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Supporting Information

Synthesis of the Fused Tetracyclic Spiroindoles via Palladium-Catalysed Cascade Cyclisation

Iwata Akira, Shinsuke Inuki, Shinya Oishi, Nobutaka Fujii,* and Hiroaki Ohno*

Graduate School of Pharmaceutical Sciences, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

E-mail: hohno@pharm.kyoto-u.ac.jp; nfujii@pharm.kyoto-u.ac.jp

Table of Contents

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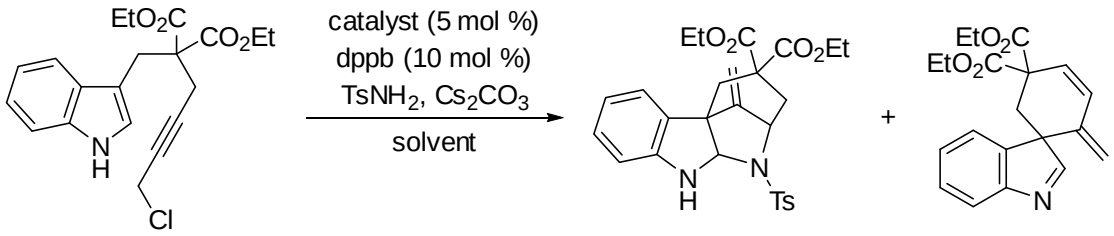
Optimization of Reaction Conditions



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

entry	catalyst (mol %)	$TsNH_2$ (equiv)	Cs_2CO_3 (equiv)	solvent (M)	temp. (^oC)	yield (%)[a]	
						2a	**3a**
1	$Pd(dba)_2$ (5)	$TsNH_2$ (1)	Cs_2CO_3 (2)	THF (0.1)	rt	*ca.* 72	3
2	$Pd(dba)_2$ (5)	$TsNH_2$ (1)	Cs_2CO_3 (2)	dioxane (0.1)	70	*ca.* 13	<1
3	$Pd(dba)_2$ (5)	$TsNH_2$ (1)	Cs_2CO_3 (2)	DMF (0.1)	rt	*ca.* 59	<1
4	$Pd(dba)_2$ (5)	$TsNH_2$ (1)	Cs_2CO_3 (2)	CH_3CN (0.1)	40	*ca.* 54	-
5	$Pd(dba)_2$ (2.5)	$TsNH_2$ (1)	Cs_2CO_3 (2)	THF (0.1)	rt	37	<5
6	$Pd_2(dba)_3{\cdot}CHCl_3$ (2.5)	$TsNH_2$ (1)	Cs_2CO_3 (2)	THF (0.1)	rt	59	7
7	$Pd_2(dba)_3{\cdot}CHCl_3$ (2.5)	$TsNH_2$ (1.5)	Cs_2CO_3 (2)	THF (0.1)	rt	68	4
8	$Pd_2(dba)_3{\cdot}CHCl_3$ (2.5)	$TsNH_2$ (1.5)	Cs_2CO_3 (1)	THF (0.1)	rt	69	5
9	$Pd_2(dba)_3{\cdot}CHCl_3$ (2.5)	$TsNH_2$ (1.5)	Cs_2CO_3 (2)	THF (0.067)	rt	72	5
10	$Pd_2(dba)_3{\cdot}CHCl_3$ (2.5)	$TsNH_2$ (1.5)	Cs_2CO_3 (1)	THF (0.067)	rt	61	9

[a] Isolated yields.

Experimental Section

General Methods.

