (s, 1H), 4.24 (d, *J* = 5.1 Hz, 2H), 3.79 (s, 3H), 1.33 (s, 10H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.7, 167.5, 155.4, 130.8, 127.0, 125.6, 52.5, 41.7, 35.0, 31.2; **IR** (KBr) υ 3253, 2957, 1730, 1609, 1248, 1012, 852 cm^{-1}; **HRMS** (ESI) $C_{14}H_{20}NO_3$ $[M+H]^+$ calcd for 250.1443, found 250.1437.

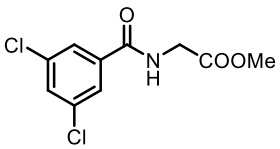
Methyl (4-(benzyloxy)benzoyl)glycinate (1m)



1m

885 mg (74%); yellow solid; mp =115 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.9 Hz, 2H), 7.45 – 7.32 (m, 4H), 7.03 – 6.96 (m, 2H), 6.64 (s, 1H), 5.11 (s, 2H), 4.23 (d, *J* = 5.1 Hz, 2H), 3.79 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.8, 167.0, 161.6, 136.4, 129.0, 128.7, 128.3, 127.5, 126.2, 114.8, 70.2, 52.5, 41.8**; IR** (KBr) υ 3674, 3299, 2946, 1739, 1605, 1245, 751 cm^{-1}; **HRMS** (ESI) $C_{17}H_{18}NO_4$ $[M+H]^+$ calcd for 300.1236, found 300.1229.

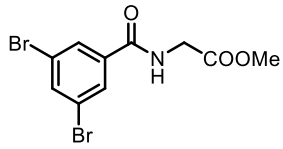
Methyl (3,5-dichlorobenzoyl)glycinate (1q)



1q

897 mg (86%); White solid; mp =91 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 1.9 Hz, 2H), 7.47 (t, *J* = 1.9 Hz, 1H), 6.90 (s, 1H), 4.21 (d, *J* = 5.2 Hz, 2H), 3.79 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.3, 165.1, 136.5, 135.5, 131.7, 125.8, 52.7, 41.8; **IR** (KBr) υ 3290, 2954, 1741, 1539, 1207, 763 cm^{-1}; **HRMS** (ESI) $C_{10}H_{10}Cl_2NO_3$ $[M+H]^+$ calcd for 262.0038, found 262.0033.

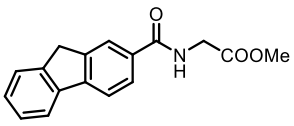
Methyl (3,5-dibromobenzoyl)glycinate (1r)



1r

1.2 g (86%); White solid; mp =105 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 1.7 Hz, 2H), 7.77 (t, *J* = 1.7 Hz, 1H), 6.91 (s, 1H), 4.20 (d, *J* = 5.2 Hz, 2H), 3.79 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.3, 164.9, 137.1, 136.8, 129.1, 123.2, 52.7, 41.8.; **IR** (KBr) υ 3277, 2952, 1740, 1629, 1205, 732 cm-^{1}; **HRMS** (ESI) $C_{10}H_{10}Br_2NO_3$ $[M+H]^+$ calcd for 349.9027, found 349.9021.

Methyl (9H-fluorene-2-carbonyl)glycinate (1t)

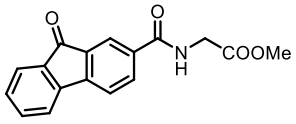


1t

663 mg (59%); White solid; mp =147 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 0.7 Hz, 1H), 7.85 – 7.77 (m, 3H), 7.56 (dd, *J* = 6.6, 0.8 Hz, 1H), 7.44 – 7.32 (m, 2H), 6.80 (s, 1H), 4.28 (d, *J* = 5.1 Hz, 2H), 3.92 (s, 2H), 3.82 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.8, 167.8, 145.4, 144.2, 143.6, 140.7, 131.9, 127.8, 127.1, 126.1, 125.3,

124.1, 120.7, 119.9, 52.6, 41.9, 37.0; **IR** (KBr) υ 3289, 2955, 1744, 1647, 1540, 1213, 760 cm^{-1}; **HRMS** (ESI) $C_{17}H_{16}NO_3$ $[M+H]^+$ calcd for 282.1130, found 282.1126.

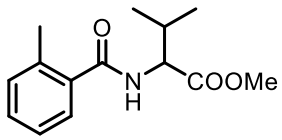
Methyl (9-oxo-9H-fluorene-2-carbonyl)glycinate (1u)



1u

790 mg (67%); yellow solid; mp =170 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 – 7.99 (m, 2H), 7.68 (d, *J* = 7.4 Hz, 1H), 7.55 (dt, *J* = 14.7, 7.6 Hz, 3H), 7.36 (t, *J* = 7.3 Hz, 1H), 6.86 (s, 1H), 4.27 (d, *J* = 5.1 Hz, 2H), 3.81 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.8, 170.4, 166.2, 147.6, 143.5, 135.1, 134.7, 134.6, 134.4, 134.4, 130.1, 124.8, 122.3, 121.2, 120.7, 52.7, 41.9; **IR** (KBr) υ 3405, 2956, 1734, 1656, 1530, 1220, 744 cm^{-1}; **HRMS** (ESI) $C_{17}H_{14}NO_4$ $[M+H]^+$ calcd for 296.0923, found 296.0917.

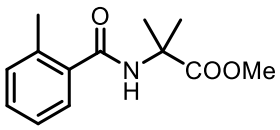
Methyl (2-methylbenzoyl)valinate (1w)



1w

866 mg (87%); Sticky liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 1H), 7.32 (td, *J* = 7.6, 1.4 Hz, 1H), 7.24 – 7.18 (m, 2H), 6.27 (d, *J* = 8.4 Hz, 1H), 4.77 (dd, *J* = 8.9, 4.8 Hz, 1H), 3.77 (s, 3H), 2.45 (s, 3H), 2.32 – 2.22 (m, 1H), 1.03 (d, *J* = 6.9 Hz, 3H), 0.95 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.5, 169.9, 136.2, 136.0, 131.0, 130.1, 126.8, 125.7, 57.3, 52.2, 31.3, 19.8, 19.1, 17.8; **IR** (KBr) υ 3361, 2926, 1721, 1656, 1209, 752 cm^{-1}; **HRMS** (ESI) $C_{14}H_{20}NO_3$ $[M+H]^+$ calcd for 250.1443, found 250.1437.

Methyl 2-methyl-2-(2-methylbenzamido)propanoate (1x)



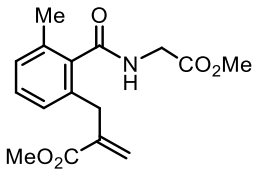
1x

705 mg (75%); White solid; mp =95 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.6 Hz, 1H), 7.29 (td, *J* = 7.5, 1.4 Hz, 1H), 7.21 – 7.15 (m, 2H), 6.33 (s, 1H), 3.76 (s, 3H), 2.43 (s, 3H), 1.64 (s, 7H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.0, 169.5, 136.3, 136.1, 130.9, 129.8, 126.8, 125.6, 56.7, 52.6, 24.9, 19.6; **IR** (KBr) υ s3267, 2991, 1736, 1630, 1151, 726 cm-^{1}; **HRMS** (ESI) $C_{13}H_{18}NO_3$ $[M+H]^+$ calcd for 236.1287, found 236.1281.

General procedure for the synthesis and characterization of C(sp^2)–H allylated intermediate (3a, 3x and 3z)

To an oven-dried screw cap sealed tube charged with methyl *N*-aroyl aminoester or *N*-alkyl arylamide (**1**) (0.2 mmol, 100 mol%), [Ru(*p*-cymene) $Cl_2]_2$ (3.05 mg, 0.005 mmol, 2.5 mol%), $AgSbF_6$ (6.8 mg, 0.02 mmol, 10 mol%), $Cu(OAc)_2{\cdot}H_2O$ (19.96 mg, 0.10 mmol, 50 mol%), TCE (1 mL) and methyl 2-(acetoxymethyl) acrylate (**2a**) (63.2 mg, 0.4 mmol, 200 mol%) were added under air at room temperature. The reaction mixture was allowed to stir at 120 °C for 4 h. Reaction mixture was cooled to room temperature, diluted with dichloromethane (2 mL) and concentrated at reduced pressure. The residue was purified by flash column chromatography (EtOAc/*n*-hexane = 1:2) to afford allylated intermediate **3**.

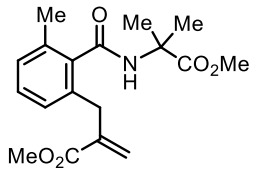
Methyl 2-(2-((2-methoxy-2-oxoethyl)carbamoyl)-3-methylbenzyl)acrylate (3a)



3a

51.0 mg (83%); white solid; mp = 84 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (t, *J* = 7.6 Hz, 1H), 7.11 (br s, 1H), 7.06 (d, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 7.7 Hz, 1H), 6.27 (s, 1H), 5.61 (s, 1H), 4.21 (d, *J* = 5.7 Hz, 2H), 3.76 (s, 3H), 3.71 (s, 2H), 3.68 (s, 3H), 2.35 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.2 (two carbons overlap), 167.4, 139.4, 136.8, 135.4, 134.9, 128.9, 128.5, 127.4, 126.3, 52.3, 52.1, 41.2, 35.4, 19.5; **IR** (KBr) υ 3311, 2957, 2346, 1755, 1722, 1659, 1214, 774, 610, 577, 535 cm^{-1}; **HRMS** (ESI) calcd for $C_{16}H_{19}NO_5$ $[M+H]^+$ 306.1341, found 306.1327.

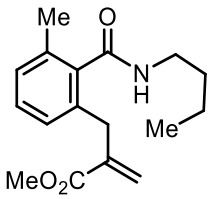
Methyl-2-(2-((2-methoxy-2-oxoethyl)carbamoyl)-3-methylbenzyl)acrylatemethyl2-(2-((1-methoxy-2-methyl-1-oxopropan-2-yl)carbamoyl)-3-methylbenzyl)acrylate (3x)



3x

45.5 mg (68%); sticky colorless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.6 Hz, 1H), 7.08 (br s, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.28 (s, 1H), 5.62 (d, *J* = 1.4 Hz, 1H), 3.76 (s, 3H), 3.73 (s, 2H), 3.71 (s, 3H), 2.35 (s, 3H), 1.61 (s, 6H)); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.9, 169.2, 167.6, 139.7, 137.1, 135.7, 134.8, 128.8, 128.6, 127.5, 126.3, 56.4, 52.5, 52.2, 35.2, 25.1, 19.3; **IR** (KBr) υ 3347, 2992, 1728, 1646, 1524, 1271, 1145, 764 cm^{-1}; **HRMS** (ESI) calcd for $C_{18}H_{25}NO_5$ $[M+H]^+$ 334.1654, found 334.1650.

Methyl 2-(2-(butylcarbamoyl)-3-methylbenzyl)acrylate (3z)



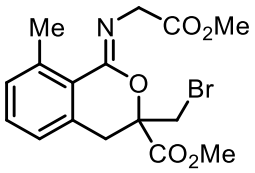
3z

33 mg (57%); white solid; mp = 93; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 7.7 Hz, 1H), 6.45 (br s, 1H), 6.26 (s, 1H), 5.58 (d, *J* = 1.3 Hz, 1H), 3.69 (s, 3H), 3.61 (s, 2H), 3.42 (td, *J* = 7.2, 6.0 Hz, 2H), 2.32 (s, 3H), 1.56 (td, *J* = 14.9, 7.4 Hz, 2H), 1.39 (qd, *J* = 14.4, 7.3 Hz, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.9, 167.4, 139.5, 138.0, 135.1, 134.6, 129.0, 128.5, 127.4, 126.4, 52.1, 39.4, 35. 6, 31.7, 20.3, 19.5, 13.8; **IR** (KBr) υ 3687, 3023, 2404, 1686, 1493, 1215, 743 cm-1 ; **HRMS** (ESI) calcd for $C_{17}H_{24}NO_3$ $[M+H]^+$ 290.1756 , found 290.1752.

General procedure for the synthesis and characterization of isochroman-1-imines (5a–5z)

To an oven-dried screw cap sealed tube charged with methyl *N*-aroyl aminoester (**1**) (0.2 mmol, 100 mol%), $[Ru(p\text{-cymene})Cl_2]_2$ (3.05 mg, 0.005 mmol, 2.5 mol%), $AgSbF_6$ (6.8 mg, 0.02 mmol, 10 mol%), $Cu(OAc)_2{\cdot}H_2O$ (19.96 mg, 0.10 mmol, 50 mol%), TCE (1 mL) and methyl 2-(acetoxymethyl) acrylate (**2**) (0.4 mmol, 200 mol %) were added under air at room temperature. The reaction mixture was allowed to stir at 120 °C for 4 h. Reaction mixture was cooled to room temperature and filtered on small celite pad with additional TCE (0.5 mL). Filtrate was collected in another screw cap sealed tube followed by addition of *N*-halogen reagent (**4**) (0.4 mmol, 200 mol%) in open atmosphere at room temperature. Reaction was further allowed to stir at room temperature for 4 h. Reaction mixture was diluted with dichloromethane (2 mL) and concentrated at reduced pressure. The residue was purified by flash column chromatography (EtOAc/*n*-hexane = 1:9) to afford isochroman-1-imines (**5**).

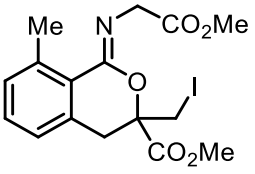
Methyl (*Z*)-3-(bromomethyl)-1-((2-methoxy-2-oxoethyl)imino)-8-methylisochromane-3-carboxylate (5a)



5a

57.5 mg, (75%); sticky colorless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 7.2 Hz, 1H), 6.96 (d, *J* = 7.0 Hz, 1H), 4.46 (d, *J* = 2.8 Hz, 2H), 3.78 (d, *J* = 10.7 Hz, 1H), 3.77 (s, 3H), 3.66 (d, *J* = 10.8 Hz, 1H), 3.60 (s, 3H), 3.26 (s, 2H), 2.71 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.9, 169.6, 152.4, 140.4, 133.0, 131.7, 130.3, 125.8, 125.2, 80.9, 53.1, 51.9, 48.8, 36.4, 35.1, 22.9; **IR** (KBr) υ 2960, 1752, 1666, 1442, 1204, 1063, 776, 684 cm^{-1}; **HRMS** (ESI) calcd for $C_{16}H_{19}BrNO_5$ $[M+H]^+$ 384.0447, found 384.0428.

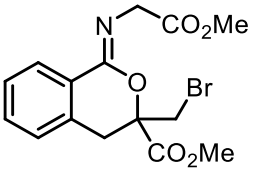
Methyl (*Z*)-3-(iodomethyl)-1-((2-methoxy-2-oxoethyl)imino)-8-methylisochromane-3-carboxylate (5b)



5b

53.5 mg, (62%); sticky colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 7.2 Hz, 1H), 4.46 (d, *J* = 4.4 Hz, 2H), 3.77 (s, 3H), 3.65 (d, *J* = 10.6 Hz, 1H), 3.58 (s, 3H), 3.49 (d, *J* = 10.6 Hz, 1H), 3.26 (d, *J* = 10.5 Hz, 2H), 2.69 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.0, 169.5, 152.5, 140.4, 133.3, 131.7, 130.3, 125.9, 125.2, 80.3, 53.20, 51.9, 49.1, 37.8, 23.1, 8.4; **IR** (KBr) υ 2953, 1751, 1661, 1435, 1201, 758 cm^{-1} ; **HRMS** (ESI) calcd for $C_{16}H_{19}INO_5$ $[M+H]^+$ 432.0308, found 432.0290.

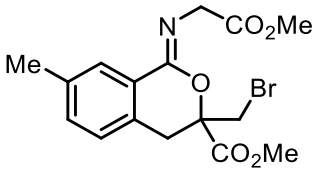
Methyl (*Z*)-3-(bromomethyl)-1-((2-methoxy-2-oxoethyl)imino)isochromane-3-carboxylate (5c)



5c

50.0 mg, (67%); sticky colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.7 Hz, 1H), 7.39 (td, *J* = 7.5, 1.4 Hz, 1H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 4.44 (d, *J* = 3.8 Hz, 2H), 3.82 (d, *J* = 10.9 Hz, 1H), 3.78 (s, 3H), 3.70 (d, *J* = 10.9 Hz, 1H), 3.64 (s, 3H), 3.31 (d, *J* = 3.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.9, 169.7, 153.2, 131.9, 131.6, 128.2, 128.1, 127.6, 126.7, 81.5, 53.4, 52.1, 48.9, 35.3, 35.1; **IR** (KBr) υ 2924, 1744, 1660, 1206, 750 cm^{-1}; **HRMS** (ESI) calcd for $C_{15}H_{17}BrNO_5$ $[M+H]^+$ 370.0290, found 370.0284.

Methyl (*Z*)-3-(bromomethyl)-1-((2-methoxy-2-oxoethyl)imino)-7-methylisochromane-3-carboxylate (5d)

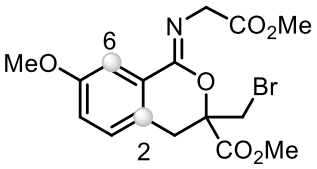


5d

58.5 mg, (76%); sticky colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 7.8 Hz, 1H), 4.45 (s, 2H), 3.82 (d, *J* = 10.9 Hz, 1H), 3.79 (s, 3H), 3.70 (d, *J* = 11.0 Hz, 1H), 3.65 (s, 3H), 3.28 (d, *J* = 4.1 Hz, 2H), 2.35 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.9, 169.8, 153.5, 138.0, 132.6, 128.9, 128.3, 127.6, 127.5, 81.6, 53.4, 52.1, 48.8, 35.4, 34.8, 21.2; **IR** (KBr) υ 2920, 2851, 1750, 1709, 1463, 1091, 724; **HRMS** (ESI) calcd for $C_{16}H_{19}BrNO_5$ $[M+H]^+$ 384.0447, found 384.0428.

Methyl (*Z*)-3-(bromomethyl)-7-methoxy-1-((2-methoxy-2-oxoethyl)imino)isochromane-3-carboxylate (5e)

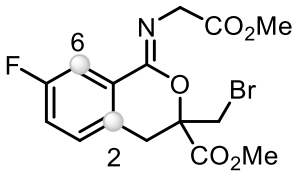
61.0 mg, (76%); white solid; mp 161 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 6.96 (dd, *J* = 8.4, 2.7 Hz, 1H), 4.44 (d, *J* = 5.9 Hz, 2H), 3.85 (s, 3H), 3.82 (d, *J* = 11.0 Hz, 1H), 3.79 (s, 3H), 3.69 (d, *J* = 10.9 Hz, 1H), 3.65 (s, 3H), 3.24 (d, *J* = 7.2 Hz, 2H); **^{13}C NMR** of **5e**(C_2) and **5e'**(C_6) (101 MHz, $CDCl_3$) δ 171.9, 171.8, 169.9, 169.7, 159.3, 155.8, 153.5, 153.3, 128.8, 128.2, 127.6, 127.5, 124.1, 120.9, 119.9, 119.8, 112.6, 110.6, 81.7, 81.3, 55.7, 55.7, 53.4 (two carbons overlap), 52.0 (two carbons overlap), 48.9, 48.8, 35.6, 35.3, 34.4, 28.9; **IR** (KBr) υ 2956, 1737, 1593, 1288, 1046, 768 cm^{-1}; **HRMS** (ESI) calcd for $C_{16}H_{19}BrNO_6$ $[M+H]^+$ 400.0396, found 400.0377.



5e(C_2) and 5e'(C_6)
5e:5e' = 1:1

Methyl (*Z*)-3-(bromomethyl)-7-fluoro-1-((2-methoxy-2-oxoethyl)imino)isochromane-3-carboxylate (5f)

57.9 mg, (74%); sticky colourless liquid; **^{1}H NMR** of **5f** (C_2) (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.9 Hz, 1H), 7.31–7.27 (m, 1H), 7.13 (t, *J* = 8.6 Hz, 1H), 4.43 (d, *J* = 4.4 Hz, 2H), 3.84 (d, *J* = 11.0 Hz, 1H), 3.78 (s, 3H), 3.72 (d, *J* = 11.0 Hz, 1H), 3.67 (s, 3H), 3.54 (d, *J* = 16.4 Hz, 1H), 3.11 (d, *J* = 16.5 Hz, 1H). **^{13}C NMR** of **5f**(C_2) and **5f'**(C_6) (101 MHz, $CDCl_3$) δ 171.6 (two carbons overlap), 169.5, 169.4, 162.2 (d, $J_{C\text{-}F}$ = 246.8 Hz), 159.2 (d, $J_{C\text{-}F}$ = 246.4 Hz), 152.2 (d, $J_{C\text{-}F}$ = 3.2 Hz), 152.1 (d, $J_{C\text{-}F}$ = 3.6 Hz), 129.4 (d, $J_{C\text{-}F}$ = 7.7 Hz), 128.7 (d, $J_{C\text{-}F}$ = 8.0 Hz), 128.5 (d, $J_{C\text{-}F}$ = 4.3 Hz), 127.6 (d, $J_{C\text{-}F}$ = 2.2 Hz), 123.7 (d, $J_{C\text{-}F}$ = 3.1 Hz) (two carbons overlap), 119.6 (d, $J_{C\text{-}F}$ = 19.3 Hz), 119.0 (d, $J_{C\text{-}F}$ = 22.2 Hz), 117.9 (d, $J_{C\text{-}F}$ = 20.9 Hz), 114.6 (d, $J_{C\text{-}F}$ = 24.1 Hz), 81.6, 81.0, 53.6, 53.5, 52.0 (two carbons overlap), 48.8 (two carbons overlap), 35.2, 34.5, 28.2, 28.1; **IR** (KBr) υ 2923, 1742, 1665, 1437, 1143, 749 cm^{-1}; **HRMS** (ESI) calcd for $C_{15}H_{16}BrFNO_5$ $[M+H]^+$ 388.0196, found 388.0178.

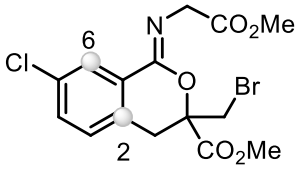


5f(C_2) and 5f'(C_6)
5f:5f' = 1:0.22

Methyl (*Z*)-3-(bromomethyl)-7-chloro-1-((2-methoxy-2-oxoethyl)imino)isochromane-3-carboxylate (5g)

40 mg, (49%); sticky colourless liquid; **IR** (KBr) υ 2923, 1744, 1663, 1207, 751 cm^{-1}; **HRMS** (ESI) calcd for $C_{15}H_{16}BrClNO_5$ $[M+H]^+$ 403.9900, found 403.9882.

5g(C_2) major: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 2.2 Hz, 1H), 7.35 (dd, *J* = 8.1, 2.2 Hz, 1H), 7.08 (d, *J* = 8.2 Hz, 1H), 4.42 (d, *J* = 6.1 Hz, 2H), 3.81 (d, *J* = 11.0 Hz, 1H), 3.79 (s, 3H), 3.70 (d, *J* = 11.0 Hz, 1H), 3.65 (s, 3H), 3.30 (d, *J* = 16.0 Hz, 1H), 3.25 (d, *J* = 16.0 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.5, 169.4, 152.0, 134.1, 131.7, 130.2, 129.0, 128.2, 127.9, 81.4, 53.5, 52.1, 48.8, 35.1, 34.5.

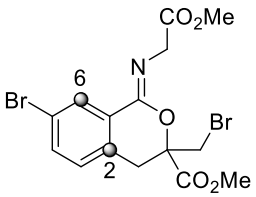


5g(C_2) and 5g'(C_6)
5g:5g' = 1:0.62

5g'(C_6) minor: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 7.5, 1H), 7.47 (d, *J* = 6.8 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 4.44 (d, *J* = 2.2 Hz, 2H), 3.86 (d, *J* = 11.0 Hz, 1H), 3.78 (s, 3H), 3.73 (d, *J* = 11.0 Hz, 1H), 3.67 (s, 3H), 3.65 (d, *J* = 16.7 Hz, 6H), 3.17 (d, J = 16.7 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.6, 169.3, 152.3, 132.9, 132.0, 130.1, 128.6 128.5, 126.6, 81.0, 53.6, 52.0, 49.0, 35.2, 32.4.

Methyl (Z)-7-bromo-3-(bromomethyl)-1-((2-methoxy-2-oxoethyl)imino)isochromane-3-carboxylate (5h)

50 mg (56%); sticky colorless liquid; **IR** (KBr) υ 2923, 1743, 1662, 1206, 752 cm^{-1}; **HRMS** (ESI) calcd for $C_{15}H_{16}Br_2NO_5$ $[M+H]^+$ 447.9395, found 447.9376

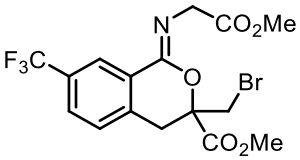


5h(C2) and 5h'(C6)
5h:5h' = 1:0.62

5h (major)**: ^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.51 (d, *J* = 6.8 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 4.43 (s, 2H), 3.83 (d, *J* = 3.0 Hz, 1H), 3.79 (s, 3H), 3.68 (s, 1H), 3.66 (s, 3H), 3.27 (s, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.5, 169.4, 152.1, 137.4, 134.7, 133.9, 129.3, 128.3, 122.0, 81.5, 53.9, 52.1, 48.8, 35.1, 34.6.
5h' (minor)**: ^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 2.0 Hz, 1H), 7.66 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.13 (d, *J* = 8.1 Hz, 1H), 4.45 (s, 2H), 3.85 (s, 1H), 3.79 (s, 3H), 3.70 (s, 1H), 3.68 (s, 3H), 3.32 (d, J = 10.9 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.5, 169.1, 161.9, 138.0, 133.1, 130.8, 129.4, 127.5, 122.3, 83.3, 53.7, 53.6, 48.8, 34.7, 34.1.

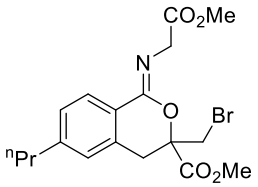
Methyl (Z)-3-(bromomethyl)-1-((2-methoxy-2-oxoethyl)imino)-7-(trifluoromethyl)isochromane-3-carboxylate (5i)

55.0 mg, (63%); sticky colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.63 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.27 (d, *J* = 8.1 Hz, 1H), 4.44 (d, *J* = 5.9 Hz, 2H), 3.83 (d, *J* = 11.0 Hz, 1H), 3.79 (s, 3H), 3.71 (d, *J* = 11.0 Hz, 1H), 3.65 (s, 3H), 3.37 (d, *J* = 5.6 Hz, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.5, 169.3, 151.9, 135.6, 130.7 (q, J_{C-F} = 33.0 Hz), 128.0 (q, J_{C-F} = 3.3 Hz), 127.5, 125.3 (q, J_{C-F} = 3.4 Hz), 123.7 (q, J_{C-F} = 273.2 Hz), 81.3, 53.6, 52.1, 48.9, 35.0, 34.9, 31.1; **IR** (KBr) υ 2923, 1746, 1667, 1269, 1125, 756 cm^{-1}; **HRMS** (ESI) calcd for $C_{16}H_{16}BrF_3NO_5$ $[M+H]^+$ 438.0164, found 438.0143.



5i

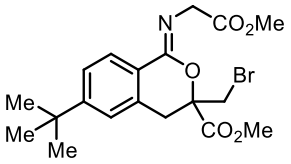
Methyl (Z)-3-(bromomethyl)-1-((2-methoxy-2-oxoethyl)imino)-6-propylisochromane-3-carboxylate (5j)



5j

62 mg (75%); sticky colorless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.29 – 7.23 (m, 1H), 6.99 (s, 1H), 4.48 (d, *J* = 1.9 Hz, 2H), 3.87 (d, *J* = 11.2 Hz, 1H), 3.77 (s, 3H), 3.74 (d, *J* = 11.2 Hz, 1H), 3.66 (s, 3H), 3.37 (d, *J* = 8.0 Hz, 2H), 2.66 – 2.55 (m, 2H), 1.62 (dd, *J* = 15.1, 7.5 Hz, 2H), 0.90 (d, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.5, 168.6, 163.3, 150.2, 135.2, 132.5, 130.4, 129.3, 127.9, 83.2, 53.8, 52.4, 46.9, 38.1, 34.8, 34.5, 24.0, 13.8; **IR** υ 2958, 2921, 1752, 1441, 1290, 1215, 1074, 749 cm^{-1}; **HRMS** (ESI) calcd for $C_{18}H_{23}BrNO_5$ $[M+H]^+$ 412.0760, found 412.0750.

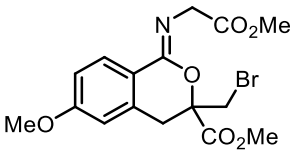
Methyl (*Z*)-3-(bromomethyl)-6-(tert-butyl)-1-((2-methoxy-2-oxoethyl)imino)isochromane-3-carboxylate (5k)



5k

63.0 mg, (74%); sticky colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.3 Hz, 1H), 7.35 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.10 (s, 1H), 4.44 (d, *J* = 4.1 Hz, 2H), 3.82 (d, *J* = 10.9 Hz, 1H), 3.78 (s, 3H), 3.70 (d, *J* = 10.9 Hz, 1H), 3.66 (s, 3H), 3.31 (d, *J* = 4.6 Hz, 2H), 1.29 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.7, 169.8, 155.6, 153.9, 131.7, 128.0, 125.5, 124.3, 123.5, 81.7, 53.4, 52.1, 48.6, 35.4, 35.3, 35.1, 31.2; **IR** (KBr) υ 2923, 1741, 1662, 1206, 755 cm^{-1}; **HRMS** (ESI) $C_{19}H_{25}BrNO_5$ $[M+H]^+$ calcd for 426.0916, found 426.0897.

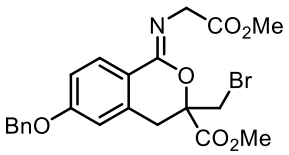
Methyl (*Z*)-3-(bromomethyl)-6-methoxy-1-((2-methoxy-2-oxoethyl)imino)isochromane-3-carboxylate (5l)



5l

58.0 mg, (72%); sticky colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.8 Hz, 1H), 6.84 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.60 (d, *J* = 2.5 Hz, 1H), 4.41 (d, *J* = 4.1 Hz, 2H), 3.82 (s, 3H), 3.79 (d, *J* = 10.9 Hz, 1H), 3.77 (s, 3H), 3.68 (d, *J* = 10.9 Hz, 1H), 3.65 (s, 3H), 3.27 (d, *J* = 2.1 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.0, 169.7, 162.2, 153.3, 133.9, 130.2, 119.2, 114.1, 112.3, 81.4, 55.5, 53.4, 52.0, 48.7, 35.3, 35.2; **IR** (KBr) υ 2954, 1747, 1663, 1438, 1202, 830 cm^{-1}; **HRMS** (ESI) calcd for $C_{16}H_{19}BrNO_6$ $[M+H]^+$ 400.0396, found 400.0376.

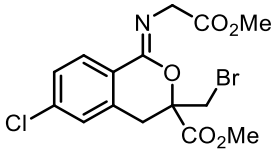
Methyl (*Z*)-6-(benzyloxy)-3-(bromomethyl)-1-((2-methoxy-2-oxoethyl)imino)isochromane-3-carboxylate (5m)



5m

71.7 mg, (75%); sticky colourless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.6 Hz, 1H), 7.44–7.33 (m, 5H), 6.93 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.69 (d, *J* = 2.4 Hz, 1H), 5.07 (d, *J* = 2.2 Hz, 2H), 4.42 (d, *J* = 4.8 Hz, 2H), 3.80 (d, *J* = 10.9 Hz, 1H), 3.78 (s, 3H), 3.69 (d, *J* = 10.9 Hz, 1H), 3.66 (s, 3H), 3.28 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.9, 169.7, 161.5, 136.3, 134.0, 130.3, 129.0, 128.8, 128.4, 127.7, 119.3, 114.9, 113.3, 81.5, 70.3, 53.5, 52.1, 48.6, 35.2 (two carbons overlap); **IR** (KBr) υ 2924, 1745, 1608, 1204, 748 cm^{-1}; **HRMS** (ESI) $C_{22}H_{23}BrNO_6$ $[M+H]^+$ calcd for 476.0709, found 476.0689.

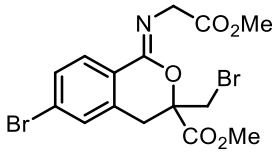
Methyl (*Z*)-3-(bromomethyl)-6-chloro-1-((2-methoxy-2-oxoethyl)imino)isochromane-3-carboxylate (5n)



5n

61.0 mg, (75%); sticky colourless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.5 Hz, 1H), 7.29 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.13 (d, *J* = 1.7 Hz, 1H), 4.41 (d, *J* = 4.6 Hz, 2H), 3.81 (d, *J* = 11.0 Hz, 1H), 3.78 (s, 3H), 3.69 (d, *J* = 11.0 Hz, 1H), 3.66 (s, 3H), 3.28 (s, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.7, 168.4, 151.3, 136.7, 132.6, 128.7, 127.5, 126.6, 124.3, 80.3, 52.6, 51.1, 47.8, 34.1, 33.8; **IR** (KBr) υ 2923, 1742, 1663, 1208, 752 cm^{-1}; **HRMS** (ESI) $C_{15}H_{16}BrClNO_5$ $[M+H]^+$ calcd for 403.9900, found 403.9882.

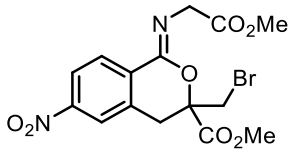
Methyl (*Z*)-6-bromo-3-(bromomethyl)-1-((2-methoxy-2-oxoethyl)imino)isochromane-3-carboxylate (5o)



5o

67.0 mg, (52%); white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.5 Hz, 1H), 7.45 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.30 (d, *J* = 1.5 Hz, 1H), 4.40 (d, *J* = 2.9 Hz, 2H), 3.81 (d, *J* = 11.0 Hz, 1H), 3.78 (s, 3H), 3.69 (d, *J* = 11.0 Hz, 1H), 3.66 (s, 3H), 3.28 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.7, 169.4, 152.4, 133.8, 131.4, 130.5, 129.8, 126.2, 125.7, 81.4, 53.6, 52.1, 48.8, 35.1, 34.7; **IR** (KBr) υ 2955, 1753, 1668, 1438, 1203, 834 cm^{-1}; **HRMS** (ESI) $C_{15}H_{16}Br_2NO_5$ $[M+H]^+$ calcd for 447.9395, found 447.9376.

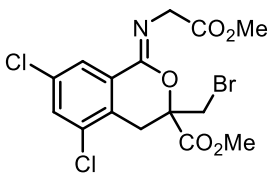
Methyl (*Z*)-3-(bromomethyl)-1-((2-methoxy-2-oxoethyl)imino)-6-nitroisochromane-3-carboxylate (5p)



5p

45.0 mg, (54%); sticky colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.7 Hz, 1H), 8.15 (dd, *J* = 8.7, 2.3 Hz, 1H), 8.04 (d, *J* = 2.1 Hz, 1H), 4.46 (d, *J* = 1.8 Hz, 2H), 3.86 (d, *J* = 11.0 Hz, 1H), 3.80 (s, 3H), 3.74 (d, *J* = 11.1 Hz, 1H), 3.67 (s, 3H), 3.43 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.3, 169.0, 151.4, 149.5, 133.4, 132.4, 129.7, 123.0, 122.9, 81.4, 53.8, 52.2, 49.1, 35.0, 34.8; **IR** (KBr) υ 2924, 1747, 1666, 1530, 1209, 759 cm^{-1}; **HRMS** (ESI) $C_{15}H_{16}BrN_2O_7$ $[M+H]^+$ calcd for 415.0141, found 415.0121.

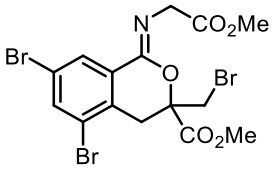
Methyl (*Z*)-3-(bromomethyl)-5,7-dichloro-1-((2-methoxy-2-oxoethyl)imino)isochromane-3-carboxylate (5q)



5q

47.4 mg, (54%); sticky colourless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 2.1 Hz, 1H), 7.46 (d, *J* = 2.1 Hz, 1H), 4.42 (d, *J* = 3.8 Hz, 2H), 3.85 (d, *J* = 11.0 Hz, 1H), 3.78 (s, 3H), 3.72 (d, *J* = 11.0 Hz, 1H), 3.68 (s, 3H), 3.59 (d, *J* = 16.7 Hz, 1H), 3.11 (d, *J* = 16.8 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.4, 169.2, 151.3, 134.3, 133.7, 131.8, 129.7, 128.6, 126.7, 81.0, 53.7, 52.2, 49.0, 35.0, 32.1; **IR** (KBr) υ 2923, 1747, 1667, 1182, 755 cm^{-1}; **HRMS** (ESI) $C_{15}H_{15}BrCl_2NO_5$ $[M+H]^+$calcd for 437.9511, found 437.9491.

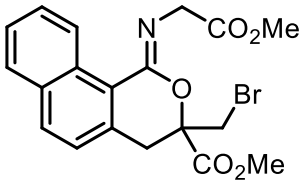
Methyl (*Z*)-3-(bromomethyl)-5,7-dibromo-1-((2-methoxy-2-oxoethyl)imino)isochromane-3-carboxylate (5r)



5r

53.8 mg, (51%); sticky colourless liquid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.35 (d, *J* = 1.9 Hz, 1H), 7.78 (d, *J* = 2.0 Hz, 1H), 4.42 (d, *J* = 0.7 Hz, 2H), 3.85 (d, *J* = 11.1 Hz, 1H), 3.78 (s, 3H), 3.71 (d, *J* = 11.1 Hz, 1H), 3.69 (s, 3H), 3.56 (d, *J* = 16.7 Hz, 1H), 3.09 (d, *J* = 16.7 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.4, 169.1, 151.3, 137.5, 130.8, 130.2, 130.1, 123.8, 122.2, 81.1, 53.7, 52.2, 49.1, 35.0, 34.8; **IR** (KBr) υ 2925, 1747, 1667, 1213, 749 cm^{-1}; **HRMS** (ESI) $C_{15}H_{15}Br_3NO_5$ $[M+H]^+$ calcd for 525.8500, found 525.8477.

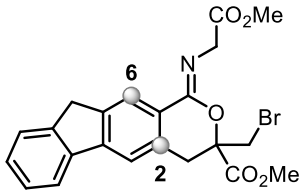
Methyl (*Z*)-3-(bromomethyl)-1-((2-methoxy-2-oxoethyl)imino)-3,4-dihydro-1H-benzo[h]isochromene-3-carboxylate (5s)



5s

35.5 mg, (42%); sticky colourless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.53 (d, *J* = 8.7 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.66 (ddd, *J* = 8.5, 6.9, 1.3 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 8.3 Hz, 1H), 4.65 (d, *J* = 18.5 Hz, 1H), 4.55 (d, *J* = 18.5 Hz, 1H), 3.85 (d, *J* = 10.9 Hz, 1H), 3.82 (s, 3H), 3.75 (d, *J* = 10.9 Hz, 1H), 3.56 (s, 3H), 3.49 (d, *J* = 16.0 Hz, 1H), 3.44 (d, *J* = 15.9 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.9, 169.7, 152.3, 133.8, 132.8, 132.6, 130.9, 128.4 (two carbons overlap), 127.3, 126.3, 125.0, 122.5, 80.6, 53.4, 52.1, 49.1, 36.6, 35.1; **IR** (KBr) υ 2954, 2924, 1747, 1657, 1202, 755 cm^{-1}; **HRMS**(ESI) $C_{19}H_{19}BrNO_5$ $[M+H]^+$ calcd for 420.0447, found 420.0426.

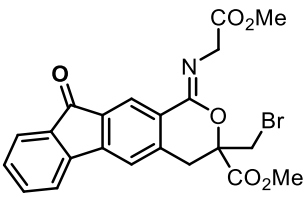
Methyl (*Z*)-3-(bromomethyl)-1-((2-methoxy-2-oxoethyl)imino)-1,3,4,10-tetrahydroindeno[1,2-g]isochromene-3-carboxylate (5u)



5t(C_2) and 5t'(C_6)
5t:5t' = 1:0.33

54.0 mg, (59%); sticky colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.76 (d, *J* = 6.7 Hz, 1H), 7.56 (d, *J* = 6.8 Hz, 1H), 7.51 (s, 1H), 7.44–7.32 (m, 2H), 4.47 (d, *J* = 1.1 Hz, 2H), 3.90 (s, 2H), 3.86 (d, *J* = 10.9 Hz, 1H), 3.80 (s, 3H), 3.74 (d, *J* = 10.9 Hz, 1H), 3.64 (s, 3H), 3.44 (d, *J* = 15.7 Hz, 1H), 3.38 (d, *J* = 15.7 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.0, 169.8, 154.0, 145.2, 144.5, 143.0, 140.4, 130.9, 128.1, 127.3, 127.1, 125.4, 124.6, 120.7, 118.8, 81.6, 53.4, 52.1, 48.9, 36.8, 35.6, 35.3; **IR**(KBr) υ 2924, 1744, 1618, 1438, 1207, 748 cm^{-1}; **HRMS** (ESI) $C_{22}H_{21}BrNO_5$ $[M+H]^+$ calcd for 458.0603, found 458.0583.

Methyl (*Z*)-3-(bromomethyl)-1-((2-methoxy-2-oxoethyl)imino)-10-oxo-1,3,4,10-tetrahydroindeno[1,2-g]isochromene-3-carboxylate (5u)

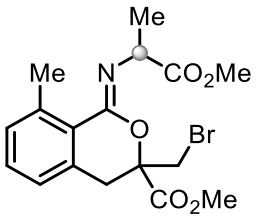


5u
5u:5u' = 1:0.33

26.0 mg, (27%); sticky colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.69 (d, *J* = 7.4 Hz, 1H), 7.52 (m, 2H), 7.36 (td, *J* = 7.2, 1.7 Hz, 1H), 7.31 (s, 1H), 4.44 (d, *J* = 2.9 Hz, 2H), 3.84 (d, *J* = 10.9 Hz, 1H), 3.80 (s, 3H), 3.73 (d, *J* = 11.0 Hz, 1H), 3.67 (s, 3H), 3.43 (d, *J* = 16.3 Hz, 1H), 3.35 (d, *J* = 16.2 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 13C NMR (101 MHz, CDCl3) δ 192.2, 171.6, 169.5, 152.2, 146.6, 143.3, 138.9, 135.0, 134.9, 134.1, 130.2, 127.7, 124.7, 124.6, 121.0, 119.7, 81.2, 53.6, 52.2, 49.0, 35.8, 35.1; **IR** (KBr) υ 2954, 1748, 1620, 1441, 1207, 761 cm^{-1}; **HRMS**(ESI) $C_{22}H_{19}BrNO_6$ $[M+H]^+$ calcd for 472.0396, found 472.0376.

Methyl (*Z*)-3-(bromomethyl)-1-((1-methoxy-1-oxopropan-2-yl)imino)-8-methylisochromane-3-carboxylate (5v)

55.0mg, (69%); sticky colourless liquid; **IR** (KBr) υ 2955, 1737, 1658, 1437, 1199, 1055, 758 cm^{-1}; **HRMS**(ESI) $C_{17}H_{21}BrNO_5$ $[M+H]^+$ calcd for 398.0603, found 398.0583.

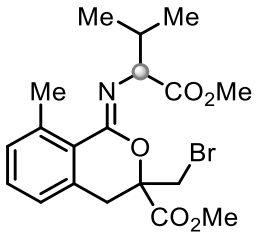


5v
dr = 1.14:1

5v (major): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (m, 2H), 6.94 (m, 1H), 4.81 (m, 1H), 3.76 (d, *J* = 10.8 Hz, 1H), 3.73 (s, 3H), 3.63 (d, *J* = 10.8 Hz, 1H), 3.59 (s, 3H), 2.67 (s, 2H), 2.67 (s, 3H), 1.56 (d, J = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.8, 169.7, 151.2, 140.4, 133.2, 131.8, 130.2, 126.0, 125.3, 80.9, 54.5, 53.1, 52.0, 36.6, 35.2, 23.3, 19.3.
5v (minor): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (m, 2H), 6.94 (m, 1H), 4.81 (m, 1H), 3.77 (d, *J* = 10.8 Hz, 1H), 3.75 (s, 3H), 3.65 (d, *J* = 10.9 Hz, 1H), 3.59 (s, 3H), 3.25 (d, *J* = 2.7 Hz, 2H), 2.69 (s, 3H), 1.50 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.7, 169.6, 150.9, 140.5, 133.1, 131.7, 130.3, 126.0, 125.4, 80.9, 54.4, 53.3, 51.9, 36.4, 35.2, 22.9, 19.1.

Methyl (*Z*)-3-(bromomethyl)-1-((1-methoxy-3-methyl-1-oxobutan-2-yl)imino)-8-methylisochromane-3-carboxylate (5w)

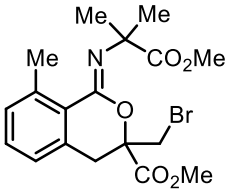
53.0mg, (62%); sticky colourless liquid; **IR** (KBr) υ 2960, 1736, 1659, 1464, 1197 1055, 758 cm^{-1}; **HRMS**(ESI) $C_{19}H_{25}BrNO_5$ $[M+H]^+$ calcd for 426.0916, found 426.0899.



5w
dr = 1:0.71

5w (major): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25–7.13 (m, 2H), 6.94 (d, *J* = 7.2 Hz, 1H), 4.56 (d, *J* = 4.9 Hz, 1H), 3.75 (d, *J* = 10.7 Hz, 1H), 3.72 (s, 3H), 3.60 (d, *J* = 10.6 Hz, 1H), 3.57 (s, 3H), 3.22 (s, 2H), 2.70 (s, 3H), 2.37–2.20 (m, 1H), 1.08 (d, *J* = 2.2 Hz, 3H), 1.06 (d, *J* = 2.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.6, 169.8, 152.1, 140.3, 133.3, 131.7, 130.2, 126.3, 125.3, 80.9, 64.8, 53.1, 51.7, 36.6, 35.2, 32.3, 23.8, 20.1, 18.4.
5w (minor): **^{1}H NMR** (400 MHz, $CDCl_3$) 7.25–7.13 (m, 2H), 6.97 (d, *J* = 7.3 Hz, 1H), 4.48 (d, *J* = 5.1 Hz, 1H), 3.71 (s, 3H), 3.69 (d, *J* = 10.8 Hz, 1H), 3.62 (d, *J* = 10.6 Hz, 1H), 3.61 (s, 3H), 3.25 (d, *J* = 5.3 Hz, 2H), 2.71 (s, 3H), 2.37–2.20 (m, 1H), 1.03 (d, *J* = 6.7 Hz, 3H), 1.00 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.4, 169.6, 151.3, 140.6, 133.3, 131.7, 130.2, 126.1, 125.5, 80.9, 64.8, 53.1, 51.6, 36.1, 34.9, 32.3, 23.5, 19.9, 18.5.

Methyl (*Z*)-3-(bromomethyl)-1-((1-methoxy-2-methyl-1-oxopropan-2-yl)imino)-8-methylisochromane-3-carboxylate (5x)



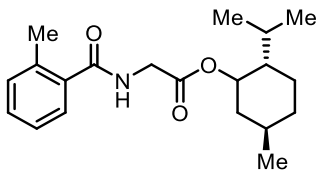
5x

53.8 mg, (65%); sticky colourless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 7.3 Hz, 1H), 3.71 (s, 3H), 3.68 (d, *J* = 10.8 Hz, 1H), 3.58 (s, 3H), 3.56 (d, *J* = 10.8 Hz, 1H), 3.22 (d, *J* = 15.3 Hz, 1H), 3.18 (d, *J* = 15.3 Hz, 1H), 2.65 (s, 3H), 1.62 (s, 3H), 1.57 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 176.7, 169.5, 149.3, 140.1, 133.2, 131.7, 130.2, 126.4, 125.3, 81.5, 60.5, 53.0, 51.9, 36.5, 34.5, 28.0, 26.4, 23.0; **IR** (KBr) υ 2951, 1733, 1661, 1436, 1143, 1054, 756, 686 cm^{-1}; **HRMS**(ESI) $C_{18}H_{23}BrNO_5$ $[M+H]^+$ calcd for 412.0760, found 412.0740.

Procedure for synthesis of (2S,5R)-2-isopropyl-5-methylcyclohexyl (2-methylbenzoyl)glycinate (1y)

step i) To an oven-dried screw cap pressure tube charged 2-methylbenzoic acid (500 mg, 3.64 mmol, 1.0 eqv.) was dissolved in 5 mL of toluene and thionyl chloride (3.19 mL, 44.04 mmol, 12 eqv.) and 3-4 drops of dimethylformamide were added to the solution and heat at 100 °C during 4 h. The liquid was evaporated under vacuum. **step ii)** The liquid obtained previously was dissolved in 5 mL of DCM and added dropwise to a mixture of (2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl glycinate (938.60 mg, 7.34 mmol, 1.2 eqv.), TEA (1.02 mL, 7.34 mmol,

2.0 eqv.) and DCM (5 mL), and stirred overnight at room temperature. The reaction mixture was filtered through silica gel and the liquid evaporated under reduced pressure. The residue was purified by flash column chromatography (EtOAc/*n*-hexane = 1:2) to afford **(1y)**, 450 mg, yield 39%.

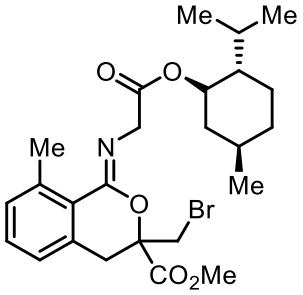


1y

450 mg, yield 38%; sticky colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.8 Hz, 1H), 7.32 (td, *J* = 7.6, 1.3 Hz, 1H), 7.22 (dd, *J* = 7.6, 2.9 Hz, 2H), 6.32 (s, 1H), 4.79 (td, *J* = 10.9, 4.4 Hz, 1H), 4.19 (d, *J* = 5.2 Hz, 2H), 2.47 (s, 3H), 2.02 (d, *J* = 11.9 Hz, 1H), 1.91– 1.83 (m, 1H), 1.69 (d, *J* = 11.6 Hz, 3H), 1.52 – 1.37 (m, 2H), 1.03 (dd, *J* = 23.2, 12.0 Hz, 2H), 0.91 (dd, *J* = 6.8, 4.4 Hz, 6H), 0.77 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 169.7, 136.5, 135.7, 131.2, 130.3, 127.1, 125.9, 76.0, 47.1, 41.9, 40.9, 34.2, 31.5, 26.4, 23.5, 22.1, 20.8, 20.0, 16.5; **IR** (KBr) υ 3303, 2954, 1738, 1650, 1521, 1200, 747 cm^{-1}; **HRMS**(ESI) $C_{20}H_{30}NO_3$ $[M+H]^+$ calcd for 332.2226, found 332.2209.

Synthesis and characterization of Methyl (*Z*)-3-(bromomethyl)-1-((2-(((2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)-2-oxoethyl)imino)-8-methylisochromane-3-carboxylate (5y)

To an oven-dried screw cap sealed tube charged with methyl (2S,5R)-2-isopropyl-5-methylcyclohexyl (2-methylbenzoyl)glycinate (**1y**) (66.29mg, 0.2 mmol, 100 mol%), $[Ru(p\text{-cymene})Cl_2]_2$ (3.05 mg, 0.005 mmol, 2.5 mol%), $AgSbF_6$ (6.8 mg, 0.02 mmol, 10 mol%), $Cu(OAc)_2 \bullet H_2O$ (19.96 mg, 0.10 mmol, 50 mol%), TCE (1 mL) and methyl 2-(acetoxymethyl) acrylate (**2**) (0.4 mmol, 200 mol %) were added under air at room temperature. The reaction mixture was allowed to stir at 120 °C for 4 h. Reaction mixture was cooled to room temperature and filtered on small celite pad with additional TCE (0.5 mL). Filtrate was collected in another screw cap sealed tube followed by addition of *N*-halogen reagent (**4**) (0.4 mmol, 200 mol%) in open atmosphere at room temperature. Reaction was further allowed to stir at room temperature for 4 h. Reaction mixture was diluted with dichloromethane (2 mL) and concentrated at reduced pressure. The residue was purified by flash column chromatography (EtOAc/*n*-hexane = 1:9) to afford isochroman-1-imines (**5y**).



5y
dr = 1:0.90

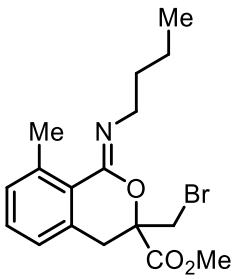
33.0 mg, (32%); sticky colourless liquid; **IR** (KBr) υ 2952, 1748, 1665, 1273, 1189, 781 cm^{-1}; **HRMS**(ESI) $C_{25}H_{35}BrNO_5$ $[M+H]^+$ calcd for 508.1699, found 508.1677.

5y (major): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (m, 2H), 6.95 (d, *J* = 7.2 Hz, 1H), 4.85–4.74 (m, 1H), 4.48–4.32 (m, 2H), 3.77 (d, *J* = 10.8 Hz, 1H), 3.65 (d, *J* = 10.8 Hz, 1H), 3.60 (s, 3H), 3.24 (s, 2H), 2.70 (s, 3H), 2.15–2.06 (m, 1H), 2.04–1.98 (m, 1H), 1.72–1.62 (m, 2H), 1.55–1.35 (m, 2H), 1.15–0.96 (m, 2H), 0.88 (d, *J* = 7.0 Hz, 6H), 0.82–0.95 (m, 1H), 0.79 (d, *J* = 1.9 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.1, 169.8, 152.1, 140.4, 133.0, 131.7, 130.2, 126.1, 125.3, 80.9, 74.5, 53.2, 49.3, 47.2, 41.1, 36.6, 35.3, 34.4, 31.5, 26.2, 23.5, 23.0, 22.2, 21.0, 16.4.

5y (minor): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (m, 2H), 6.95 (d, *J* = 7.2 Hz, 1H), 4.85–4.74 (m, 1H), 4.48–4.32 (m, 2H), 3.77 (d, *J* = 10.8 Hz, 1H), 3.66 (d, *J* = 10.8 Hz, 1H), 3.60 (s, 3H), 3.24 (s, 2H), 2.70 (s, 3H), 2.15–2.06 (m, 1H), 2.04–1.98 (m, 1H), 1.72–1.62 (m, 2H), 1.55–1.35 (m, 2H), 1.15–0.96 (m, 2H), 0.90 (d, *J* = 6.5 Hz, 6H), 0.82–0.95 (m, 1H), 0.77 (d, J = 1.9 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.0, 169.8, 152.1, 140.4, 133.0, 131.7, 130.2, 126.1, 125.3, 80.9, 74.5, 53.2, 49.4, 47.2, 41.0, 36.5, 35.3, 34.4, 31.5, 26.2, 23.5, 23.0, 22.2, 21.0, 16.4.

Synthesis and characterization of Methyl (*Z*)-3-(bromomethyl)-1-((1-methoxy-1-oxopropan-2-yl)imino)-8-methylisochromane-3-carboxylate (5z)

To an oven-dried screw cap sealed tube charged with *N*-butyl-2-methylbenzamide (**1z**) (38.25 mg, 0.2 mmol, 100 mol%), [Ru(*p*-cymene)Cl_2]$_2$ (3.05 mg, 0.005 mmol, 2.5 mol%), $AgSbF_6$ (6.8 mg, 0.02 mmol, 10 mol%), $Cu(OAc)_2 \cdot H_2O$ (19.96 mg, 0.10 mmol, 50 mol%), TCE (1 mL) and methyl 2-(acetoxymethyl) acrylate (**2**) (0.4 mmol, 200 mol %) were added under air at room temperature. The reaction mixture was allowed to stir at 120 °C for 4 h. Reaction mixture was cooled to room temperature and filtered on small celite pad with additional TCE (0.5 mL). Filtrate was collected in another screw cap sealed tube followed by addition of *N*-halogen reagent (**4**) (0.4 mmol, 200 mol %) in open atmosphere at room temperature. Reaction was further allowed to stir at room temperature for 4 h. Reaction mixture was diluted with dichloromethane (2 mL) and concentrated at reduced pressure. The residue was purified by flash column chromatography (EtOAc/*n*-hexane = 1:9) to afford isochroman-1-imines (**5z**).

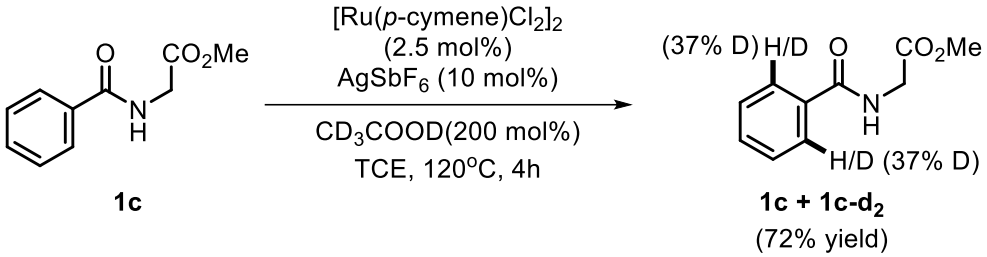


5z

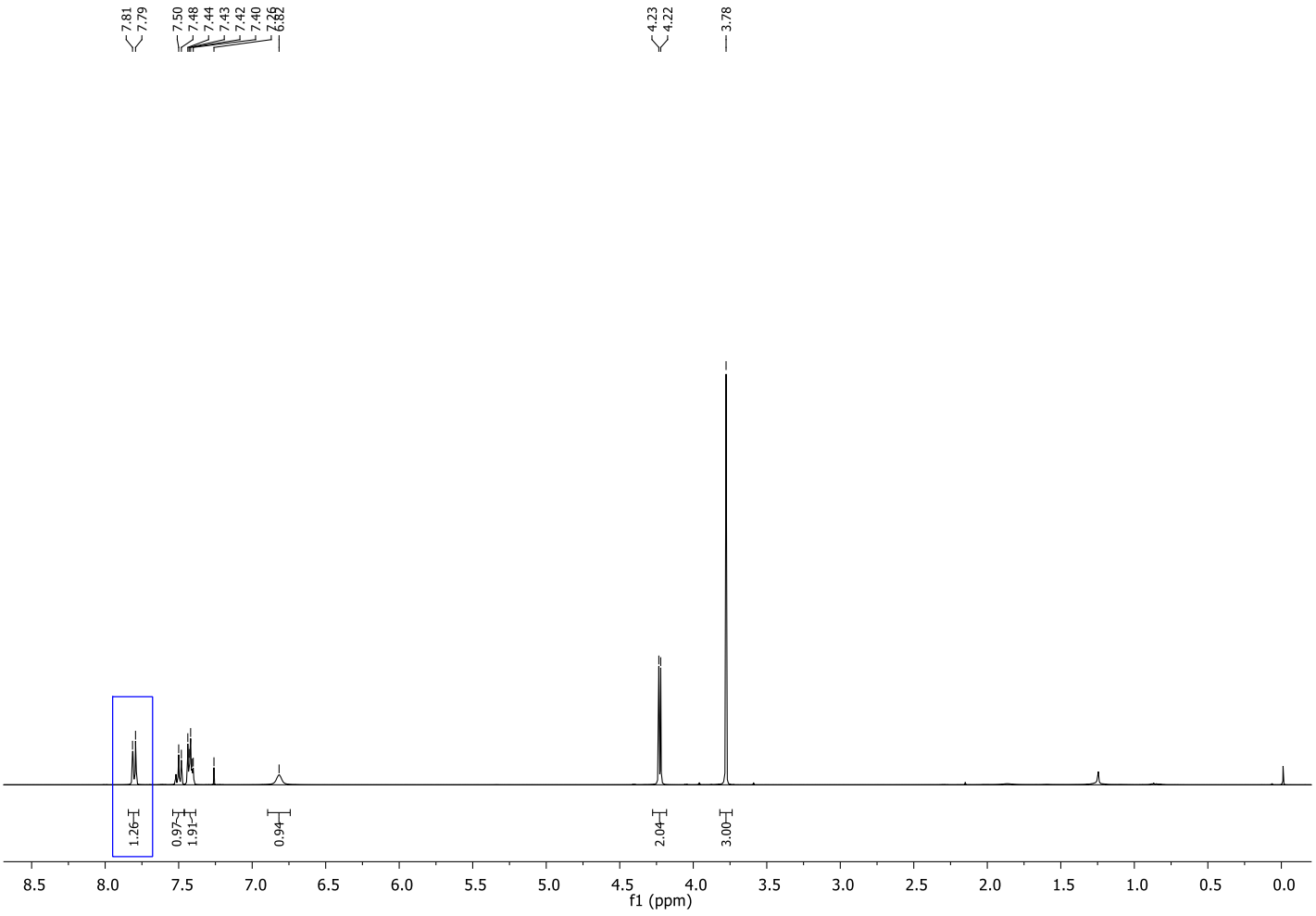
28.0 mg, (38%); sticky colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21–7.11 (m, 2H), 6.94 (d, *J* = 7.1 Hz, 1H), 3.78 (d, *J* = 10.7 Hz, 1H), 3.68 (dt, *J* = 7.0, 6.2 Hz, 1H), 3.67 (d, *J* = 10.7 Hz, 1H), 3.59 (s, 3H), 3.53 (dt, *J* = 13.8, 6.8 Hz, 1H), 3.23 (s, 2H), 2.64 (s, 3H), 1.72–1.62 (m, 2H), 1.55–1.43 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 149.4, 139.7, 133.0, 131.6, 129.7, 126.8, 125.4, 80.6, 53.1, 46.3, 36.7, 35.6, 33.2, 23.1, 21.0, 14.2; **IR** (KBr) υ 2923, 1749, 1660, 1201, 776 cm^{-1}; **HRMS**(ESI) $C_{17}H_{23}BrNO_3$ $[M+H]^+$ calcd for 368.0861, found 368.0843.

Mechanistic investigations

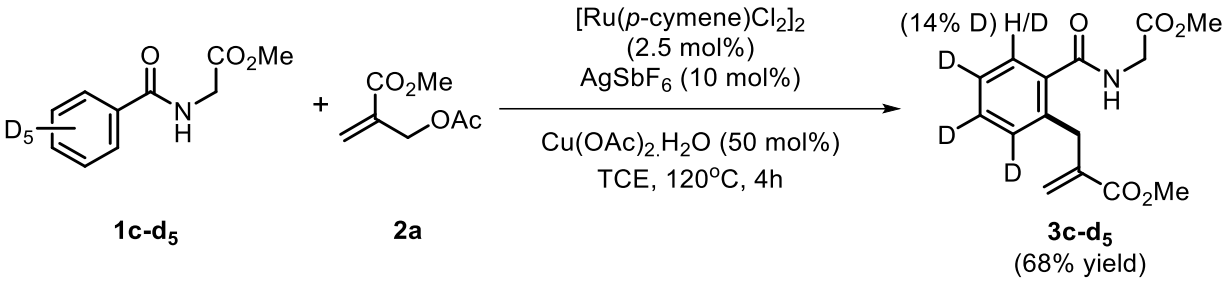
a) General procedure for H/D exchange experiment



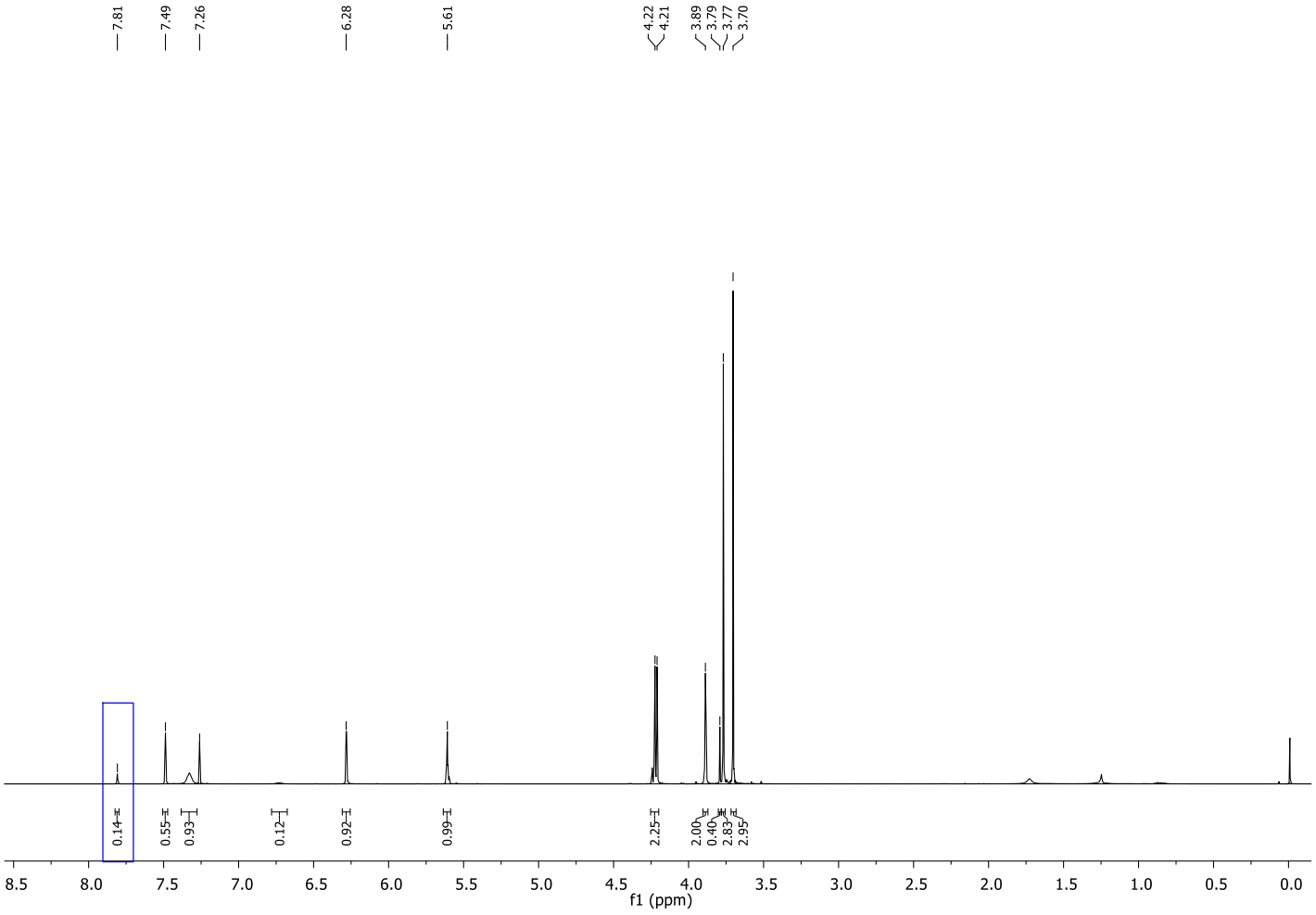
To an oven-dried screw cap sealed tube charged with methyl (2-methylbenzoyl)glycinate (**1a**) (41.4 mg, 0.2 mmol, 100 mol%), [Ru(*p*-Cymene)Cl_2]$_2$ (3.05 mg, 0.005 mmol, 2.5 mol%), $AgSbF_6$ (6.8 mg, 0.02 mmol, 10 mol%), $Cu(OAc)_2$ (19.96 mg, 0.10 mmol, 50 mol%), TCE (1 mL) and acetic acid-D4 (25.6 mg, 0.4 mmol, 200 mol %) under air at room temperature. The reaction mixture was allowed to stir at 120 °C for 4 h. Reaction tube was cooled to room temperature and diluted with dichloromethane (2 mL) and concentrated at reduced pressure. The residue was purified by flash column chromatography (EtOAc/*n*-hexane = 1:3) to afford mixture of **1c** and **1c-d$_2$** (28.2 mg, 72%) as white solid with 37% D incorporation at the *ortho*-positions.



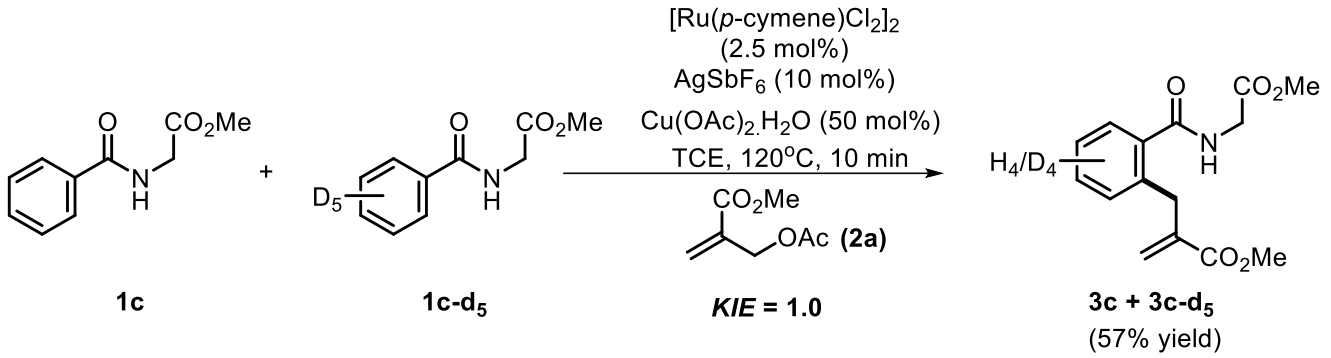
b) General procedure for C(sp^2)-D bond allylation reaction



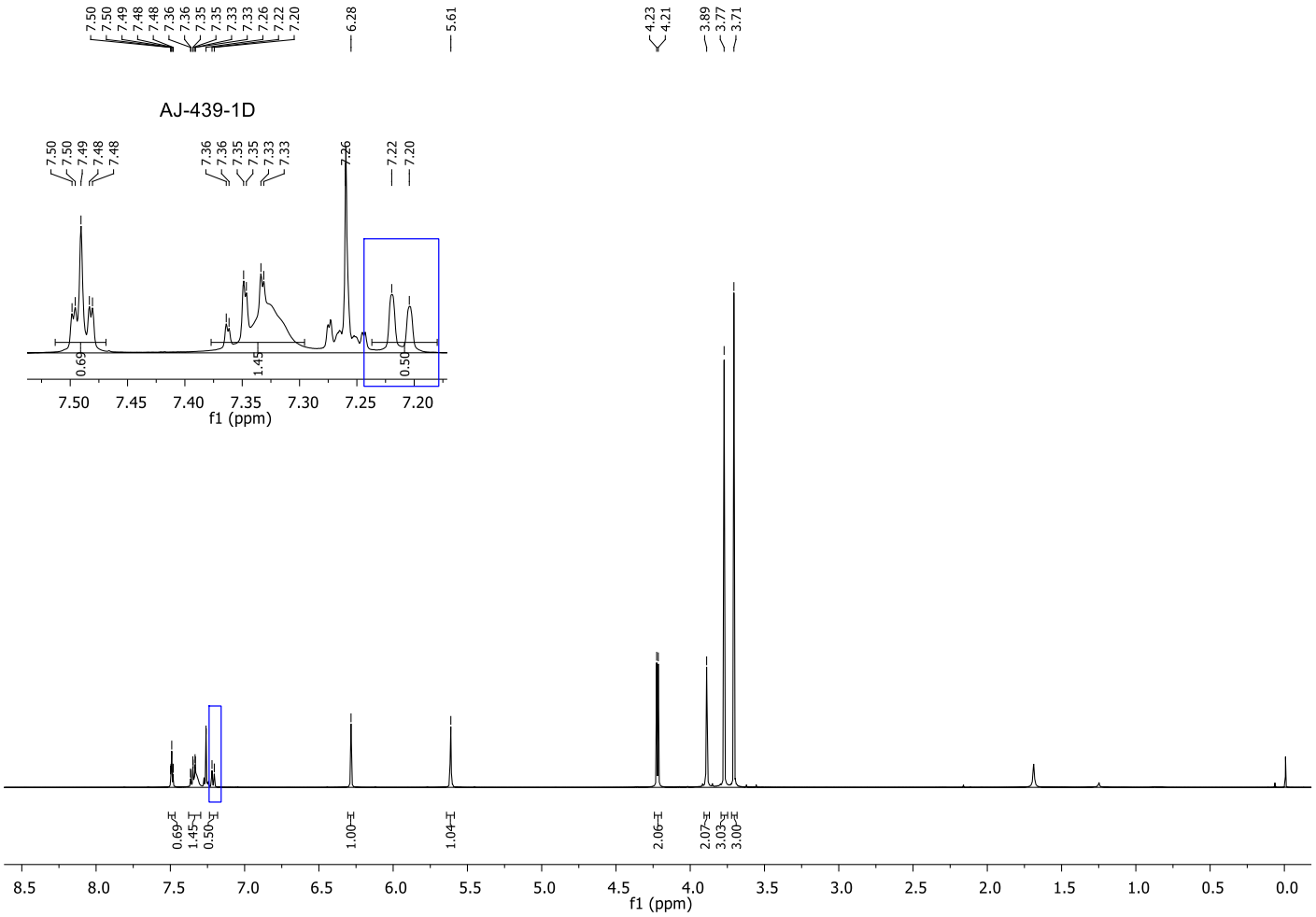
To an oven-dried sealed tube charged with methyl (2-methylbenzoyl) glycinate (**1c-d$_5$**) (39.64 mg, 0.2 mmol, 100 mol%), [Ru(*p*-Cymene)Cl_2]$_2$ (3.05 mg, 0.005 mmol, 2.5 mol%), $AgSbF_6$ (6.8 mg, 0.02 mmol, 10 mol%), $Cu(OAc)_2$ (19.96 mg, 0.10 mmol, 50 mol%) and methyl 2-(acetoxymethyl) acrylate (**2a**) (63.2 mg, 0.4 mmol, 200 mol %) followed by addition of TCE (1 mL) in open atmosphere at room temperature. The reaction mixture was allowed to stir at 120 °C for 4 h. Reaction tube was cooled to room temperature and diluted with dichloromethane (2 mL) and concentrated at reduced pressure. The residue was purified by flash column chromatography (EtOAc/*n*-hexane = 1:3) to afford mixture of **3c-d$_5$** (40.3 mg, 68%) as white solid with the partial hydrogenation (14%) at *ortho*-position.



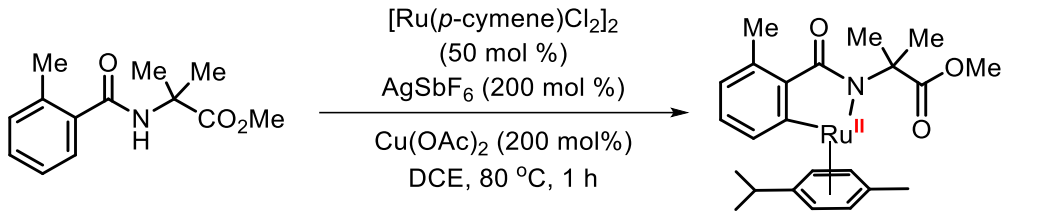
c) **Kinetic Isotope Effect (KIE) experiment**



To an oven-dried sealed tube charged with methyl (2-methylbenzoyl) glycinate (**1c**) (18.6 mg, 0.1 mmol, 50 mol%), and **1c- d$_5$** (19.64 mg, 0.1 mmol, 50 mol %), [Ru(*p*-Cymene)Cl$_2$]$_2$ (3.05 mg, 0.005 mmol, 2.5 mol%), AgSbF$_6$ (6.8 mg, 0.02 mmol, 10 mol%), Cu(OAc)$_2$ (19.96 mg, 0.10 mmol, 50 mol%) and methyl 2-(acetoxymethyl) acrylate (**2a**) (63.2 mg, 0.4 mmol, 200 mol%) followed by addition of TCE (1 mL) in open atmosphere at room temperature. The reaction mixture was allowed to stir at 120 °C for 10 min and then mixture was cooled to room temperature. Reaction mixture was diluted with dichloromethane (2 mL) and concentrated at reduced pressure. The residue was purified by flash column chromatography (EtOAc/*n*-hexane = 1:3) to afford mixture of **3c** + **3c- d$_5$** (33 mg, 57%) as white solid. The kinetic isotope effect (K_H/K_D) value was determined as KIE = 1.0 using ^{1}H NMR spectroscopy techniques.



d) Synthesis and characterization of ruthanacycle Ru(II) complex (A)

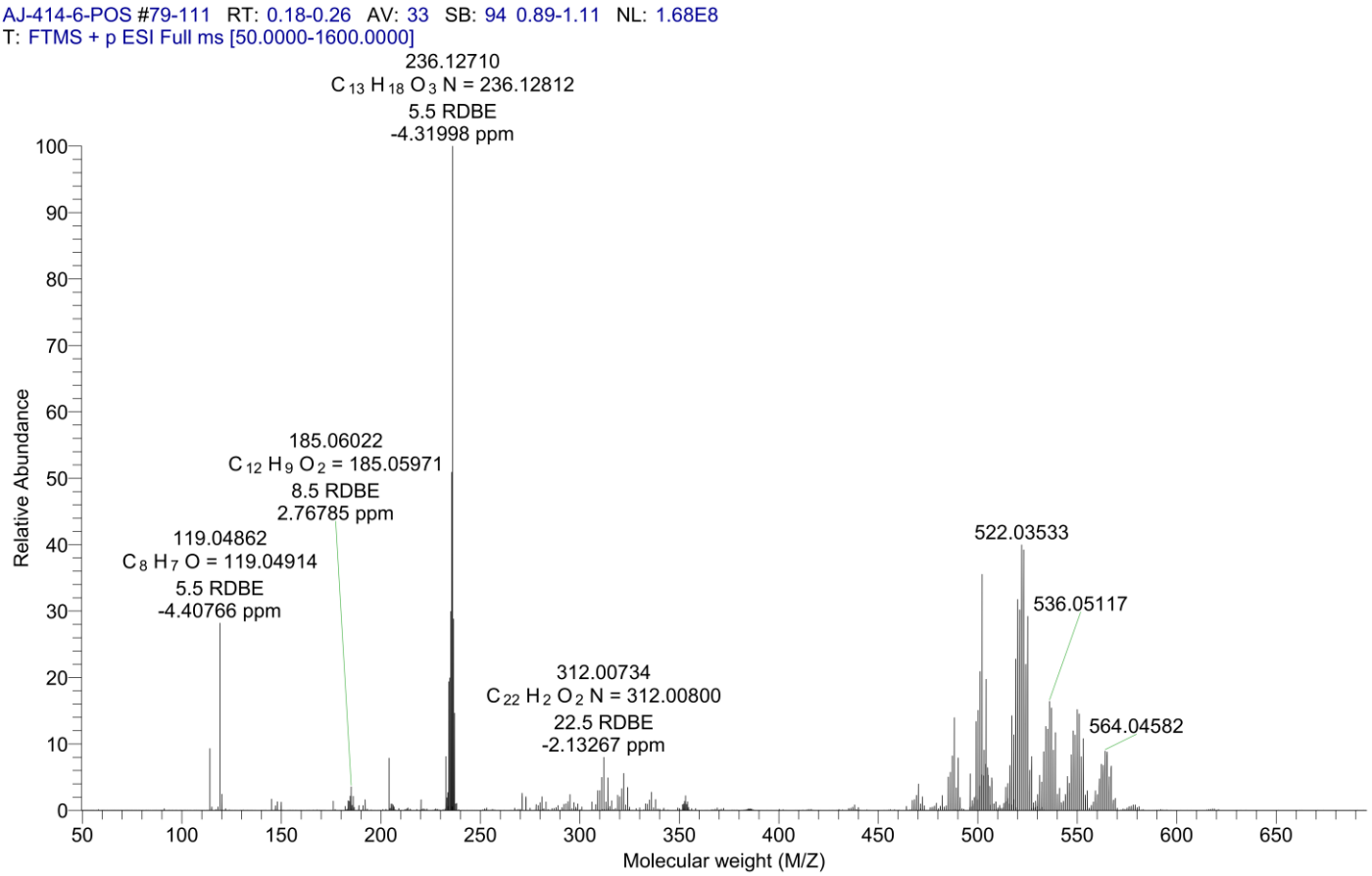


1x **A**

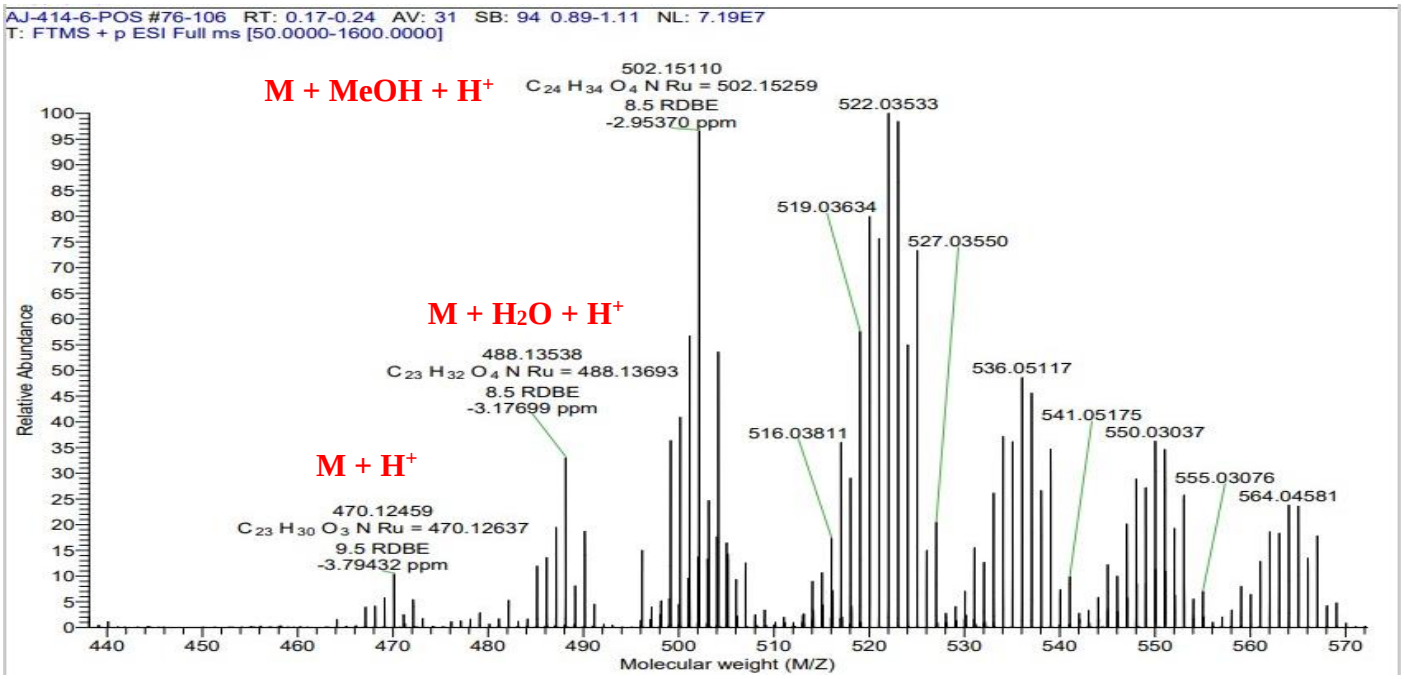
m/z (M^+ + H + MeOH) = 502.1526

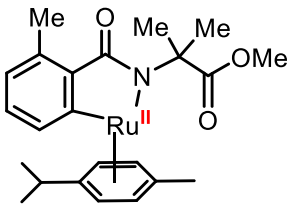
To an oven-dried sealed tube charged with methyl 2-methyl-2-(2-methylbenzamido)propanoate (**1x**) (47.05 mg, 0.2 mmol, 100 mol%), [Ru(*p*-Cymene)Cl_2]$_2$ (61.23 mg, 0.10 mmol, 50 mol%), $AgSbF_6$ (137.44 mg, 0.4 mmol, 200 mol%), $Cu(OAc)_2$ (72.65 mg, 0.4 mmol, 200 mol%) followed by addition of DCE (1 mL) in open atmosphere at room temperature. The reaction mixture was allowed to stir at 80 °C for 1 h and then mixture was cooled to room temperature. Reaction mixture was filtered on celite pad using dichloromethane and concentrated at reduced pressure. Orange sticky oil crude mixture was directly submitted for HRMS to characterize Ru(II) complex **A**. Notably, washing of crude mixture with diethyl ether, ethyl acetate, petroleum ether, acetonitrile etc. or isolation of **A** using column chromatography (silica and neutral alumina) was unsuccessful to obtain pure compound of Ru(II) complex **A**.

Full HRMS spectrum of complex A



Zoom HRMS spectrum of complex A

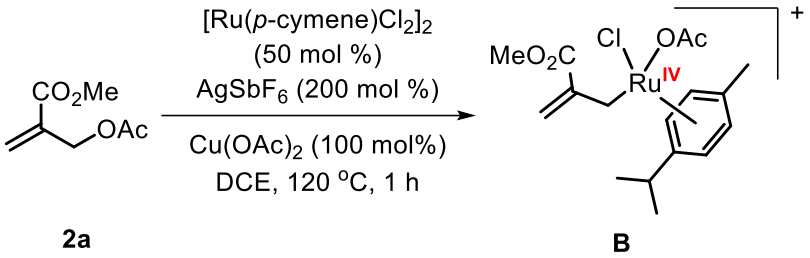




M ($C_{23}H_{29}NO_3Ru$, m/z = 469.1191)

M + H$^+$ (m/z = 470.1269)
M + H$_2$O + H$^+$ (m/z = 488.1375)
M + MeOH + H$^+$ (m/z = 502.1531)

e) Synthesis and characterization of Ru(IV)allyl complex (B)



2a B

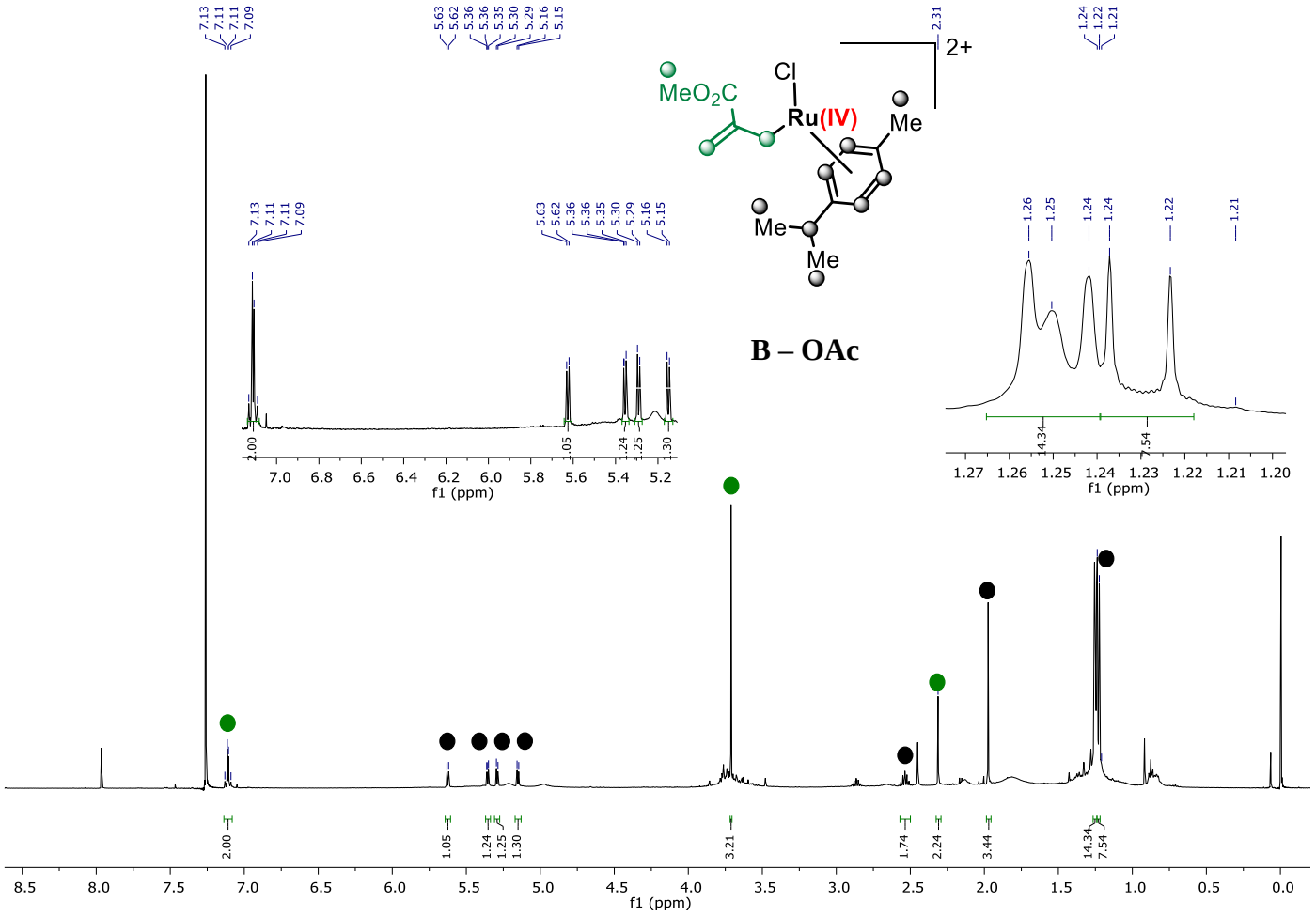
To an oven-dried sealed tube charged with methyl 2-(acetoxymethyl) acrylate (**2a**) (31.62 mg, 0.2 mmol, 100 mol%), [Ru(*p*-Cymene)Cl_2]$_2$ (122.47 mg, 0.2 mmol, 50 mol%), $AgSbF_6$ (137.44 mg, 0.4 mmol, 200 mol%), $Cu(OAc)_2$ (36.32 mg, 0.2 mmol, 100 mol%) followed by addition of DCE (1 mL) in open atmosphere at room temperature. The reaction mixture was allowed to stir at 120 °C for 1h and then mixture was cooled to room temperature. Reaction mixture was diluted with dichloromethane (2 mL) and concentrated at reduced pressure. The residue was purified by using neutral alumina column chromatography (Et_2O/CH_3CN =4:1) to afford Ru(IV) complex **B-OAc** (7.00 mg, 11%) as orange sticky oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.16–7.07 (m, 2H), 5.63 (d, *J* = 5.7 Hz, 1H), 5.35 (dd, *J* = 5.8, 1.0 Hz, 1H), 5.29 (d, *J* = 5.3 Hz, 1H), 5.15 (d, *J* = 5.7 Hz, 1H), 3.74–3.67 (s, 3H), 2.56–2.50 (m, 1H), 2.31 (s, 2H), 1.97 (s, 3H), 1.25 (d, *J* = 6.9 Hz, 1H), 1.23 (d, *J* = 6.9 Hz, 1H).

Note:

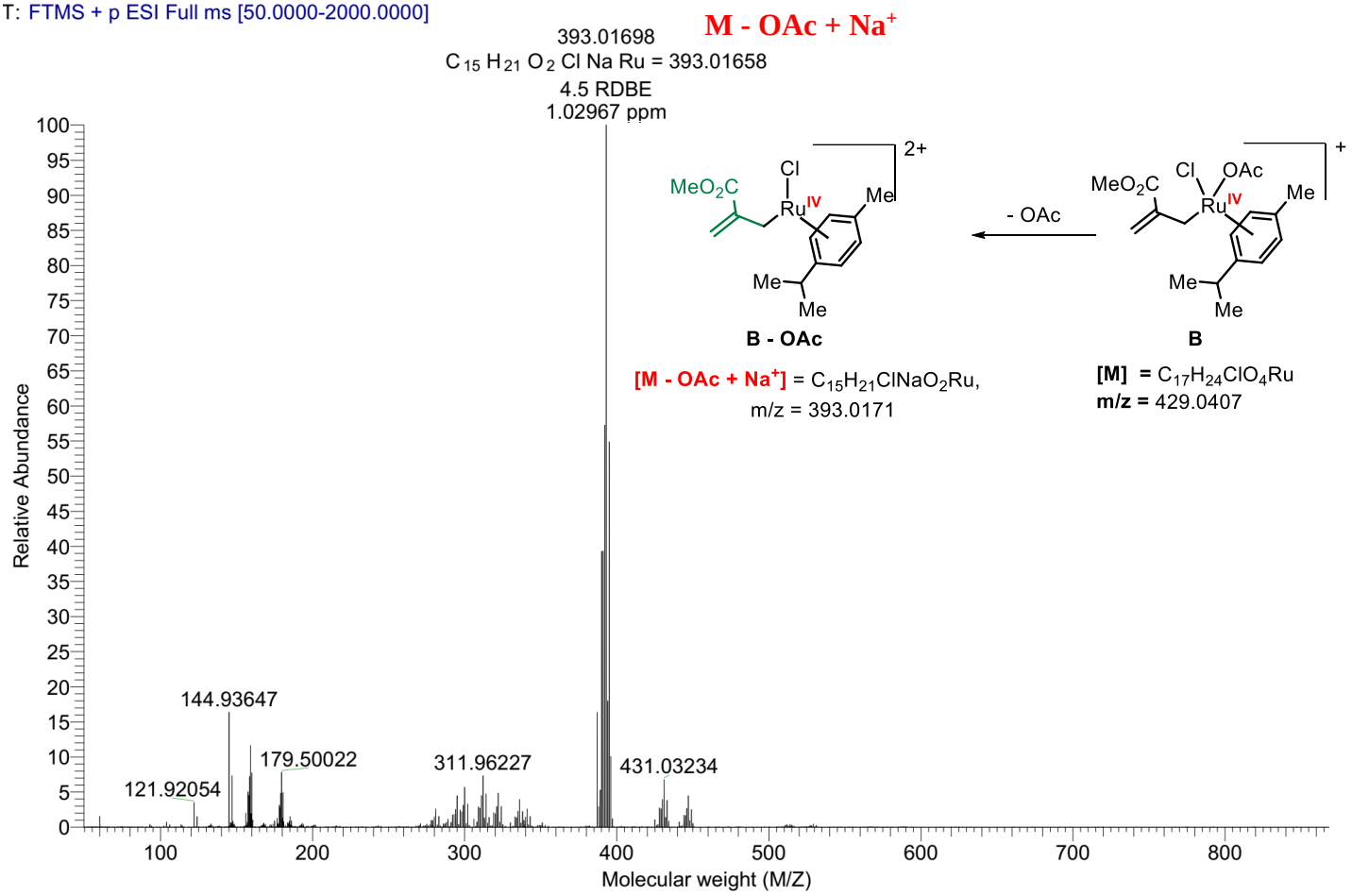
1. During column chromatography using flash silica, Ru(IV) complex (**B**) was decomposed. However, we could be able to isolate Ru(IV) complex **B-OAc** in a trace amount using neutral alumina along with the decomposition of complex **B-OAc**.

2. Ru(IV) complex (**B-OAc**) was very unstable in chloroform-d while it was completely decomposed in methanol-d4 during NMR studies.

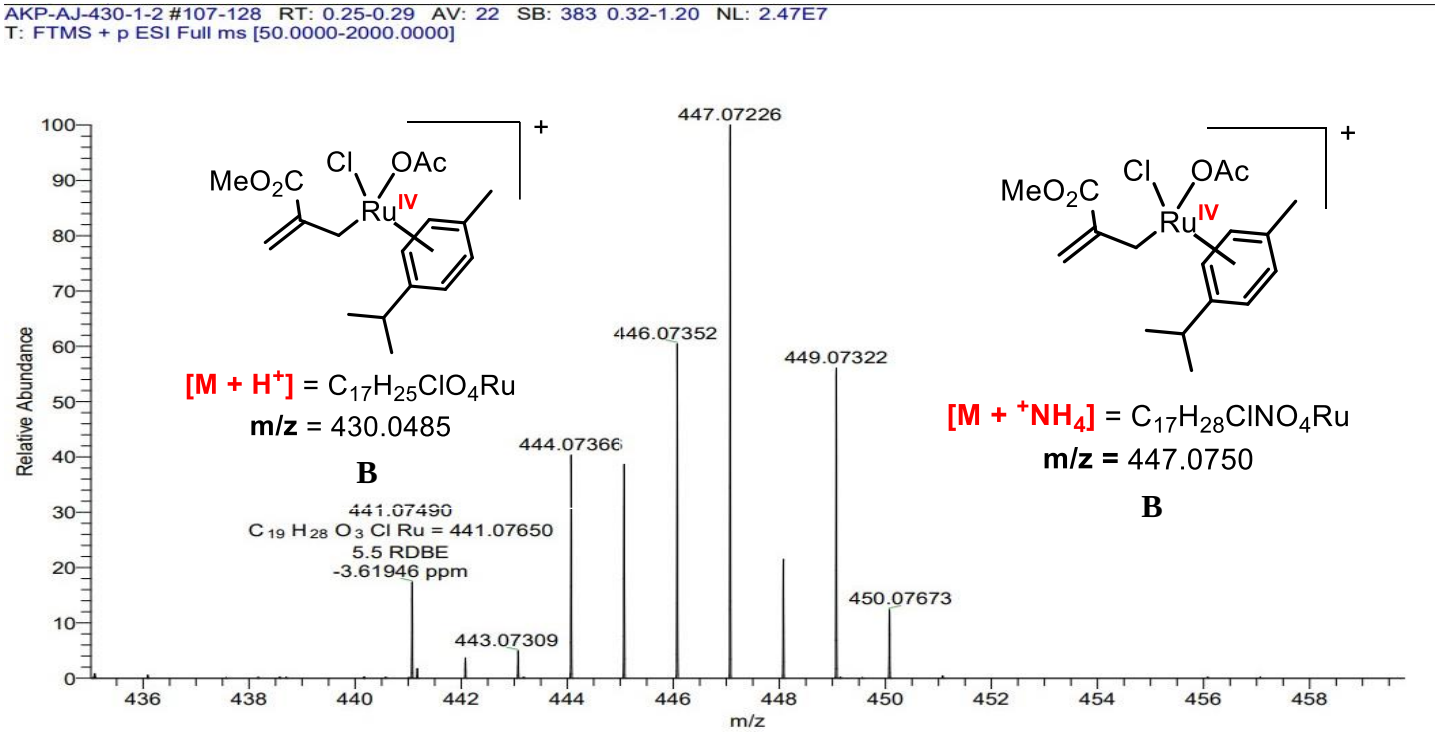
3. For further characterization, the crude mixture was submitted to HRMS for exact mass analysis. The detail of spectra (^{1}H NMR and HRMS) are given below.



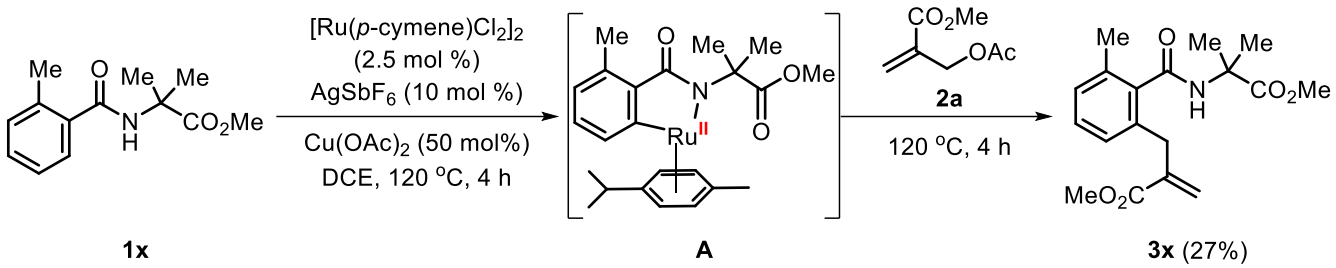
Full HRMS spectrum of complex B



Zoom HRMS spectrum of complex B

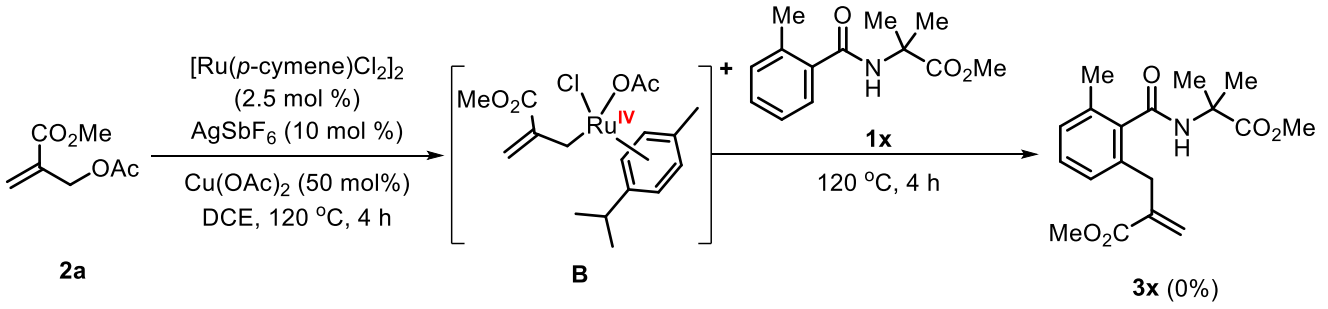


f) Reactivity of Ru(II) complex (A) in C(sp^2)-H allylation with MBH acetate (2a)



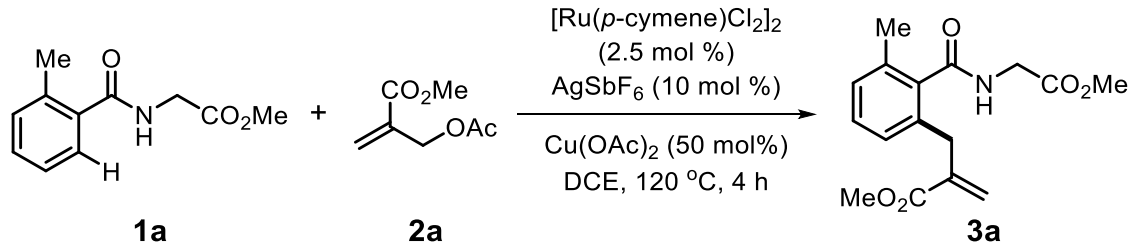
To an oven-dried screw cap sealed tube charged with 2-methyl-2-(2-methylbenzamido)propanoate (**1x)** (47.10 mg, 0.2 mmol, 100 mol%), [Ru(*p*-Cymene)Cl_2]$_2$ (3.05 mg, 0.005 mmol, 2.5 mol%), $AgSbF_6$ (6.8 mg, 0.02 mmol, 10 mol%) and $Cu(OAc)_2$ (19.96 mg, 0.10 mmol, 50 mol%), DCE (1 mL) were added under air at room temperature. The reaction mixture was allowed to stir at 120 °C for 4 h. Reaction mixture was cooled to room temperature and methyl 2-(acetoxymethyl) acrylate (**2a**) (62.2 mg, 0.4 mmol, 200 mol%) were added under air at room temperature. The reaction mixture was allowed to stir at 120 °C for 4 h. Reaction mixture was cooled to room and filtered on celite. The solvent was evaporated at reduced pressure and residue was dried on high vacuum. Crude mixture was taken to determine the yield using TCE as internal reference. The ^{1}H NMR yield of **3x** was 27%.

g) Reactivity of Ru(IV)allyl complex (B) in C(sp^2)-H allylation reaction with (1x)

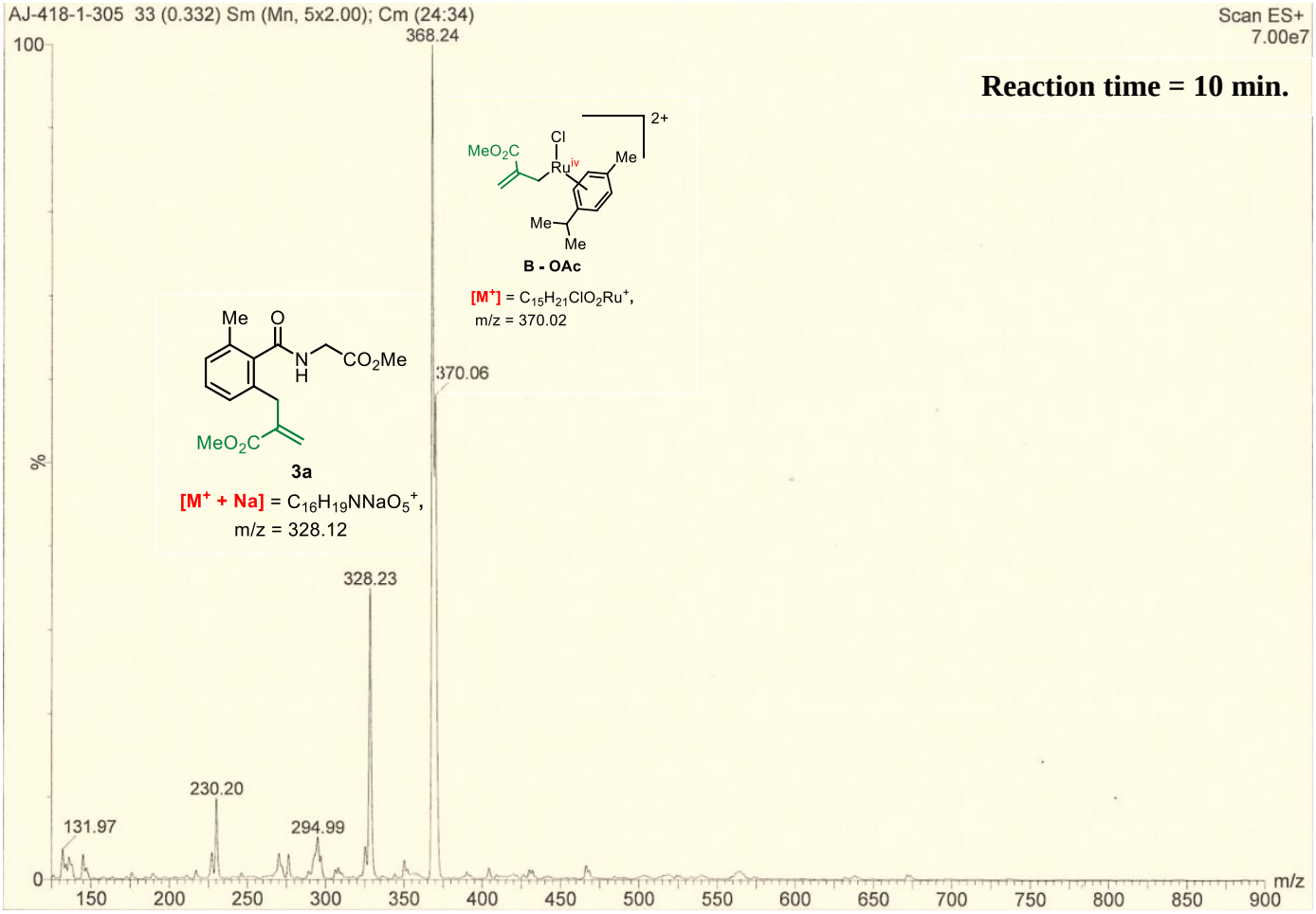


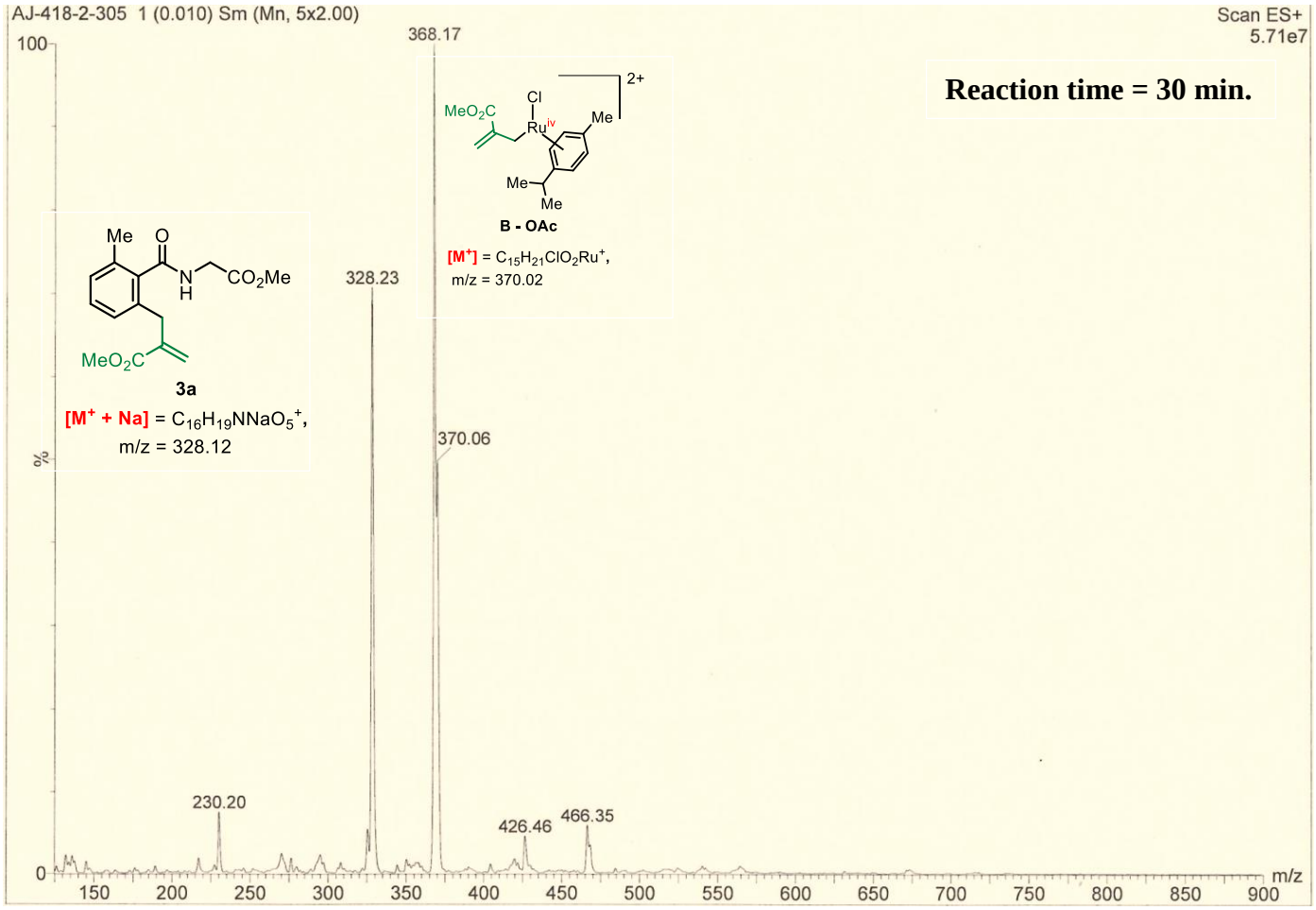
To an oven-dried screw cap sealed tube charged with methyl 2-(acetoxymethyl) acrylate (**2a**) (63.2 mg, 0.4 mmol, 200 mol%), [Ru(*p*-Cymene)Cl_2]$_2$ (3.05 mg, 0.005 mmol, 2.5 mol%), $AgSbF_6$ (6.8 mg, 0.02 mmol, 10 mol %) and $Cu(OAc)_2$ (19.96 mg, 0.10 mmol, 50 mol%), DCE (1 mL) were added under air at room temperature. The reaction mixture was allowed to stir at 120 °C for 4 h. Reaction mixture was cooled to room temperature and 2-methyl-2-(2-methylbenzamido)propanoate (**1x**) (47.10 mg, 0.2 mmol, 100 mol%) was added to the reaction under air at room temperature. The reaction mixture was allowed to stir at 120 °C for 4 h and monitored by thin layer chromatography (TLC). Compound 3v was neither detected on TLC nor in ^{1}H NMR spectroscopy.

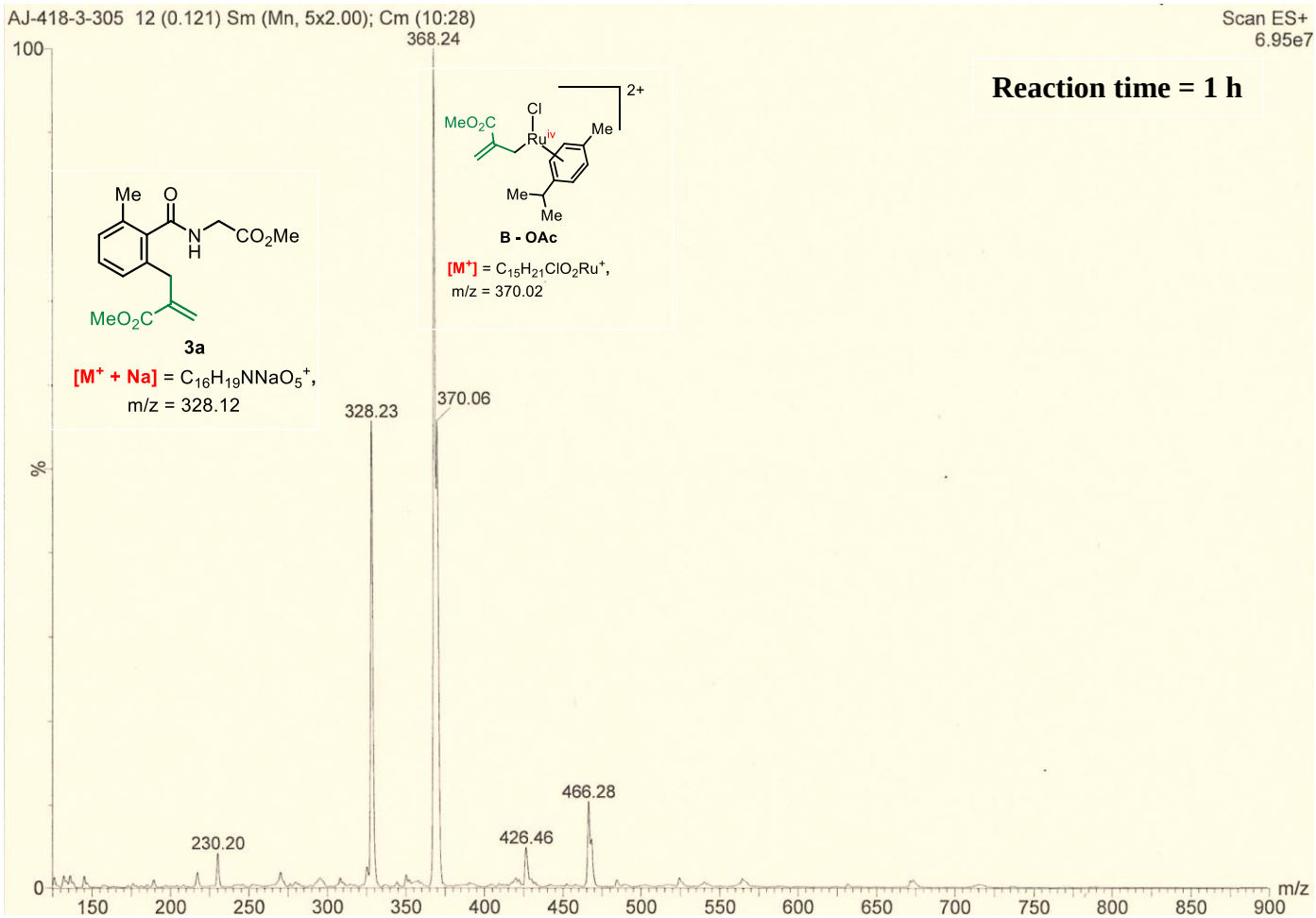
h) Progress of reaction monitored at variable time using MS-ESI

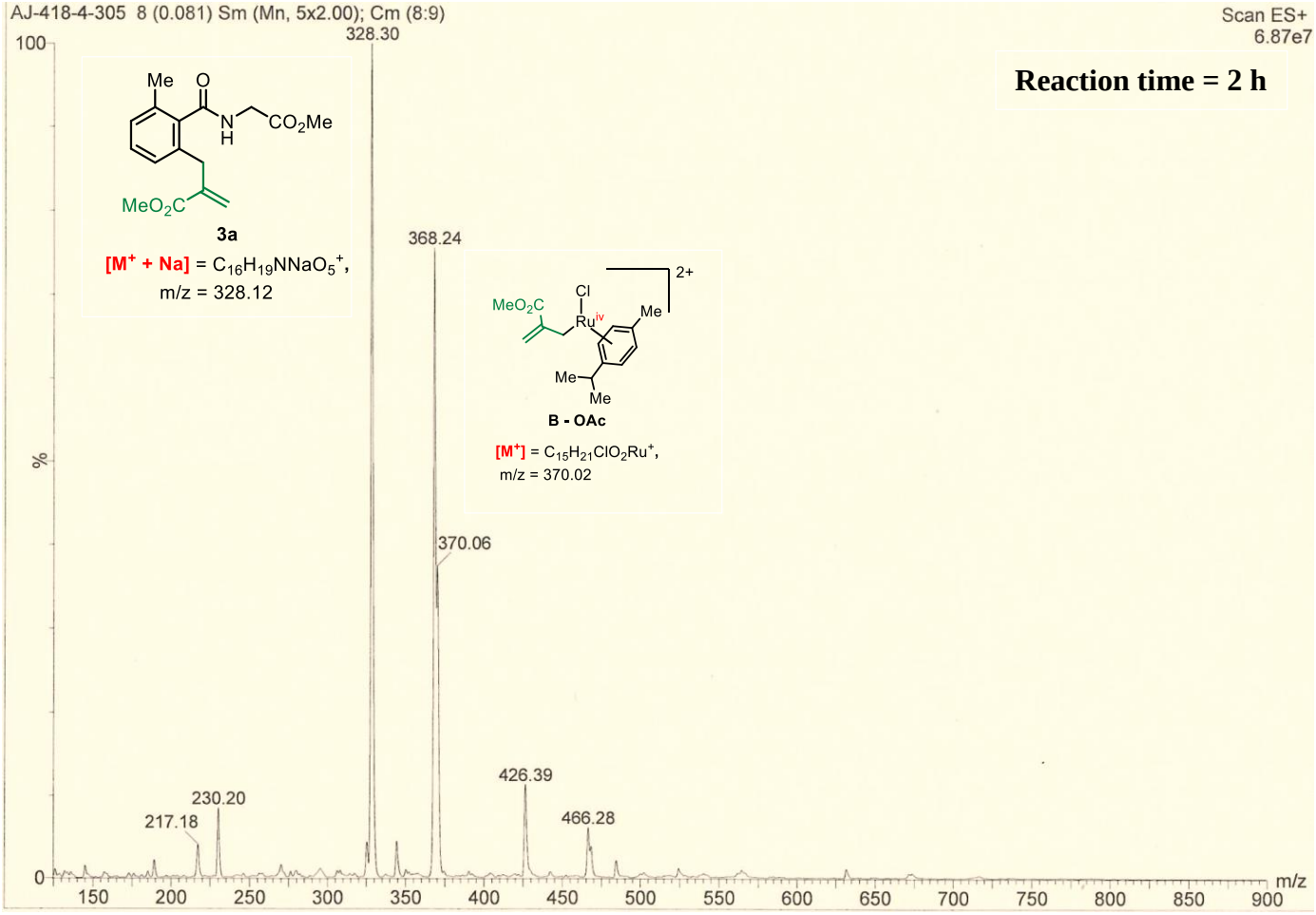


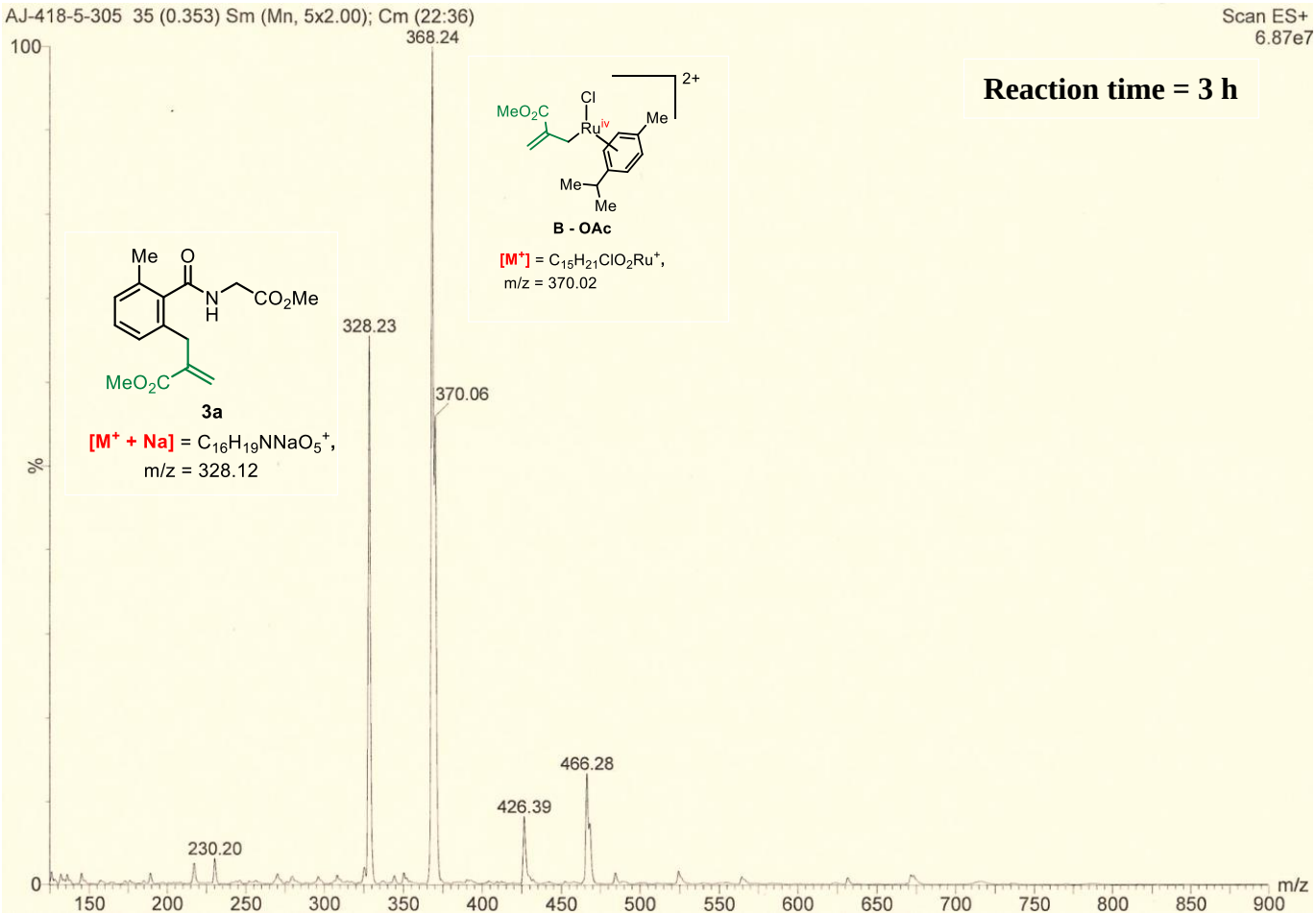
To an oven-dried sealed tube charged with methyl (2-methylbenzoyl)glycinate (**1a**) (41.44 mg, 0.2 mmol, 100 mol %), [Ru(*p*-Cymene)Cl_2]$_2$ (3.05 mg, 0.005 mmol, 2.5 mol%), $AgSbF_6$ (6.87 mg, 0.02 mmol, 10 mol%), $Cu(OAc)_2$ (18.16 mg, 0.10 mmol, 50 mol %) and methyl 2-(acetoxymethyl) acrylate (**2a**) (63.2 mg, 0.4 mmol, 200 mol%) followed by addition of DCE (1 mL) in open atmosphere at room temperature. The reaction mixture was started to stir at 120 °C and reaction samples (20 µL each) were collect from reaction tube for MS-ESI analysis in variable time (10 min., 30 min., 1 h, 2 h, 3 h and 4 h) Volatile mixture was evaporated at reduce pressure and dried crude samples were dissolved in acetonitrile and submitted for MS-ESI data collection. All the collected MS-ESI spectra have incorporated below.

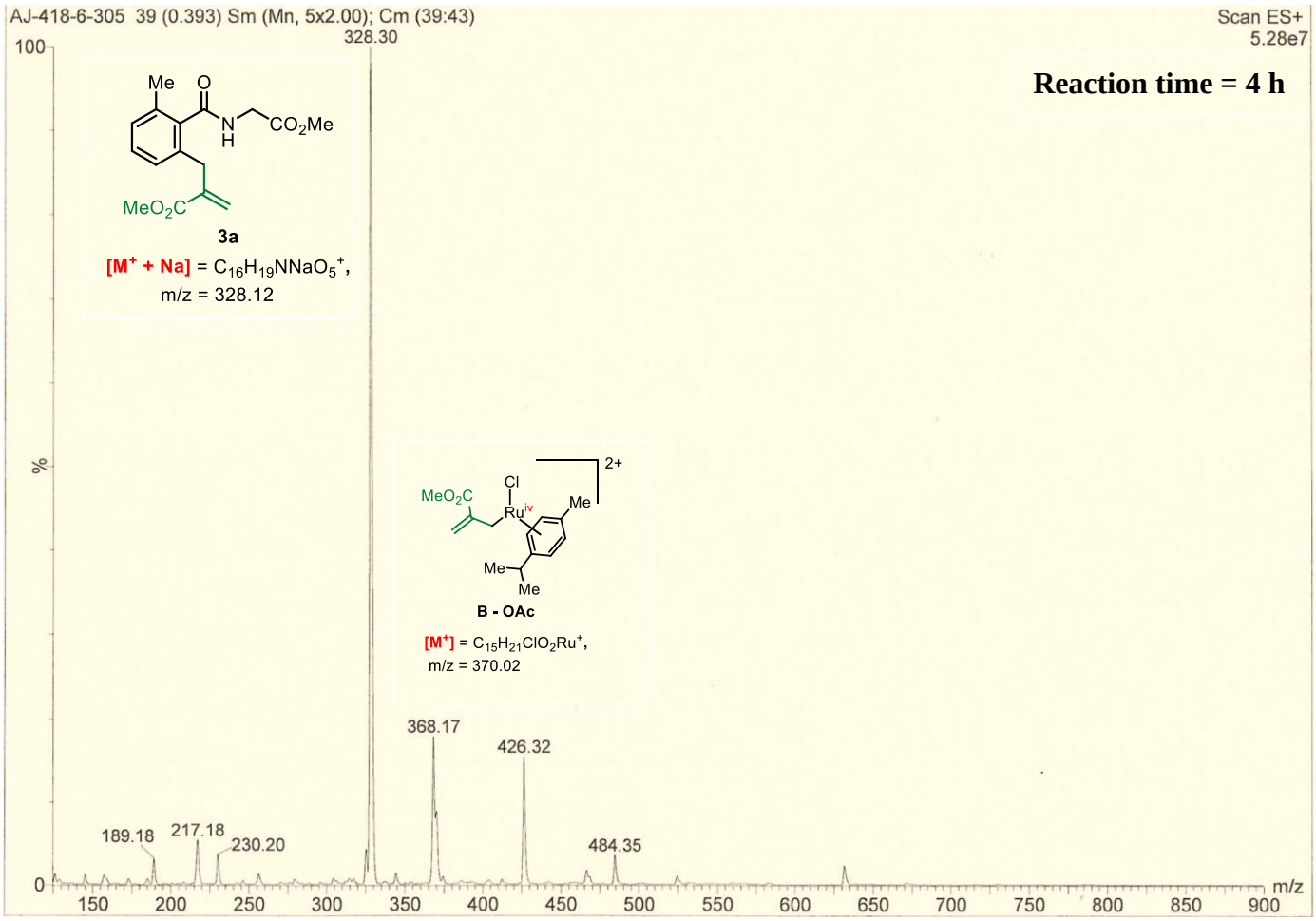



AJ-418-2-305 1 (0.010) Sm (Mn, 5x2.00)
Scan ES+
5.71e7
Reaction time = 30 min.
368.17
328.23
370.06
230.20
426.46
466.35
B - OAc
[M+] = C15H21ClO2Ru+,
m/z = 370.02
3a
[M+ + Na] = C16H19NNaO5+,
m/z = 328.12
%
m/z


AJ-418-3-305 12 (0.121) Sm (Mn, 5x2.00); Cm (10:28)
Scan ES+
6.95e7
Reaction time = 1 h
368.24
328.23
370.06
230.20
426.46
466.28
B - OAc
[M+] = C15H21ClO2Ru+,
m/z = 370.02
3a
[M+ + Na] = C16H19NNaO5+,
m/z = 328.12
%
m/z

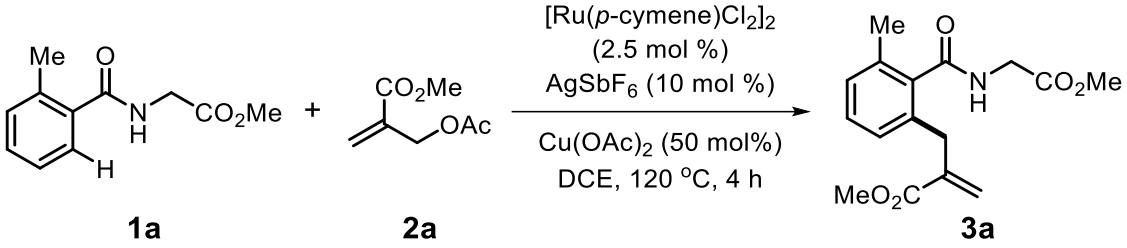

AJ-418-4-305 8 (0.081) Sm (Mn, 5x2.00); Cm (8:9)
Scan ES+
6.87e7
Reaction time = 2 h
328.30
368.24
370.06
426.39
466.28
230.20
217.18
3a
[M+ + Na] = C16H19NNaO5+,
m/z = 328.12
B - OAc
[M+] = C15H21ClO2Ru+,
m/z = 370.02
%
m/z


AJ-418-5-305 35 (0.353) Sm (Mn, 5x2.00); Cm (22:36)
Scan ES+
6.87e7
Reaction time = 3 h
368.24
328.23
370.06
466.28
426.39
230.20
3a
[M+ + Na] = C16H19NNaO5+,
m/z = 328.12
B - OAc
[M+] = C15H21ClO2Ru+,
m/z = 370.02
%
m/z


AJ-418-6-305 39 (0.393) Sm (Mn, 5x2.00); Cm (39:43)
Scan ES+
5.28e7
328.30
100
%
0
Reaction time = 4 h
Me
O
N
H
CO2Me
MeO2C
3a
[M+ + Na] = C16H19NNaO5+,
m/z = 328.12
2+
Cl
MeO2C
Ruiv
Me
Me
Me
B - OAc
[M+] = C15H21ClO2Ru+,
m/z = 370.02
368.17
426.32
189.18
217.18
230.20
484.35
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
m/z

i) Progress of reaction monitored at variable time using LC-MS

I. Reaction progress at 0.7 equivalent of (2a)



1a **2a** **3a**

To an oven-dried sealed tube charged with methyl (2-methylbenzoyl)glycinate (**1a**) (41.44 mg, 0.2 mmol, 100 mol%), [Ru(*p*-Cymene)Cl_2]$_2$ (3.05 mg, 0.005 mmol, 2.5 mol%), $AgSbF_6$ (6.87 mg, 0.02 mmol, 10 mol%), $Cu(OAc)_2$ (18.16 mg, 0.10 mmol, 50 mol%) and methyl 2-(acetoxymethyl) acrylate (**2a**) (22.14 mg, 0.14 mmol, 70 mol%) followed by addition of DCE (1 mL) in open atmosphere at room temperature. The reaction mixture was started to stir at 120 °C and reaction samples (20 µL each) were collect from reaction tube for LC-MS analysis in variable time (10 min., 30 min., 1 h, 2 h, 3 h and 4 h) Volatile mixture was evaporated at reduced pressure and dried crude samples were dissolved in acetonitrile and submitted for LC-MS data collection.
Method: RP-18 HPLC column (5µm), Flow rate = 0.2 mL/min., Eluent = acetonitrile/water
All the collected LC-MS spectra have been incorporated below.

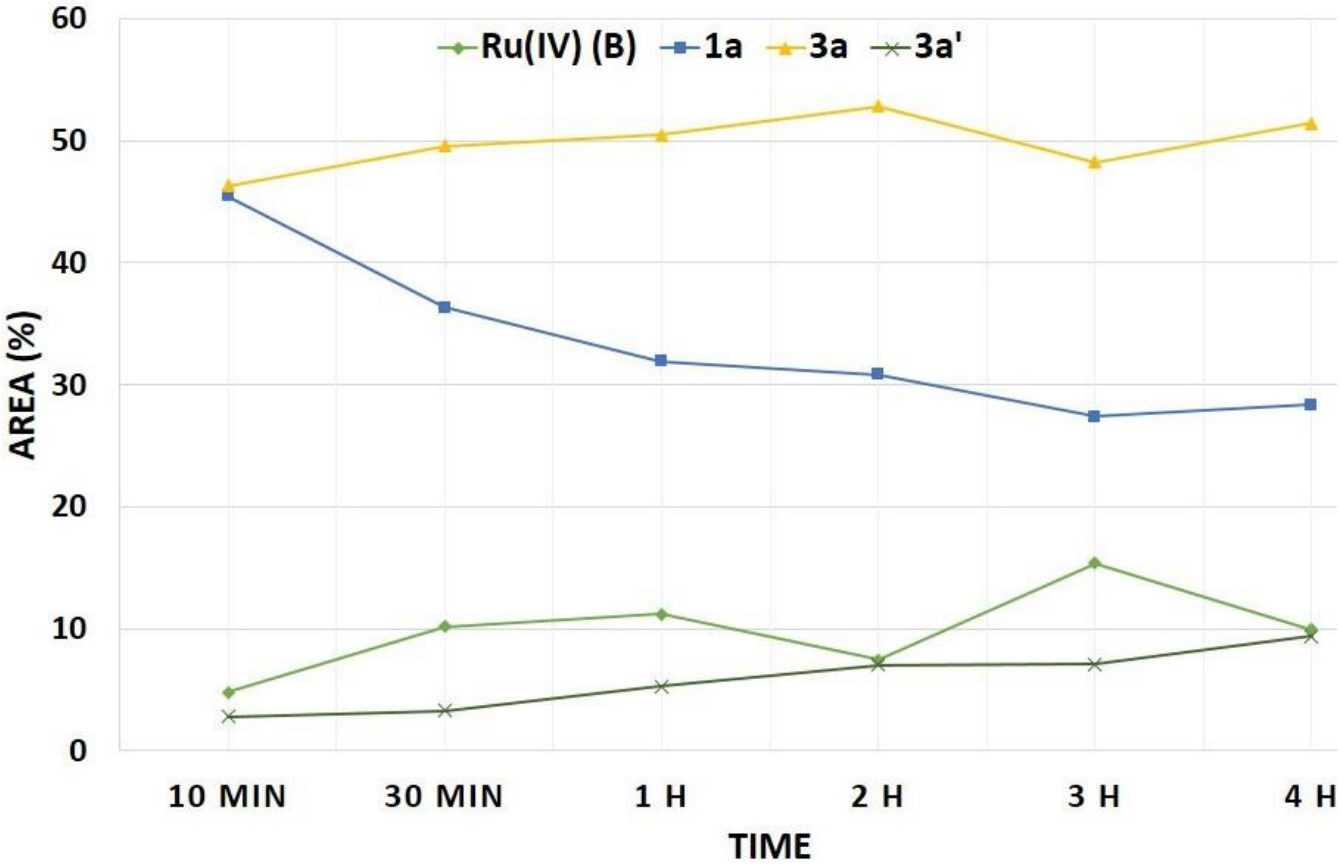
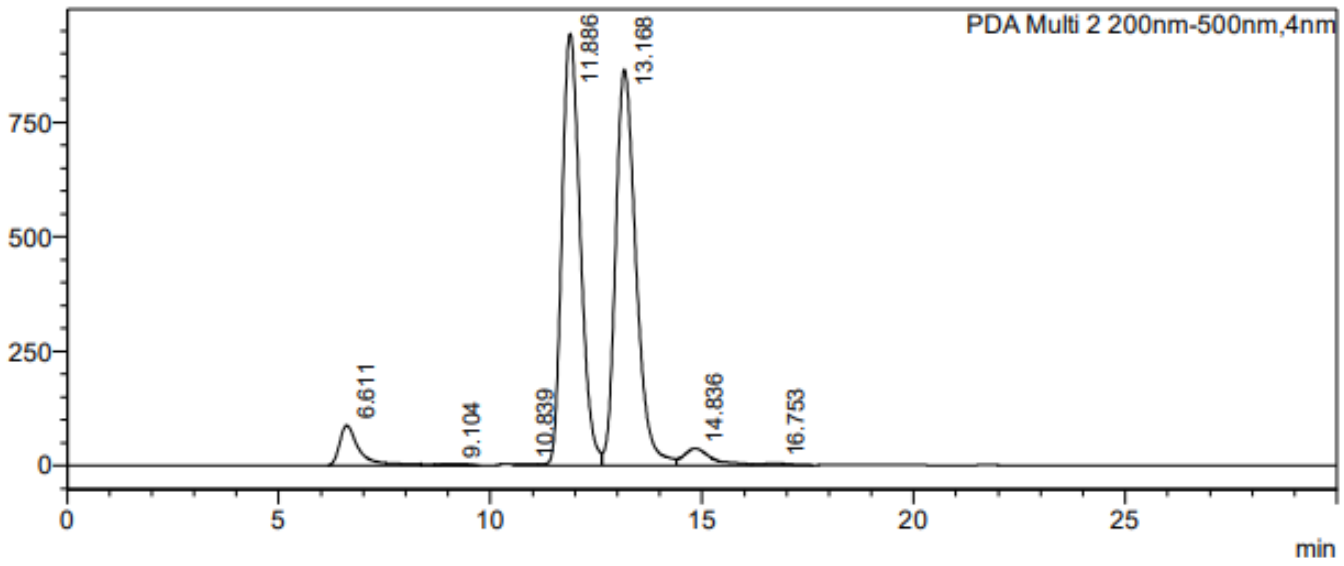


Fig. 1. Reaction progress at variable time (LC-MS data)

<Chromatogram>

Reaction time = 10 min.



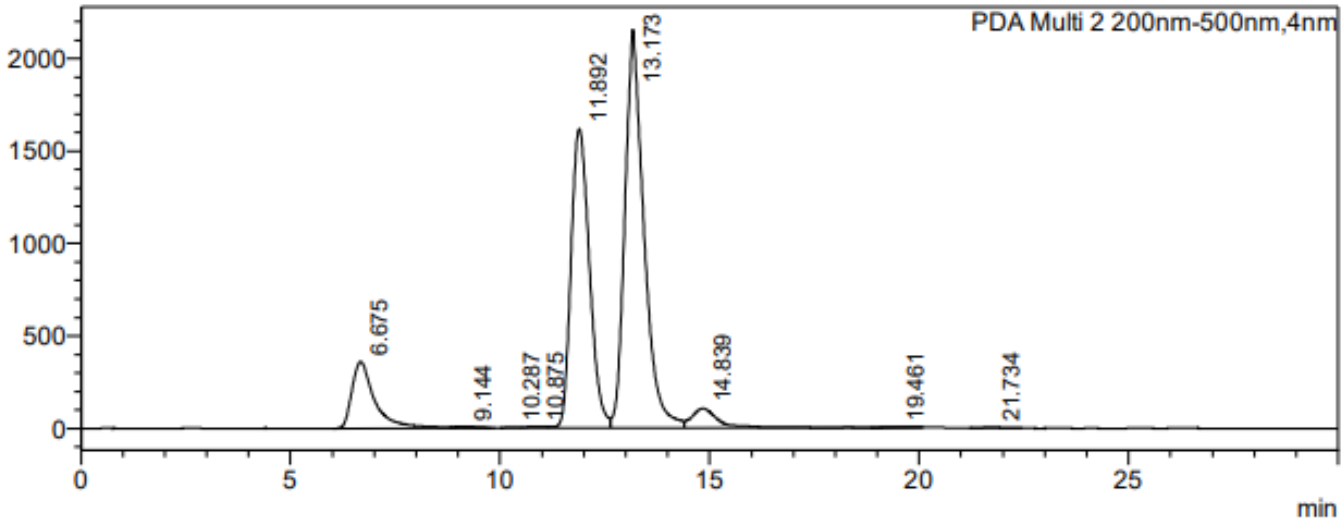
Peak Table

PDA Ch2 200nm-500nm

Peak#	Ret. Time	Area	Height	Name	Area%
1	6.611	2991944	88002	RT:6.611	4.789
2	9.104	107036	2669	RT:9.104	0.171
3	10.839	108264	3412	RT:10.839	0.173
4	11.886	28406256	943824	RT:11.886	45.468
5	13.168	28934426	864044	RT:13.168	46.313
6	14.836	1723083	37272	RT:14.836	2.758
7	16.753	204894	3804	RT:16.753	0.328
Total		62475904	1943027		100.000

<Chromatogram>

Reaction time = 30 min.



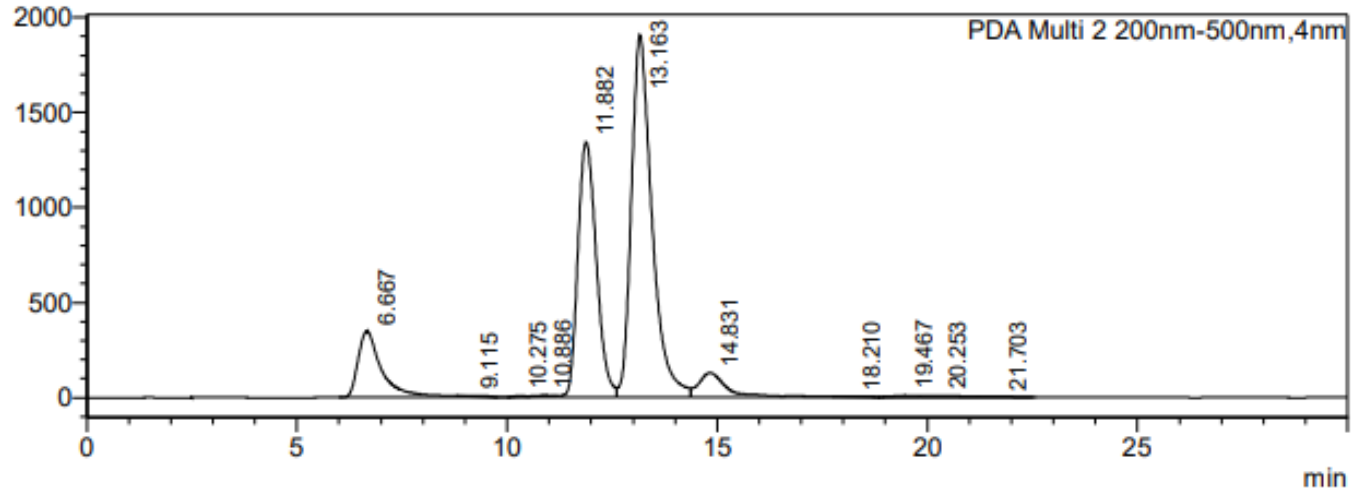
Peak Table

PDA Ch2 200nm-500nm

Peak#	Ret. Time	Area	Height	Name	Area%
1	6.675	13875548	360073	RT:6.675	10.160
2	9.144	214860	5341	RT:9.144	0.157
3	10.287	176140	7312	RT:10.287	0.129
4	10.875	305116	9322	RT:10.875	0.223
5	11.892	49585061	1619459	RT:11.892	36.309
6	13.173	67693827	2156085	RT:13.173	49.569
7	14.839	4451968	104992	RT:14.839	3.260
8	19.461	117163	3867	RT:19.461	0.086
9	21.734	145105	4457	RT:21.734	0.106
Total		136564788	4270909		100.000

<Chromatogram>

Reaction time = 1 h



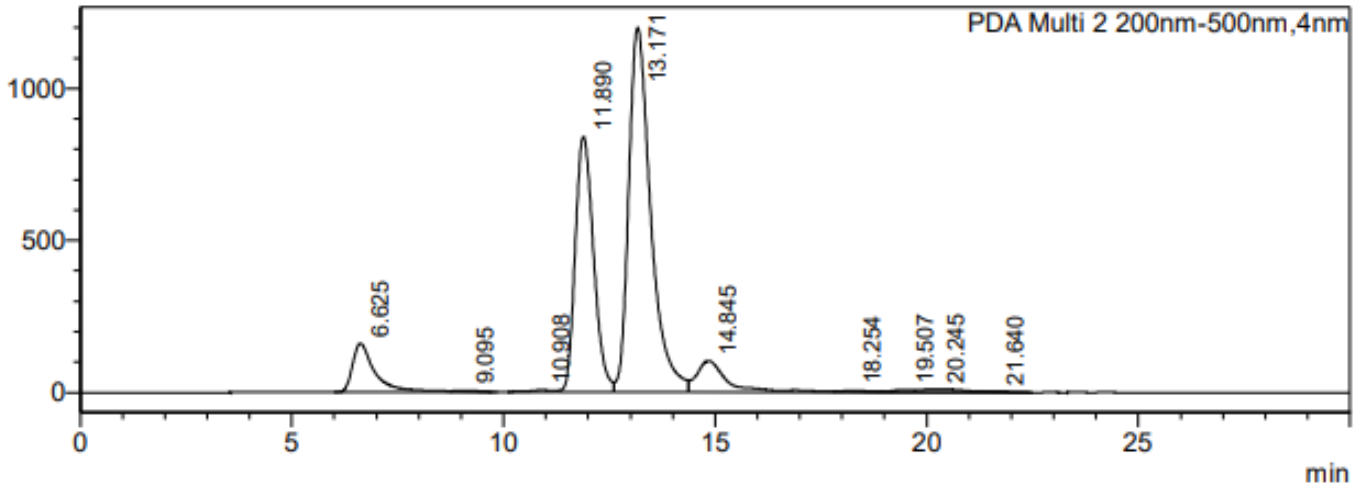
Peak Table

PDA Ch2 200nm-500nm

Peak#	Ret. Time	Area	Height	Name	Area%
1	6.667	14406580	349241	RT:6.667	11.174
2	9.115	224675	4905	RT:9.115	0.174
3	10.275	116244	5265	RT:10.275	0.090
4	10.886	104711	3525	RT:10.886	0.081
5	11.882	41107642	1341795	RT:11.882	31.884
6	13.163	65064474	1906565	RT:13.163	50.465
7	14.831	6794443	129114	RT:14.831	5.270
8	18.210	100223	3063	RT:18.210	0.078
9	19.467	294977	8178	RT:19.467	0.229
10	20.253	498636	7979	RT:20.253	0.387
11	21.703	217871	5826	RT:21.703	0.169
Total		128930474	3765456		100.000

<Chromatogram>

Reaction time = 2 h



Peak Table

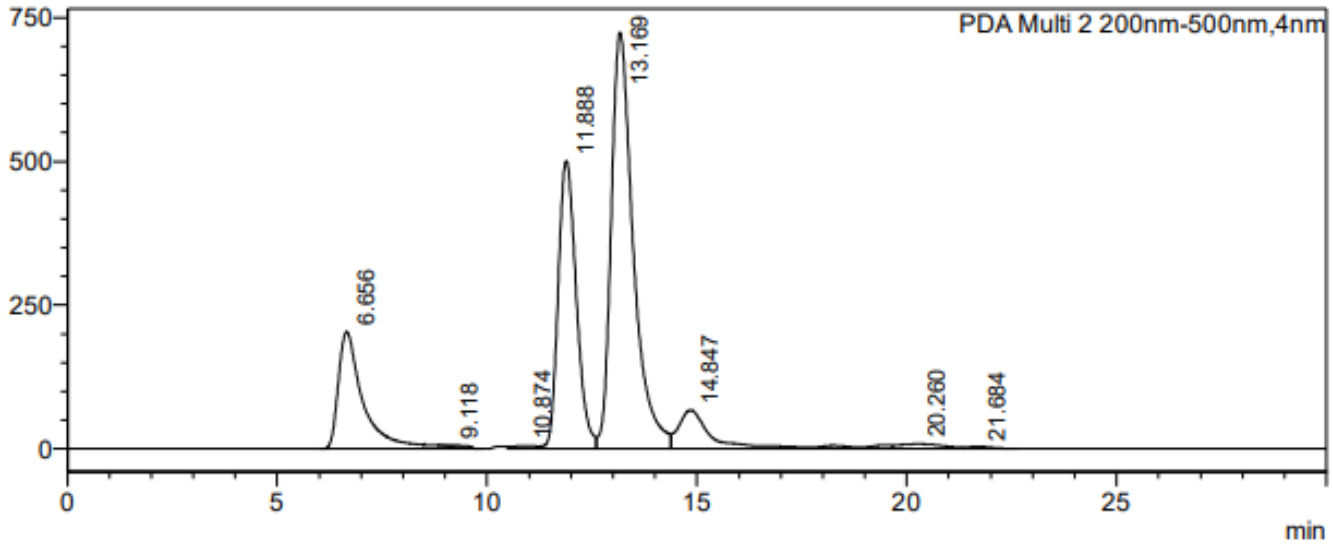
PDA Ch2 200nm-500nm

Peak#	Ret. Time	Area	Height	Name	Area%
1	6.625	6141634	160879	RT:6.625	7.446
2	9.095	122384	2711	RT:9.095	0.148
3	10.908	315182	7032	RT:10.908	0.382
4	11.890	25447484	840661	RT:11.890	30.852
5	13.171	43562945	1199306	RT:13.171	52.815
6	14.845	5764560	103862	RT:14.845	6.989
7	18.254	118743	3398	RT:18.254	0.144
8	19.507	217686	7180	RT:19.507	0.264
9	20.245	648151	9367	RT:20.245	0.786
10	21.640	143426	3624	RT:21.640	0.174
Total		82482196	2338020		100.000

<Chromatogram>

mAU

Reaction time = 3 h



Peak Table

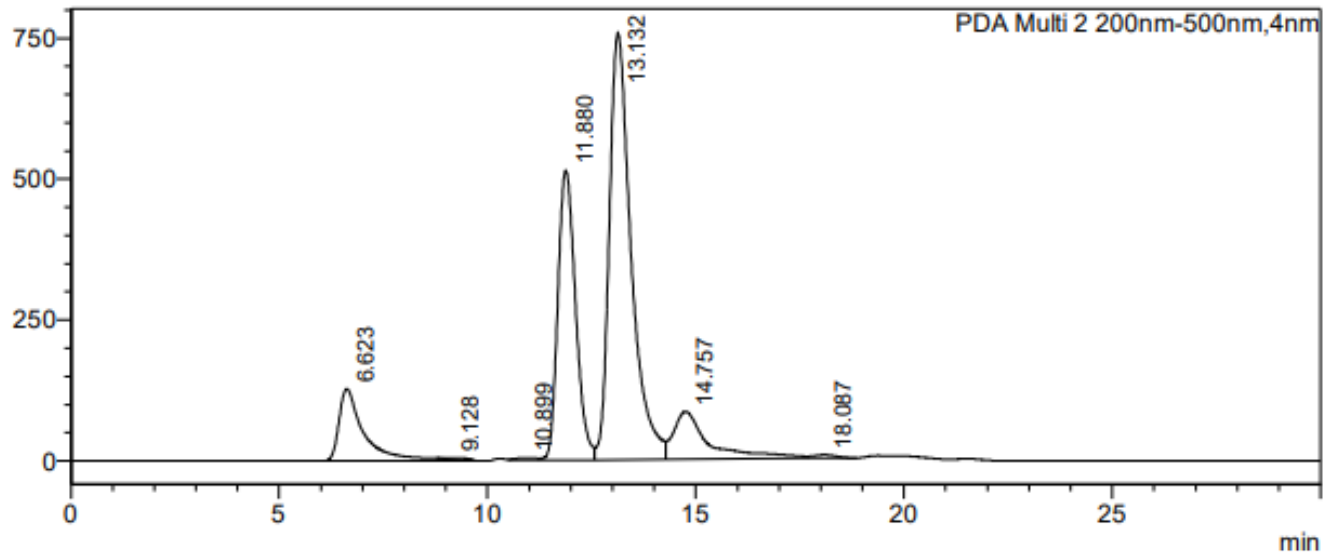
PDA Ch2 200nm-500nm

Peak#	Ret. Time	Area	Height	Name	Area%
1	6.656	8448983	203807	RT:6.656	15.372
2	9.118	122301	2434	RT:9.118	0.223
3	10.874	198238	5402	RT:10.874	0.361
4	11.888	15040941	500636	RT:11.888	27.366
5	13.169	26516633	724169	RT:13.169	48.246
6	14.847	3903900	67226	RT:14.847	7.103
7	20.260	587859	8073	RT:20.260	1.070
8	21.684	142930	3461	RT:21.684	0.260
Total		54961784	1515208		100.000

<Chromatogram>

mAU

Reaction time = 4 h

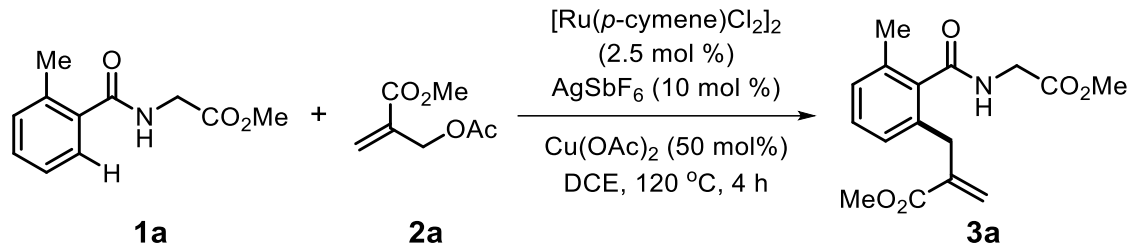


Peak Table

PDA Ch2 200nm-500nm

Peak#	Ret. Time	Area	Height	Name	Area%
1	6.623	5307280	128117	RT:6.623	9.894
2	9.128	100361	2081	RT:9.128	0.187
3	10.899	162760	4491	RT:10.899	0.303
4	11.880	15203094	514220	RT:11.880	28.343
5	13.132	27582218	757395	RT:13.132	51.422
6	14.757	5041354	84613	RT:14.757	9.399
7	18.087	241666	6112	RT:18.087	0.451
Total		53638733	1497030		100.000

II. Reaction progress at standard condition



To an oven-dried sealed tube charged with methyl (2-methylbenzoyl)glycinate (**1a**) (41.44 mg, 0.2 mmol, 100 mol%), [Ru(*p*-Cymene)Cl_2]$_2$ (3.05 mg, 0.005 mmol, 2.5 mol%), $AgSbF_6$ (6.87 mg, 0.02 mmol, 10 mol%), $Cu(OAc)_2$ (18.16 mg, 0.10 mmol, 50 mol%) and methyl 2-(acetoxymethyl) acrylate (**2a**) (63.2 mg, 0.4 mmol, 200 mol %) followed by addition of DCE (1 mL) in open atmosphere at room temperature. The reaction mixture was started to stir at 120 °C and reaction samples (20 µL each) were collect from reaction tube for LC-MS analysis in variable time (10 min., 30 min., 1 h, 2 h, 3 h and 4 h) Volatile mixture was evaporated at reduce pressure and dried crude samples were dissolved in acetonitrile and submitted for LC-MS data collection.
Method: RP-18 HPLC column (5µm), Flow rate = 0.2 mL/min., Eluent = acetonitrile/water
All the collected LC-MS spectra have incorporated below.

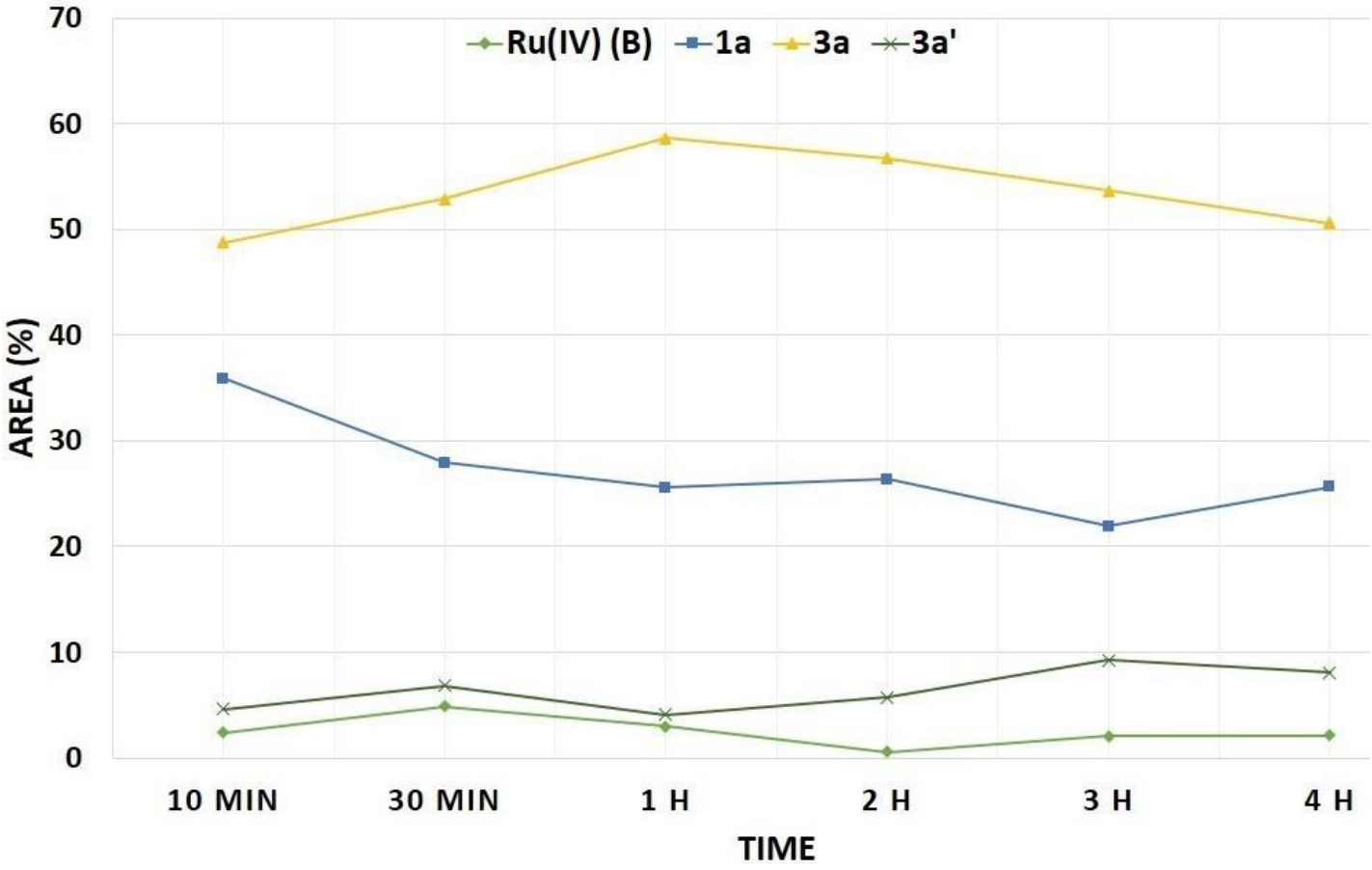
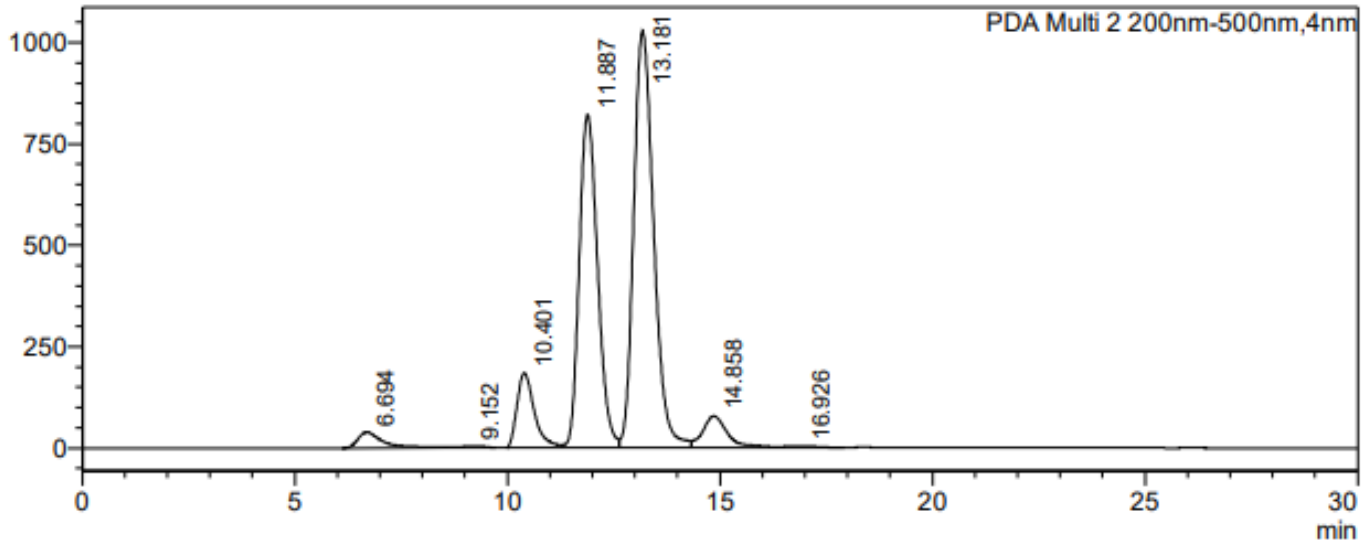


Fig. 2. Reaction progress at variable time (LC-MS data)

<Chromatogram>

mAU

Reaction time = 10 min.



Peak Table

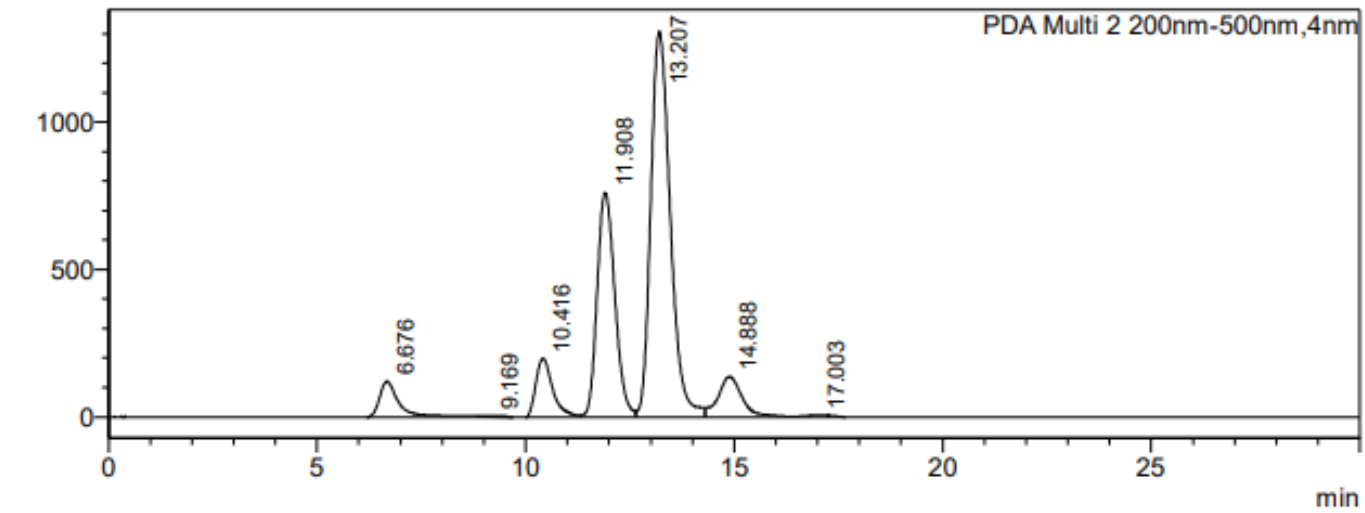
PDA Ch2 200nm-500nm

Peak#	Ret. Time	Area	Height	Name	Area%
1	6.694	1652961	39140	RT:6.694	2.404
2	9.152	197443	4170	RT:9.152	0.287
3	10.401	5279877	184932	RT:10.401	7.678
4	11.887	24700654	822398	RT:11.887	35.919
5	13.181	33546047	1028533	RT:13.181	48.782
6	14.858	3181822	78094	RT:14.858	4.627
7	16.926	208566	4007	RT:16.926	0.303
Total		68767371	2161275		100.000

<Chromatogram>

mAU

Reaction time = 30 min.



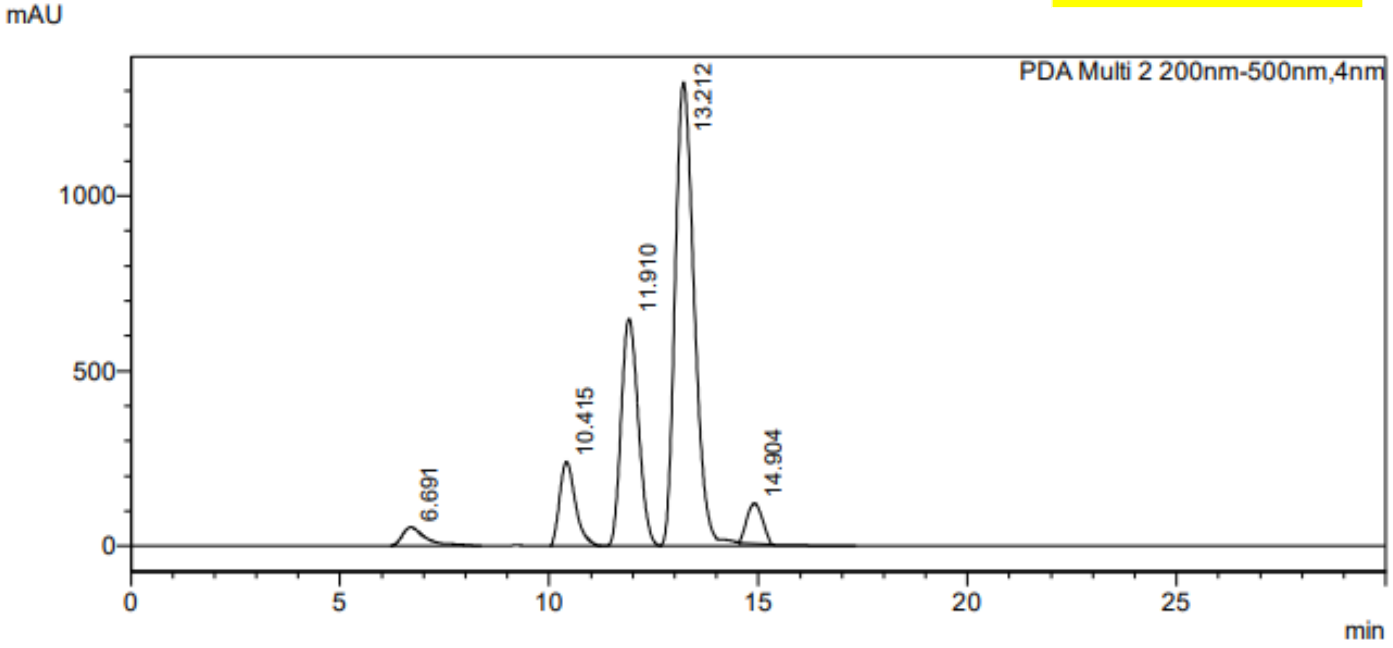
Peak Table

PDA Ch2 200nm-500nm

Peak#	Ret. Time	Area	Height	Area%
1	6.676	3924482	120306	4.879
2	9.169	130698	3804	0.162
3	10.416	5562164	199690	6.915
4	11.908	22484347	761945	27.952
5	13.207	42538182	1307852	52.882
6	14.888	5515489	136802	6.857
7	17.003	284732	6246	0.354
Total		80440094	2536645	100.000

<Chromatogram>

Reaction time = 1 h



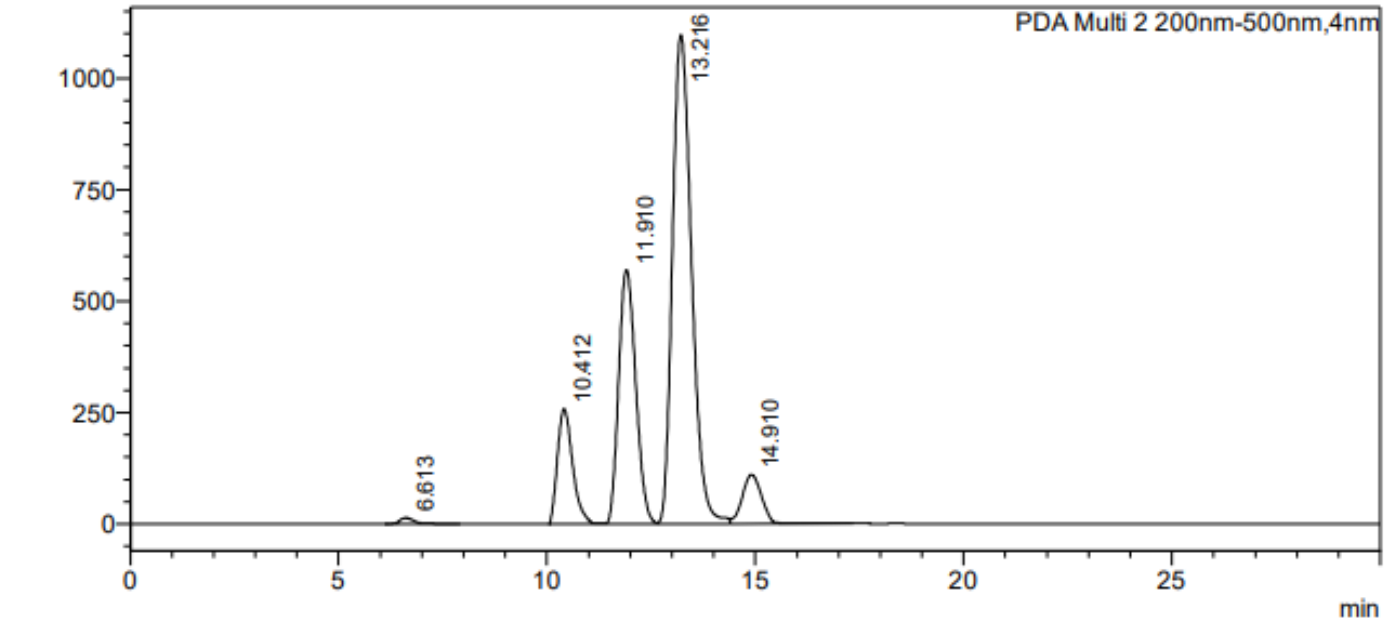
Peak Table

PDA Ch2 200nm-500nm

Peak#	Ret. Time	Area	Height	Area%
1	6.691	2136092	54129	2.955
2	10.415	6308812	240300	8.727
3	11.910	18473709	648342	25.554
4	13.212	42392882	1321715	58.641
5	14.904	2980544	114714	4.123
Total		72292039	2379201	100.000

<Chromatogram>

Reaction time = 2 h



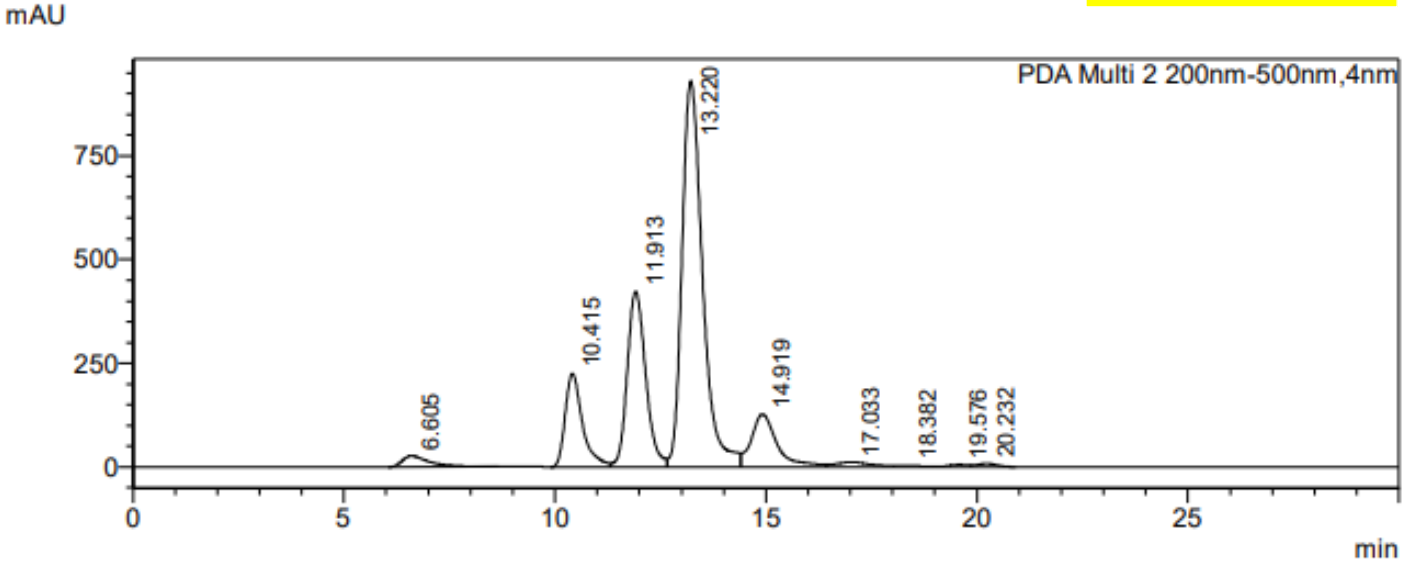
Peak Table

PDA Ch2 200nm-500nm

Peak#	Ret. Time	Area	Height	Area%
1	6.613	339592	13544	0.552
2	10.412	6508810	257403	10.571
3	11.910	16221359	569571	26.346
4	13.216	34958805	1096568	56.778
5	14.910	3542849	109765	5.754
Total		61571415	2046851	100.000

<Chromatogram>

Reaction time = 3 h



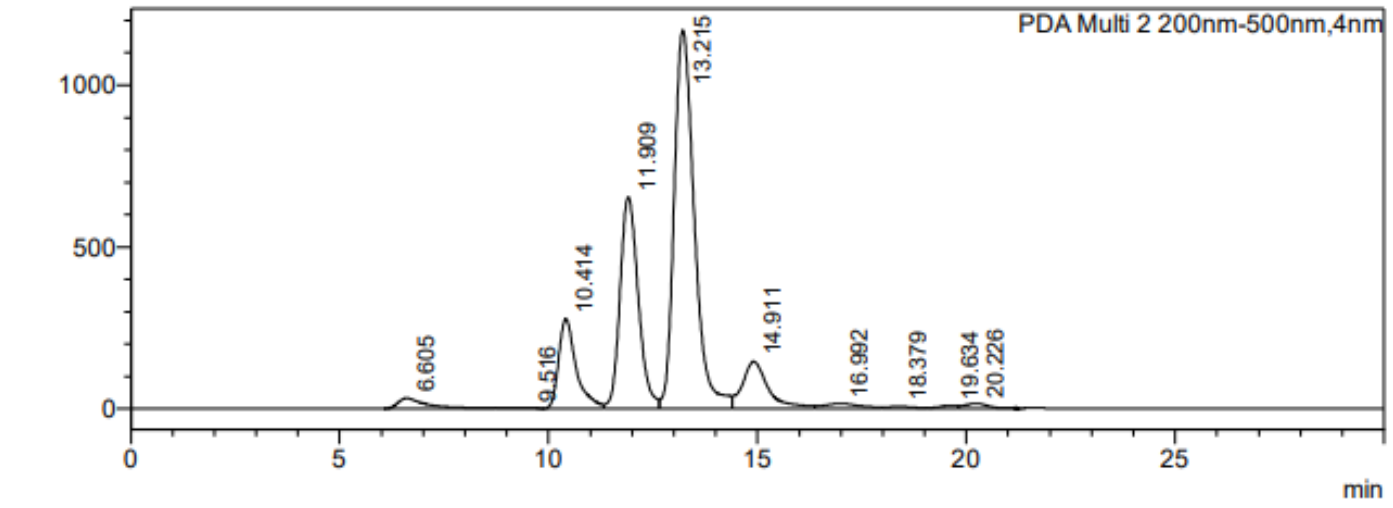
Peak Table

PDA Ch2 200nm-500nm

Peak#	Ret. Time	Area	Height	Area%
1	6.605	1198189	26642	2.046
2	10.415	6417997	225055	10.962
3	11.913	12846950	422657	21.942
4	13.220	31434952	930138	53.690
5	14.919	5405785	127004	9.233
6	17.033	673959	11600	1.151
7	18.382	127630	3362	0.218
8	19.576	179117	5489	0.306
9	20.232	264218	7905	0.451
Total		58548797	1759851	100.000

<Chromatogram>

Reaction time = 4 h

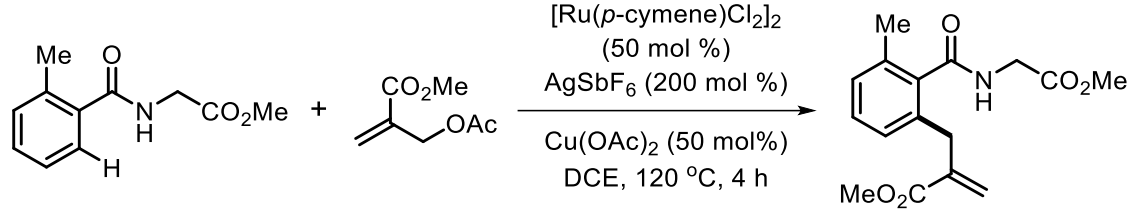


Peak Table

PDA Ch2 200nm-500nm

Peak#	Ret. Time	Area	Height	Area%
1	6.605	1633891	32455	2.104
2	9.516	169141	3087	0.218
3	10.414	8160175	277476	10.508
4	11.909	19900109	653905	25.625
5	13.215	39278134	1170092	50.577
6	14.911	6294094	145454	8.105
7	16.992	975185	15571	1.256
8	18.379	306874	6876	0.395
9	19.634	300706	9369	0.387
10	20.226	641821	16072	0.826
Total		77660129	2330358	100.000

III. Reaction progress at 50 mol % of $[Ru(p\text{-cymene})Cl_2]_2$ scale



1a **2a** **3a**

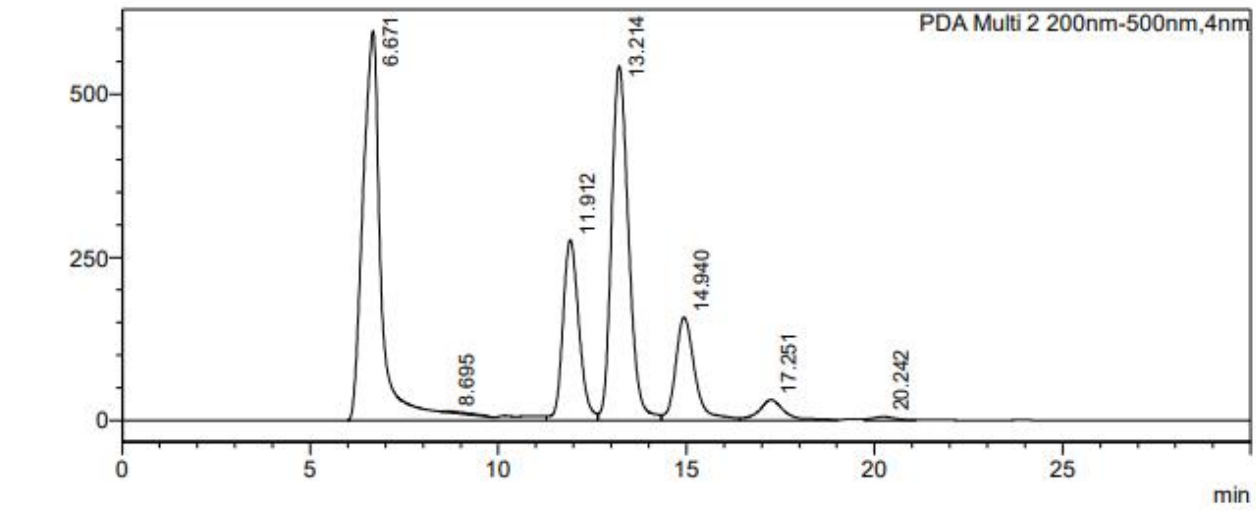
To an oven-dried sealed tube charged with methyl (2-methylbenzoyl)glycinate (**1a**) (41.44 mg, 0.2 mmol, 100 mol%), $[Ru(p\text{-Cymene})Cl_2]_2$ (61.23 mg, 0.10 mmol, 50 mol%), $AgSbF_6$ (137.44 mg, 0.4 mmol, 200 mol%), $Cu(OAc)_2$ (18.16 mg, 0.10 mmol, 50 mol%) and methyl 2-(acetoxymethyl) acrylate (**2a**) (63.2 mg, 0.4 mmol, 200 mol%) followed by addition of DCE (1 mL) in open atmosphere at room temperature. The reaction mixture was started to stir at 120 °C and reaction samples (20 µL each) were collect from reaction tube for LC-MS analysis in variable time (10 min., 30 min., 1 h, 2 h, 3 h and 4 h). Volatile mixture was evaporated at reduce pressure and dried crude samples were dissolved in acetonitrile and submitted for LC-MS data collection.

Method: RP-18 HPLC column (5µm), Flow rate = 0.2 mL/min., Eluent = acetonitrile/water

All the collected LC-MS spectra have incorporated below.

<Chromatogram>

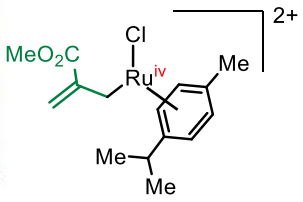
Reaction time = 10 min.



Peak Table

PDA Ch2 200nm-500nm

Peak#	Ret. Time	Area	Height	Area%
1	6.671	20923526	596534	38.904
2	8.695	132108	2088	0.246
3	11.912	8197519	276652	15.242
4	13.214	17135141	543331	31.860
5	14.940	5642011	158225	10.490
6	17.251	1510016	31606	2.808
7	20.242	242667	5535	0.451
Total		53782989	1613970	100.000



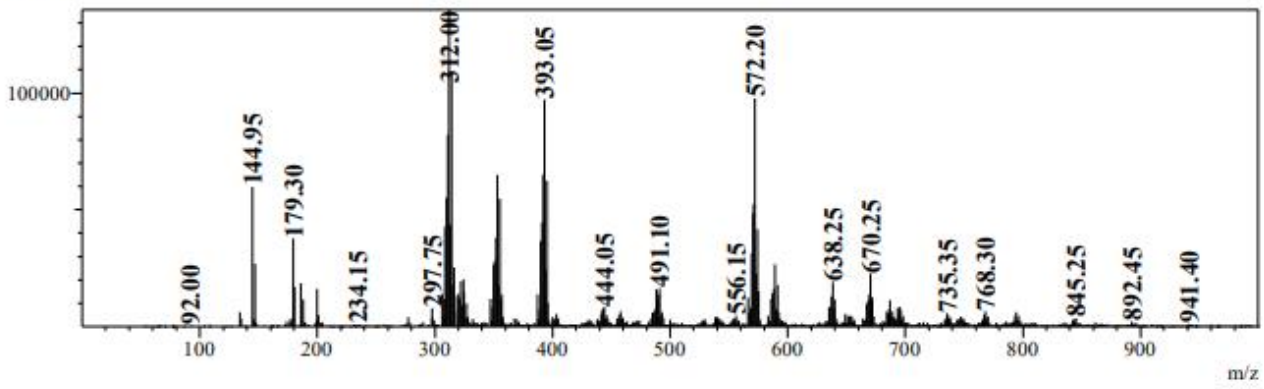
B - OAc

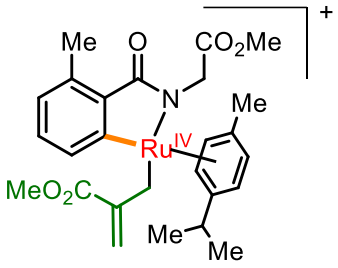
[M⁺+Na] = $C_{15}H_{21}ClO_2NaRu$

m/z = 393.01

MS Spectrum

Line#:1 R.Time:6.867(Scan#:413)
MassPeaks:1048
Spectrum Mode:Averaged 6.833-6.900(411-415) Base Peak:312.00(135691)
BG Mode:Calc Segment 1 - Event 1

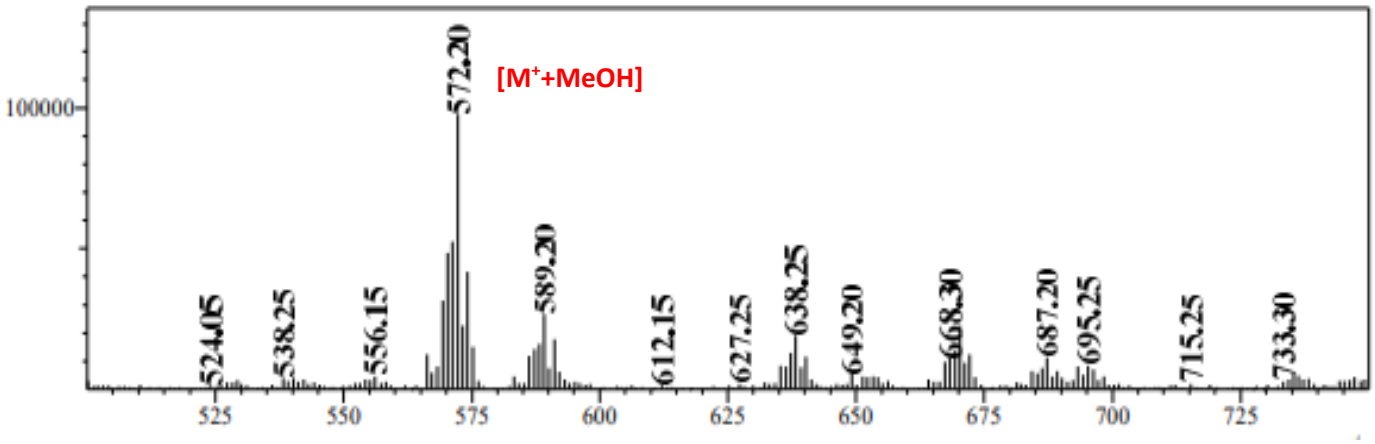


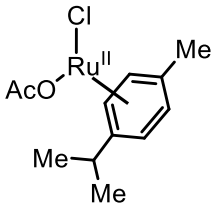


D

[M⁺+MeOH]: $C_{27}H_{36}NO_6Ru$

m/z = 572.16



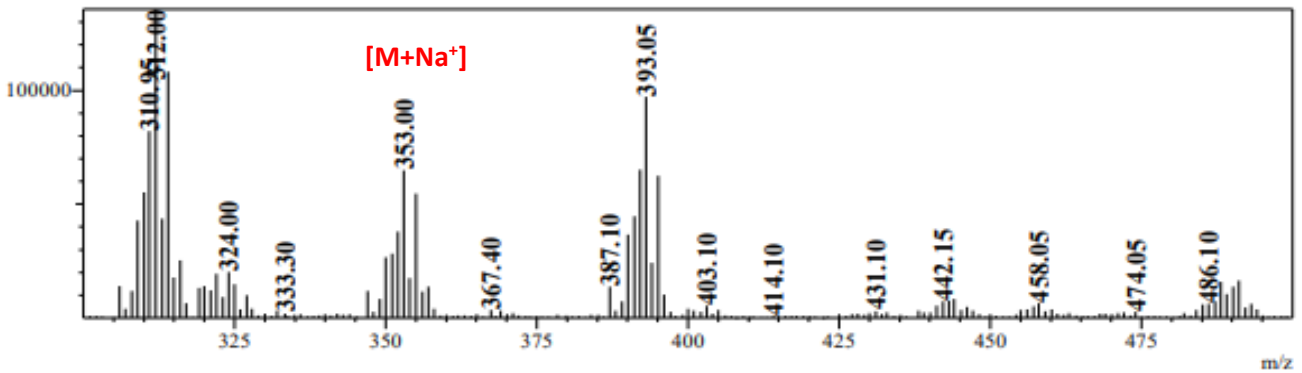


E

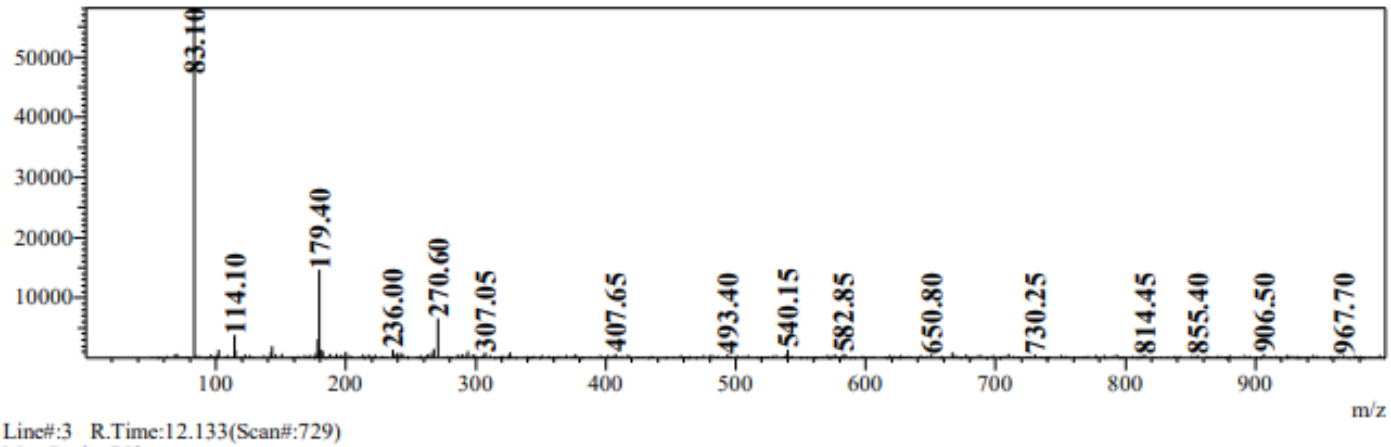
[M+Na⁺]: $C_{12}H_{17}ClNaO_2Ru$

m/z = 352.99

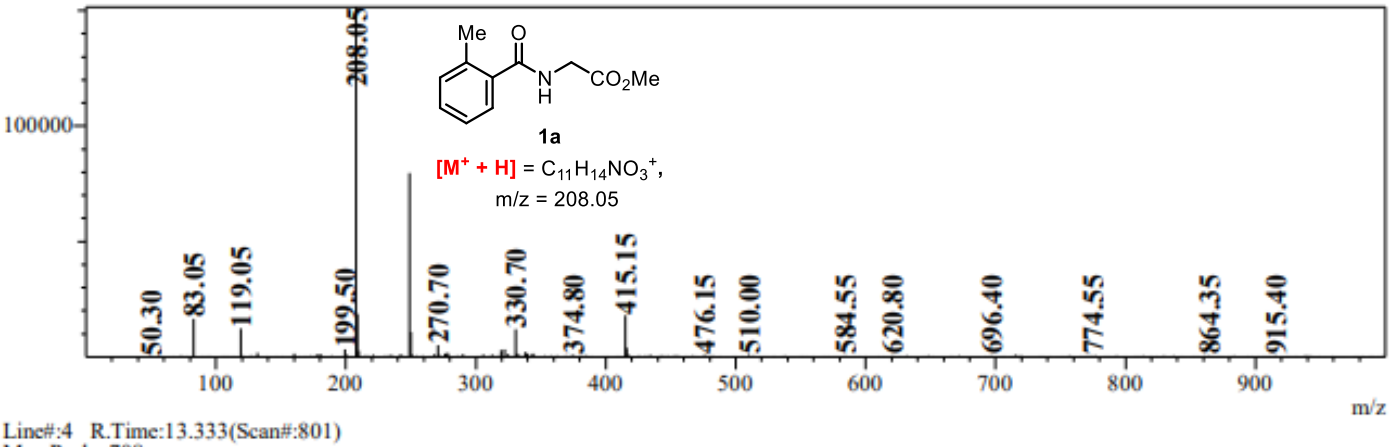
Line#:1 R.Time:6.867(Scan#:413)
MassPeaks:1048
Spectrum Mode:Averaged 6.833-6.900(411-415) Base Peak:312.00(135691)
BG Mode:Calc Segment 1 - Event 1



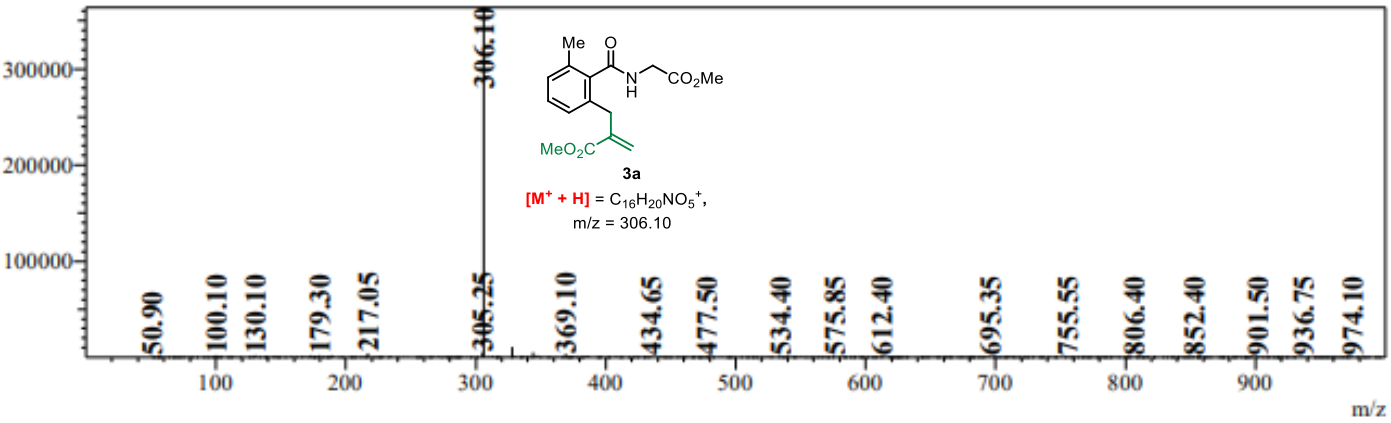
Line#:2 R.Time:11.233(Scan#:675)
MassPeaks:691
Spectrum Mode:Averaged 11.200-11.267(673-677) Base Peak:83.10(58142)
BG Mode:Calc Segment 1 - Event 1



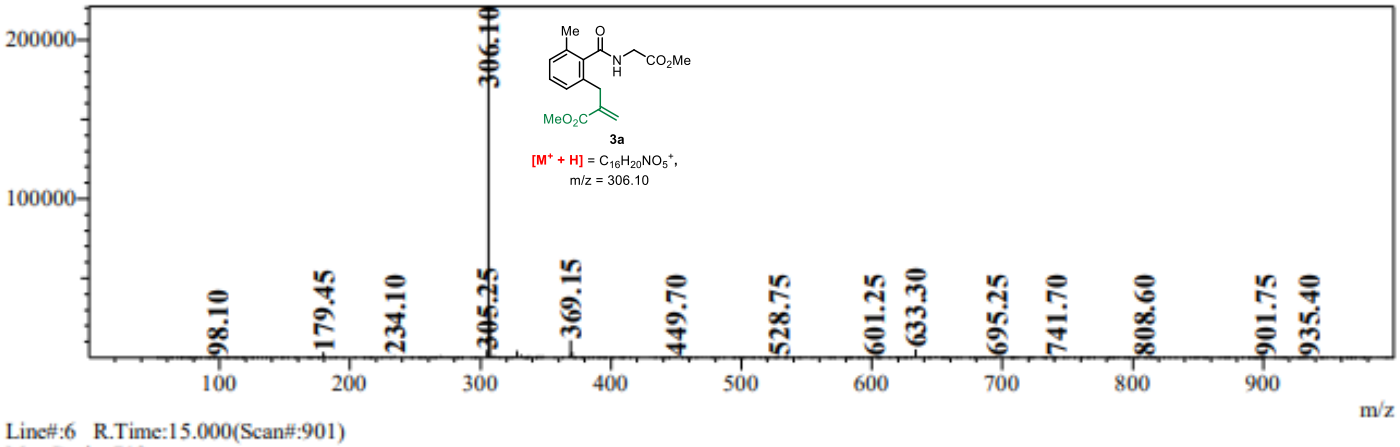
Line#:3 R.Time:12.133(Scan#:729)
MassPeaks:753
Spectrum Mode:Averaged 12.100-12.167(727-731) Base Peak:208.05(151571)
BG Mode:Calc Segment 1 - Event 1



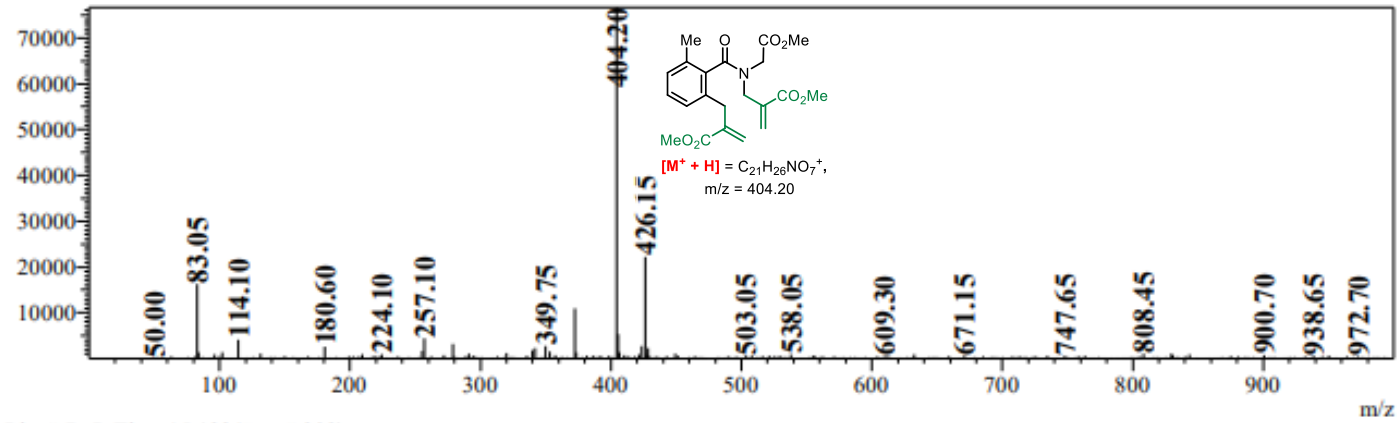
Line#:4 R.Time:13.333(Scan#:801)
MassPeaks:708
Spectrum Mode:Averaged 13.300-13.367(799-803) Base Peak:306.10(363948)
BG Mode:Calc Segment 1 - Event 1



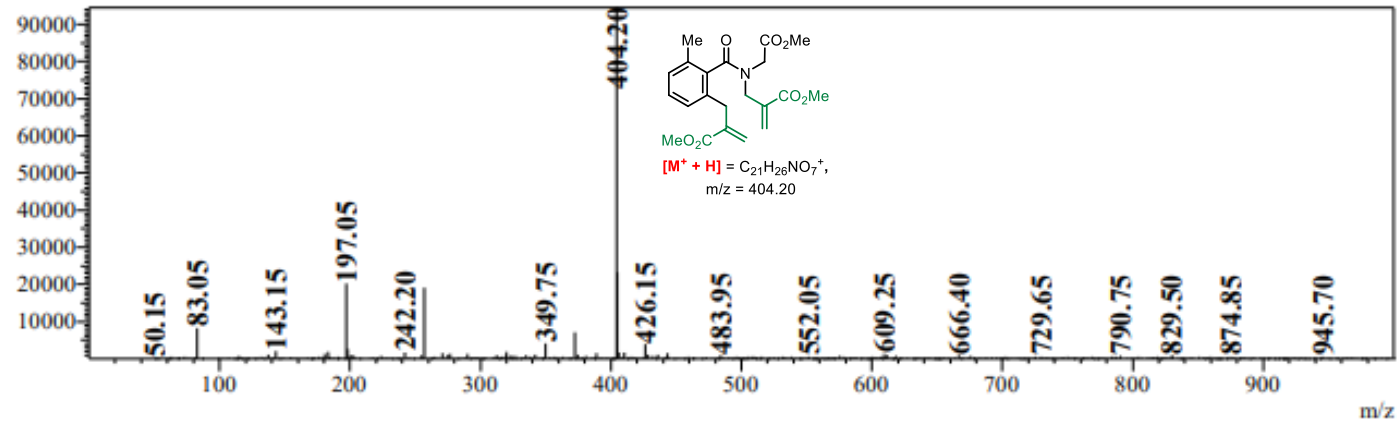
Line#:5 R.Time:13.500(Scan#:811)
MassPeaks:711
Spectrum Mode:Averaged 13.467-13.533(809-813) Base Peak:306.10(221094)
BG Mode:Calc Segment 1 - Event 1



Line#:6 R.Time:15.000(Scan#:901)
MassPeaks:719
Spectrum Mode:Averaged 14.967-15.033(899-903) Base Peak:404.20(76664)
BG Mode:Calc Segment 1 - Event 1

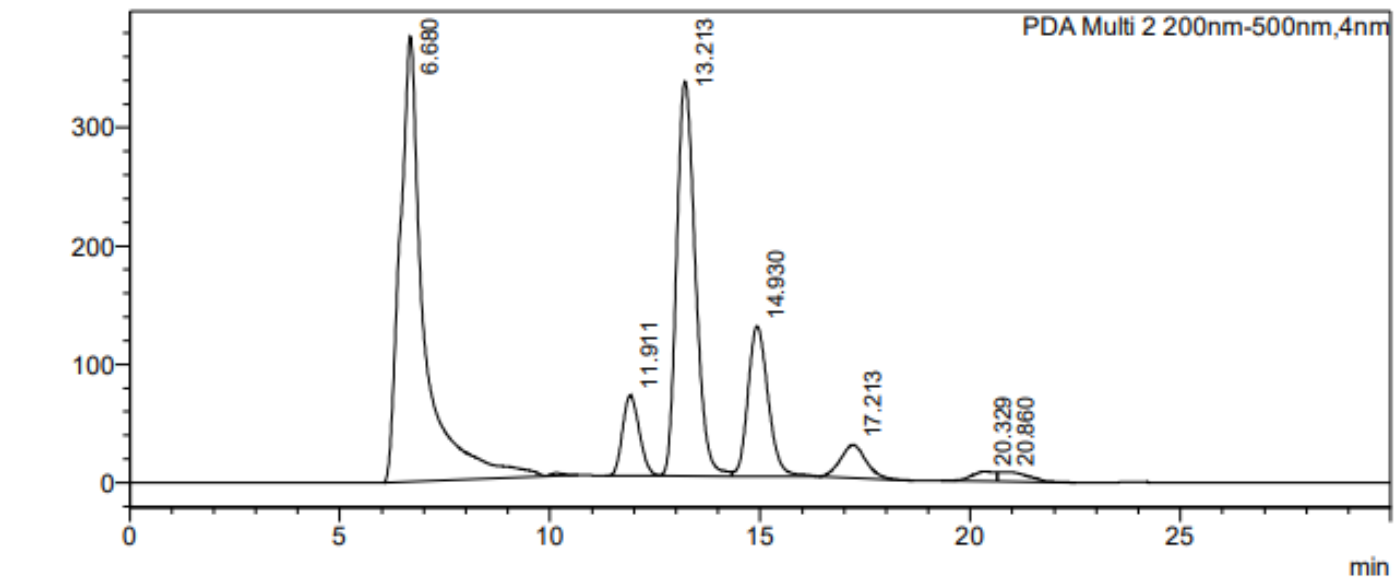


Line#:7 R.Time:15.133(Scan#:909)
MassPeaks:743
Spectrum Mode:Averaged 15.100-15.167(907-911) Base Peak:404.20(94500)
BG Mode:Calc Segment 1 - Event 1



<Chromatogram>

Reaction time = 30 min.



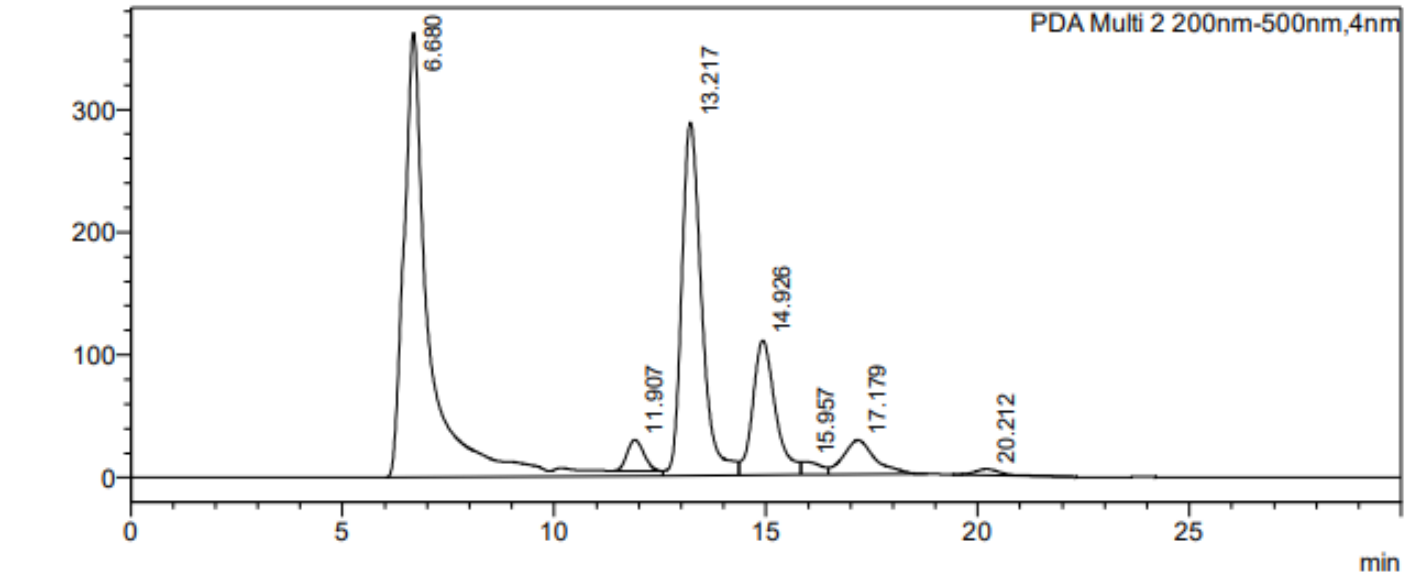
Peak Table

PDA Ch2 200nm-500nm

Peak#	Ret. Time	Area	Height	Area%
1	6.680	15107140	376210	45.080
2	11.911	1896958	67830	5.661
3	13.213	10338152	333668	30.849
4	14.930	4247141	126725	12.674
5	17.213	1188368	28009	3.546
6	20.329	333710	8223	0.996
7	20.860	400482	8177	1.195
Total		33511950	948840	100.000

<Chromatogram>

Reaction time = 1 h



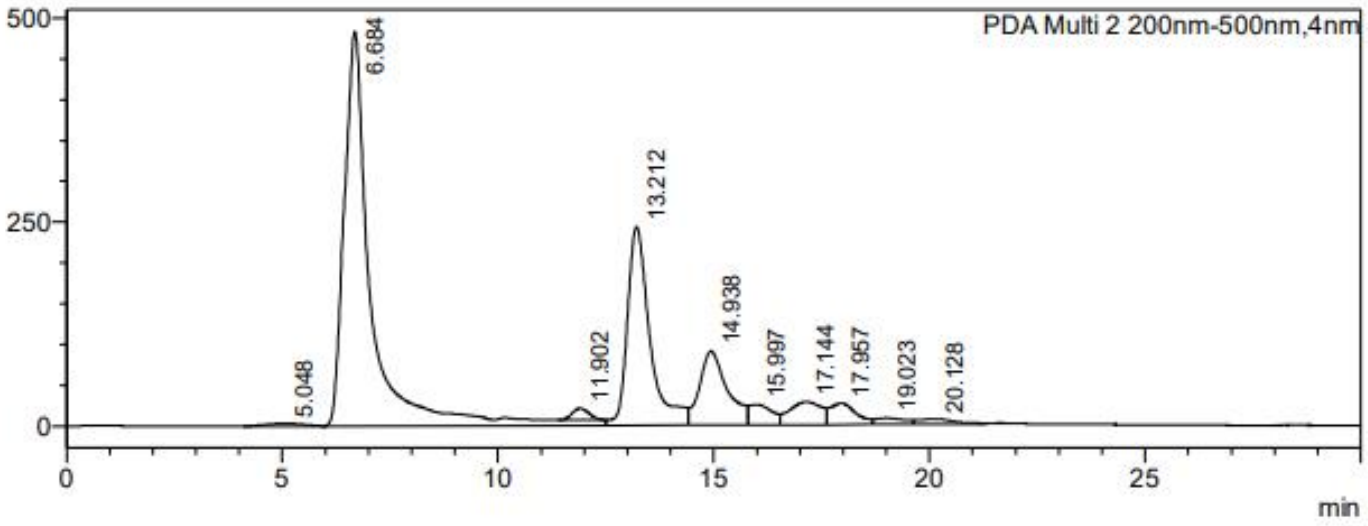
Peak Table

PDA Ch2 200nm-500nm

Peak#	Ret. Time	Area	Height	Area%
1	6.680	15276841	362413	48.477
2	11.907	694782	25381	2.205
3	13.217	9416597	287722	29.881
4	14.926	4088466	109712	12.974
5	15.957	338565	10454	1.074
6	17.179	1467653	27991	4.657
7	20.212	230387	5099	0.731
Total		31513290	828771	100.000

<Chromatogram>

Reaction time = 2 h



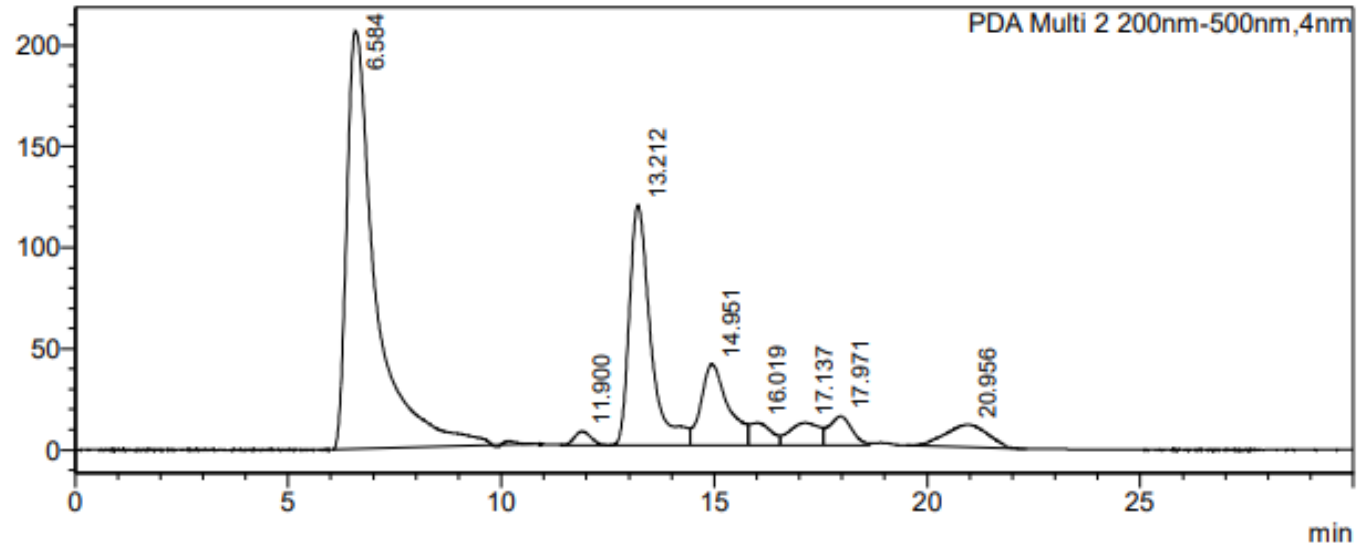
Peak Table

PDA Ch2 200nm-500nm

Peak#	Ret. Time	Area	Height	Area%
1	5.048	204591	3335	0.529
2	6.684	20980732	482847	54.278
3	11.902	378156	14033	0.978
4	13.212	8818207	242738	22.813
5	14.938	4033997	90155	10.436
6	15.997	914762	24658	2.367
7	17.144	1452530	28079	3.758
8	17.957	1094682	26202	2.832
9	19.023	378998	7827	0.980
10	20.128	397719	6625	1.029
Total		38654374	926500	100.000

<Chromatogram>

Reaction time = 3 h



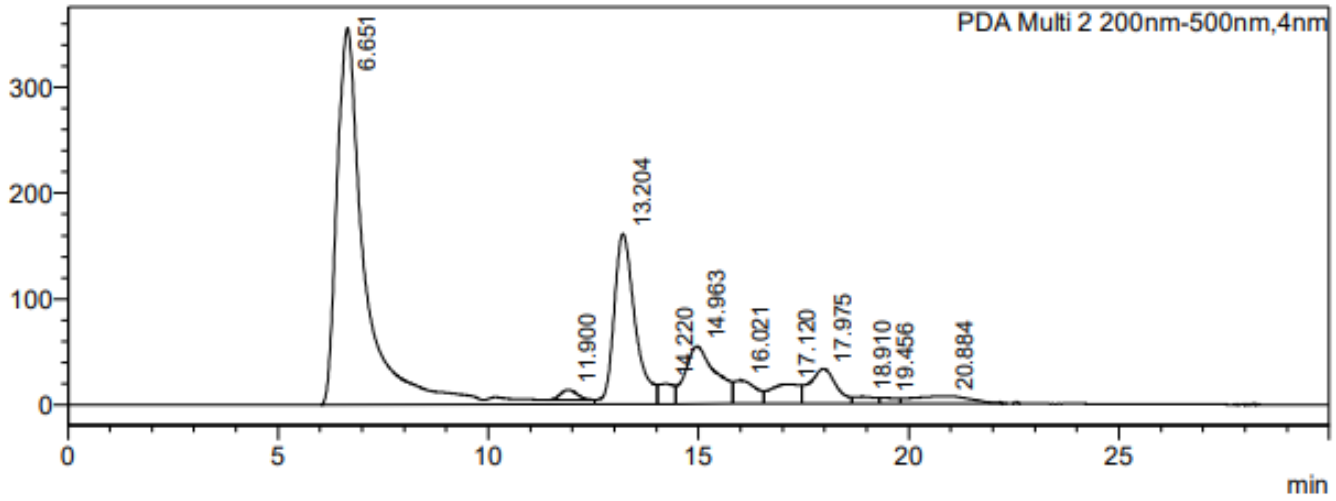
Peak Table

PDA Ch2 200nm-500nm

Peak#	Ret. Time	Area	Height	Area%
1	6.584	9723263	206709	53.816
2	11.900	177395	6708	0.982
3	13.212	4117534	118538	22.790
4	14.951	1788765	40113	9.900
5	16.019	384515	11082	2.128
6	17.137	548236	11135	3.034
7	17.971	541373	14450	2.996
8	20.956	786409	11156	4.353
Total		18067491	419890	100.000

<Chromatogram>

Reaction time = 4 h



Peak Table

PDA Ch2 200nm-500nm

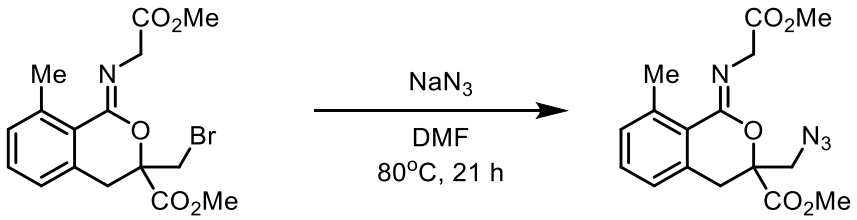
Peak#	Ret. Time	Area	Height	Area%
1	6.651	16723112	355999	55.801
2	11.900	256222	9487	0.855
3	13.204	5597046	160988	18.676
4	14.220	480412	18983	1.603
5	14.963	2779307	54318	9.274
6	16.021	798658	21951	2.665
7	17.120	894604	18441	2.985
8	17.975	1424997	33080	4.755
9	18.910	232984	6395	0.777
10	19.456	145637	5102	0.486
11	20.884	636229	6839	2.123
Total		29969208	691584	100.000

General procedure for scale-up experiment:

To an oven-dried round bottom flask charged with methyl (2-methylbenzoyl)glycinate (**1a**) (1 g, 4.8 mmol, 100 mol%), [Ru(*p*-cymene)Cl_2]$_2$ (73.5 mg, 0.12 mmol, 2.5 mol%), $AgSbF_6$ (164.9 mg, 0.48 mmol, 10 mol%), Cu(OAc)$_2$•H_2O (481.1 mg, 2.4 mmol, 50 mol%), methyl 2-(acetoxymethyl) acrylate (**2a**) (1.52 g, 9.6 mmol, 200 mol%) followed by addition of TCE (24.1 mL) under air at room temperature. The reaction mixture was allowed to stir at 120 °C for 4 h. Reaction mixture was cooled to room temperature and filtered on small celite pad with additional TCE (12.5 mL). Filtrate was collected in another round bottom flask followed by addition of *N*-bromosuccinamide (**4a**) (428.9 mg, 9.6 mmol, 200 mol%) in open atmosphere at room temperature. Reaction was further allowed to stir at room temperature for 4 h. Reaction mixture was diluted with dichloromethane (10 mL) and concentrated at reduced pressure. The residue was purified by flash column chromatography (EtOAc/*n*-hexane = 1:9) to afford isochroman-1-imines (**5a**) (1.15 g, 63%) as sticky colourless liquid.