All reactions under argon atmosphere were performed using syringe-septum cap techniques and all glassware was dried in an oven at 80 °C for 2 h prior to use. For flash chromatography, silica gel (Wakosil C-200: Wako Pure Chemical Industries, Ltd) or NH_2 silica gel (Chromatorex NH-DM1020: Fuji Silysia Chemical Ltd.) was employed. Thin layer chromatography was performed on Merck TLC silica gel 60 F_{254} or Wako NH_2 silica gel 60 F_{254} plate (layer thickness 0.25 mm), which were developed using standard visualizing agents: UV fluorescence (254 nm) and anisaldehyde with heating. Melting points were measured by a hot stage melting point apparatus (uncorrected). ^{1}H NMR spectra were recorded using a JEOL AL-400 or JEOL ECA-500 spectrometer, and chemical shifts are reported in δ (ppm) relative to TMS as internal standard. ^{13}C NMR spectra were recorded using a JEOL AL-400 or JEOL ECA-500 spectrometer and referenced to the residual solvent signal. ^{1}H NMR spectra are tabulated as follows: chemical shift, multiplicity (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), number of protons, and coupling constant(s). Exact mass (HRMS) spectra were recorded on a JMS-HX/HX 110A mass spectrometer. Infrared (IR) spectra were obtained on a JASCO FT/IR-4100 FT-IR spectrometer with JASCO ATR PRO410-S.

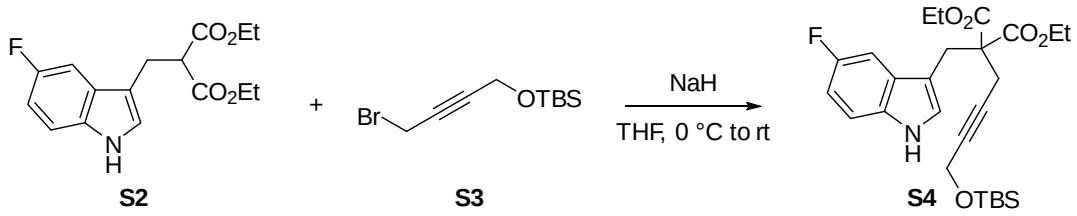
Preparation of the Substrates.

The known compounds **S1**,[1] **S6-8**[2] and **S9**[3] were prepared according to the literature procedure.

1 Jones, D. T.; Artman, G. D.; Williams, R. M. *Tetrahedron Lett.* **2007**, *48*, 1291–1294.

2 Cera, G.; Crispino, P.; Monari, M.; Bandini, M. *Chem. Commun*. **2011**, *47*, 7803–7805.

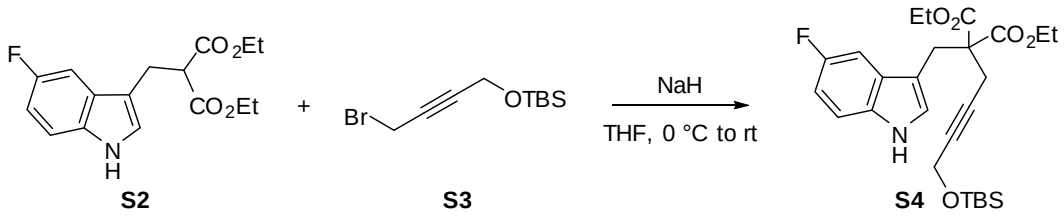
3 Miyake, Y.; Endo, S.; Moriyama, T.; Sakata, K.; Nishibayashi, Y. *Angew. Chem. Int. Ed*. **2013**, *52*, 1758–1762.



Diethyl 2-[(5-Fluoro-1*H*-indol-3-yl)methyl]malonate (S2).

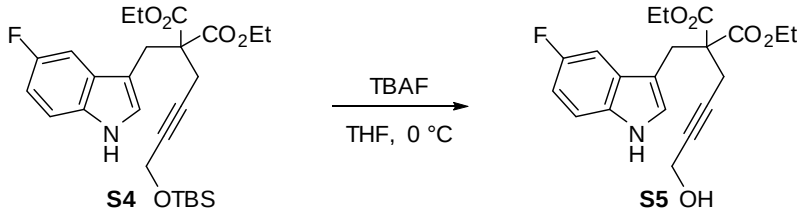
The malonate **S2** was prepared by use of a slight modification of the Williams' procedure.[1] To a stirred mixture of **S1** (1.0 g, 5.20 mmol) and diethyl malonate (736 μL, 4.85 mmol) in Et_2O (2.6 mL) was added dropwise ethylpropiolate (529 μL, 5.20 mmol) at room temperature. The mixture was stirred for 45 min at this temperature, followed by quenching with H_2O. The whole was extracted with Et_2O. The extract was washed successively with H_2O and brine, and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (8:1) to give **S2** as a pale yellow needle (1.27 g, 77% yield): mp 60–61 °C; IR (neat): 3410 (NH), 1726 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.21 (t, J = 7.2 Hz, 6H), 3.33 (d, J = 7.7 Hz, 2H), 3.72 (t, J = 7.7 Hz, 1H), 4.12-4.20 (m, 4H), 6.93 (ddd, J = 9.2, 9.2, 2.5 Hz, 1H), 7.09 (d, J = 2.3 Hz, 1H), 7.23-7.26 (m, 2H), 8.00 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9 (2C), 24.4, 52.9, 61.4 (2C), 103.5 (d, J = 24.0 Hz), 110.4 (d, J = 26.4 Hz), 111.8 (d, J = 9.6 Hz), 112.3 (d, J = 4.8 Hz) 124.4,