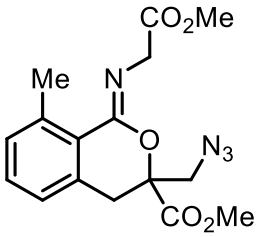
Synthetic transformations

a) Methyl (*Z*)-3-(azidomethyl)-1-((2-methoxy-2-oxoethyl)imino)-8-methylisochromane-3-carboxylate (6)



5a **6**

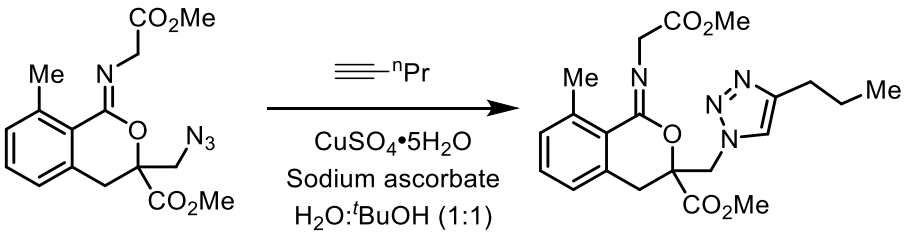
To an oven-dried screw cap sealed tube charged with methyl (*Z*)-3-(bromomethyl)-1-((2-methoxy-2-oxoethyl)imino)-8-methylisochromane-3-carboxylate (**5a**) (76.84 mg,0.2 mmol, 100 mol%.), sodium azid (65.0 mg, 1.0 mmol, 500 mol%), DMF (1 mL) were added under air at room temperature. The reaction mixture was allowed to stir at 80 °C for 21 h. Reaction mixture was cooled to room temperature, diluted with dichloromethane (3 mL) and washed with H_2O (3 x 3 mL). Organic layer was dried over anhydrous Na_2SO_4 and concentrated at reduced pressure. The residue was purified by flash column chromatography (EtOAc/*n*-hexane = 1:4) to afford **6** (38.8 mg, 54%) as sticky colourless liquid.



6

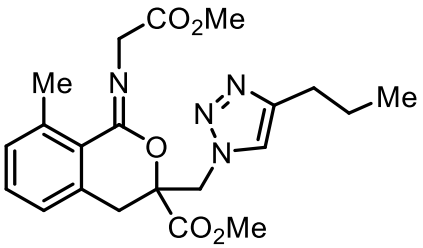
38.0 mg, (55%); sticky colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 6.4 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 4.47 (d, *J* = 18.5 Hz, 1H), 4.39 (d, *J* = 18.5 Hz, 1H), 3.77 (s, 3H), 3.63 (d, *J* = 1.5 Hz, 2H), 3.58 (s, 3H), 3.23 (d, *J* = 15.4 Hz, 1H), 3.14 (d, *J* = 15.5 Hz, 1H), 2.70 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.9, 170.2, 152.2, 140.6, 133.0, 131.8, 130.3, 126.0, 125.4, 82.8, 56.7, 53.2, 52.0, 49.2, 35.1, 23.2 ; **IR** (KBr) υ 2926, 2107, 1750, 1666, 1227, 780 cm^{-1}; **HRMS**(ESI) calcd for $C_{16}H_{19}N_4O_5$ $[M+H]^+$ 347.1355, found 347.1339.

b) Methyl 1-((2-methoxy-2-oxoethyl)imino)-8-methyl-3-((4-propyl-1*H*-1,2,3-triazol-1-yl)methyl)isochromane-3-carboxylate (7)



6 **7**

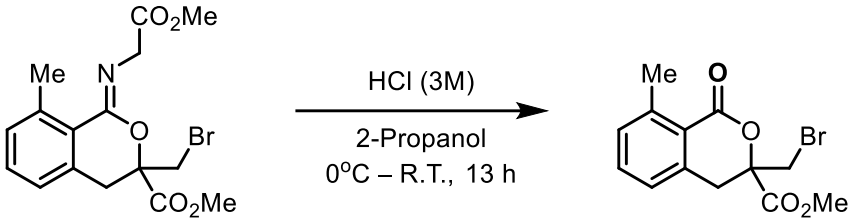
Methyl (Z)-3-(azidomethyl)-1-((2-methoxy-2-oxoethyl)imino)-8-methylisochromane-3-carboxylate (**6**) (69.26 mg, 0.2 mmol) and 1- Pentyne (27.24 mg, 0.4 mmol) were dissolved in a 1:2 tert-butyl alcohol/water mixture (2 mL). Sodium ascorbate (19.81 mg, 0.1 mmol,) was added, followed by copper(II) sulfate pentahydrate (12.48 mg, 0.50 mmol). The heterogeneous mixture was stirred vigorously 2h , at room temperature which point it cleared and TLC analysis indicated complete consumption of the reactants. The reaction mixture was diluted with diluted with water (3mL) and extracted with Et_2O. The organic phase was dried over Na_2SO_4 (anhy.), concentrated at reduced pressure. The residue was purified by flash column chromatography (EtOAc/*n*-hexane = 1:2) to afford colourless sticky liquid, **7** (52.1 mg, 78%).



7

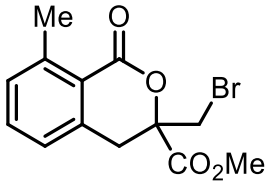
(52.1 mg, 62%) as sticky colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.3 Hz, 1H), 4.87 (d, *J* = 14.3 Hz, 1H), 4.74 (d, *J* = 14.4 Hz, 1H), 4.37 (d, *J* = 2.3 Hz, 2H), 3.78 (s, 3H), 3.54 (s, 3H), 3.32 (d, *J* = 15.6 Hz, 1H), 3.01 (d, *J* = 15.5 Hz, 1H), 2.72 – 2.68 (m, 2H), 2.66 (s, 3H), 1.71 (dd, *J* = 15.0, 7.5 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.8, 169.5, 152.2, 148.7, 140.7, 132.9, 131.9, 130.6, 125.6, 125.5, 122.5, 81.3, 55.1, 53.4, 52.0, 49.2, 35.0, 27.7, 23.3, 22.7, 13.9; **IR** (KBr) υ 3019, 1753, 1438, 1214, 744 cm^{-1}; **HRMS** (ESI) $C_{21}H_{27}N_4O_5$ $[M+H]^+$ calcd for 415.1981 found 415.1981.

c) Methyl 3-(bromomethyl)-8-methyl-1-oxoisochromane-3-carboxylate (8)



5a **8**

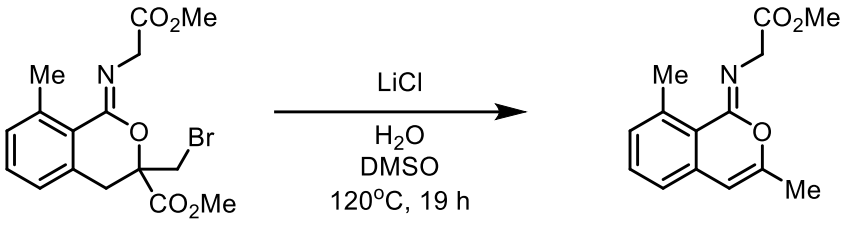
To an oven-dried screw cap sealed tube charged with methyl (*Z*)-3-(bromomethyl)-1-((2-methoxy-2-oxoethyl)imino)-8-methylisochromane-3-carboxylate (**5a**) (76.84 mg,0.2 mmol, 100 mol%.), HCl (12 µL, 3 Molar) followed by 2-propanol (1 mL) under air at room temperature. The reaction mixture was allowed to stir from 0°C to room temperature for 21 h. Reaction mixture was quenched with saturated aq. $NaHCO_3$ (3 mL) and three times extract with EtOAc. Organic layer was dried over anhydrous Na_2SO_4 and concentrated at reduced pressure. The residue was purified by flash column chromatography (EtOAc/*n*-hexane = 3:7) to afford **8** (55.5 mg, 88%) as sticky colourless liquid.



8

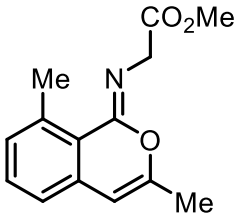
55.5 mg, (88%); sticky colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 3.81 (d, *J* = 11.0 Hz, 1H), 3.75 (d, *J* = 11.0 Hz, 1H), 3.64 (s, 3H), 3.43 (d, *J* = 15.9 Hz, 1H), 3.32 (d, *J* = 15.9 Hz, 1H), 2.67 (s, 3H**)**; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.4, 162.4, 143.3, 136.1, 133.3, 131.9, 125.6, 123.0, 82.6, 53.5, 35.6, 34.7, 22.3; **IR** (KBr) υ 2959, 1730, 1595, 1437, 1204, 798 cm^{-1}; **HRMS**(ESI) $C_{13}H_{14}BrO_4$ $[M+H]^+$ calcd for 313.0075, found 313.0061.

d) Methyl (Z)-2-((3-(bromomethyl)-3-(hydroxymethyl)-8-methylisochroman-1-ylidene)amino)acetate (9)



5a **9**

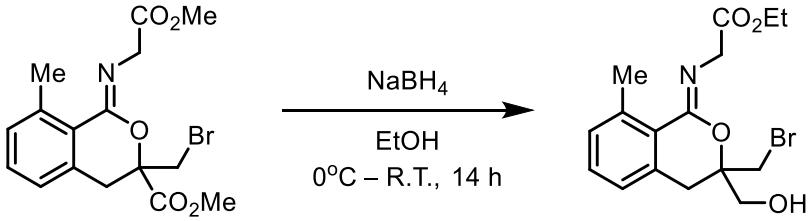
To an oven-dried screw cap sealed tube charged with methyl (*Z*)-3-(bromomethyl)-1-((2-methoxy-2-oxoethyl)imino)-8-methylisochromane-3-carboxylate (**5a**) (76.84 mg,0.2 mmol, 100 mol%.), LiCl (25.44 mg, 0.6 mmol, 300 mol%), H_2O (10 µL) followed by DMSO (1 mL) were added under air at room temperature. The reaction mixture was allowed to stir at 120 °C for 19 h. Reaction mixture was cooled to room temperature, diluted with EtOAc (3 mL) and washed with H_2O (3 x 3 mL). Organic layer was dried over anhydrous Na_2SO_4 and concentrated at reduced pressure. The residue was purified by flash column chromatography (EtOAc/*n*-hexane = 1:4) to afford **9** (25.5 mg, 52%) as white solid; mp 146-148 °C



9

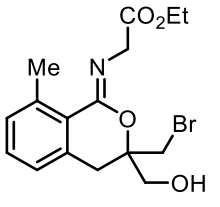
25.5 mg, (52%); white solid; mp 146-148 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.16 (d, *J* = 7.3 Hz, 1H), 6.31 (s, 1H), 4.79 (s, 2H), 3.78 (s, 3H), 2.88 (s, 3H), 2.32 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.5, 163.0, 141.0, 137.7, 137.3, 130.9, 128.3, 122.7, 121.7, 105.8, 51.7, 44.5, 22.9, 19.7; **IR** (KBr) υ 3851, 3056, 2922, 1740, 1659, 1230 806 cm-1; **HRMS** (ESI) calcd for $C_{14}H_{16}NO_3$ $[M+H]^+$ 246.1130, found 246.1119.

e) Ethyl 3-(bromomethyl)-8-methyl-1-oxoisochromane-3-carboxylate (10)



5a 10

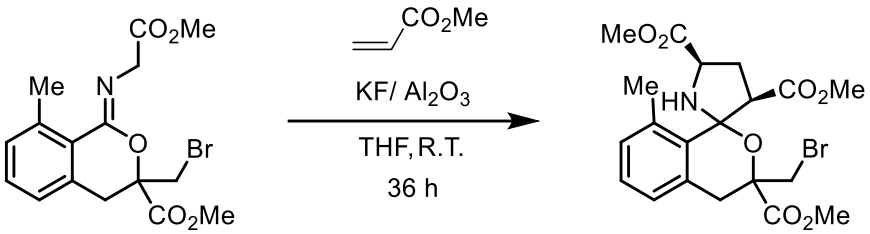
To an oven-dried screw cap sealed tube charged with methyl (*Z*)-3-(bromomethyl)-1-((2-methoxy-2-oxoethyl)imino)-8-methylisochromane-3-carboxylate (**5a**) (76.84 mg,0.2 mmol, 100 mol%), $NaBH_4$ (22.69 mg,0.6 mmol, 300 mol%), followed by EtOH (1 mL) under air at room temperature. The reaction mixture was allowed to stir from 0°C to room temperature for 14 h. Reaction mixture was diluted with DCM (3 mL) and washed with H_2O (3 x 2 mL). Organic layer was dried over anhydrous Na_2SO_4 and concentrated at reduced pressure. The residue was purified by flash column chromatography (EtOAc/*n*-hexane = 1:4) to afford **10** (44.2 mg, 62%) as sticky colourless liquid.



10

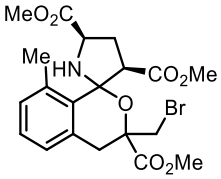
44.2 mg, (59%); sticky colourless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.4 Hz, 1H), 4.42 (d, *J* = 16.8 Hz, 1H), 4.28 (d, *J* = 16.8 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.78 (d, *J* = 12.2 Hz, 1H), 3.74 (d, *J* = 12.2 Hz, 1H), 3.51 (d, *J* = 10.6 Hz, 1H), 3.39 (d, *J* = 10.6 Hz, 1H), 3.18 (d, *J* = 16.1 Hz, 1H), 3.13 (d, *J* = 16.1 Hz, 1H), 2.67 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.1, 153.7, 140.5, 134.6, 131.4, 130.7, 126.3, 125.5, 80.4, 65.0, 61.2, 49.1, 33.7, 32.92, 23.4, 14.4; **IR** (KBr) υ 3472, 2923, 1732, 1653, 1191, 779 cm-1; **HRMS** (ESI) calcd for $C_{16}H_{21}BrNO_4$ $[M+H]^+$ 370.0654 found 370.0649.

f) Trimethyl-(1R,3'R,5'S)-3-(bromomethyl)-8-methyl-3,4-dihydro-2H-spiro[naphthalene-1,2'-pyrrolidine]-3,3',5'-tricarboxylate (11a)



5a **11a**

To an oven-dried screw cap sealed tube charged with methyl (*Z*)-3-(bromomethyl)-1-((2-methoxy-2-oxoethyl)imino)-8-methylisochromane-3-carboxylate (**5a**) (76.84 mg,0.2 mmol, 100 mol%.), KF/Al_2O_3 (40% w/w), followed by THF (2 mL) under air at room temperature. The reaction mixture was allowed to stir at room temperature for 36 h. Reaction mixture was diluted with DCM (3 mL) and washed with H_2O (3 x 2 mL). Organic layer was dried over anhydrous Na_2SO_4 and concentrated at reduced pressure. The residue was purified by flash column chromatography (EtOAc/*n*-hexane = 1:4) to afford **11a** (55.5 mg, 58%) as sticky colourless liquid.

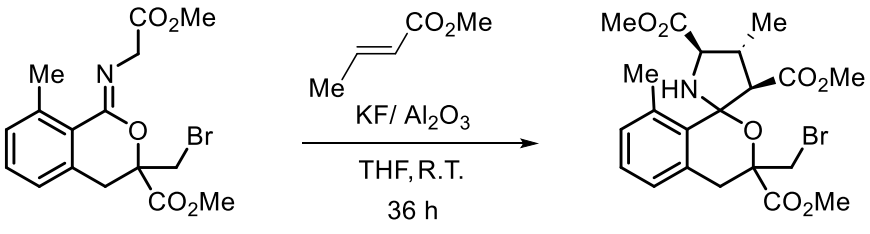


11a
dr = 1.0 : 0.5

11a (major): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (m, 1H), 7.16 (m, 1H), 6.96 (m, 1H), 4.75 (m, 1H), 3.76 (d, *J* = 10.9 Hz, 1H), 3.74 (s, 3H), 3.65 (d, *J* = 10.8 Hz, 1H), 3.63 (s, 3H), 3.60 (s, 3H), 3.26 (s, 2H), 2.67 (s, 3H), 2.63–2.40 (m, 1H), 2.38–2.11 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.9, 173.3, 169.5, 151.7, 140.6, 133.3, 131.7, 130.4, 125.9, 125.4, 81.1, 58.0, 53.1, 52.0, 51.7, 36.3, 35.0, 30.9, 28.9, 23.2; **IR** (KBr) υ 3526, 2924, 1735, 1646, 1437, 1209, 758 cm^{-1}; **HRMS** (ESI) $C_{20}H_{25}BrNO_7$ $[M+H]^+$ calcd for 470.0814 found 470.0810.

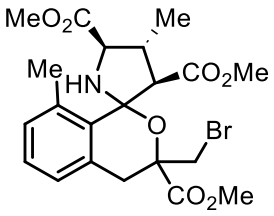
11a (minor): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (m, 1H), 7.16 (m, 1H), 6.96 (m, 1H), 4.75 (m, 1H), 3.73 (s, 3H), 3.72 (d, *J* = 10.8 Hz, 1H), 3.68 (s, 3H), 3.65 (d, *J* = 10.8 Hz, 1H), 3.59 (s, 2H), 3.23 (s, 3H), 2.67 (s, 2H), 2.63–2.40 (m, 2H), 2.3 –2.11 (m, 1H); **^{13}C NMR** (101 MHz, CDCl3) δ 174.0, 173.4, 169.6, 152.3, 140.4, 133.2, 131.8, 130.4, 125.8, 125.4, 81.1, 58.1, 53.1, 52.0, 51.6, 36.5, 35.1, 30.9, 29.0, 23.5.

g) Trimethyl (3'R,4'R,5'R)-3-(bromomethyl)-4',8-dimethylspiro[isochromane-1,2'-pyrrolidine]-3,3',5'-tricarboxylate (11b)



5a **11b**

To an oven-dried screw cap sealed tube charged with methyl (*Z*)-3-(bromomethyl)-1-((2-methoxy-2-oxoethyl)imino)-8-methylisochromane-3-carboxylate (**5a**) (76.84 mg,0.2 mmol, 100 mol%.), KF/Al_2O_3 (40% w/w), followed by THF (2 mL) and methyl (E)-but-2-enoate (40 mg, 0.8 mmol, 400 mol%) under air at room temperature. The reaction mixture was allowed to stir at room temperature for 36 h. Reaction mixture was diluted with DCM (3 mL) and washed with H_2O (3 x 2 mL). Organic layer was dried over anhydrous Na_2SO_4 and concentrated at reduced pressure. The residue was purified by flash column chromatography (EtOAc/*n*-hexane = 1:4) to afford **11b** (56 mg, 58%) as sticky colourless liquid.



11b

11b (major): **^{1}H NMR** δ 7.26–7.12 (m, 2H), 6.96 (t, *J* = 7.7 Hz, 1H), 4.61 (d, *J* = 4.3 Hz, 1H), 3.75 (d, *J* = 10.8 Hz, 1H), 3.72 (s, 3H), 3.68 (d, *J* = 10.8 Hz, 1H), 3.67 (s, 3H), 3.59 (s, 3H), 3.23 (s, 2H), 2.69 (s, 3H), 2.46–2.32 (m, 1H), 1.13 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** δ 173.9, 173.0, 169.7, 152.7, 140.4, 133.3, 131.8, 130.4, 125.9, 125.5, 81.0, 63.6, 53.1, 51.9, 51.6, 37.4, 36.5, 35.1, 34.1, 24.0, 18.0; **IR** (KBr) υ 2957, 1733, 1658, 1435, 1169, 756 cm^{-1}; **HRMS (ESI)** $C_{21}H_{27}BrNO_7$ $[M+H]^+$ calcd for 484.0971 found 484.0964.

11b (minor): **^{1}H NMR** δ 7.26–7.12 (m, 2H), 6.96 (t, *J* = 7.7 Hz, 1H), 4.53 (d, *J* = 4.7 Hz, 1H), 3.72 (s, 3H), 3.65 (d, *J* = 10.8 Hz, 1H), 3.64 (s, 3H), 3.61 (d, *J* = 10.8 Hz, 1H), 3.60 (s, 3H), 3.25 (d, *J* = 3.0 Hz, 2H), 2.68 (s, 3H), 2.44–2.29 (m, 1H), 1.05 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** δ 173.8, 172.7, 169.5, 151.9, 140.7, 133.3, 131.7, 130.4, 125.7, 125.5, 81.1, 63.6, 53.1, 51.8, 51.5, 37.6, 36.2, 34.9, 34.2, 23.6 , 17.8.

Single crystal X-Ray crystallography data of 5o (CCDC 2111276):

Compound **5o** was dissolved in isopropanol and crystallized in a 5 mL glass at room temperature. Appropriate single crystal was selected under microscope and mounted with paratone oil on a Cryoloop. X-Ray data was collected at 293K on Bruker D8 QUEST Photon 100 difractometer using monochromated Mo Kα radiation (λ = 0.71073 Å). Integrations and scaling were performed using SAINT program[7a] and adsorption correction was done applying SADABS program.[7b] The crystal structure was solved by SHELXT 2018/2 (Sheldrick, 2018) and refined by full matrix least square method using SHELXL-2018/3 (Sheldrick, 2018)[7c] and WinGX v2021.3[7d]. All the non-hydrogen atoms in the structure were refined anisotropically. The hydrogen atoms were fixed by HFIX in their ideal positions and refined using riding model with isotropic thermal parameters. CCDC 2111276 contains supplementary Crystallographic data for the structure. This dataset can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0) 1223 336 033; Email: deposit@ccdc.cam.ac.uk]

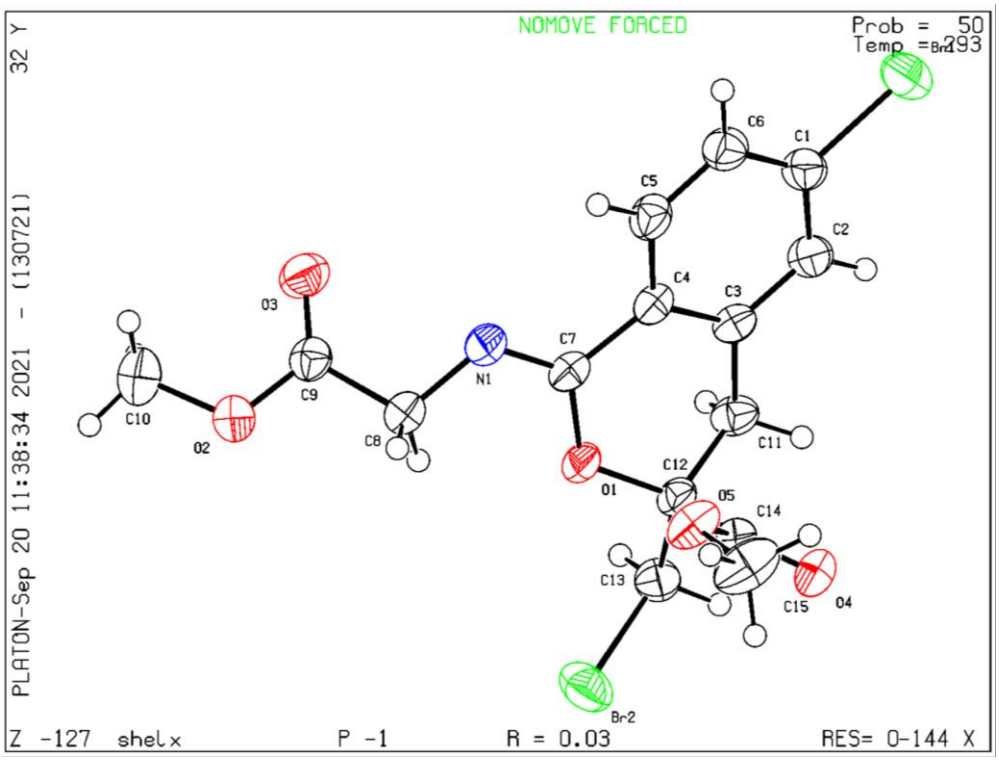


Figure S2. Ellipsoid plot of **5o**

Crystal data of 5o

Mol. Formula = $C_{15}H_{15}Br_2NO_5$	D_c = 1.779 g cm^{-3}	R_{int} = 0.049
M_r = 449.10 g/mol	V = 838.33 (9) Å^3	Least-squares matrix: full
Triclinic, P-1	Z = 2	$R[F^2 > 2\sigma(F^2)]$ = 0.032
a = 8.1671 (5) Å	Mo $K\alpha$ radiation, λ = 0.71073 Å	$wR(F^2)$ = 0.087
b = 9.9200 (6) Å	$\theta_{min} - \theta_{max}$ = 1.9–27.5°	S = 1.04
c = 11.5668 (6) Å	μ = 4.86 mm^{-1}	$(\Delta/\sigma)_{max}$ = 0.001
α = 109.881 (2)°	T = 293 K	$\Delta\rho_{max}$ = 0.52 e Å^{-3}
β = 98.181 (2)°	Measured reflections = 27035	$\Delta\rho_{min}$ = −0.69 e Å^{-3}
γ = 102.053 (2)°	Independent reflections = 3754	
F(000) = 444	Reflections with $I > 2\sigma(I)$ = 3136	

$w = 1/[\sigma^2(F_o^2) + (0.0398P)^2 + 0.5367P]$, where $P = (F_o^2 + 2F_c^2)/3$

$Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

[Extinction correction: SHELXL-2018/3 (Sheldrick 2018); Extinction coefficient: 0.050 (6)]

Bond length:

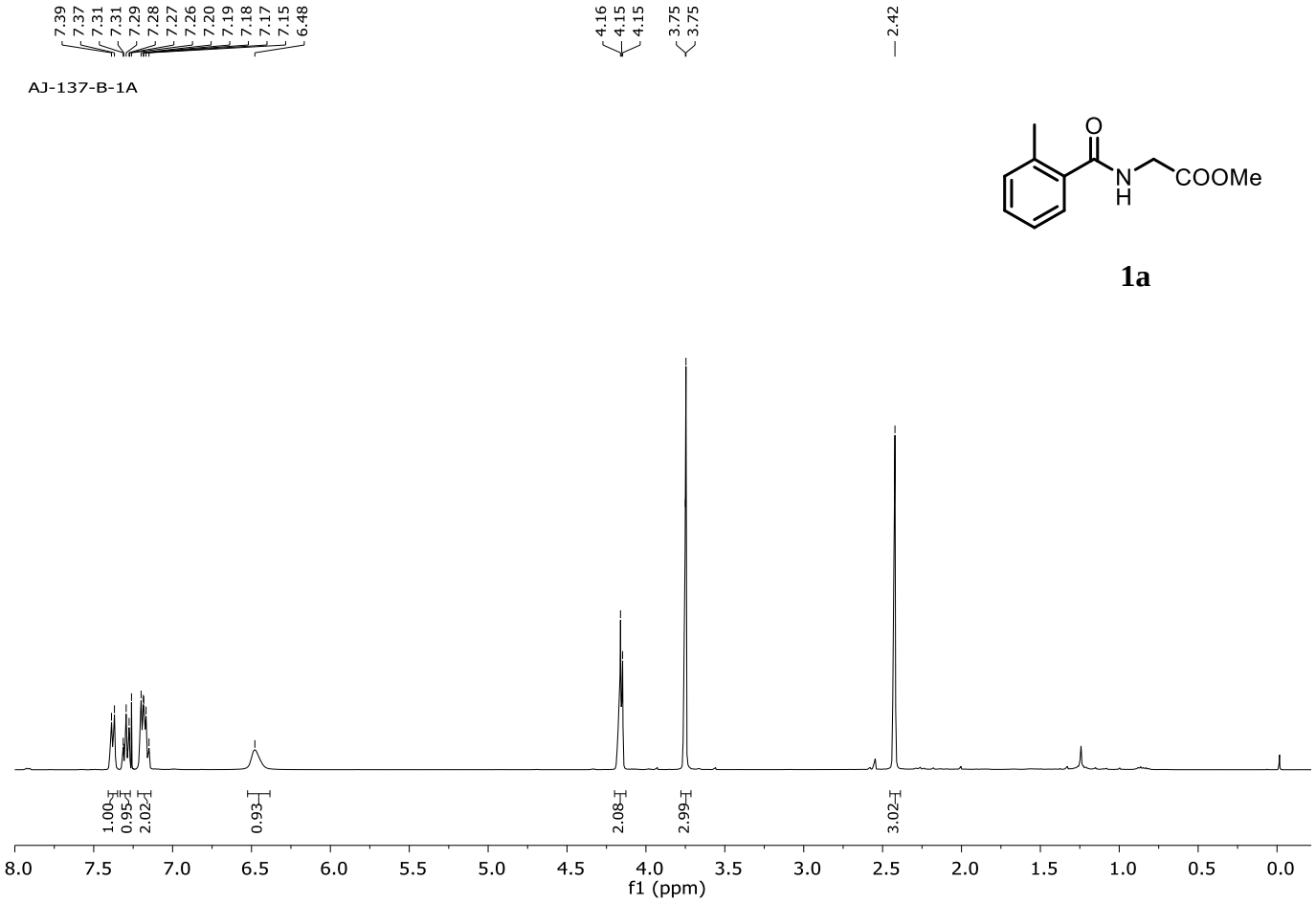
Atom 1	Atom 2	Length (Å)	Atom 1	Atom 2	Length (Å)
Br2	C13	1.936(2)	C12	C11	1.526(3)
Br1	C1	1.898(2)	C12	C14	1.530(4)
O1	C7	1.368(3)	C11	H11A	0.970
O1	C12	1.438(3)	C11	H11B	0.970
O5	C14	1.317(3)	C2	H2	0.930
O5	C15	1.452(5)	C2	C1	1.382(3)
O4	C14	1.202(3)	C8	H8A	0.970
O3	C9	1.198(3)	C8	H8B	0.970
N1	C7	1.265(3)	C8	C9	1.510
N1	C8	1.449(3)	C15	H15A	0.960
O2	C9	1.334(3)	C15	H15B	0.960
O2	C10	1.438(5)	C15	H15C	0.960
C3	C4	1.401(4)	C5	H5	0.930
C3	C11	1.504(3)	C5	C6	1.381(3)
C3	C2	1.385(3)	C1	C6	1.384(4)
C7	C4	1.469(2)	C6	H6	0.930
C4	C5	1.401(3)	C10	H10A	0.960
C13	H13A	0.970	C10	H10B	0.960
C13	H13B	0.970	C10	H10C	0.960
C13	C12	1.520(3)			

Bond angels:

Atom1	Atom2	Atom3	Angle (º)	Atom1	Atom2	Atom3	Angle (º)
C7	O1	C12	120.9(2)	N1	C8	H8A	109.5
C14	O5	C15	115.1(2)	N1	C8	H8B	109.5
C7	N1	C8	118.7(2)	N1	C8	C9	110.7(2)
C9	O2	C10	116.0(2)	H8A	C8	H8B	108.1
C4	C3	C11	118.8(2)	H8A	C8	C9	109.5
C4	C3	C2	119.7(2)	H8B	C8	C9	109.5
C11	C3	C2	121.4(2)	O5	C14	O4	125.3(2)
O1	C7	N1	120.1(2)	O5	C14	C12	114.3(2)
O1	C7	C4	118.3(2)	O4	C14	C12	120.4(2)
N1	C7	C4	121.5(2)	O3	C9	O2	124.0(2)
C3	C4	C7	119.7(2)	O3	C9	C8	125.8(2)
C3	C4	C5	119.4(2)	O2	C9	C8	110.2(2)
C7	C4	C5	120.7(2)	O5	C15	H15A	109.5
Br2	C13	H13A	109.2	O5	C15	H15B	109.5
Br2	C13	H13B	109.2	O5	C15	H15C	109.5
Br2	C13	C12	111.9(2)	H15A	C15	H15B	109.4
H13A	C13	H13B	107.9	H15A	C15	H15C	109.4
H13A	C13	C12	109.2	H15B	C15	H15C	109.5
H13B	C13	C12	109.2	C4	C5	H5	119.6
O1	C12	C13	105.3(2)	C4	C5	C6	120.7(2)
O1	C12	C11	111.2(2)	H5	C5	C6	119.7
O1	C12	C14	112.2(2)	Br1	C1	C2	118.5(2)
C13	C12	C11	109.8(2)	Br1	C1	C6	119.7(2)
C13	C12	C14	109.3(2)	C2	C1	C6	121.8(2)
C11	C12	C14	109.0(2)	C5	C6	C1	118.8(2)

C3	C11	C12	110.6(2)	C5	C6	H6	120.6
C3	C11	H11A	109.5	C1	C6	H6	120.6
C3	C11	H11B	109.5	O2	C10	H10A	109.4
C12	C11	H11A	109.5	O2	C10	H10B	109.4
C12	C11	H11B	109.5	O2	C10	H10C	109.5
H11A	C11	H11B	108.1	H10A	C10	H10B	109.5
C3	C2	H2	120.2	H10A	C10	H10C	109.5
C3	C2	C1	119.6(2)	H10B	C10	H10C	109.5
H2	C2	C1	120.2				

^{1}H and ^{13}C NMR spectra of synthesized compounds (1a, 1d, 1h to 1k, 1m, 1q, 1r, 1t, 1u, 1w, 1x, 3a, 3x, 3z, 5a to 5x, 1y, 5y to 5z, 6, 7, 8, 9, 10, 11a and 11b)



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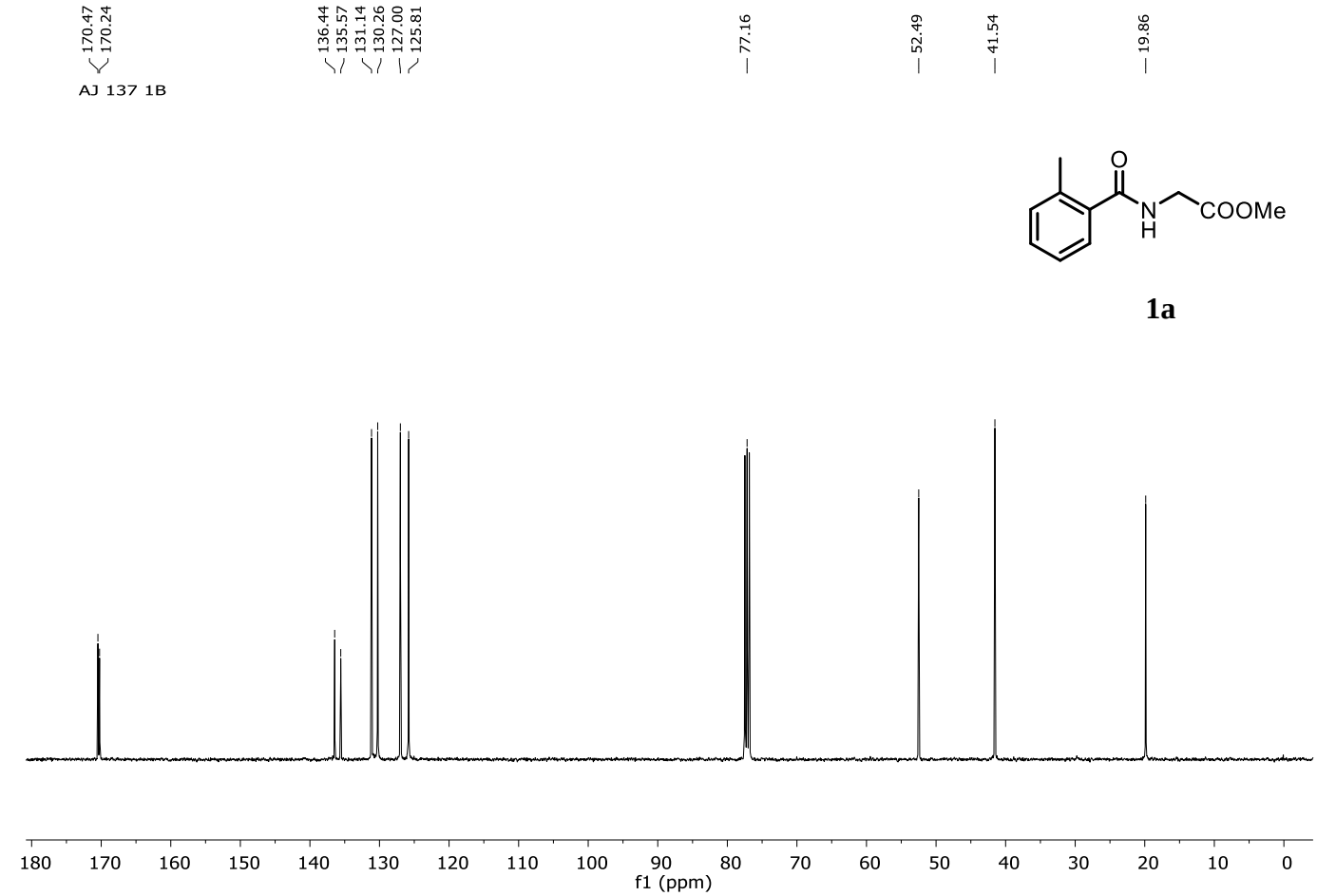

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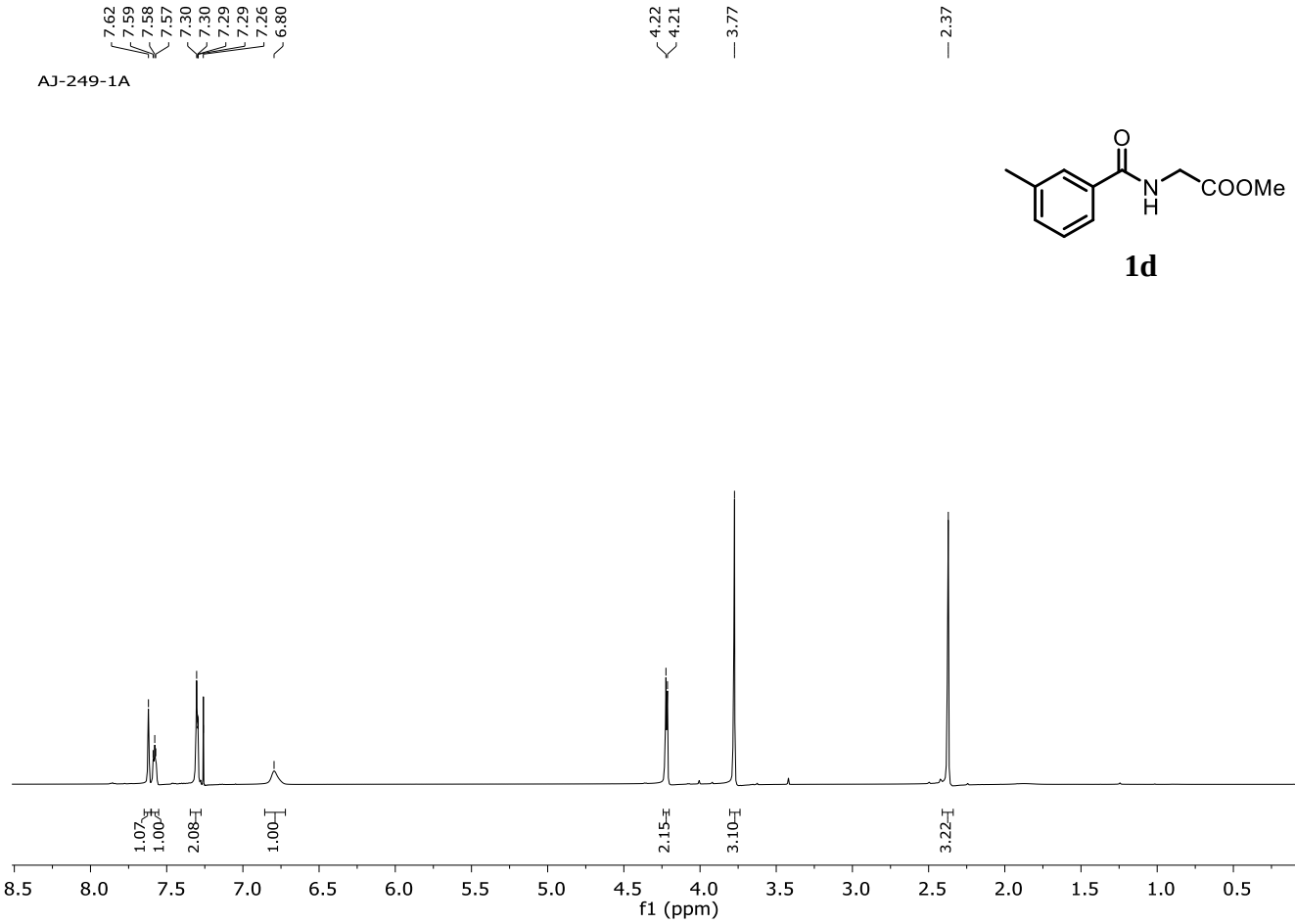
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H
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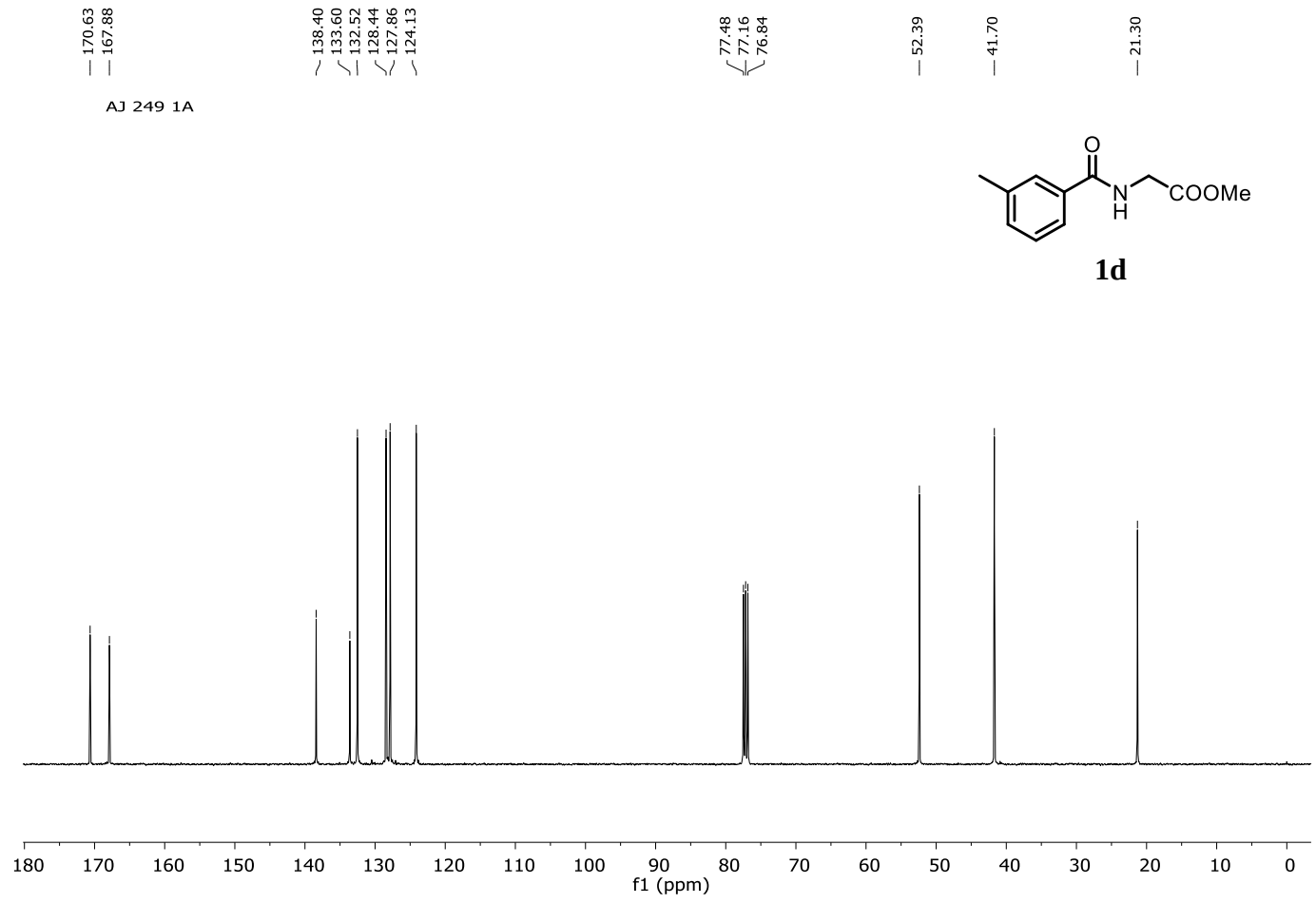
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AJ 249 1A
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N
H
COOMe
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100
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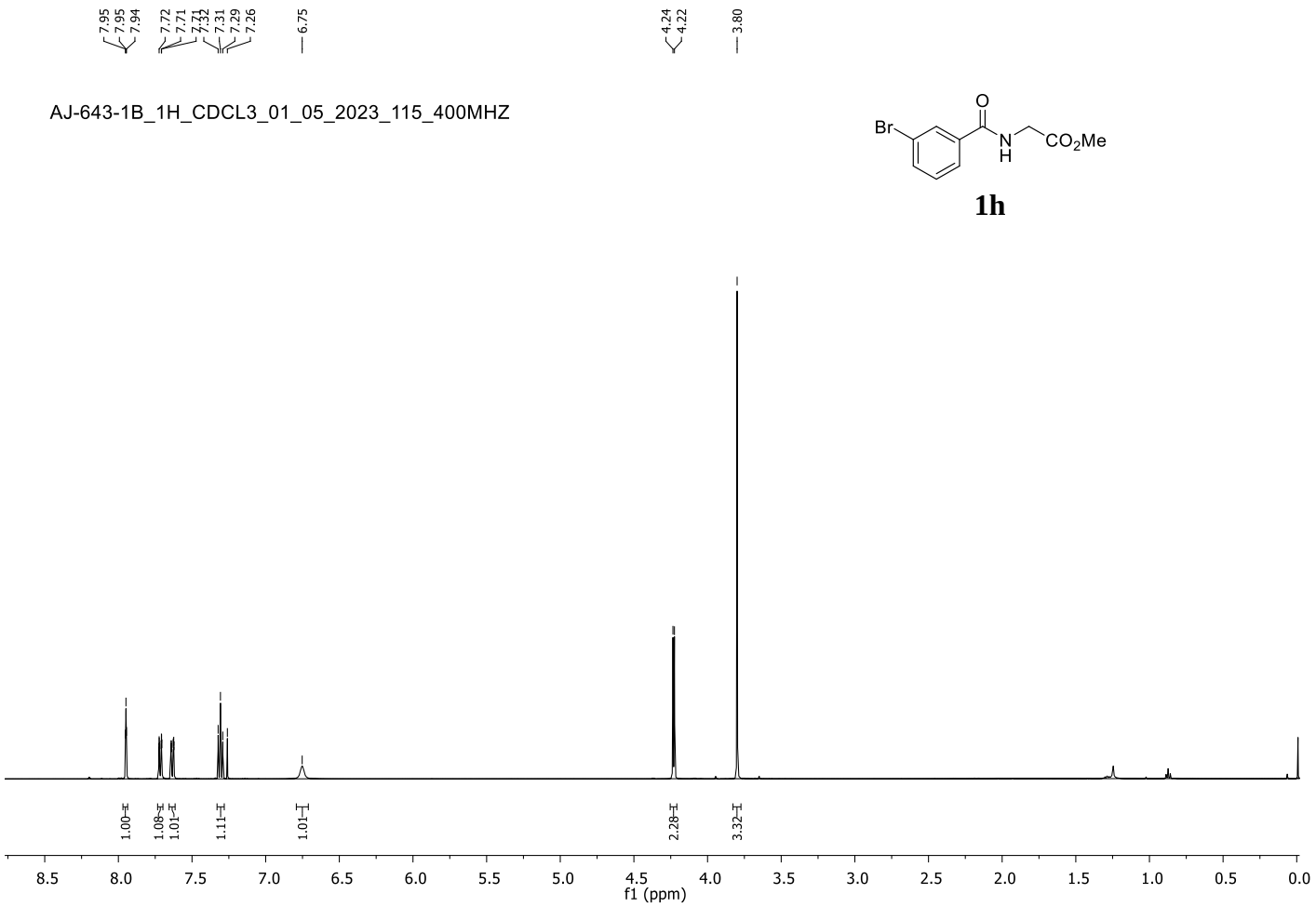
f1 (ppm)

1d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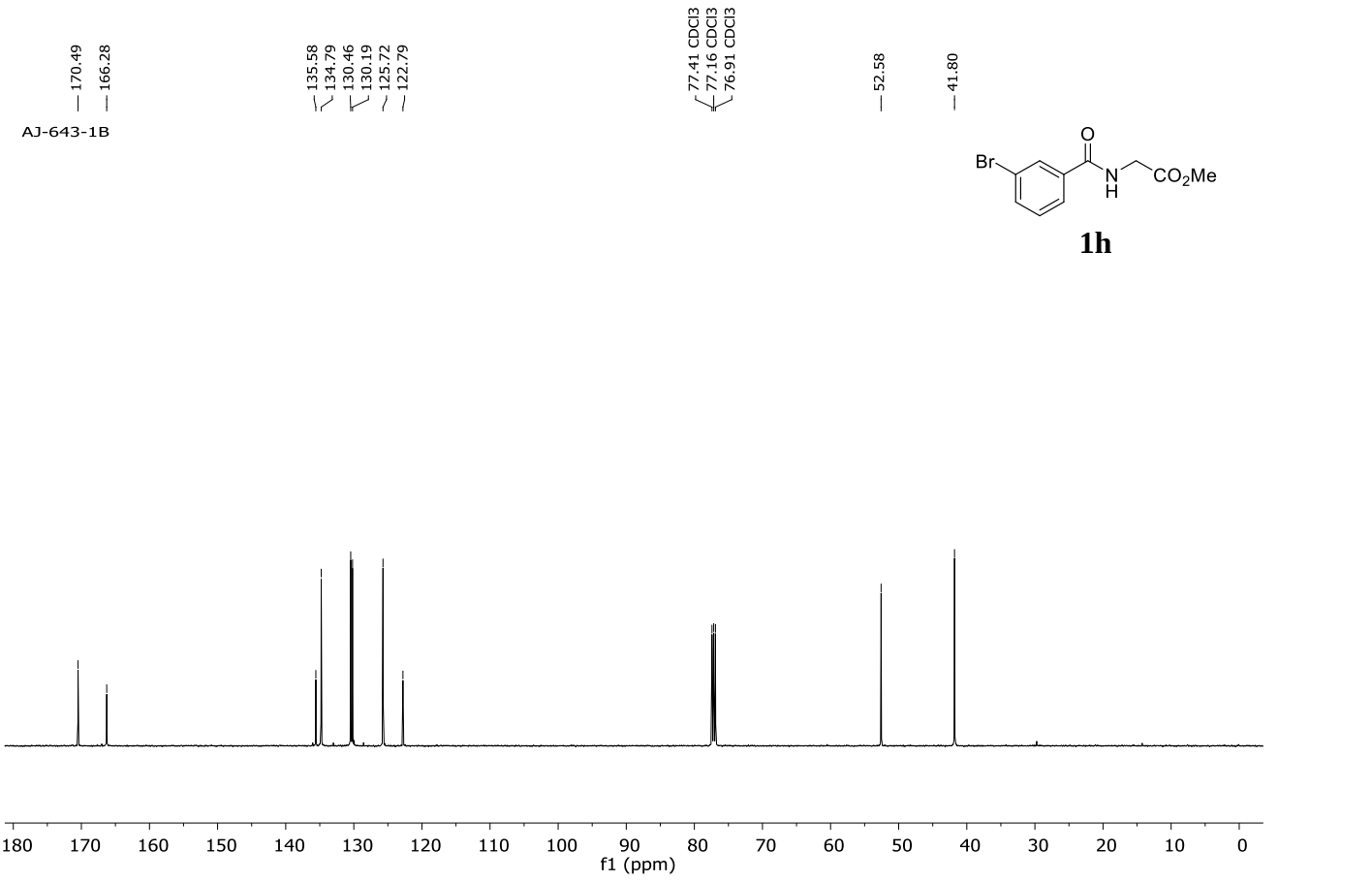
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41.80
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O
N
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1h
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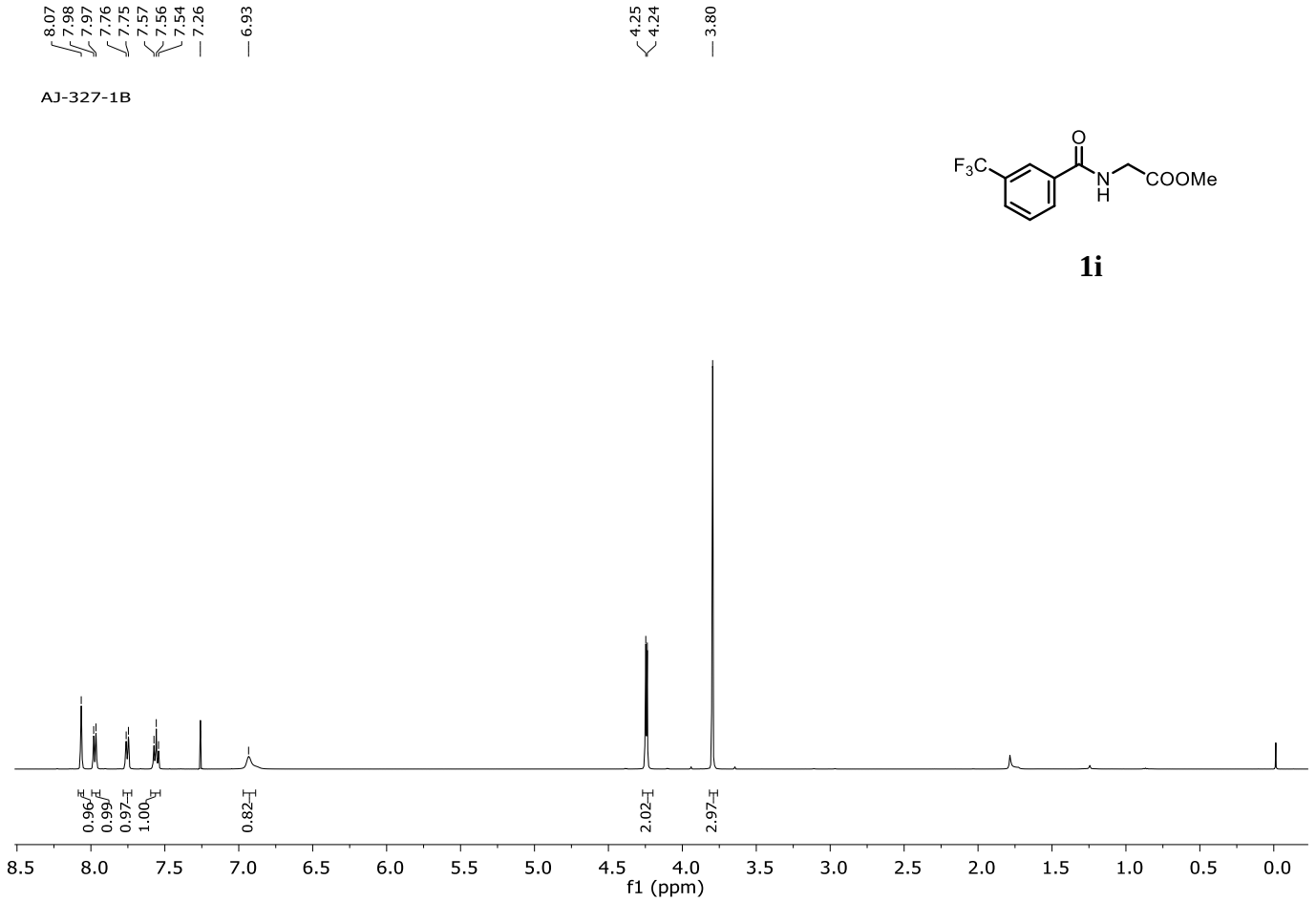
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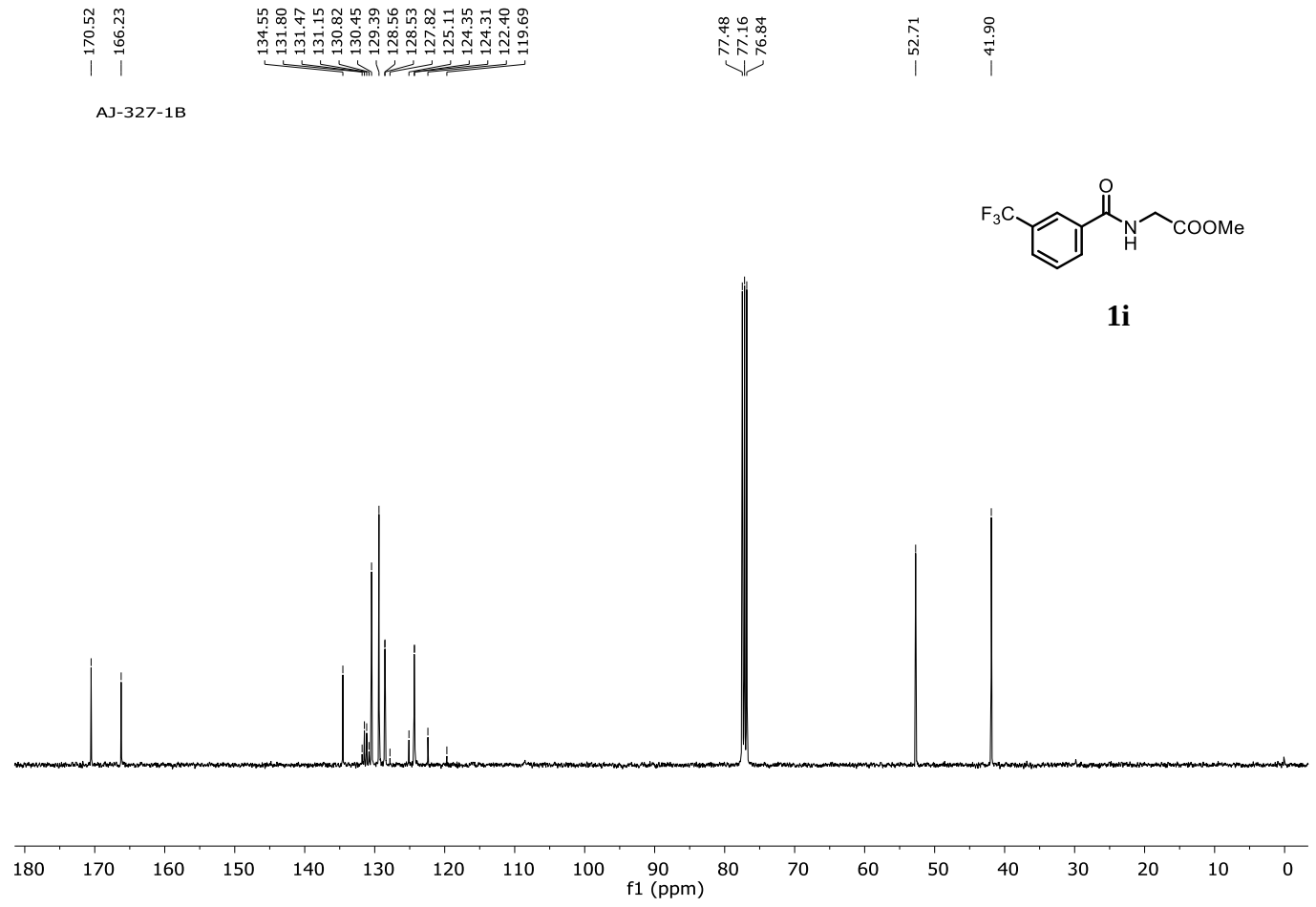
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124.35
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122.40
119.69
77.48
77.16
76.84
52.71
41.90
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O
N
H
COOMe
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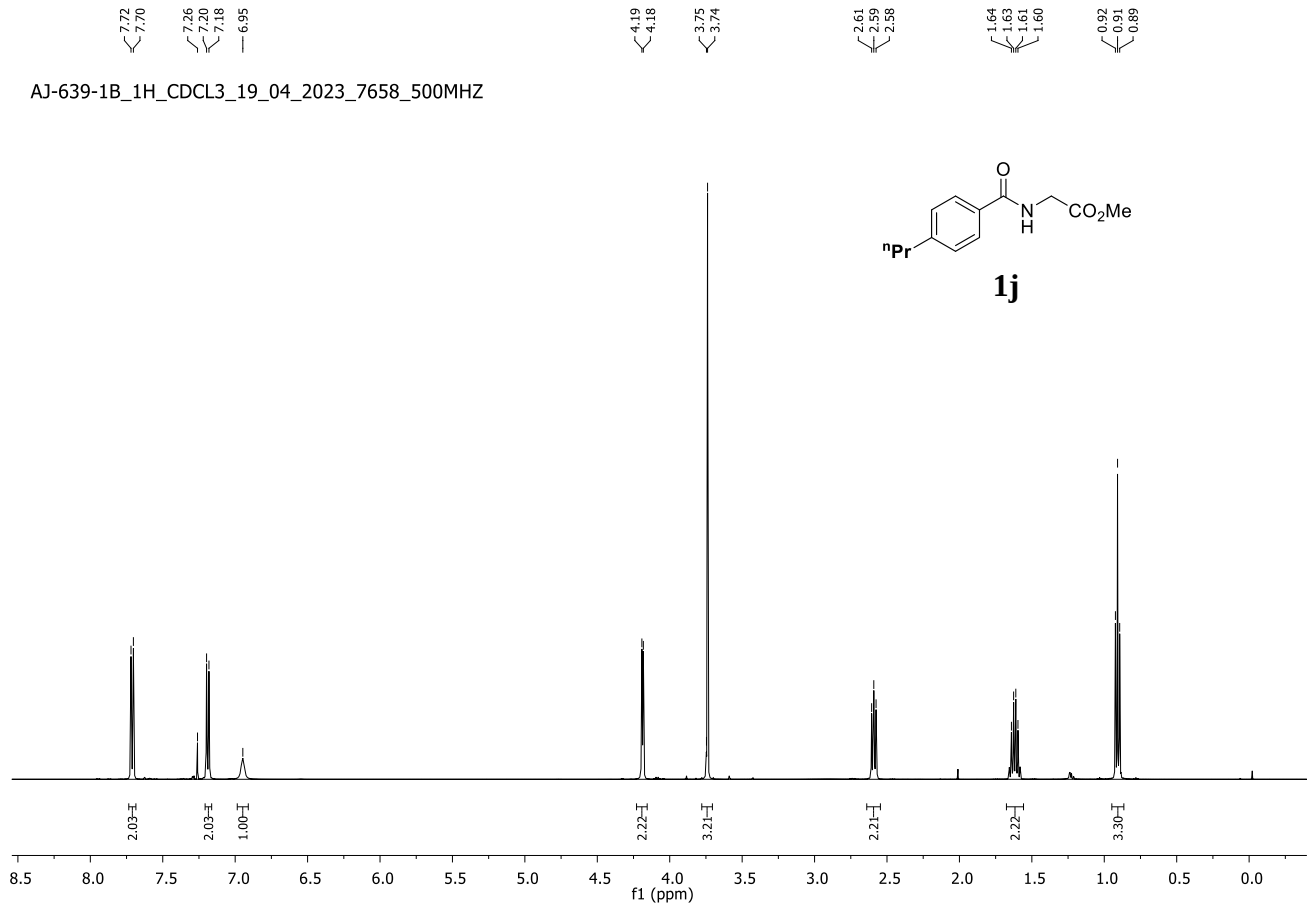
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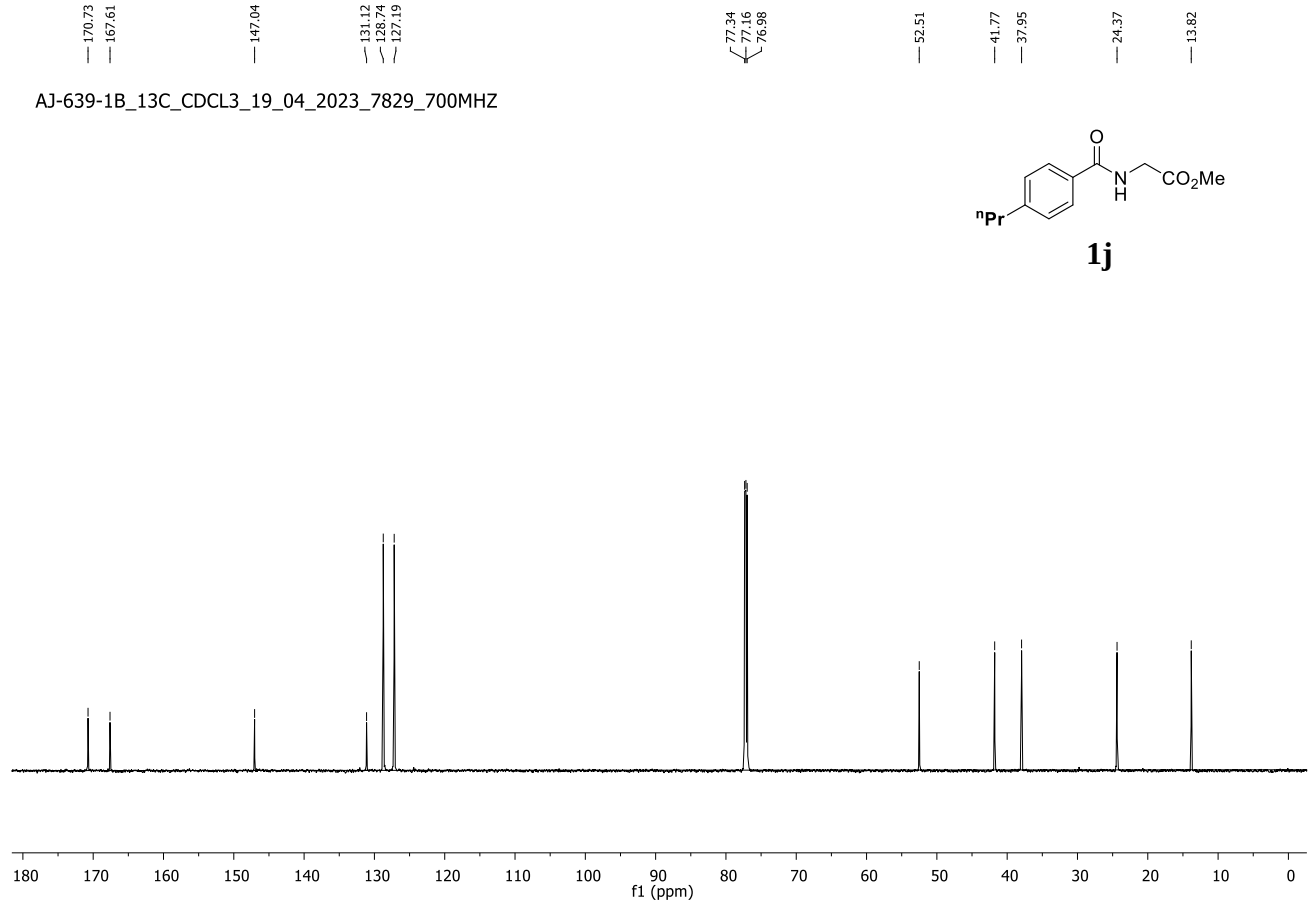
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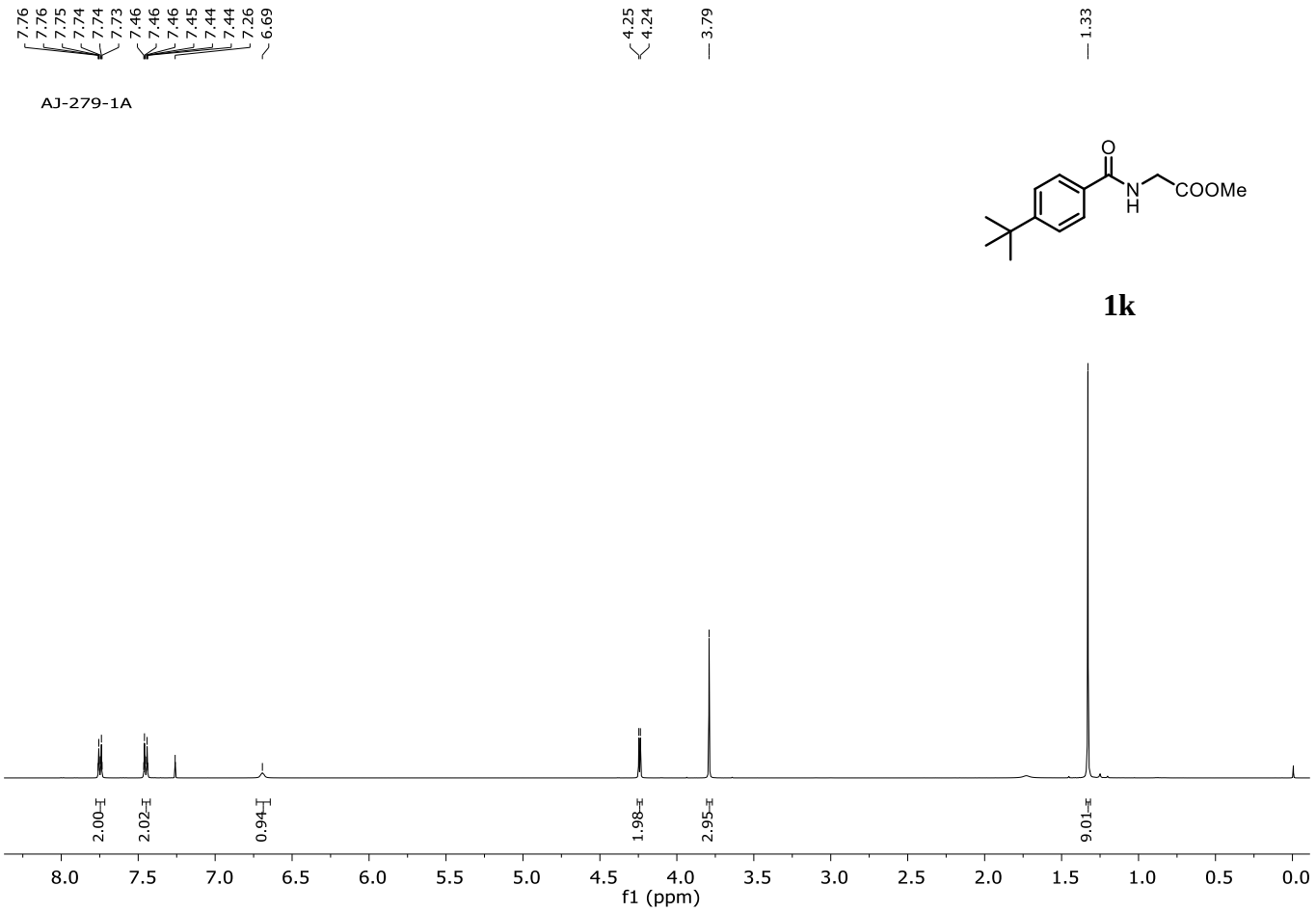
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COOMe
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6.0
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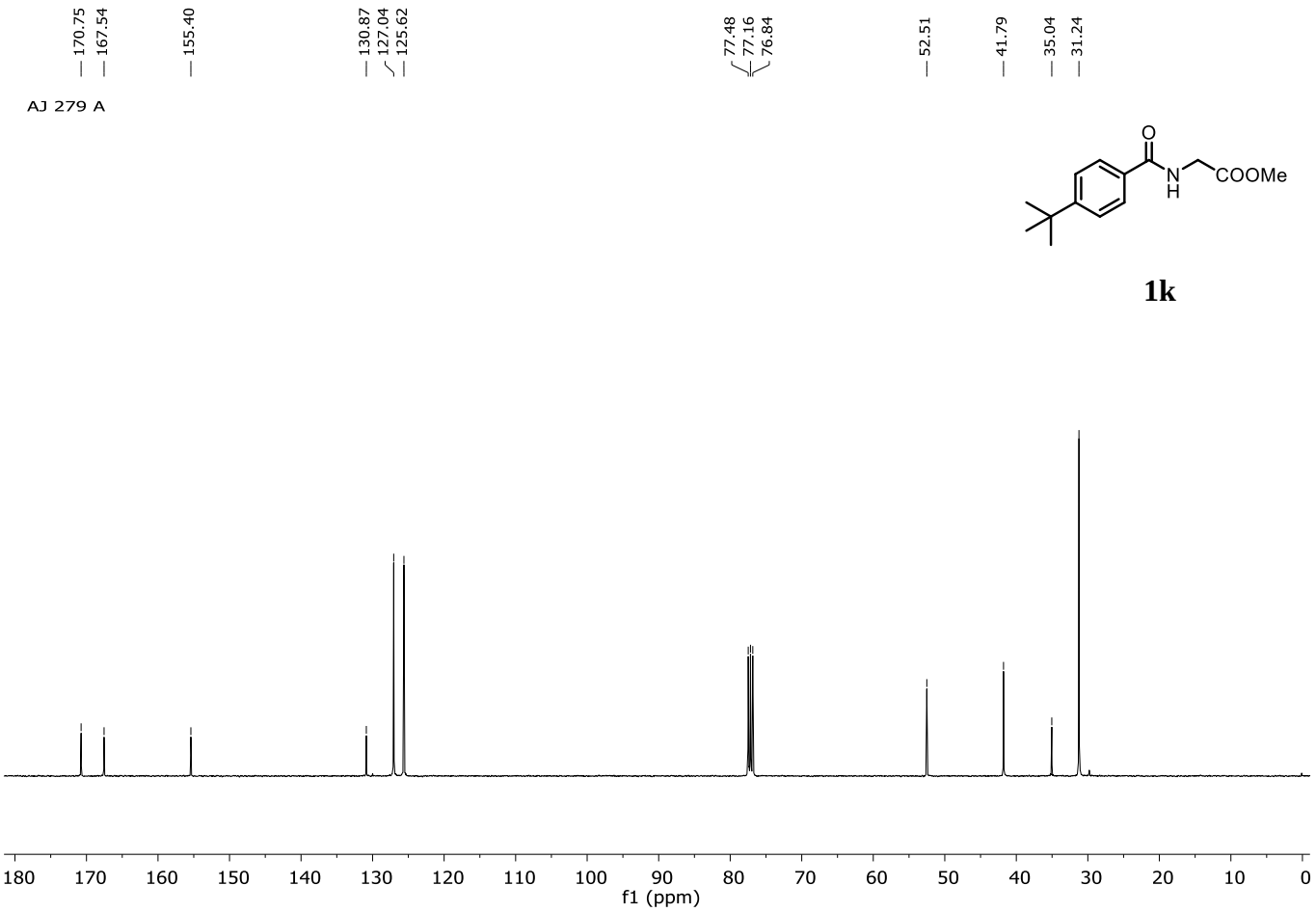
1k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H
COOMe
180
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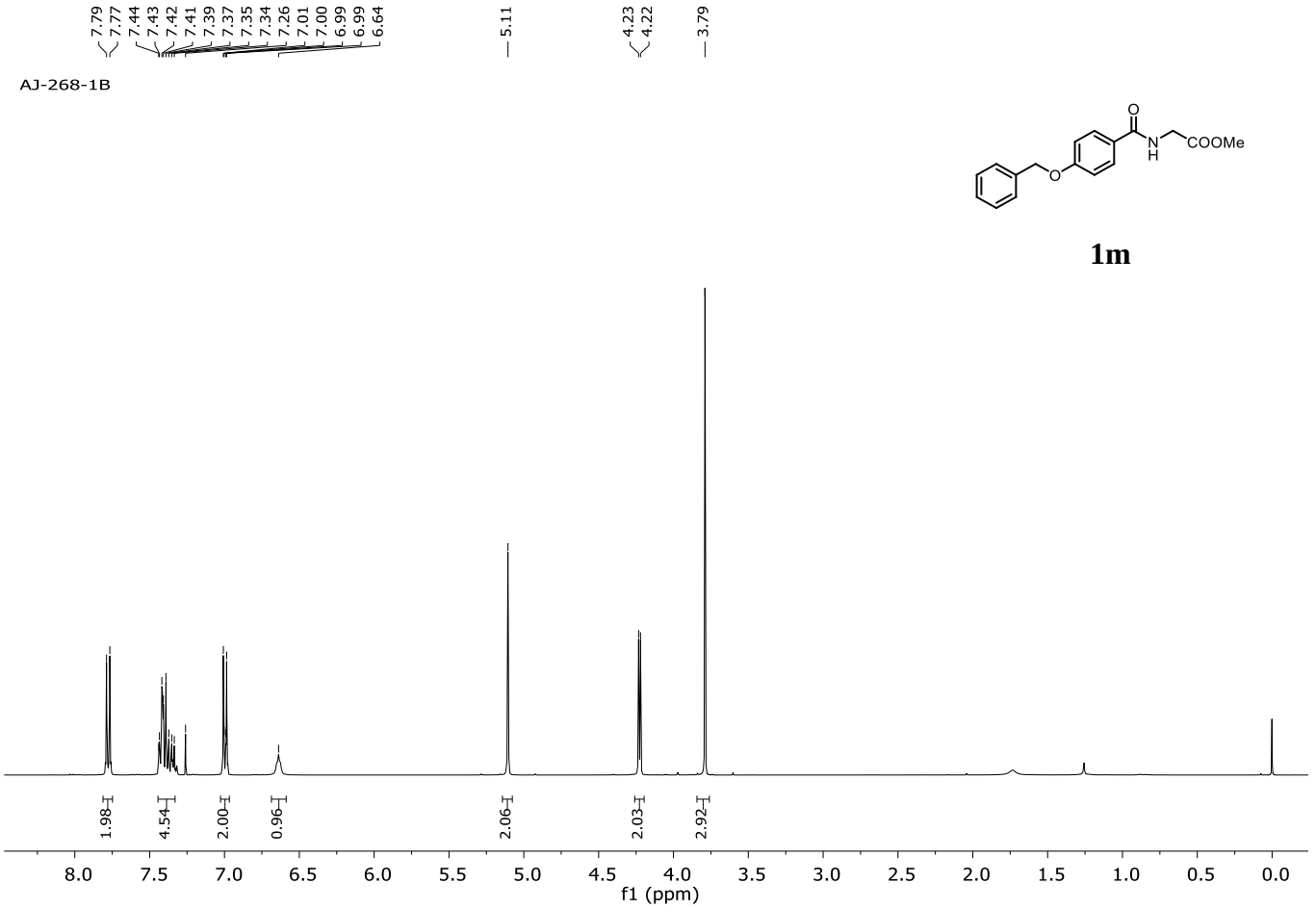
f1 (ppm)

1k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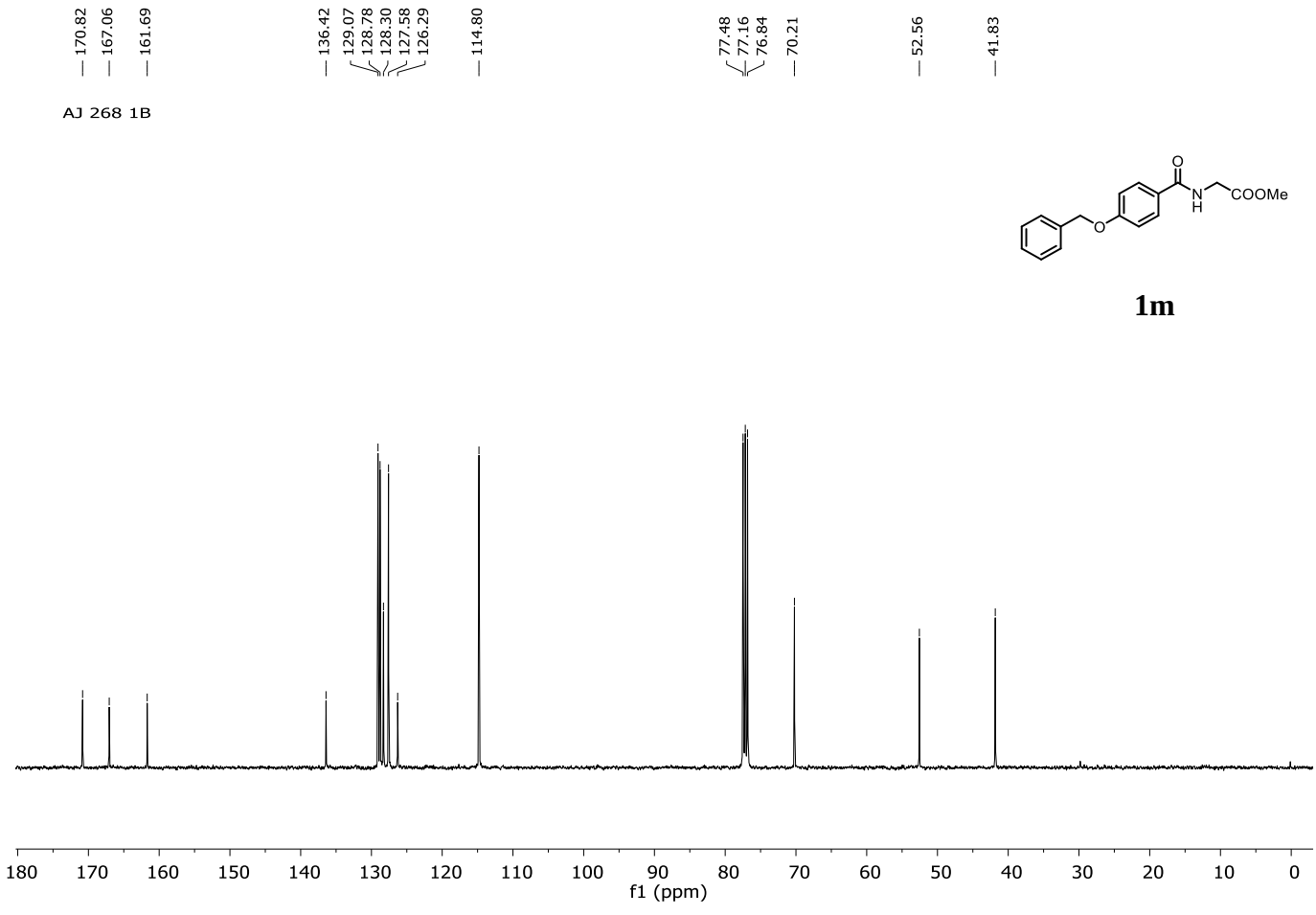
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70.21
52.56
41.83
AJ 268 1B
O
N
H
COOMe
O
1m
180
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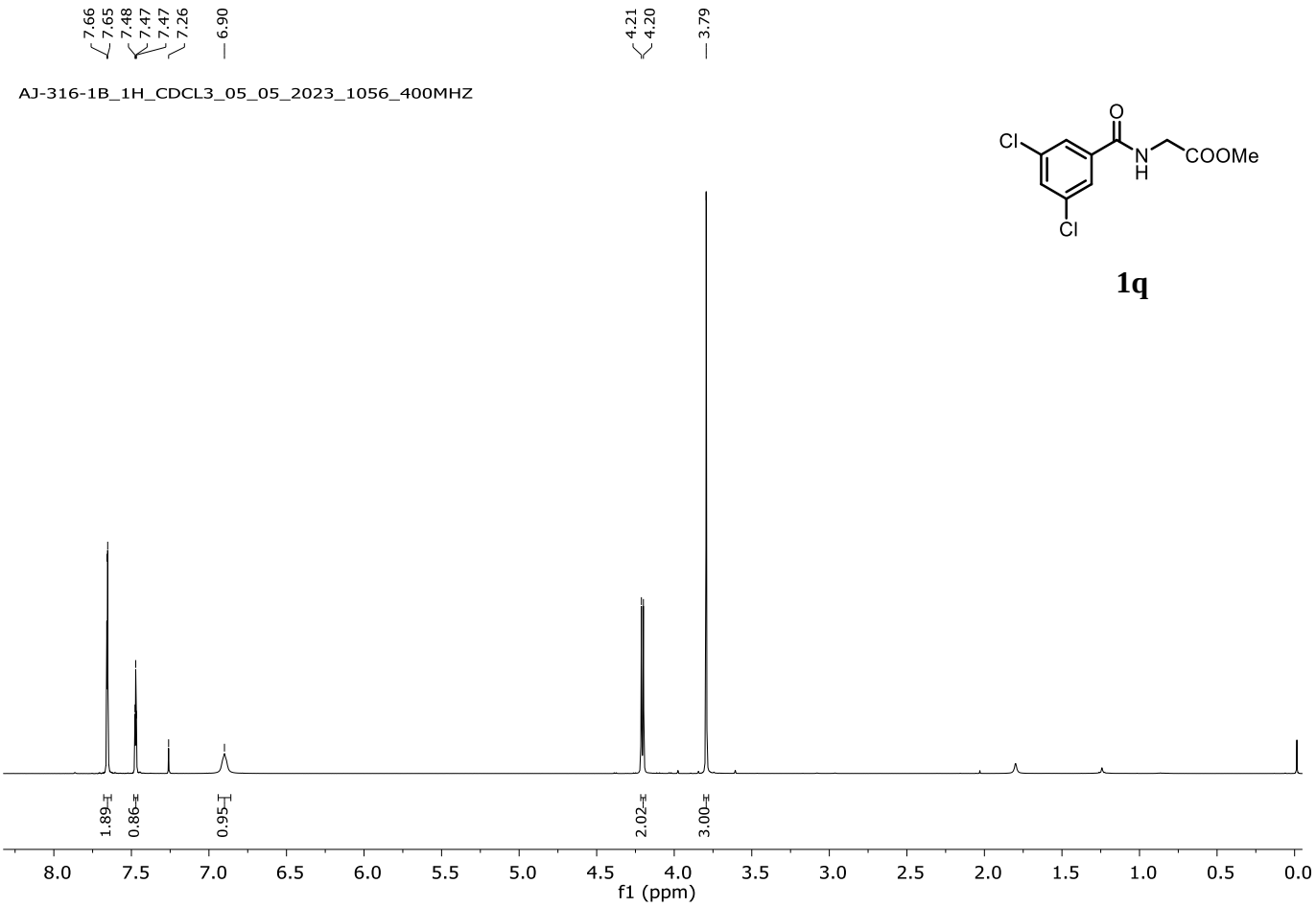
f1 (ppm)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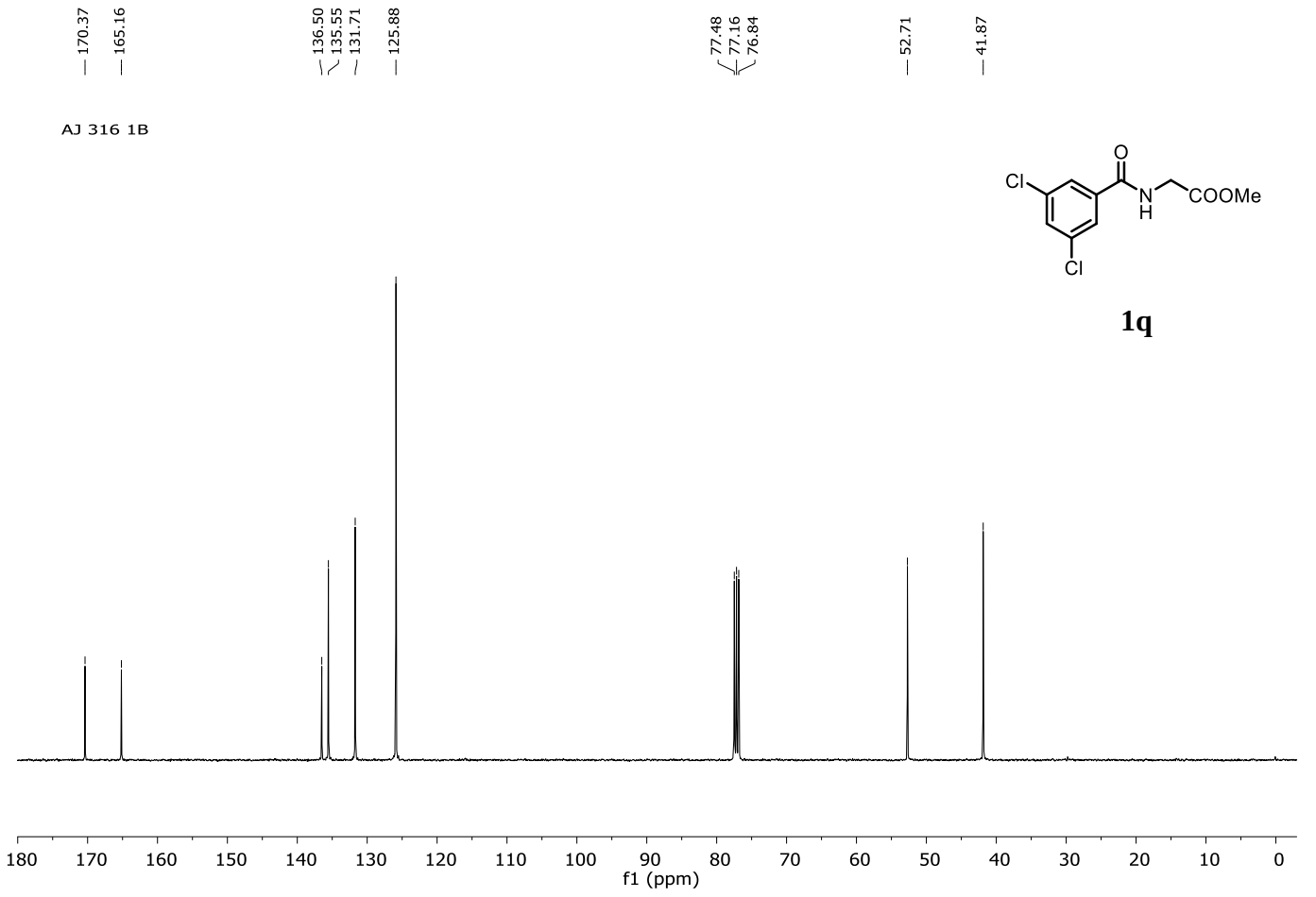
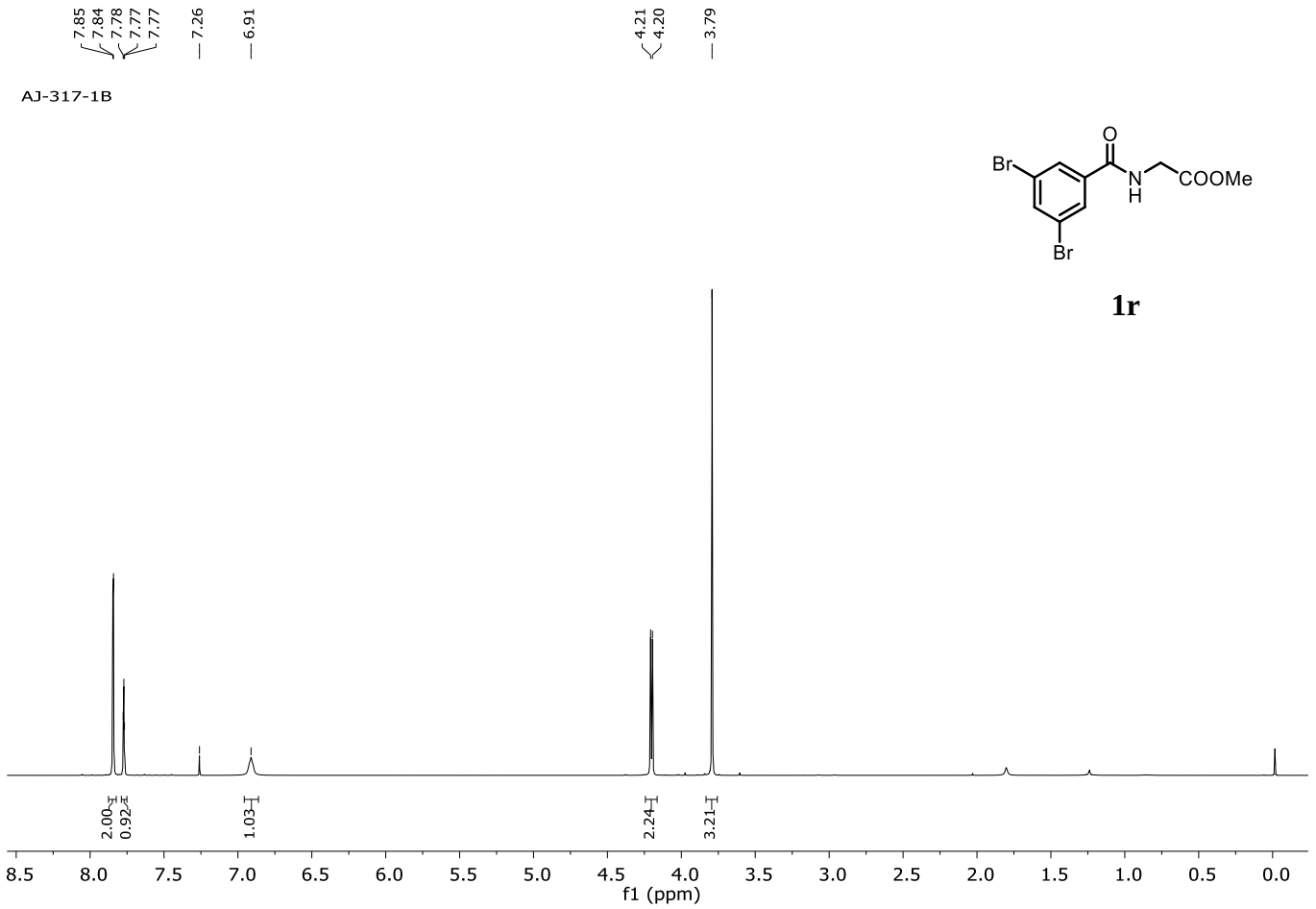
4.21
4.20
3.79
AJ-316-1B_1H_CDCL3_05_05_2023_1056_400MHZ
Cl
O
N
H
COOMe
Cl
1.89
0.86
0.95
2.02
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

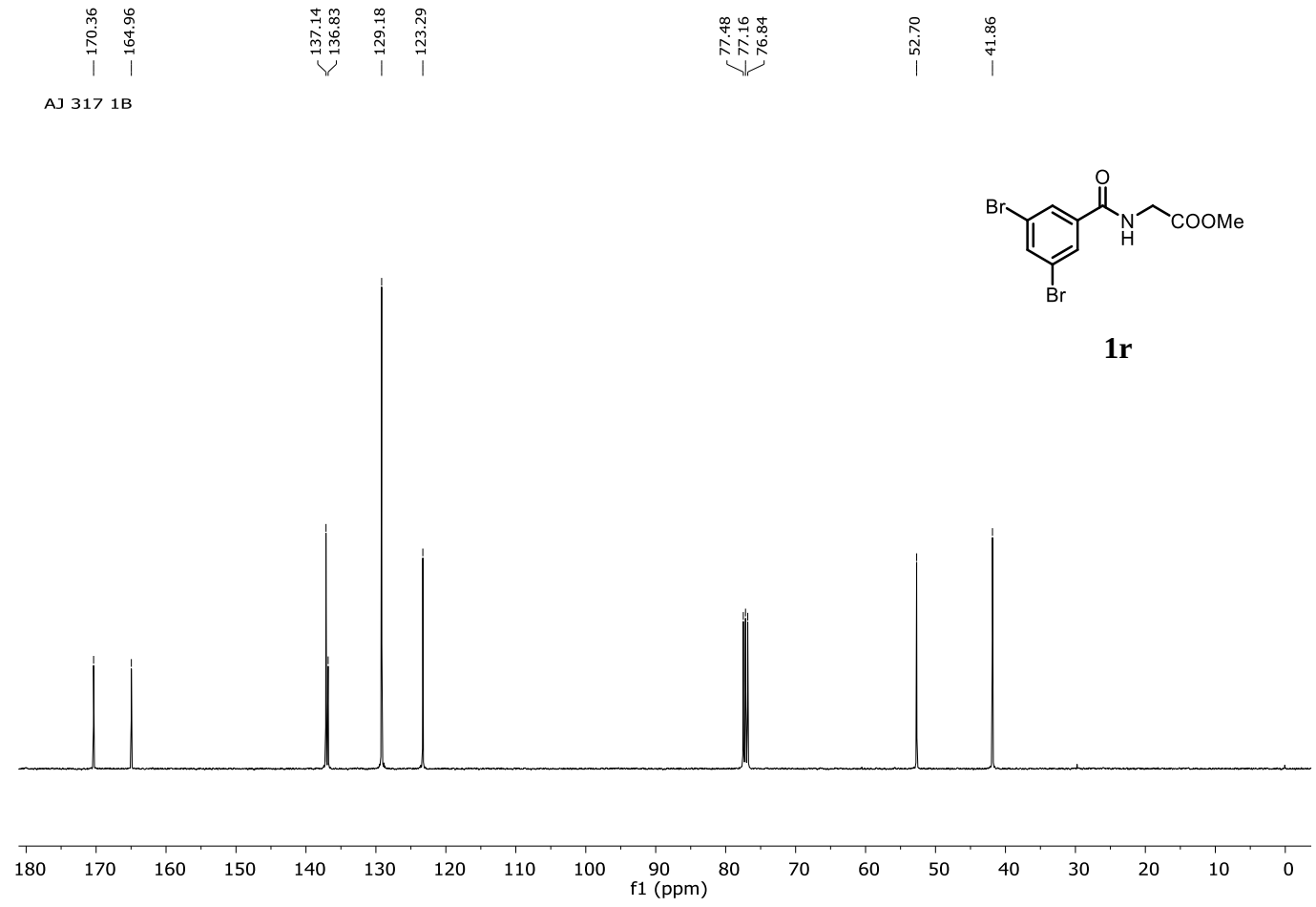
1q


170.37
165.16
136.50
135.55
131.71
125.88
77.48
77.16
76.84
52.71
41.87
AJ 316 1B
Cl
O
N
H
COOMe
Cl
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

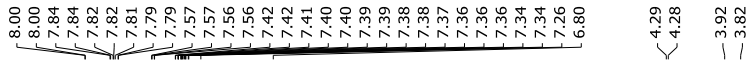
1q


7.85
7.84
7.78
7.77
7.77
7.26
6.91
4.21
4.20
3.79
AJ-317-1B
Br
O
N
H
COOMe
Br
2.00
0.92
1.03
2.24
3.21
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

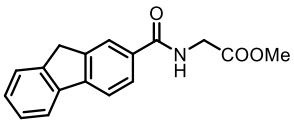
1r


170.36
164.96
137.14
136.83
129.18
123.29
77.48
77.16
76.84
52.70
41.86
AJ 317 1B
Br
O
N
H
COOMe
Br
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

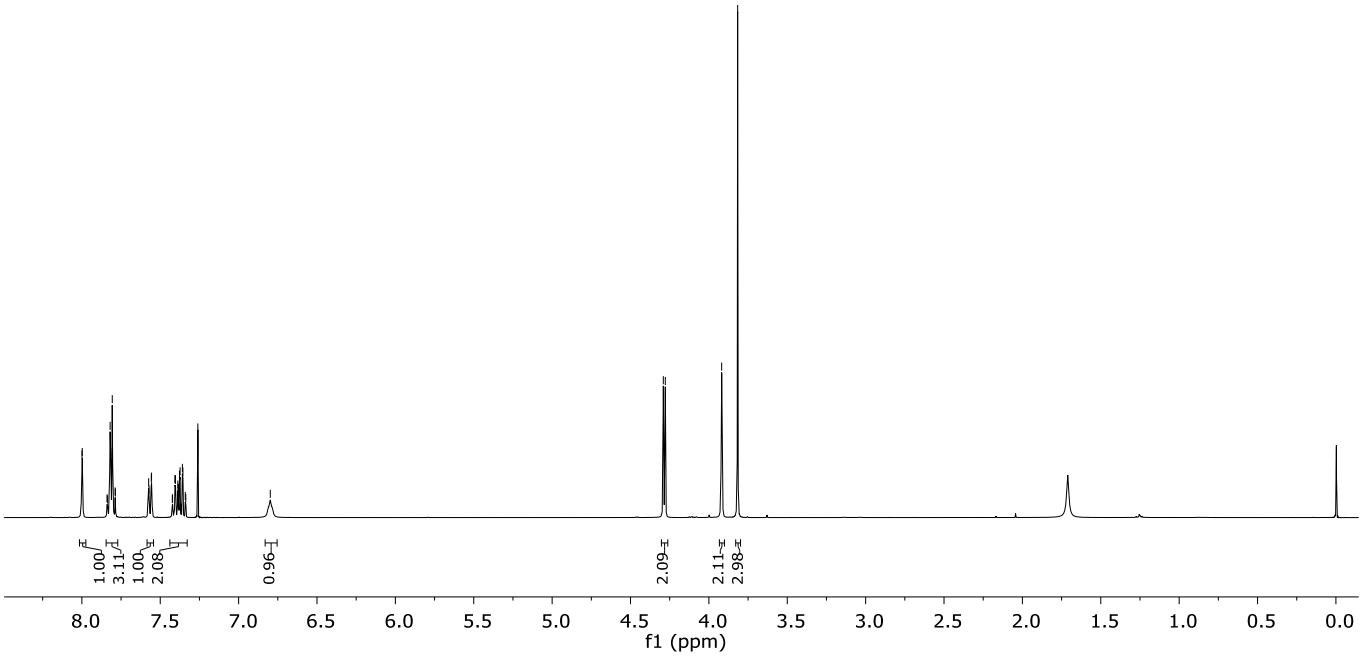
1r



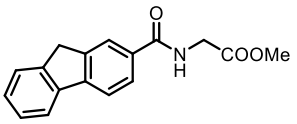
AJ-330-1D



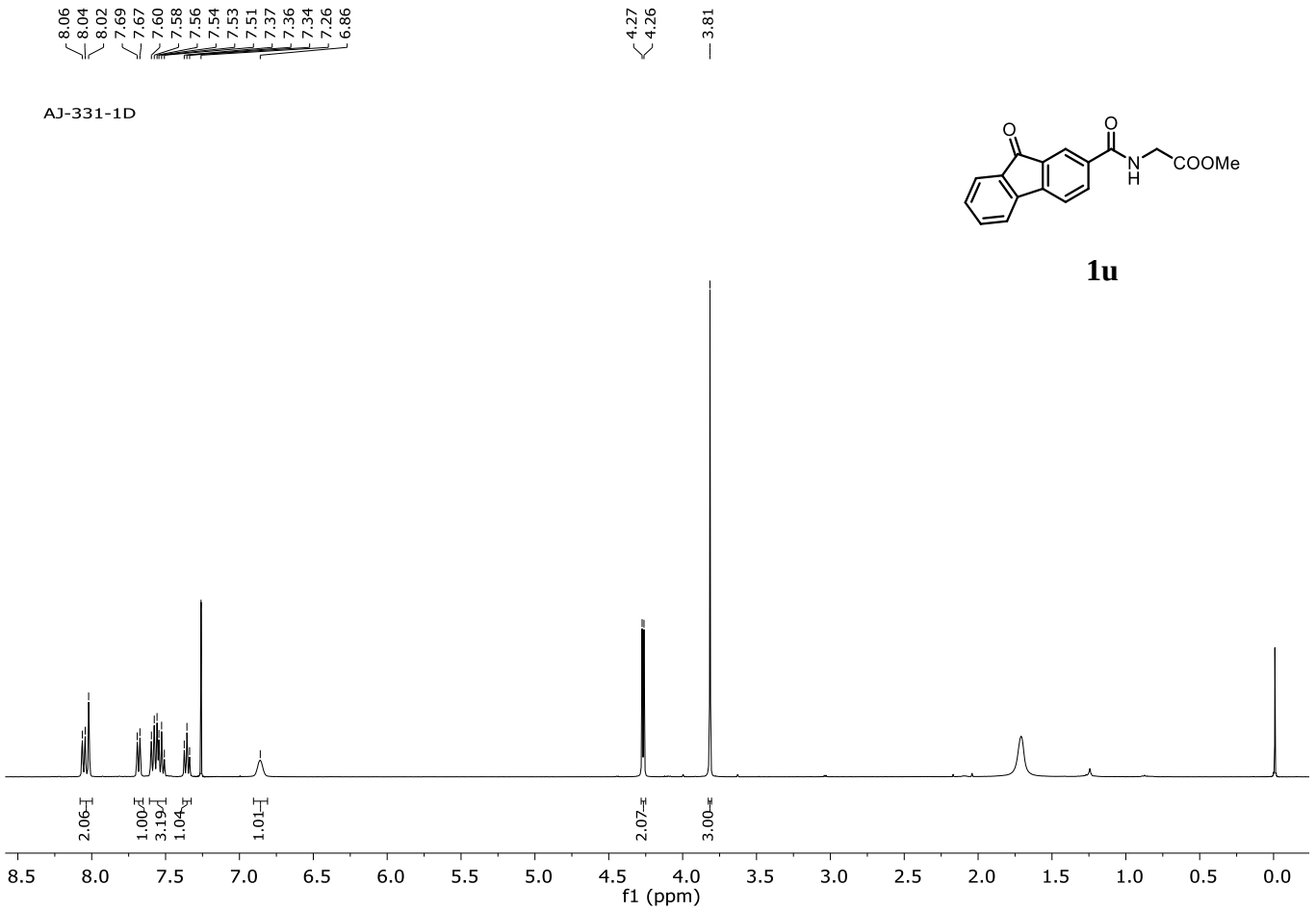
1t



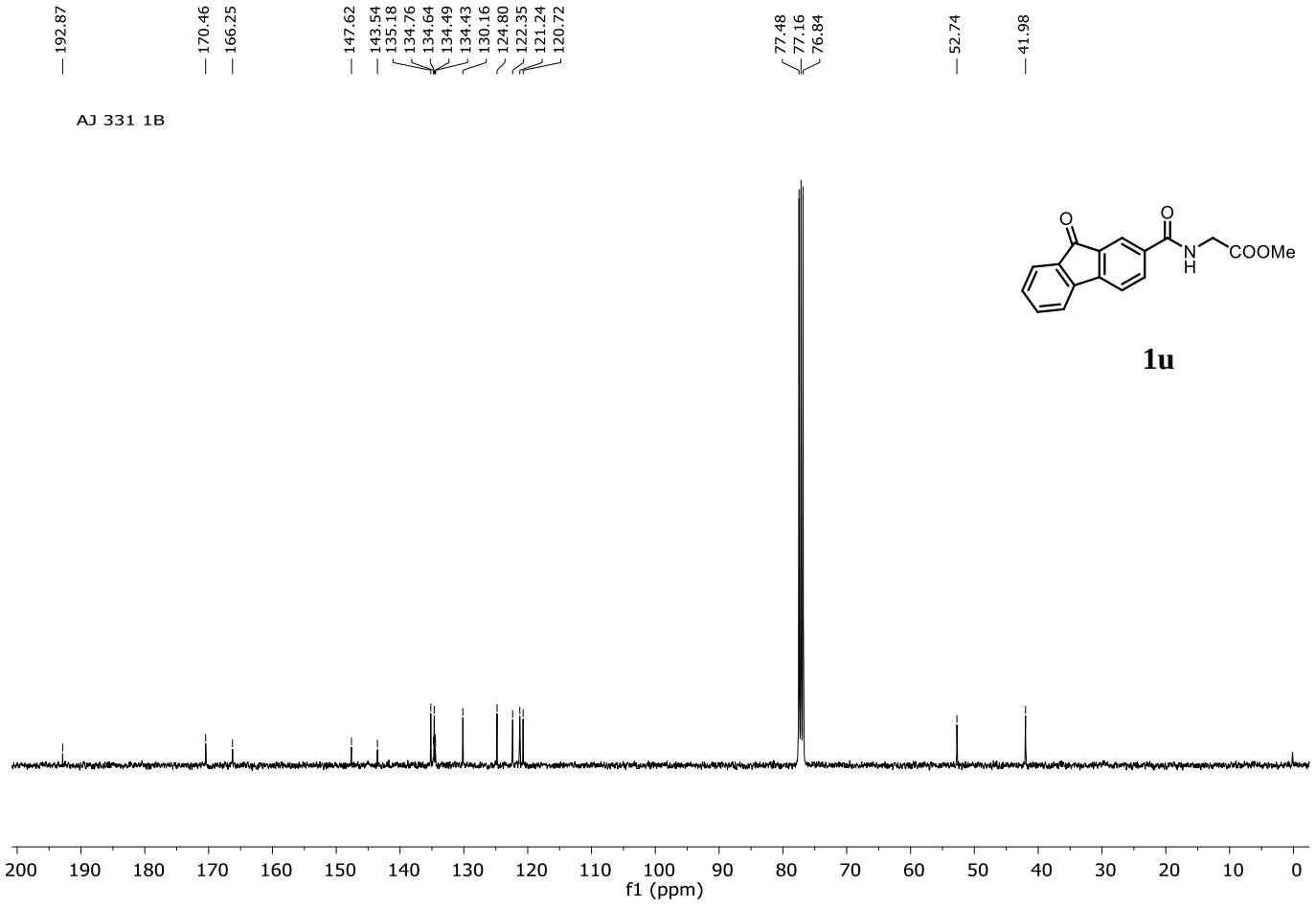
AJ 330 1B



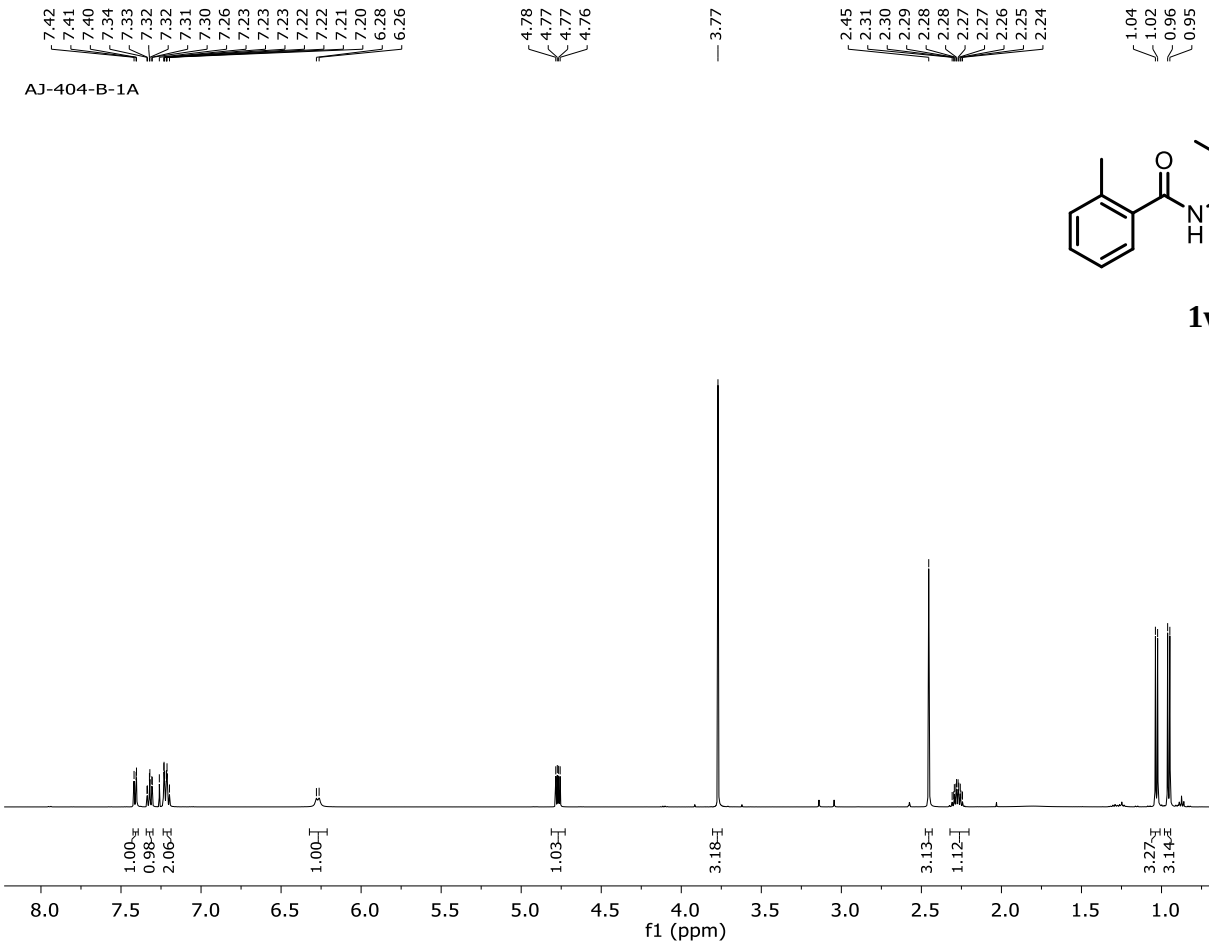
1t

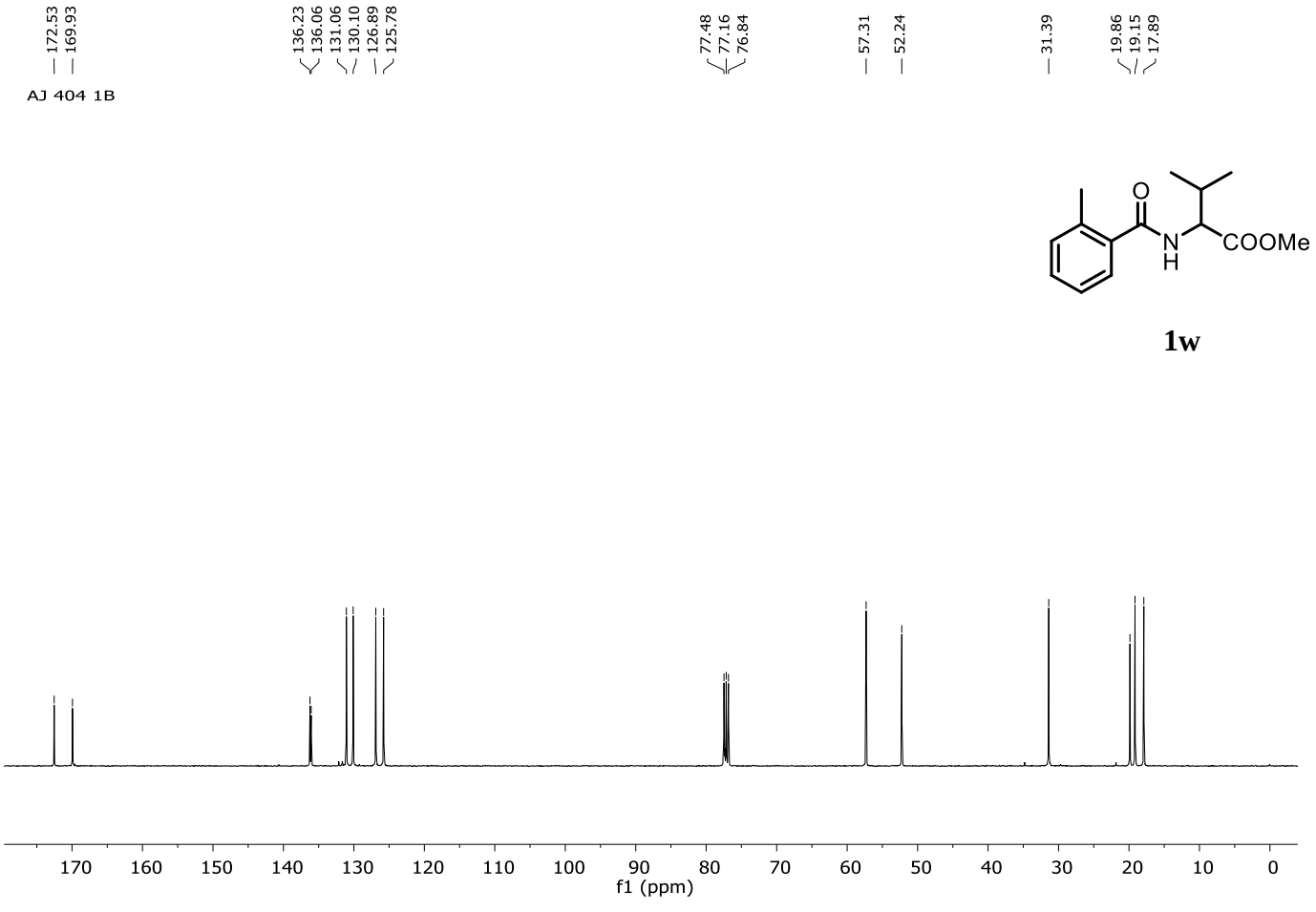

8.06
8.04
8.02
7.69
7.67
7.60
7.58
7.56
7.54
7.53
7.51
7.37
7.36
7.34
7.26
6.86
4.27
4.26
3.81
AJ-331-1D
O
O
N
H
COOMe
2.06
1.00
3.19
1.04
1.01
2.07
3.00
f1 (ppm)

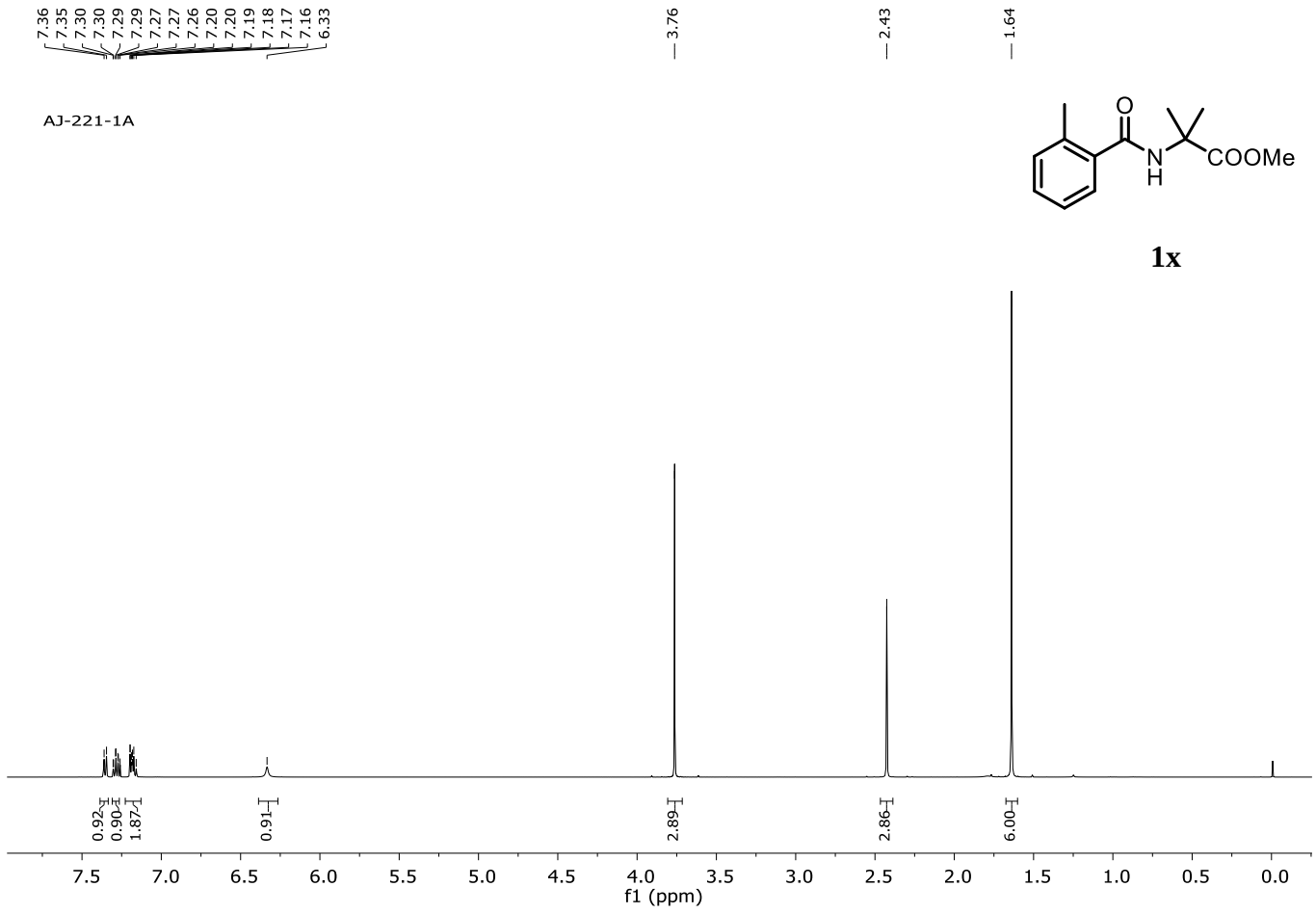
1u

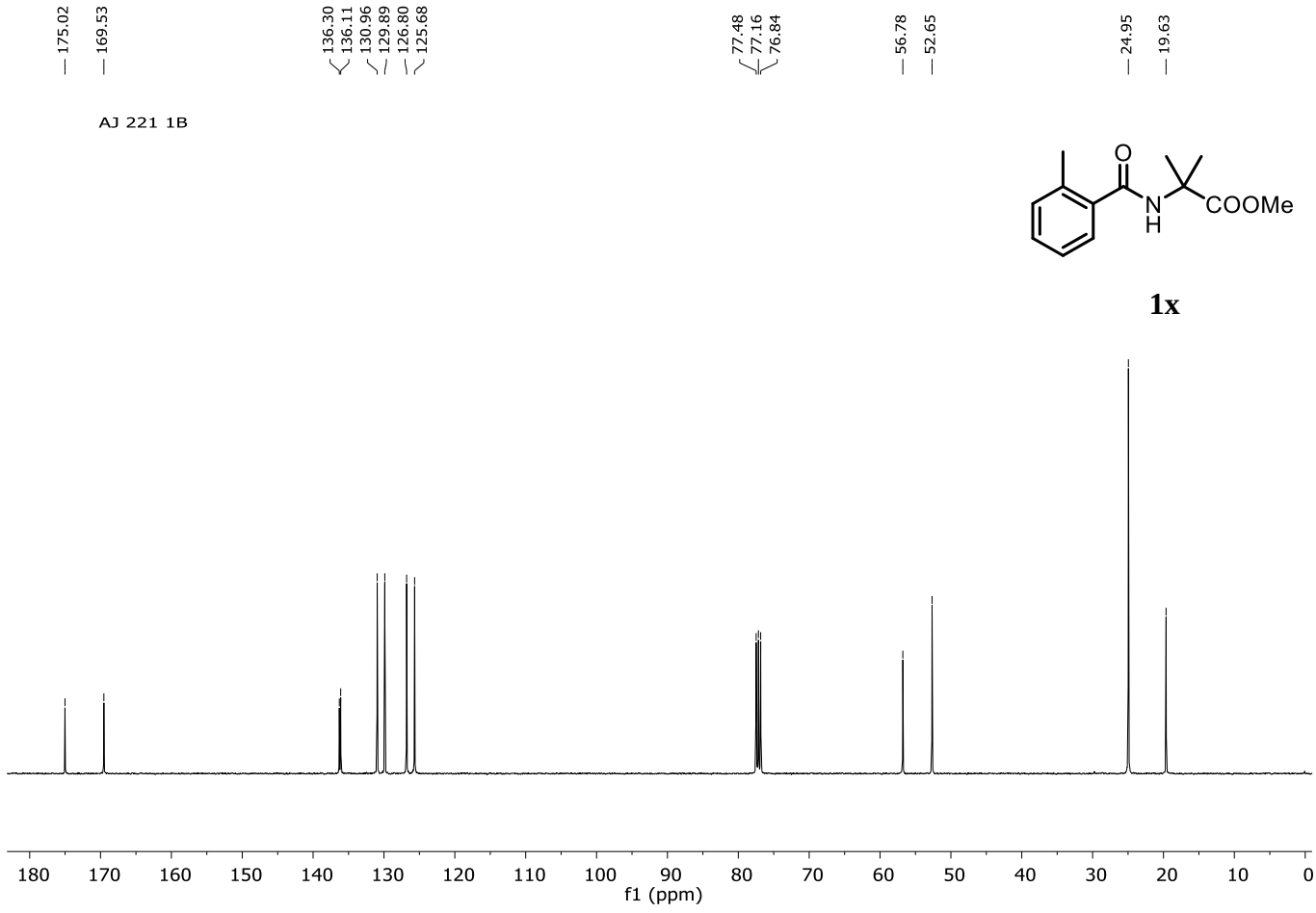

192.87
170.46
166.25
147.62
143.54
135.18
134.76
134.64
134.49
134.43
130.16
124.80
122.35
121.24
120.72
77.48
77.16
76.84
52.74
41.98
AJ 331 1B
O
O
N
H
COOMe
f1 (ppm)

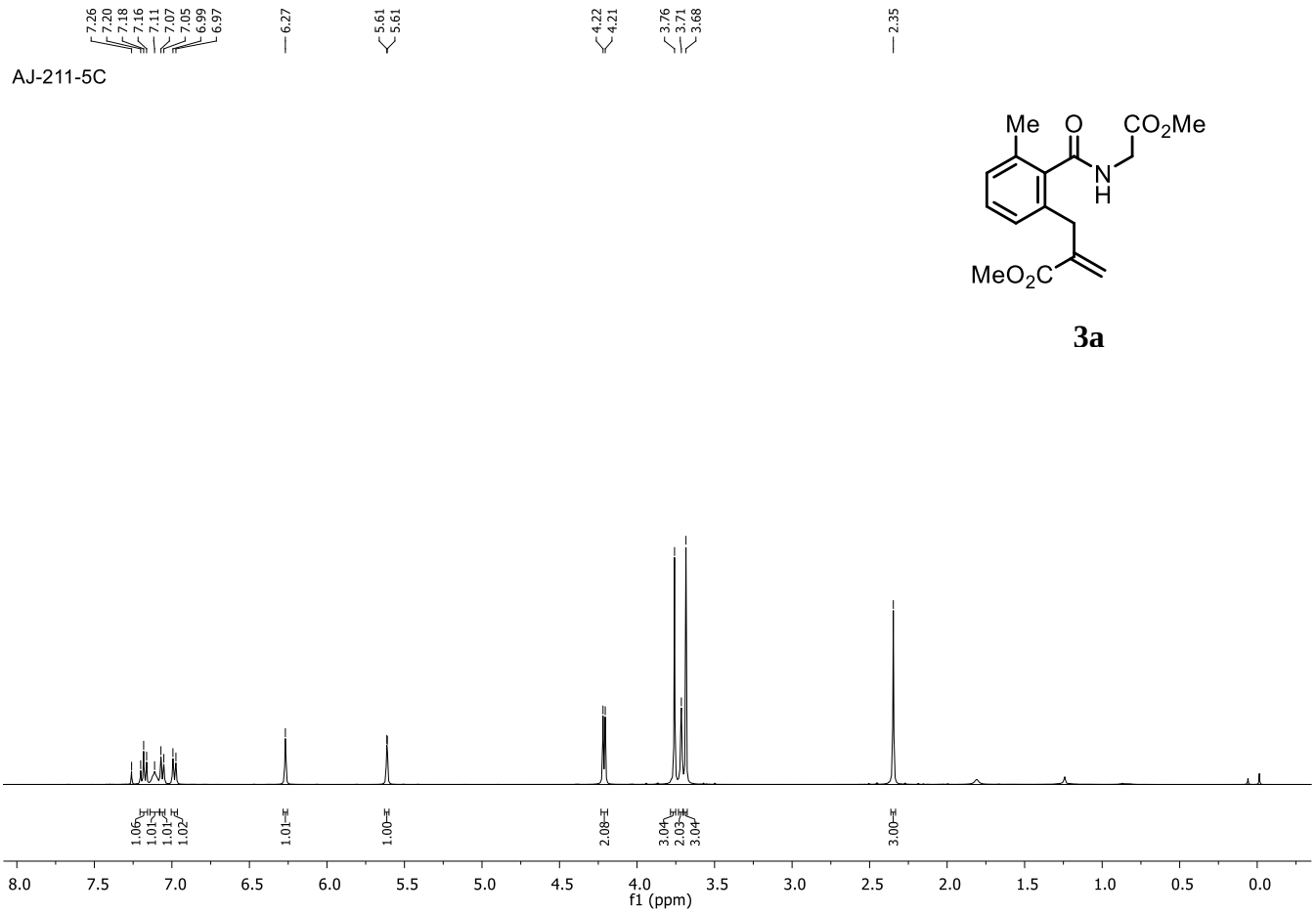
1u


7.42
7.41
7.40
7.34
7.33
7.32
7.32
7.31
7.30
7.26
7.23
7.23
7.23
7.22
7.22
7.21
7.20
6.28
6.26
4.78
4.77
4.77
4.76
3.77
2.45
2.31
2.30
2.29
2.28
2.28
2.27
2.27
2.26
2.25
2.24
1.04
1.02
0.96
0.95
AJ-404-B-1A
O
N
H
COOMe
1w
1.00
0.98
2.06
1.00
1.03
3.18
3.13
1.12
3.27
3.14
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

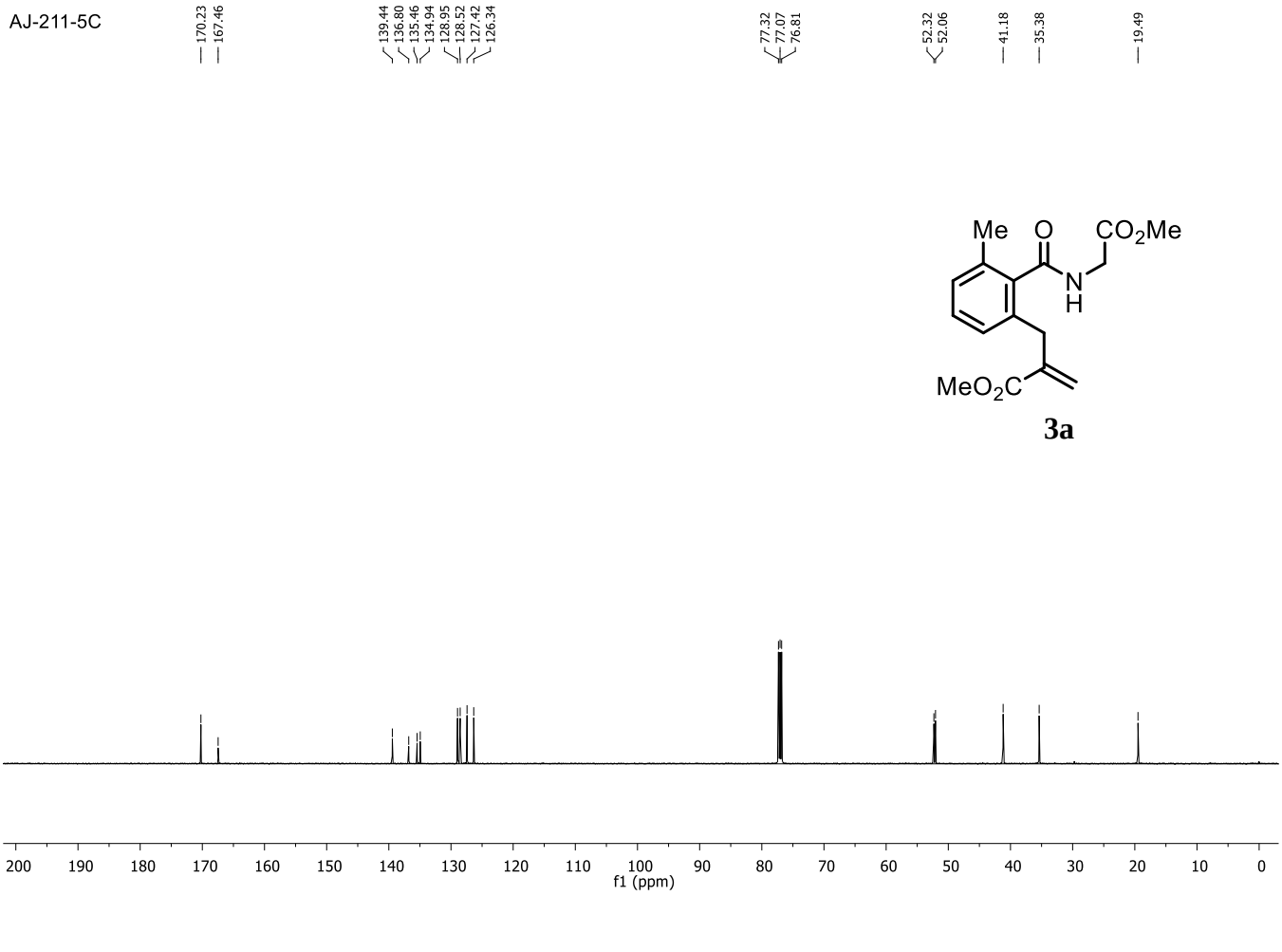

172.53
169.93
136.23
136.06
131.06
130.10
126.89
125.78
77.48
77.16
76.84
57.31
52.24
31.39
19.86
19.15
17.89
AJ 404 1B
O
N
H
COOMe
1w
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.36
7.35
7.30
7.30
7.29
7.29
7.27
7.27
7.26
7.20
7.20
7.19
7.18
7.17
7.16
6.33
3.76
2.43
1.64
AJ-221-1A
COOMe
1x
0.92
0.90
1.87
0.91
2.89
2.86
6.00
f1 (ppm)

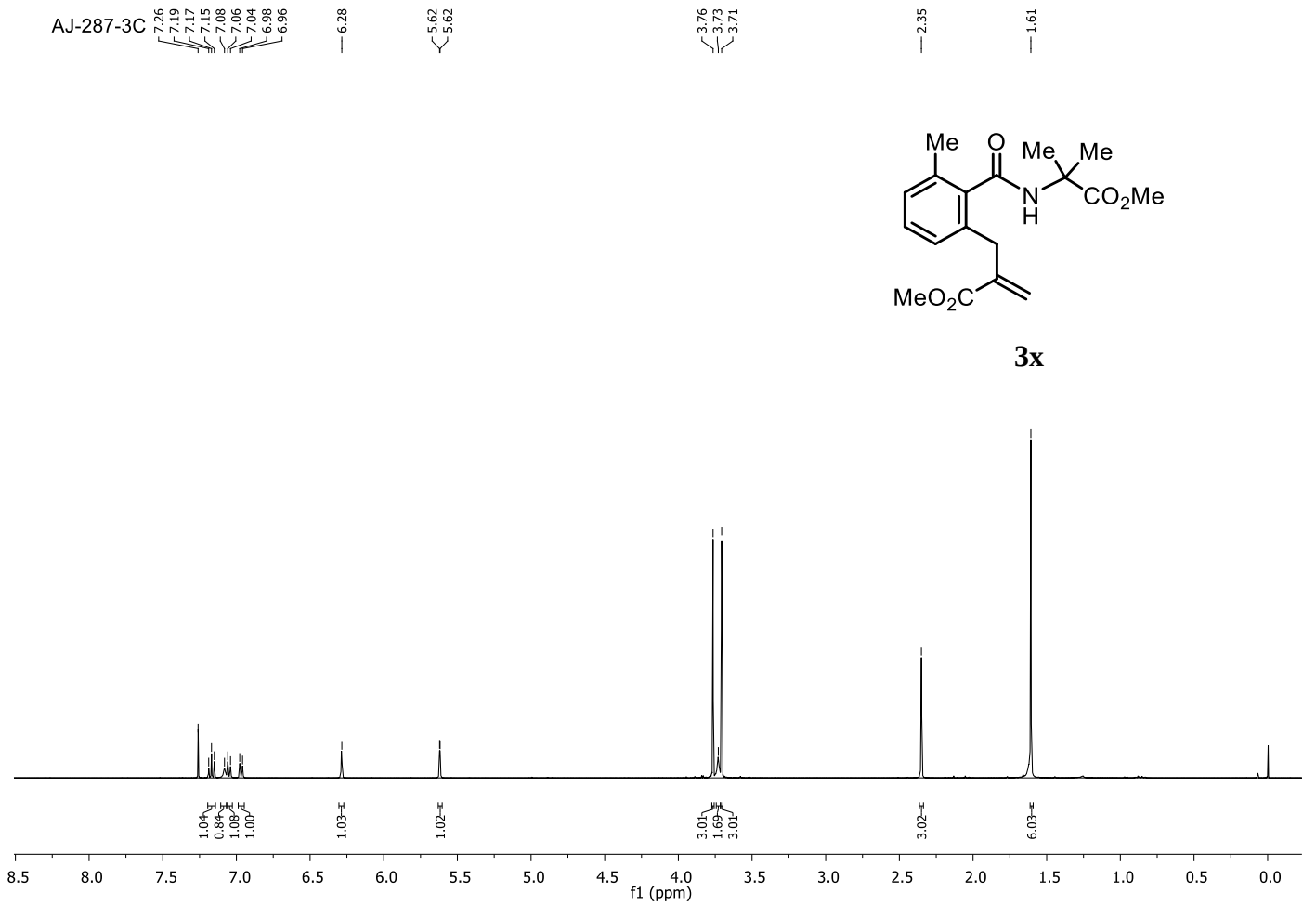

175.02
169.53
136.30
136.11
130.96
129.89
126.80
125.68
77.48
77.16
76.84
56.78
52.65
24.95
19.63
AJ 221 1B
COOMe
1x
f1 (ppm)


7.26
7.20
7.18
7.16
7.11
7.07
7.05
6.99
6.97
6.27
5.61
5.61
4.22
4.21
3.76
3.71
3.68
2.35
AJ-211-5C
Me
O
CO2Me
N
H
MeO2C
1.06
1.01
1.01
1.02
1.01
1.00
2.08
3.04
2.03
3.04
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

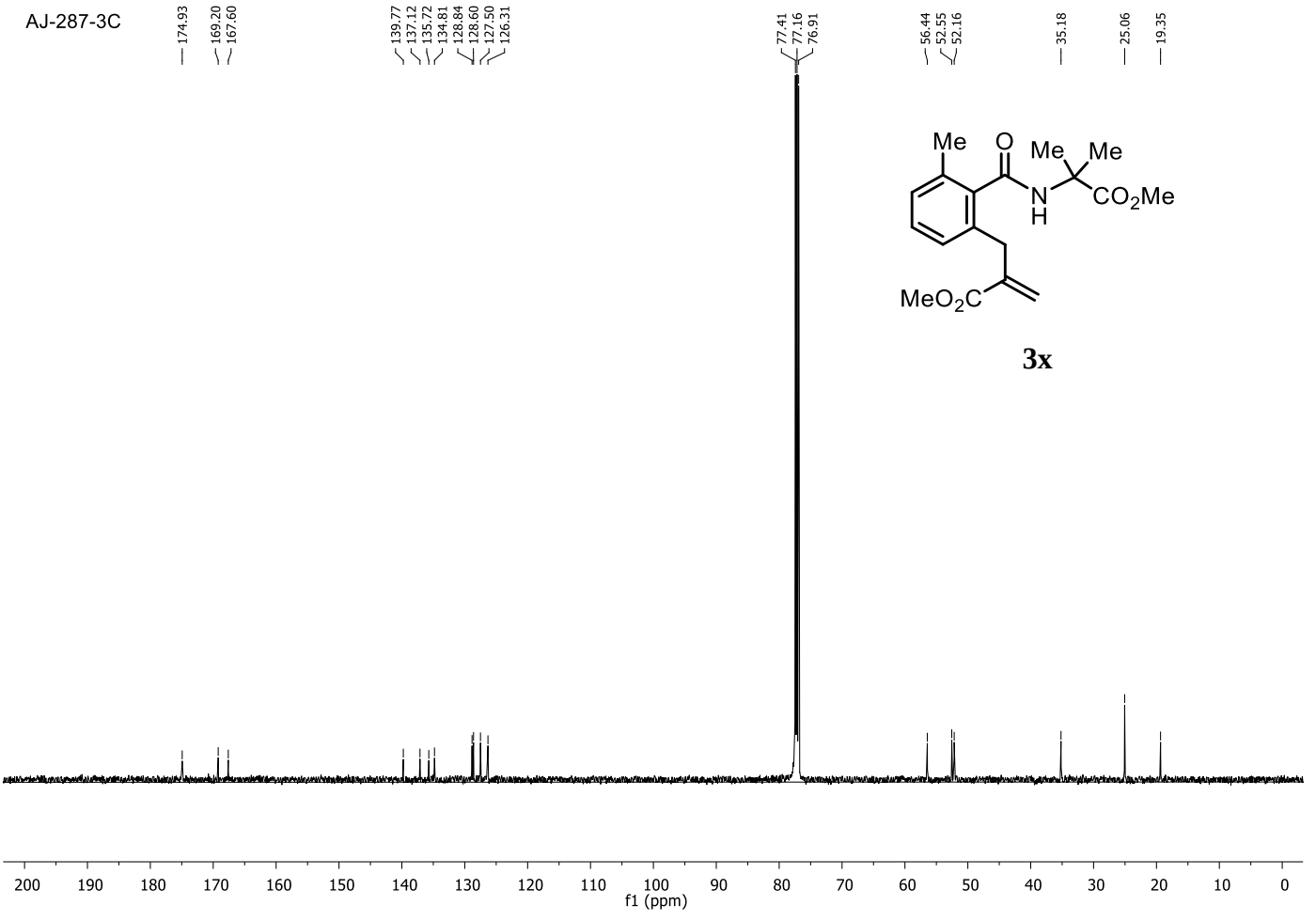
3a


AJ-211-5C
170.23
167.46
139.44
136.80
135.46
134.94
128.95
128.52
127.42
126.34
77.32
77.07
76.81
52.32
52.06
41.18
35.38
19.49
Me
O
CO2Me
N
H
MeO2C
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3a

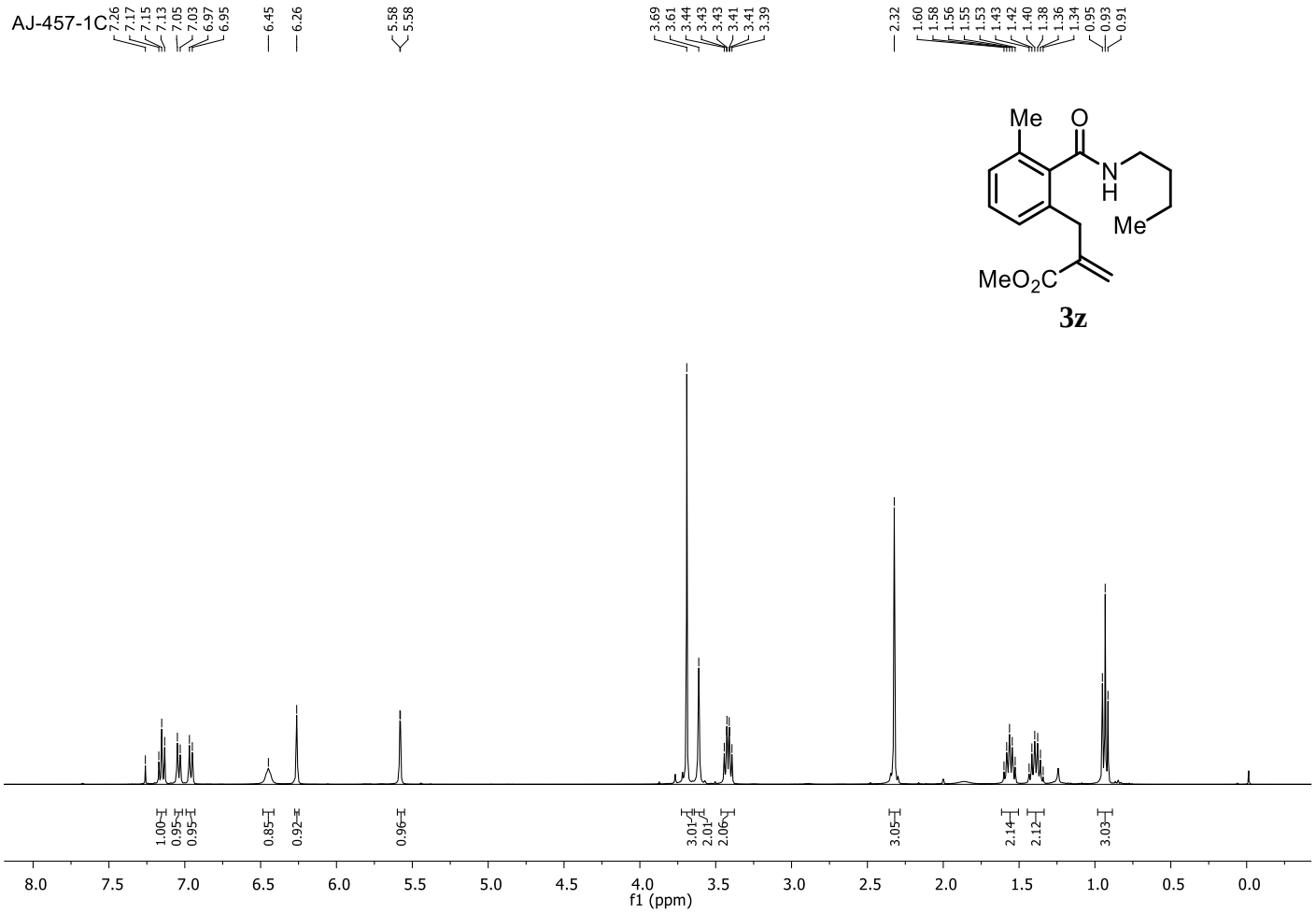

AJ-287-3C
7.26
7.19
7.17
7.15
7.08
7.06
7.04
6.98
6.96
6.28
5.62
5.62
3.76
3.73
3.71
2.35
1.61
Me
O
Me
Me
N
H
CO2Me
MeO2C
1.04
0.84
1.08
1.00
1.03
1.02
3.01
1.69
3.01
3.02
6.03
f1 (ppm)

3x


AJ-287-3C
174.93
169.20
167.60
139.77
137.12
135.72
134.81
128.84
128.60
127.50
126.31
77.41
77.16
76.91
56.44
52.55
52.16
35.18
25.06
19.35
Me
O
Me
Me
N
H
CO2Me
MeO2C
f1 (ppm)

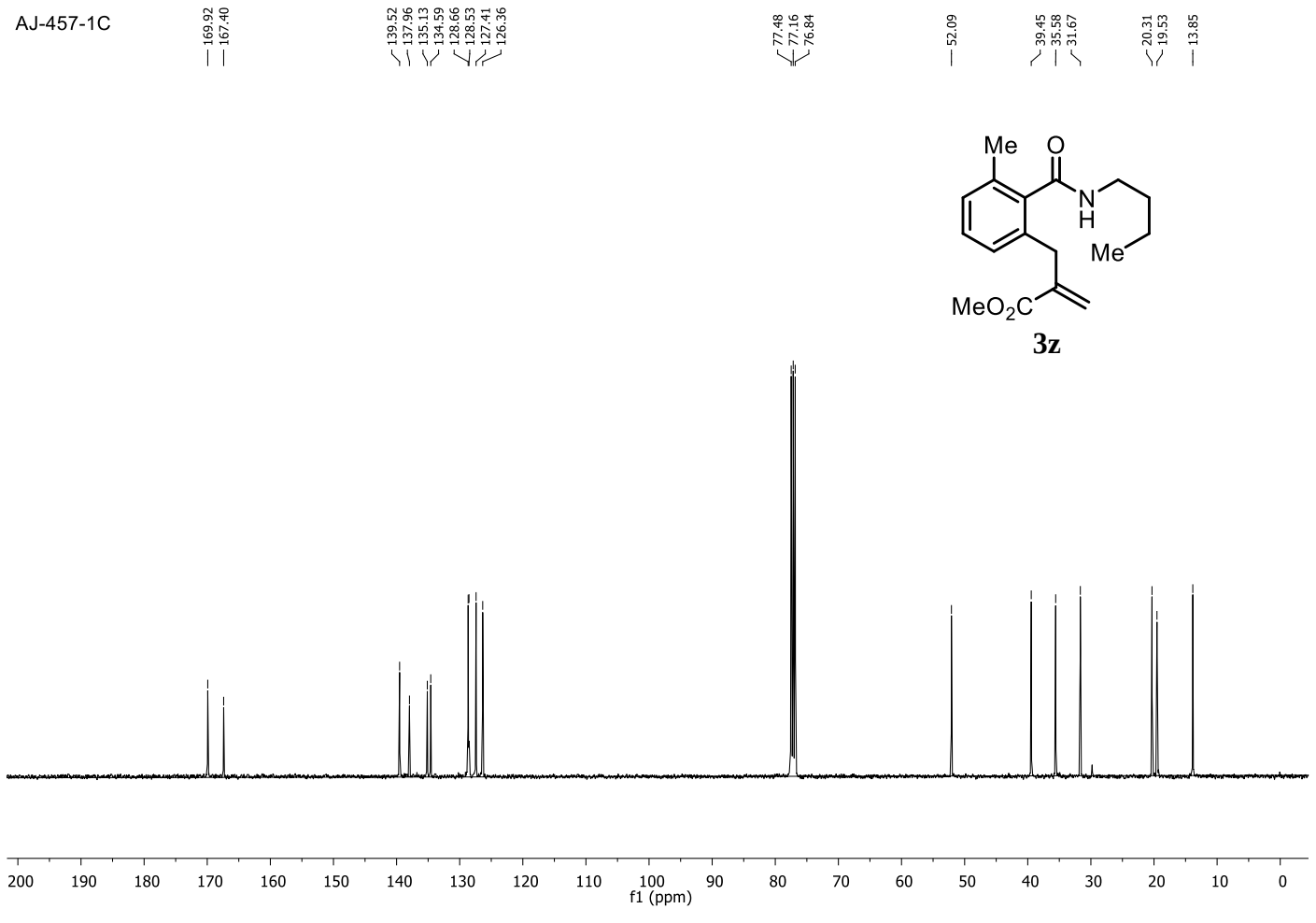
3x

AJ-457-1C

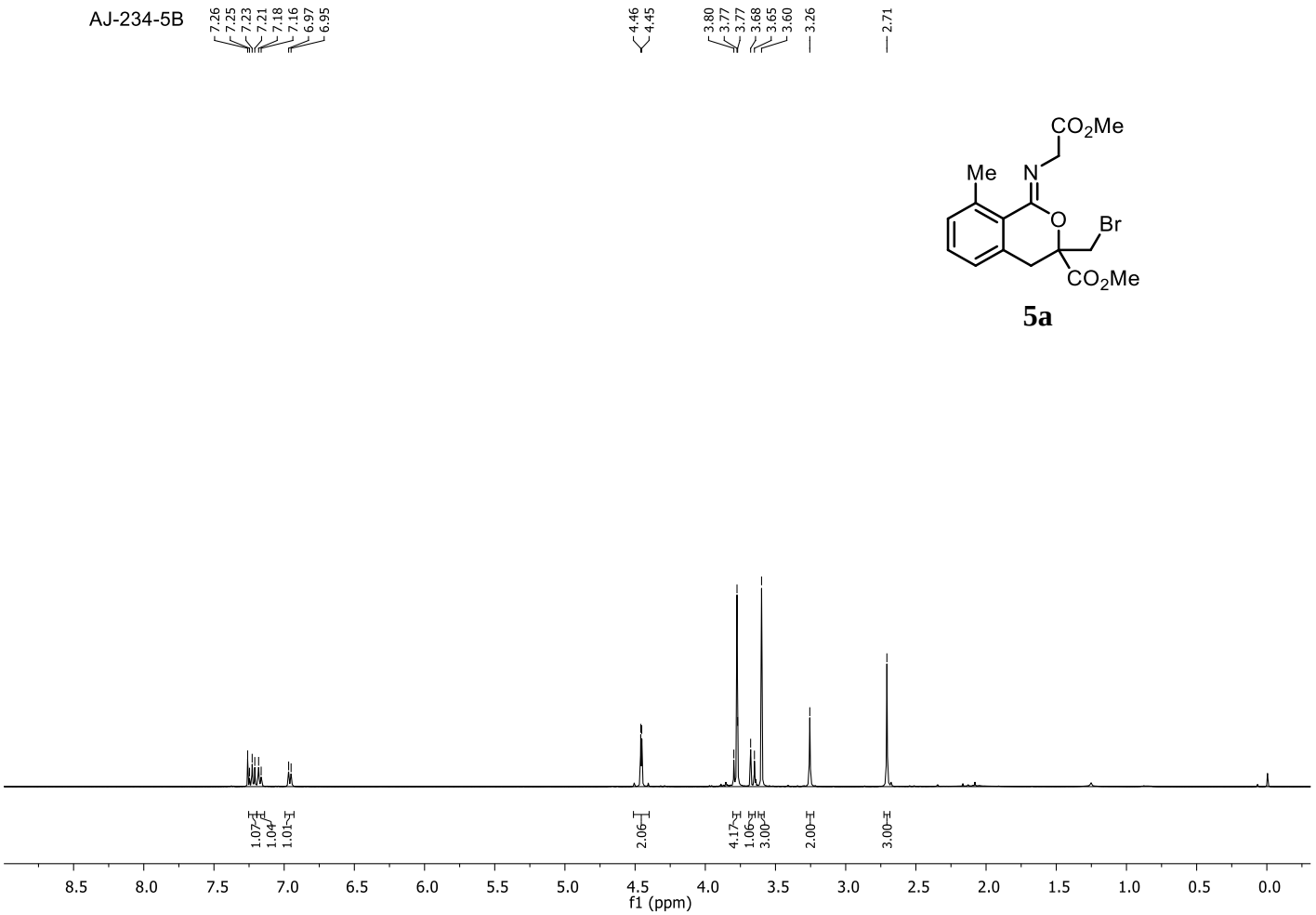


3z

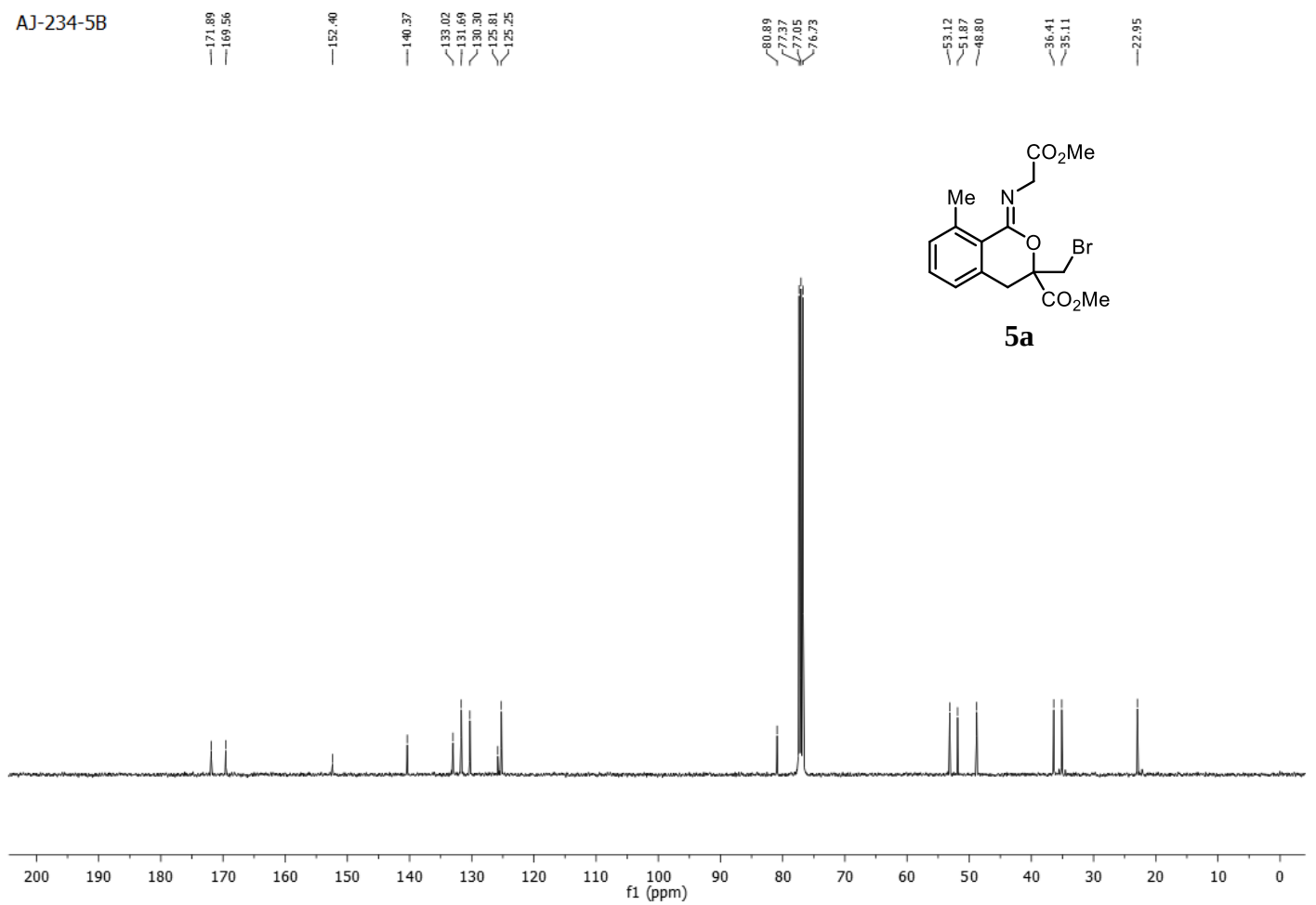
AJ-457-1C



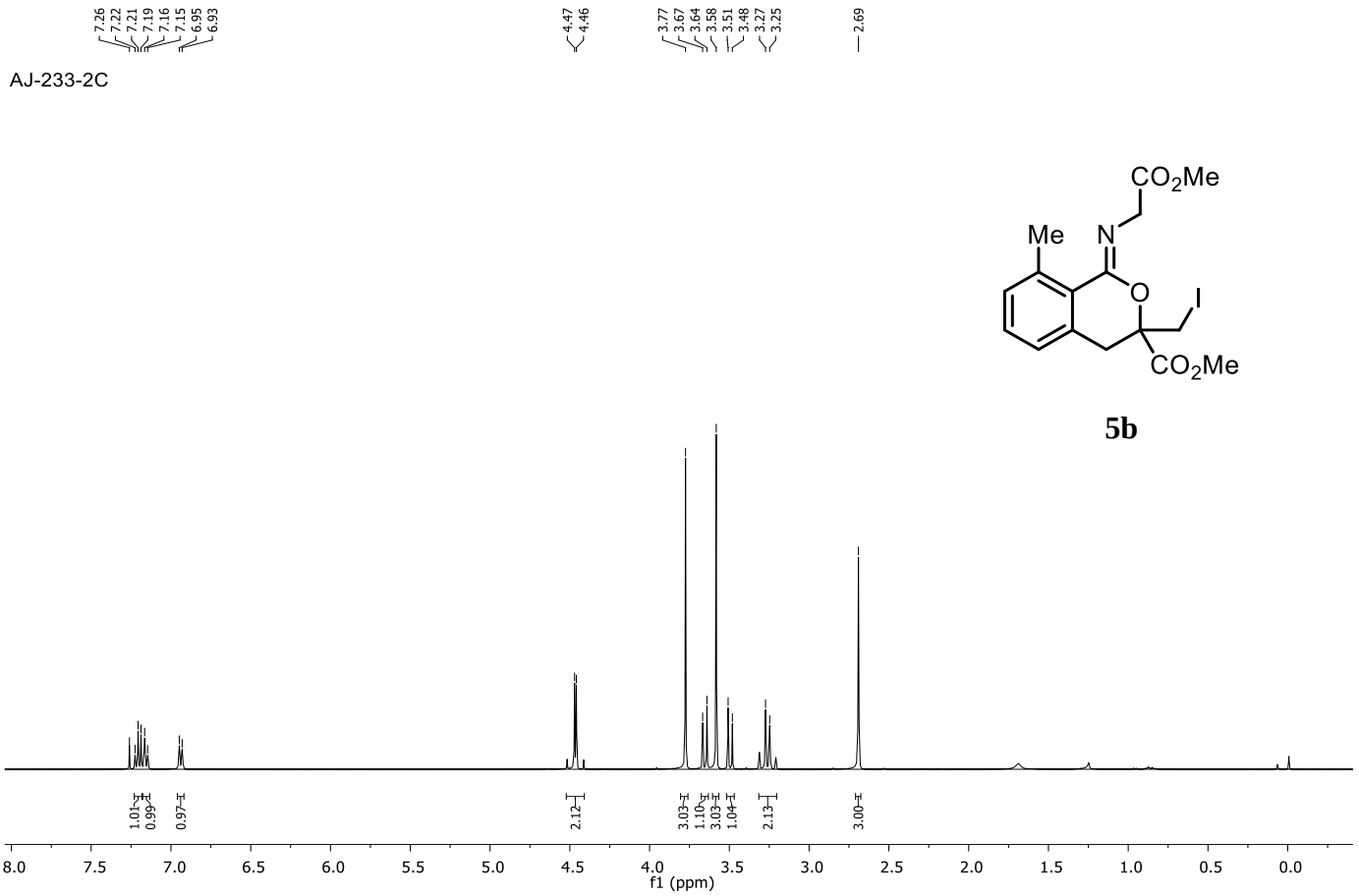
3z


AJ-234-5B
7.26
7.25
7.23
7.21
7.18
7.16
6.97
6.95
4.46
4.45
3.80
3.77
3.77
3.68
3.65
3.60
3.26
2.71
CO2Me
Me
N
O
Br
CO2Me
1.07
1.04
1.01
2.06
4.17
1.06
3.00
2.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

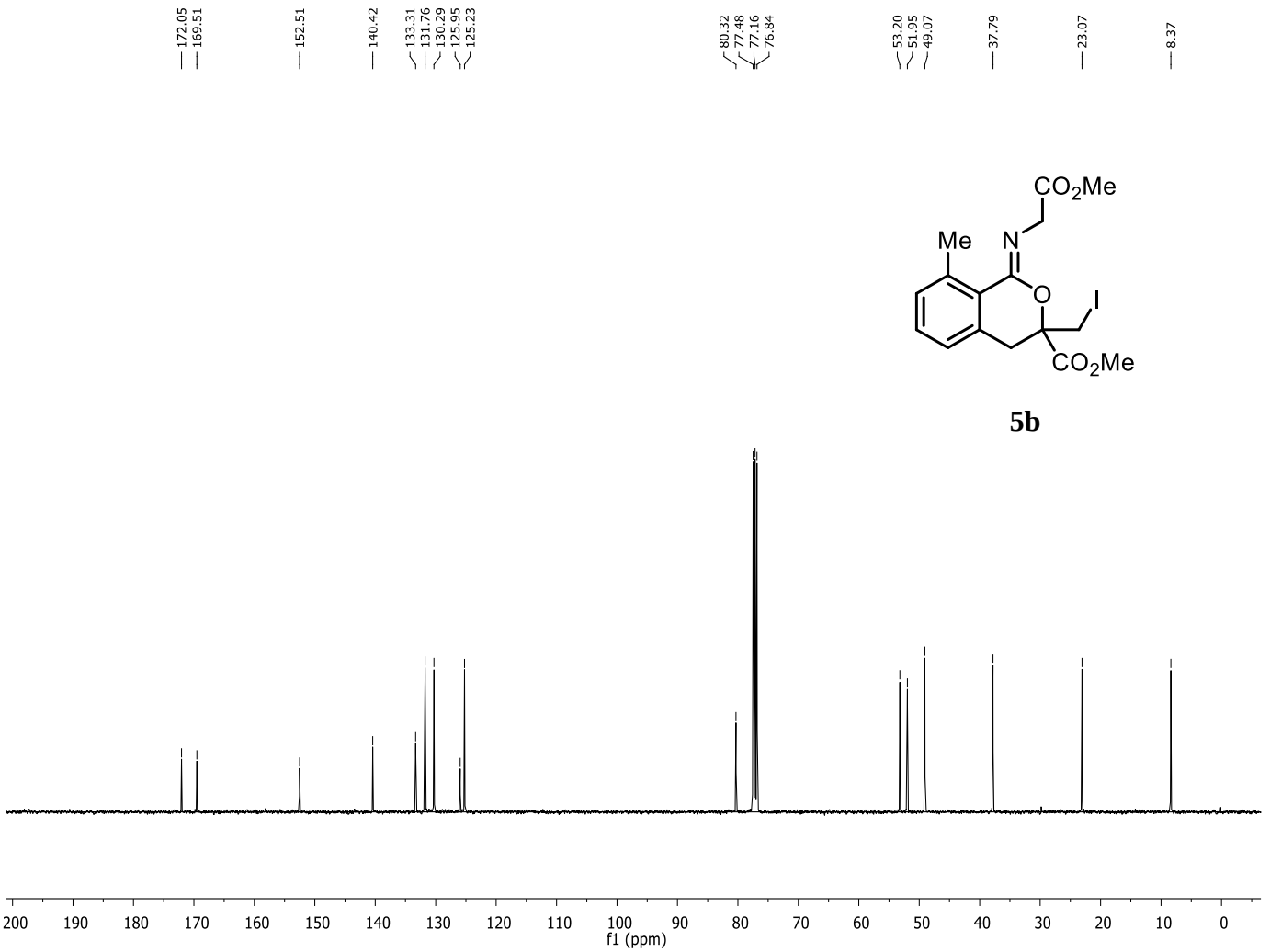
5a


AJ-234-5B
171.89
169.56
152.40
140.37
133.02
131.69
130.30
125.81
125.25
80.89
77.37
77.05
76.73
53.12
51.87
48.80
36.41
35.11
22.95
CO2Me
Me
N
O
Br
CO2Me
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

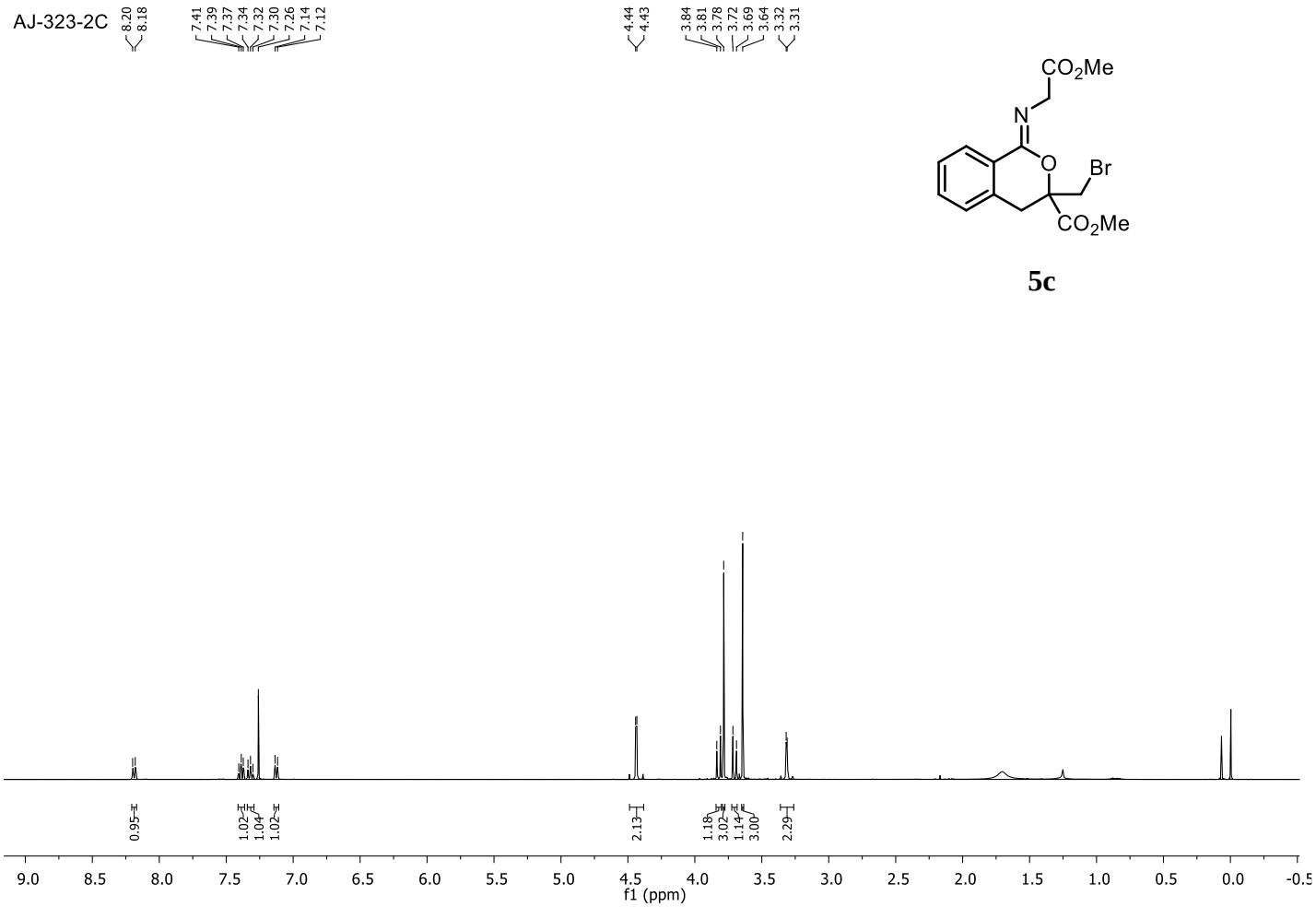
5a


7.26
7.22
7.21
7.19
7.16
7.15
6.95
6.93
4.47
4.46
3.77
3.67
3.64
3.58
3.51
3.48
3.27
3.25
2.69
AJ-233-2C
CO2Me
Me
N
O
I
CO2Me
1.01
0.99
0.97
2.12
3.03
1.10
3.03
1.04
2.13
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

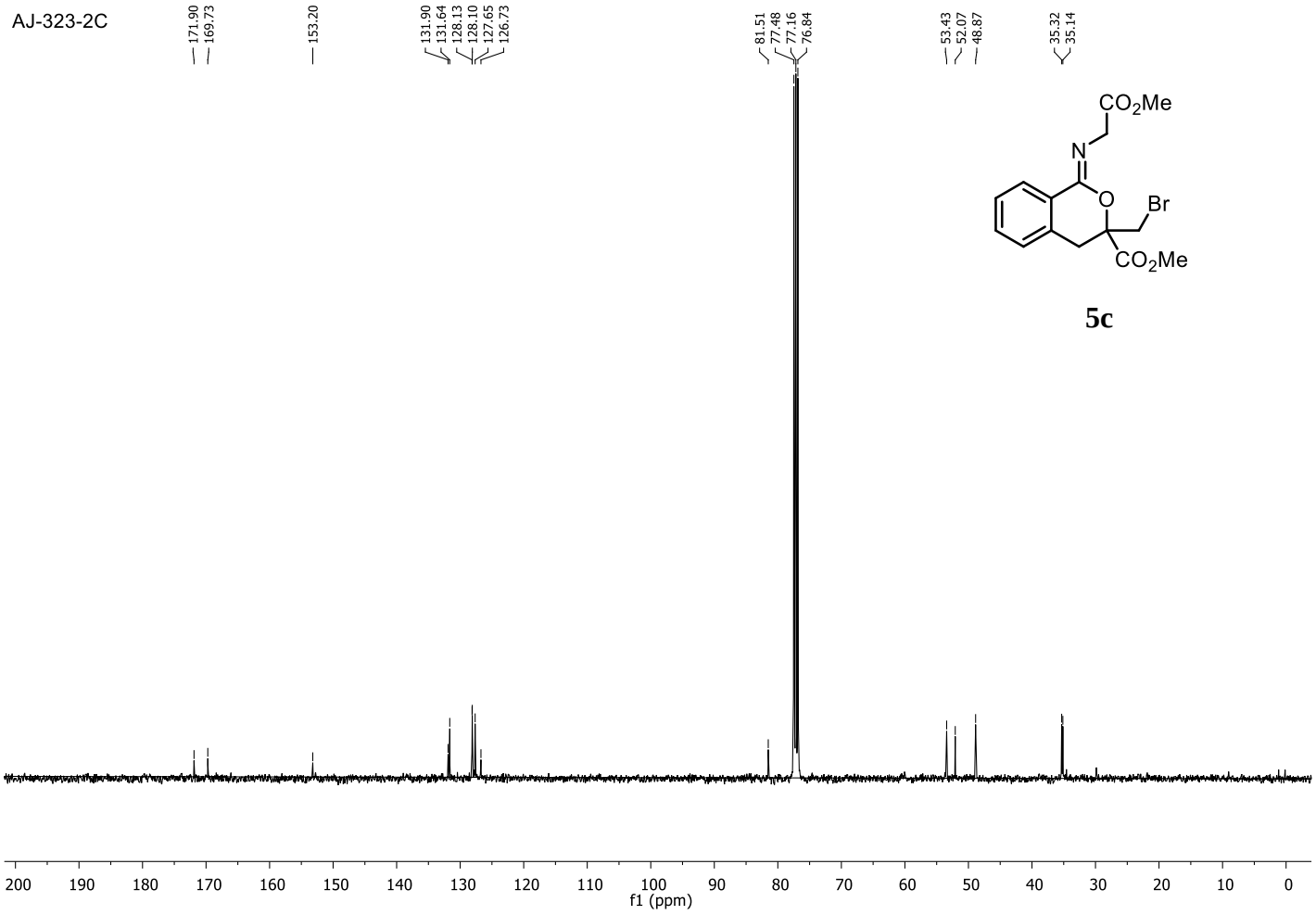
5b


172.05
169.51
152.51
140.42
133.31
131.76
130.29
125.95
125.23
80.32
77.48
77.16
76.84
53.20
51.95
49.07
37.79
23.07
8.37
CO2Me
Me
N
O
I
CO2Me
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

5b

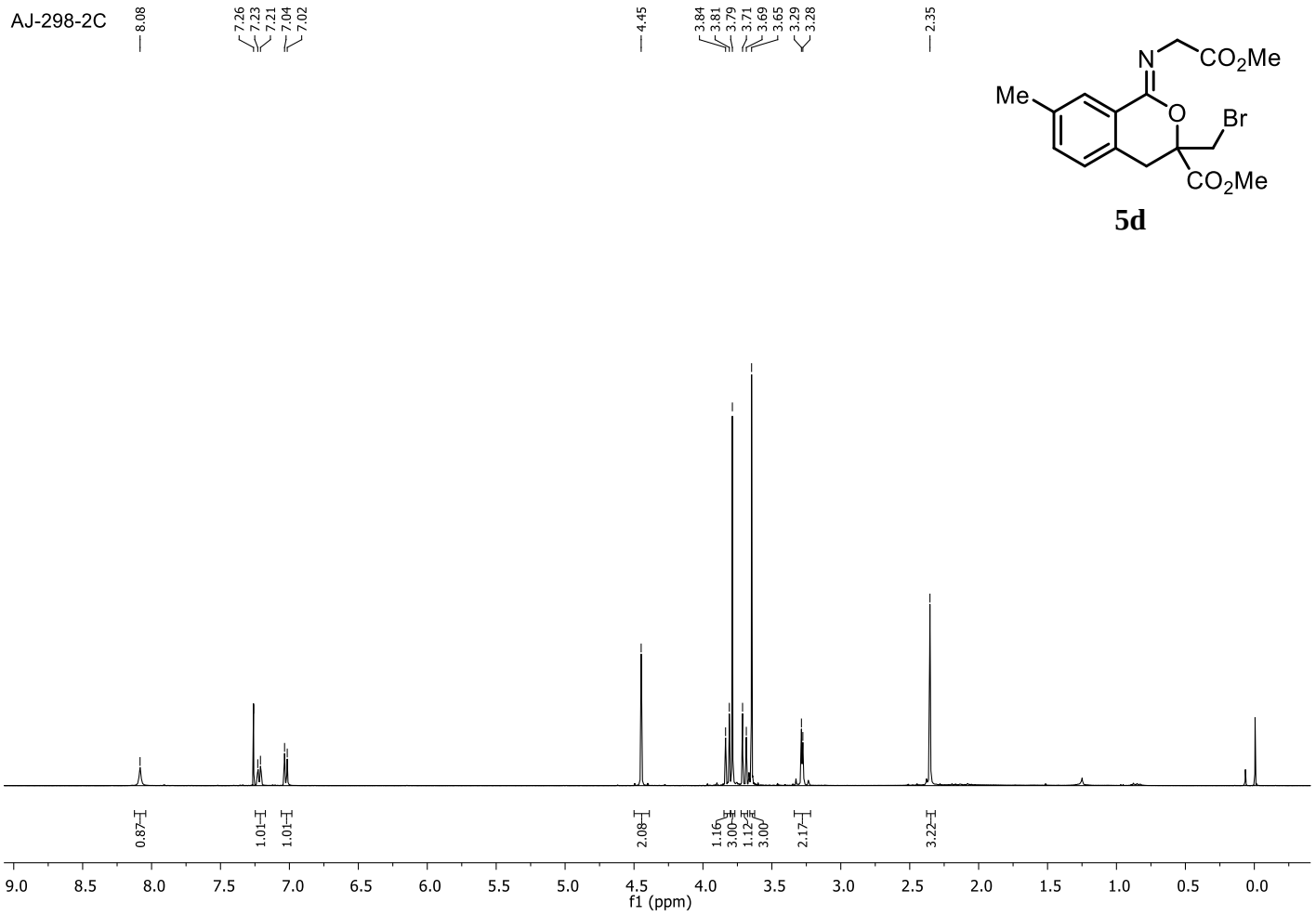

AJ-323-2C
8.20
8.18
7.41
7.39
7.37
7.34
7.32
7.30
7.26
7.14
7.12
4.44
4.43
3.84
3.81
3.78
3.72
3.69
3.64
3.32
3.31
CO2Me
N
O
Br
CO2Me
0.95
1.02
1.04
1.02
2.13
1.18
3.02
1.14
3.00
2.29
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

5c


AJ-323-2C
171.90
169.73
153.20
131.90
131.64
128.13
128.10
127.65
126.73
81.51
77.48
77.16
76.84
53.43
52.07
48.87
35.32
35.14
CO2Me
N
O
Br
CO2Me
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

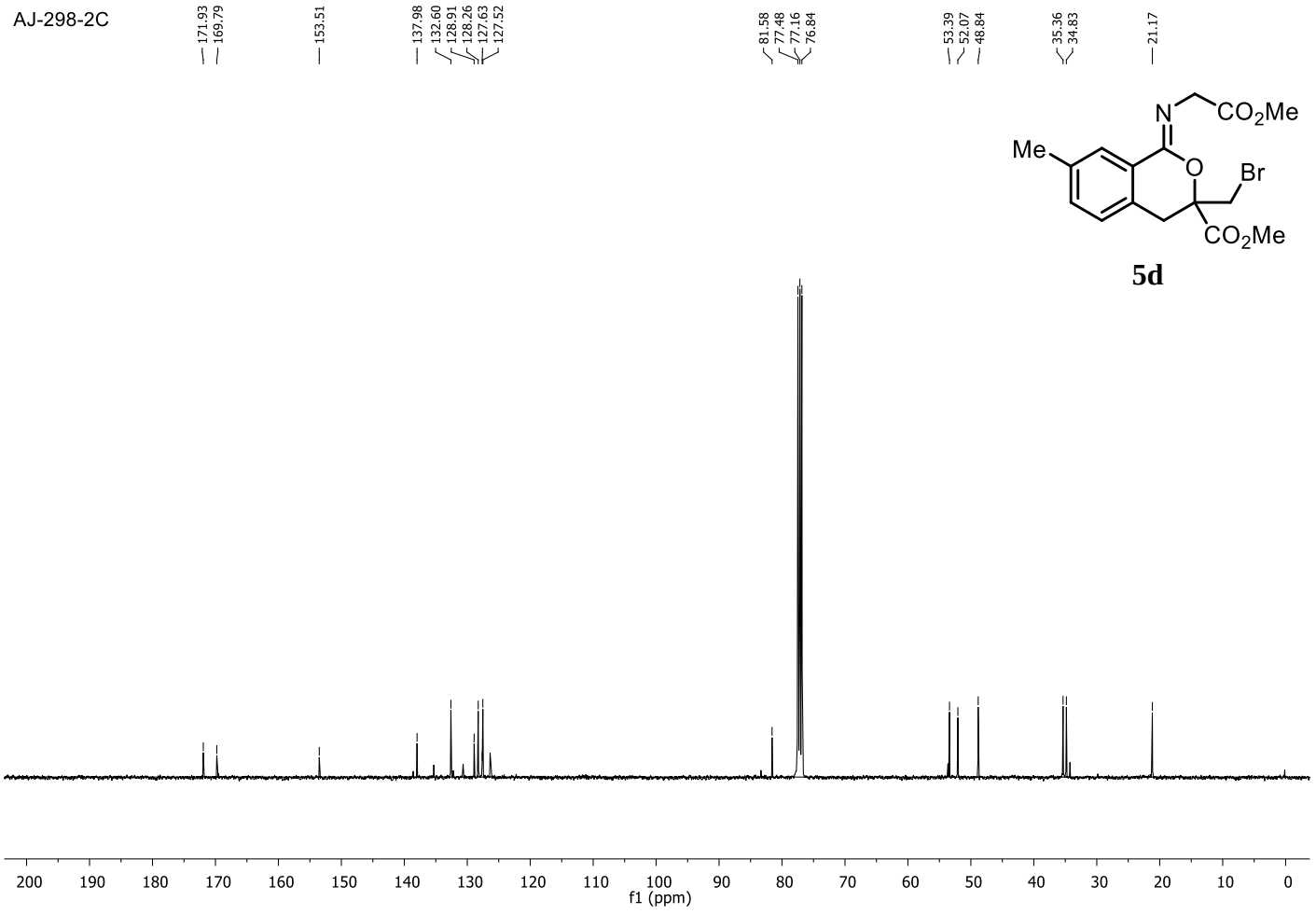
5c

AJ-298-2C



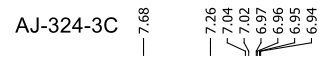
5d

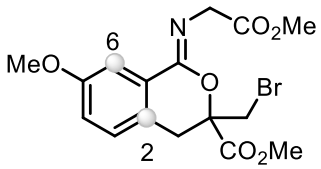
AJ-298-2C



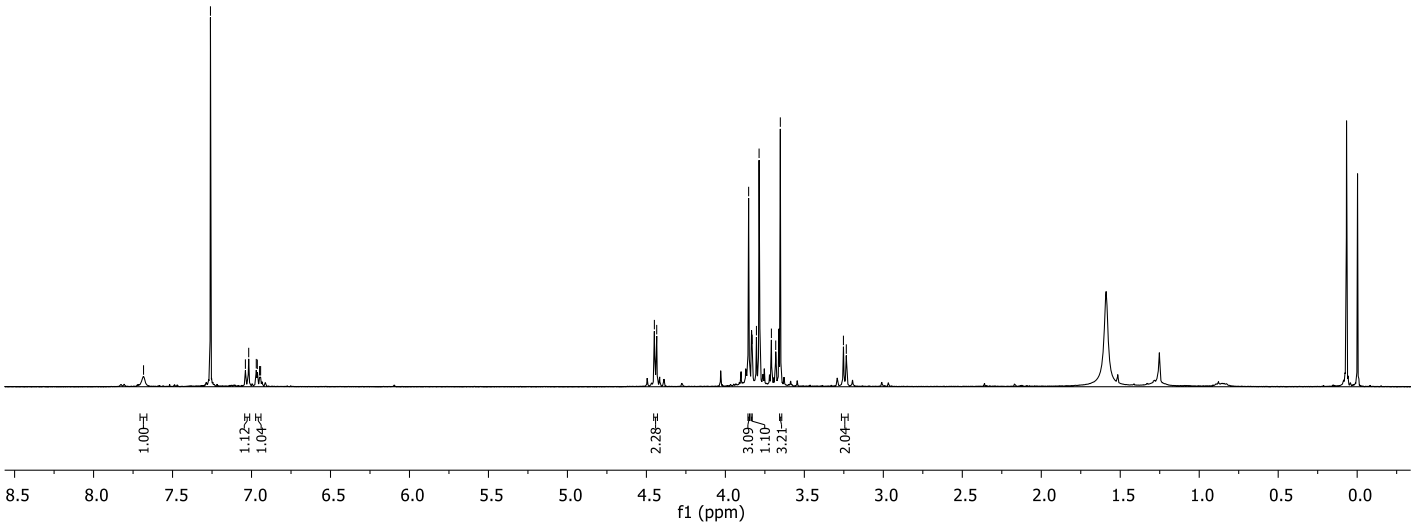
5d

AJ-324-3C

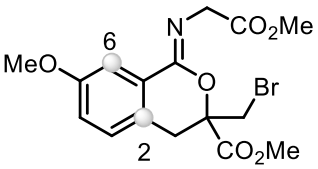




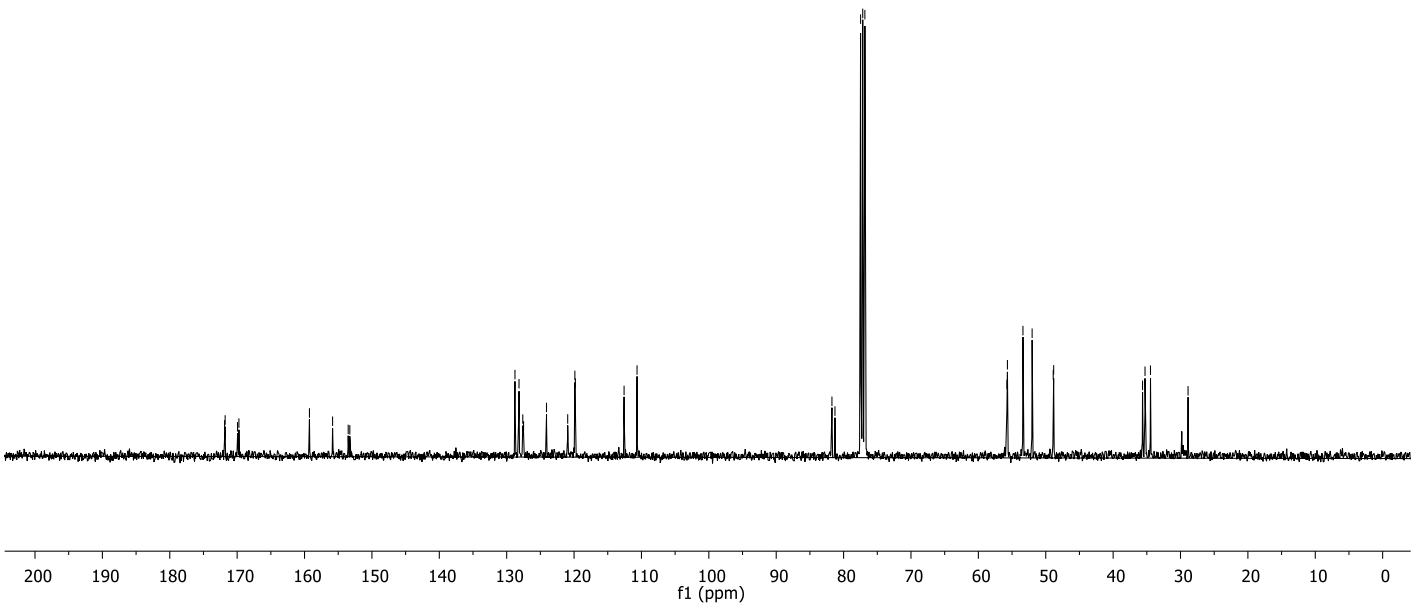
5e(C2) and 5e'(C6)
5e:5e' = 1:1



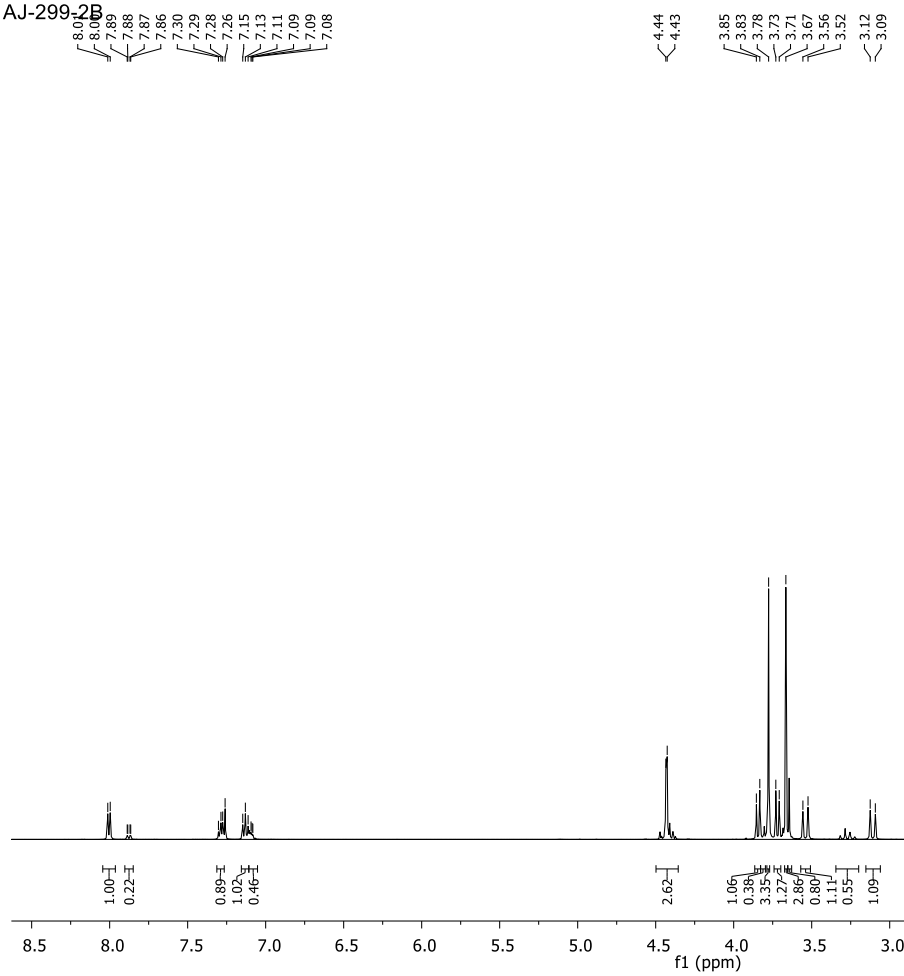
AJ-324-3C

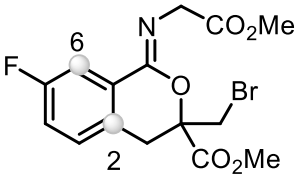


5e(C2) and 5e'(C6)
5e:5e' = 1:1



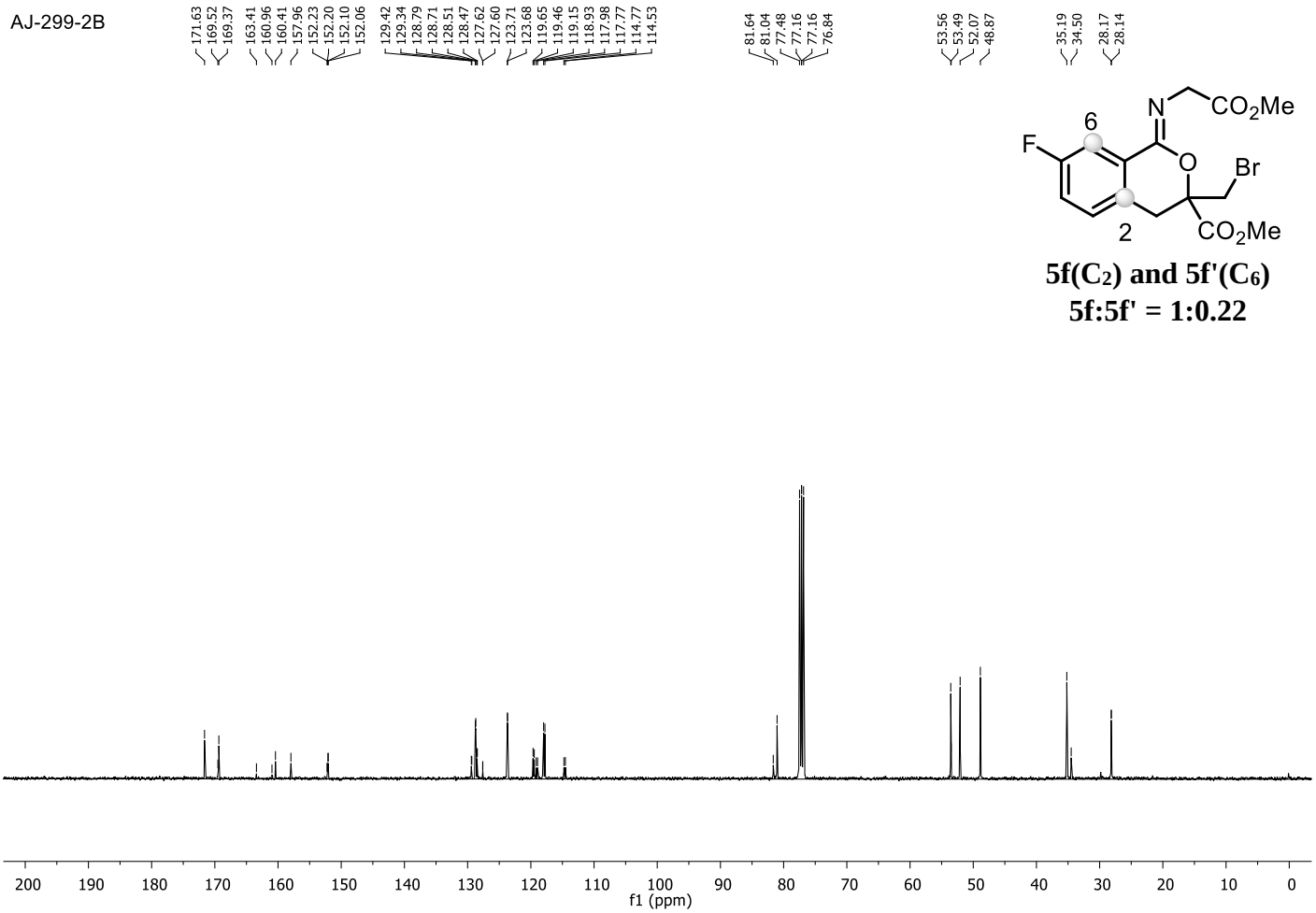
AJ-299-2B





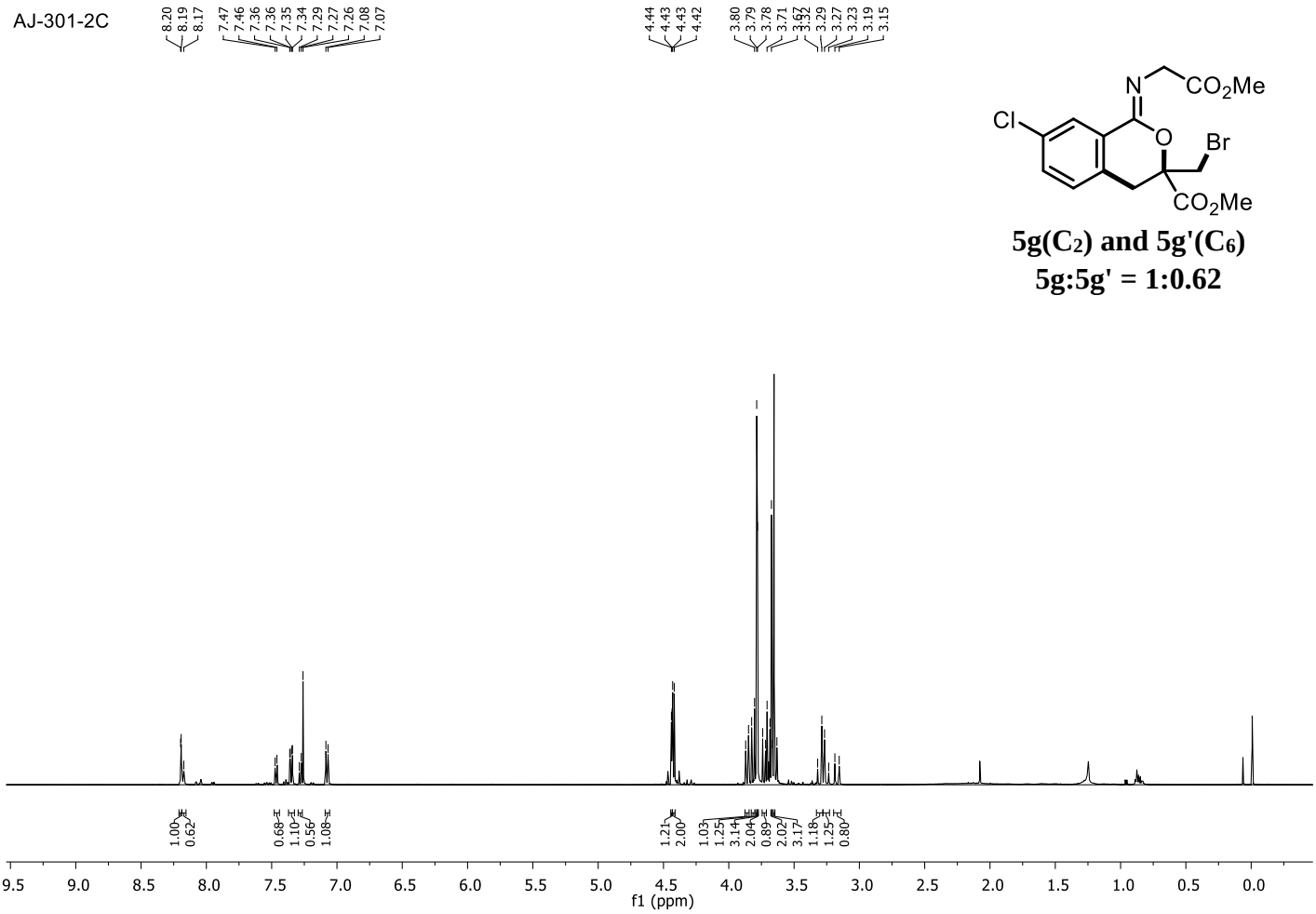
5f(C_2) and 5f'(C_6)
5f:5f' = 1:0.22

AJ-299-2B



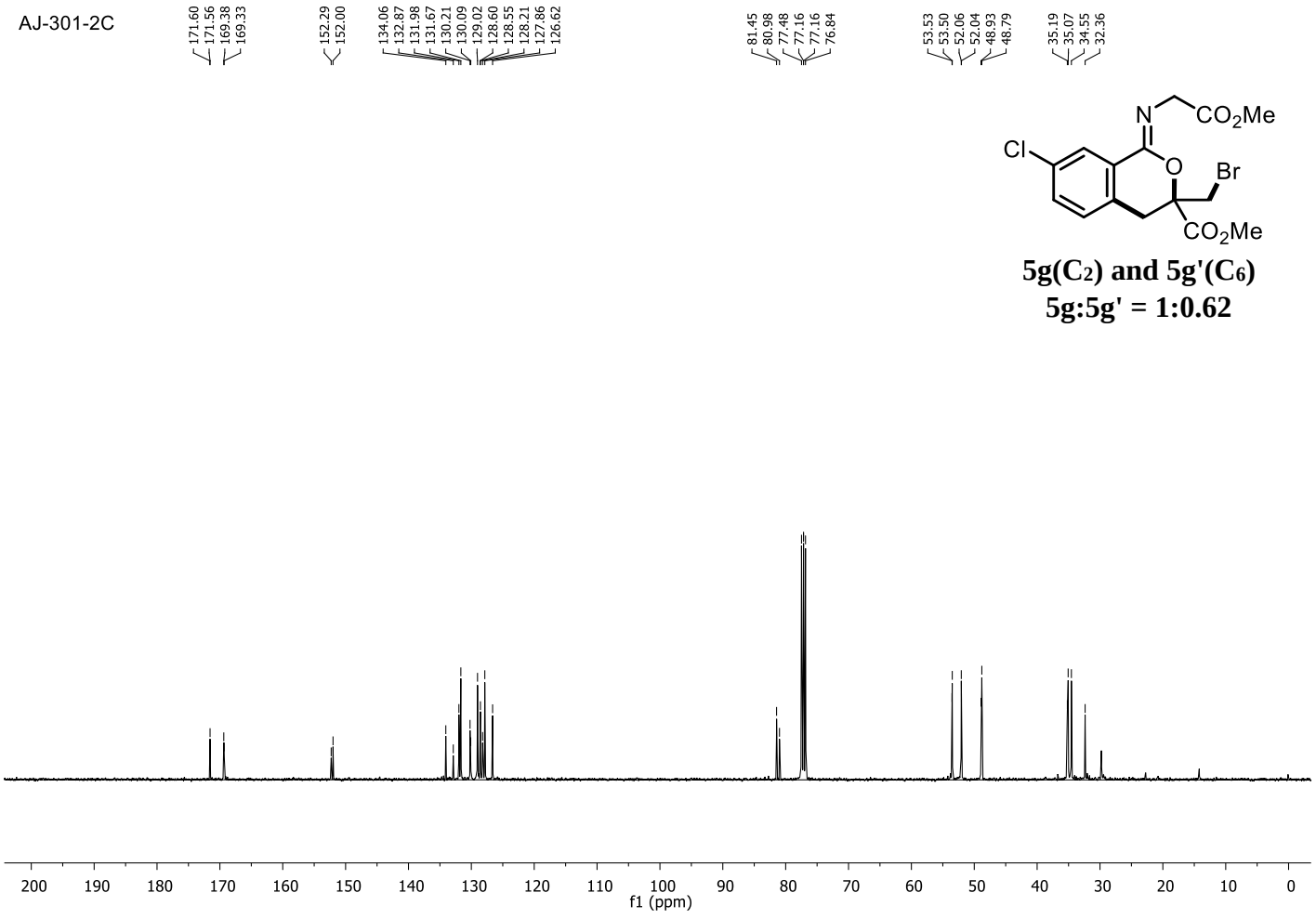
5f(C_2) and 5f'(C_6)
5f:5f' = 1:0.22

AJ-301-2C

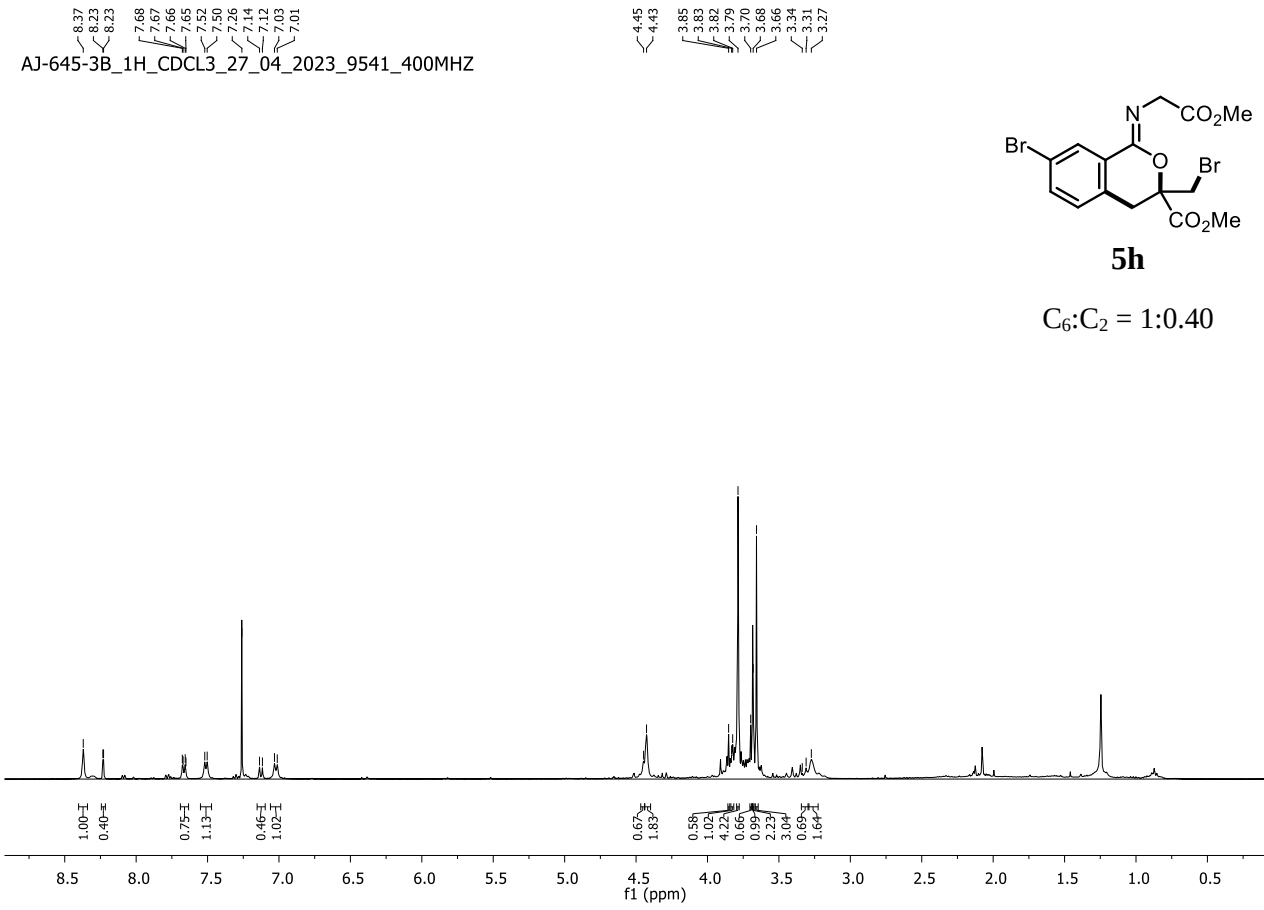


5g(C2) and 5g'(C6)
5g:5g' = 1:0.62

AJ-301-2C

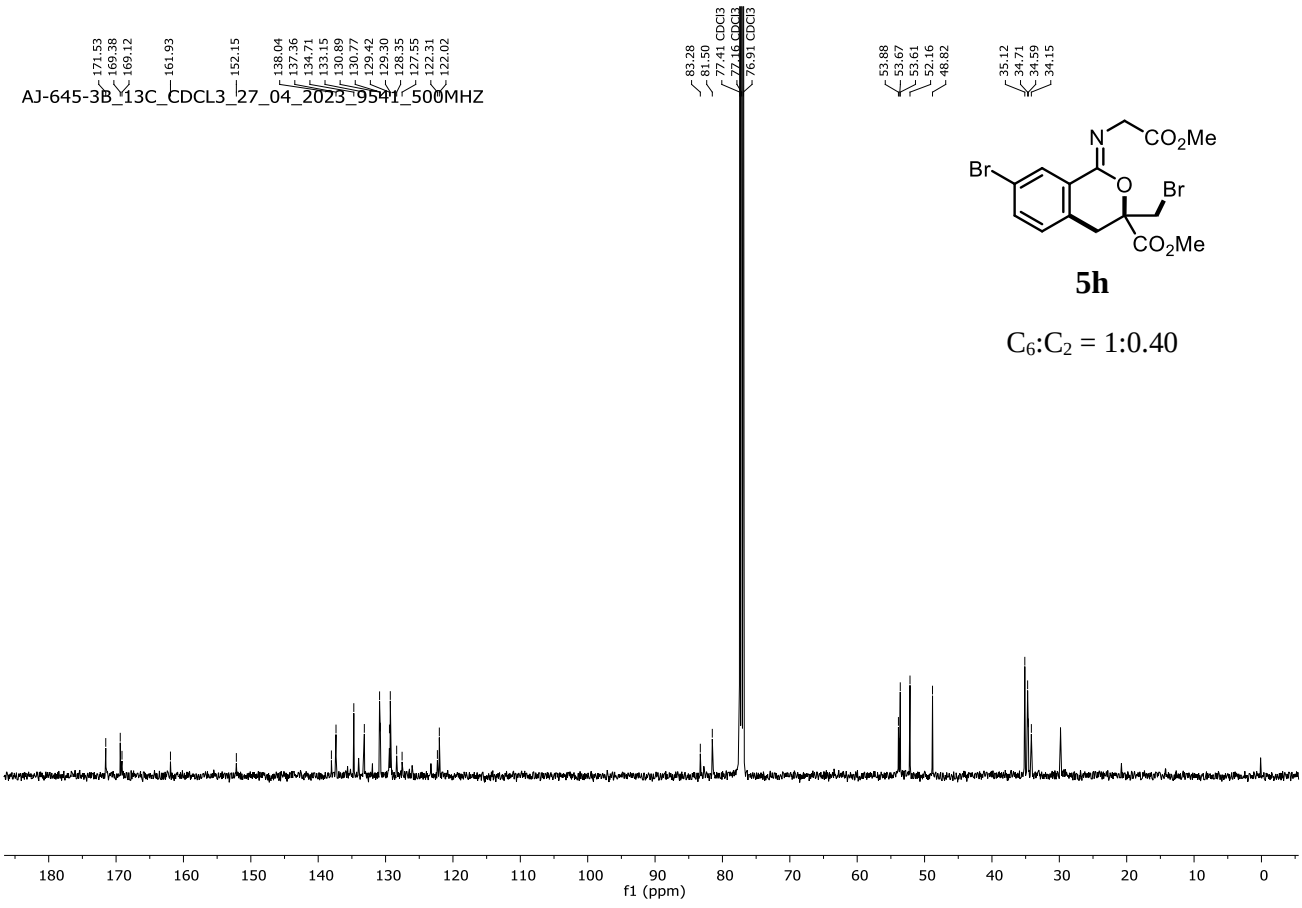


5g(C2) and 5g'(C6)
5g:5g' = 1:0.62



5h

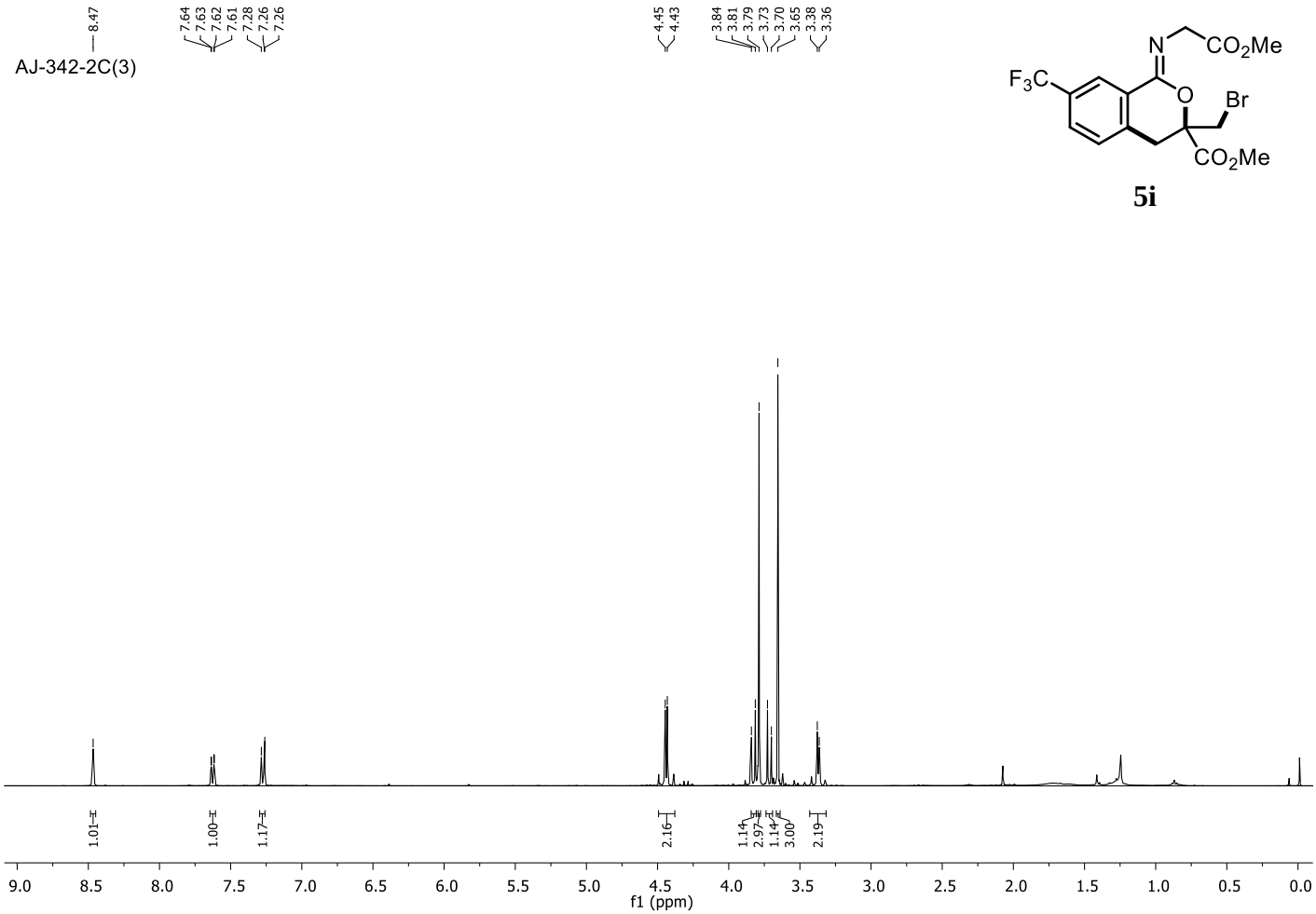
C_6:C_2 = 1:0.40



5h

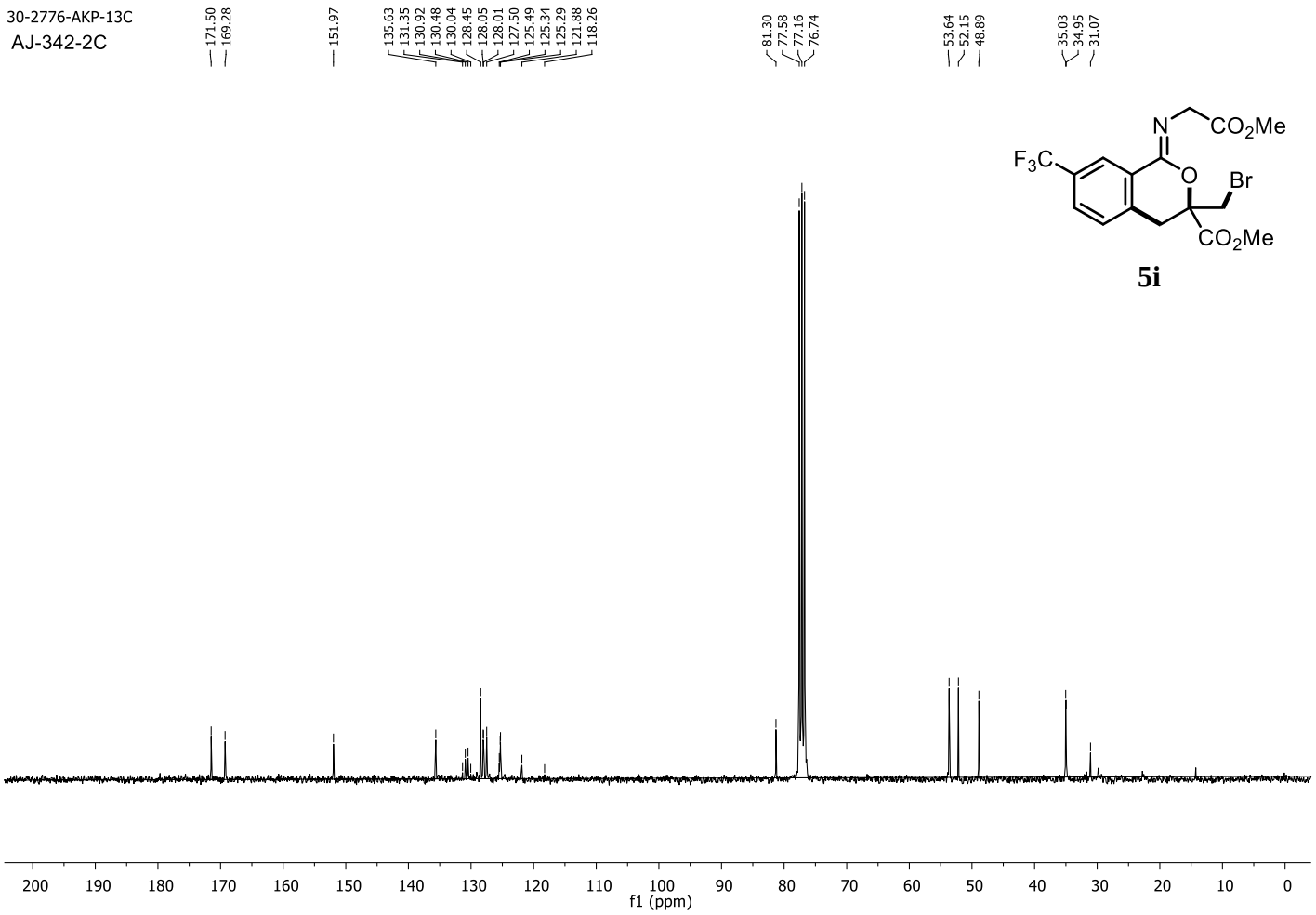
C_6:C_2 = 1:0.40

AJ-342-2C(3)



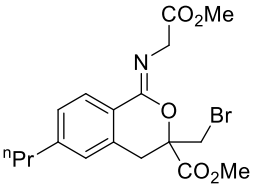
5i

30-2776-AKP-13C
AJ-342-2C

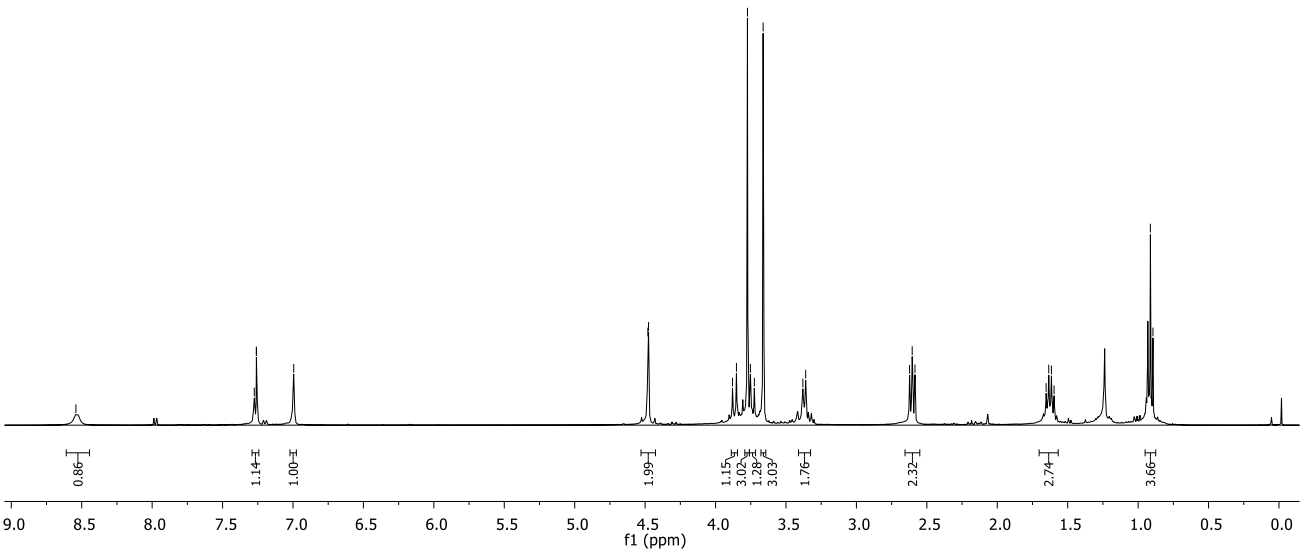


5i

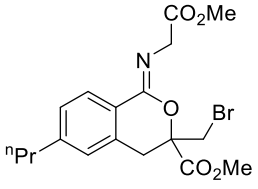
AJ-645-2B_1H_CDCL3_28_04_2023_9829_400MHZ



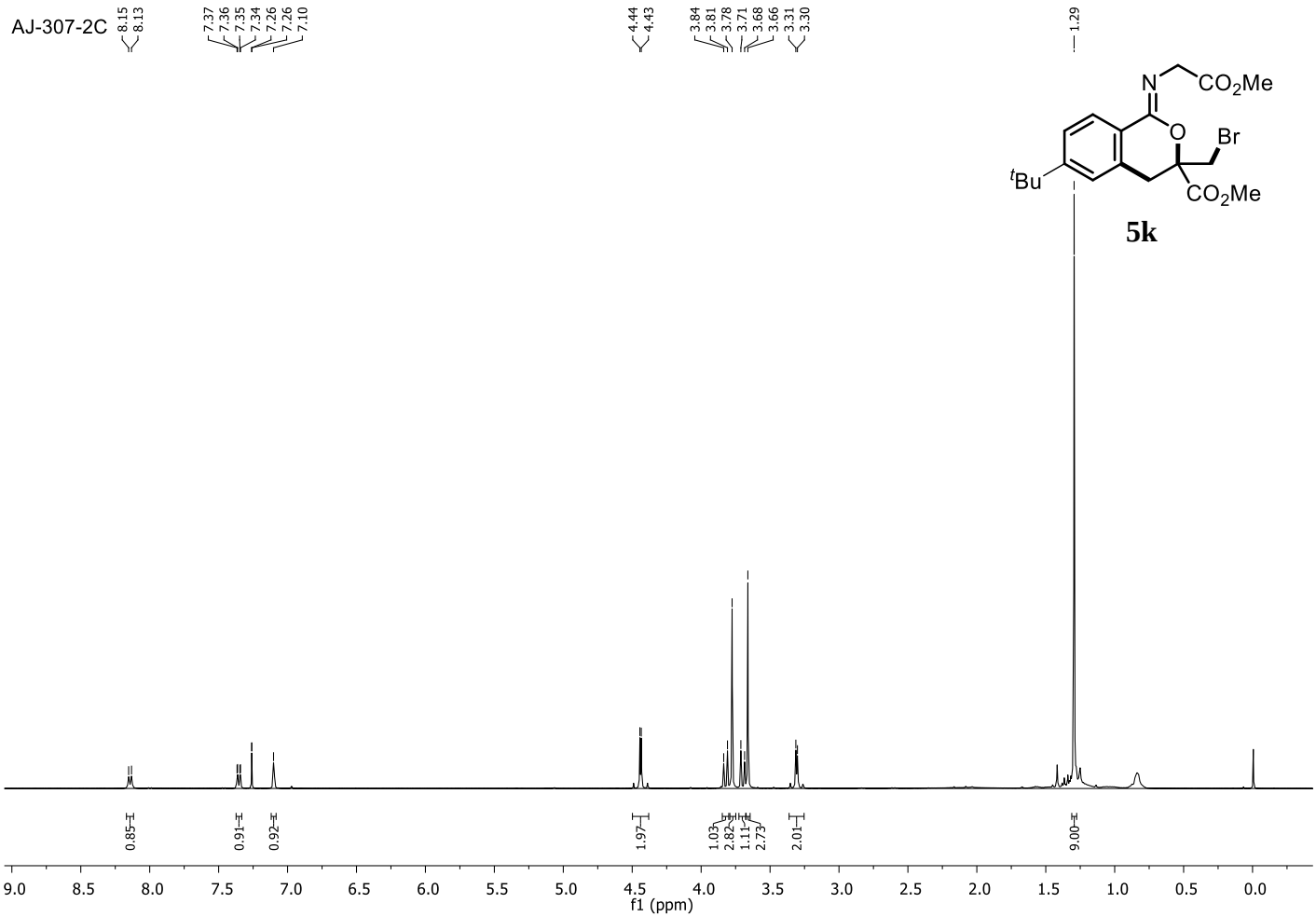
5j



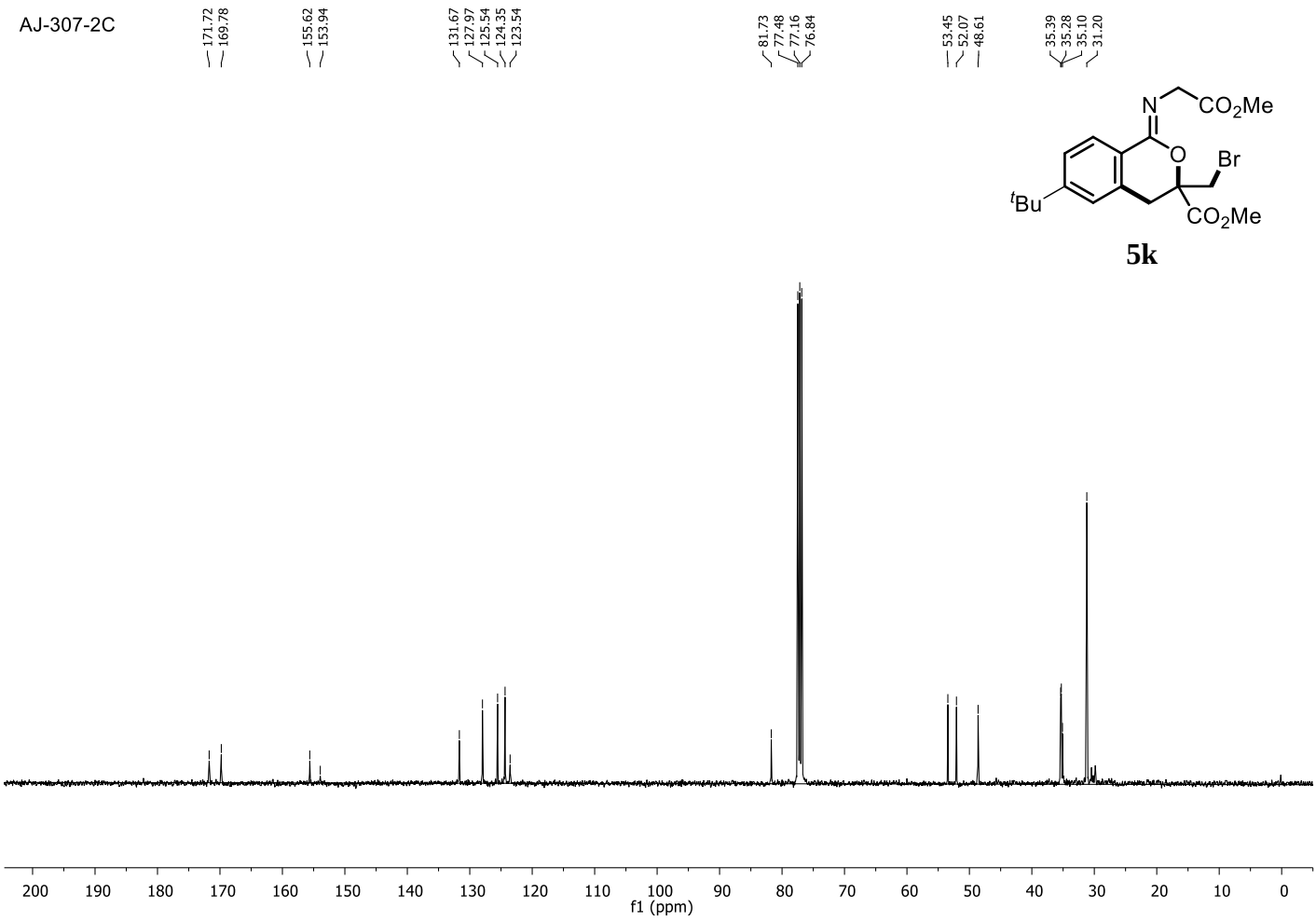
AJ-645-2B



5j

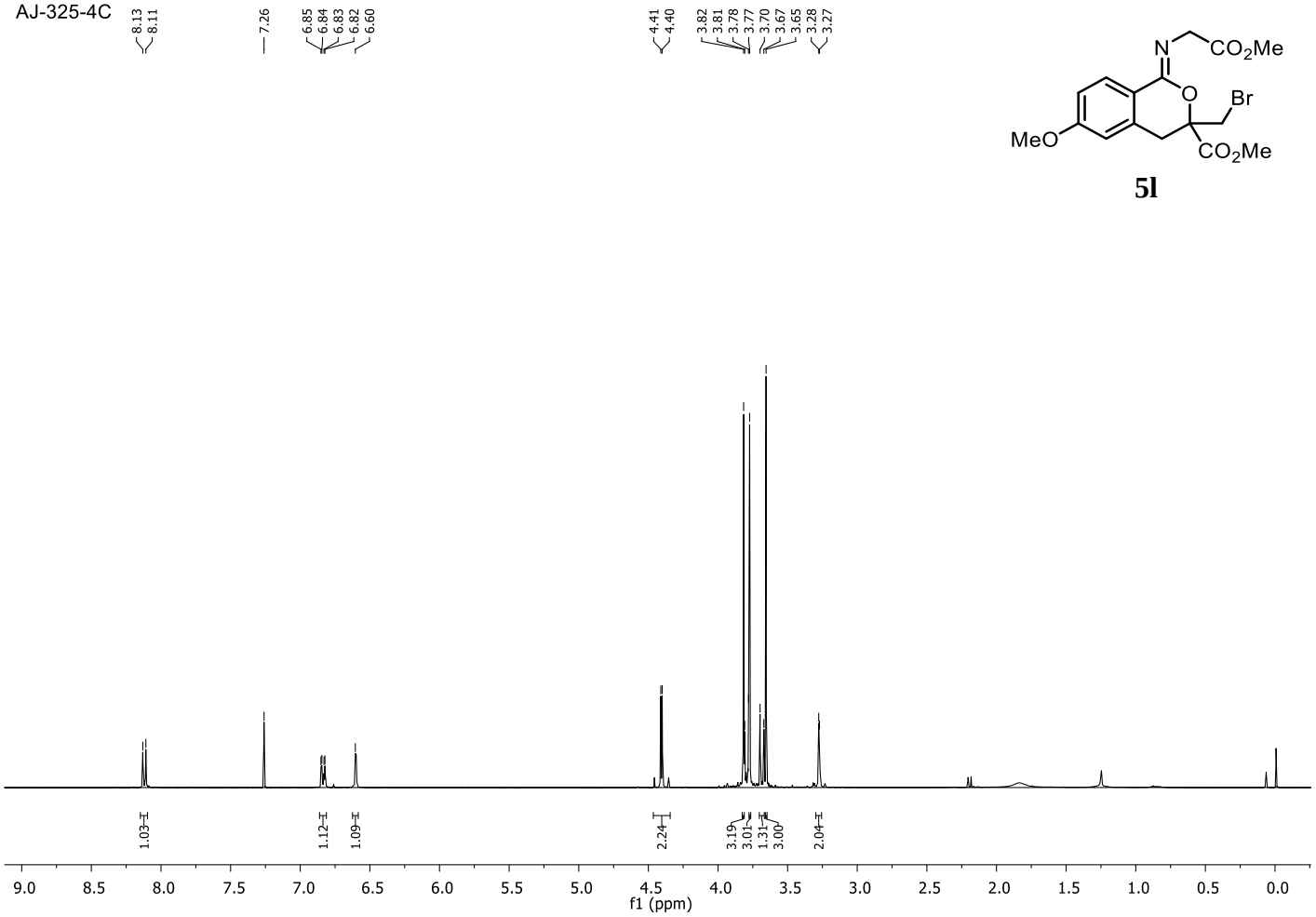

AJ-307-2C
8.15
8.13
7.37
7.36
7.35
7.34
7.26
7.26
7.10
4.44
4.43
3.84
3.81
3.78
3.71
3.68
3.66
3.31
3.30
1.29
N
CO2Me
O
Br
tBu
CO2Me
0.85
0.91
0.92
1.97
1.03
2.82
1.11
2.73
2.01
9.00
f1 (ppm)

5k


AJ-307-2C
171.72
169.78
155.62
153.94
131.67
127.97
125.54
124.35
123.54
81.73
77.48
77.16
76.84
53.45
52.07
48.61
35.39
35.28
35.10
31.20
N
CO2Me
O
Br
tBu
CO2Me
f1 (ppm)

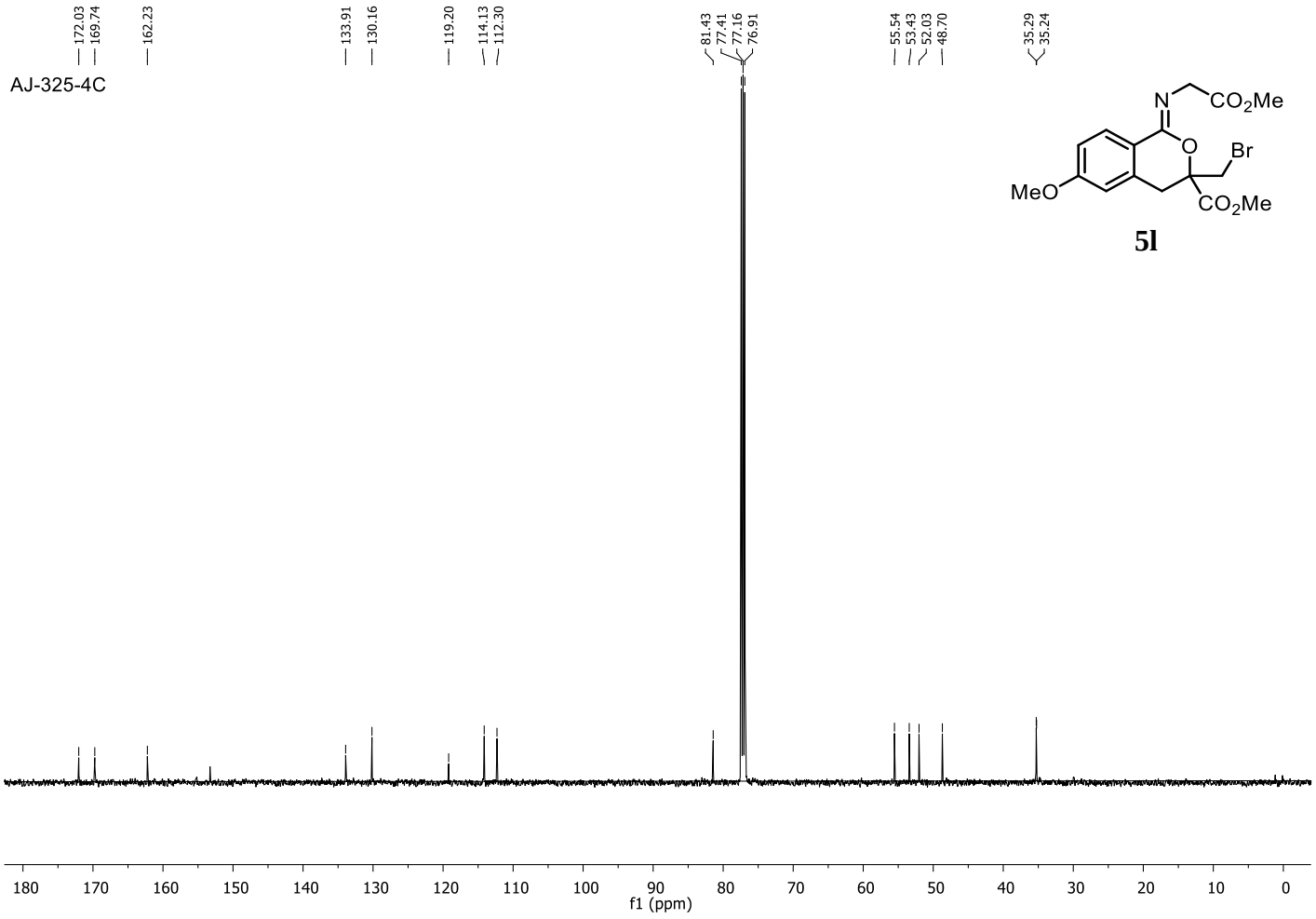
5k

AJ-325-4C



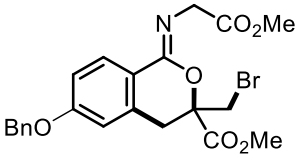
5l

AJ-325-4C

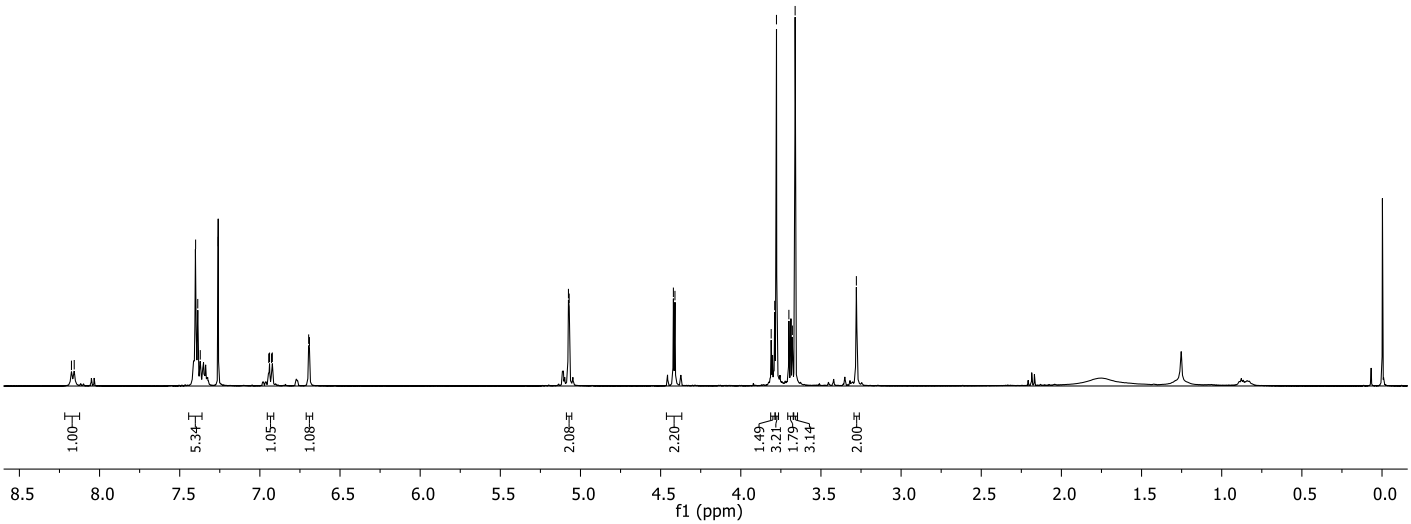


5l

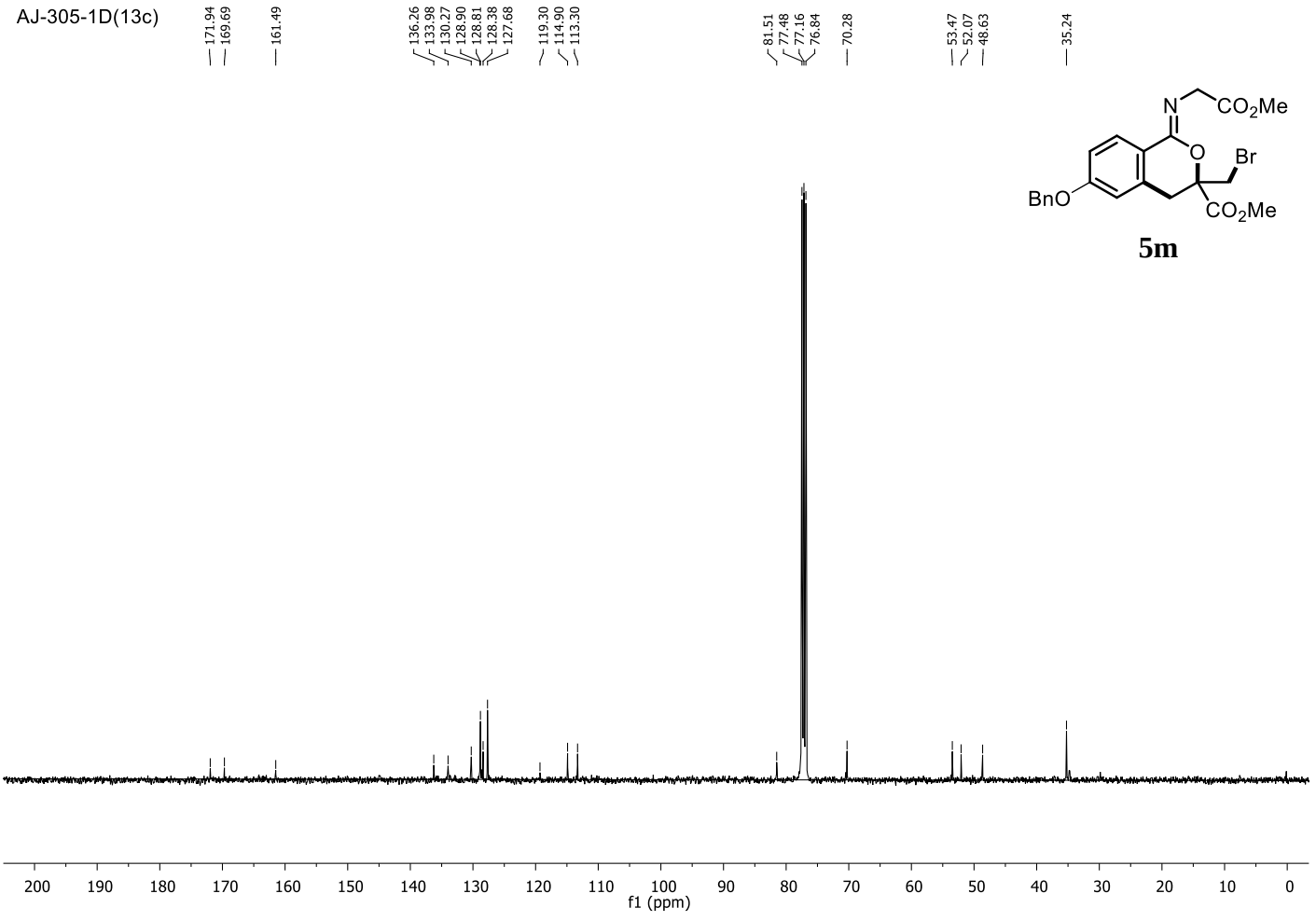
AJ-305-1D



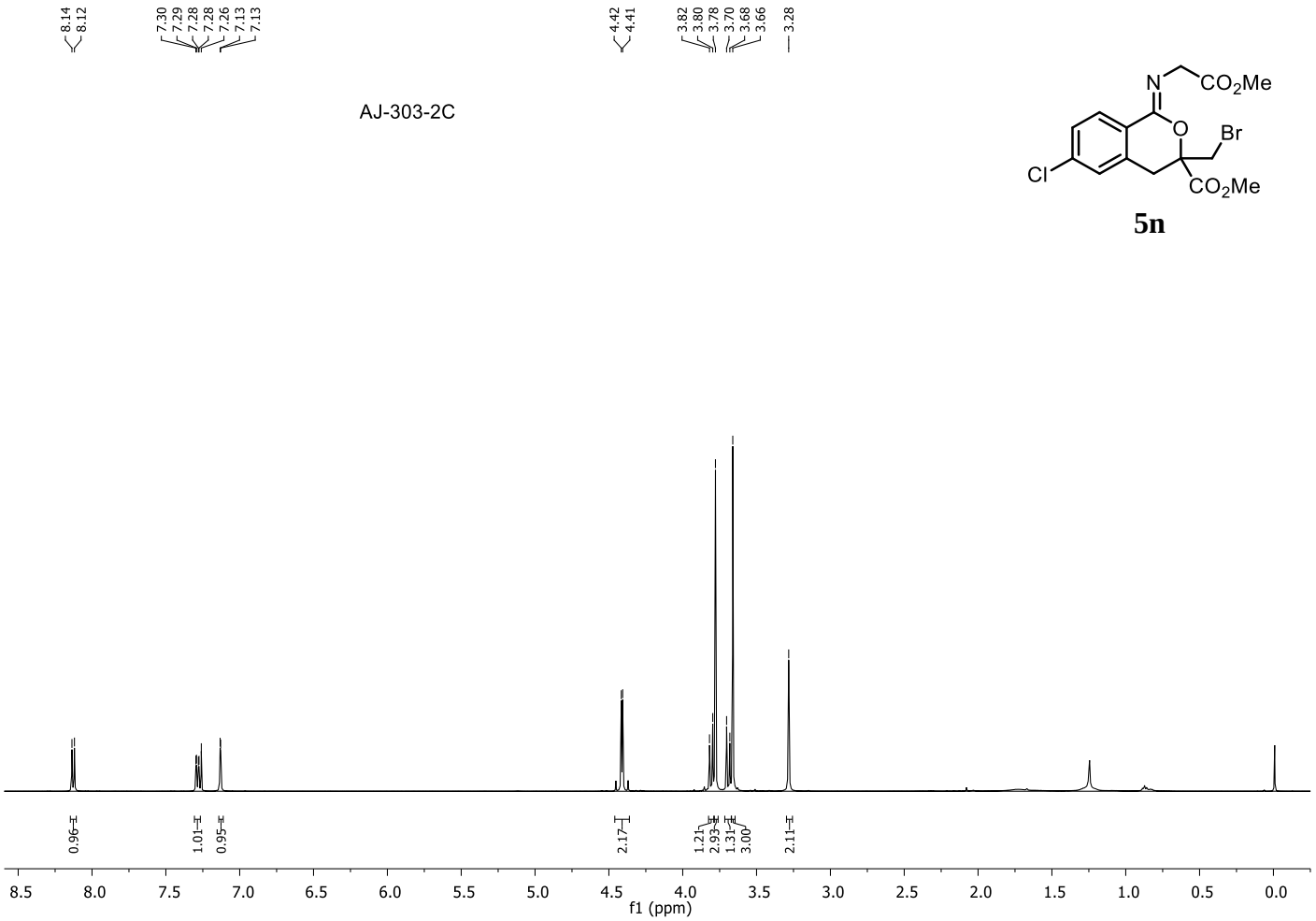
5m



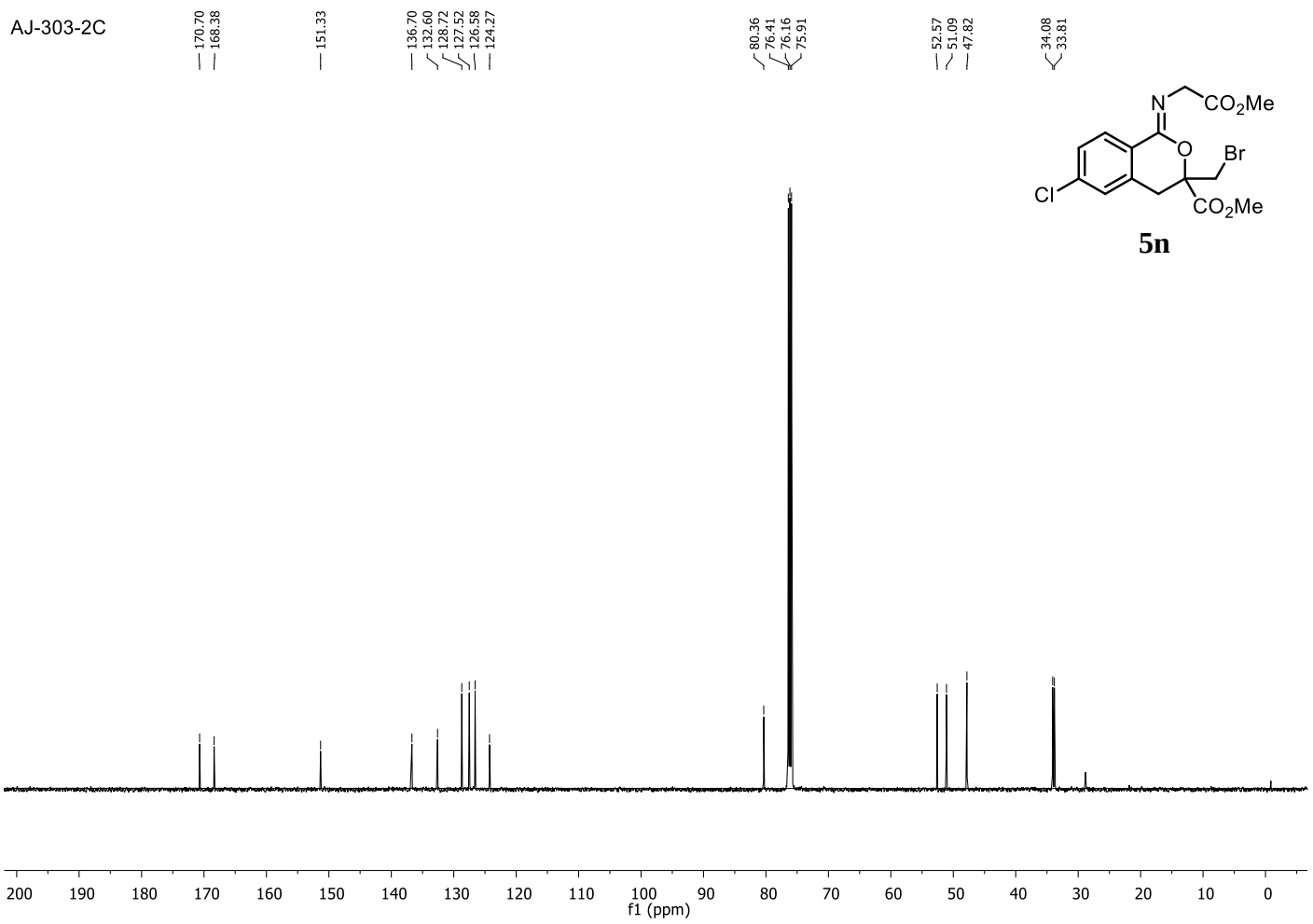
AJ-305-1D(13c)



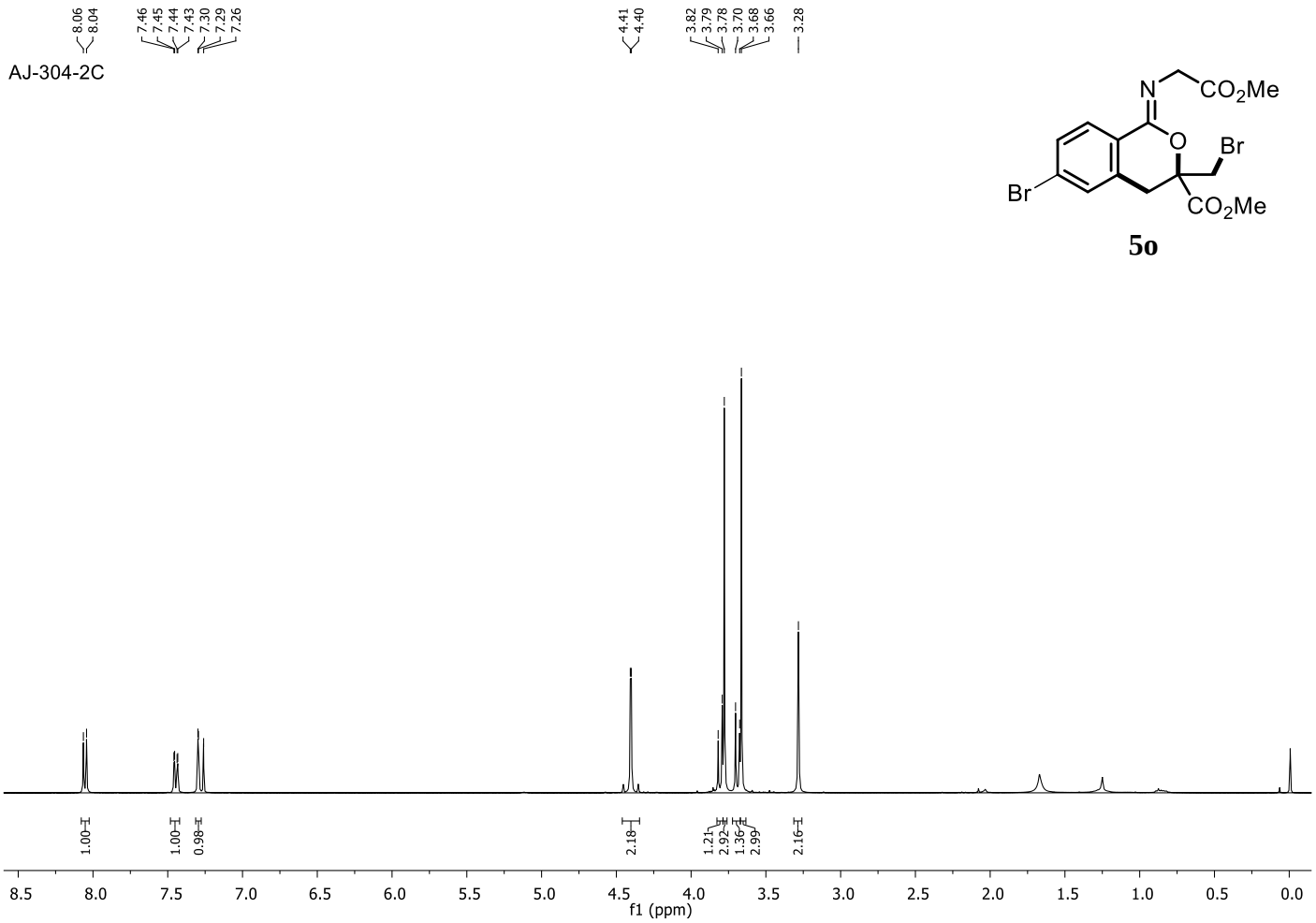
5m


8.14
8.12
7.30
7.29
7.28
7.28
7.26
7.13
7.13
4.42
4.41
3.82
3.80
3.78
3.70
3.68
3.66
3.28
AJ-303-2C
N
CO2Me
O
Br
Cl
CO2Me
0.96
1.01
0.95
2.17
1.21
2.93
1.31
3.00
2.11
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

5n

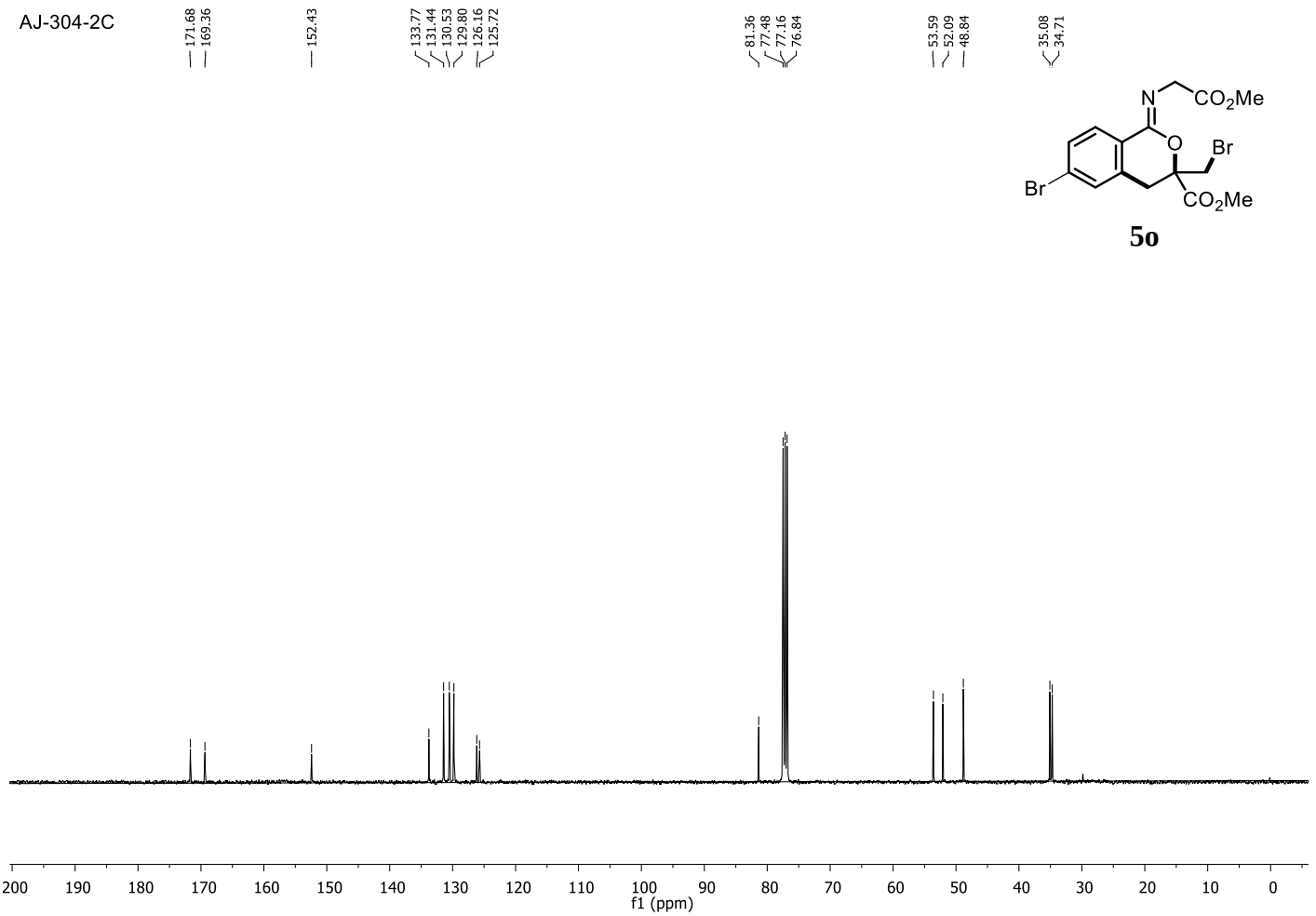

AJ-303-2C
170.70
168.38
151.33
136.70
132.60
128.72
127.52
126.58
124.27
80.36
76.41
76.16
75.91
52.57
51.09
47.82
34.08
33.81
N
CO2Me
O
Br
Cl
CO2Me
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

5n


AJ-304-2C
8.06
8.04
7.46
7.45
7.44
7.43
7.30
7.29
7.26
4.41
4.40
3.82
3.79
3.78
3.70
3.68
3.66
3.28
1.00
1.00
0.98
2.18
1.21
2.92
1.36
2.99
2.16
f1 (ppm)

N
CO2Me
O
Br
Br
CO2Me

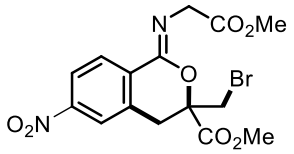
5o


AJ-304-2C
171.68
169.36
152.43
133.77
131.44
130.53
129.80
126.16
125.72
81.36
77.48
77.16
76.84
53.59
52.09
48.84
35.08
34.71
f1 (ppm)

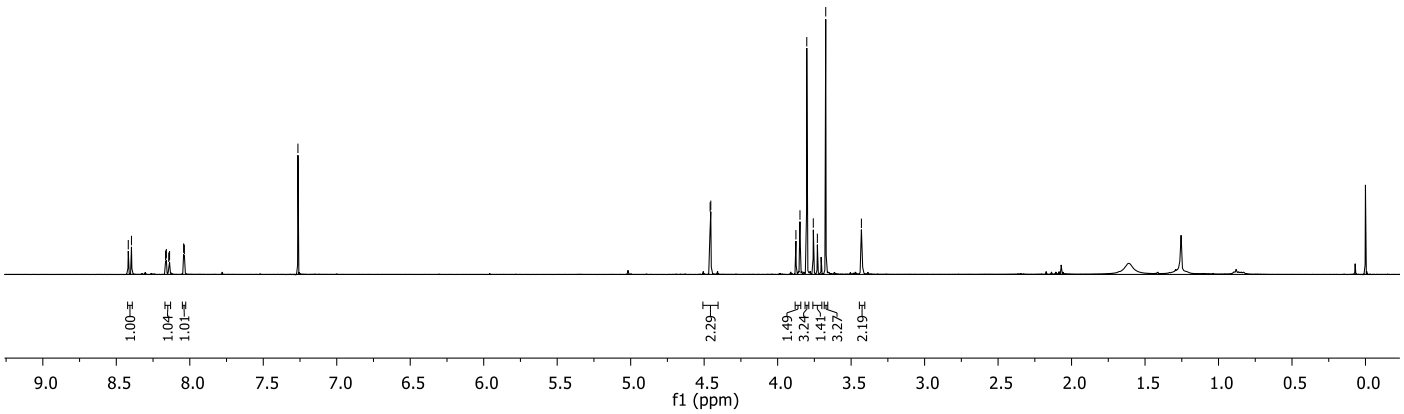
N
CO2Me
O
Br
Br
CO2Me

5o

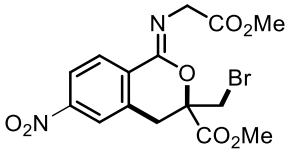
AJ-295-3B(2)



5p

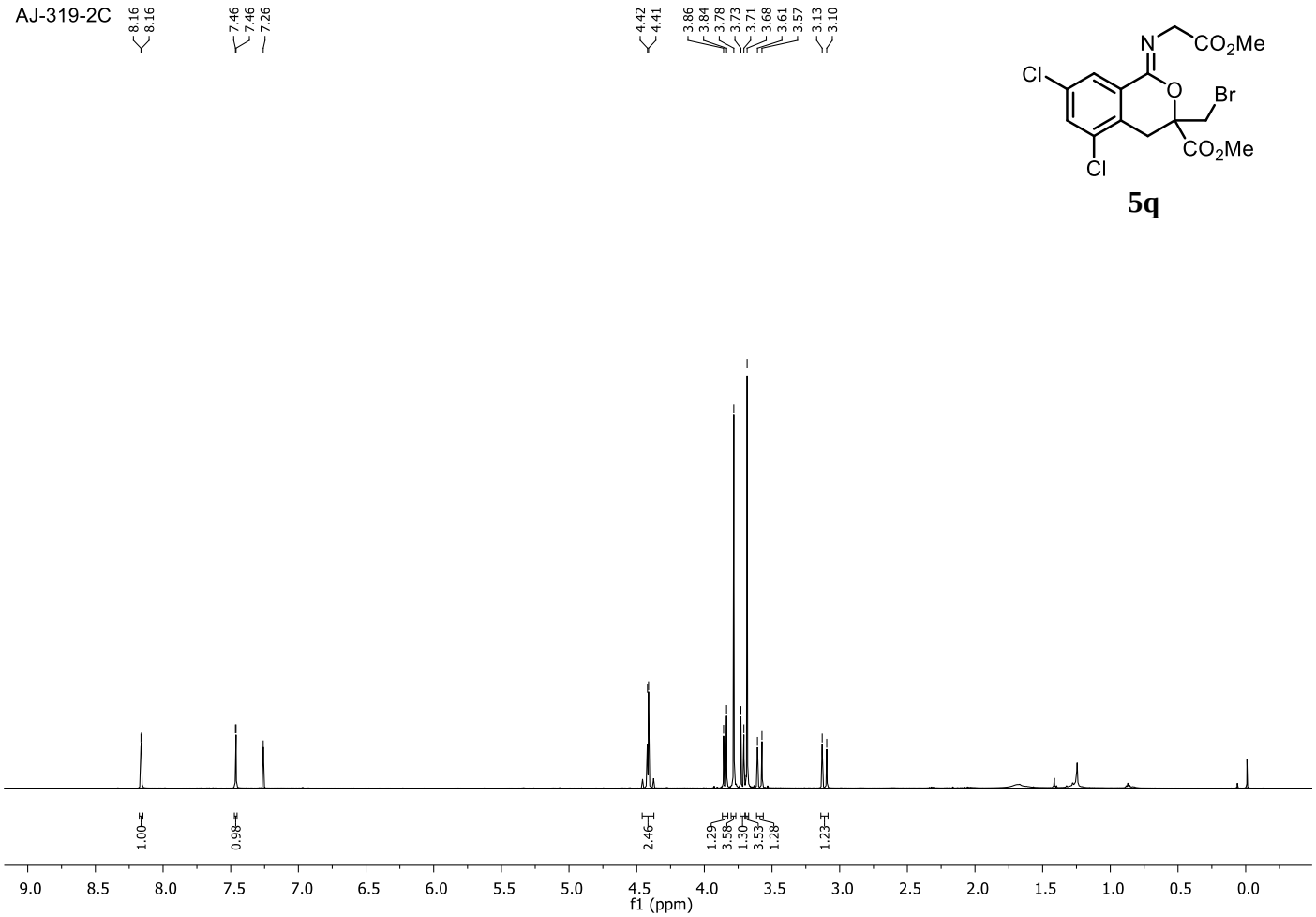


AJ-295-3B



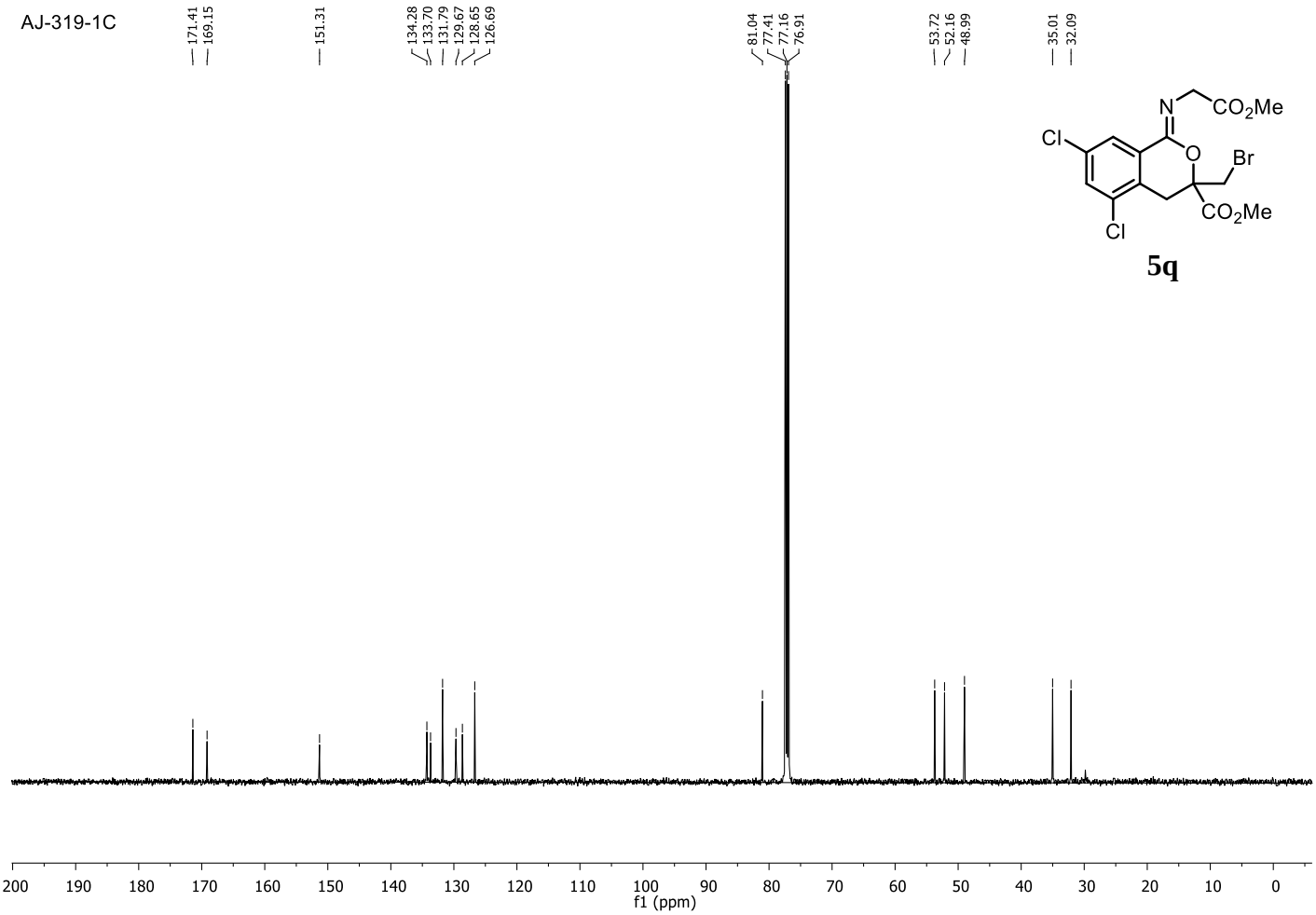
5p

AJ-319-2C

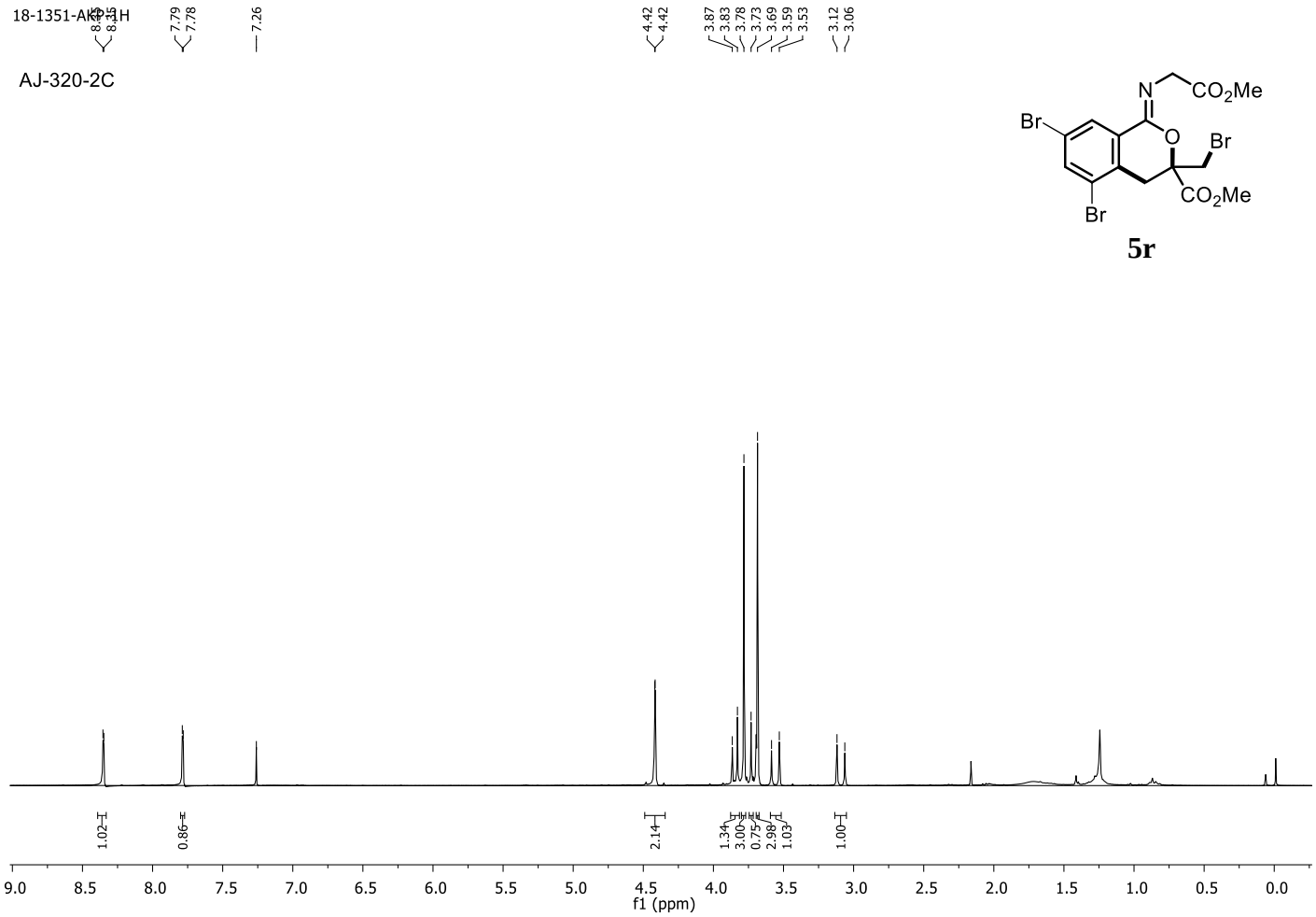


5q

AJ-319-1C

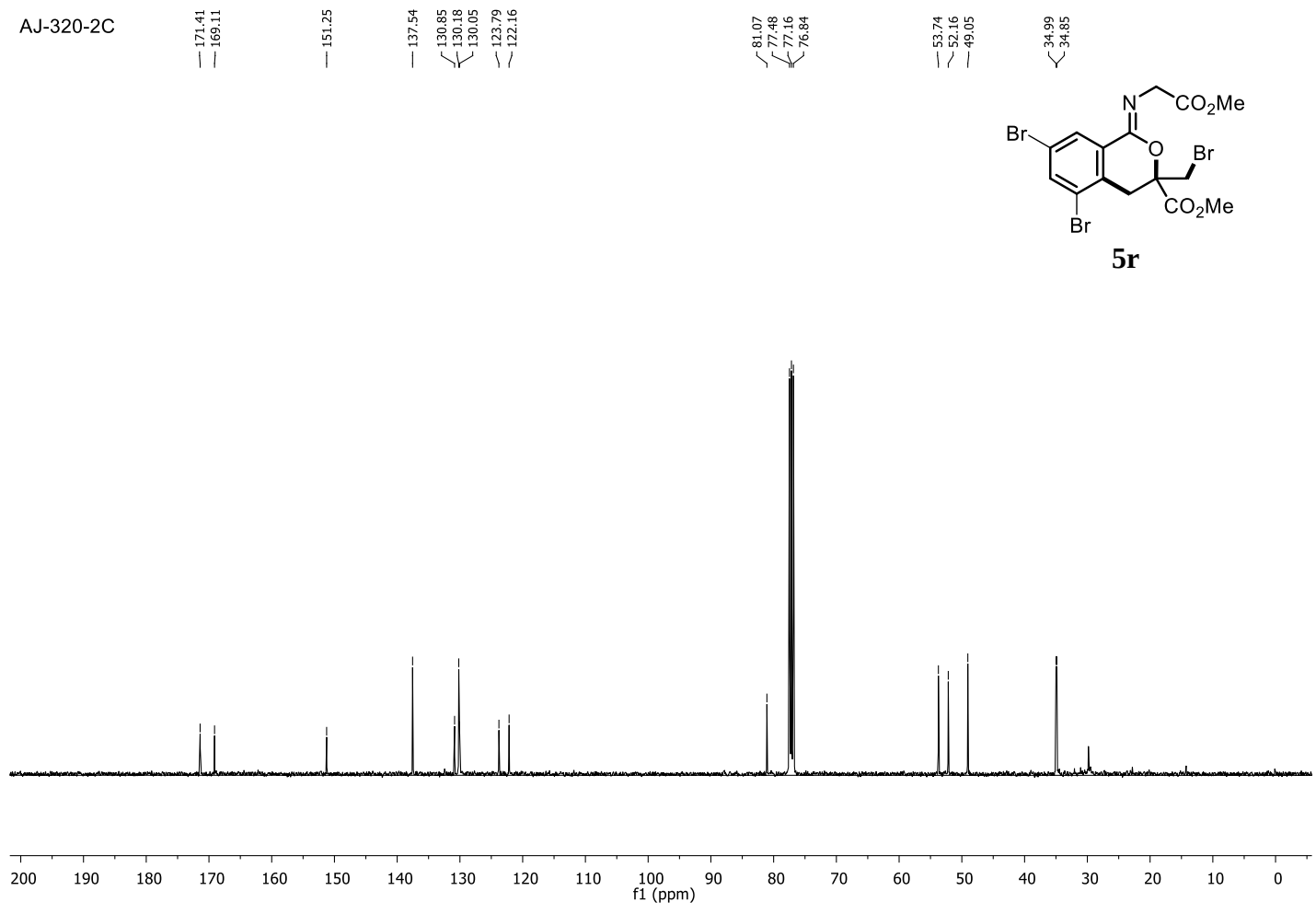


5q


18-1351-AKS 1H
AJ-320-2C
8.33
8.31
7.79
7.78
7.26
4.42
4.42
3.87
3.83
3.78
3.73
3.69
3.59
3.53
3.12
3.06
1.02
0.86
2.14
1.34
3.00
0.75
2.98
1.03
1.00
f1 (ppm)

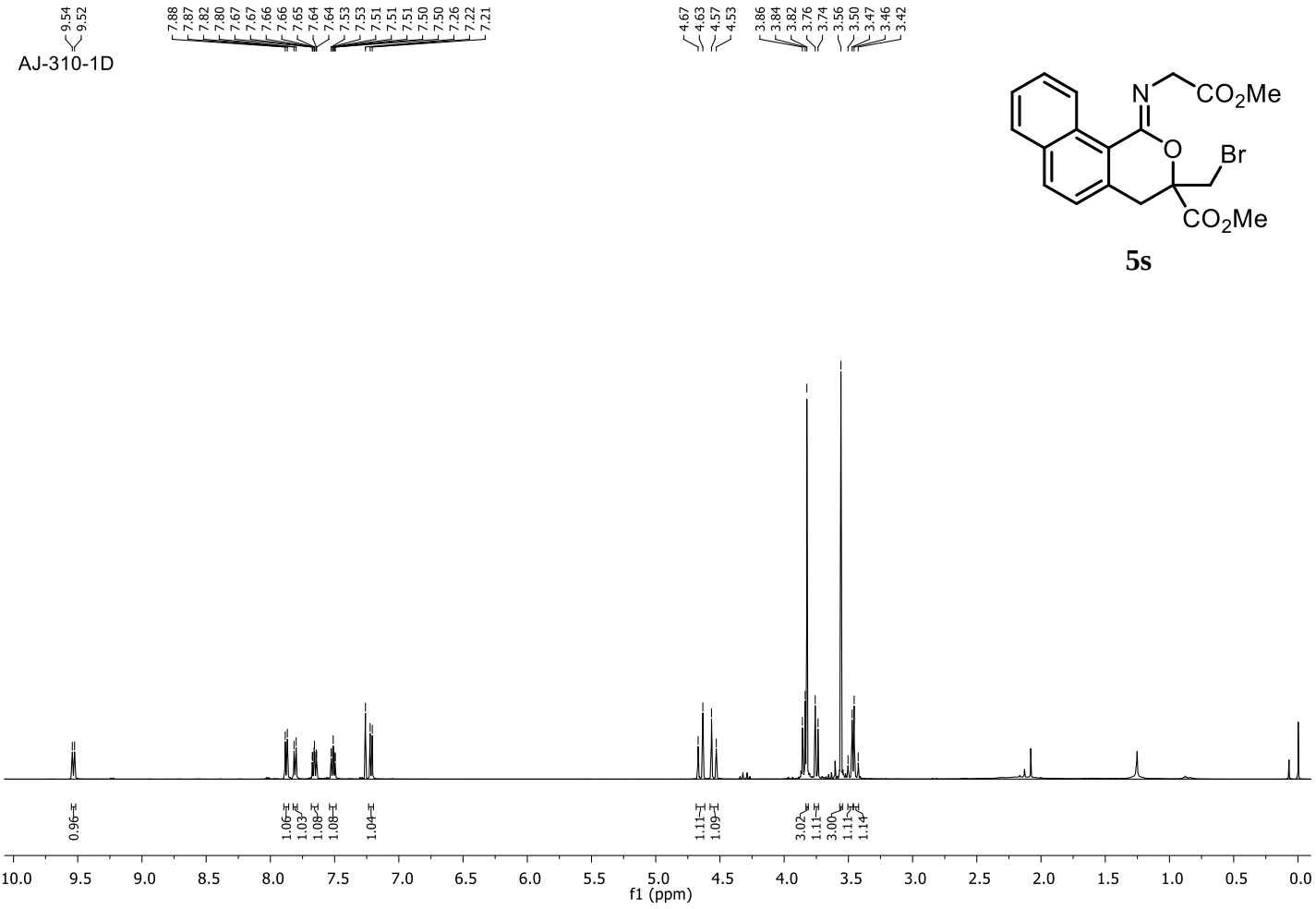
N
CO2Me
Br
O
Br
CO2Me
Br

5r

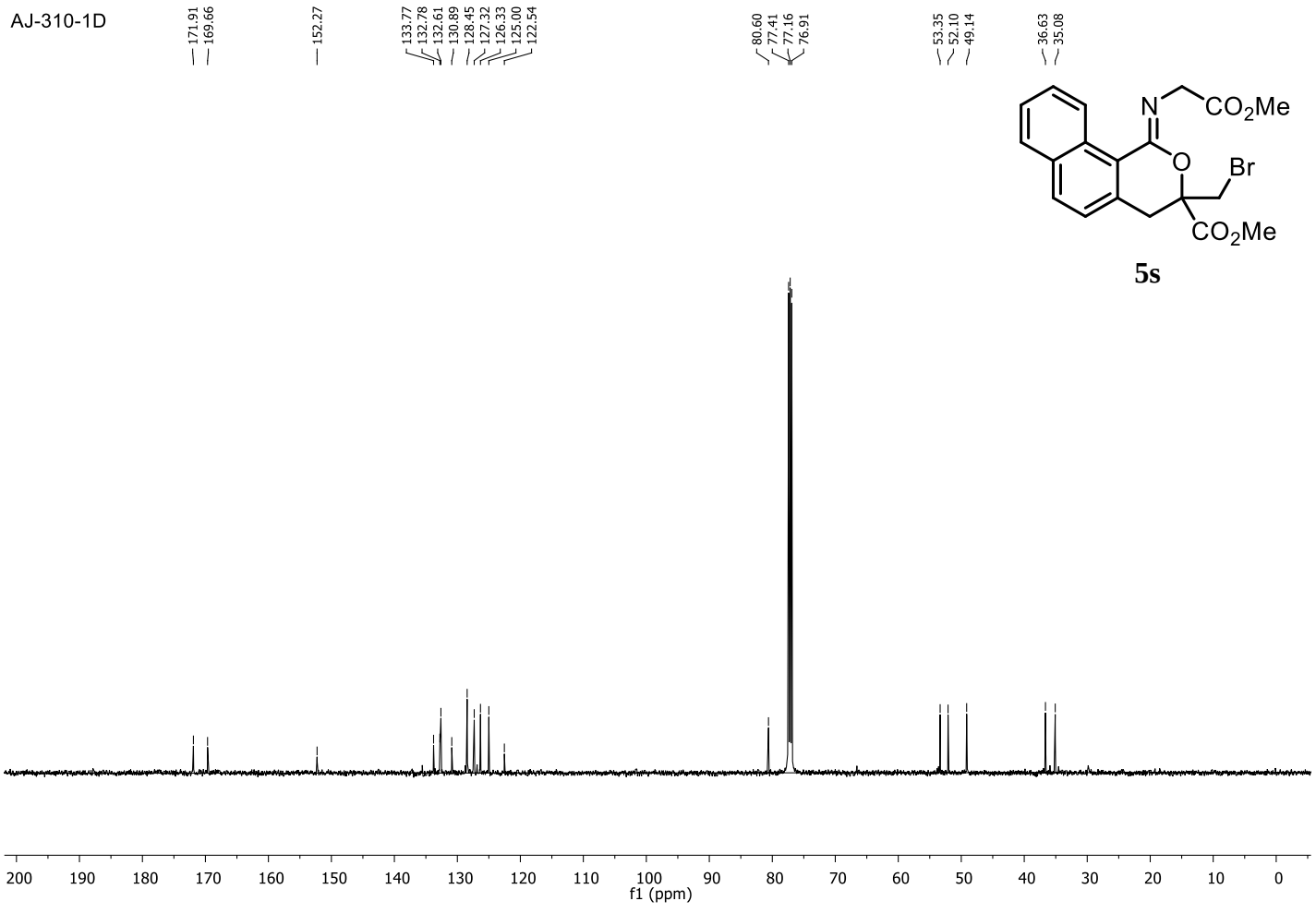

AJ-320-2C
171.41
169.11
151.25
137.54
130.85
130.18
130.05
123.79
122.16
81.07
77.48
77.16
76.84
53.74
52.16
49.05
34.99
34.85
f1 (ppm)

N
CO2Me
Br
O
Br
CO2Me
Br

5r

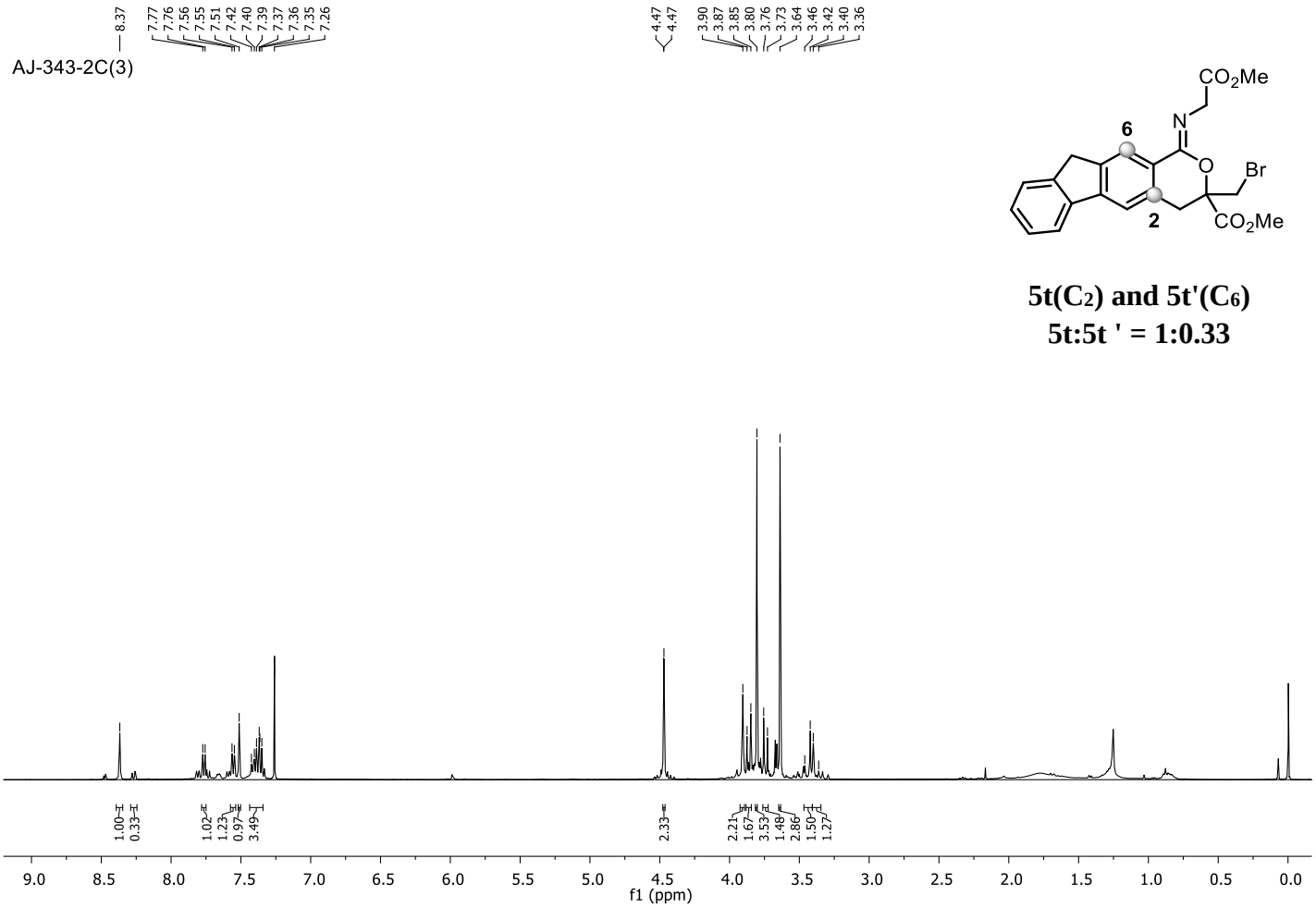

AJ-310-1D
9.54
9.52
7.88
7.87
7.82
7.80
7.67
7.67
7.66
7.66
7.65
7.64
7.64
7.53
7.53
7.51
7.51
7.51
7.50
7.50
7.26
7.22
7.21
4.67
4.63
4.57
4.53
3.86
3.84
3.82
3.76
3.74
3.56
3.50
3.47
3.46
3.42
N
CO2Me
O
Br
CO2Me
0.96
1.06
1.03
1.08
1.08
1.04
1.11
1.09
3.02
1.11
3.00
1.11
1.14
f1 (ppm)

5s


AJ-310-1D
171.91
169.66
152.27
133.77
132.78
132.61
130.89
128.45
127.32
126.33
125.00
122.54
80.60
77.41
77.16
76.91
53.35
52.10
49.14
36.63
35.08
N
CO2Me
O
Br
CO2Me
f1 (ppm)

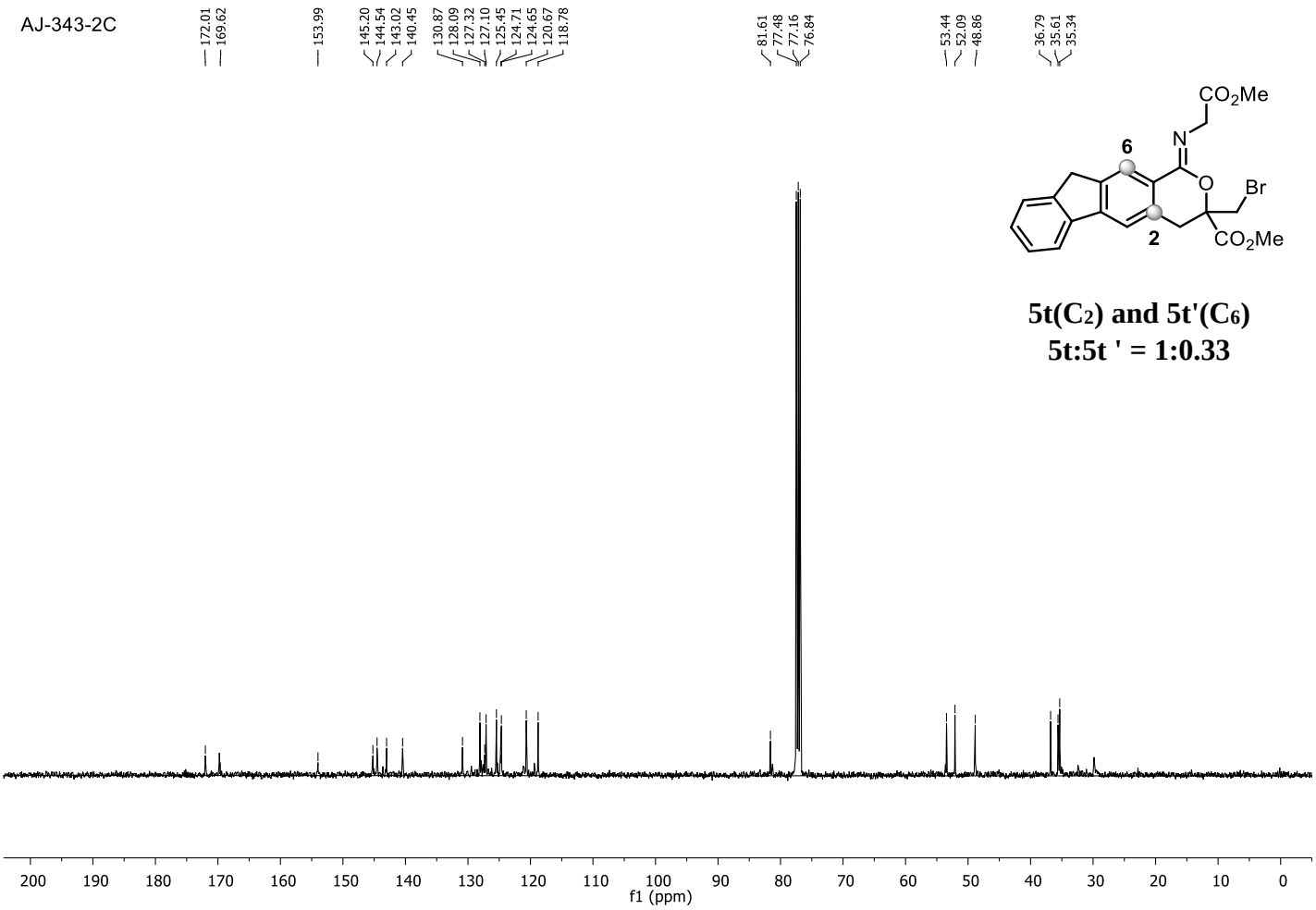
5s

AJ-343-2C(3)



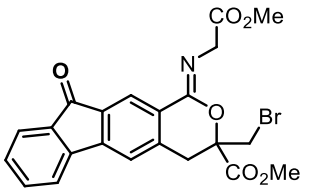
5t(C2) and 5t'(C6)
5t:5t ' = 1:0.33

AJ-343-2C

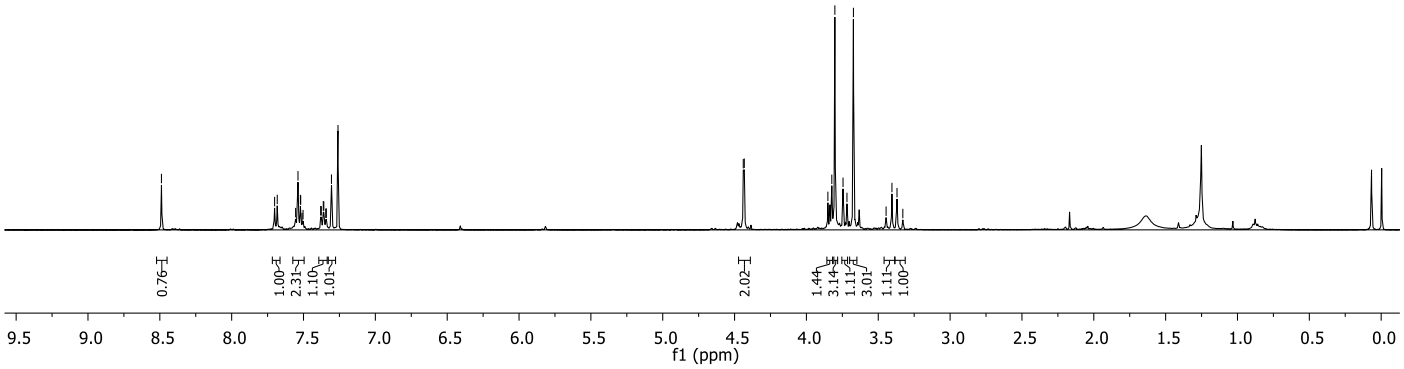


5t(C2) and 5t'(C6)
5t:5t ' = 1:0.33

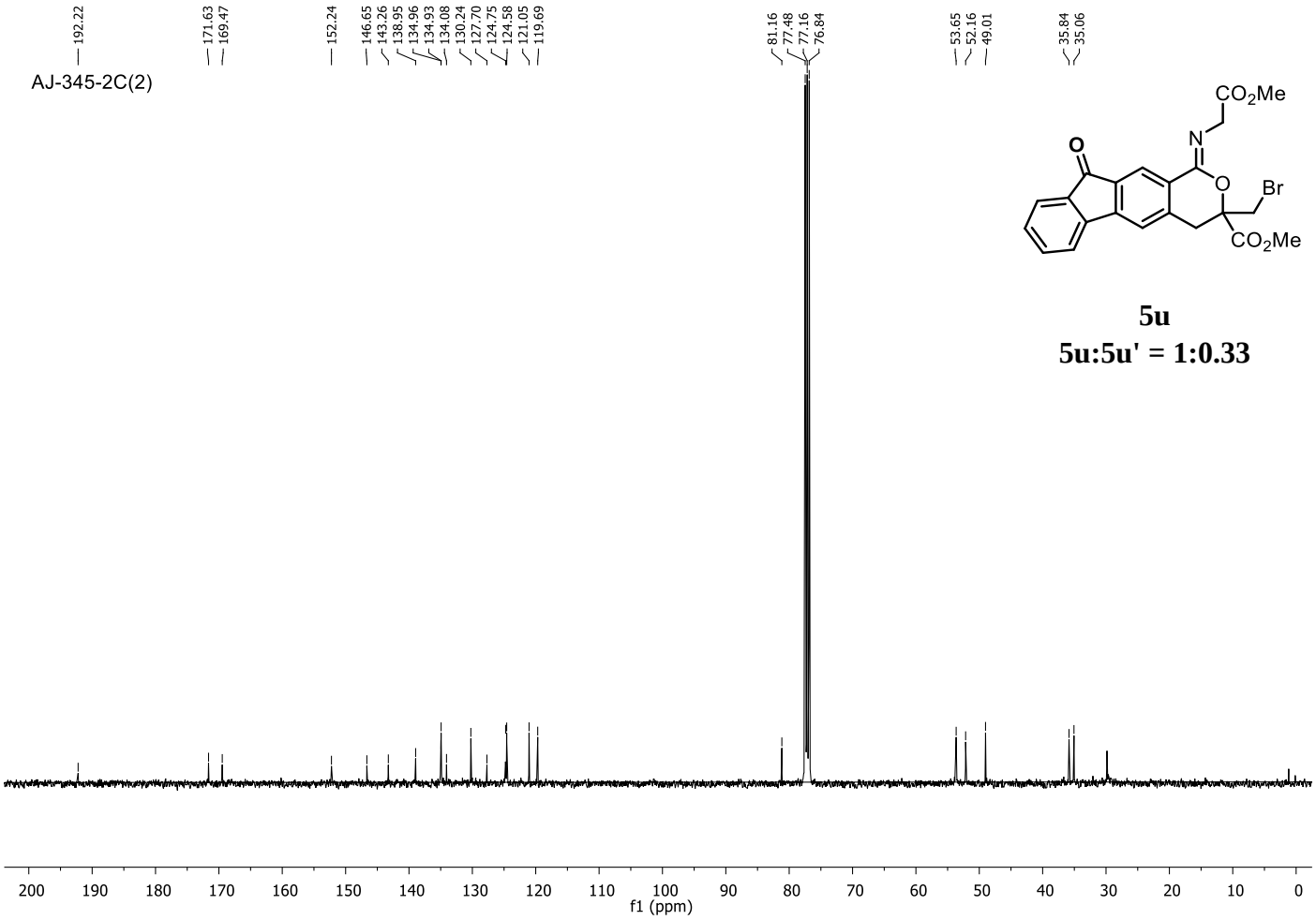
AJ-345-2C



5u
5u:5u' = 1:0.33

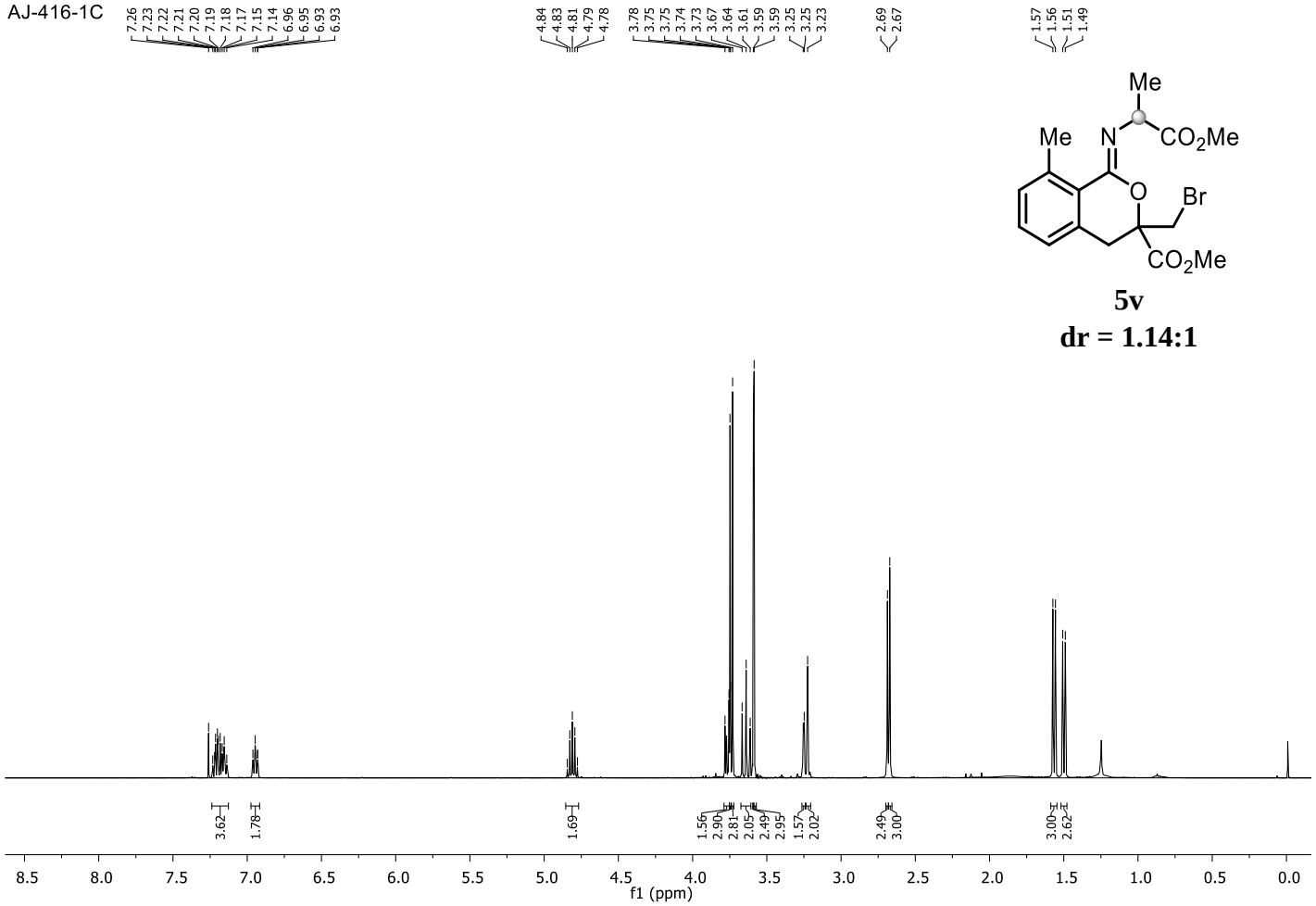


AJ-345-2C(2)



5u
5u:5u' = 1:0.33

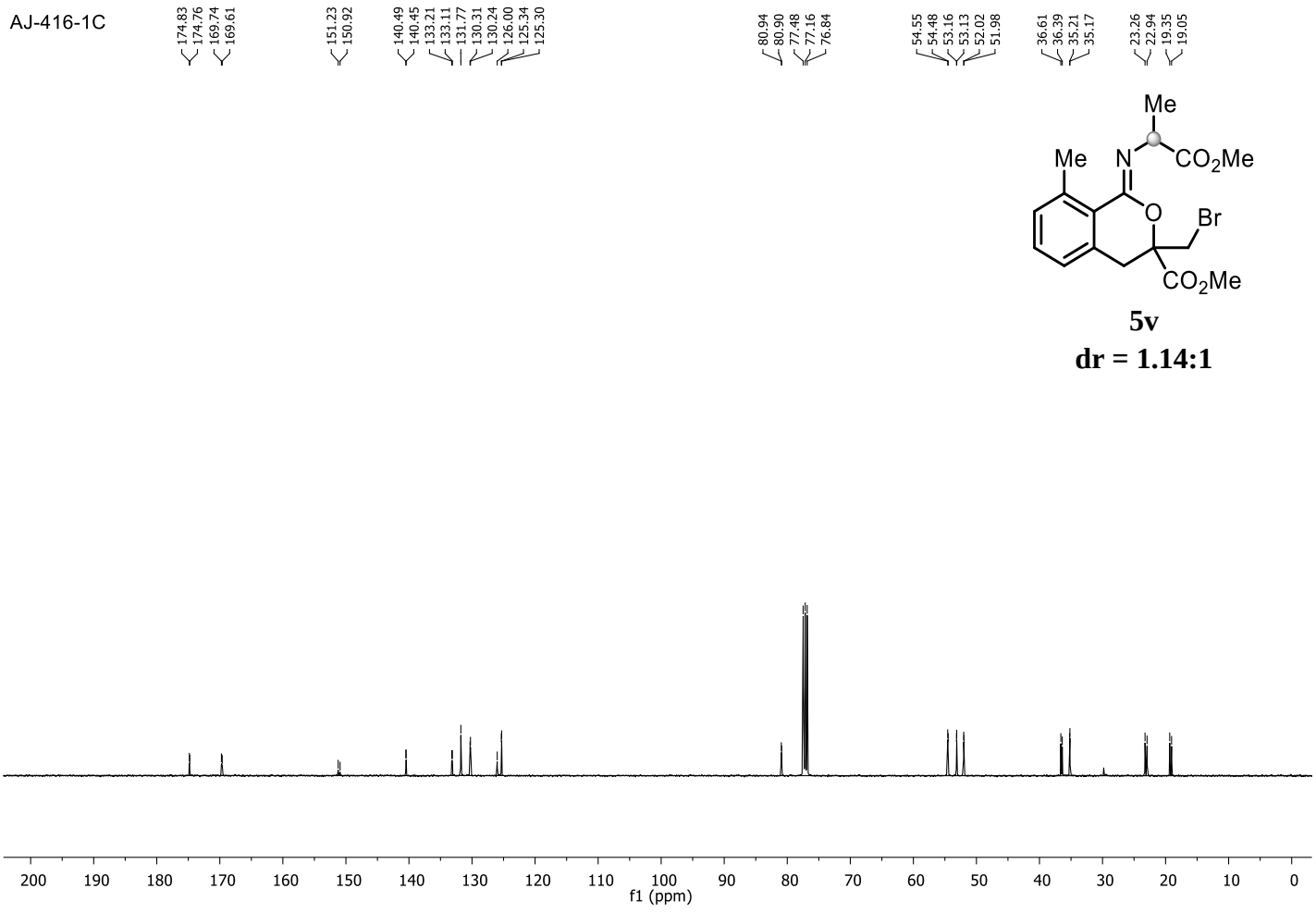
AJ-416-1C



5v

dr = 1.14:1

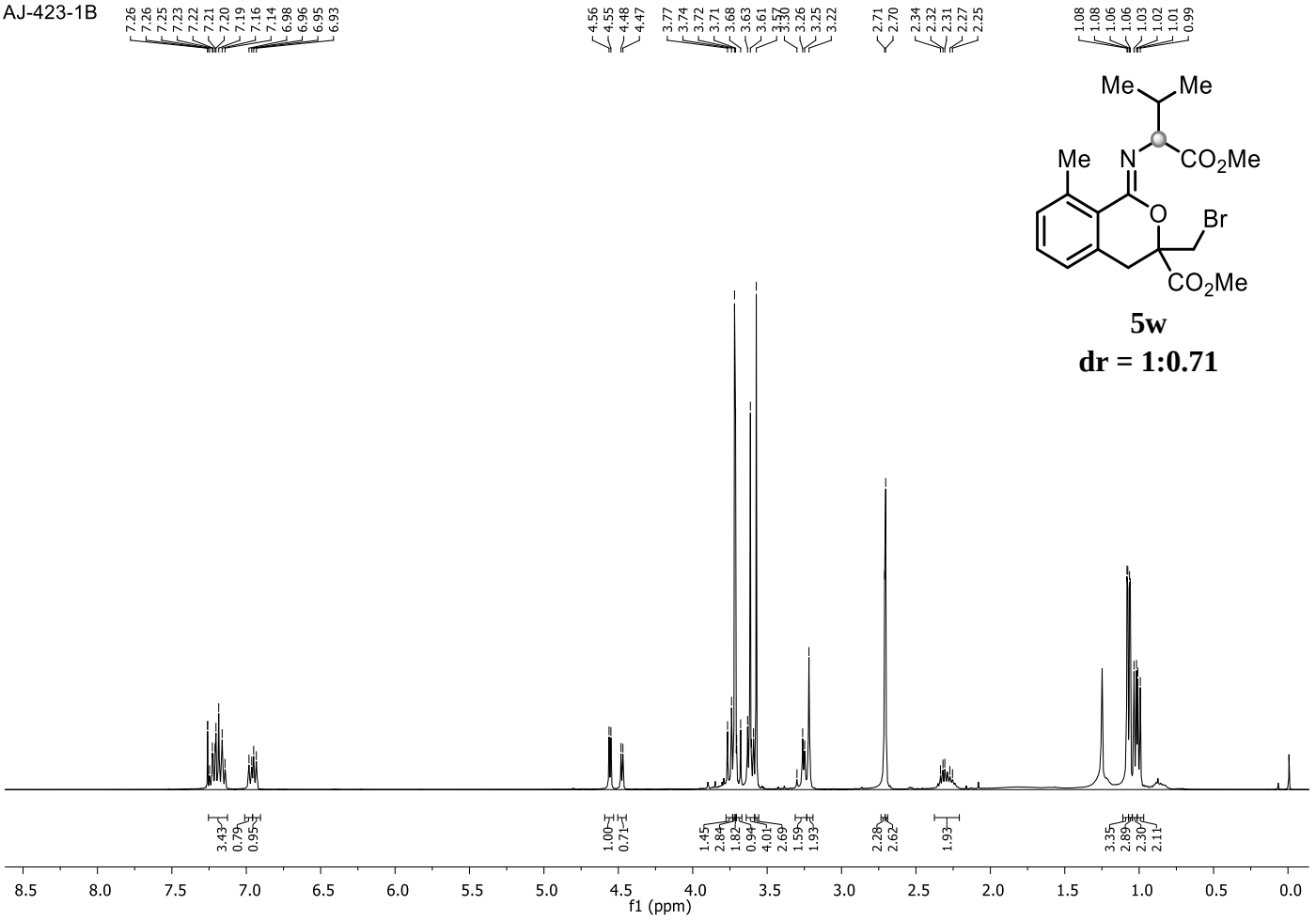
AJ-416-1C



5v

dr = 1.14:1

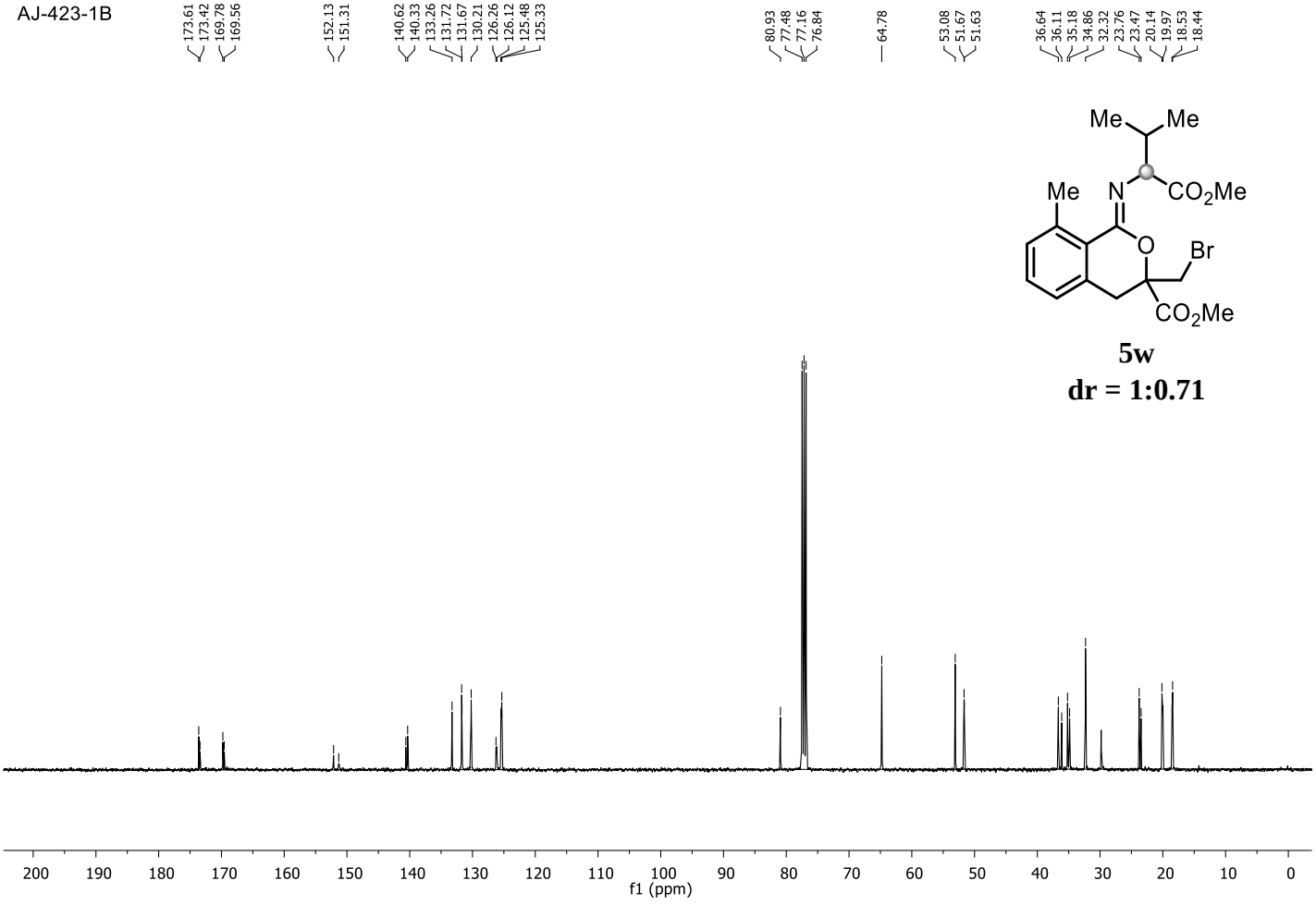
AJ-423-1B



5w

dr = 1:0.71

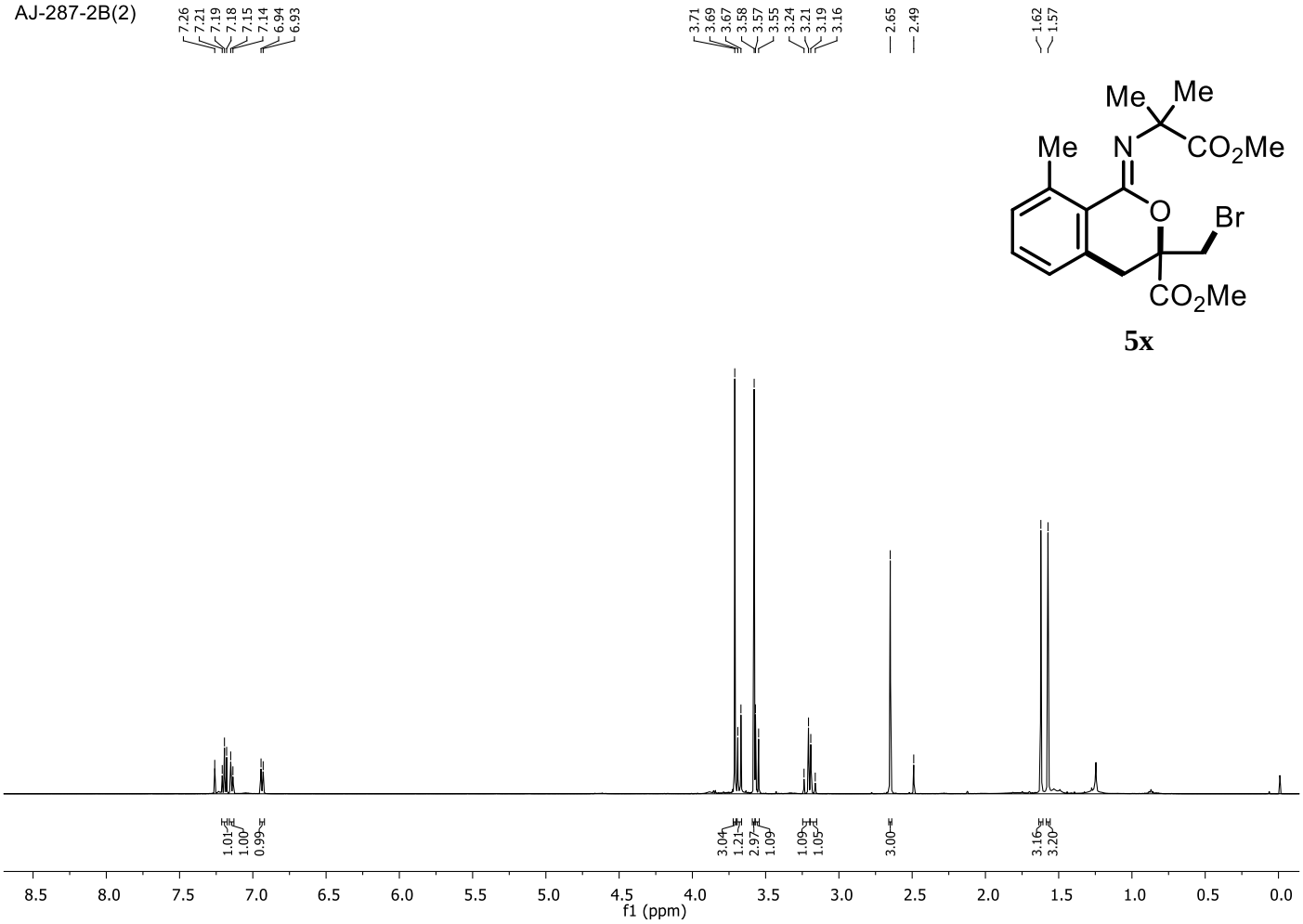
AJ-423-1B



5w

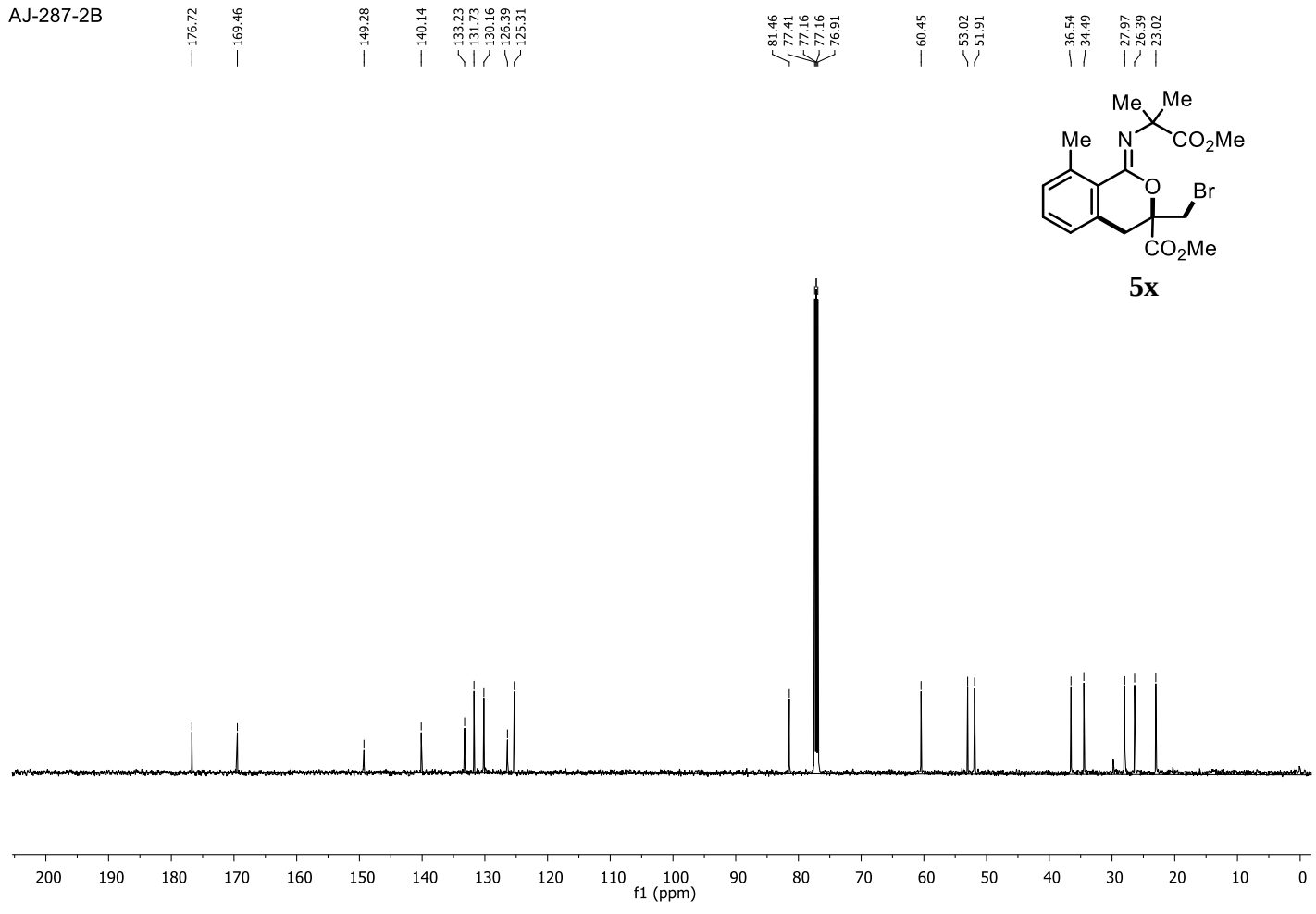
dr = 1:0.71

AJ-287-2B(2)



5x

AJ-287-2B



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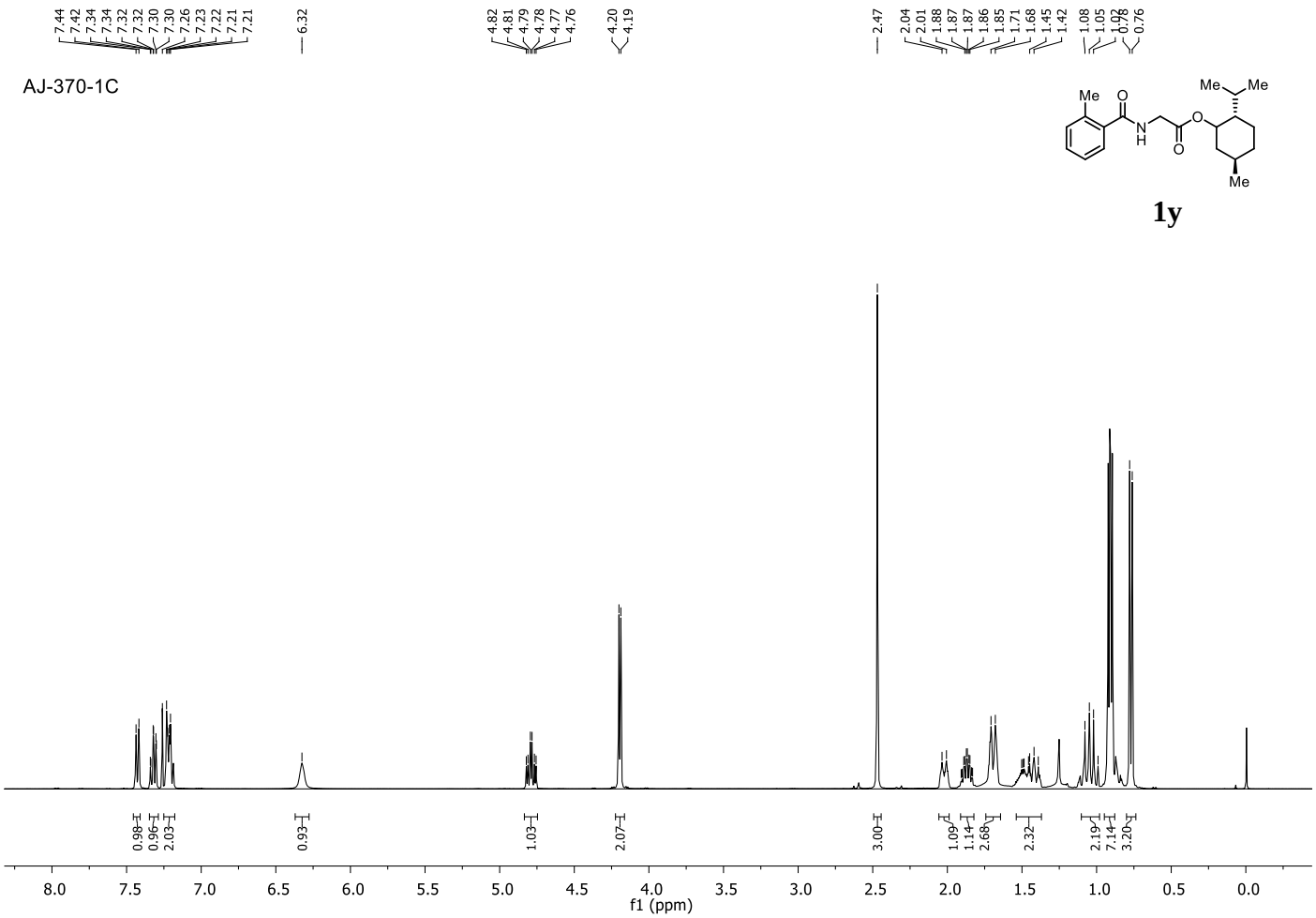
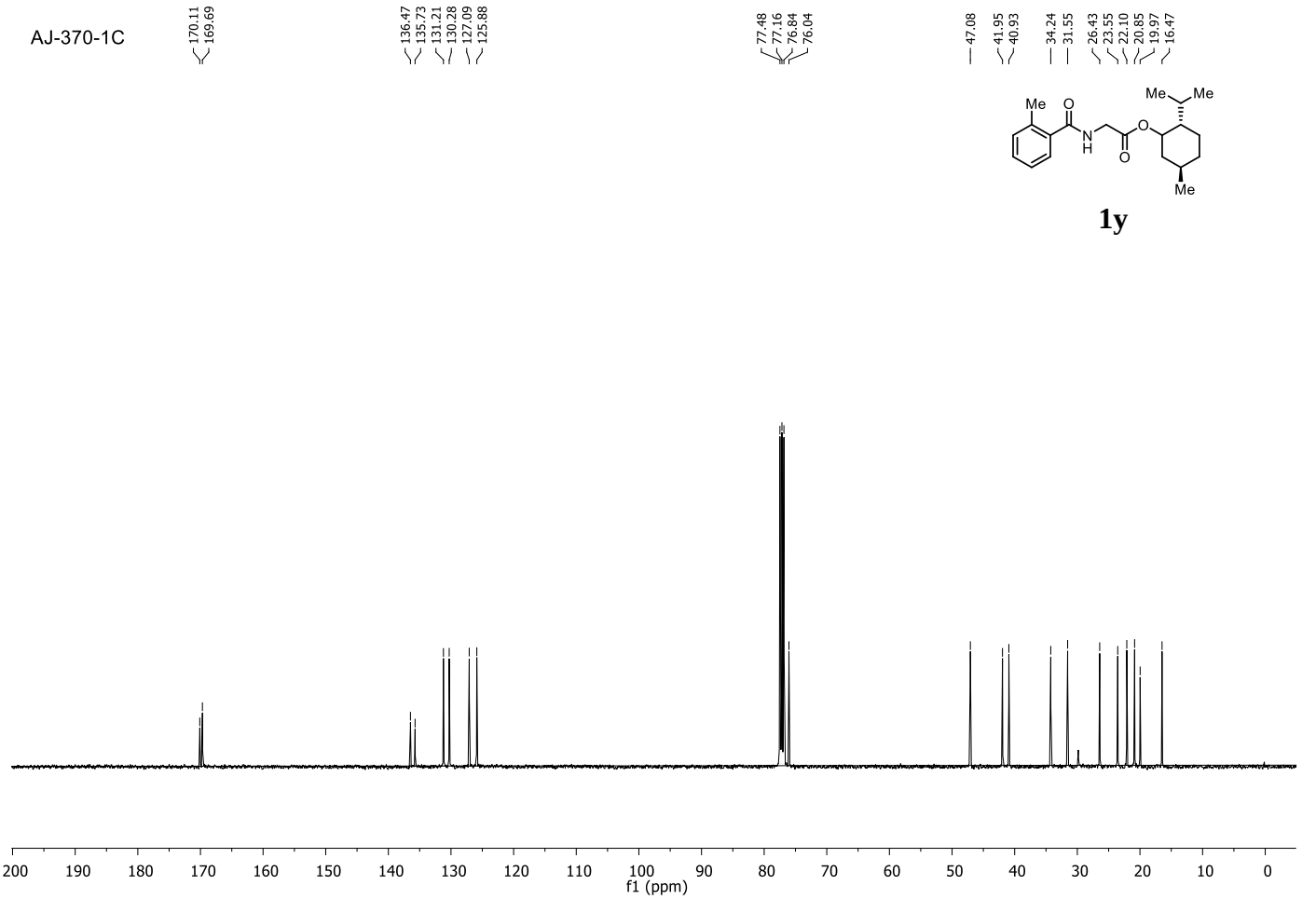

AJ-370-1C
7.44
7.42
7.34
7.34
7.32
7.32
7.30
7.30
7.26
7.23
7.22
7.21
7.21
6.32
4.82
4.81
4.79
4.78
4.77
4.76
4.20
4.19
2.47
2.04
2.01
1.88
1.87
1.87
1.86
1.85
1.71
1.68
1.45
1.42
1.08
1.05
1.02
0.78
0.76
Me
O
N
H
O
O
Me
Me
Me
0.98
0.96
2.03
0.93
1.03
2.07
3.00
1.09
1.14
2.68
2.32
2.19
7.14
3.20
f1 (ppm)

1y


AJ-370-1C
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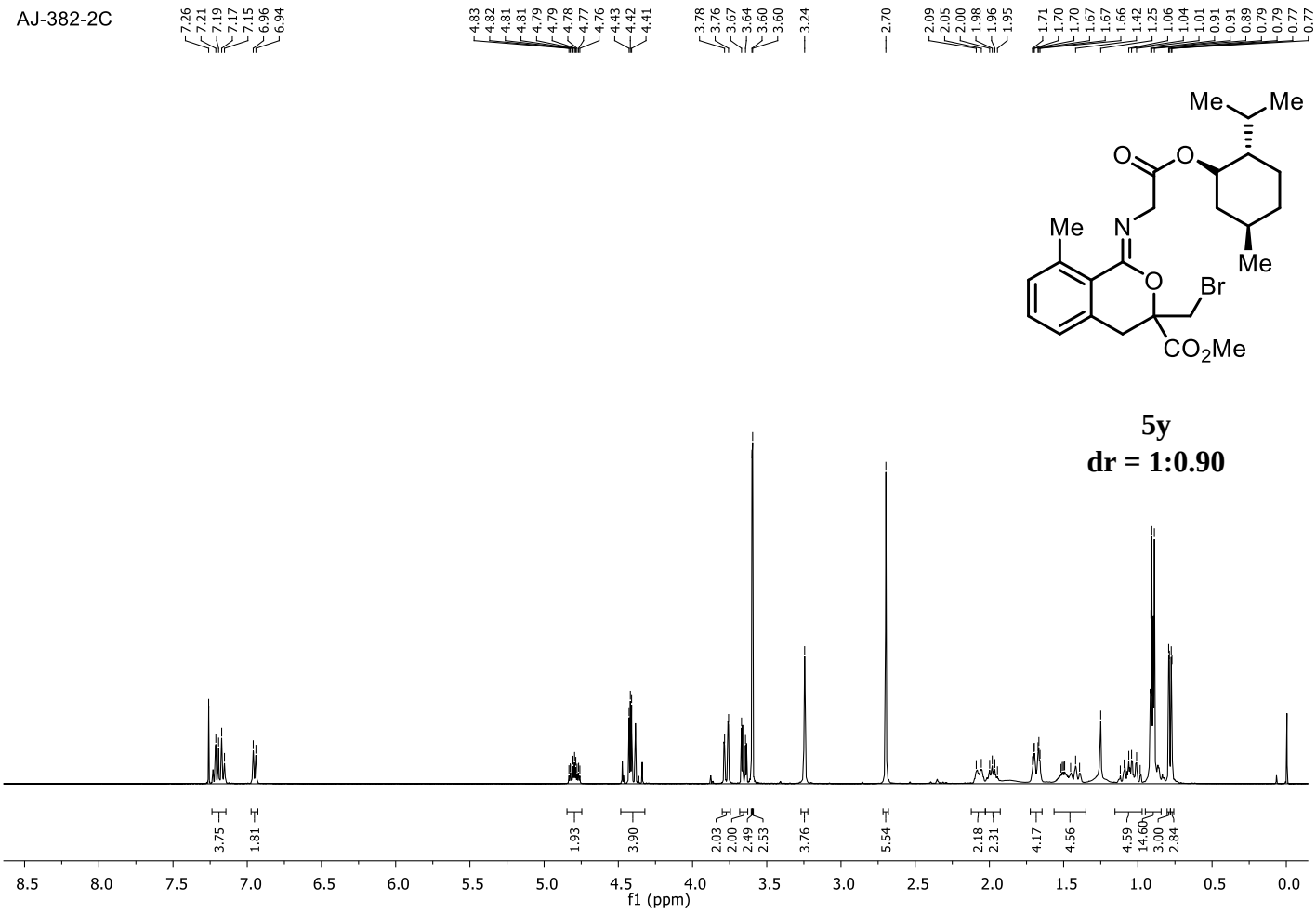
169.69
136.47
135.73
131.21
130.28
127.09
125.88
77.48
77.16
76.84
76.04
47.08
41.95
40.93
34.24
31.55
26.43
23.55
22.10
20.85
19.97
16.47
Me
O
N
H
O
O
Me
Me
Me
f1 (ppm)

1y

AJ-382-2C



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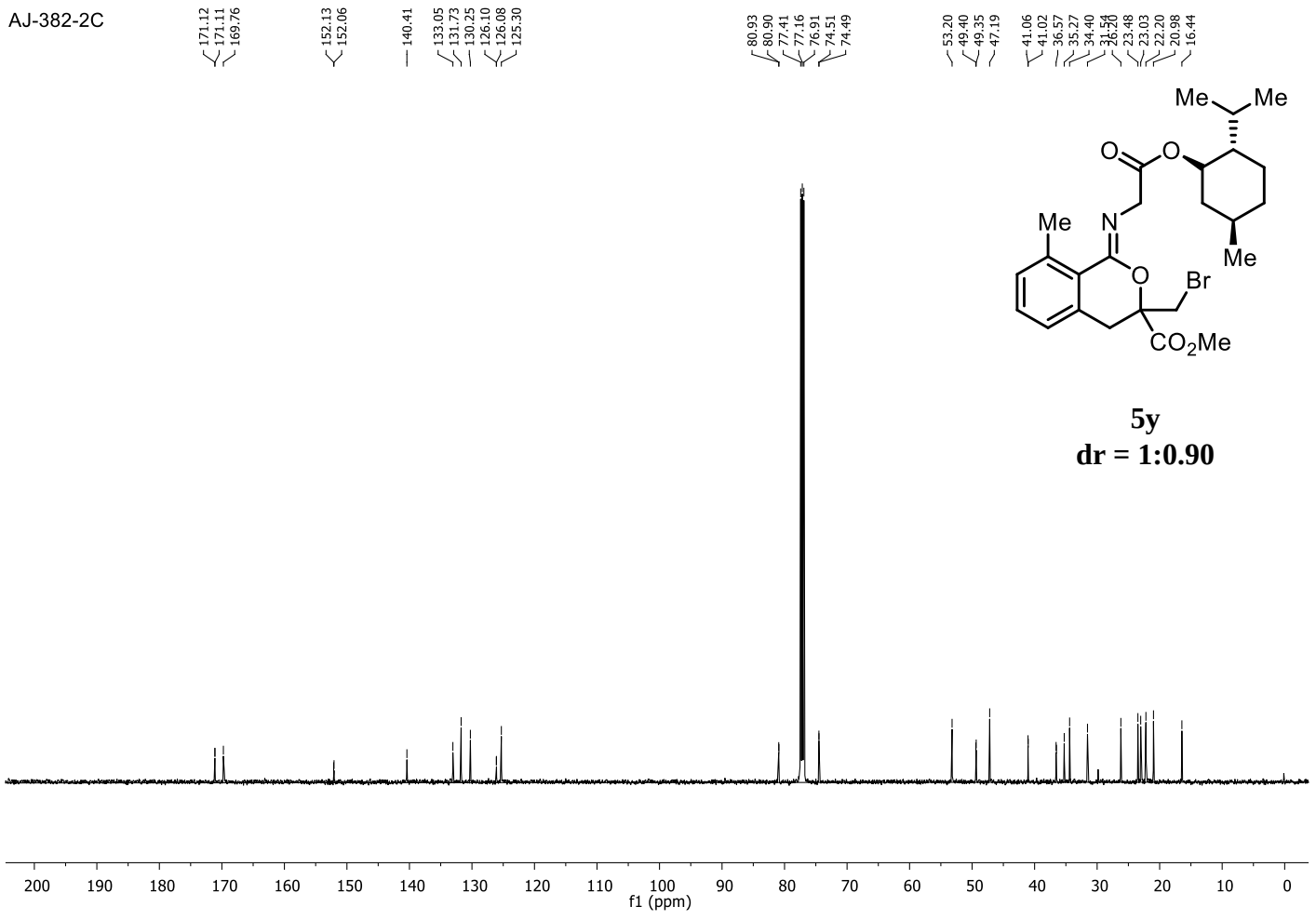
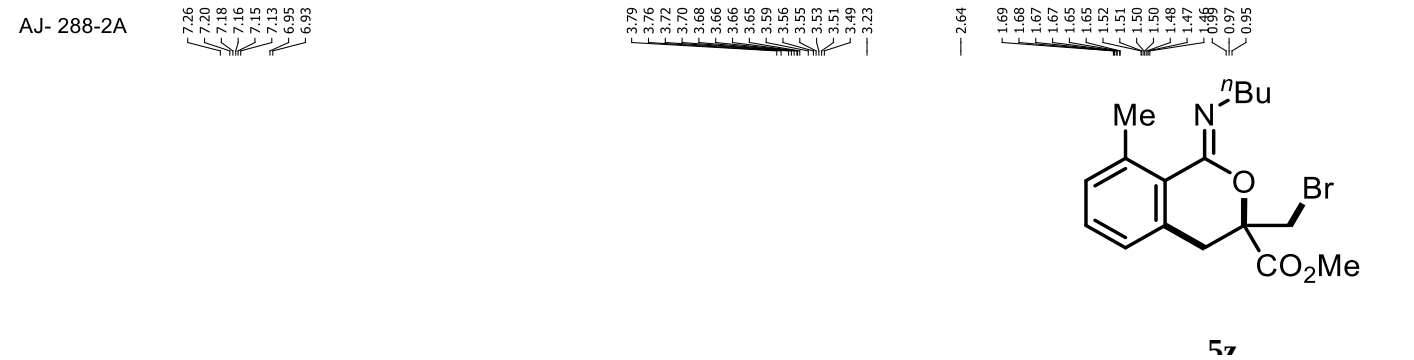
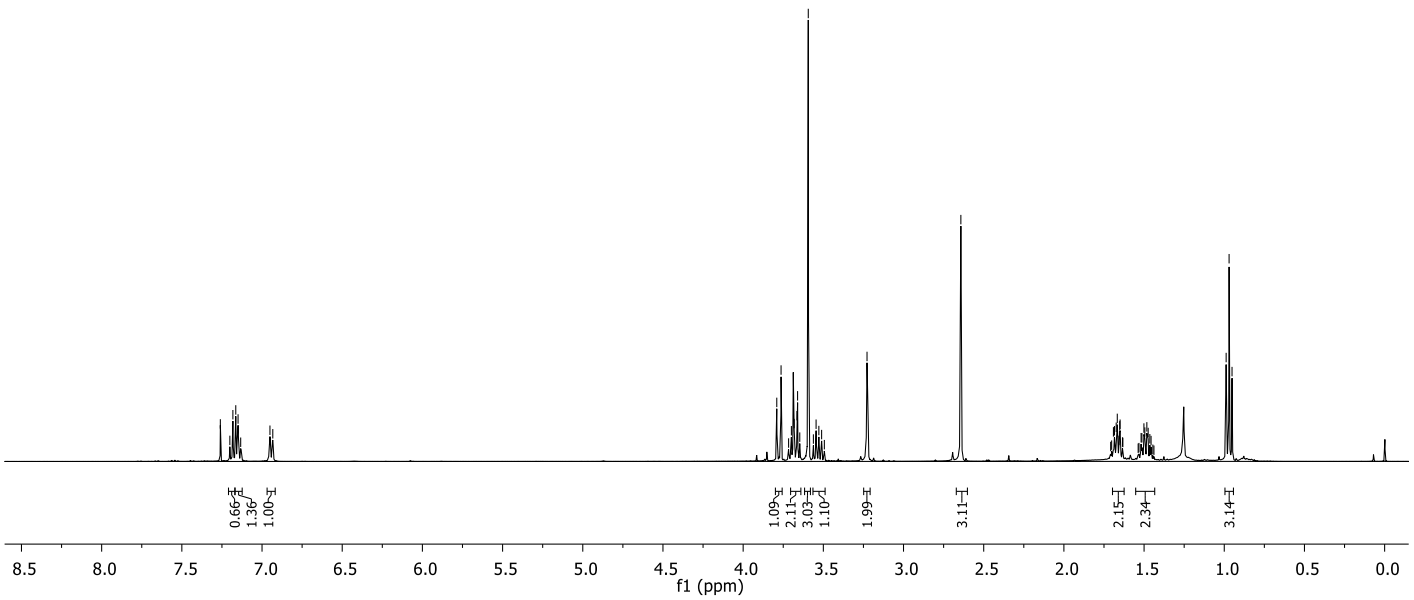


5y
dr = 1:0.90

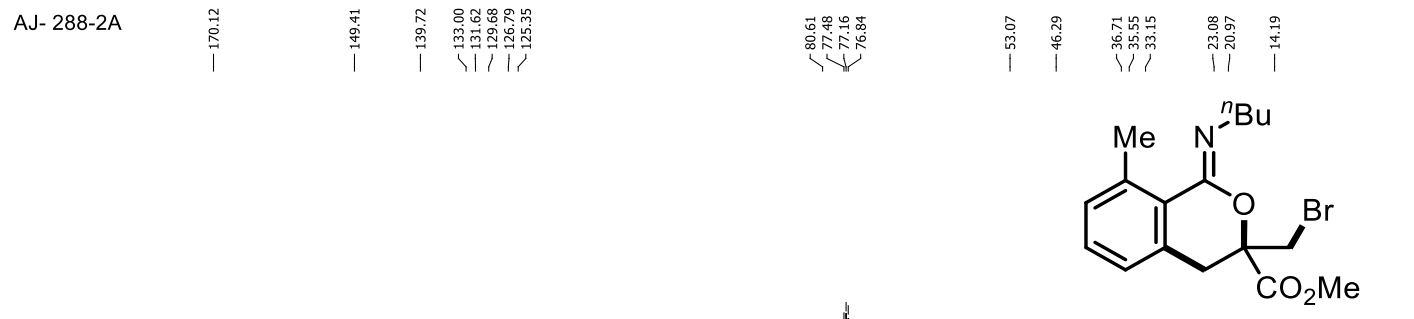
AJ- 288-2A

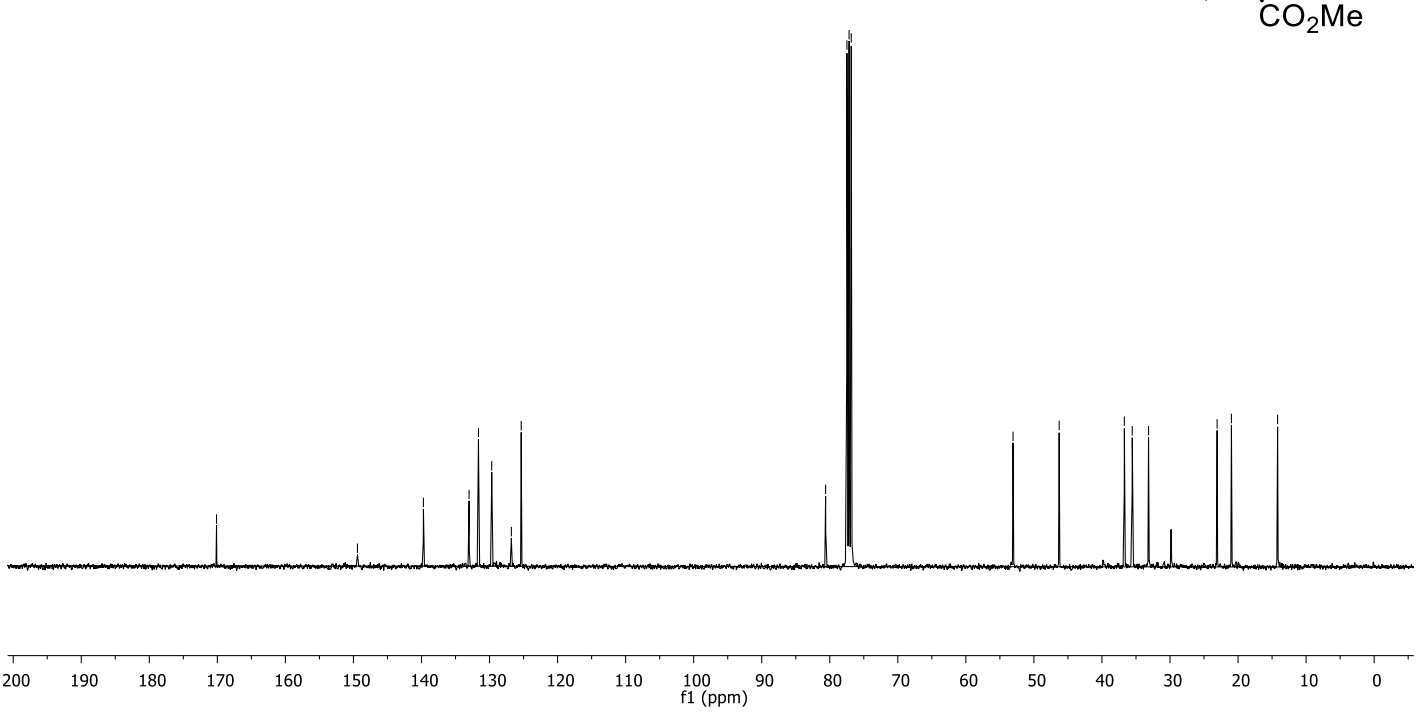


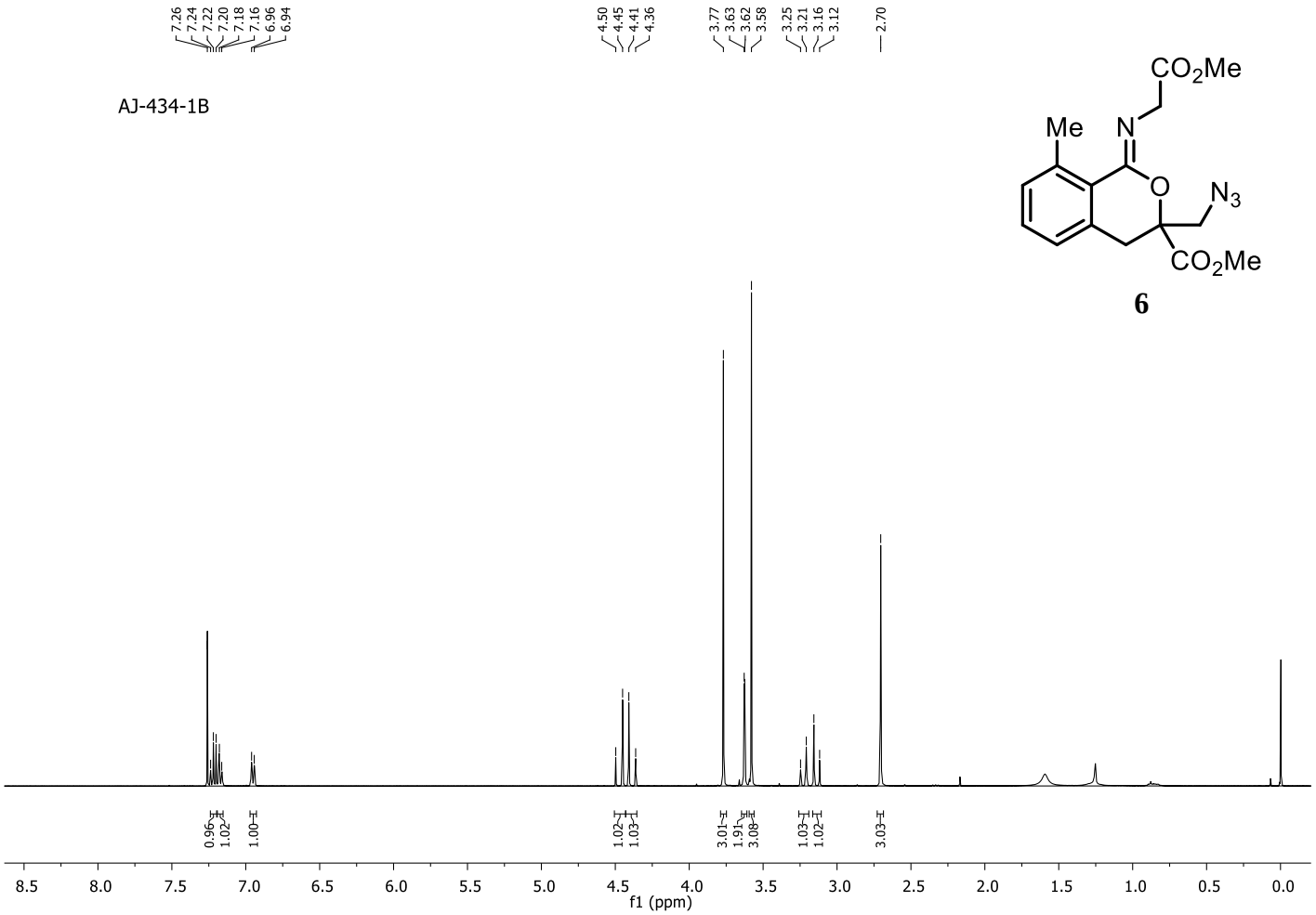
5z



AJ- 288-2A

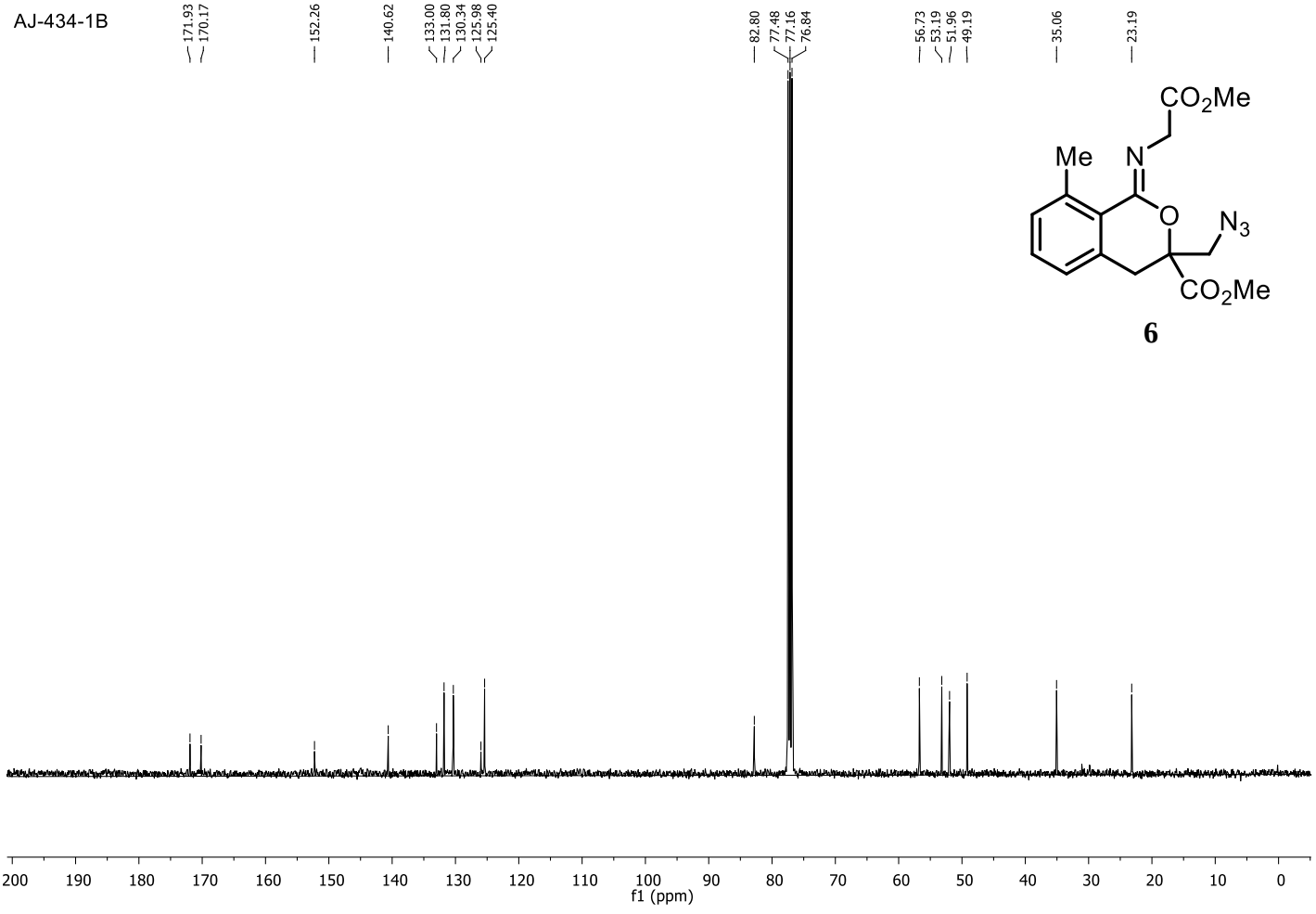





AJ-434-1B
7.26
7.24
7.22
7.20
7.18
7.16
6.96
6.94
4.50
4.45
4.41
4.36
3.77
3.63
3.62
3.58
3.25
3.21
3.16
3.12
2.70
0.96
1.02
1.00
1.02
1.03
3.01
1.91
3.08
1.03
1.02
3.03
f1 (ppm)

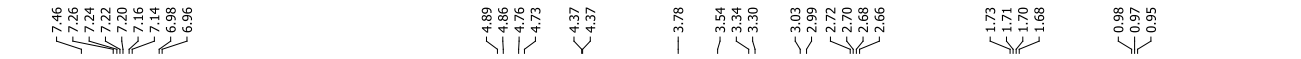
CO2Me
Me
N
O
N3
CO2Me

6

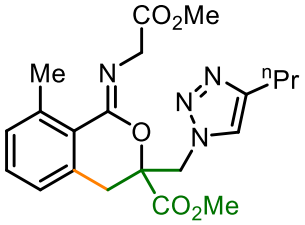

AJ-434-1B
171.93
170.17
152.26
140.62
133.00
131.80
130.34
125.98
125.40
82.80
77.48
77.16
76.84
56.73
53.19
51.96
49.19
35.06
23.19
f1 (ppm)

CO2Me
Me
N
O
N3
CO2Me

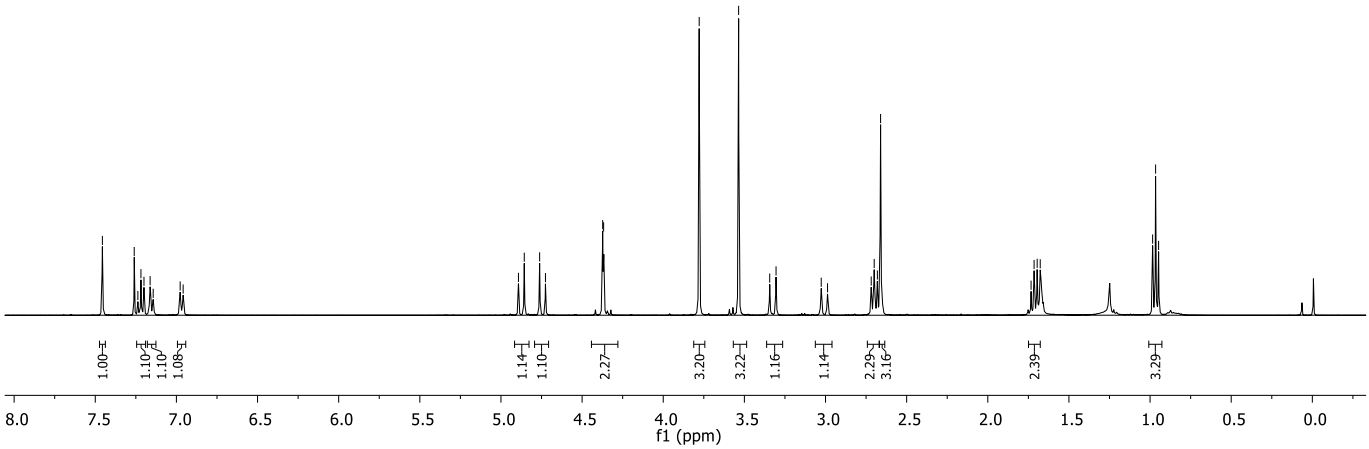
6

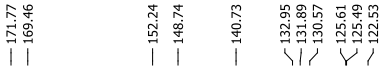


AJ-540-2B-LC_1H_CDCL3_07-01_2023_871_400MHZ

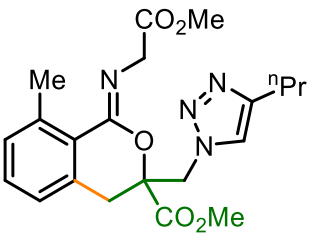


7

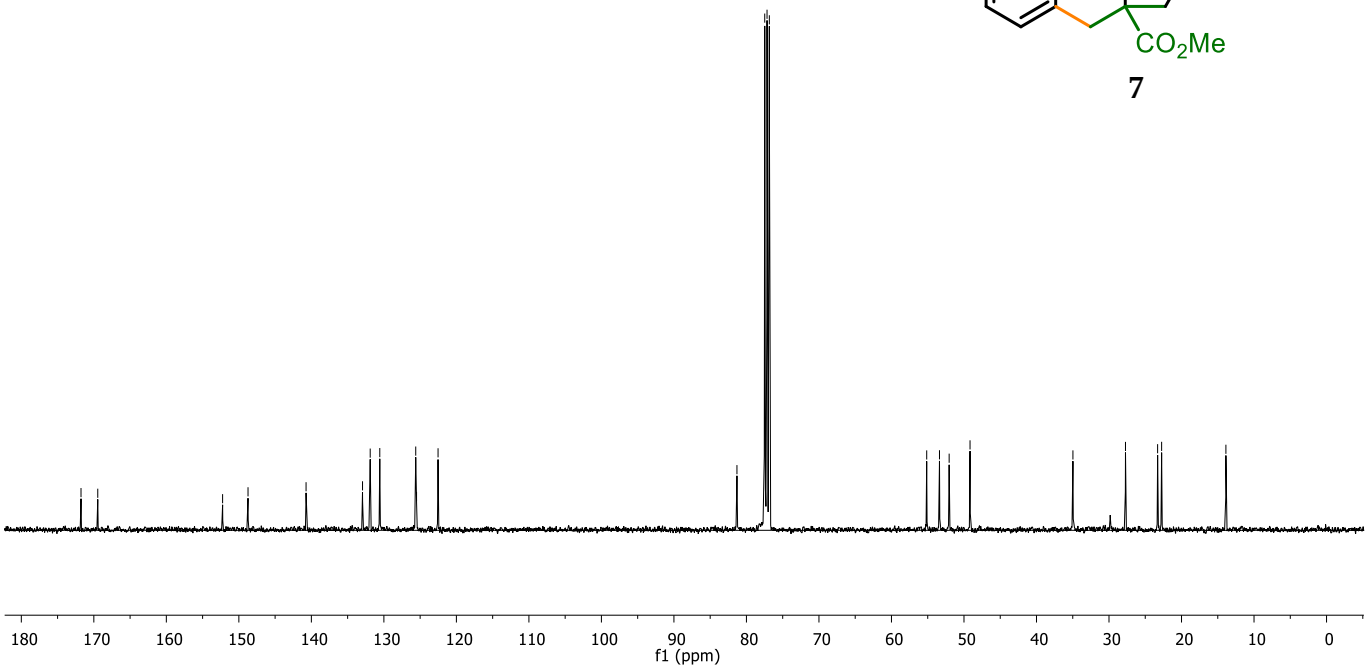




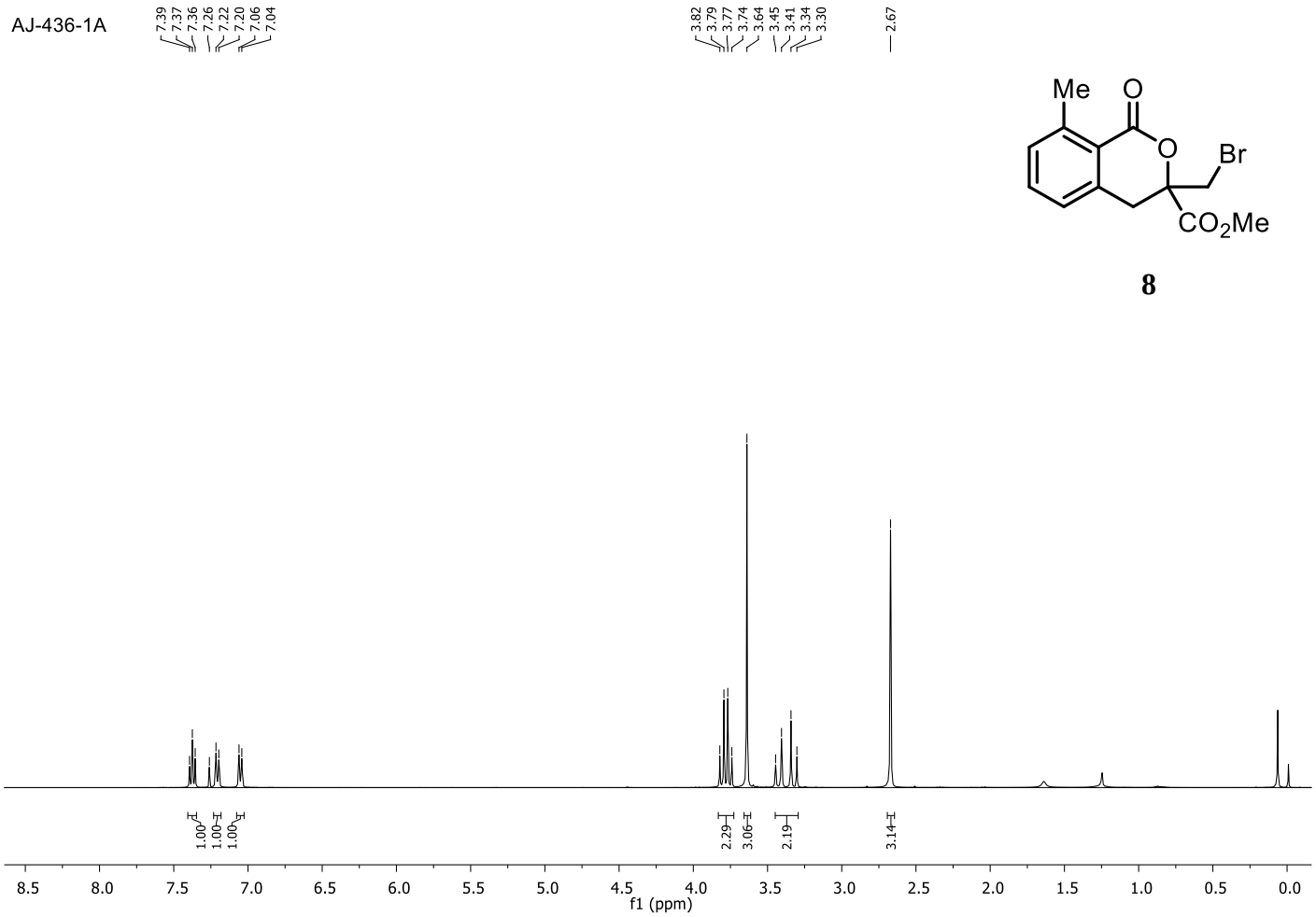
AJ-540-2B-LC_13C_CDCL3_07-01_2023_871_400MHZ



7

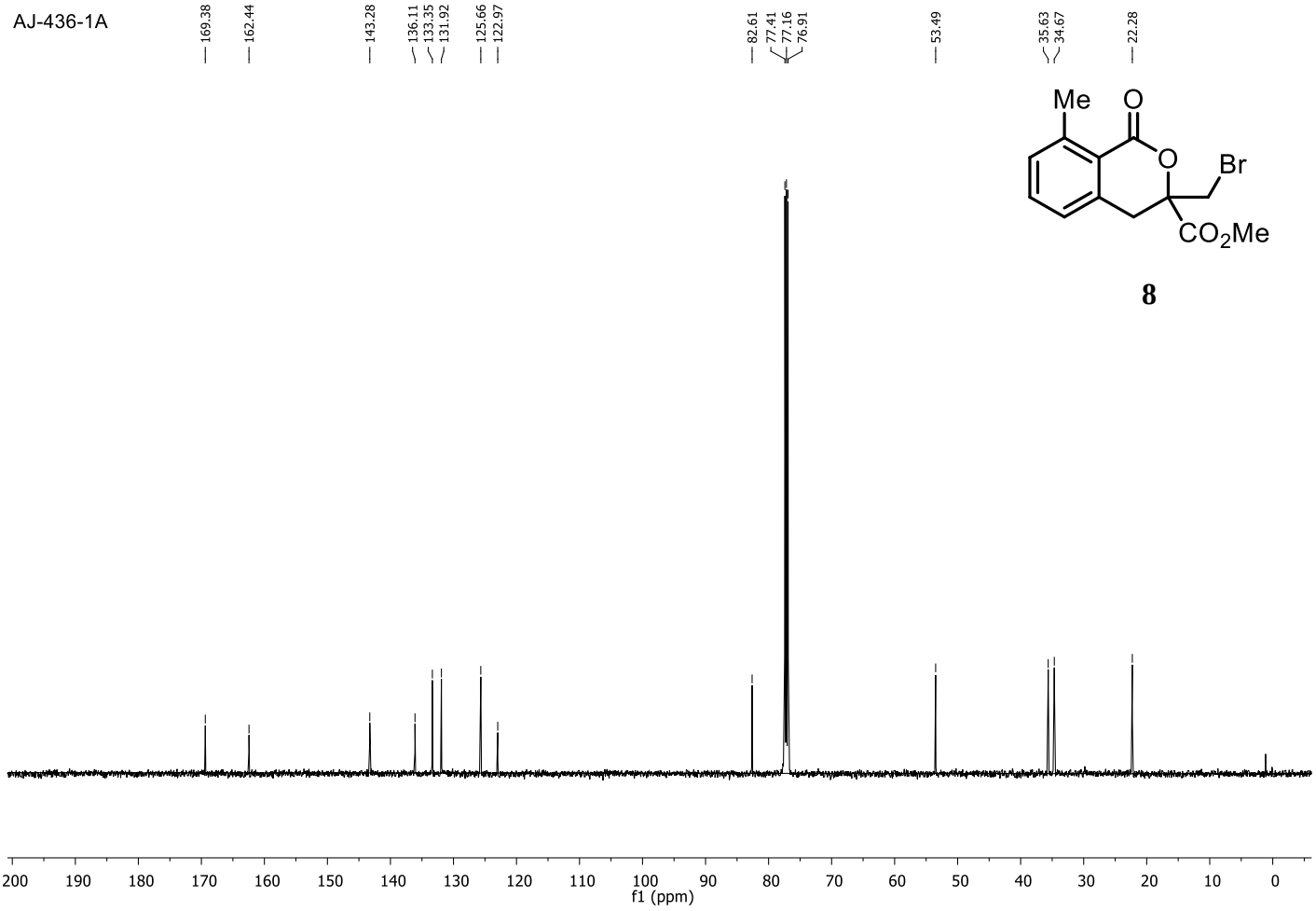


AJ-436-1A



8

AJ-436-1A



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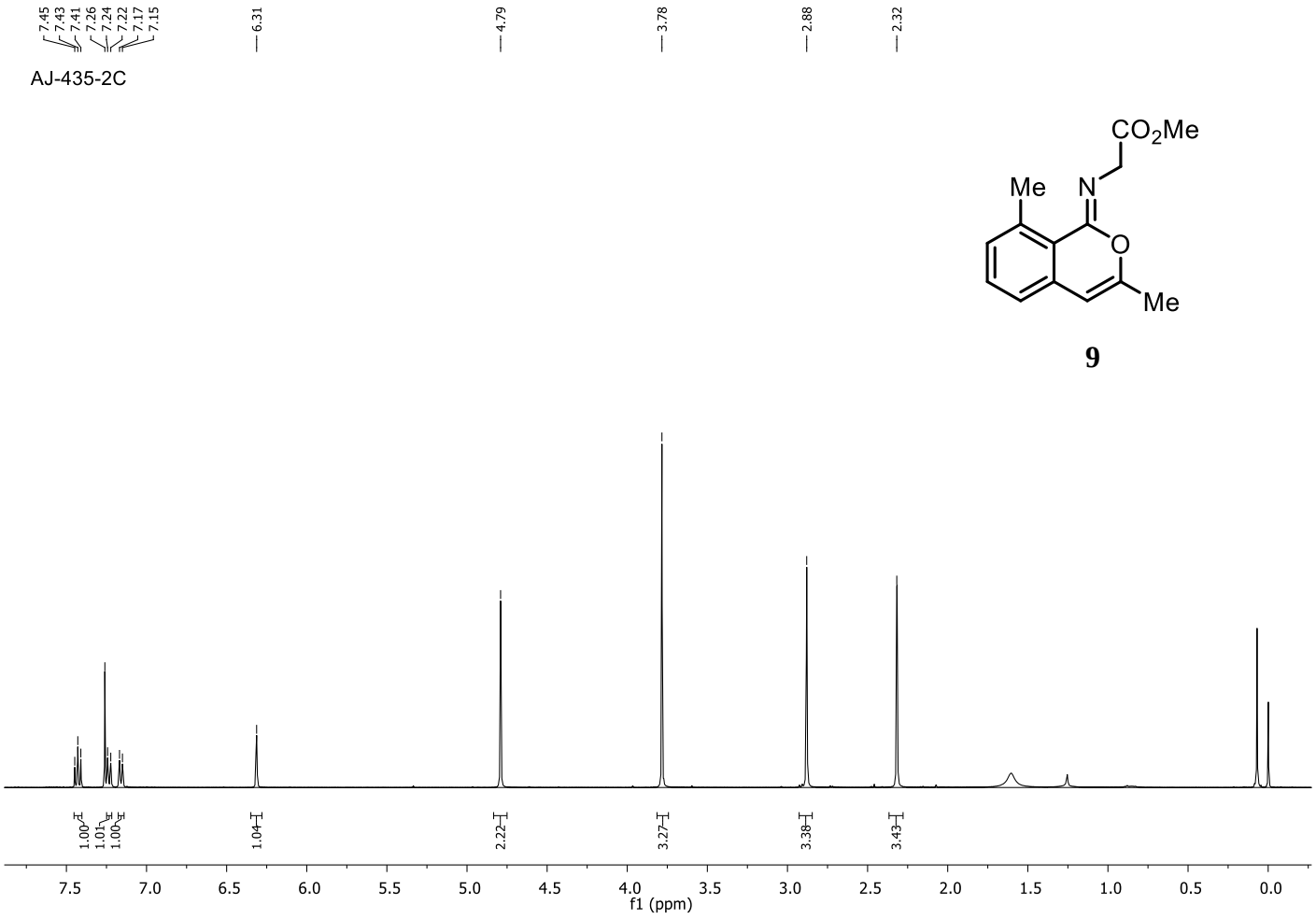
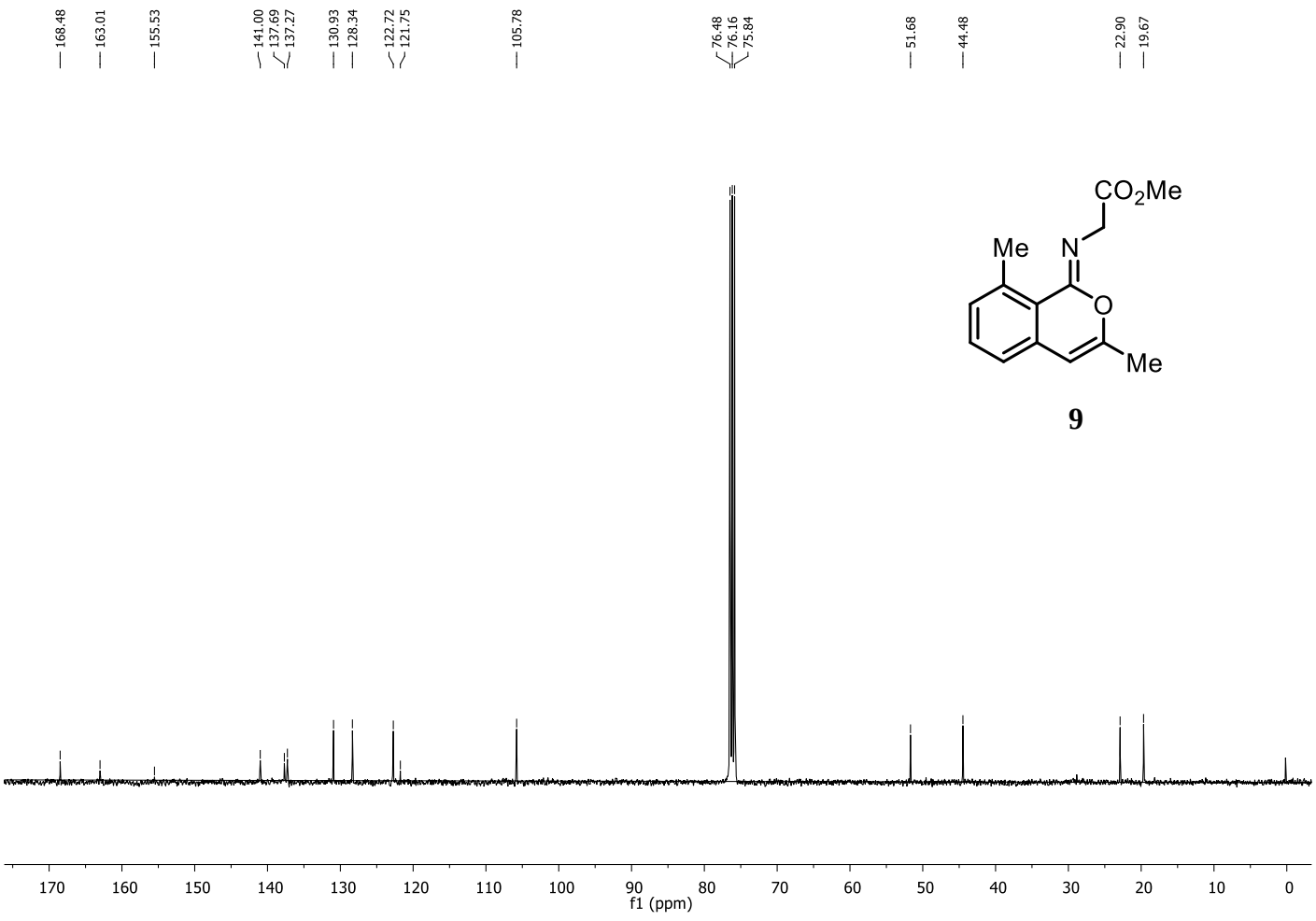
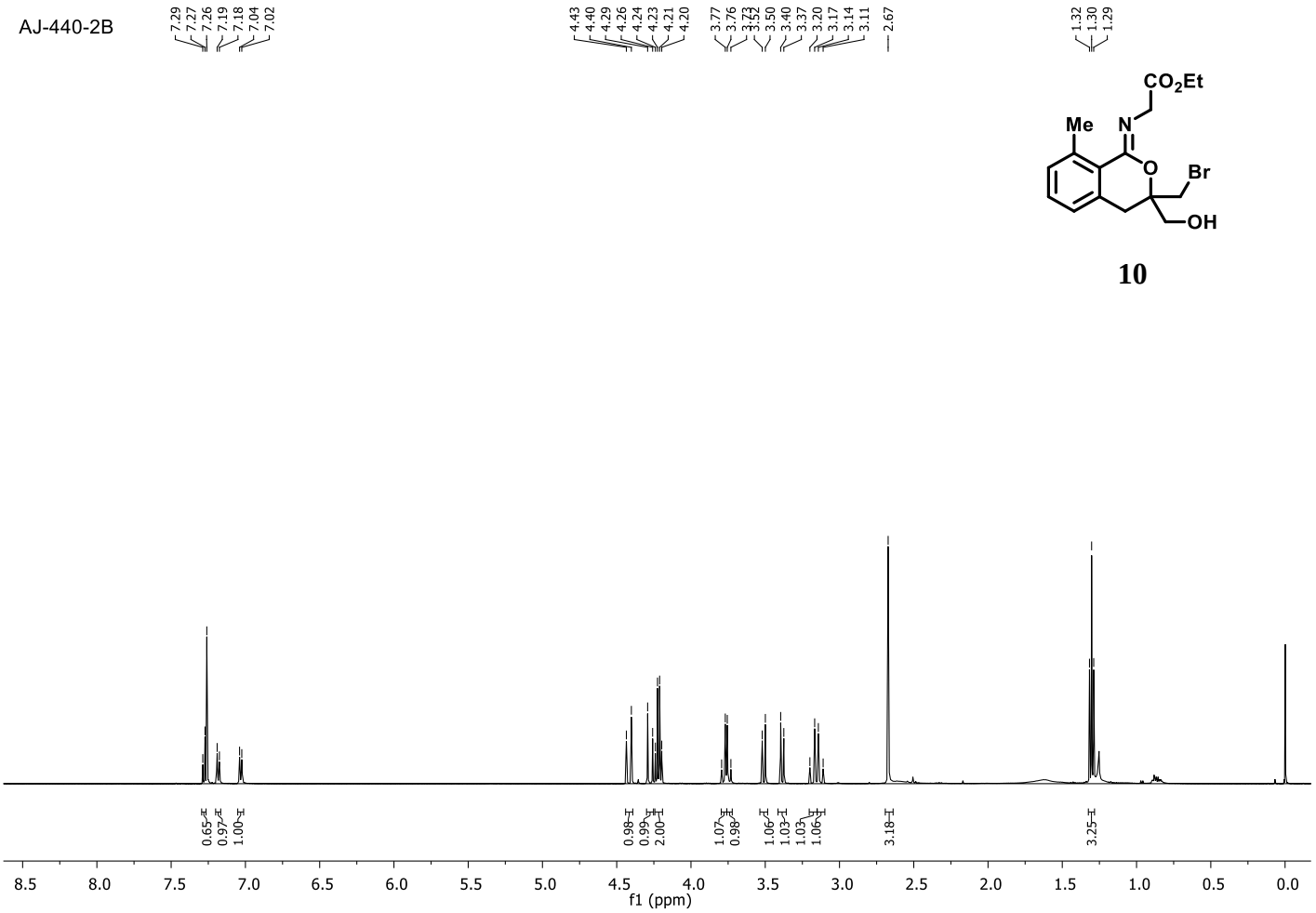

7.45
7.43
7.41
7.26
7.24
7.22
7.17
7.15
6.31
4.79
3.78
2.88
2.32
AJ-435-2C
CO2Me
Me
N
O
Me
1.00
1.01
1.00
1.04
2.22
3.27
3.38
3.43
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

9


168.48
163.01
155.53
141.00
137.69
137.27
130.93
128.34
122.72
121.75
105.78
76.48
76.16
75.84
51.68
44.48
22.90
19.67
CO2Me
Me
N
O
Me
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

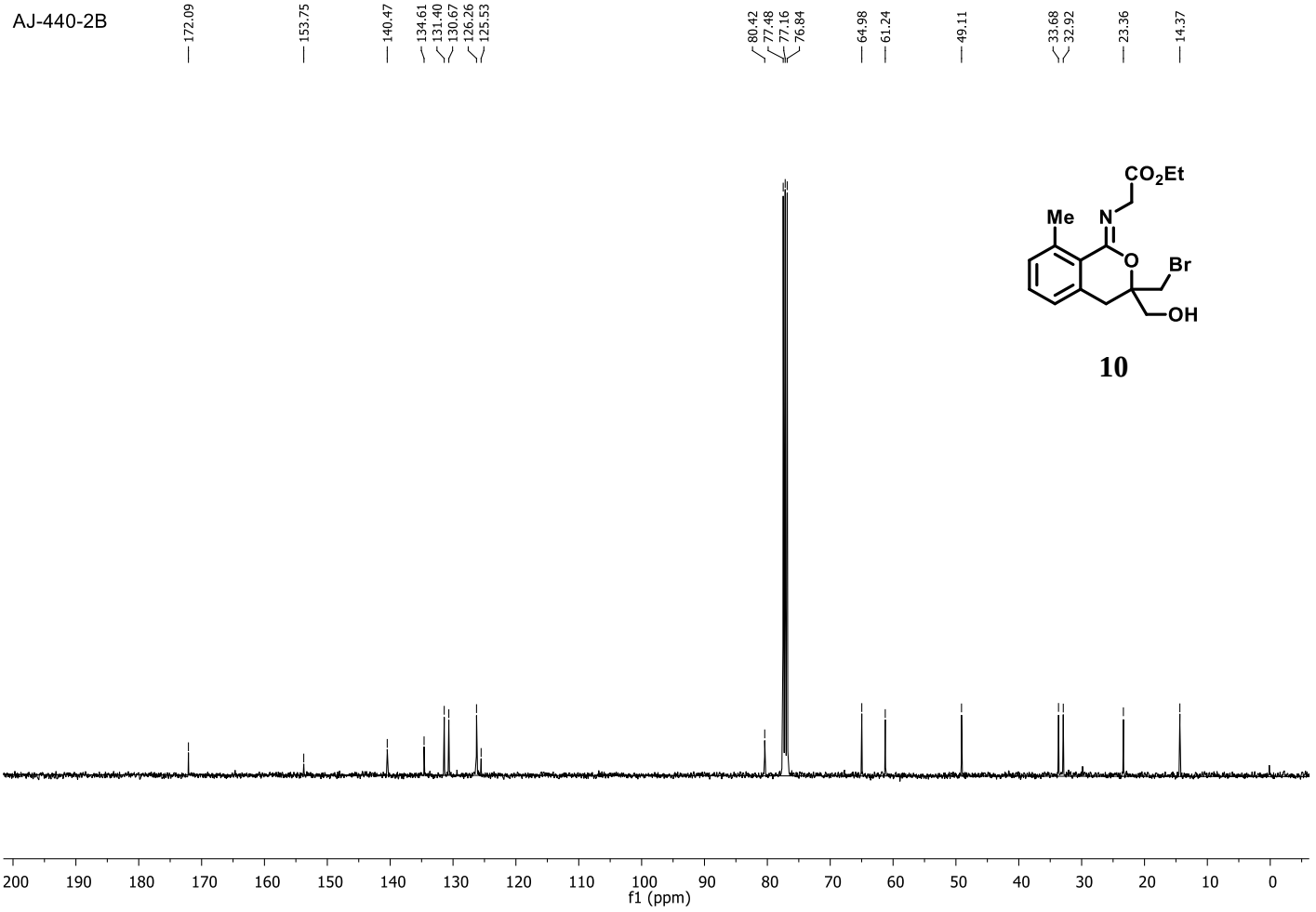
9

AJ-440-2B



10

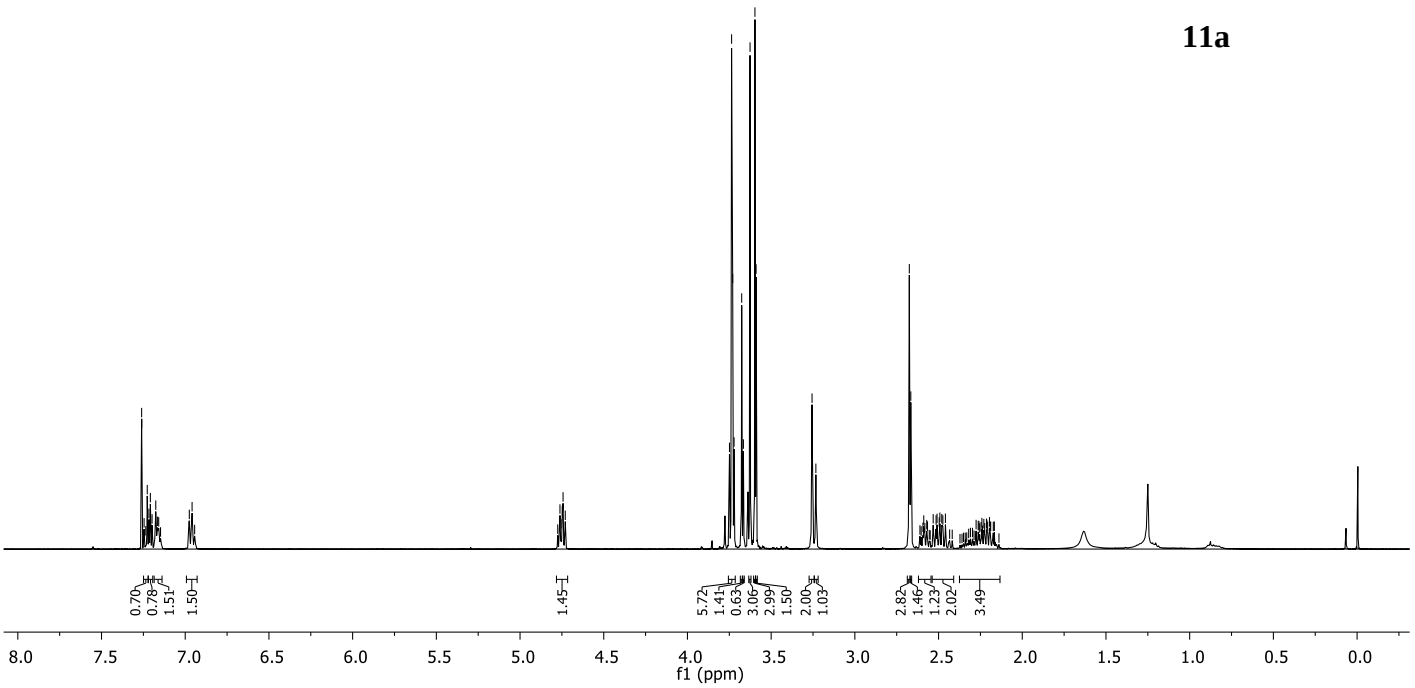
AJ-440-2B

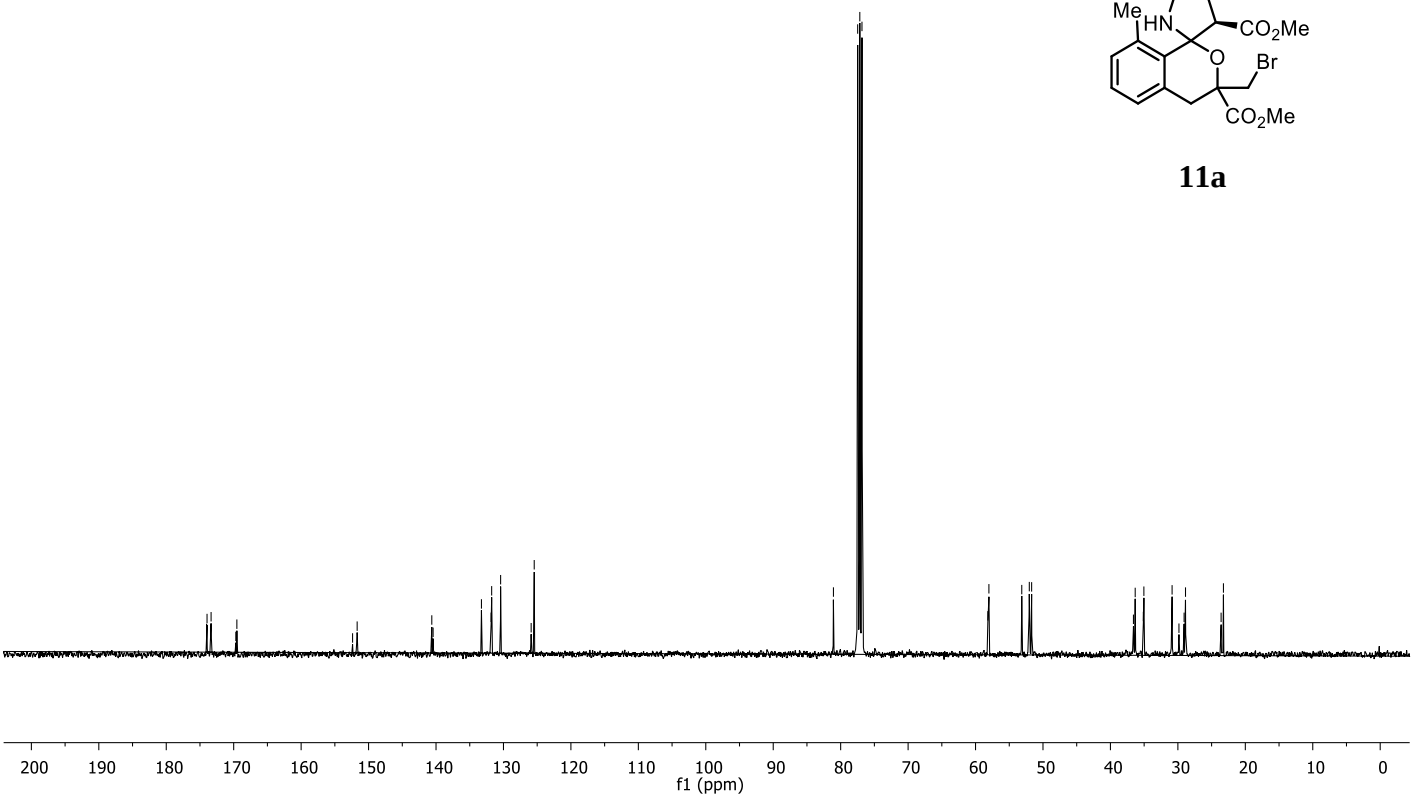


10

AJ-445-1B(1H)

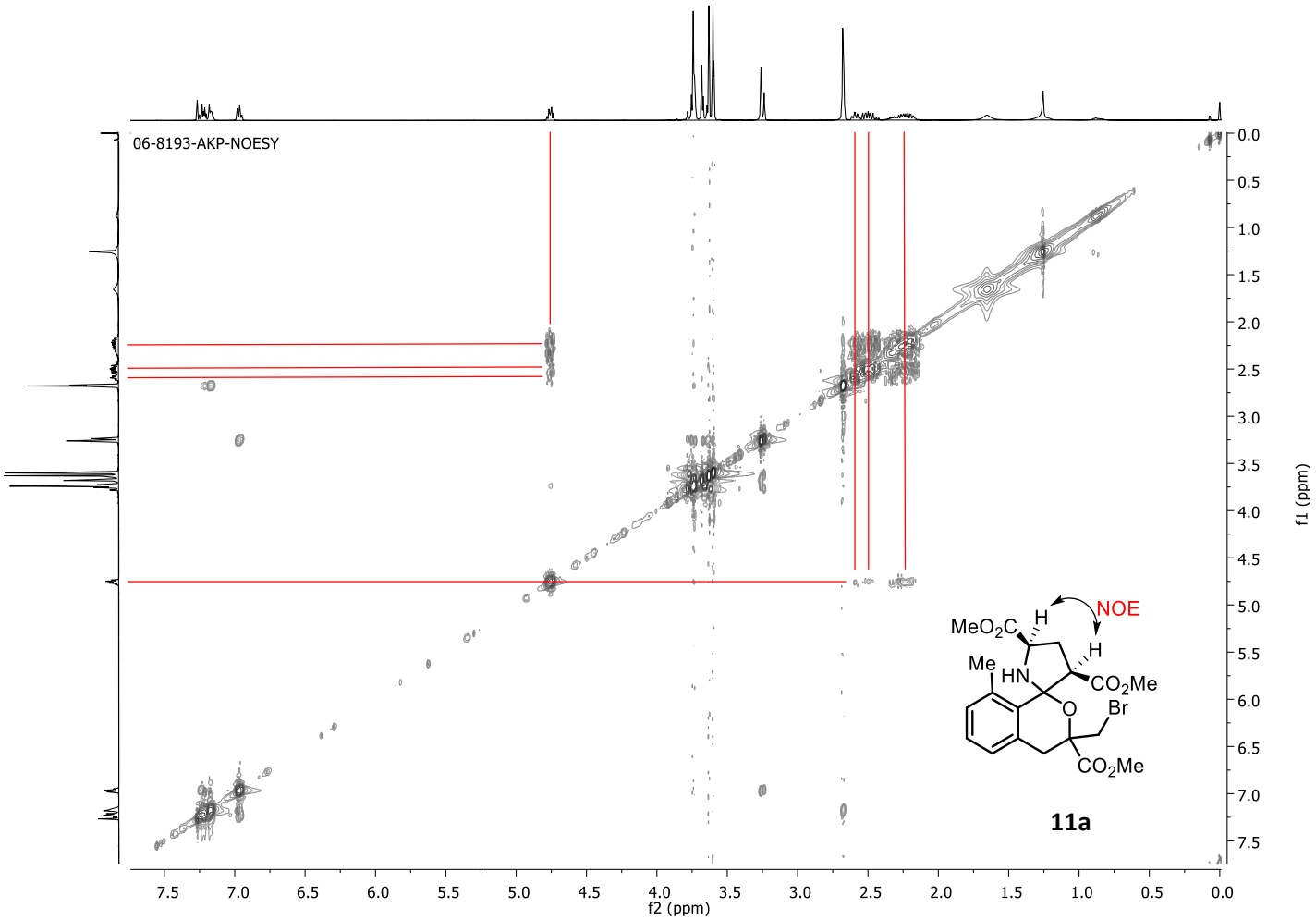
11a



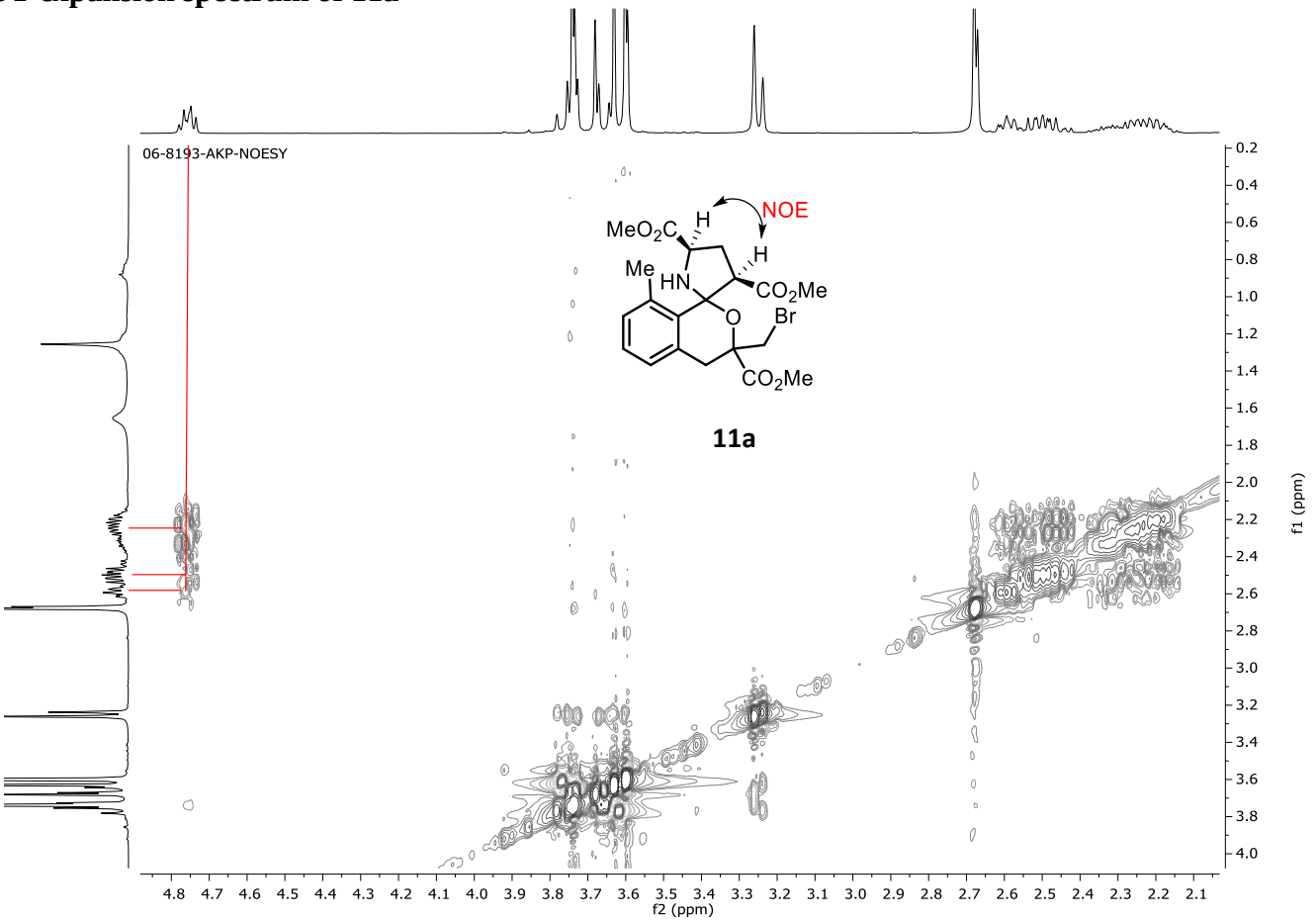


11a

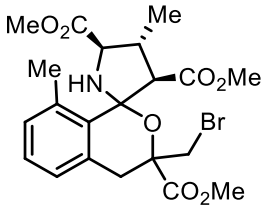
NOESY spectrum of 11a



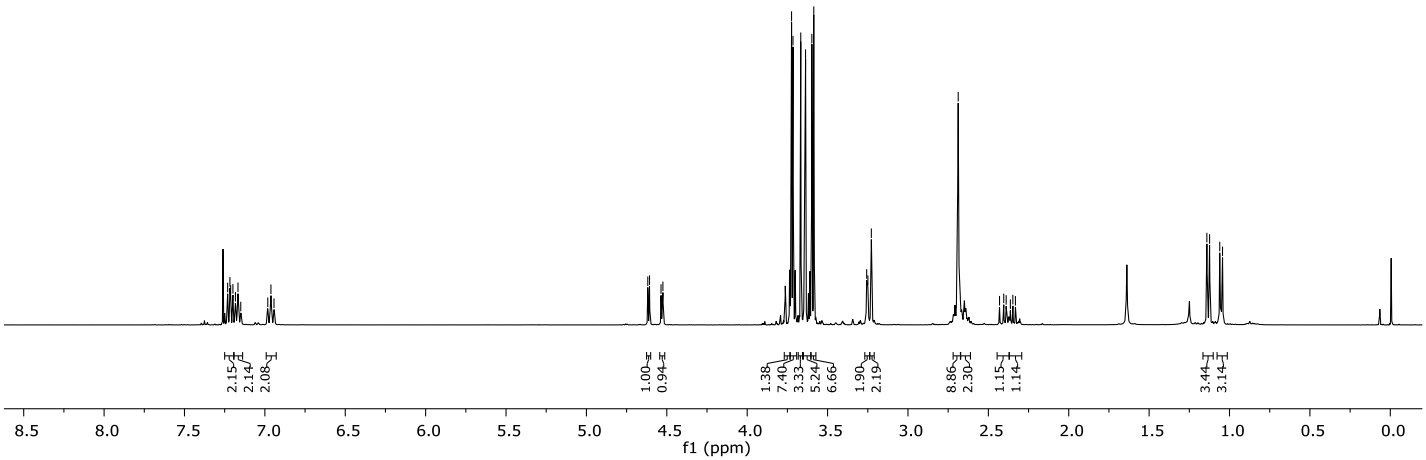
NOESY expansion spectrum of 11a



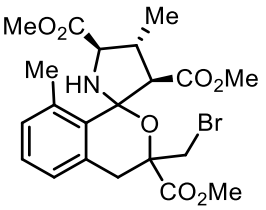
AJ-561-3C_1H



11b

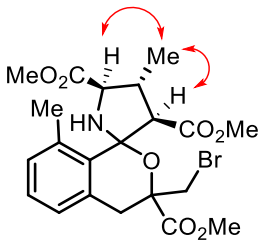


AJ-561-3C_13C

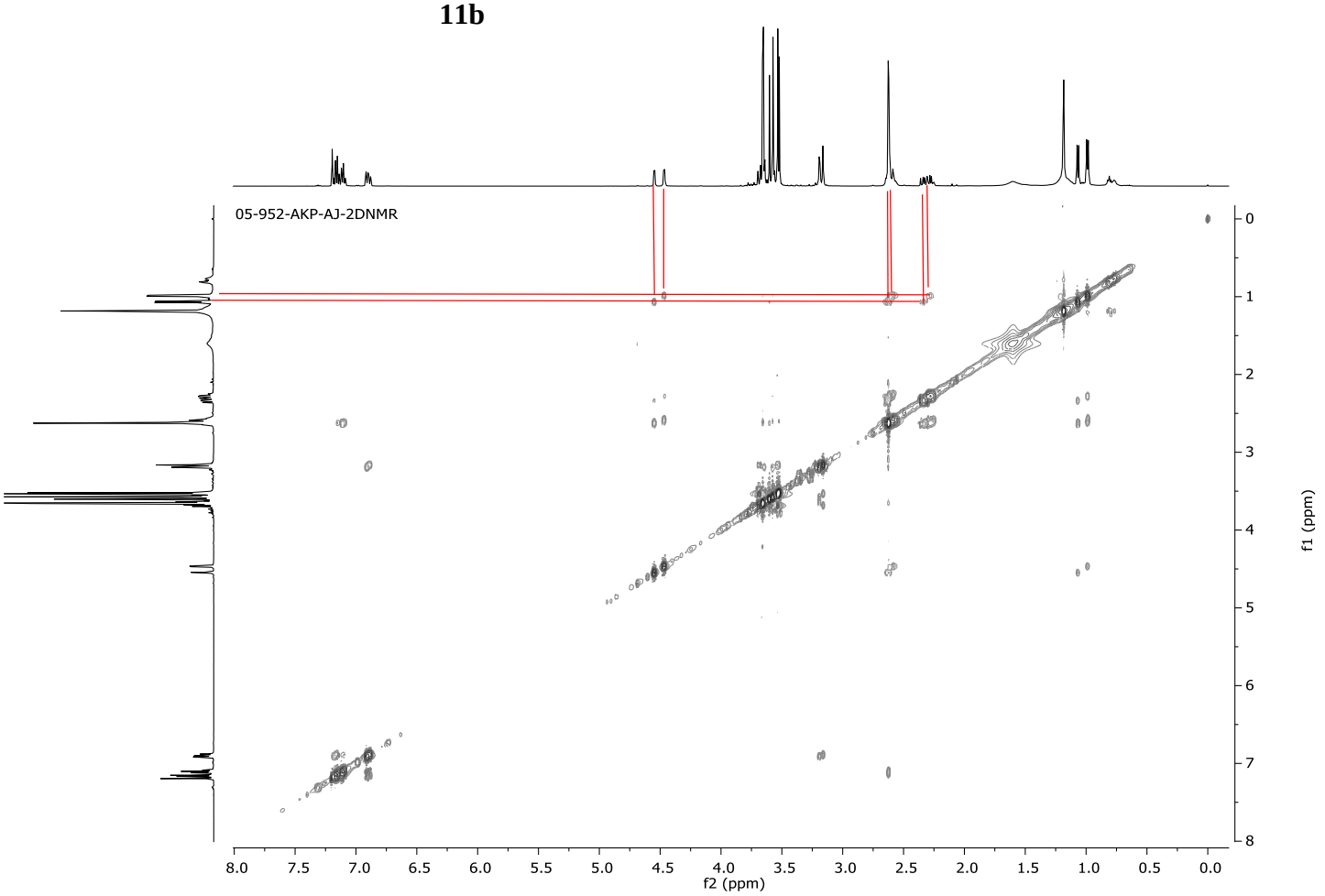


11b

NOESY spectrum of 11a



11b



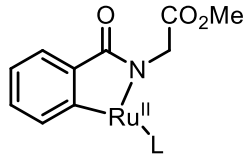
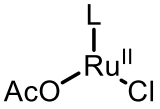
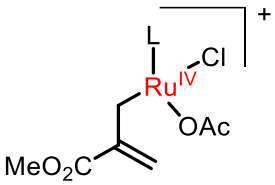
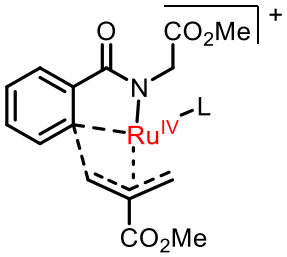
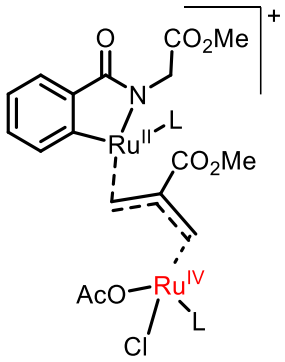
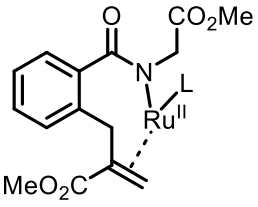
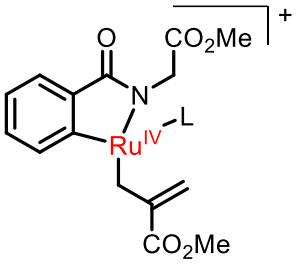
Computational Details

All the calculations were carried out in the Gaussian 09 program[8]. For geometry optimization, we have used M06L functional[9], including dispersion[10] with the SDD basis set for Ru and Cl[11] and 6-31G**[12] for all other atoms (called BS-I). The optimized geometries were characterized as stationary points on the potential energy surface by evaluating the vibrational frequencies. The transition states were characterized by one and only one imaginary frequency corresponding to the change occurring in the system. Also, intrinsic reaction coordinate (IRC) calculations were carried out to verify that the transition state connects the correct forward and backward minima. Solvent effects (dichloroethane (DCE)) were incorporated using the SMD model[13] by performing single-point energy calculations on the gas-phase optimized geometry. All the solvent-incorporated single-point energy calculations were carried out at the M06L level of theory with SDD basis set for Ru and Cl and def2-TZVP[14] basis set for the rest of the atoms (called BS-II). Natural Bonding Orbital (NBO) analysis was carried out using Weinhold's NBO 3.1 code[15] as implemented in Gaussian 09. To further probe the nature of bonding, we have carried out the topological analysis of electronic density with bond path and bond critical points using the Multiwfn code.[16] Here, we have used Bader's quantum theory of atoms in molecules (QTAIM) approach to compute the Laplacian electron density (QTAIM) approach[17, 18].

Energy decomposition analysis (EDA) has been carried out on ADF 2021[19] code to understand the nature of the interaction energy. Here have M06L functional and all-electron TZ2P basis set. Scalar relativistic effects were considered using zeroth-order regular approximation (ZORA). The EDA framework divides the total binding energy (BE) into three terms: electrostatic, Pauli repulsion, orbital interaction terms and dispersion terms (see equation 1). The attractive electrostatic term ΔE_{elstat} corresponds to the classical electrostatic interaction between the unperturbed charge distributions of the prepared fragments. The orbital interaction term (ΔE_{orb}) is attractive in nature and accounts for charge transfer and polarization terms. The Pauli term (ΔE_{Pauli}) is the repulsive term, which accounts for the destabilizing interactions between occupied orbitals and is responsible for the steric repulsion. The final dispersion term (ΔE_{disp}) accounts for the dispersion interactions, which are always attractive in nature.

$$(\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb} + \Delta E_{disp}) \ldots \quad (1)$$

Table S6: Corresponding species labels in the main text and DFT scheme

Species in the main text	Labelling in DFT calculations	Species in the main text	Labeling in DFT calculations
 **A**	**4**	 **E**	**[Ru^{II}(p-cymene)Cl(OAc)]**
 **B**	**11**	 **F**	**TS7**
 **C**	**12**	 **G**	**14**
 **D**	**13**		

Energetics for [RuCl$_2$(p-cymene)]$_2$ dimer opening:

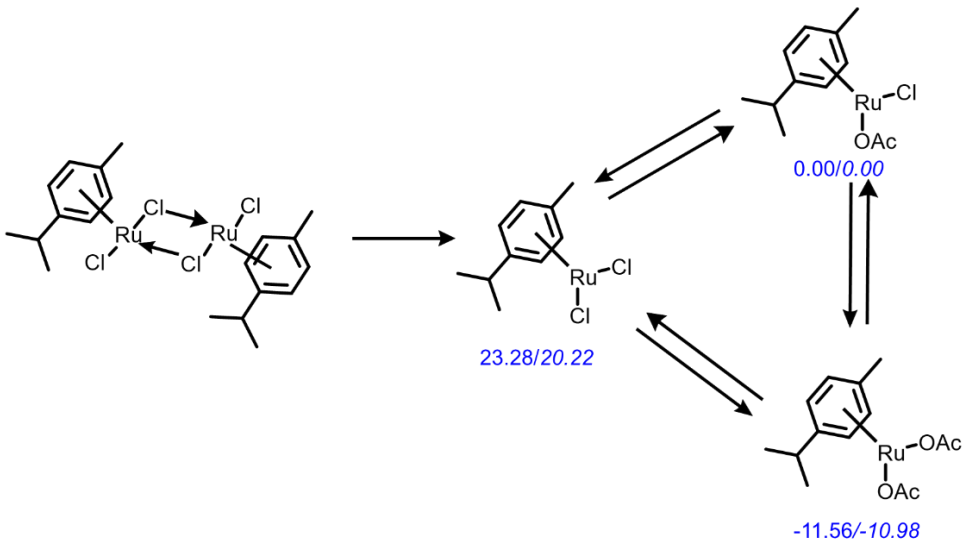


Figure S3. DFT computed energetics for the ring opening of the [RuCl$_2$(*p*-cymene)]$_2$ complex. Relative free energies are provided in the kcal/mol corrected for dichloromethane solvent and for the gas phase (in italics

Formation of Ru(II) ruthanacycle (Species 4)

The proposed reaction pathway for forming the Ru(II) ruthanacycle via the C-H activation is provided in Figure S4. In the first step, our active form of the catalyst [Ru(p-cymene)$(OAc)_2$] interacts with **1a** and forms a reactive complex (**RC1**), where the NH proton of **1a** is weakly coordinated to the O atom of the attached η^2-acetate group. In the next step, **RC1** rearranges to yield species **1**, where the N atom of the **1a** weakly coordinates with Ru, resulting in the opening of one of the O arms of the attached η^2-acetate involved in the weak hydrogen bonding with NH proton. Species **1** is ~ 2.7 kcal/mol more stable compared to **RC1**. In the next step, NH deprotonation occurs via the six-membered transition state (**TS1**), where the acetate group abstracts the NH proton and generates species **2,** which is ~ 3.8 kcal/mol destabilized compared to species **1**. The **TS1** is ~8.4 kcal/mol higher than the preceding intermediate. NBO computed second-order perturbation analysis indicates a donor-acceptor interaction of –282.5 kcal/mol from the $2p_z$ orbital of O3 (of the acetate group) to the 1s orbital of H2 of **1a** (see Figure S5). The formation of **2** by removing the AcOH group is required to achieve the C-H activation step, as Ru-C bond formation and the AcOH group violate the $18e^-$ rule. In the next step, the C-H activation occurs via a concerted metalation–deprotonation (CMD) mechanism, where the acetate ligand (the second one) acts as an intramolecular base and abstracts a proton from the phenyl ring. The proton transfer occurs via a 6-membered transition state (**TS2**) with a barrier height of ~8.4 kcal/mol. The **TS2** leads to species **3**, where we observe a formation of the Ru-C bond (C from the phenyl ring). NBO analysis of the **TS2** shows a significant donation of –79.8 kcal/mol from the lone pair of O3 to the σ* orbital comprised of the C–H bond (27%C1 ($2p_y$) + 72%H2(1s)), which facilitates the C-H activation (see Figure S6). Subsequently, the AcOH group leaves and generates species **4**. We have also studied the effect of solvent in the formation of ruthanacyle by comparing the DCE and methanol solvents. Compared to the chlorinated DCE solvent, the protic methanol solvent unfavours the formation of the ruthancycle (**4**) reaction pathway, and this observation is in line with the experimental results (see Figure S5). DFT-optimized structures of all the intermediates with relevant structural parameters are depicted in Figure S7.

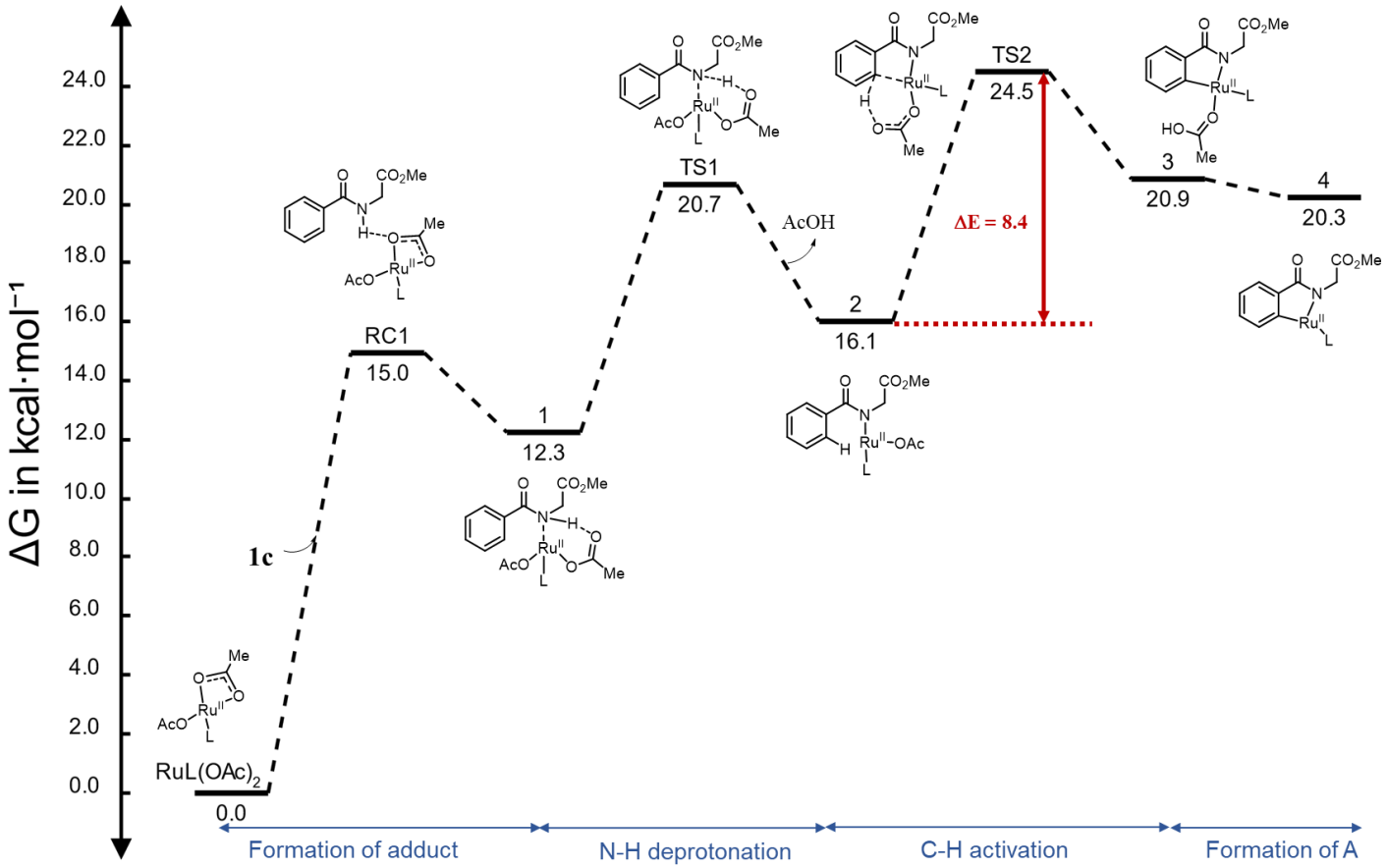


Figure S4: Solvent-corrected (dichloroethane) free energy profile for the formation of **4(A)** at M06L/BS-II level of theory

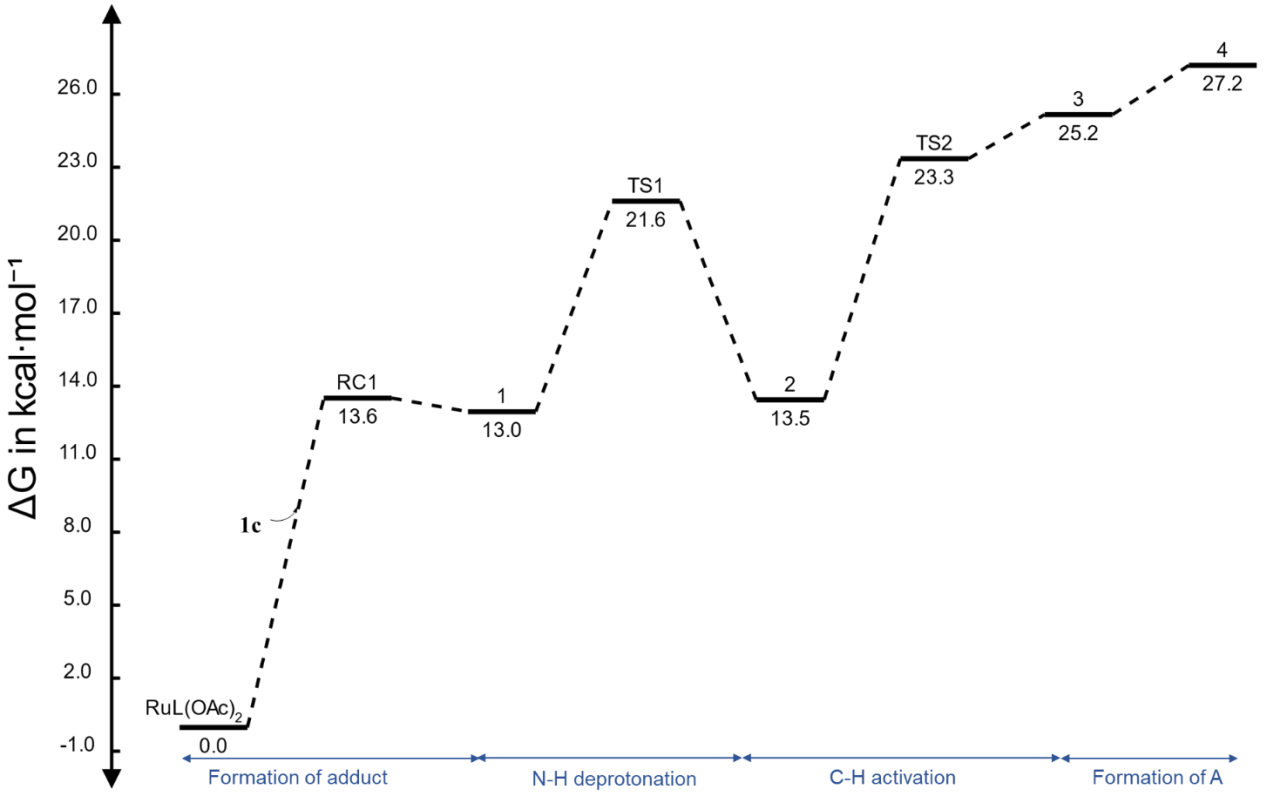


Figure S5: Solvent-corrected (methanol) free energy profile for the formation of **4(A)** at M06L/BS-II level of theory

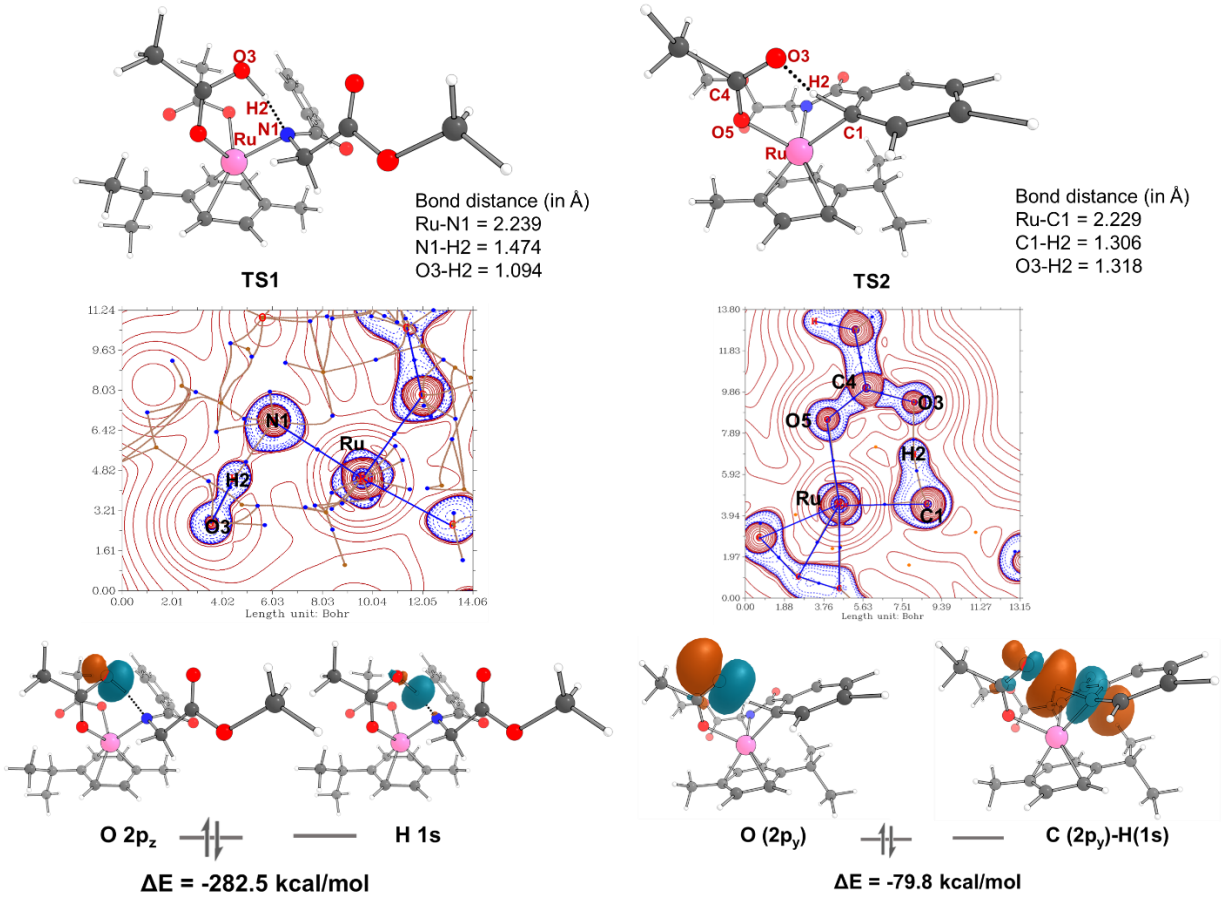


Figure S6: DFT-optimized structures of **TS1** and **TS2** with relevant structural parameters (top); Contour plot of the Laplacian of the electron density along with the bond critical points (blue dots) and bond path (center); NBO representing the most stabilizing interaction involved in the transition state (bottom). The ΔE here represents donor–acceptor interactions obtained from second-order perturbation analysis. Color code: Ru (pink), O (red), C (grey), N (blue) and H (white)

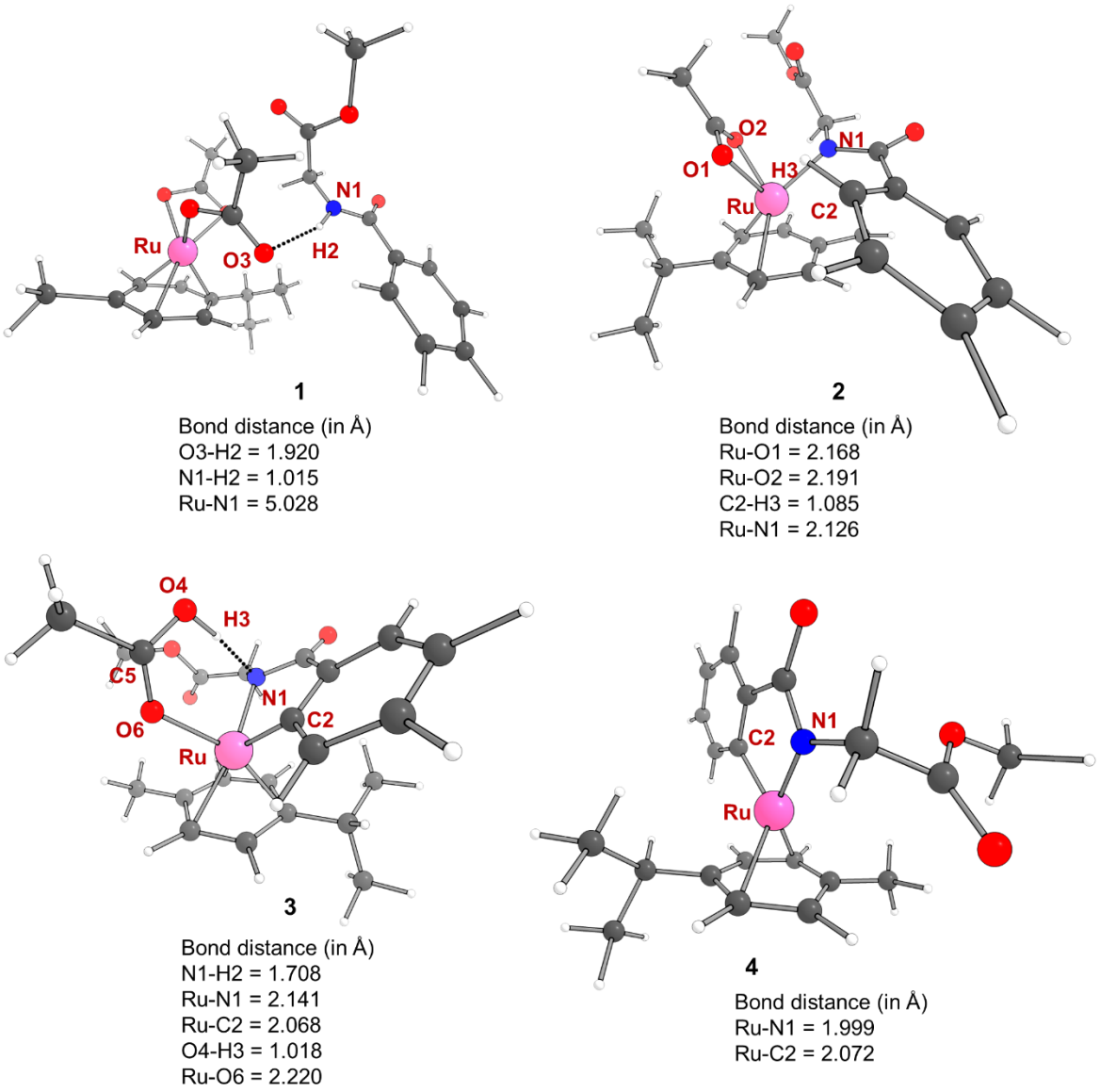


Figure S7: DFT optimized structures of species **1-4** with relevant structural parameters which are involved in the formation of ruthanacyle (**4**). Color code: Ru (pink), O (red), C (grey), N (blue) and H (white)

Conformational analysis of species 4:

Careful observation of species **4** suggests four possible orientations for the arrangement of *p*-cymene and *N*-aryl glycine methyl ester attachment. Here we have computed the relative free energies of all four conformations, which lie within the energy span of 5 kcal/mol. Our calculations indicate that the conformers **A-IV** and **A-III**, where the *N* and *O* atoms of the *N*-aryl glycine methyl ester bind with the Ru(II) center, are highly destabilized, irrespective of the orientation of the *p*-cymene. On the other hand, the **A-I** and **A-II** conformers are relatively lower in energy where the *O* atom of the ester group is not coordinated with the Ru(II) center. Thus, the coordination of the *N* and *O* atoms of the *N*-aryl glycine methyl is not favourable in species **4.** Among all the studied four conformers, the **A-I** conformer is the most stable one, where the isopropyl group of the *p*-cymene and aryl group of the **1a** are next to each other (see Figure S8 and DFT optimized geometry). We have considered the most stable form of the species, i.e. **A-I,** throughout the calculations.

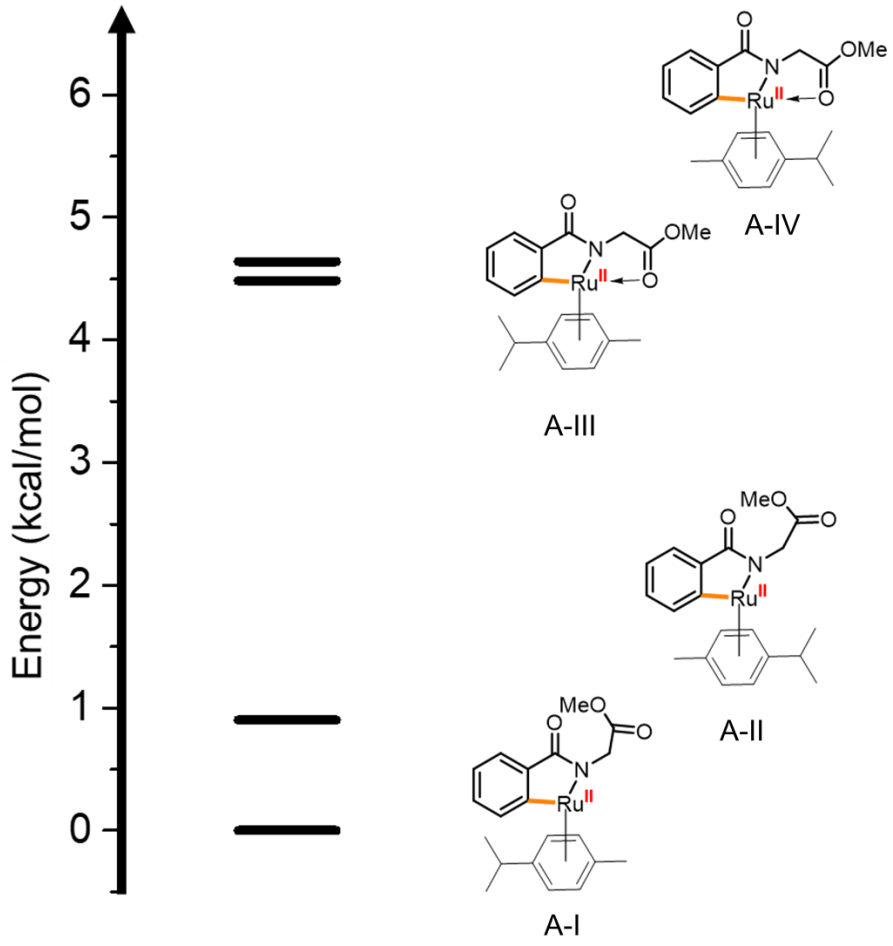


Figure S8: DFT calculated relative free energies of the four possible conformers of species **4**

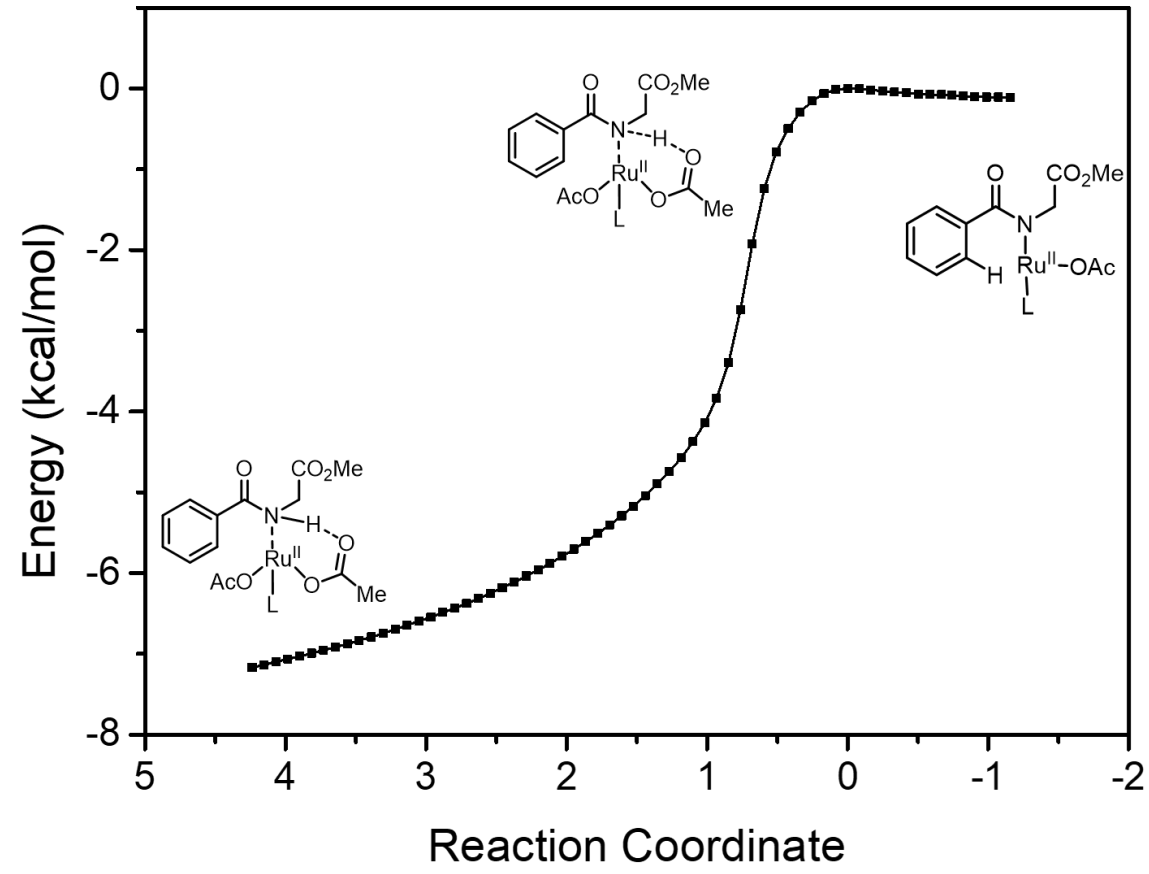


Figure S9: IRC path corresponding to **TS1** involving N-H deprotonation

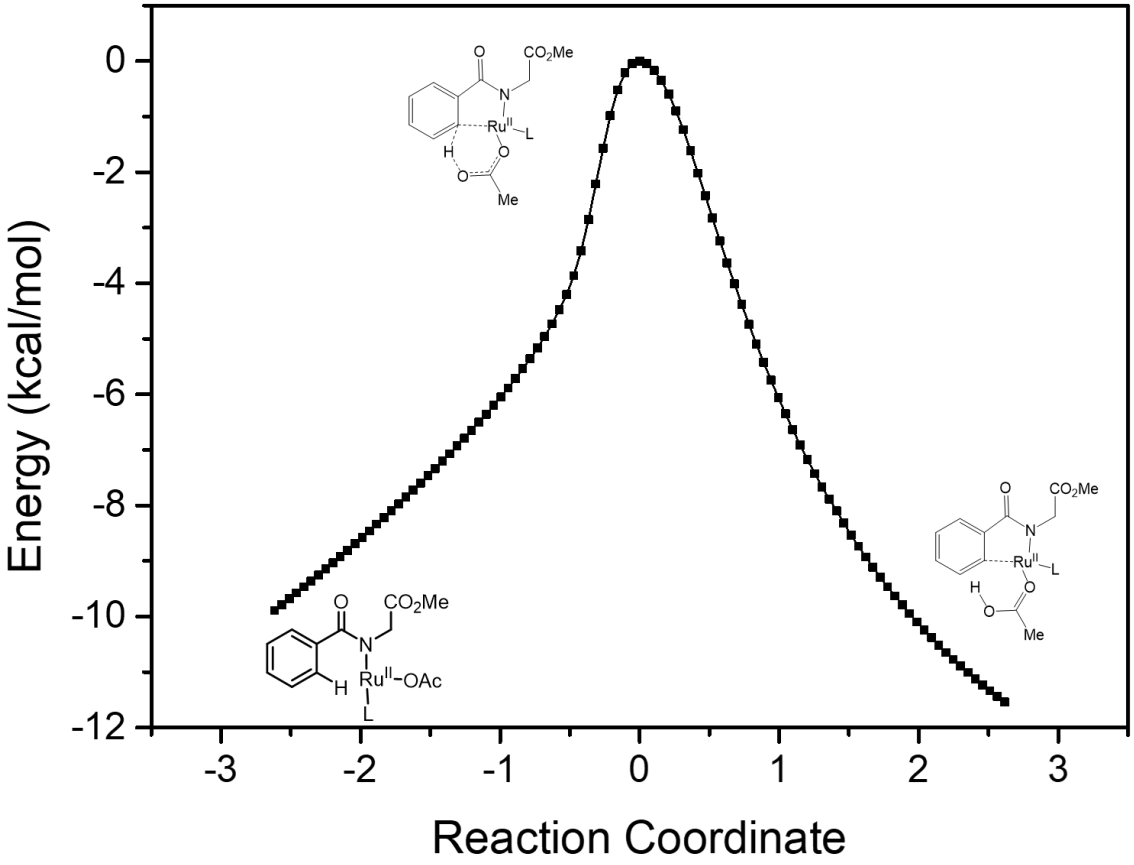


Figure S10: IRC path corresponding to **TS2** involving C-H activation

C(sp^2)–H Allylation via olefin insertion mechanism (*Path I*)

Path I begins with the reaction between species **4** and olefin **2a**, generating a reaction complex (**RC2**) that is marginally more stable than the unreactive species **4** and **2a** species by about 0.6 kcal/mol (see Figure S11). In the next step, **RC2** further rearranges and generates species **5,** where olefin is coordinated to Ru(II) center in the a η^2 fashion. The observed free energy change suggests that species **5** is marginally destabilized compared to **RC2** by 0.04 kcal/mol. In the next step, olefin insertion occurs in the Ru-C bond of **5** via a 1,2 migratory insertion mechanism and generates species **6**, which is stabilized by ~4.1 kcal/mol more than species **5**. The 1,2 migratory insertion goes via a four-membered transition state (**TS3**) with a barrier height of ~8.2 kcal/mol. The seven-membered ring formation in intermediate **6** reduces the strain energy and stabilizes this species compared to **5**.

To further undergo *β*-acetate elimination, an intramolecular rearrangement takes place where the *O* atom of the acetate group (**2a**) weakly forms a bond with the Ru(II) center and generates an intermediate **7**, which is ~4.3 kcal/mol destabilized compared to **6**. This rearrangement breaks the Ru-C4 bond and slightly weakens the C5-C6 bond (see Figure S13), which is necessary to facilitate the β-acetate elimination. Finally, β-acetate elimination occurs via the **TS4**, located at ~13.2 kcal/mol higher in energy than intermediate **7**, forming intermediate **8**. In **TS4**, the C7-O8 bond ruptures (1.997 Å) while the C6-C7 bond (1.415 Å) comes closer to the Ru(II) center in the η^2-fashion. This is well reflected in the computed NBO, where the donor-acceptor interaction of ~ 50.7 kcal/mol from the σ C7-O8 bond to the vacant antibonding orbital of C9 results in the weakening of the C-O bond. Simultaneously, we noticed a donation of ~ 27.8 kcal/mol from the π Ru-C6 bond to the σ*C7-O8 bond, representing the role of the Ru(II) center in breaking the C-O bond (see Figure S14). In species **8**, the C6-C7 bond (1.382 Å) strengthens and binds with the Ru(II) center in the η^2-fashion, resulting in the formation of a much larger ring that significantly stabilizes species **8** compared to preceding intermediates (see Figure S13). In the next step, species **8** interacts with the AcOH, which protonates the N and generates the allylated product (3b). At the same time, the OAc- attaches to the Ru(II) center to regenerate the catalyst [Ru(*p*-cymene)$(OAc)_2$] for the subsequent cycle (see Figures S10 and S11). The rate-determining step is the β-acetate elimination process which includes the intramolecular rearrangement, resulting in the activation energy barrier of ~ 17.5 kcal/mol. DFT-optimized geometries of all the intermediates with relevant structural parameters are depicted in Figure S13.

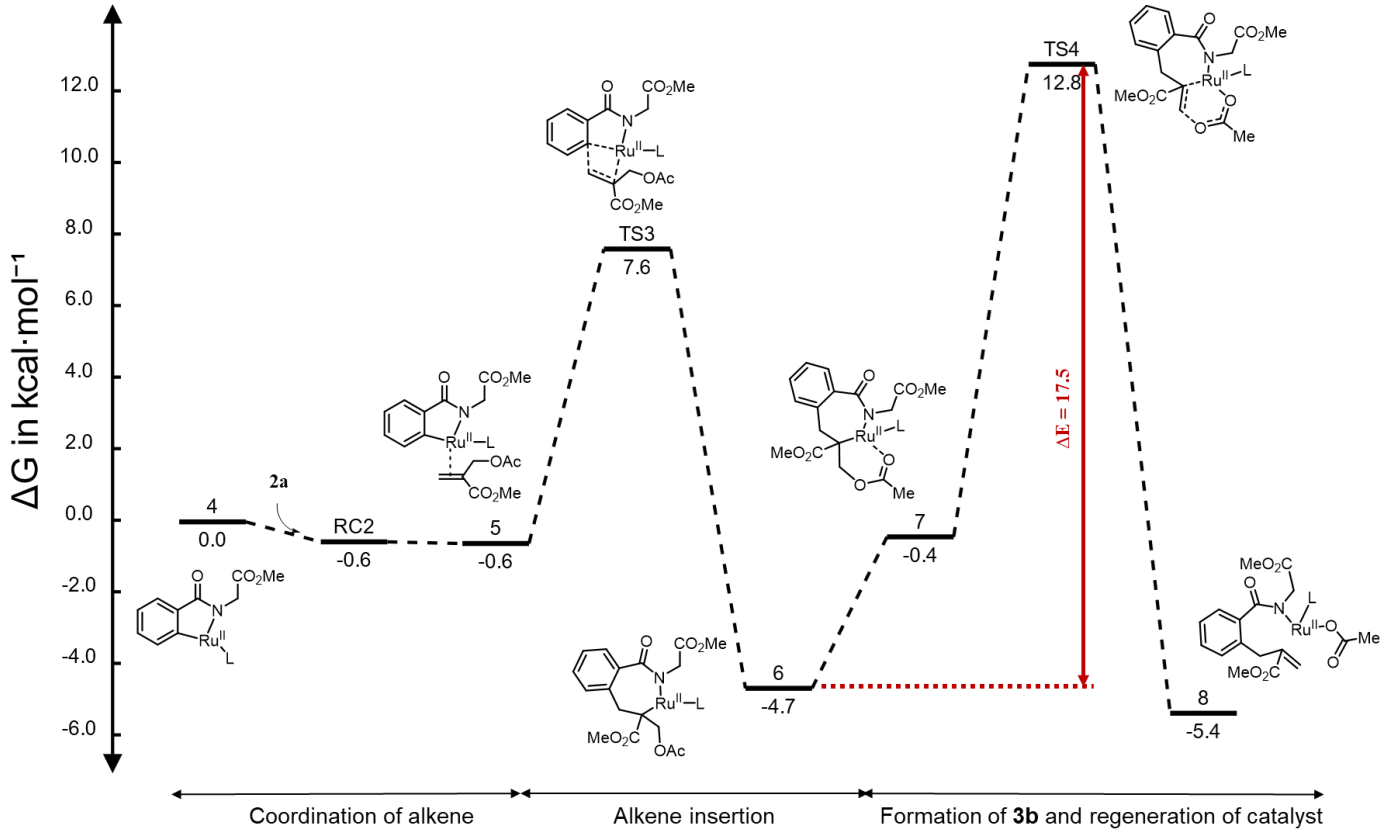


Figure S11: Solvent-corrected (dichloroethane) free energy profile for the known mechanism at M06L/BS-II level of theory

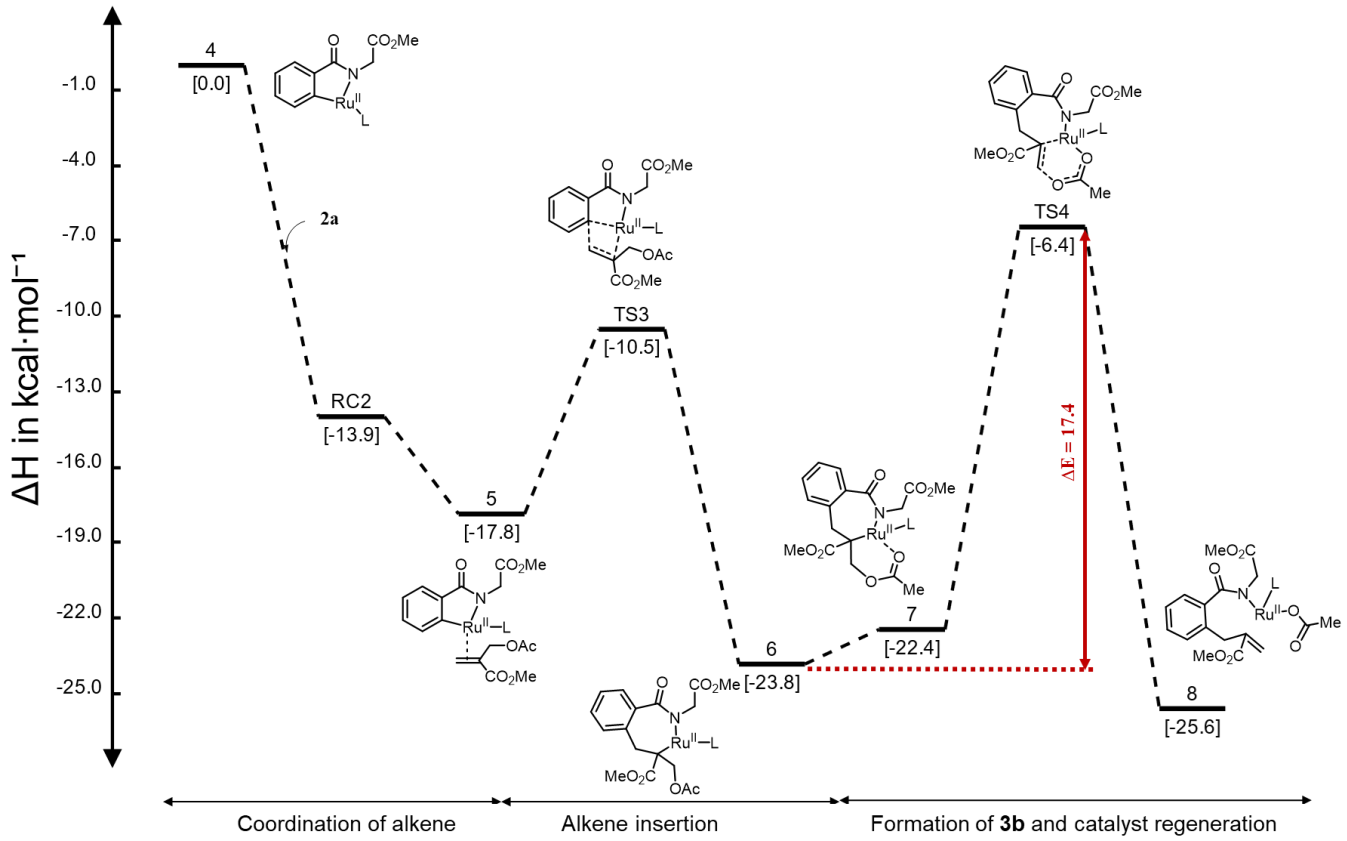


Figure S12: Solvent-corrected (dichloroethane) enthalpy profile for the known mechanism at M06L/BS-II level of theory

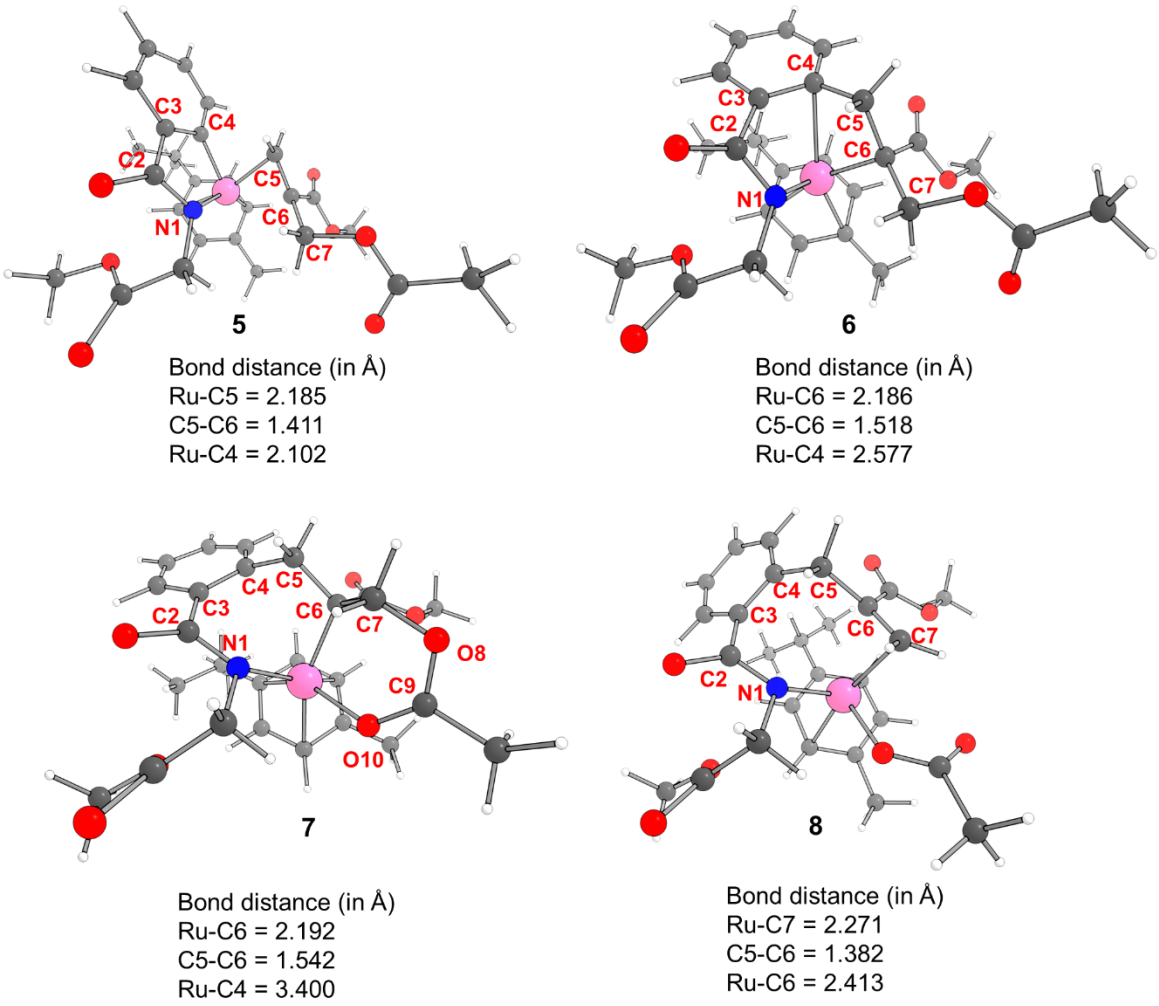


Figure S13: DFT optimized structures of species **5-8** with relevant structural parameters which are involved in *path I* (olefin insertion mechanism). Color code: Ru (pink), O (red), C (grey), N (blue) and H (white)

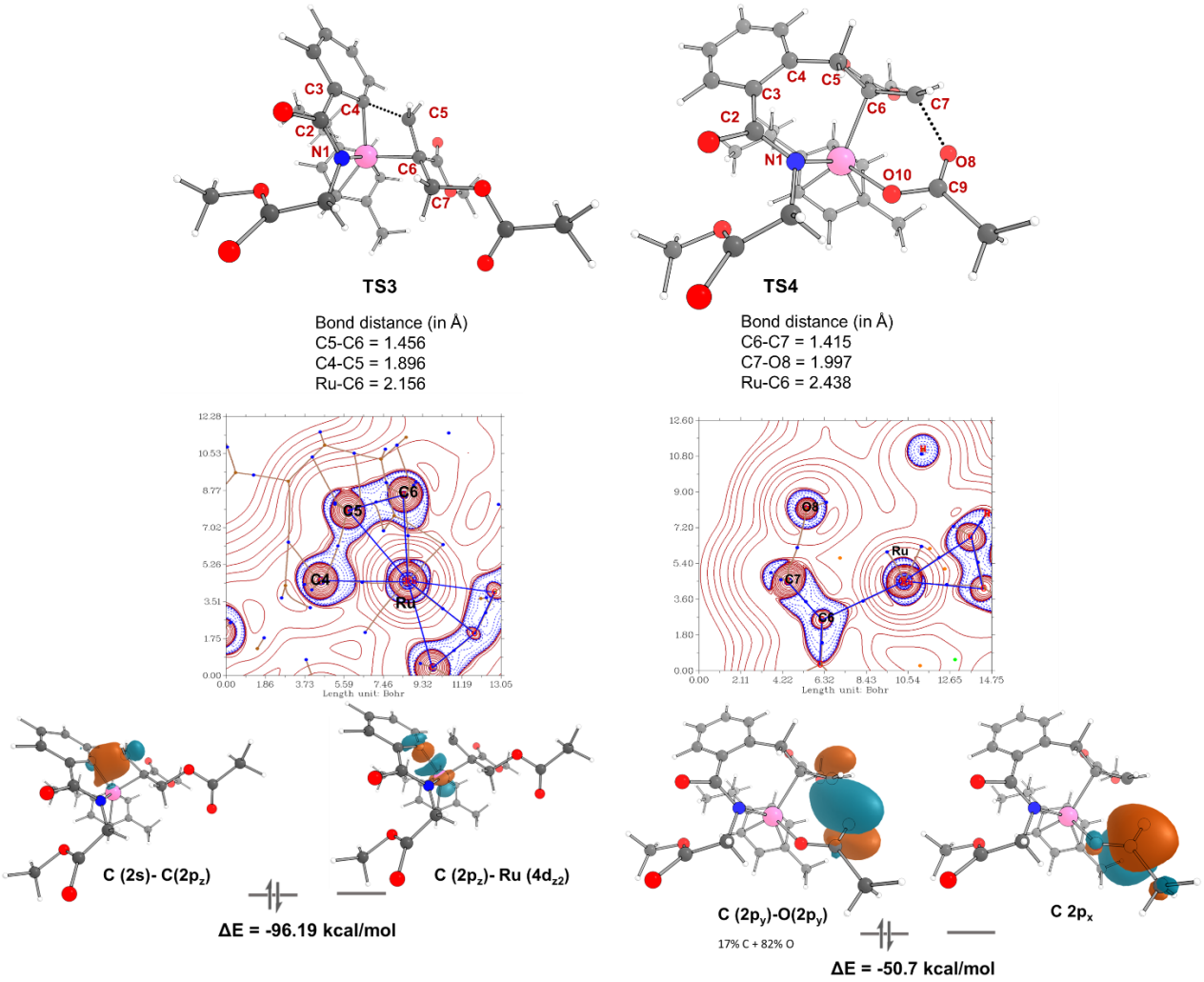


Figure S14: DFT-optimized structures of **TS3** and **TS4** with relevant structural parameters (left); Contour plot of the Laplacian of the electron density along with the bond critical points (blue dots) and bond path (center); NBO representing the most stabilizing interaction involved in the transition state (right). The ΔE here represents donor–acceptor interactions obtained from second-order perturbation analysis. Color code: Ru (pink), O (red), C (grey), N (blue) and H (white)

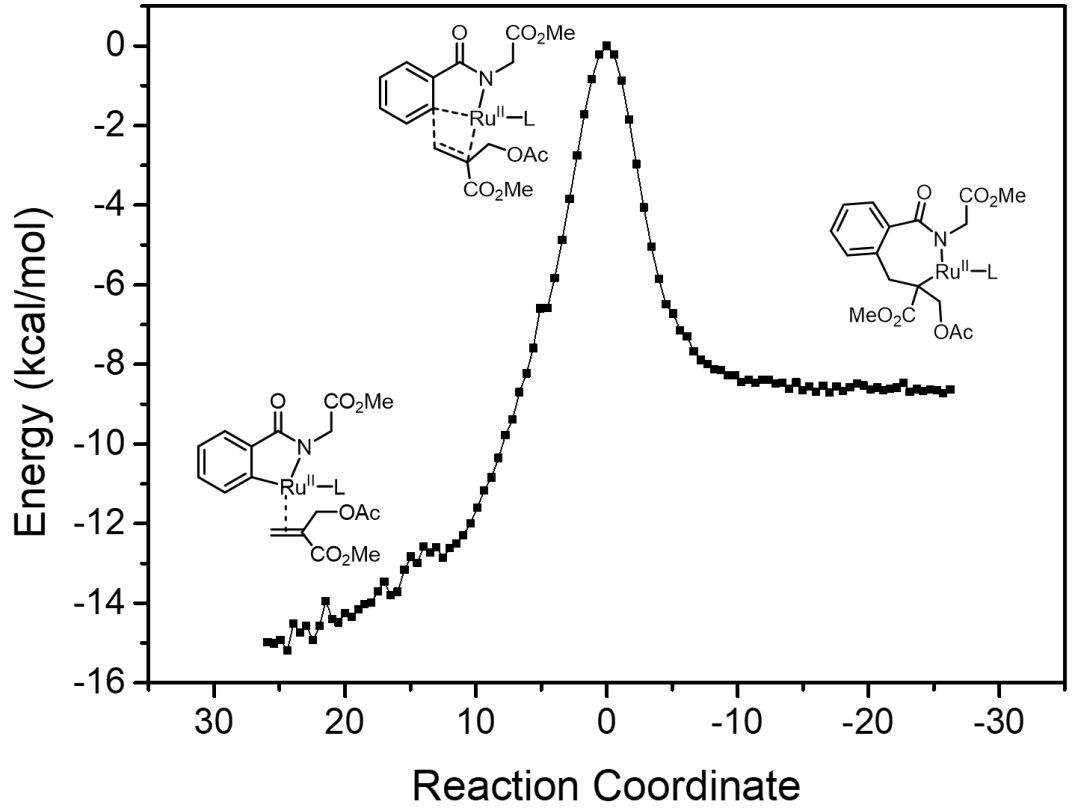


Figure S15: IRC path corresponding to the TS3 involves the migration of the alkene to the Ru – C bond (alkene insertion)

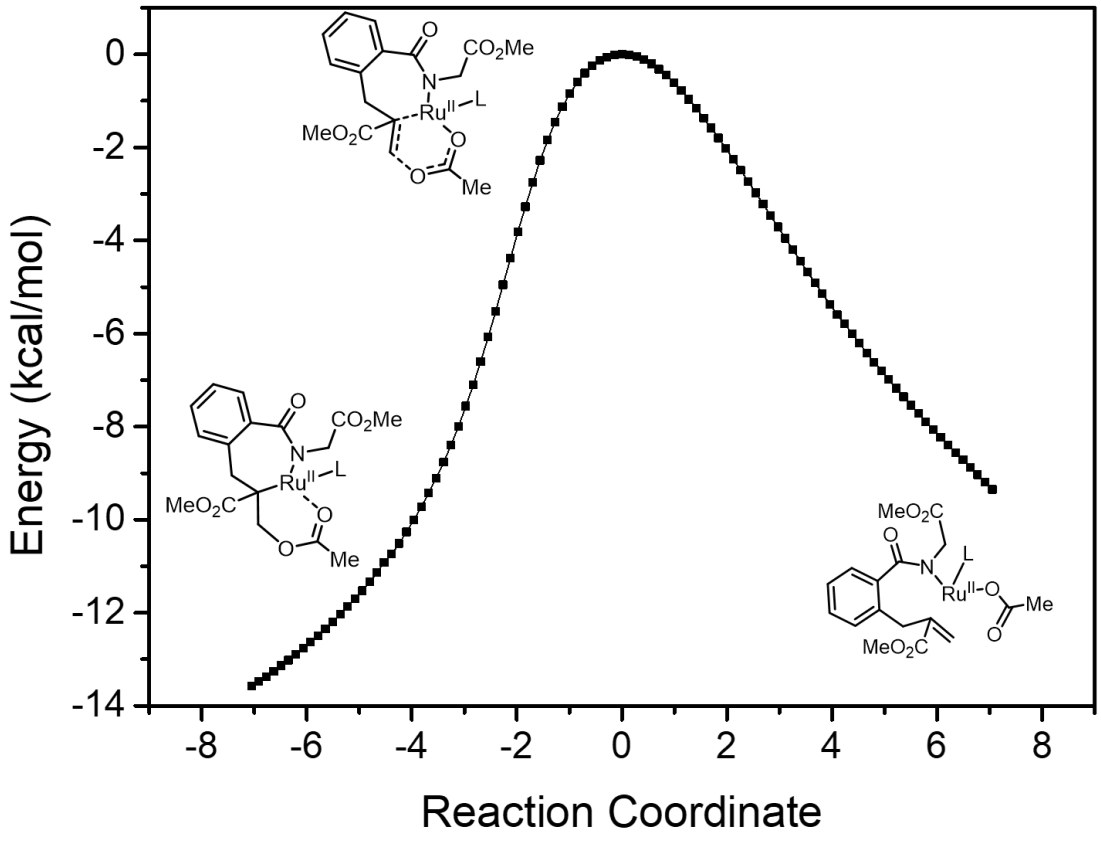


Figure S16: IRC path corresponding to the **TS4**, which involves the cleavage of the C-O bond to eliminate the β-acetate.

Formation of η^1-Ru(IV)allyl species 10

Control experiments revealed that the formation of the η^1-Ru(IV)allyl complex (**B**) takes place with the reaction of [Ru(*p*-cymene)Cl_2]$_2$ and **2a,** and ^{1}H NMR, MS-ESI, HRMS, and LC-MS techniques well characterize this. Here we hypothesize the formation of the η^1-Ru(IV)allyl intermediate, where the [Ru(*p*-cymene)Cl_2] (after breaking the dimer) initially interacts with **2a** and forms a reaction complex (**RC3**) which is ~2.6 kcal/mol higher than the unreacted species. The **RC3** becomes unstable as a result of species **2a**'s inability to attach to the Ru(II) center due to the coordinatively saturated environment in [$RuCl_2$(p-cymene)] species. On the other hand, the formation of **RC3** is a highly enthalpically driven process where **RC3** is stabilized by ~12.8 kcal/mol compared to unreacted species. The next step involves the removal of one of the Cl^- ions from [$RuCl_2$(p-cymene)] by the Ag^+ ions present in the solution, resulting in the formation of charged species **9**. In species **9**, Ru(II) center interacts with C=C bond in η^2-fashion, while the O atom of the acetate group is weakly attached to the Ru(II) center. The Ru-C2/Ru-C3 bond distances are 2.574Å/2.686Å, while the Ru-O7 bond distance is 2.258Å, further confirming the binding of both acetate and C=C bond with the Ru(II) center in **9** (see Figure S20). Interestingly, we have observed a lengthening of the C4-O5 bond (1.533 Å) in **9** compared to the **2a** present in the **RC3** (1.442 Å), indicative of the weakening of the C-O bond in species **9** (see Figure S20). In the next step, a paltry energy barrier (**TS5**) causes the C-O bond cleavage resulting in the formation of species **10**, which is stabilized by ~1.5 kcal/mol compared to species **9**. As a result of the C-O bond cleavage, we observed the formation of the allyl cation and acetate anion where the former is coordinated in the η^3-fashion to the Ru(II) center (see Figure S20). The Ru-C2/C3/C4 bond distances are 2.234 Å/2.251 Å/2.321Å in species **10**, representing highly symmetric allyl coordination to the Ru(II) center. Finally, η^3-Ru(II) allyl complex rearranges and forms the η^1-Ru(IV)allyl complex (**11**) via the transition state (**TS6**) with a barrier height of ~4.7 kcal/mol. In **TS6**, we noticed a slipping of allyl carbon atoms from η^3-mode to η^1-mode, followed by two-electron transfer to generate species **11**, which is stabilized by ~26.5 kcal/mol compared to species **10** (see Figure S17). In species **11**, we have noticed that C3-C4/C2-C3 bond distances (1.355 Å /1.434 Å) are asymmetric in nature compared to **10** (where both the C3-C4/C2-C3 bond distances (1.393 Å /1.420 Å), which indicates a η^1-type coordination of the allyl group in **11**. Additionally, we have also checked the formation of the η^1-Ru(IV)allyl complex with [Ru(*p*-cymene)Cl_2]$_2$ and allyl agent **2** (allyl acetate) without the ester group at β-position (see Figure S19). Our calculations indicate that the formation of η^3-Ru(II)allyl or η^1-Ru(IV)allyl complex is a highly endergonic process when species **2** has no ester group at β-position. The electron-withdrawing nature of the ester group facilitates the two-electron transfers from Ru(II) center and helps in stabilizing the η^1-Ru(IV)allyl complex.

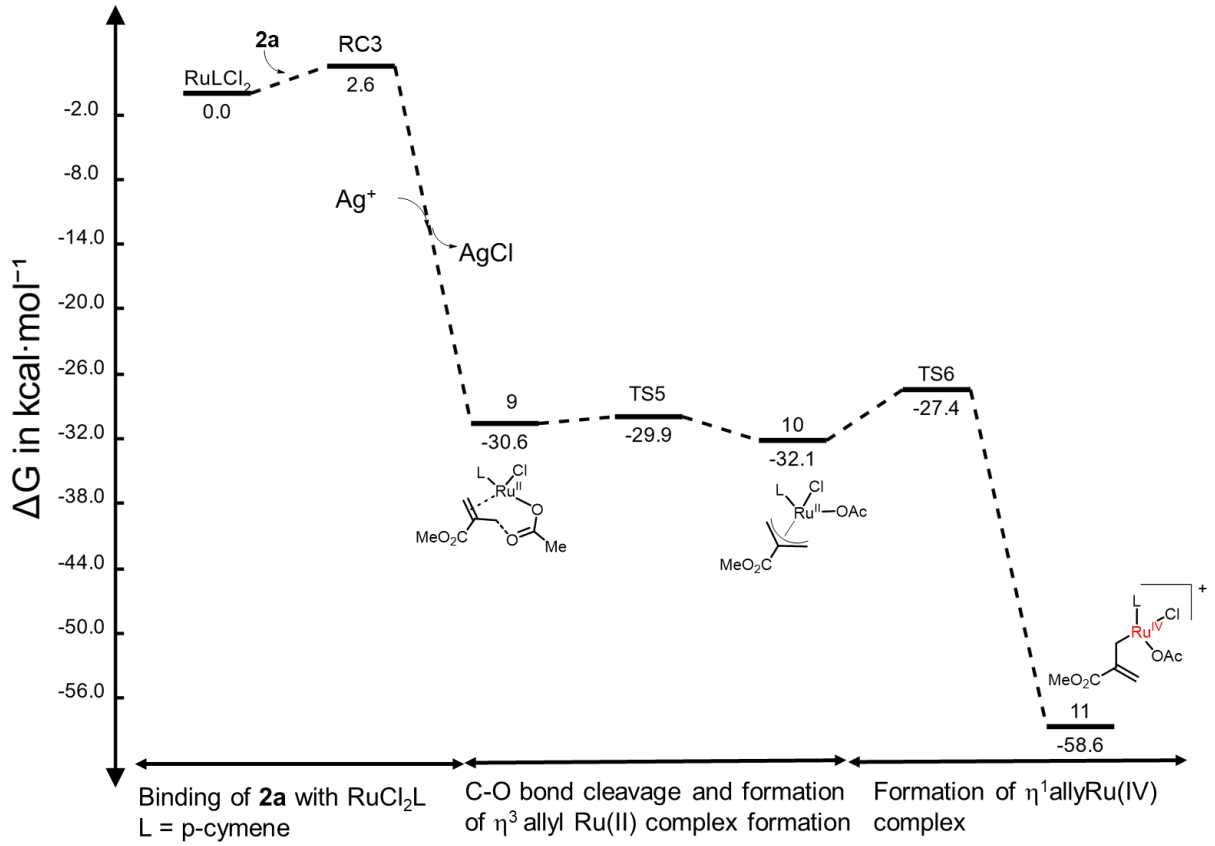


Figure S17: Solvent-corrected free energy profile for the formation of species **11** computed at M06L/BS-II level of theory

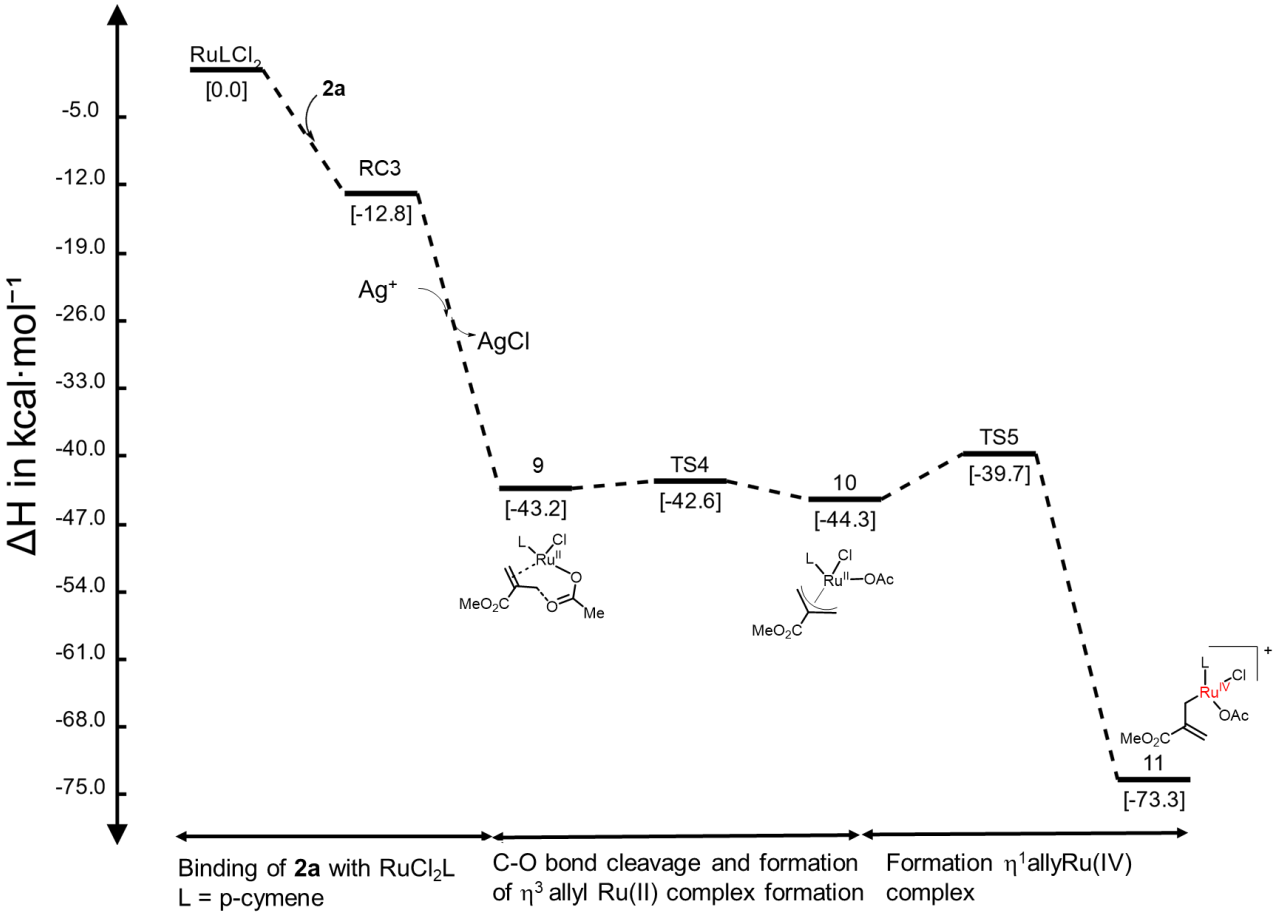


Figure S18: Solvent-corrected enthalpy profile for the formation of species **11** computed at M06L/BS-II level of theory

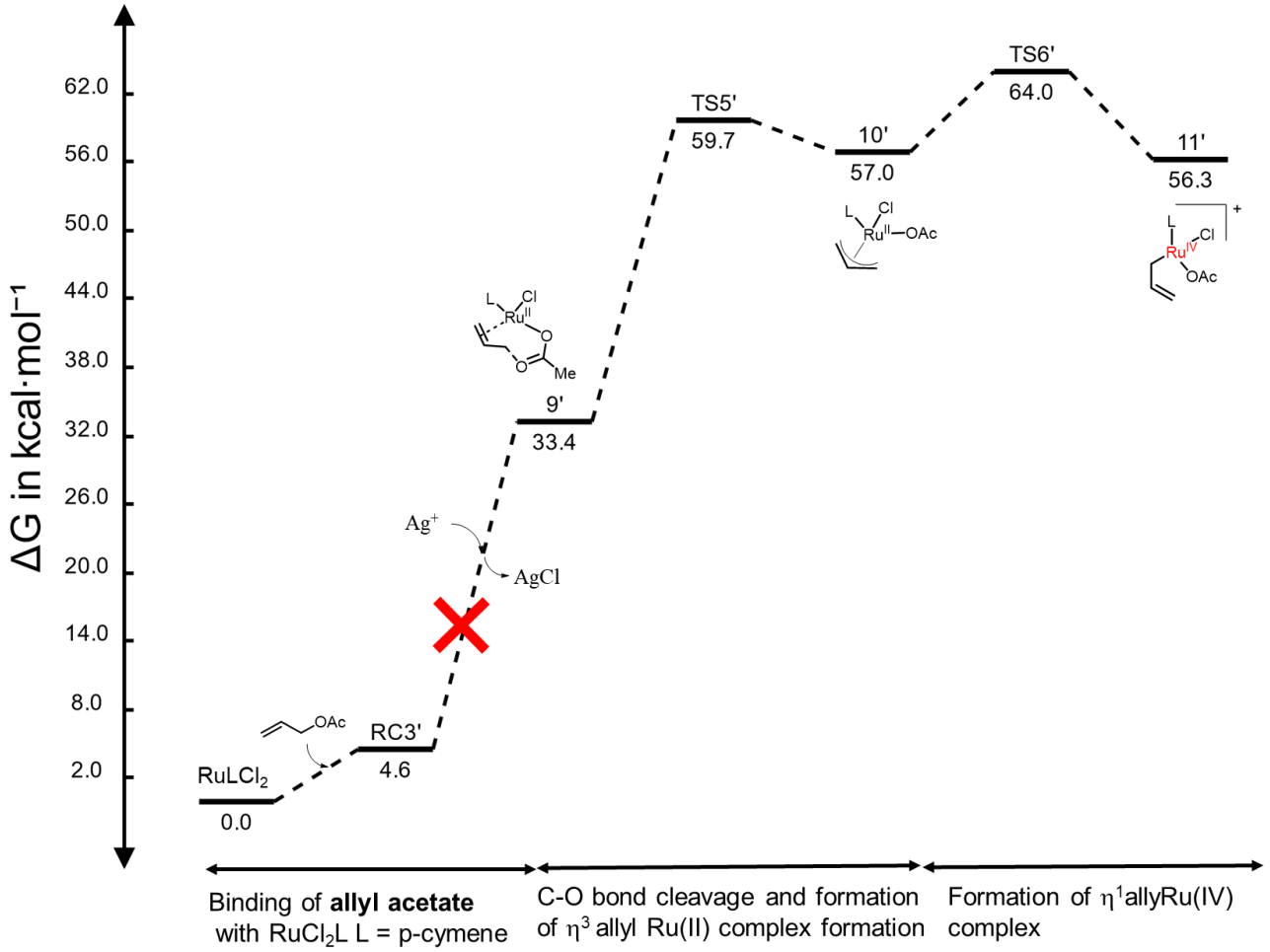


Figure S19: Solvent-corrected free energy profile for the formation of η^1-Ru(IV)allyl complex from [Ru(*p*-cymene)Cl_2]$_2$ and allyl acetate **2** without the ester group at β-position computed at M06L/BS-II level of theory

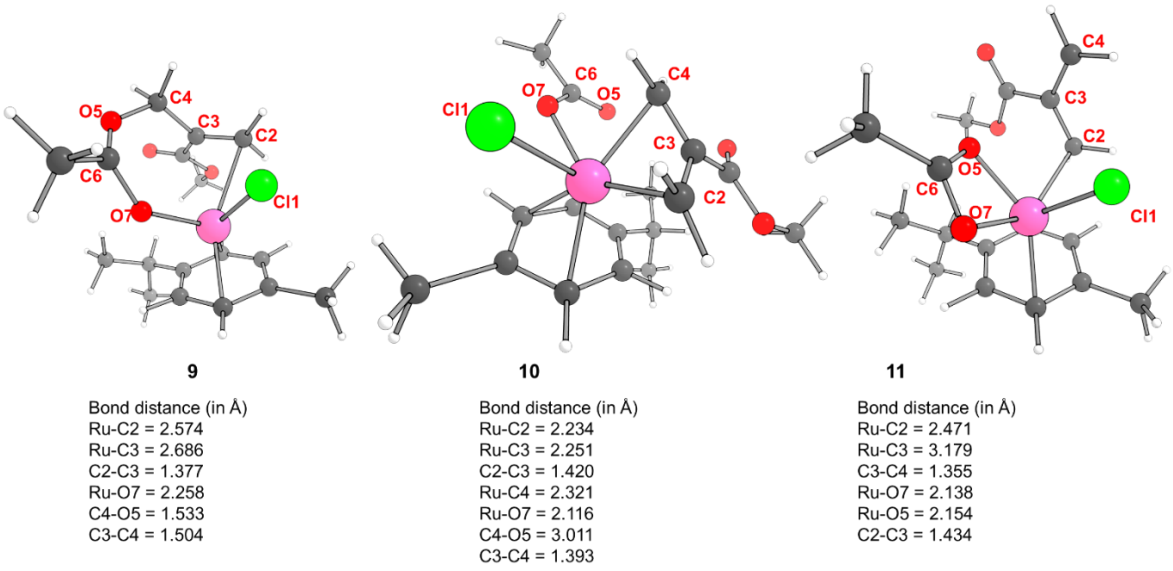


Figure S20: DFT optimized structures for all intermediates involved in the formation of η^1-Ru(IV)allyl complex (**11**). Colour code: Color code: Ru (pink), Cl (green), O (red), C (grey), N (blue) and H (white)

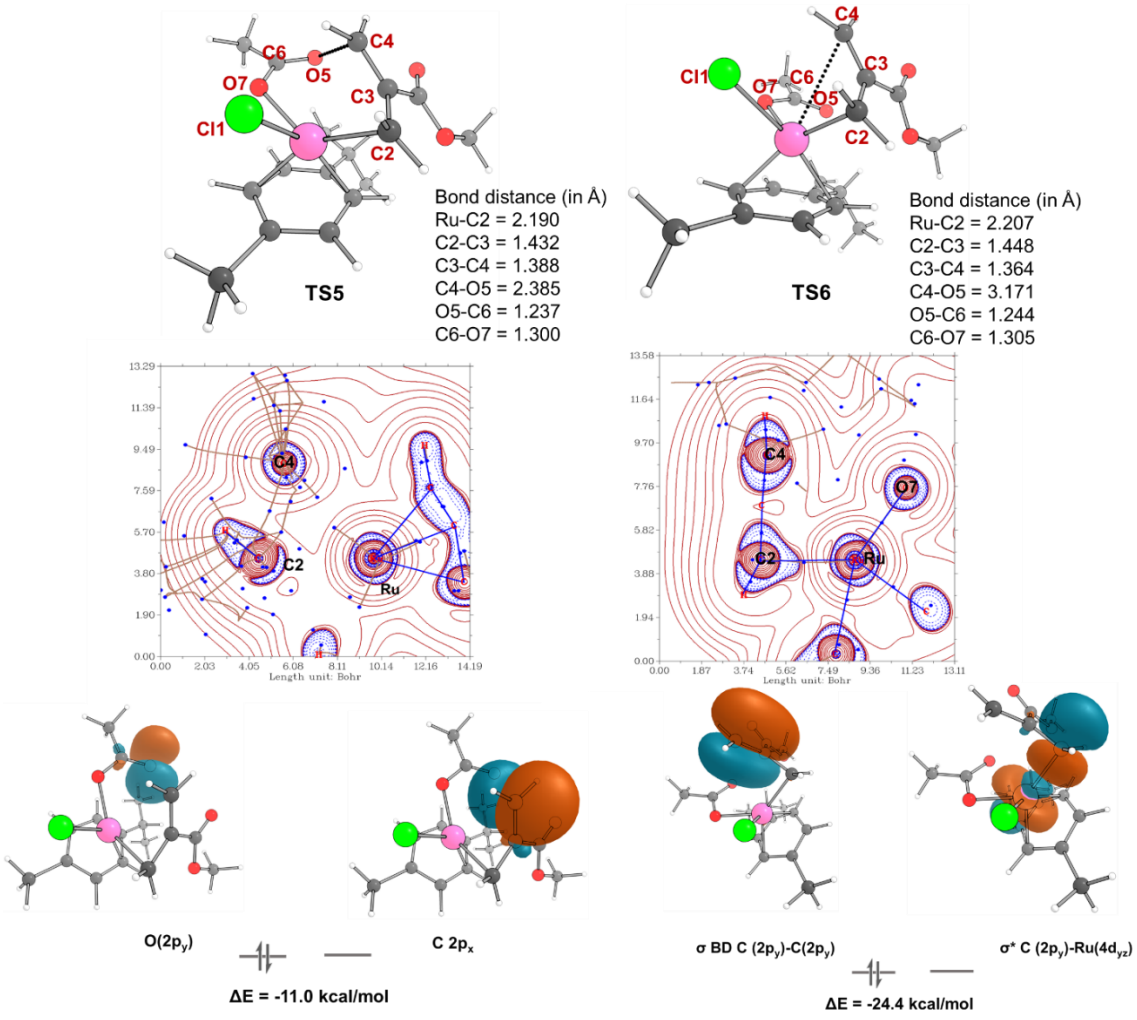


Figure S21: DFT optimized structures of **TS5** and **TS6** with relevant structural parameters (left); Contour plot of the Laplacian of the electron density along with the bond critical points (blue dots) and bond path (center); NBO representing the most stabilizing interaction involved in the transition state (right). The ΔE here represents donor–acceptor interactions obtained from second-order perturbation analysis. Color code: Ru (pink), Cl (green), O (red), C (grey), N (blue) and H (white)

C(sp^2)–H Allylation from Ru(IV)allyl complex (11) via redox mechanism (*Path II*)

The free energy charge for forming species **11** is substantial, and the process is highly exergonic in nature. It is clear from the estimated energy profile that, in contrast to species **4** (ruthanacycle), the formation of species **11** is a relatively faster process. Here, we have hypothesized that species **11** acts as an allyl source for the C–H allylation step by transferring the allyl group to the ruthanacyle (**4**) intermediate. In this step, **11** binds with species **4** (ruthanacyle) and forms a stable adduct (**12**), which is ~7.2 kcal/mol more stable than the unreacted species **11** and **4**. In species **12**, we have observed that the terminal carbon (C4) of the allyl group in species **11** forms a bond with the Ru(II) center of species **4** (see Figure S22a). In species **12**, the C3-C4 bond distance is significantly elongated (1.461 Å) compared to the C3-C4 bond distance in species **11** (1.355 Å), indicating the breaking of terminal C=C bond upon formation of the Ru2-C4 bond (2.201 Å) in **12** (see Figure S26). In **12**, the C2-C3 and C3-C4 bond distances are 1.410 Å and 1.461 Å, respectively, indicating the shortening of the C2-C3 bond in **12** compared to **11**. We have plotted the Laplacian of the electron density, which shows the presence of the bond critical points (BCPs) between the Ru2-C4 bond and Ru1-C2 bond, indicating the binding of allyl group with both the Ru centers (see Figure S28). We have also computed the energy decomposition analysis to understand the nature of binding energy in species **12** by fragmenting species **12** in the form of species **11** and **4** (ruthanacyle) (see Figure S22). EDA analysis shows the total binding energy of -95.6 kcal/mol between the two fragments, which is in line with the observed large negative free energy for **12** (see Table S7). The total intermolecular interaction energy is decomposed into the orbital (-126.7 kcal/mol), electrostatic (-60.9 kcal/mol), Pauli repulsion (107.5 kcal/mol) and dispersion (-15.9 kcal/mol) interactions. The most substantial stabilizing interaction is the orbital interaction, followed by the electrostatics and dispersion interactions which strongly stabilize the species **12**. To further understand the origin of the orbital interactions, we have further decomposed the orbital interactions using the ETS-NOCV approach as implemented in ADF 2021. Among numerous interactions, we observed the two most stabilizing orbital interactions of -53.7 kcal/mol and -4.5 kcal/mol (see Figure S22), contributing nearly ~ 60% of the total binding energy. NOCV difference density of the first interaction (-53.7 kcal/mol) shows electron flow from the Ru(II) center to the Ru(IV) center, which helps in stabilizing the species **12**. In the next step, [Ru^{II}Cl(OAc)(*p*-cymene)] leaves the adduct as a consequence of the two-electron redox process leading to the formation of species **13**. This redox process is highly exergonic, and species **13** is stabilized by ~ 30.2 kcal/mol compared to its predecessor. In the next step, the reductive elimination process occurs via the **TS7,** where the Ru-C4/ Ru-C9 bond breaks, followed by the formation of the C2-C9 bond. The activation energy barrier for this process is ~8.5 kcal/mol, and species **14** is stabilized by ~4.9 kcal/mol compared to species **13** (see Figure S23). Finally, the charged species takes an acetate anion from the coordination sphere and forms neutral species **15,** which is stabilized by ~9.4 kcal/mol compared to the charged species **14**. The final step involves species **15** interacting with the AcOH, where *N* is protonated, and the allylated product (**3b**) is released. At the same time, the OAc attaches to the Ru(II) centers and regenerates the catalyst [Ru (*p*-cymene)$(OAc)_2$] for the subsequent cycle.

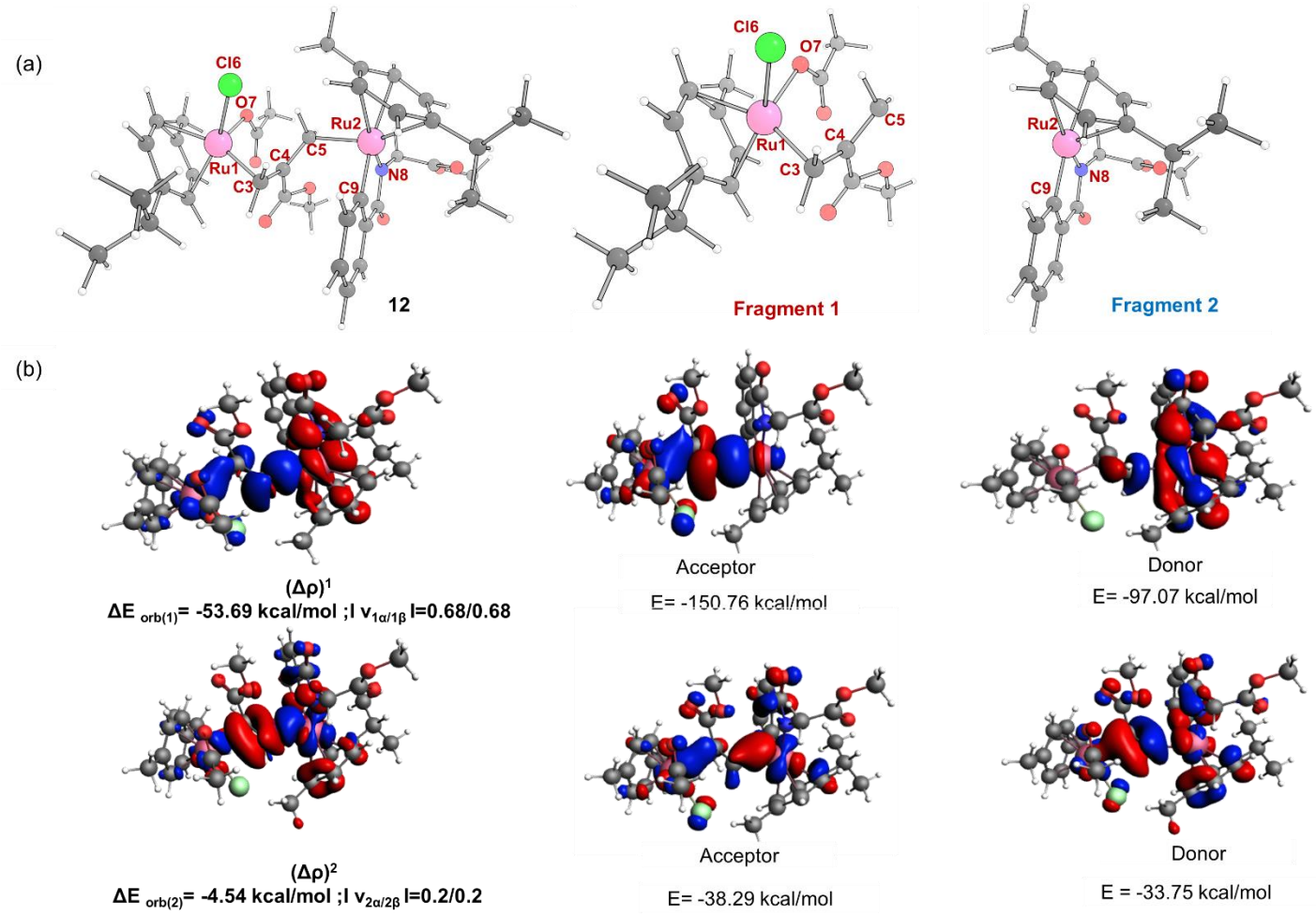


Figure S22: (a) DFT optimized structure of **12** (left), along with fragments used in EDA analysis (middle and right). (b) Contours of representative NOCV deformation densities (isovalue = 0.03 au) for **12** (left) and NOCV donor-acceptor orbitals. Color code: Ru (pink), Cl (green), O (red), C (grey), N (blue) and H (white)

Table S7: EDA analysis for species **12** using scalar relativistic DFT method. All the values are reported here in kcal/mol.

Parameters (kcal/mol)	**12**
Pauli Repulsion	107.5
Dispersion Interaction	-15.9
Electrostatic Interaction	-60.9
Orbital Interaction	-126.7
Total Binding Energy	-95.6
enthalpy of complexation	-80.3
free energy of complexation	-81.6
*The free energy and enthalpy of the formation of species **12** are taken directly from the calculations. The binding energy is calculated by fragmenting species **12** (see species **12**)*	

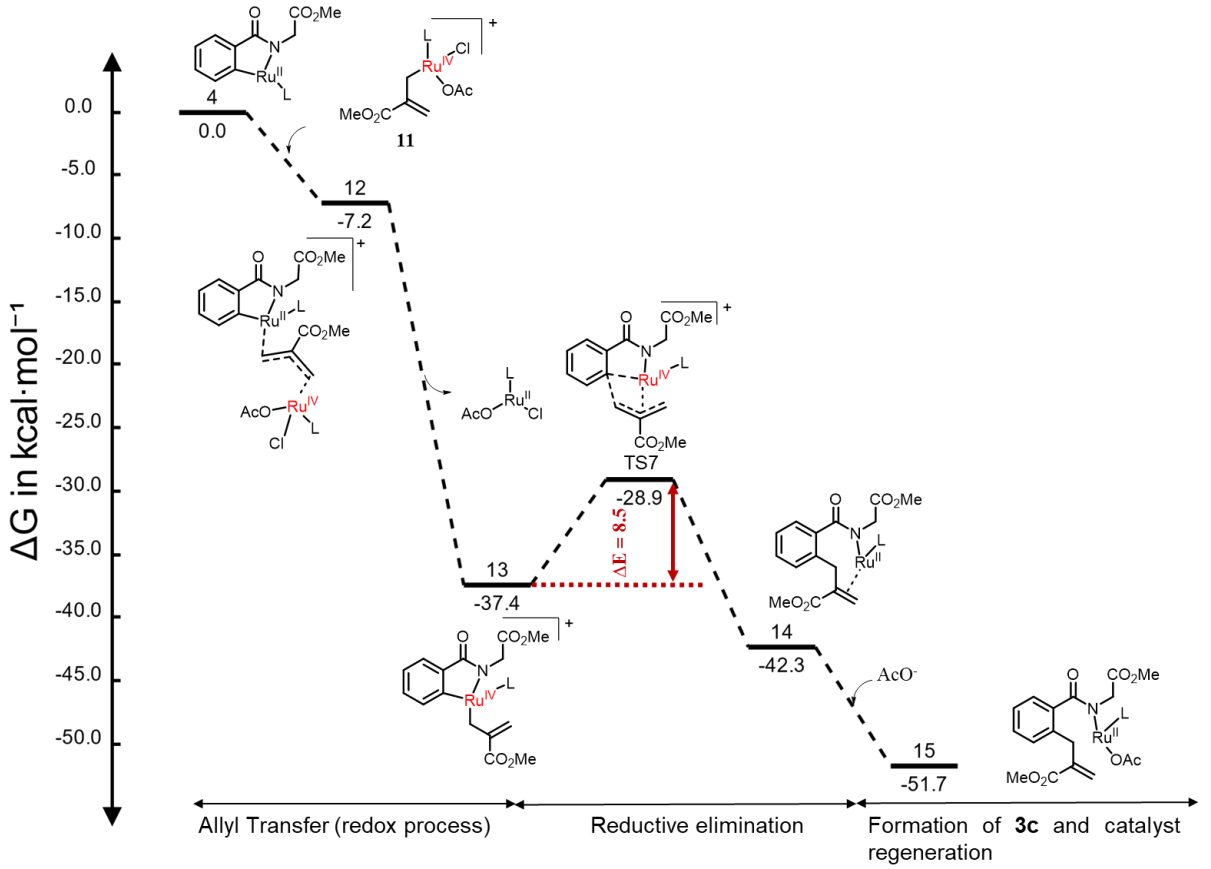


Figure S23: Solvent-corrected free energy profile for the proposed mechanism at M06L/BS-II level of theory

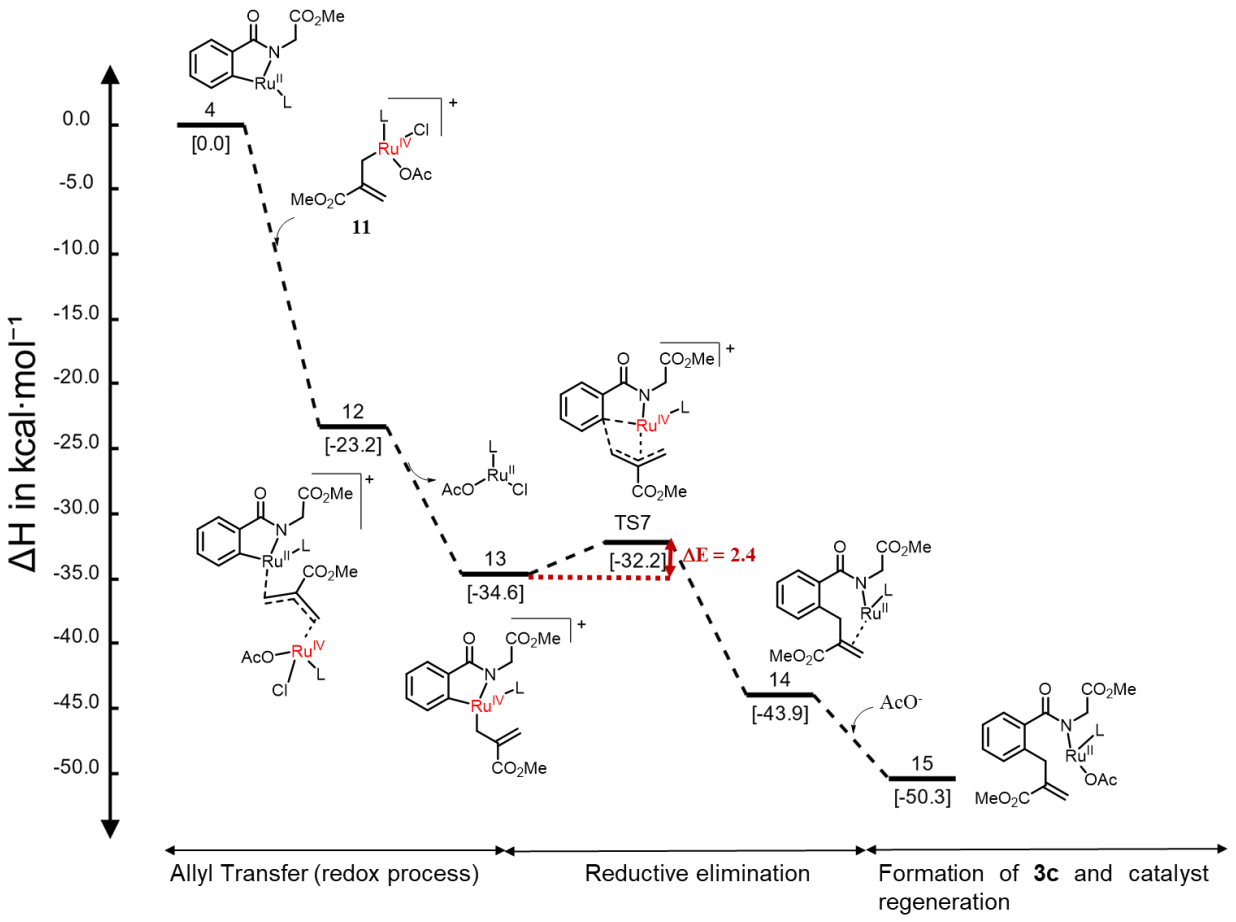


Figure S24: Solvent-corrected free energy profile for the proposed mechanism at M06L/BS-II level of theory

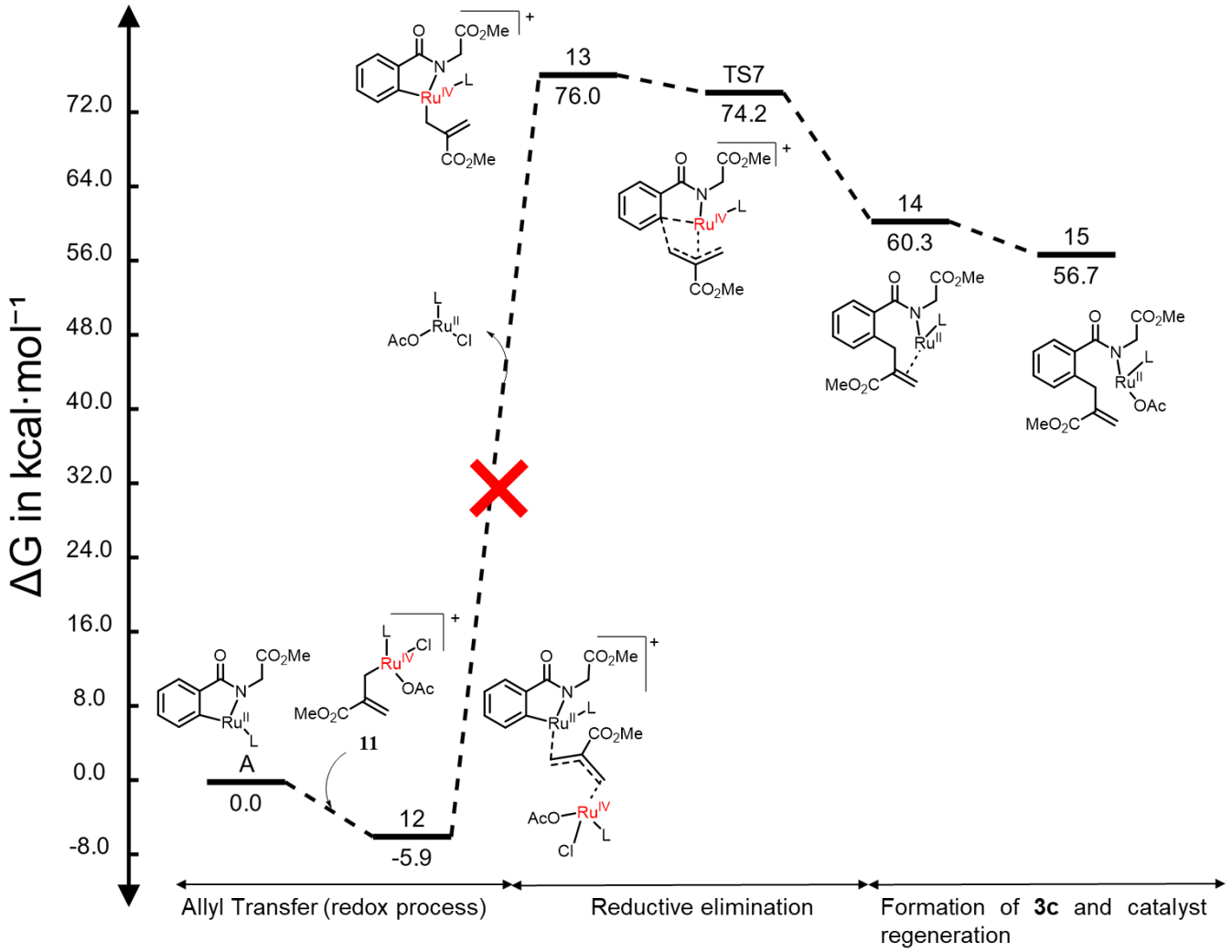
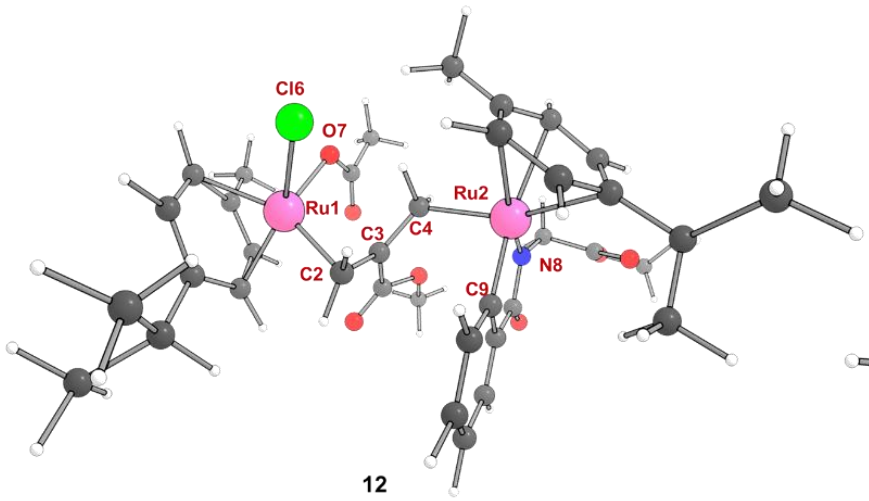
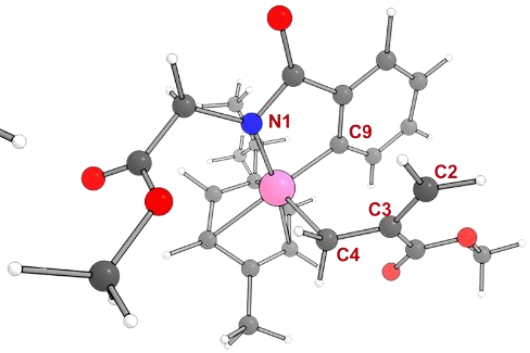


Figure S25: Solvent-corrected (methanol) free energy profile for the formation of **3c** computed at M06/BS-II level of theory



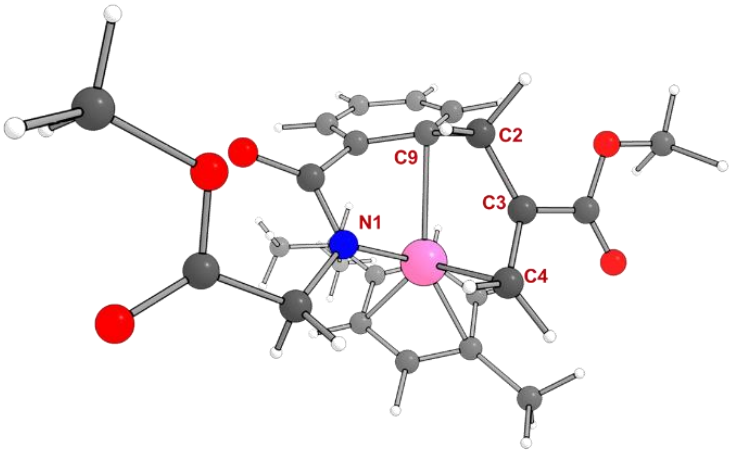
12

Bond distance (in Å)
Ru1-C3 = 2.200
Ru2-C9 = 2.201
Ru1-O7 = 2.096
C2-C3 = 1.410
C3-C4 = 1.461



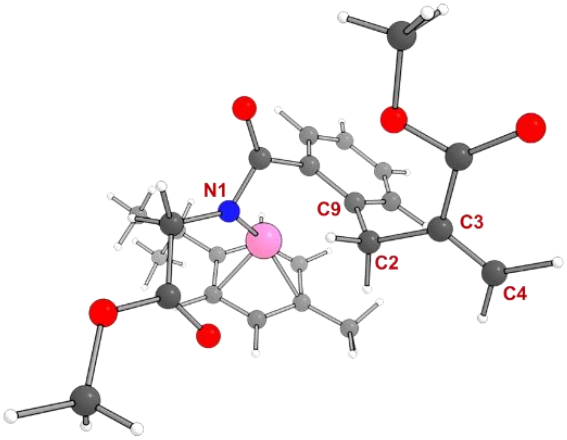
13

Bond distance (in Å)
Ru-C9 = 2.063
Ru-C4 = 2.193
C2-C3 = 1.458
C3-C4 = 1.348



14

Bond distance (in Å)
Ru-N1 = 2.086
Ru-C9 = 2.591
Ru-C4 = 2.263
Ru-C3 = 2.293
C2-C9 = 1.526
C2-C3 = 1.504
C3-C4 = 1.391



15

Bond distance (in Å)
Ru-N1 = 1.961
Ru-C9 = 2.646
C9-C2 = 1.517
C2-C3 = 1.505
C3-C4 = 1.336

Figure S26: DFT optimized structures for all the intermediates (**12-15**) involved in the *path II* mechanism. Colour code: Ru (pink), O (red), N (blue), Cl(light green), C (grey) and H (white)

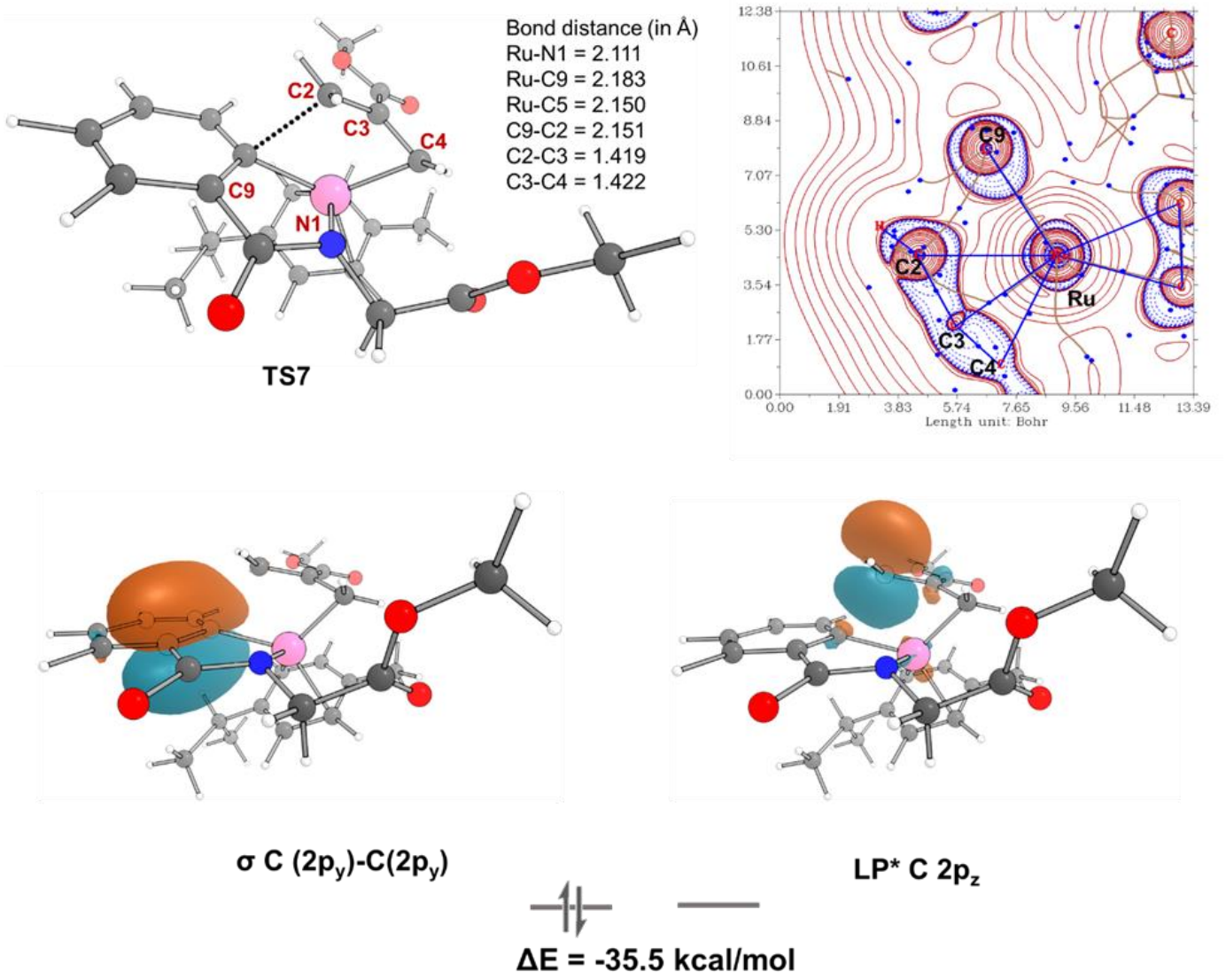


Figure S27: DFT-optimized structures of **TS7** with relevant structural parameters (top left); Contour plot of the Laplacian of the electron density along with the bond critical points (blue dots) and bond path (center); NBO representing the most stabilizing interaction involved in the transition state (bottom). The ΔE here represents donor–acceptor interactions obtained from second-order perturbation analysis. Color code: Ru (pink), O (red), C (grey), N (blue) and H (white)

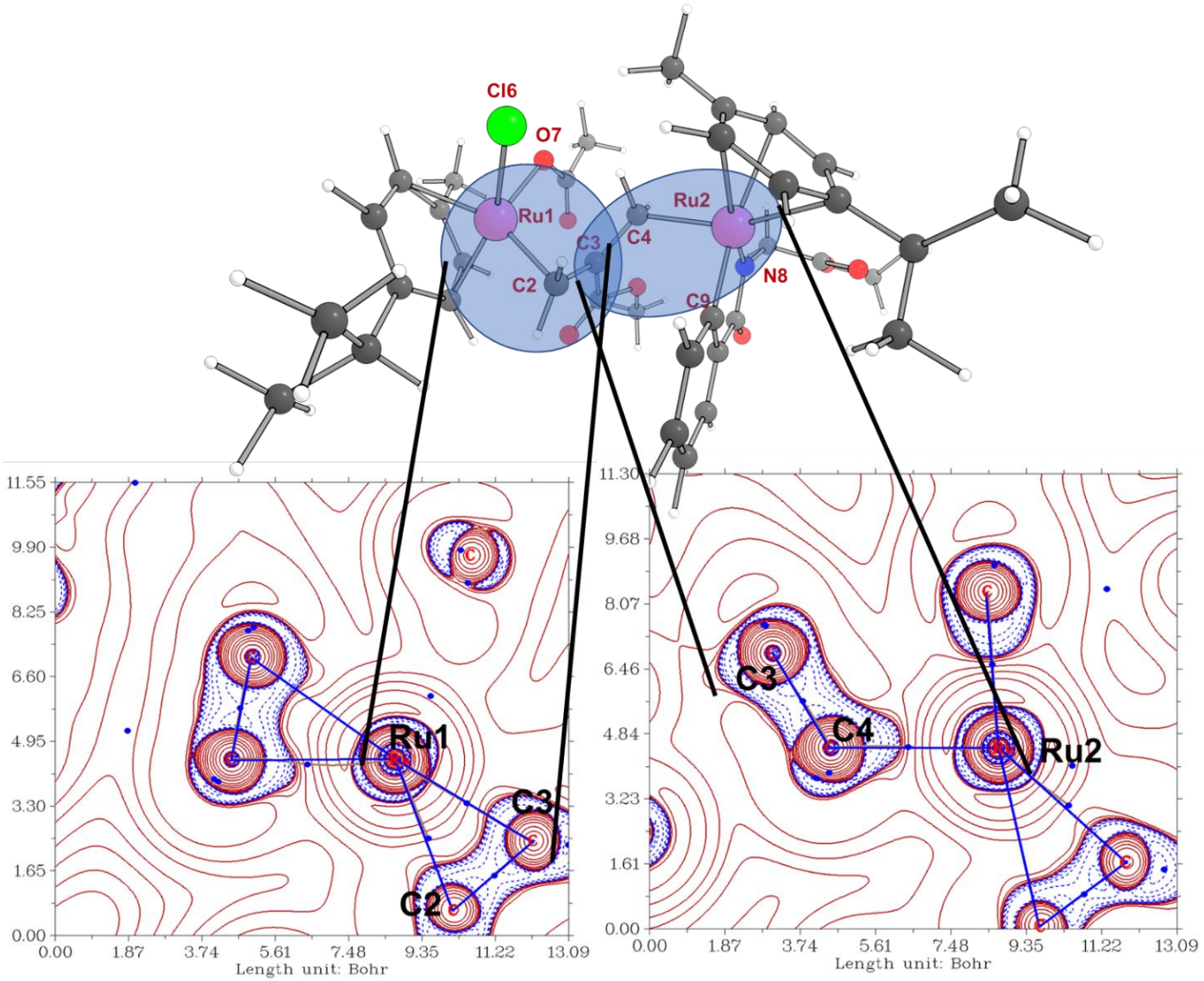


Figure S28: Contour plot of the Laplacian of the electron density along with the bond critical points (blue dots) and bond path (blue lines) for species **12** representing the formation of Ru1-C2 and Ru2-C4 bond in the adduct. Colour code: Ru (pink), O (red), N (blue), Cl(light green), C (grey) and H (white)

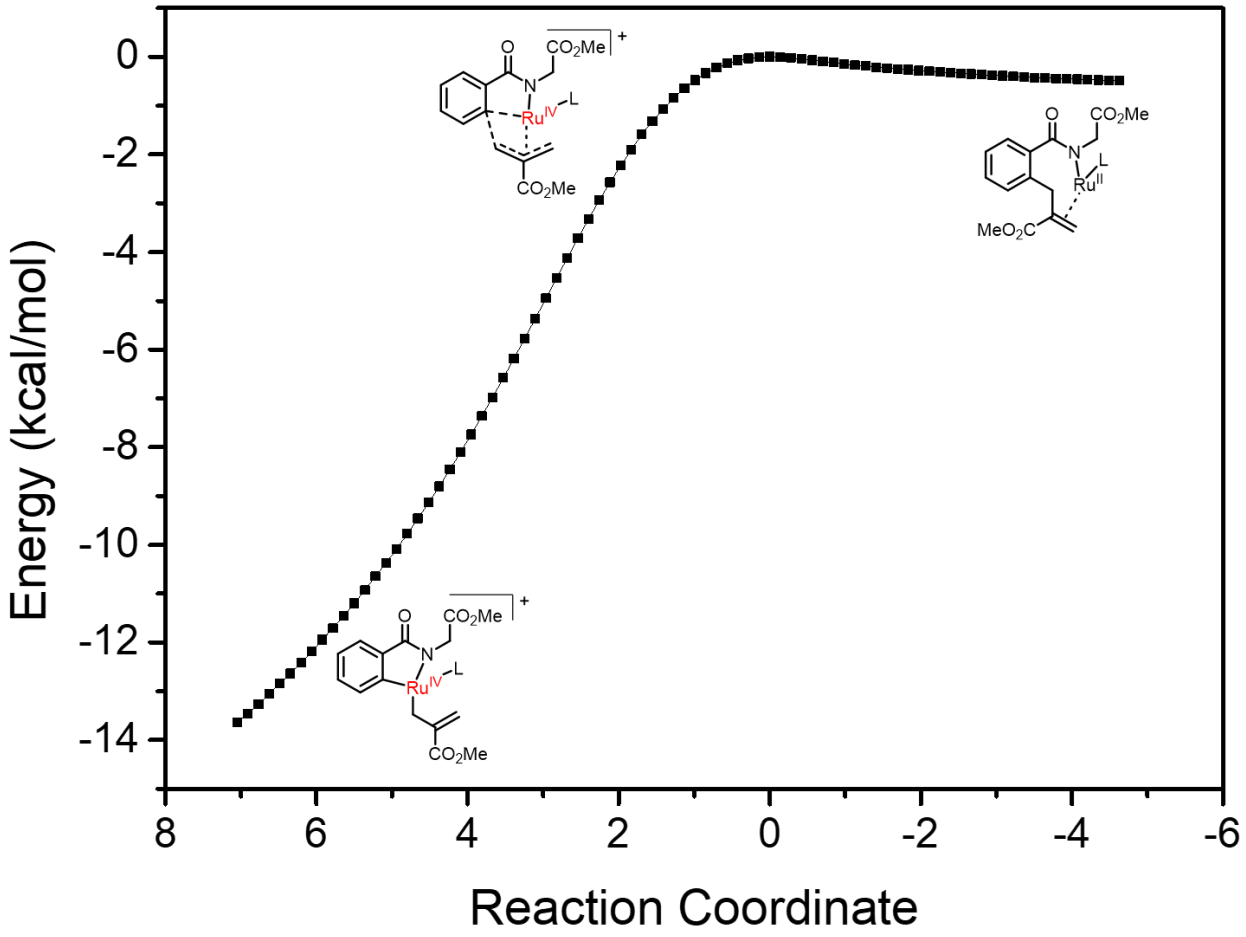


Figure S29: IRC path corresponding to TS7, which is the migration of alkene to the Ru – C bond (alkene insertion)

Coordinates for all optimized geometry in DFT calculations:

$[RuCl_2(p\text{-cymene})]_2$

E = -1028.441955 Eh
H = -1027.972307 Eh
G = -1027.597499 Eh
E_{sol} = -1028.193180 Eh
H_{sol} = -1027.723532 Eh
G_{sol} = -1027.348724 Eh

Ru	1.869793	-0.582014	0.457109
Cl	0.53903	1.644134	0.41663
Cl	1.944567	-0.321596	2.886479
C	3.501851	0.304056	-0.612955
C	2.528468	-0.176022	-1.555056
H	2.02333	0.533051	-2.206801
C	2.046111	-1.500035	-1.498876
H	1.186261	-1.76832	-2.106275
C	2.513054	-2.408366	-0.491603
C	3.499461	-1.949098	0.425882
H	3.771069	-2.57355	1.27192
C	3.992547	-0.609446	0.360674
H	4.617412	-0.247407	1.17112
C	3.89752	1.759767	-0.618016
H	3.034109	2.30668	-1.019147
C	5.077446	1.956338	-1.571002
H	5.959214	1.409178	-1.2187
H	5.346823	3.014605	-1.632676
H	4.849583	1.607331	-2.582887
C	4.198409	2.305068	0.771692
H	3.399662	2.063891	1.480898
H	4.306359	3.392223	0.73224
H	5.138383	1.905891	1.169481
C	1.89812	-3.760064	-0.344658
H	1.937311	-4.102616	0.691952
H	2.439037	-4.484768	-0.96355
H	0.853585	-3.751241	-0.662696
Ru	-1.738519	0.586236	-0.021643
Cl	-0.515631	-1.538592	0.722951
Cl	-0.952446	0.092206	-2.317233
C	-3.666558	-0.279258	0.36572
C	-3.116301	0.243375	1.586304
H	-2.914422	-0.445894	2.402504
C	-2.642574	1.570142	1.679921
H	-2.091864	1.880203	2.563212
C	-2.690806	2.441041	0.540986
C	-3.256369	1.941739	-0.666048
H	-3.191433	2.540305	-1.5698
C	-3.740643	0.599602	-0.748641
H	-4.007747	0.204122	-1.723887
C	-4.03833	-1.738753	0.279513
H	-3.386281	-2.259585	0.994216
C	-5.489012	-1.919032	0.729082
H	-6.175642	-1.406042	0.046224
H	-5.758999	-2.978767	0.736689
H	-5.65936	-1.521622	1.734485
C	-3.79183	-2.338336	-1.097803
H	-2.773996	-2.131624	-1.445174
H	-3.933456	-3.421878	-1.065106
H	-4.493192	-1.946922	-1.843334

C	-2.071207	3.796858	0.595218
H	-1.712401	4.107384	-0.388459
H	-2.811092	4.52988	0.935417
H	-1.226494	3.81812	1.286691

$RuCl_2$(p-cymene)

E = -514.207366 Eh
H = -513.973590 Eh
G = -513.798475 Eh
E_{sol} = -514.068755 Eh
H_{sol} = -513.834979 Eh
G_{sol} = -513.659864 Eh

Ru	0.521470000000	-0.130920000000	-0.018300000000
Cl	0.514120000000	-2.258660000000	1.048500000000
C	0.497060000000	1.893680000000	-0.820270000000
C	-0.705870000000	1.217090000000	-1.129380000000
C	-1.505100000000	0.592330000000	-0.110490000000
C	-1.063700000000	0.690030000000	1.237060000000
C	0.188110000000	1.283490000000	1.535400000000
C	0.997260000000	1.888660000000	0.512080000000
C	-2.748140000000	-0.160920000000	-0.514550000000
C	-3.131610000000	-1.278080000000	0.444090000000
C	2.356890000000	2.417070000000	0.826370000000
Cl	2.249640000000	-0.851120000000	-1.485910000000
C	-3.892750000000	0.839980000000	-0.695370000000
H	-2.530330000000	-0.608970000000	-1.494570000000
H	1.143710000000	2.228770000000	-1.625160000000
H	0.597380000000	1.183990000000	2.537220000000
H	-0.981030000000	1.071100000000	-2.171280000000
H	-1.574690000000	0.126520000000	2.010650000000
H	-4.792490000000	0.329060000000	-1.048980000000
H	-4.136940000000	1.324760000000	0.256200000000
H	-3.645080000000	1.624530000000	-1.416910000000
H	-3.958530000000	-1.858710000000	0.027410000000
H	-2.294600000000	-1.957600000000	0.632130000000
H	-3.475600000000	-0.881660000000	1.405940000000
H	3.021440000000	2.332660000000	-0.035880000000
H	2.296130000000	3.473970000000	1.109040000000
H	2.809560000000	1.874920000000	1.659670000000

RuCl(OAc) (p-cymene)

E = -727.634514 Eh
H = -727.346545 Eh
G = -727.123949 Eh
E_{sol} = -727.434678 Eh
H_{sol} = -727.146709 Eh
G_{sol} = -726.924113 Eh

Ru	0.242980000000	0.225820000000	0.016870000000

Cl	0.858140000000	-0.904010000000	2.090930000000
C	-0.265460000000	1.755830000000	-1.424500000000
C	-1.165280000000	0.671080000000	-1.538740000000
C	-1.865130000000	0.150750000000	-0.395550000000
C	-1.653120000000	0.793420000000	0.850800000000
C	-0.735620000000	1.880650000000	0.978500000000
C	-0.009650000000	2.356850000000	-0.147190000000
C	-2.696890000000	-1.101090000000	-0.537490000000
C	-2.676010000000	-1.974980000000	0.709030000000
C	1.063940000000	3.383280000000	0.004450000000
O	0.998430000000	-1.574810000000	-0.928620000000
C	2.189220000000	-1.127010000000	-0.853500000000
O	2.354100000000	0.076800000000	-0.471920000000
C	3.354630000000	-2.003570000000	-1.154250000000
C	-4.122200000000	-0.729290000000	-0.947360000000
H	3.637270000000	-2.522470000000	-0.233390000000
H	3.093200000000	-2.757450000000	-1.897860000000
H	4.210430000000	-1.415380000000	-1.487110000000
H	-2.241050000000	-1.674090000000	-1.357850000000
H	0.345540000000	2.040320000000	-2.276350000000
H	-0.474570000000	2.239720000000	1.969070000000
H	-1.223880000000	0.126320000000	-2.478160000000
H	-2.050270000000	0.344670000000	1.755940000000
H	-4.720720000000	-1.628640000000	-1.118450000000
H	-4.613780000000	-0.148160000000	-0.159290000000
H	-4.143030000000	-0.131560000000	-1.864000000000
H	-3.159840000000	-2.933560000000	0.504310000000
H	-1.652310000000	-2.167750000000	1.047310000000
H	-3.224760000000	-1.511390000000	1.536430000000
H	1.898990000000	3.182230000000	-0.670950000000
H	0.673670000000	4.379820000000	-0.229720000000
H	1.450370000000	3.402770000000	1.025480000000

Ru(p-cymene) $(OAc)_2$

E = -940.780236 Eh
H = -940.438284 Eh
G = -940.169971 Eh
E_{sol} = -941.045285 Eh
H_{sol} = -940.703333 Eh
G_{sol} = -940.435020 Eh

Ru	0.207740000000	-0.451260000000	-0.119120000000
O	1.177120000000	1.281420000000	-0.713340000000
C	0.555910000000	2.377900000000	-1.054580000000
C	1.518310000000	3.499860000000	-1.381020000000
C	-0.655940000000	-1.246750000000	-1.924520000000

O	-0.662790000000	2.547450000000	-1.093780000000
C	-2.779640000000	0.911800000000	0.483160000000
C	0.781420000000	-3.306330000000	-1.542700000000
O	1.086300000000	0.164810000000	1.771430000000
C	2.220040000000	-0.278120000000	1.396580000000
C	3.452120000000	0.019620000000	2.181330000000
O	2.280250000000	-0.952340000000	0.318150000000
H	1.937180000000	3.896790000000	-0.451640000000
H	2.357030000000	3.138800000000	-1.979830000000
H	1.001390000000	4.306830000000	-1.900420000000
H	-2.834200000000	1.674350000000	-0.300630000000
H	1.412460000000	-2.883610000000	-2.327590000000
H	3.889100000000	0.947430000000	1.801060000000
H	3.216600000000	0.165970000000	3.236110000000
H	4.191570000000	-0.772840000000	2.059880000000
C	-0.235440000000	-2.317750000000	-1.075920000000
C	-0.734310000000	-2.371210000000	0.260410000000
C	-1.515010000000	-0.229480000000	-1.427640000000
C	-1.958890000000	-0.223710000000	-0.080310000000
C	-1.536820000000	-1.312520000000	0.752570000000
H	-1.753340000000	-1.273770000000	1.817800000000
H	-1.697530000000	0.656360000000	-2.025840000000
H	-0.223530000000	-1.153670000000	-2.915750000000
H	-0.355500000000	-3.127160000000	0.941560000000
C	-4.188940000000	0.419270000000	0.808600000000
H	-4.811690000000	1.246080000000	1.162580000000
H	-4.681080000000	-0.022760000000	-0.063370000000
H	-4.171910000000	-0.339450000000	1.600290000000
C	-2.111560000000	1.550720000000	1.694860000000
H	-1.126850000000	1.940620000000	1.425750000000
H	-2.721250000000	2.377090000000	2.072260000000
H	-1.980250000000	0.837810000000	2.517310000000
H	0.288410000000	-4.197300000000	-1.946660000000
H	1.429930000000	-3.618380000000	-0.721230000000

RC1

E = -1608.460917Eh
H = -1607.902003 Eh
G = -1607.447904 Eh
E_{sol} = -1608.929481 Eh
H_{sol} = -1608.370567 Eh
G_{sol} = -1607.916468 Eh

Ru	2.493520000000	-0.047110000000	-0.098380000000
O	1.337370000000	1.106620000000	-1.420770000000
C	0.136150000000	0.737050000000	-1.723570000000
C	-0.601990000000	1.715830000000	-2.608480000000
C	2.790340000000	-1.607790000000	-1.544790000000
O	-0.406830000000	-0.321230000000	-1.361850000000
C	1.262840000000	-2.281700000000	1.937410000000
C	4.933940000000	-0.442300000000	-2.274080000000
O	1.365180000000	1.072080000000	1.357880000000
C	2.087710000000	2.107660000000	1.141190000000
C	1.689090000000	3.428440000000	1.690450000000
O	3.124880000000	1.958080000000	0.418720000000
H	-1.678430000000	1.643520000000	-2.434880000000
H	-0.258360000000	2.739150000000	-2.447940000000

H	-0.416710000000	1.459370000000	-3.655950000000
H	1.471160000000	-1.564660000000	2.743790000000
H	4.353890000000	-0.126820000000	-3.144200000000
H	2.485880000000	4.161520000000	1.568510000000
H	0.791260000000	3.769370000000	1.159910000000
H	1.420540000000	3.333390000000	2.745140000000
C	4.052620000000	-1.039510000000	-1.227090000000
C	4.402650000000	-0.969910000000	0.163570000000
C	1.900050000000	-2.079820000000	-0.540130000000
C	2.246530000000	-1.964560000000	0.836150000000
C	3.538620000000	-1.448870000000	1.177020000000
H	3.785940000000	-1.280240000000	2.221360000000
H	0.887310000000	-2.339720000000	-0.821340000000
H	2.430860000000	-1.541040000000	-2.568710000000
H	5.296830000000	-0.420310000000	0.447420000000
C	-0.189160000000	-2.104920000000	1.514280000000
H	-0.848700000000	-2.154670000000	2.384840000000
H	-0.346380000000	-1.144790000000	1.015130000000
H	-0.509860000000	-2.894110000000	0.824400000000
C	1.532910000000	-3.691530000000	2.464810000000
H	2.563510000000	-3.811420000000	2.813800000000
H	0.865030000000	-3.920170000000	3.299970000000
H	1.354670000000	-4.438340000000	1.683390000000
H	5.682060000000	-1.167430000000	-2.613200000000
H	5.466900000000	0.431100000000	-1.889500000000
C	-4.072150000000	-1.260810000000	0.349190000000
C	-3.437490000000	-1.886780000000	-0.731270000000
C	-5.206920000000	-1.854550000000	0.909470000000
C	-3.936620000000	-3.085000000000	-1.233970000000
C	-5.701610000000	-3.051250000000	0.406930000000
C	-5.066690000000	-3.670130000000	-0.667820000000
H	-5.682390000000	-1.345580000000	1.742380000000
H	-3.440970000000	-3.562120000000	-2.075400000000
H	-6.584870000000	-3.502660000000	0.851200000000
H	-5.452550000000	-4.605220000000	-1.065380000000
C	-3.617500000000	0.027680000000	0.959280000000
O	-4.243280000000	0.565480000000	1.872020000000
N	-2.467360000000	0.555020000000	0.454820000000
C	-1.904840000000	1.759690000000	0.992110000000
H	-2.427000000000	1.966900000000	1.934800000000
H	-0.839170000000	1.630270000000	1.209610000000
C	-2.046320000000	2.987010000000	0.124870000000
O	-1.268860000000	3.921870000000	0.131700000000
O	-3.154470000000	2.950080000000	-0.636490000000
C	-3.355020000000	4.113800000000	-1.441640000000
H	-3.396950000000	5.011100000000	-0.820050000000
H	-2.539500000000	4.229480000000	-2.161000000000
H	-4.300740000000	3.958330000000	-1.958200000000
H	-1.927620000000	0.080480000000	-0.262060000000
H	-2.556840000000	-1.449650000000	-1.198810000000

1

E = -1608.458439 Eh
H = -1607.899894 Eh
G = -1607.448832 Eh
E_{sol} = -1608.930461 Eh

H_{sol} = -1608.371916 Eh
G_{sol} = -1607.920854 Eh

Ru	2.495080000000	-0.050560000000	-0.104580000000
O	1.336530000000	1.105990000000	-1.422570000000
C	0.134260000000	0.737810000000	-1.722830000000
C	-0.606830000000	1.720340000000	-2.601140000000
C	2.788660000000	-1.609720000000	-1.553290000000
O	-0.407650000000	-0.321800000000	-1.363440000000
C	1.264890000000	-2.287060000000	1.930000000000
C	4.932200000000	-0.444880000000	-2.283580000000
O	1.371500000000	1.069250000000	1.354940000000
C	2.094370000000	2.104210000000	1.136440000000
C	1.698120000000	3.425300000000	1.686640000000
O	3.129730000000	1.953670000000	0.411600000000
H	-1.682950000000	1.644320000000	-2.427290000000
H	-0.265540000000	2.743450000000	-2.434370000000
H	-0.421640000000	1.471130000000	-3.650370000000
H	1.474920000000	-1.571490000000	2.737240000000
H	4.351230000000	-0.127880000000	-3.152540000000
H	2.494430000000	4.158290000000	1.561020000000
H	0.797880000000	3.766130000000	1.160090000000
H	1.434210000000	3.330750000000	2.742550000000
C	4.051820000000	-1.043060000000	-1.236380000000
C	4.403610000000	-0.975560000000	0.153940000000
C	1.899140000000	-2.082250000000	-0.548120000000
C	2.247270000000	-1.969050000000	0.827840000000
C	3.540240000000	-1.454850000000	1.167760000000
H	3.788980000000	-1.287710000000	2.212010000000
H	0.885800000000	-2.340710000000	-0.828490000000
H	2.427920000000	-1.541280000000	-2.576660000000
H	5.298620000000	-0.427140000000	0.437450000000
C	-0.187630000000	-2.108670000000	1.509370000000
H	-0.845850000000	-2.159690000000	2.380870000000
H	-0.345180000000	-1.147660000000	1.012070000000
H	-0.509650000000	-2.896530000000	0.818620000000
C	1.534650000000	-3.697930000000	2.454810000000
H	2.565660000000	-3.819160000000	2.802160000000
H	0.867780000000	-3.927400000000	3.290540000000
H	1.354770000000	-4.443350000000	1.672440000000
H	5.679540000000	-1.169890000000	-2.624640000000
H	5.466040000000	0.427710000000	-1.898400000000
C	-4.071710000000	-1.258210000000	0.352080000000
C	-3.440790000000	-1.882080000000	-0.731780000000
C	-5.205830000000	-1.851960000000	0.913690000000
C	-3.942880000000	-3.078200000000	-1.236480000000
C	-5.703510000000	-3.046530000000	0.409090000000
C	-5.072280000000	-3.663300000000	-0.669020000000
H	-5.678340000000	-1.344720000000	1.749350000000
H	-3.449990000000	-3.553750000000	-2.080430000000
H	-6.586230000000	-3.497930000000	0.854430000000
H	-5.460430000000	-4.596800000000	-1.068100000000
C	-3.613340000000	0.027800000000	0.964640000000
O	-4.234870000000	0.563350000000	1.881590000000
N	-2.464920000000	0.555890000000	0.456930000000
C	-1.898500000000	1.757520000000	0.996920000000
H	-2.413600000000	1.959280000000	1.944690000000
H	-0.831310000000	1.626830000000	1.206150000000

C	-2.046540000000	2.990320000000	0.138470000000
O	-1.270690000000	3.926500000000	0.147850000000
O	-3.158180000000	2.956430000000	-0.617750000000
C	-3.365310000000	4.125450000000	-1.413480000000
H	-3.409240000000	5.017770000000	-0.784900000000
H	-2.552120000000	4.250060000000	-2.133920000000
H	-4.311780000000	3.970320000000	-1.928770000000
H	-1.927900000000	0.081680000000	-0.262170000000
H	-2.560520000000	-1.445140000000	-1.200240000000

2

E = -1379.490388 Eh
H = -1379.002224 Eh
G = -1378.603826 Eh
E_{sol} = -1379.889111 Eh
H_{sol} = -1379.400947 Eh
G_{sol} = -1379.002549 Eh

Ru	1.146087000000	-0.302970000000	-0.336150000000
O	1.234789000000	1.233749000000	-1.863940000000
C	1.621347000000	0.385972000000	-2.740250000000
C	1.817231000000	0.790359000000	-4.157810000000
C	1.177822000000	-1.747040000000	1.288213000000
O	1.827927000000	-0.808190000000	-2.356660000000
C	4.489456000000	-0.281850000000	-0.067290000000
C	-0.949840000000	-0.699410000000	2.196678000000
H	2.538918000000	0.137520000000	-4.649760000000
H	2.138467000000	1.831864000000	-4.219140000000
H	0.853995000000	0.698529000000	-4.668020000000
H	4.465774000000	-1.023590000000	-0.878610000000
H	-1.416610000000	-1.622840000000	1.845578000000
C	0.460814000000	-0.589810000000	1.720504000000
C	1.088708000000	0.675267000000	1.578368000000
C	2.465579000000	-1.614700000000	0.707299000000
C	3.138256000000	-0.354990000000	0.600468000000
C	2.407197000000	0.781110000000	1.026497000000
H	2.794734000000	1.772747000000	0.808876000000
H	2.919168000000	-2.489560000000	0.243850000000
H	0.681958000000	-2.713100000000	1.283177000000
H	0.528465000000	1.578351000000	1.803889000000
C	5.581923000000	-0.693970000000	0.920226000000
H	6.560691000000	-0.708510000000	0.431598000000
H	5.399554000000	-1.689150000000	1.336936000000
H	5.637279000000	0.011523000000	1.756717000000
C	4.786760000000	1.078012000000	-0.682770000000
H	3.980287000000	1.412171000000	-1.343370000000
H	5.709789000000	1.036394000000	-1.266770000000
H	4.931052000000	1.844763000000	0.086976000000

H	-0.979150000000	-0.700740000000	3.291524000000
H	-1.556140000000	0.138121000000	1.842054000000
C	-1.046690000000	-2.924480000000	-0.724160000000
C	0.081975000000	-3.295390000000	-1.461860000000
C	-1.621710000000	-3.848750000000	0.153608000000
C	0.649101000000	-4.555520000000	-1.288660000000
C	-1.039650000000	-5.098320000000	0.345391000000
C	0.102896000000	-5.452590000000	-0.371750000000
H	-2.531110000000	-3.562800000000	0.677091000000
H	1.518927000000	-4.839770000000	-1.876060000000
H	-1.481830000000	-5.801850000000	1.046066000000
H	0.552877000000	-6.431860000000	-0.230640000000
C	-1.687440000000	-1.578120000000	-0.854480000000
O	-2.922520000000	-1.495620000000	-0.787040000000
N	-0.849730000000	-0.517660000000	-1.038000000000
C	-1.529220000000	0.748480000000	-1.216400000000
H	-1.122020000000	1.526580000000	-0.559280000000
H	-2.591110000000	0.621155000000	-0.959440000000
C	-1.464300000000	1.256350000000	-2.631910000000
O	-1.241340000000	0.600441000000	-3.626380000000
O	-1.732490000000	2.583338000000	-2.659460000000
C	-1.710120000000	3.160055000000	-3.963070000000
H	-2.380170000000	2.624520000000	-4.639960000000
H	-0.698440000000	3.128029000000	-4.379710000000
H	-2.031330000000	4.193905000000	-3.842140000000
H	0.506422000000	-2.591830000000	-2.171340000000

3

E = -1379.486591 Eh
H = -1378.999357 Eh
G = -1378.602066 Eh
E_{sol} = -1379.879420 Eh
H_{sol} = -1379.392186 Eh
G_{sol} = -1378.994895 Eh

C	-0.046420000000	1.673572000000	1.512121000000
C	1.144369000000	0.939656000000	1.373130000000
C	-0.199830000000	2.648427000000	2.495890000000
C	2.167201000000	1.175265000000	2.297746000000
C	0.834900000000	2.881025000000	3.396307000000
C	2.008790000000	2.132640000000	3.304204000000
H	-1.133960000000	3.205105000000	2.536779000000
H	3.101685000000	0.615630000000	2.237147000000
H	0.728772000000	3.634135000000	4.172317000000
H	2.813881000000	2.301780000000	4.016883000000
C	-1.134770000000	1.344239000000	0.560697000000
O	-2.150180000000	2.014753000000	0.381819000000
N	-0.863330000000	0.136169000000	-0.070472000000
C	-1.762810000000	-0.188674000000	-1.162323000000
H	-2.788870000000	0.094529000000	-0.887149000000
H	-1.524670000000	0.367200000000	-2.080585000000
C	-1.709790000000	-1.654749000000	-1.499418000000
O	-1.576420000000	-2.129592000000	-2.609875000000
O	-1.841310000000	-2.407631000000	-0.386023000000
C	-1.723020000000	-3.815650000000	-0.582310000000

H	-2.370910000000	-4.153595000000	-1.393650000000
H	-0.687150000000	-4.077040000000	-0.821863000000
H	-2.014140000000	-4.273338000000	0.363276000000
Ru	1.226979000000	-0.265052000000	-0.306155000000
C	1.248006000000	-0.626488000000	-2.551467000000
C	1.369597000000	0.755914000000	-2.184057000000
C	2.410562000000	1.220434000000	-1.332438000000
C	3.286007000000	0.229629000000	-0.770638000000
C	3.086287000000	-1.140855000000	-1.042245000000
C	2.085313000000	-1.591058000000	-1.975879000000
C	2.610097000000	2.676567000000	-0.986658000000
C	3.821727000000	3.213478000000	-1.750277000000
C	1.879666000000	-3.049577000000	-2.223160000000
C	1.384097000000	3.542764000000	-1.234619000000
H	2.837565000000	2.708662000000	0.089100000000
H	0.418872000000	-0.945170000000	-3.177080000000
H	3.669104000000	-1.881849000000	-0.501093000000
H	0.631605000000	1.463672000000	-2.551521000000
H	4.031745000000	0.534208000000	-0.039671000000
H	1.553526000000	4.551680000000	-0.849318000000
H	1.170253000000	3.639818000000	-2.305438000000
H	0.490227000000	3.149654000000	-0.740789000000
H	4.025977000000	4.250956000000	-1.469924000000
H	4.723950000000	2.627010000000	-1.550801000000
H	3.642709000000	3.190013000000	-2.831222000000
H	2.620537000000	-3.436378000000	-2.932073000000
H	1.988978000000	-3.620710000000	-1.295591000000
H	0.884685000000	-3.238110000000	-2.635617000000
O	-0.859430000000	-1.480867000000	2.116683000000
C	0.239008000000	-2.165004000000	1.984502000000
O	1.062996000000	-2.001616000000	1.067521000000
H	1.175487000000	-3.941403000000	2.704824000000
C	0.472701000000	-3.184172000000	3.049484000000
H	-0.465650000000	-3.640288000000	3.367790000000
H	0.907128000000	-2.685253000000	3.920946000000
H	-0.956640000000	-0.876629000000	1.302732000000

4

E = -1150.514815 Eh
H = -1150.096698 Eh
G = -1149.758575 Eh
E_{sol} = -1150.839824 Eh
H_{sol} = -1150.421707 Eh
G_{sol} = -1150.083584 Eh

C	0.946950000000	2.314055000000	-0.201300000000
C	-0.091750000000	1.549392000000	-0.763700000000
C	1.017834000000	3.694624000000	-0.347010000000
C	-1.078300000000	2.237738000000	-1.477220000000
C	0.021808000000	4.356375000000	-1.063610000000
C	-1.024800000000	3.626800000000	-1.624390000000
H	1.848460000000	4.228525000000	0.109697000000
H	-1.907070000000	1.694796000000	-1.934530000000
H	0.058545000000	5.435901000000	-1.182870000000

H	-1.805030000000	4.142243000000	-2.180530000000
C	1.958892000000	1.569908000000	0.588044000000
O	2.915587000000	2.086534000000	1.156371000000
N	1.672444000000	0.205784000000	0.624733000000
C	2.518790000000	-0.598340000000	1.485488000000
H	3.207461000000	0.064837000000	2.024918000000
H	1.914989000000	-1.152680000000	2.212073000000
C	3.326064000000	-1.611620000000	0.715261000000
O	3.304189000000	-2.814970000000	0.895355000000
O	4.101624000000	-1.014690000000	-0.209540000000
C	4.939493000000	-1.900170000000	-0.953430000000
H	5.559336000000	-2.499870000000	-0.282810000000
H	4.341822000000	-2.577890000000	-1.569390000000
H	5.557990000000	-1.264360000000	-1.584440000000
Ru	0.116288000000	-0.484620000000	-0.424800000000
C	0.035978000000	-2.676530000000	0.157623000000
C	-0.990020000000	-1.878620000000	0.739857000000
C	-1.907060000000	-1.113140000000	-0.061460000000
C	-1.713700000000	-1.125770000000	-1.469110000000
C	-0.588230000000	-1.768370000000	-2.030190000000
C	0.288493000000	-2.577990000000	-1.225080000000
C	-3.024510000000	-0.301170000000	0.548044000000
C	-4.256960000000	-1.186490000000	0.733452000000
C	1.461691000000	-3.253090000000	-1.856860000000
C	-2.633670000000	0.388108000000	1.848742000000
H	-3.268410000000	0.482443000000	-0.184200000000
H	0.744006000000	-3.205220000000	0.789865000000
H	-0.364540000000	-1.639910000000	-3.085510000000
H	-1.071850000000	-1.832930000000	1.823093000000
H	-2.332020000000	-0.485060000000	-2.091970000000
H	-3.445130000000	1.036085000000	2.191209000000
H	-2.443710000000	-0.334610000000	2.650176000000
H	-1.736120000000	1.001064000000	1.720135000000
H	-5.099590000000	-0.604340000000	1.118193000000
H	-4.568760000000	-1.651630000000	-0.206610000000
H	-4.054650000000	-1.990410000000	1.450424000000
H	2.196742000000	-3.559760000000	-1.109300000000
H	1.135289000000	-4.144430000000	-2.404790000000
H	1.950111000000	-2.591290000000	-2.579350000000

RC2

E = -1723.789767 Eh
H = -1723.189635Eh
G = -1722.701420 Eh
E_{sol} = -1724.294798 Eh
H_{sol} = -1723.694666 Eh
G_{sol} = -1723.206451 Eh

C	0.199058000000	-0.203912000000	2.383972000000
C	0.105243000000	-1.562754000000	2.026773000000
C	0.054638000000	0.234628000000	3.695528000000
C	-0.175787000000	-2.471441000000	3.052598000000
C	-0.209756000000	-0.695327000000	4.700598000000
C	-0.333818000000	-2.045146000000	4.373713000000
H	0.141751000000	1.299092000000	3.905510000000
H	-0.285175000000	-3.533712000000	2.829965000000

H	-0.326521000000	-0.370673000000	5.731166000000
H	-0.554472000000	-2.771287000000	5.153432000000
C	0.382411000000	0.758531000000	1.268132000000
O	0.455553000000	1.976373000000	1.417588000000
N	0.416380000000	0.118043000000	0.034493000000
C	0.521867000000	0.970460000000	-1.129716000000
H	-0.319134000000	0.801019000000	-1.811715000000
H	0.498560000000	2.023247000000	-0.813995000000
C	1.780498000000	0.731343000000	-1.924104000000
O	1.835276000000	0.606819000000	-3.132587000000
O	2.865127000000	0.683307000000	-1.125832000000
C	4.098412000000	0.465969000000	-1.810445000000
H	4.107864000000	-0.519343000000	-2.287530000000
H	4.253758000000	1.222436000000	-2.582863000000
H	4.875578000000	0.524591000000	-1.050504000000
Ru	0.438096000000	-1.887686000000	0.010692000000
C	1.346678000000	-2.525903000000	-1.973473000000
C	1.929430000000	-3.165591000000	-0.834054000000
C	1.159320000000	-3.975879000000	0.058097000000
C	-0.244412000000	-3.960226000000	-0.112662000000
C	-0.841652000000	-3.149397000000	-1.122817000000
C	-0.046059000000	-2.502057000000	-2.134396000000
C	1.808391000000	-4.764438000000	1.170122000000
C	2.292201000000	-6.107787000000	0.621890000000
C	-0.695337000000	-1.744778000000	-3.243937000000
C	2.936889000000	-4.016865000000	1.868536000000
H	1.025749000000	-4.966476000000	1.914714000000
H	1.965982000000	-1.932189000000	-2.640706000000
H	-1.920900000000	-3.023097000000	-1.150634000000
H	2.997630000000	-3.059541000000	-0.660546000000
H	-0.875283000000	-4.441928000000	0.630682000000
H	3.296058000000	-4.591112000000	2.727037000000
H	3.795073000000	-3.869696000000	1.203353000000
H	2.608391000000	-3.036182000000	2.224691000000
H	2.722206000000	-6.720298000000	1.420068000000
H	1.479301000000	-6.675041000000	0.159110000000
H	3.068256000000	-5.960176000000	-0.137759000000
H	-0.876696000000	-2.413297000000	-4.093789000000
H	-1.664001000000	-1.351343000000	-2.924609000000
H	-0.058759000000	-0.925560000000	-3.592827000000
C	-2.905796000000	0.580179000000	0.741124000000
C	-2.911380000000	-0.460845000000	1.582251000000
H	-2.992327000000	-1.475764000000	1.202908000000
C	-2.745717000000	1.996719000000	1.194029000000
H	-2.805284000000	-0.326751000000	2.654695000000
C	-3.031372000000	0.306980000000	-0.709779000000
O	-3.154365000000	-0.790685000000	-1.225905000000
O	-2.994844000000	1.457632000000	-1.415737000000
C	-3.110973000000	1.329318000000	-2.831286000000
H	-2.186940000000	0.926192000000	-3.258467000000
H	-3.939791000000	0.668464000000	-3.095677000000
H	-3.278406000000	2.338552000000	-3.205747000000
O	-3.975984000000	2.709692000000	0.939217000000
C	-3.886703000000	3.817875000000	0.161965000000
O	-2.855766000000	4.302152000000	-0.242901000000
C	-5.262731000000	4.328341000000	-0.143359000000
H	-5.906036000000	4.292851000000	0.737410000000

H	-5.719981000000	3.683807000000	-0.900643000000
H	-5.205472000000	5.343234000000	-0.533792000000
H	-2.553342000000	2.033952000000	2.270517000000
H	-1.928849000000	2.510482000000	0.679176000000

5

E = -1723.796448 Eh
H = -1723.195809 Eh
G = -1722.701487 Eh
E_{sol} = -1724.302404 Eh
H_{sol} = -1723.701765 Eh
G_{sol} = -1723.207443 Eh

C	-1.399410000000	0.965797000000	1.893611000000
C	-0.121740000000	1.494298000000	1.687722000000
C	-2.227740000000	1.462451000000	2.900195000000
C	0.348456000000	2.481864000000	2.552935000000
C	-1.773110000000	2.481644000000	3.729045000000
C	-0.481220000000	2.981742000000	3.559223000000
H	-3.218190000000	1.024799000000	3.006715000000
H	1.363334000000	2.867648000000	2.448611000000
H	-2.410210000000	2.876885000000	4.515461000000
H	-0.108720000000	3.761040000000	4.220810000000
C	-1.822950000000	-0.136470000000	1.007357000000
O	-2.952030000000	-0.645990000000	1.009387000000
N	-0.815970000000	-0.528200000000	0.176165000000
C	-1.223250000000	-1.504230000000	-0.811180000000
H	-0.398760000000	-1.667530000000	-1.517280000000
H	-1.443750000000	-2.480060000000	-0.358380000000
C	-2.467880000000	-1.155990000000	-1.605090000000
O	-3.241370000000	-1.964740000000	-2.060060000000
O	-2.579220000000	0.182504000000	-1.819350000000
C	-3.814360000000	0.564660000000	-2.425550000000
H	-3.949430000000	0.072927000000	-3.392100000000
H	-4.647470000000	0.292733000000	-1.772670000000
H	-3.768200000000	1.647609000000	-2.547160000000
Ru	0.865070000000	0.732169000000	-0.005130000000
C	0.445014000000	0.971701000000	-2.229200000000
C	-0.131000000000	2.060518000000	-1.508110000000
C	0.673631000000	2.939736000000	-0.746430000000
C	2.043143000000	2.599797000000	-0.567600000000
C	2.583423000000	1.474863000000	-1.233140000000
C	1.817584000000	0.696960000000	-2.167620000000
C	0.125175000000	4.211548000000	-0.149690000000
C	0.582966000000	5.377169000000	-1.034130000000
C	2.430890000000	-0.405920000000	-2.968030000000
C	-1.385400000000	4.223177000000	0.027527000000
H	0.589385000000	4.334883000000	0.836880000000
H	-0.210760000000	0.339681000000	-2.821340000000
H	3.630434000000	1.236582000000	-1.072660000000
H	-1.205170000000	2.193339000000	-1.551710000000
H	2.680195000000	3.205214000000	0.071552000000
H	-1.690650000000	5.126485000000	0.562143000000
H	-1.901930000000	4.231155000000	-0.939390000000

H	-1.738790000000	3.360345000000	0.599250000000
H	0.245165000000	6.327450000000	-0.611310000000
H	1.672040000000	5.418312000000	-1.130210000000
H	0.161171000000	5.292525000000	-2.041650000000
H	3.128982000000	0.005200000000	-3.705900000000
H	2.992523000000	-1.109500000000	-2.347270000000
H	1.668305000000	-0.968790000000	-3.511250000000
C	2.153894000000	-0.957810000000	0.720614000000
C	1.614344000000	-0.234860000000	1.806039000000
H	2.262349000000	0.428279000000	2.371662000000
C	1.622459000000	-2.311400000000	0.333632000000
H	0.781520000000	-0.671720000000	2.349545000000
C	3.596967000000	-0.699470000000	0.450827000000
O	4.274426000000	0.183285000000	0.942598000000
O	4.101712000000	-1.600280000000	-0.427160000000
C	5.492067000000	-1.461400000000	-0.719910000000
H	5.673457000000	-0.565850000000	-1.323150000000
H	6.074390000000	-1.381670000000	0.200345000000
H	5.764008000000	-2.354130000000	-1.282480000000
O	2.433449000000	-3.329580000000	0.962485000000
C	3.032092000000	-4.227770000000	0.141060000000
O	2.865223000000	-4.291960000000	-1.056000000000
C	3.949157000000	-5.104400000000	0.937922000000
H	4.243625000000	-5.971140000000	0.348392000000
H	3.482447000000	-5.419060000000	1.872849000000
H	4.844883000000	-4.534860000000	1.205204000000
H	0.607909000000	-2.430180000000	0.715299000000
H	1.635279000000	-2.487310000000	-0.746200000000

6

E = -1723.807101 Eh
H = -1723.205323 Eh
G = -1722.707944 Eh
E_{sol} = -1724.311939 Eh
H_{sol} = -1723.710161 Eh
G_{sol} = -1723.212782 Eh

C	-0.920867000000	0.702814000000	1.821823000000
C	0.416659000000	0.480678000000	2.246015000000
C	-1.602717000000	1.857283000000	2.237737000000
C	1.051188000000	1.492396000000	2.999307000000
C	-0.962647000000	2.823178000000	2.993431000000
C	0.380681000000	2.649960000000	3.354756000000
H	-2.648486000000	1.951936000000	1.957375000000
H	2.075791000000	1.320393000000	3.316517000000
H	-1.501034000000	3.714462000000	3.306836000000
H	0.886369000000	3.407999000000	3.946970000000
C	-1.662267000000	-0.282254000000	0.965358000000
O	-2.858025000000	-0.543911000000	1.143945000000
N	-0.880834000000	-0.746428000000	-0.029254000000
C	-1.546870000000	-1.600216000000	-0.983240000000
H	-0.860051000000	-1.811184000000	-1.813527000000
H	-1.808052000000	-2.568863000000	-0.538040000000
C	-2.843493000000	-1.067128000000	-1.560326000000

O	-3.779863000000	-1.751801000000	-1.898367000000
O	-2.806195000000	0.280738000000	-1.728671000000
C	-4.051132000000	0.838395000000	-2.150876000000
H	-4.399173000000	0.369032000000	-3.073966000000
H	-4.807252000000	0.691489000000	-1.375031000000
H	-3.870087000000	1.903230000000	-2.304758000000
Ru	0.754228000000	0.583229000000	-0.307300000000
C	0.438769000000	0.808752000000	-2.405160000000
C	-0.203466000000	1.962477000000	-1.863912000000
C	0.479428000000	2.774365000000	-0.946385000000
C	1.845534000000	2.449039000000	-0.634740000000
C	2.519754000000	1.391365000000	-1.281037000000
C	1.821449000000	0.526024000000	-2.187890000000
C	-0.171758000000	3.943820000000	-0.252004000000
C	0.464450000000	5.246455000000	-0.744197000000
C	2.499772000000	-0.607141000000	-2.883758000000
C	-1.683815000000	3.984818000000	-0.410012000000
H	0.060235000000	3.839912000000	0.818168000000
H	-0.148957000000	0.115759000000	-3.004086000000
H	3.549930000000	1.170753000000	-1.019139000000
H	-1.261013000000	2.102941000000	-2.045681000000
H	2.357829000000	3.003816000000	0.148483000000
H	-2.110124000000	4.771200000000	0.219462000000
H	-1.969252000000	4.206238000000	-1.445221000000
H	-2.151678000000	3.037146000000	-0.123984000000
H	0.048174000000	6.103548000000	-0.207036000000
H	1.548723000000	5.254641000000	-0.599391000000
H	0.270135000000	5.394991000000	-1.812068000000
H	2.966770000000	-0.247066000000	-3.807981000000
H	3.277884000000	-1.061047000000	-2.266308000000
H	1.786080000000	-1.387712000000	-3.162293000000
C	1.822951000000	-0.993298000000	0.766263000000
C	1.081517000000	-0.876646000000	2.094714000000
H	1.755459000000	-1.033453000000	2.945243000000
C	1.688347000000	-2.325844000000	0.078305000000
H	0.309521000000	-1.650206000000	2.135599000000
C	3.219212000000	-0.521645000000	0.906036000000
O	3.637993000000	0.270948000000	1.734711000000
O	4.044545000000	-1.076242000000	-0.030689000000
C	5.413420000000	-0.692503000000	0.057223000000
H	5.553189000000	0.354395000000	-0.235283000000
H	5.786064000000	-0.811202000000	1.077336000000
H	5.948463000000	-1.347580000000	-0.630818000000
O	2.503823000000	-3.318848000000	0.763151000000
C	3.432529000000	-3.958133000000	0.017871000000
O	3.551920000000	-3.858249000000	-1.184324000000
C	4.317142000000	-4.785271000000	0.902203000000
H	4.846352000000	-5.530887000000	0.310337000000
H	3.749803000000	-5.263199000000	1.702253000000
H	5.053858000000	-4.129662000000	1.377768000000
H	0.655214000000	-2.675106000000	0.139692000000
H	2.003167000000	-2.304289000000	-0.965912000000

7

E = -1723.805716 Eh
H = -1723.203148 Eh
G = -1722.701203 Eh
E_{sol} = -1724.305211 Eh
H_{sol} = -1723.702643 Eh
G_{sol} = -1723.200698 Eh

C	0.910003000000	2.147240000000	-0.666533000000
C	-0.383111000000	2.427035000000	-1.145204000000
C	1.681069000000	3.185455000000	-0.133400000000
C	-0.920306000000	3.699913000000	-0.931408000000
C	1.145474000000	4.454637000000	0.052124000000
C	-0.177249000000	4.701849000000	-0.311752000000
H	2.706354000000	2.958422000000	0.145468000000
H	-1.927556000000	3.901396000000	-1.289727000000
H	1.753529000000	5.245516000000	0.484075000000
H	-0.615306000000	5.684438000000	-0.156722000000
C	1.545242000000	0.794734000000	-0.734569000000
O	2.771668000000	0.709452000000	-0.937006000000
N	0.764077000000	-0.298687000000	-0.535328000000
C	1.534944000000	-1.529393000000	-0.651156000000
H	0.896584000000	-2.376734000000	-0.382387000000
H	1.875057000000	-1.693943000000	-1.682150000000
C	2.788611000000	-1.627922000000	0.187144000000
O	3.784781000000	-2.235814000000	-0.129471000000
O	2.628716000000	-1.053557000000	1.410309000000
C	3.823088000000	-1.026650000000	2.189120000000
H	4.237817000000	-2.030486000000	2.308657000000
H	4.571488000000	-0.393697000000	1.703361000000
H	3.544640000000	-0.605292000000	3.156207000000
Ru	-1.166814000000	-0.503998000000	0.389993000000
C	-1.233194000000	-1.584839000000	2.336568000000
C	-0.385941000000	-0.482599000000	2.498153000000
C	-0.820473000000	0.832684000000	2.128474000000
C	-2.127788000000	0.988661000000	1.589271000000
C	-3.017858000000	-0.120611000000	1.497393000000
C	-2.568714000000	-1.417218000000	1.829679000000
C	-0.005664000000	2.062667000000	2.432899000000
C	-0.613700000000	2.742071000000	3.665496000000
C	-3.450849000000	-2.604813000000	1.622005000000
C	1.473564000000	1.791573000000	2.658552000000
H	-0.129107000000	2.751629000000	1.590815000000
H	-0.854208000000	-2.589952000000	2.503260000000
H	-4.007615000000	0.011297000000	1.071749000000
H	0.648679000000	-0.640664000000	2.783248000000
H	-2.443845000000	1.964000000000	1.222853000000
H	2.019014000000	2.736506000000	2.735365000000
H	1.630808000000	1.249451000000	3.600063000000
H	1.922062000000	1.203039000000	1.853603000000
H	-0.066622000000	3.661659000000	3.895089000000
H	-1.664509000000	3.005041000000	3.510909000000
H	-0.555606000000	2.091156000000	4.545761000000
H	-3.968535000000	-2.861648000000	2.552990000000
H	-4.211906000000	-2.404519000000	0.861633000000
H	-2.871165000000	-3.478541000000	1.314103000000
C	-1.861093000000	0.250875000000	-1.546783000000
C	-1.076340000000	1.470664000000	-2.071847000000
H	-1.752735000000	2.056436000000	-2.708927000000

C	-1.603734000000	-0.794920000000	-2.628119000000
H	-0.296050000000	1.084547000000	-2.739599000000
C	-3.277631000000	0.619602000000	-1.326131000000
O	-3.687089000000	1.727640000000	-1.020921000000
O	-4.136632000000	-0.445125000000	-1.447884000000
C	-5.507434000000	-0.121186000000	-1.233105000000
H	-5.688703000000	0.185271000000	-0.196589000000
H	-5.824504000000	0.697233000000	-1.883378000000
H	-6.069130000000	-1.028628000000	-1.456112000000
O	-2.307476000000	-2.063655000000	-2.581537000000
C	-2.060440000000	-2.839841000000	-1.554154000000
O	-1.340769000000	-2.525353000000	-0.599712000000
C	-2.759145000000	-4.154526000000	-1.635789000000
H	-2.755693000000	-4.538796000000	-2.656318000000
H	-3.805222000000	-4.012797000000	-1.345025000000
H	-2.302323000000	-4.871059000000	-0.954715000000
H	-1.885359000000	-0.415054000000	-3.617209000000
H	-0.530452000000	-1.016786000000	-2.629431000000

8

E = -1723.809804 Eh
H = -1723.208152 Eh
G = -1722.709071 Eh
E_{sol} = -1724.311010 Eh
H_{sol} = -1723.709358 Eh
G_{sol} = -1723.210277 Eh

C	1.133840000000	1.927243000000	-0.514835000000
C	0.076432000000	2.545831000000	-1.199349000000
C	1.926870000000	2.687485000000	0.354448000000
C	-0.142445000000	3.915700000000	-1.015477000000
C	1.670216000000	4.035302000000	0.566579000000
C	0.637193000000	4.657013000000	-0.134269000000
H	2.772105000000	2.195051000000	0.830871000000
H	-0.951546000000	4.391761000000	-1.561935000000
H	2.287871000000	4.606220000000	1.255203000000
H	0.443456000000	5.717908000000	-0.000228000000
C	1.616935000000	0.543790000000	-0.813478000000
O	2.836495000000	0.419104000000	-1.028085000000
N	0.759849000000	-0.508393000000	-0.874822000000
C	1.488532000000	-1.735695000000	-1.171202000000
H	0.806852000000	-2.585389000000	-1.103470000000
H	1.882094000000	-1.718731000000	-2.194004000000
C	2.690250000000	-2.009483000000	-0.298487000000
O	3.655590000000	-2.653082000000	-0.636677000000
O	2.530233000000	-1.532693000000	0.972816000000
C	3.706713000000	-1.629051000000	1.771313000000
H	4.067124000000	-2.659144000000	1.826696000000
H	4.497308000000	-1.004156000000	1.345811000000
H	3.430672000000	-1.265081000000	2.762724000000
Ru	-1.154013000000	-0.648004000000	0.106806000000
C	-0.330684000000	-1.364670000000	1.986867000000
C	-0.173951000000	0.052400000000	1.960755000000
C	-1.291862000000	0.911596000000	1.862362000000

C	-2.549214000000	0.280466000000	1.593666000000
C	-2.739311000000	-1.115207000000	1.641782000000
C	-1.619817000000	-1.954318000000	1.891959000000
C	-1.168959000000	2.411524000000	2.050899000000
C	-2.510340000000	3.088078000000	2.315672000000
C	-1.766158000000	-3.435843000000	1.971400000000
C	-0.197772000000	2.728906000000	3.188822000000
H	-0.758791000000	2.840276000000	1.131523000000
H	0.553499000000	-1.989922000000	2.037227000000
H	-3.708130000000	-1.550114000000	1.425386000000
H	0.833448000000	0.459131000000	2.003831000000
H	-3.409137000000	0.907126000000	1.388587000000
H	-0.116782000000	3.812546000000	3.312839000000
H	-0.546471000000	2.306844000000	4.138820000000
H	0.810667000000	2.355678000000	2.994770000000
H	-2.344501000000	4.148581000000	2.524060000000
H	-3.182739000000	3.040353000000	1.456330000000
H	-3.016378000000	2.655674000000	3.187772000000
H	-1.752644000000	-3.732110000000	3.026138000000
H	-2.706032000000	-3.771242000000	1.531690000000
H	-0.936918000000	-3.946333000000	1.475940000000
C	-1.880058000000	0.920433000000	-1.577971000000
C	-0.762951000000	1.758063000000	-2.163147000000
H	-1.234990000000	2.452094000000	-2.870573000000
C	-2.061810000000	-0.396150000000	-1.960166000000
H	-0.125108000000	1.086509000000	-2.745022000000
C	-3.045037000000	1.702986000000	-1.080058000000
O	-3.042864000000	2.909592000000	-0.922124000000
O	-4.148114000000	0.941612000000	-0.883292000000
C	-5.302157000000	1.667847000000	-0.458952000000
H	-5.136715000000	2.128612000000	0.521458000000
H	-5.544986000000	2.460511000000	-1.169924000000
H	-6.106838000000	0.937097000000	-0.401651000000
O	-3.438500000000	-2.848847000000	-0.734366000000
C	-2.302658000000	-3.225950000000	-1.016950000000
O	-1.191180000000	-2.560491000000	-0.830289000000
C	-2.062271000000	-4.582425000000	-1.644691000000
H	-2.426506000000	-4.567334000000	-2.675604000000
H	-2.645756000000	-5.336800000000	-1.111619000000
H	-1.007937000000	-4.861573000000	-1.650649000000
H	-3.019591000000	-0.892443000000	-1.858730000000
H	-1.311971000000	-0.864608000000	-2.590603000000

RC3

E = -1087.655713 Eh
H = -1087.239100 Eh
G = -1086.910726 Eh
E_{sol} = -1087.342719 Eh
H_{sol} = -1086.926106 Eh
G_{sol} = -1086.597732 Eh

Ru	4.384914000000	4.602034000000	3.168398000000
Cl	6.415967000000	3.371324000000	2.817877000000
C	5.240374000000	6.501759000000	2.547361000000
C	4.339345000000	6.044682000000	1.563451000000
C	3.001410000000	5.652595000000	1.907661000000

C	2.578271000000	5.798540000000	3.260286000000
C	3.498954000000	6.204466000000	4.255190000000
C	4.857292000000	6.535077000000	3.921812000000
C	2.121112000000	5.059998000000	0.836646000000
C	1.082313000000	4.087394000000	1.373983000000
C	5.853564000000	6.833733000000	4.992028000000
C	1.483101000000	6.194903000000	0.032616000000
H	2.793440000000	4.519430000000	0.159156000000
H	6.286591000000	6.637260000000	2.289579000000
H	3.216777000000	6.134075000000	5.302175000000
H	4.680621000000	5.851663000000	0.547937000000
H	1.615617000000	5.404586000000	3.569104000000
H	0.884427000000	5.782024000000	-0.784361000000
H	0.822313000000	6.803720000000	0.660477000000
H	2.241058000000	6.847199000000	-0.409297000000
H	0.561651000000	3.603470000000	0.542665000000
H	1.538132000000	3.305559000000	1.992640000000
H	0.316837000000	4.594661000000	1.972695000000
H	6.858161000000	6.528146000000	4.692060000000
H	5.873205000000	7.910012000000	5.197849000000
H	5.602437000000	6.320567000000	5.923112000000
Cl	3.399579000000	2.718051000000	4.282209000000
C	3.926160000000	1.548243000000	0.304247000000
C	3.919017000000	1.046455000000	1.547117000000
H	4.801049000000	1.094826000000	2.179600000000
C	2.735055000000	1.545405000000	-0.570188000000
O	2.715609000000	2.034342000000	-1.688852000000
O	1.663159000000	0.944035000000	-0.015321000000
C	0.504167000000	0.918188000000	-0.848870000000
H	0.184537000000	1.933074000000	-1.101495000000
H	0.708431000000	0.382374000000	-1.779046000000
H	-0.265559000000	0.408044000000	-0.272366000000
H	3.027734000000	0.596457000000	1.970602000000
C	5.146594000000	2.168206000000	-0.298850000000
H	6.002089000000	2.049633000000	0.370275000000
H	5.372781000000	1.720027000000	-1.270018000000
O	4.935063000000	3.588463000000	-0.440894000000
C	4.905982000000	4.223997000000	-1.634561000000
O	4.567129000000	5.390645000000	-1.630328000000
C	5.318495000000	3.483468000000	-2.869225000000
H	4.604863000000	2.683828000000	-3.079526000000
H	6.310292000000	3.036042000000	-2.760879000000
H	5.330216000000	4.186001000000	-3.700249000000

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E = -1072.433133Eh
H = -1072.021119Eh
G = -1071.690066 Eh
E_{sol} = -1072.069827 Eh
H_{sol} = -1071.657813 Eh
G_{sol} = -1071.326760 Eh

Ru	2.358515000000	4.802510000000	2.731755000000
Cl	3.427880000000	2.653440000000	2.304576000000
C	4.200240000000	5.927320000000	2.517627000000

C	3.127240000000	6.736020000000	2.063778000000
C	1.986450000000	7.012240000000	2.868801000000
C	1.956220000000	6.391960000000	4.147593000000
C	3.041020000000	5.598510000000	4.629454000000
C	4.199430000000	5.379530000000	3.840264000000
C	0.852380000000	7.879020000000	2.387230000000
C	1.126460000000	9.324400000000	2.814241000000
C	5.314660000000	4.520470000000	4.314266000000
C	0.601240000000	7.772670000000	0.889045000000
H	-0.047840000000	7.535280000000	2.912498000000
H	5.013960000000	5.677030000000	1.843129000000
H	2.952220000000	5.093750000000	5.587002000000
H	3.131950000000	7.076780000000	1.031564000000
H	1.047790000000	6.459430000000	4.741490000000
H	-0.322870000000	8.292990000000	0.629462000000
H	1.403000000000	8.243780000000	0.309618000000
H	0.490530000000	6.732950000000	0.567522000000
H	0.292910000000	9.966060000000	2.518997000000
H	1.257940000000	9.418570000000	3.895787000000
H	2.029090000000	9.711530000000	2.329898000000
H	5.746940000000	3.939460000000	3.498491000000
H	6.098270000000	5.162500000000	4.732517000000
H	4.991030000000	3.830620000000	5.094801000000
C	0.154980000000	3.268470000000	2.640723000000
C	1.092510000000	2.683400000000	3.462622000000
H	1.523340000000	1.717040000000	3.222452000000
C	-0.721740000000	4.398930000000	3.082440000000
O	-1.593910000000	4.867380000000	2.382255000000
O	-0.460360000000	4.792270000000	4.341744000000
C	-1.380230000000	5.769840000000	4.869698000000
H	-1.329580000000	6.698340000000	4.295241000000
H	-2.399870000000	5.385420000000	4.825480000000
H	-1.072470000000	5.934930000000	5.899410000000
H	1.258110000000	3.079020000000	4.460094000000
C	-0.195920000000	2.677020000000	1.302448000000
H	0.103910000000	1.630420000000	1.218493000000
H	-1.246430000000	2.802060000000	1.039488000000
O	2.171270000000	4.446460000000	0.509800000000
C	1.495760000000	3.528670000000	-0.328440000000
O	0.401840000000	3.156240000000	-0.026500000000
C	2.308820000000	3.185420000000	-1.523360000000
H	3.068040000000	2.452960000000	-1.229840000000
H	2.805640000000	4.066780000000	-1.935060000000
H	1.666160000000	2.736730000000	-2.278580000000

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E = -1072.432422 Eh
H = -1072.020450 Eh
G = -1071.690140 Eh
E_{sol} = -1072.071480 Eh
H_{sol} = -1071.659508 Eh
G_{sol} = -1071.329198 Eh

Ru	2.579268100000	4.285131600000	2.474560000000
Cl	4.037260100000	2.327095500000	2.525102000000
C	4.085297500000	5.918927300000	2.174023000000
C	2.804263600000	6.499638600000	1.898518000000
C	1.796747000000	6.529083000000	2.879740000000
C	2.065955100000	5.774554000000	4.058922000000
C	3.339408900000	5.206801900000	4.346447000000
C	4.418767500000	5.359335900000	3.429456000000
C	0.517413800000	7.307805000000	2.755629000000
C	0.686040500000	8.581657200000	3.599472000000
C	5.774622200000	4.835061100000	3.722031000000
C	0.098513700000	7.630322200000	1.332306000000
H	-0.268723000000	6.708190800000	3.231062000000
H	4.819382000000	5.869105100000	1.375348000000
H	3.494345200000	4.653688800000	5.268305000000
H	2.601388400000	6.907291700000	0.913575000000
H	1.253435200000	5.631659000000	4.769775000000
H	-0.872255000000	8.130775000000	1.345876000000
H	0.803183500000	8.320923300000	0.856160000000
H	0.015035400000	6.737386000000	0.712571000000
H	-0.245340000000	9.152515700000	3.585392000000
H	0.932336000000	8.366011000000	4.643653000000
H	1.472918000000	9.222582000000	3.189604000000
H	6.291233000000	4.527596000000	2.812053000000
H	6.362933000000	5.629656000000	4.195643000000
H	5.738983000000	3.984723000000	4.403828000000
C	0.573292000000	3.307851000000	2.764550000000
C	1.423429000000	2.958198000000	3.848140000000
H	1.974089000000	2.023983000000	3.822897000000
C	-0.633299000000	4.196427000000	2.900167000000
O	-1.258308000000	4.625735000000	1.959519000000
O	-0.939365000000	4.395417000000	4.193286000000
C	-2.186143000000	5.091142000000	4.411807000000
H	-2.150458000000	6.090606000000	3.971684000000
H	-3.003673000000	4.534680000000	3.952074000000
H	-2.307594000000	5.143526000000	5.490658000000
H	1.193013000000	3.353489000000	4.832663000000
C	0.977921000000	2.929618000000	1.485854000000
H	1.644738000000	2.084279000000	1.341677000000
H	0.457784000000	3.351869000000	0.632093000000
O	3.129636000000	4.026216000000	0.445671000000
C	2.426499000000	4.574668000000	-0.527170000000
O	1.416133000000	5.250401000000	-0.381780000000
C	3.011024000000	4.246250000000	-1.879020000000
H	2.358586000000	3.513788000000	-2.361410000000
H	4.014963000000	3.830289000000	-1.814720000000
H	3.004264000000	5.144805000000	-2.497640000000

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E = -1072.428005 Eh
H = -1072.014191 Eh
G = -1071.679785 Eh
E_{sol} = -1072.119577 Eh
H_{sol} = -1071.705763 Eh

G_{sol} = -1071.371357 Eh

Ru	2.630727000000	4.515814000000	2.551902000000
Cl	3.827866000000	2.424472000000	2.286581000000
C	4.237945000000	5.960899000000	2.549181000000
C	3.038416000000	6.648356000000	2.167166000000
C	1.890856000000	6.668897000000	2.990461000000
C	1.966516000000	5.887616000000	4.173009000000
C	3.178209000000	5.257742000000	4.589803000000
C	4.359259000000	5.318207000000	3.808818000000
C	0.636881000000	7.414997000000	2.620367000000
C	0.883539000000	8.911812000000	2.833522000000
C	5.610137000000	4.623920000000	4.211586000000
C	0.149747000000	7.119153000000	1.206427000000
H	-0.137940000000	7.086007000000	3.324770000000
H	5.056913000000	5.890446000000	1.838434000000
H	3.184839000000	4.669611000000	5.502552000000
H	2.991043000000	7.085912000000	1.173469000000
H	1.063526000000	5.757309000000	4.764069000000
H	-0.743210000000	7.710809000000	0.991457000000
H	0.896541000000	7.386464000000	0.449858000000
H	-0.104950000000	6.063242000000	1.087773000000
H	-0.038450000000	9.470523000000	2.657157000000
H	1.222029000000	9.135636000000	3.848715000000
H	1.637412000000	9.289067000000	2.134680000000
H	6.115506000000	4.187378000000	3.348190000000
H	6.291562000000	5.343631000000	4.677484000000
H	5.414318000000	3.827521000000	4.931056000000
C	0.553257000000	2.308271000000	3.486508000000
C	1.592854000000	3.010738000000	4.185719000000
H	2.471887000000	2.434240000000	4.457333000000
C	-0.785060000000	2.942691000000	3.298271000000
O	-1.735430000000	2.401738000000	2.785500000000
O	-0.807850000000	4.213274000000	3.778045000000
C	-2.081940000000	4.858729000000	3.620451000000
H	-2.308130000000	4.994990000000	2.560168000000
H	-2.872970000000	4.258788000000	4.072184000000
H	-1.997510000000	5.820388000000	4.125809000000
H	1.235135000000	3.697764000000	4.944588000000
C	0.727817000000	1.052858000000	3.009505000000
H	1.688362000000	0.553073000000	3.079925000000
H	-0.108680000000	0.527289000000	2.558343000000
O	2.802860000000	4.412018000000	0.422608000000
C	1.613089000000	3.964225000000	0.291515000000
O	0.946616000000	3.865129000000	1.375096000000
C	1.045492000000	3.616491000000	-1.027930000000
H	0.162324000000	2.988668000000	-0.912670000000
H	1.794844000000	3.112644000000	-1.640160000000
H	0.756656000000	4.533489000000	-1.550770000000

12

E = -2223.310404 Eh
H = -2222.478926 Eh
G = -2221.784808Eh

E_{sol} = -2222.654074 Eh
H_{sol} = -2221.822596 Eh
G_{sol} = -2221.128478 Eh

Ru	-9.578100000000	5.426622000000	-4.244080000000
C	-10.154000000000	3.081221000000	-3.826360000000
C	-10.256600000000	3.366660000000	-5.225410000000
C	-9.175710000000	3.893750000000	-5.937730000000
C	-7.962470000000	4.238822000000	-5.278090000000
C	-7.880450000000	3.954931000000	-3.872510000000
C	-8.930460000000	3.340697000000	-3.172420000000
H	-11.217800000000	3.210171000000	-5.713430000000
H	-9.279800000000	4.113313000000	-6.996720000000
H	-6.966490000000	4.238049000000	-3.354410000000
H	-8.825330000000	3.109620000000	-2.115780000000
C	-11.295300000000	2.472020000000	-3.086600000000
H	-11.150700000000	1.386270000000	-3.047970000000
H	-11.342700000000	2.830376000000	-2.054970000000
H	-12.258900000000	2.652181000000	-3.572250000000
C	-6.742910000000	4.716469000000	-6.029150000000
C	-6.182030000000	3.528917000000	-6.818900000000
H	-5.241130000000	3.810426000000	-7.298430000000
H	-5.986440000000	2.662754000000	-6.180120000000
C	-6.990460000000	5.916670000000	-6.931780000000
H	-7.290510000000	6.796439000000	-6.356450000000
H	-6.075880000000	6.162858000000	-7.477040000000
H	-7.770850000000	5.721009000000	-7.676410000000
H	-6.007460000000	5.011884000000	-5.272910000000
H	-6.873780000000	3.214583000000	-7.608490000000
C	-9.670210000000	9.381304000000	-5.882760000000
C	-10.155600000000	9.272551000000	-7.179250000000
C	-10.485100000000	8.013664000000	-7.685580000000
C	-10.352800000000	6.862668000000	-6.904300000000
C	-9.875530000000	6.955860000000	-5.597070000000
C	-9.530530000000	8.223922000000	-5.113790000000
H	-9.385390000000	10.339660000000	-5.454920000000
H	-10.268600000000	10.155850000000	-7.799540000000
H	-10.851900000000	7.923378000000	-8.705460000000
H	-10.644100000000	5.903101000000	-7.329360000000
C	-8.975800000000	8.237397000000	-3.767040000000
O	-8.556140000000	9.186007000000	-3.127410000000
N	-8.918700000000	6.903326000000	-3.230440000000
C	-8.146470000000	6.809294000000	-2.008890000000
H	-8.470180000000	7.580332000000	-1.303910000000
H	-8.313690000000	5.829969000000	-1.549680000000
C	-6.660690000000	6.971524000000	-2.287980000000
O	-6.122640000000	6.580727000000	-3.304760000000
O	-6.045390000000	7.550551000000	-1.262320000000
C	-4.623160000000	7.717762000000	-1.418540000000
H	-4.277070000000	8.157429000000	-0.486430000000
H	-4.144530000000	6.753094000000	-1.595730000000
H	-4.416490000000	8.381573000000	-2.259340000000
Ru	-14.774300000000	5.776934000000	-4.468260000000
C	-16.692400000000	6.216342000000	-3.315710000000
C	-16.875600000000	5.202123000000	-4.298780000000
C	-16.592400000000	5.449541000000	-5.675440000000
C	-16.075900000000	6.689240000000	-6.106020000000

C	-15.743000000000	7.633982000000	-5.083570000000
C	-16.064500000000	7.424543000000	-3.717560000000
H	-17.206800000000	4.214046000000	-3.994840000000
H	-16.703500000000	4.632640000000	-6.382140000000
H	-15.185700000000	8.528439000000	-5.346270000000
H	-15.762700000000	8.155168000000	-2.975010000000
C	-17.017500000000	5.951721000000	-1.888230000000
H	-16.456900000000	6.609997000000	-1.223190000000
H	-18.086400000000	6.131759000000	-1.728990000000
H	-16.815300000000	4.911903000000	-1.620810000000
C	-15.808300000000	6.999464000000	-7.556070000000
C	-15.457000000000	5.768908000000	-8.380730000000
H	-15.120400000000	6.065035000000	-9.377050000000
H	-14.668800000000	5.171473000000	-7.909830000000
C	-17.021600000000	7.736872000000	-8.130590000000
H	-17.252000000000	8.647329000000	-7.570090000000
H	-16.834800000000	8.019993000000	-9.169570000000
H	-17.910600000000	7.097681000000	-8.114880000000
H	-14.958300000000	7.695552000000	-7.581390000000
H	-16.326600000000	5.118710000000	-8.522020000000
O	-14.236800000000	4.859126000000	-2.661860000000
Cl	-14.017400000000	3.558035000000	-5.362770000000
C	-13.950400000000	5.617666000000	-1.634130000000
C	-13.649100000000	4.823906000000	-0.383950000000
H	-14.274400000000	5.188378000000	0.434891000000
H	-13.807500000000	3.753410000000	-0.517550000000
H	-12.611800000000	5.004922000000	-0.086690000000
O	-13.911800000000	6.848039000000	-1.637530000000
C	-13.102200000000	6.473710000000	-5.717870000000
H	-13.361000000000	7.387631000000	-6.246020000000
C	-12.560900000000	6.615045000000	-4.423380000000
C	-11.731700000000	5.577701000000	-3.814330000000
H	-11.551900000000	5.739220000000	-2.745440000000
H	-12.151800000000	4.596685000000	-3.999720000000
C	-12.554600000000	7.998339000000	-3.850500000000
O	-13.228300000000	8.922760000000	-4.267130000000
O	-11.668400000000	8.118825000000	-2.849750000000
C	-11.662300000000	9.403270000000	-2.209840000000
H	-10.849400000000	9.368025000000	-1.486770000000
H	-11.486400000000	10.192460000000	-2.943890000000
H	-12.620900000000	9.565384000000	-1.712770000000
H	-12.810700000000	5.623631000000	-6.326630000000

13

E = -1495.197154 Eh
H = -1494.656390 Eh
G = -1494.214715 Eh
E_{sol} = -1495.690063 Eh
H_{sol} = -1495.149299 Eh
G_{sol} = -1494.707624 Eh

C	0.595458000000	-0.719610000000	2.089649000000
C	-0.485860000000	-0.022440000000	1.535953000000
C	0.936474000000	-0.609190000000	3.440668000000

C	-1.254380000000	0.782124000000	2.375361000000
C	0.165432000000	0.198996000000	4.266227000000
C	-0.928960000000	0.880624000000	3.732364000000
H	1.790805000000	-1.166050000000	3.817624000000
H	-2.076970000000	1.379316000000	1.986011000000
H	0.407654000000	0.296821000000	5.319385000000
H	-1.534890000000	1.513232000000	4.376594000000
C	1.336576000000	-1.554730000000	1.157420000000
O	2.334168000000	-2.222470000000	1.354535000000
N	0.713889000000	-1.506550000000	-0.146330000000
C	1.152576000000	-2.542460000000	-1.071650000000
H	2.154945000000	-2.862690000000	-0.760250000000
H	0.500421000000	-3.421140000000	-1.002280000000
C	1.176656000000	-2.077780000000	-2.505520000000
O	0.653847000000	-2.660430000000	-3.429390000000
O	1.865060000000	-0.925030000000	-2.626980000000
C	1.998650000000	-0.443450000000	-3.973660000000
H	2.553786000000	-1.160390000000	-4.580370000000
H	1.015713000000	-0.291830000000	-4.428320000000
H	2.539554000000	0.498111000000	-3.899660000000
Ru	-0.681360000000	-0.248630000000	-0.505850000000
C	-1.650420000000	-0.593610000000	-2.736440000000
C	-1.973300000000	-1.597400000000	-1.808860000000
C	-2.648460000000	-1.297420000000	-0.574990000000
C	-2.964650000000	0.066218000000	-0.325350000000
C	-2.541860000000	1.077503000000	-1.191040000000
C	-1.875360000000	0.762168000000	-2.413960000000
C	-3.106820000000	-2.373080000000	0.378036000000
C	-4.459720000000	-2.904220000000	-0.110150000000
C	-1.476400000000	1.850517000000	-3.350690000000
C	-2.101560000000	-3.500860000000	0.561686000000
H	-3.258040000000	-1.886080000000	1.350853000000
H	-1.159630000000	-0.867100000000	-3.667100000000
H	-2.663530000000	2.118453000000	-0.906190000000
H	-1.706070000000	-2.625910000000	-2.043430000000
H	-3.458450000000	0.322736000000	0.607703000000
H	-2.480210000000	-4.226680000000	1.284215000000
H	-1.924550000000	-4.049640000000	-0.370280000000
H	-1.142350000000	-3.129950000000	0.935815000000
H	-4.851160000000	-3.639040000000	0.597092000000
H	-5.201200000000	-2.107300000000	-0.212610000000
H	-4.359970000000	-3.399340000000	-1.081750000000
H	-0.483530000000	1.681054000000	-3.775870000000
H	-2.181810000000	1.887156000000	-4.187960000000
H	-1.494200000000	2.830109000000	-2.868310000000
C	0.774218000000	2.383150000000	0.547637000000
C	1.921660000000	2.227954000000	1.239287000000
H	2.664002000000	1.495073000000	0.933246000000
C	-0.268410000000	3.359997000000	0.966321000000
O	-1.313420000000	3.521155000000	0.354366000000
O	0.049849000000	4.021264000000	2.083318000000
C	-0.941110000000	4.955529000000	2.535064000000
H	-1.131670000000	5.709832000000	1.769748000000
H	-1.876330000000	4.436002000000	2.759075000000
H	-0.529400000000	5.411156000000	3.432650000000
H	2.144483000000	2.835544000000	2.108791000000
C	0.453719000000	1.622562000000	-0.654300000000

H	1.312778000000	1.104337000000	-1.097910000000
H	-0.064360000000	2.231481000000	-1.390550000000

14

E = -1495.232642 Eh
H = -1494.688439 Eh
G = -1494.239808 Eh
E_{sol} = -1495.708302 Eh
H_{sol} = -1495.164099 Eh
G_{sol} = -1494.715468 Eh

C	0.634594000000	-0.774020000000	1.364102000000
C	0.463766000000	0.636133000000	1.455388000000
C	0.287253000000	-1.592630000000	2.449085000000
C	-0.188280000000	1.151600000000	2.602575000000
C	-0.322610000000	-1.055810000000	3.568605000000
C	-0.590590000000	0.320938000000	3.630404000000
H	0.514372000000	-2.652640000000	2.380983000000
H	-0.292770000000	2.228210000000	2.698675000000
H	-0.587920000000	-1.697300000000	4.404017000000
H	-1.058560000000	0.742530000000	4.515008000000
C	1.213998000000	-1.404480000000	0.140019000000
O	2.077349000000	-2.279620000000	0.179655000000
N	0.630399000000	-0.920650000000	-0.978160000000
C	1.046155000000	-1.503760000000	-2.232610000000
H	0.873816000000	-2.587330000000	-2.265140000000
H	0.463080000000	-1.053900000000	-3.045410000000
C	2.514511000000	-1.297640000000	-2.565090000000
O	3.144219000000	-2.025850000000	-3.289600000000
O	2.997633000000	-0.165080000000	-2.007130000000
C	4.387183000000	0.074577000000	-2.291480000000
H	4.992137000000	-0.754000000000	-1.920150000000
H	4.545787000000	0.175514000000	-3.366740000000
H	4.640788000000	0.998578000000	-1.774840000000
Ru	-1.073920000000	0.218694000000	-0.588310000000
C	-2.350310000000	-0.428880000000	-2.212740000000
C	-2.372110000000	-1.484080000000	-1.258930000000
C	-2.701150000000	-1.235520000000	0.084703000000
C	-3.011270000000	0.126265000000	0.444880000000
C	-3.140430000000	1.146704000000	-0.518590000000
C	-2.811830000000	0.883296000000	-1.876470000000
C	-2.730700000000	-2.322450000000	1.124531000000
C	-4.191540000000	-2.714620000000	1.377531000000
C	-2.946410000000	1.927907000000	-2.928360000000
C	-1.887370000000	-3.535020000000	0.757214000000
H	-2.338790000000	-1.883140000000	2.052015000000
H	-2.025330000000	-0.626300000000	-3.230770000000
H	-3.391690000000	2.160536000000	-0.223350000000
H	-2.021260000000	-2.468830000000	-1.554080000000
H	-3.158590000000	0.361575000000	1.497399000000
H	-1.807030000000	-4.212670000000	1.610131000000
H	-2.342550000000	-4.107630000000	-0.057740000000
H	-0.871180000000	-3.261250000000	0.450424000000
H	-4.244640000000	-3.471020000000	2.164095000000
H	-4.800690000000	-1.862080000000	1.690635000000

H	-4.643970000000	-3.139160000000	0.475607000000
H	-2.337570000000	1.702238000000	-3.806320000000
H	-3.991590000000	1.947264000000	-3.257070000000
H	-2.695550000000	2.919457000000	-2.549580000000
C	0.176232000000	2.137166000000	-0.460840000000
C	1.185026000000	1.602020000000	0.518960000000
H	1.977020000000	1.081478000000	-0.025440000000
C	-0.647370000000	3.340065000000	-0.111340000000
O	-1.548480000000	3.785546000000	-0.795720000000
O	-0.226960000000	3.912916000000	1.025839000000
C	-0.908800000000	5.131364000000	1.381055000000
H	-0.826100000000	5.857329000000	0.571548000000
H	-1.964880000000	4.931244000000	1.572654000000
H	-0.413620000000	5.492020000000	2.279556000000
H	1.634173000000	2.409030000000	1.102589000000
C	0.147707000000	1.703580000000	-1.782600000000
H	0.980846000000	1.125383000000	-2.170210000000
H	-0.480650000000	2.236719000000	-2.489250000000

15

E = -1495.232886 Eh
H = -1494.689340 Eh
G = -1494.245398 Eh
E_{sol} = -1495.717903 Eh
H_{sol} = -1495.174357 Eh
G_{sol} = -1494.730415 Eh

C	0.520314000000	-0.062100000000	2.405403000000
C	0.636885000000	1.317602000000	2.065805000000
C	-0.309520000000	-0.460060000000	3.479848000000
C	-0.099990000000	2.241610000000	2.831351000000
C	-1.036650000000	0.476723000000	4.195395000000
C	-0.924490000000	1.833216000000	3.867981000000
H	-0.345000000000	-1.513960000000	3.744191000000
H	0.031078000000	3.302528000000	2.626924000000
H	-1.669620000000	0.162543000000	5.019088000000
H	-1.468160000000	2.575020000000	4.445931000000
C	1.346663000000	-1.105040000000	1.686917000000
O	2.218908000000	-1.790100000000	2.184141000000
N	0.856874000000	-1.188040000000	0.393069000000
C	1.550008000000	-2.012810000000	-0.561910000000
H	2.508854000000	-2.333290000000	-0.139670000000
H	0.990375000000	-2.933980000000	-0.772700000000
C	1.770031000000	-1.300580000000	-1.880690000000
O	1.259005000000	-0.249420000000	-2.211640000000
O	2.596096000000	-2.020950000000	-2.637950000000
C	2.885787000000	-1.469190000000	-3.935700000000
H	1.973137000000	-1.398140000000	-4.530250000000
H	3.325662000000	-0.476080000000	-3.833480000000
H	3.590355000000	-2.158480000000	-4.394220000000
Ru	-0.841600000000	-0.210930000000	0.489951000000
C	-1.489940000000	0.604498000000	-1.378510000000
C	-1.849990000000	-0.768060000000	-1.318050000000
C	-2.600040000000	-1.270300000000	-0.212830000000

C	-3.005480000000	-0.339000000000	0.796895000000
C	-2.686420000000	1.031287000000	0.709473000000
C	-1.912450000000	1.529450000000	-0.369210000000
C	-2.948230000000	-2.731720000000	-0.078240000000
C	-4.139310000000	-3.031470000000	-0.992790000000
C	-1.499490000000	2.961719000000	-0.429790000000
C	-1.777600000000	-3.664510000000	-0.356060000000
H	-3.265940000000	-2.886800000000	0.961543000000
H	-0.799240000000	0.934778000000	-2.147400000000
H	-2.906490000000	1.684113000000	1.550176000000
H	-1.452100000000	-1.452280000000	-2.061880000000
H	-3.491320000000	-0.718340000000	1.691937000000
H	-2.078770000000	-4.703620000000	-0.205230000000
H	-1.425400000000	-3.584780000000	-1.390660000000
H	-0.936290000000	-3.459810000000	0.314257000000
H	-4.464370000000	-4.066280000000	-0.860910000000
H	-4.992980000000	-2.382070000000	-0.781730000000
H	-3.868150000000	-2.899020000000	-2.045490000000
H	-0.619910000000	3.103363000000	-1.061700000000
H	-2.309740000000	3.558075000000	-0.862980000000
H	-1.293950000000	3.366306000000	0.565274000000
C	2.611662000000	2.810108000000	1.681690000000
C	1.643183000000	1.840512000000	1.057394000000
H	1.115978000000	2.343614000000	0.238058000000
C	3.577658000000	2.285084000000	2.689237000000
O	4.392822000000	2.945127000000	3.293079000000
O	3.416746000000	0.951098000000	2.835919000000
C	4.299734000000	0.331177000000	3.782606000000
H	5.338501000000	0.472101000000	3.477422000000
H	4.163793000000	0.773685000000	4.771554000000
H	4.029530000000	-0.722720000000	3.781177000000
H	2.187980000000	1.007818000000	0.604185000000
C	2.647535000000	4.111972000000	1.381552000000
H	1.970791000000	4.549134000000	0.651909000000
H	3.372994000000	4.761003000000	1.861484000000

Product

E = -1012.008195 Eh
H = -1011.681709 Eh
G = -1011.426903 Eh
E_{sol} = -1012.321374 Eh
H_{sol} = -1011.994888 Eh
G_{sol} = -1011.740082 Eh

C	2.410760000000	-0.799800000000	0.126980000000
C	2.363284000000	0.590722000000	0.353766000000
C	3.592947000000	-1.385100000000	-0.339540000000
C	3.502541000000	1.347003000000	0.057599000000
C	4.706940000000	-0.614860000000	-0.641380000000
C	4.658462000000	0.762917000000	-0.447190000000
H	3.609546000000	-2.465310000000	-0.452210000000
H	3.475466000000	2.419244000000	0.244495000000
H	5.610960000000	-1.086020000000	-1.016430000000
H	5.524262000000	1.379865000000	-0.671020000000

C	1.289908000000	-1.753630000000	0.410180000000
O	1.489743000000	-2.873160000000	0.873517000000
N	0.035449000000	-1.322430000000	0.098858000000
C	-1.102600000000	-2.165230000000	0.327150000000
H	-0.956800000000	-3.165820000000	-0.101320000000
H	-1.269260000000	-2.333490000000	1.399049000000
C	-2.329880000000	-1.531780000000	-0.266210000000
O	-2.349130000000	-0.480890000000	-0.874280000000
O	-3.410150000000	-2.294480000000	-0.036670000000
C	-4.635310000000	-1.768520000000	-0.558620000000
H	-4.922710000000	-0.863910000000	-0.017050000000
H	-4.530910000000	-1.526310000000	-1.618080000000
H	-5.380000000000	-2.548200000000	-0.411340000000
C	0.154880000000	1.778045000000	-0.075890000000
C	1.165436000000	1.293001000000	0.934812000000
H	1.507781000000	2.159736000000	1.516779000000
C	0.404500000000	1.938763000000	-1.381490000000
H	0.635343000000	0.660550000000	1.652837000000
C	-1.212390000000	1.990113000000	0.474930000000
O	-1.574270000000	1.584673000000	1.562904000000
O	-2.012870000000	2.669315000000	-0.370610000000
C	-3.364470000000	2.785228000000	0.073249000000
H	-3.803970000000	1.794475000000	0.210895000000
H	-3.416550000000	3.326303000000	1.021161000000
H	-3.888650000000	3.331876000000	-0.709000000000
H	1.388382000000	1.729717000000	-1.793650000000
H	-0.373310000000	2.268128000000	-2.060230000000
H	-0.119570000000	-0.482690000000	-0.445350000000

2a

E = -573.250870 Eh
H = -573.070717 Eh
G = -572.941948 Eh
E_{sol} = -573.467095 Eh
H_{sol} = -573.286942 Eh
G_{sol} = -573.158173 Eh

C	-0.721950000000	1.207930000000	0.190410000000
C	-1.455410000000	2.297800000000	-0.054120000000
H	-1.012730000000	3.289270000000	-0.013650000000
C	-1.288990000000	-0.162430000000	0.164490000000
O	-0.686730000000	-1.143890000000	0.559790000000
O	-2.541350000000	-0.208240000000	-0.327110000000
C	-3.114370000000	-1.519540000000	-0.353750000000
H	-2.515380000000	-2.185410000000	-0.978670000000
H	-3.163570000000	-1.939160000000	0.653640000000
H	-4.112880000000	-1.397850000000	-0.769530000000
H	-2.510190000000	2.229310000000	-0.295510000000
C	0.732280000000	1.265090000000	0.540310000000
H	1.056070000000	2.305430000000	0.651420000000
H	0.910580000000	0.743850000000	1.485070000000
O	1.489090000000	0.685430000000	-0.527760000000
C	2.325410000000	-0.381590000000	-0.346450000000
O	2.875480000000	-0.827570000000	-1.321860000000
C	2.516160000000	-0.919390000000	1.043230000000

H	1.573100000000	-1.308810000000	1.435450000000
H	2.880940000000	-0.153660000000	1.734110000000
H	3.247090000000	-1.723890000000	0.990820000000

1a

E = -667.666920 Eh
H = -667.453145 Eh
G = -667.295080 Eh
E_{sol} = -667.877198 Eh
H_{sol} = -667.663423 Eh
G_{sol} = -667.505358 Eh

C	-1.877709000000	0.243876000000	-0.044758000000
C	-2.017475000000	-1.119304000000	-0.325865000000
C	-3.008335000000	0.987536000000	0.305033000000
C	-3.264983000000	-1.728799000000	-0.244364000000
C	-4.253075000000	0.377490000000	0.391754000000
C	-4.383357000000	-0.982914000000	0.119212000000
H	-2.876545000000	2.047611000000	0.500511000000
H	-3.365310000000	-2.786280000000	-0.471983000000
H	-5.125032000000	0.962580000000	0.669642000000
H	-5.357014000000	-1.460793000000	0.184056000000
C	-0.577750000000	0.972742000000	-0.116248000000
O	-0.509885000000	2.199176000000	-0.125816000000
N	0.547988000000	0.202450000000	-0.182202000000
C	1.838198000000	0.830741000000	-0.174041000000
H	2.035193000000	1.365717000000	-1.111367000000
H	1.905852000000	1.596724000000	0.610488000000
C	2.896575000000	-0.214725000000	0.040680000000
O	2.674476000000	-1.388839000000	0.252829000000
O	4.121804000000	0.326106000000	-0.031179000000
C	5.195056000000	-0.602549000000	0.168908000000
H	5.113680000000	-1.078801000000	1.148164000000
H	5.177716000000	-1.378084000000	-0.599822000000
H	6.109317000000	-0.016314000000	0.101470000000
H	0.542370000000	-0.782800000000	0.041165000000
H	-1.161094000000	-1.709734000000	-0.642429000000

AcOH

E = -228.928520 Eh
H = -228.861033 Eh
G = -228.825789 Eh
E_{sol} = -229.014961 Eh
H_{sol} = -228.947474 Eh
G_{sol} = -228.912230 Eh

O	8.998966000000	1.149463000000	0.358681000000
C	7.960580000000	0.624430000000	0.663540000000
O	7.676390000000	-0.630730000000	0.219070000000
H	6.813010000000	-0.906880000000	0.548880000000
C	6.892750000000	1.250580000000	1.523620000000
H	7.220580000000	2.231460000000	1.862520000000
H	5.960380000000	1.364280000000	0.961410000000
H	6.673370000000	0.627350000000	2.396260000000

TS1

E = -1608.443208 Eh
H = -1607.889675 Eh
G = -1607.436833 Eh
E_{sol} = -1608.913779 Eh
H_{sol} = -1608.360246 Eh
G_{sol} = -1607.907404 Eh
i=-337.9 cm^{-1}

Ru	-1.509590000000	0.237060000000	0.038051000000
O	-2.052988000000	1.404044000000	1.673107000000
C	-3.274836000000	1.379559000000	2.129074000000
C	-3.419240000000	2.193210000000	3.397559000000
C	-1.568984000000	1.765199000000	-1.466964000000
O	-4.218426000000	0.755169000000	1.642698000000
C	-4.671885000000	-0.505841000000	-1.069399000000
C	0.837294000000	1.305485000000	-2.111532000000
O	-1.989574000000	-1.389298000000	1.409212000000
C	-1.782742000000	-1.325880000000	2.647885000000
C	-2.710922000000	-2.047296000000	3.567165000000
O	-0.832252000000	-0.653146000000	3.196001000000
H	-3.000575000000	3.193929000000	3.263579000000
H	-4.465232000000	2.260295000000	3.697459000000
H	-2.844233000000	1.717357000000	4.199878000000
H	-5.159764000000	0.292103000000	-0.500070000000
H	1.038527000000	2.267024000000	-1.634138000000
H	-3.002360000000	-3.006657000000	3.137462000000
H	-2.275477000000	-2.180418000000	4.556553000000
H	-3.621953000000	-1.444802000000	3.653148000000
C	-0.550754000000	0.839059000000	-1.836348000000
C	-0.881615000000	-0.549010000000	-1.907810000000
C	-2.897356000000	1.311125000000	-1.211707000000
C	-3.249439000000	-0.058119000000	-1.295227000000
C	-2.193369000000	-0.978255000000	-1.598361000000
H	-2.388829000000	-2.044819000000	-1.515084000000
H	-3.635486000000	2.005792000000	-0.818938000000
H	-1.303724000000	2.805388000000	-1.299618000000
H	-0.098484000000	-1.277858000000	-2.093468000000
C	-5.356103000000	-0.643956000000	-2.431491000000
H	-6.408493000000	-0.914872000000	-2.303885000000
H	-5.314717000000	0.285297000000	-3.008351000000
H	-4.883719000000	-1.429851000000	-3.032863000000
C	-4.792690000000	-1.784709000000	-0.254896000000
H	-4.295968000000	-1.670928000000	0.709536000000
H	-5.847935000000	-2.014094000000	-0.080929000000
H	-4.360543000000	-2.648058000000	-0.775463000000
H	0.962497000000	1.433939000000	-3.192505000000
H	1.593407000000	0.600164000000	-1.760618000000
C	0.912108000000	2.530550000000	1.514192000000
C	0.173960000000	2.700478000000	2.688460000000
C	1.386918000000	3.661650000000	0.838689000000
C	-0.104233000000	3.980018000000	3.159400000000
C	1.077957000000	4.938606000000	1.288831000000
C	0.329155000000	5.099345000000	2.454032000000
H	2.021991000000	3.513579000000	-0.031592000000
H	-0.660837000000	4.101414000000	4.085508000000
H	1.437173000000	5.808822000000	0.745999000000

H	0.100230000000	6.096573000000	2.821049000000
C	1.330383000000	1.195659000000	1.003870000000
O	2.443234000000	1.059679000000	0.490810000000
N	0.439567000000	0.128739000000	1.134435000000
C	1.101720000000	-1.121318000000	0.769977000000
H	0.367282000000	-1.934285000000	0.827503000000
H	1.497594000000	-1.110066000000	-0.252169000000
C	2.241841000000	-1.439488000000	1.712649000000
O	2.375913000000	-0.992106000000	2.828119000000
O	3.072835000000	-2.343836000000	1.153463000000
C	4.167458000000	-2.721275000000	1.992340000000
H	4.783946000000	-1.851241000000	2.229654000000
H	3.807002000000	-3.155003000000	2.928538000000
H	4.740640000000	-3.453761000000	1.425960000000
H	-0.169613000000	1.833494000000	3.241373000000
H	-0.244268000000	-0.182397000000	2.402315000000

TS2

E = -1379.472455 Eh
H = -1378.990446 Eh
G = -1378.595234 Eh
E_{sol} = -1379.866265 Eh
H_{sol} = -1379.384256 Eh
G_{sol} = -1378.989044Eh
i=-1337.1 cm^{-1}

C	0.065650000000	1.180550000000	1.718900000000
C	1.325060000000	0.554680000000	1.807020000000
C	-0.272380000000	2.249460000000	2.542200000000
C	2.239770000000	1.037190000000	2.758310000000
C	0.654080000000	2.714420000000	3.472040000000
C	1.907140000000	2.106170000000	3.586180000000
H	-1.254060000000	2.702850000000	2.427040000000
H	3.213710000000	0.557750000000	2.860540000000
H	0.403970000000	3.555240000000	4.114050000000
H	2.620010000000	2.469650000000	4.322140000000
C	-0.876380000000	0.691930000000	0.674010000000
O	-2.034230000000	1.112290000000	0.559700000000
N	-0.304440000000	-0.249210000000	-0.126430000000
C	-1.111460000000	-0.679510000000	-1.244130000000
H	-1.241700000000	0.108980000000	-2.001450000000
H	-0.605860000000	-1.528210000000	-1.721450000000
C	-2.512060000000	-1.137520000000	-0.899030000000
O	-3.456900000000	-1.044200000000	-1.649190000000
O	-2.566380000000	-1.740200000000	0.307580000000
C	-3.884910000000	-2.113600000000	0.702490000000
H	-4.521560000000	-1.227540000000	0.772870000000
H	-4.328410000000	-2.808050000000	-0.015380000000
H	-3.784540000000	-2.586250000000	1.679800000000
Ru	1.787710000000	-0.366060000000	-0.150460000000
C	2.308050000000	-1.034690000000	-2.173960000000
C	1.904110000000	0.328470000000	-2.183500000000
C	2.492020000000	1.298200000000	-1.319970000000
C	3.541200000000	0.837160000000	-0.456840000000
C	3.968670000000	-0.511860000000	-0.440110000000
C	3.309310000000	-1.476840000000	-1.260520000000

C	2.055730000000	2.743720000000	-1.264390000000
C	3.037800000000	3.608740000000	-2.056090000000
C	3.610020000000	-2.932130000000	-1.119520000000
C	0.625480000000	2.966530000000	-1.734620000000
H	2.116870000000	3.039710000000	-0.205750000000
H	1.751770000000	-1.769550000000	-2.748260000000
H	4.694700000000	-0.844180000000	0.295660000000
H	1.035680000000	0.606850000000	-2.774740000000
H	3.941420000000	1.529210000000	0.281840000000
H	0.326980000000	4.002860000000	-1.557050000000
H	0.523730000000	2.787310000000	-2.811240000000
H	-0.088880000000	2.321600000000	-1.213910000000
H	2.771800000000	4.666900000000	-1.978350000000
H	4.065350000000	3.492700000000	-1.697670000000
H	3.023830000000	3.339650000000	-3.118100000000
H	4.331980000000	-3.245990000000	-1.881540000000
H	4.035500000000	-3.151660000000	-0.138060000000
H	2.700180000000	-3.524840000000	-1.235080000000
O	1.450120000000	-1.977520000000	1.327040000000
C	0.809840000000	-2.592480000000	0.301530000000
O	0.822690000000	-2.130220000000	-0.821640000000
H	-0.689670000000	-3.652430000000	1.344890000000
C	0.159660000000	-3.882690000000	0.693550000000
H	0.853350000000	-4.510490000000	1.257760000000
H	-0.206960000000	-4.410960000000	-0.185820000000
H	1.277210000000	-0.841970000000	1.763750000000

TS3

E = -1723.783778 Eh
H = -1723.184128 Eh
G = -1722.688442 Eh
E_{sol} = -1724.287983 Eh
H_{sol} = -1723.688333 Eh
G_{sol} = -1723.192647 Eh
i=-243.7 cm^{-1}

C	-1.243658000000	0.871707000000	1.889956000000
C	0.124410000000	1.207136000000	1.793528000000
C	-2.082802000000	1.560058000000	2.760353000000
C	0.614076000000	2.257493000000	2.585462000000
C	-1.586575000000	2.607073000000	3.531720000000
C	-0.238331000000	2.959626000000	3.431710000000
H	-3.127685000000	1.260357000000	2.791419000000
H	1.676698000000	2.499204000000	2.551517000000
H	-2.241364000000	3.148798000000	4.208403000000
H	0.157412000000	3.774634000000	4.033231000000
C	-1.773323000000	-0.178194000000	0.990257000000
O	-2.923933000000	-0.633457000000	1.066102000000
N	-0.854821000000	-0.563424000000	0.064842000000
C	-1.357222000000	-1.521028000000	-0.891211000000
H	-0.578711000000	-1.728052000000	-1.637640000000
H	-1.601493000000	-2.481091000000	-0.417185000000
C	-2.623195000000	-1.117001000000	-1.621558000000
O	-3.441006000000	-1.892314000000	-2.057865000000
O	-2.701385000000	0.227746000000	-1.799916000000
C	-3.940303000000	0.657427000000	-2.364966000000

H	-4.116916000000	0.183380000000	-3.333582000000
H	-4.763946000000	0.401143000000	-1.693864000000
H	-3.863795000000	1.739827000000	-2.472889000000
Ru	0.848793000000	0.670979000000	-0.190039000000
C	0.370351000000	0.959804000000	-2.299748000000
C	-0.130798000000	2.117479000000	-1.625553000000
C	0.718114000000	2.896283000000	-0.819038000000
C	2.074789000000	2.465291000000	-0.662384000000
C	2.567914000000	1.347056000000	-1.371593000000
C	1.731361000000	0.583343000000	-2.251458000000
C	0.250926000000	4.143010000000	-0.114323000000
C	0.696355000000	5.362403000000	-0.926672000000
C	2.251504000000	-0.597586000000	-3.003359000000
C	-1.245263000000	4.172667000000	0.154012000000
H	0.771717000000	4.174108000000	0.852531000000
H	-0.333693000000	0.335993000000	-2.844045000000
H	3.600643000000	1.045030000000	-1.222819000000
H	-1.193421000000	2.324746000000	-1.672644000000
H	2.733484000000	2.995728000000	0.021122000000
H	-1.500415000000	5.030208000000	0.782376000000
H	-1.818944000000	4.270953000000	-0.774903000000
H	-1.581255000000	3.268282000000	0.669816000000
H	0.423013000000	6.286209000000	-0.408413000000
H	1.778398000000	5.374056000000	-1.089216000000
H	0.211014000000	5.374400000000	-1.908762000000
H	2.755975000000	-0.273839000000	-3.921100000000
H	2.971277000000	-1.171824000000	-2.413075000000
H	1.440388000000	-1.269804000000	-3.296732000000
C	1.973363000000	-0.909834000000	0.750020000000
C	1.315711000000	-0.265203000000	1.877301000000
H	2.004390000000	0.208625000000	2.570591000000
C	1.559830000000	-2.291210000000	0.317334000000
H	0.566985000000	-0.891623000000	2.355923000000
C	3.416676000000	-0.582139000000	0.645563000000
O	4.002065000000	0.301561000000	1.247503000000
O	4.043949000000	-1.389887000000	-0.248384000000
C	5.441625000000	-1.156177000000	-0.408398000000
H	5.626345000000	-0.185306000000	-0.879938000000
H	5.949970000000	-1.169386000000	0.558333000000
H	5.801658000000	-1.960332000000	-1.049897000000
O	2.395184000000	-3.276207000000	0.973782000000
C	3.100906000000	-4.107316000000	0.168732000000
O	3.004454000000	-4.153684000000	-1.037294000000
C	4.037318000000	-4.937602000000	0.992922000000
H	4.396614000000	-5.784627000000	0.410415000000
H	3.560685000000	-5.280447000000	1.912655000000
H	4.894311000000	-4.323248000000	1.286963000000
H	0.533071000000	-2.485878000000	0.629133000000
H	1.645170000000	-2.444407000000	-0.762311000000

TS4

E = -1723.777411 Eh
H = -1723.177655 Eh
G = -1722.680203 Eh

E_{sol} = -1724.280417 Eh
H_{sol} = -1723.680661 Eh
G_{sol} = -1723.183209 Eh
i=-238.1 cm^{-1}

C	1.413415000000	1.944990000000	0.321307000000
C	1.194235000000	2.000406000000	-1.062924000000
C	1.183530000000	3.085433000000	1.105098000000
C	0.729938000000	3.202095000000	-1.614997000000
C	0.673559000000	4.248221000000	0.551051000000
C	0.443502000000	4.305230000000	-0.823552000000
H	1.426906000000	3.025793000000	2.162506000000
H	0.584799000000	3.256556000000	-2.689424000000
H	0.481324000000	5.114912000000	1.178444000000
H	0.068807000000	5.217022000000	-1.281233000000
C	2.004204000000	0.779252000000	1.038940000000
O	2.863487000000	1.008017000000	1.913307000000
N	1.584420000000	-0.477378000000	0.760153000000
C	2.246716000000	-1.445522000000	1.628249000000
H	1.763115000000	-2.419365000000	1.515541000000
H	3.296737000000	-1.586181000000	1.347082000000
C	2.273300000000	-1.108970000000	3.101298000000
O	3.151083000000	-1.432998000000	3.866657000000
O	1.116395000000	-0.511812000000	3.516654000000
C	1.162059000000	-0.046614000000	4.863352000000
H	1.437112000000	-0.850713000000	5.550086000000
H	1.897690000000	0.758598000000	4.951918000000
H	0.163157000000	0.329439000000	5.089769000000
Ru	-0.107126000000	-1.256691000000	-0.330775000000
C	-1.161196000000	-2.417868000000	1.156161000000
C	-1.235948000000	-1.048193000000	1.500225000000
C	-1.745293000000	-0.072268000000	0.589845000000
C	-2.122930000000	-0.545276000000	-0.695935000000
C	-2.083681000000	-1.923357000000	-1.057950000000
C	-1.581094000000	-2.871944000000	-0.137798000000
C	-1.884156000000	1.394067000000	0.943869000000
C	-3.334963000000	1.840811000000	0.754562000000
C	-1.442572000000	-4.310157000000	-0.511317000000
C	-1.416378000000	1.694642000000	2.360573000000
H	-1.264389000000	1.967495000000	0.239276000000
H	-0.682769000000	-3.116353000000	1.838183000000
H	-2.308981000000	-2.227997000000	-2.074389000000
H	-0.777915000000	-0.728406000000	2.429736000000
H	-2.414439000000	0.191768000000	-1.440021000000
H	-1.464556000000	2.769929000000	2.551850000000
H	-2.057770000000	1.194752000000	3.098272000000
H	-0.385400000000	1.373289000000	2.534971000000
H	-3.434164000000	2.904571000000	0.988888000000
H	-3.679503000000	1.697477000000	-0.273774000000
H	-4.010417000000	1.287812000000	1.417527000000
H	-2.344934000000	-4.856041000000	-0.215322000000
H	-1.313168000000	-4.431527000000	-1.589194000000
H	-0.596571000000	-4.774488000000	0.002297000000
C	0.585586000000	-0.190993000000	-2.411185000000
C	1.609613000000	0.878338000000	-1.977658000000
H	1.991243000000	1.346705000000	-2.896704000000
C	1.182038000000	-1.252293000000	-3.131899000000

H	2.451824000000	0.341587000000	-1.529238000000
C	-0.656879000000	0.315828000000	-3.038540000000
O	-1.092252000000	1.451306000000	-2.991269000000
O	-1.323401000000	-0.669895000000	-3.717524000000
C	-2.521446000000	-0.233217000000	-4.356290000000
H	-3.278304000000	0.052882000000	-3.617652000000
H	-2.332750000000	0.629327000000	-4.998754000000
H	-2.874461000000	-1.081567000000	-4.941683000000
O	0.801278000000	-3.179816000000	-2.775274000000
C	1.323838000000	-3.537365000000	-1.680746000000
O	1.346291000000	-2.830395000000	-0.630178000000
C	1.978629000000	-4.891297000000	-1.627035000000
H	2.276662000000	-5.150688000000	-0.611336000000
H	2.859898000000	-4.894973000000	-2.273690000000
H	1.296010000000	-5.647821000000	-2.021930000000
H	0.801160000000	-1.542375000000	-4.101271000000
H	2.244347000000	-1.422778000000	-2.975797000000

TS5

E = -1072.430672 Eh
H = -1072.020319 Eh
G = -1071.689166 Eh
E_{sol} = -1072.067134 Eh
H_{sol} = -1071.656781 Eh
G_{sol} = -1071.325628 Eh
i= -128.06cm^{-1}

Ru	2.440769000000	4.297418000000	2.672872000000
Cl	3.541818000000	2.120689000000	2.788506000000
C	4.237012000000	5.466261000000	2.264105000000
C	3.145971000000	6.247384000000	1.774127000000
C	2.046625000000	6.592597000000	2.585038000000
C	2.082877000000	6.075084000000	3.917229000000
C	3.220153000000	5.406371000000	4.453023000000
C	4.342446000000	5.109110000000	3.640849000000
C	0.863230000000	7.398015000000	2.108347000000
C	0.750855000000	8.671575000000	2.954165000000
C	5.519779000000	4.373186000000	4.162529000000
C	0.901826000000	7.719507000000	0.623580000000
H	-0.029592000000	6.783583000000	2.296389000000
H	4.996075000000	5.119318000000	1.569767000000
H	3.199449000000	5.049608000000	5.478604000000
H	3.119127000000	6.479109000000	0.713250000000
H	1.204131000000	6.194641000000	4.544572000000
H	0.009622000000	8.283060000000	0.345255000000
H	1.766555000000	8.342027000000	0.368459000000
H	0.914377000000	6.814914000000	0.010024000000
H	-0.141041000000	9.232858000000	2.666415000000
H	0.678412000000	8.459562000000	4.025560000000
H	1.615961000000	9.323801000000	2.799774000000
H	5.986393000000	3.764636000000	3.387527000000
H	6.257863000000	5.102568000000	4.516025000000
H	5.254760000000	3.725839000000	4.999281000000
C	0.239446000000	3.542966000000	3.133894000000

C	1.191144000000	3.313037000000	4.179073000000
H	1.622131000000	2.324786000000	4.300842000000
C	-0.882245000000	4.537468000000	3.273435000000
O	-1.745528000000	4.685261000000	2.441403000000
O	-0.828714000000	5.208910000000	4.440912000000
C	-1.935684000000	6.111030000000	4.651122000000
H	-1.958358000000	6.872689000000	3.868170000000
H	-2.875317000000	5.558066000000	4.630544000000
H	-1.769355000000	6.558722000000	5.628250000000
H	1.034509000000	3.872103000000	5.096815000000
C	0.216079000000	2.776146000000	1.976245000000
H	0.968992000000	2.006179000000	1.815678000000
H	-0.631408000000	2.842238000000	1.307494000000
O	2.641976000000	3.787608000000	0.643885000000
C	1.665535000000	4.028368000000	-0.179936000000
O	0.509204000000	4.302344000000	0.165964000000
C	2.065931000000	3.974962000000	-1.630196000000
H	2.956058000000	3.366171000000	-1.781369000000
H	2.283058000000	4.993144000000	-1.968930000000
H	1.233595000000	3.601725000000	-2.226561000000

TS6

E = -1072.423676 Eh
H = -1072.013569 Eh
G = -1071.683031 Eh
E_{sol} = -1072.062253 Eh
H_{sol} = -1071.652146 Eh
G_{sol} = -1071.321608 Eh
i = -109.46 cm^{-1}

Ru	2.609135000000	4.228818000000	2.748012000000
Cl	4.100891000000	2.294341000000	2.747297000000
C	4.164338000000	5.643193000000	2.322974000000
C	2.966521000000	6.276623000000	1.868065000000
C	1.857452000000	6.466093000000	2.715921000000
C	1.990695000000	5.920565000000	4.028824000000
C	3.232156000000	5.449115000000	4.542446000000
C	4.361692000000	5.315320000000	3.704106000000
C	0.565123000000	7.110346000000	2.290841000000
C	0.268515000000	8.305955000000	3.203690000000
C	5.655653000000	4.782163000000	4.194741000000
C	0.539756000000	7.517786000000	0.827244000000
H	-0.207411000000	6.346996000000	2.453419000000
H	4.950960000000	5.407099000000	1.611423000000
H	3.289882000000	5.093621000000	5.567250000000
H	2.876498000000	6.513875000000	0.811529000000
H	1.113699000000	5.898081000000	4.669837000000
H	-0.427713000000	7.960574000000	0.582755000000
H	1.302770000000	8.271895000000	0.604166000000
H	0.681105000000	6.662811000000	0.161097000000
H	-0.711227000000	8.723026000000	2.959329000000
H	0.256753000000	8.036386000000	4.263992000000
H	1.008794000000	9.100603000000	3.069583000000
H	6.152253000000	4.177621000000	3.434836000000
H	6.308857000000	5.627573000000	4.440537000000
H	5.530816000000	4.176871000000	5.093272000000

C	0.703069000000	2.595402000000	3.479137000000
C	1.716550000000	3.064225000000	4.400655000000
H	2.472984000000	2.347701000000	4.708131000000
C	-0.663109000000	3.218029000000	3.436929000000
O	-1.612751000000	2.699264000000	2.904001000000
O	-0.704401000000	4.397002000000	4.091557000000
C	-2.005514000000	5.017971000000	4.081751000000
H	-2.331636000000	5.187845000000	3.053210000000
H	-2.732461000000	4.376429000000	4.581543000000
H	-1.889878000000	5.959391000000	4.617481000000
H	1.354451000000	3.712103000000	5.193682000000
C	0.896628000000	1.516422000000	2.665793000000
H	1.853113000000	1.004714000000	2.622432000000
H	0.073214000000	1.177481000000	2.042477000000
O	2.576848000000	3.696540000000	0.736093000000
C	1.343493000000	3.867864000000	0.343746000000
O	0.477245000000	4.254084000000	1.149018000000
C	1.057526000000	3.536287000000	-1.082075000000
H	0.183520000000	4.089180000000	-1.427606000000
H	0.827984000000	2.468715000000	-1.153354000000
H	1.918028000000	3.728917000000	-1.723276000000

TS7

E = -1724.094705 Eh
H = -1723.485654 Eh
G = -1722.984643 Eh
E_{sol} = -1724.640921 Eh
H_{sol} = -1724.031870 Eh
G_{sol} = -1723.530859 Eh
i=-163.9 cm^{-1}

C	1.605837000000	-1.605295000000	-1.412566000000
C	1.516345000000	-0.241949000000	-1.141839000000
C	2.788471000000	-2.135032000000	-1.933129000000
C	2.592067000000	0.607609000000	-1.410396000000
C	3.866614000000	-1.299077000000	-2.193784000000
C	3.766993000000	0.070132000000	-1.932581000000
H	2.828463000000	-3.208488000000	-2.101134000000
H	2.505797000000	1.681301000000	-1.251672000000
H	4.785377000000	-1.705287000000	-2.604626000000
H	4.603089000000	0.728814000000	-2.150328000000
C	0.481558000000	-2.484586000000	-1.027699000000
O	0.512017000000	-3.705452000000	-1.156028000000
N	-0.577311000000	-1.780448000000	-0.488577000000
C	-1.558860000000	-2.633007000000	0.180422000000
H	-1.574927000000	-3.585541000000	-0.356469000000
H	-1.258944000000	-2.850402000000	1.216531000000
C	-2.950123000000	-2.054917000000	0.230872000000
O	-3.418074000000	-1.436314000000	1.171120000000
O	-3.624722000000	-2.308226000000	-0.898294000000
C	-4.966119000000	-1.791413000000	-0.940080000000
H	-5.545702000000	-2.170505000000	-0.097270000000
H	-4.954926000000	-0.698742000000	-0.898797000000
H	-5.383453000000	-2.133781000000	-1.883745000000
Ru	-0.181230000000	0.189180000000	0.162330000000
C	-0.805268000000	-0.279633000000	2.251775000000

C	0.545167000000	-0.728275000000	2.155998000000
C	1.586304000000	0.143534000000	1.805858000000
C	1.207580000000	1.476131000000	1.427402000000
C	-0.101667000000	1.956334000000	1.638858000000
C	-1.132408000000	1.093785000000	2.103150000000
C	3.032228000000	-0.266622000000	1.807904000000
C	3.705124000000	0.388983000000	3.022973000000
C	-2.511701000000	1.589189000000	2.356954000000
C	3.251004000000	-1.772068000000	1.807282000000
H	3.486856000000	0.158820000000	0.903651000000
H	-1.605294000000	-0.981277000000	2.469224000000
H	-0.347870000000	2.988869000000	1.405925000000
H	0.758018000000	-1.782541000000	2.311129000000
H	1.970896000000	2.152613000000	1.049026000000
H	4.313130000000	-1.992543000000	1.681312000000
H	2.941741000000	-2.225140000000	2.755444000000
H	2.715243000000	-2.271771000000	0.994713000000
H	4.771919000000	0.154247000000	3.023526000000
H	3.602367000000	1.477902000000	3.019665000000
H	3.281527000000	0.011946000000	3.959133000000
H	-3.247454000000	0.794624000000	2.214171000000
H	-2.578297000000	1.918308000000	3.400004000000
H	-2.755743000000	2.447420000000	1.726211000000
C	-1.103569000000	1.391099000000	-1.369709000000
C	-0.150125000000	0.679634000000	-2.144045000000
H	-0.461208000000	-0.266754000000	-2.578132000000
C	-1.039636000000	2.864096000000	-1.132736000000
O	-1.859020000000	3.472588000000	-0.474730000000
O	0.034666000000	3.414913000000	-1.716295000000
C	0.151619000000	4.840659000000	-1.544755000000
H	-0.749740000000	5.339182000000	-1.903117000000
H	0.295616000000	5.083998000000	-0.489288000000
H	1.018659000000	5.136794000000	-2.129857000000
H	0.582639000000	1.247453000000	-2.700624000000
C	-2.094060000000	0.592260000000	-0.733279000000
H	-2.418952000000	-0.301165000000	-1.256805000000
H	-2.822698000000	1.081343000000	-0.093588000000

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