127.5 (d, J = 9.6 Hz), 132.6, 157.8 (d, J = 235 Hz), 169.2 (2C). *Anal*. Calcd for $C_{16}H_{18}FNO_4$: C, 62.53; H, 5.90; N, 4.56. Found: C, 62.41; H, 5.93; N, 4.50.



Diethyl 2-{4-[(*tert*-Butyldimethylsilyl)oxy]but-2-yn-1-yl}-2-[(5-fluoro-1*H*-indol-3-yl)methyl]malonate (S4).

To a solution of **S2** (1.14 g, 3.71 mmol) in THF was added NaH (60% suspension in mineral oil; 297 mg, 7.42 mmol) at 0 °C. The suspension was stirred for 30 min at 0 °C, then **S3** (1.17 g, 4.45) in THF was added dropwise. The reaction was warmed up to room temperature and stirred for 2 h, followed by quenching with H_2O. The whole was extracted with EtOAc. The extract was washed successively with H_2O and brine, and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (5:1) to give **S4** as a colorless oil (682 mg, 38%): IR (neat): 3387 (NH), 2332 (C≡C), 1736 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.14 (s, 6H), 0.92 (s, 9H), 1.23 (t, J = 7.0 Hz, 6H), 2.81 (t, J = 2.1 Hz, 2H), 3.51 (s, 2H), 4.10-4.22 (m, 4H), 4.37 (t, J = 2.1 Hz, 2H), 6.90 (ddd, J = 9.0, 9.0, 2.5 Hz, 1H), 7.09 (d, J = 2.4 Hz, 1H), 7.21 (dd, J = 9.0, 4.3 Hz, 1H), 7.29 (dd, J = 9.9, 2.5 Hz, 1H), 8.12 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ –5.2 (2C), 13.9 (2C), 18.3, 23.1, 25.8 (3C), 27.3, 51.8, 58.0, 61.6 (2C), 80.2, 82.4, 103.8 (d, J = 24.0 Hz), 110.0 (d, J = 4.8 Hz), 110.4 (d, J = 26.4 Hz), 111.6 (d, J = 9.6 Hz), 125.3, 128.5 (d, J = 9.6 Hz), 132.3, 157.9 (d, J = 234 Hz), 170.1 (2C). HRMS (FAB) calcd $C_{26}H_{36}FNO_5Si$: [M^+], 489.2347; found: [M^+], 489.2350.

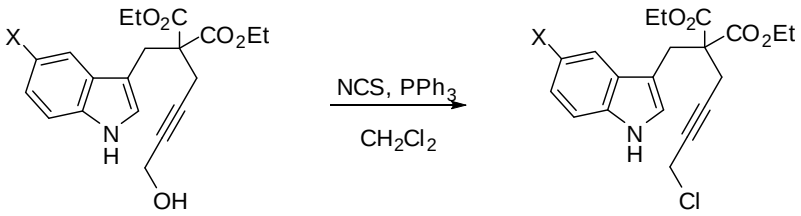


Diethyl 2-[(5-Fluoro-1*H*-indol-3-yl)methyl]-2-(4-hydroxybut-2yn-1-yl)malonate (S5).

To a stirred solution of **S4** (638 mg, 1.30 mmol) in THF (6.5 mL) was added TBAF (1.00 M solution in THF; 1.43 mL, 1.43 mmol) at 0 °C. The mixture was stirred for 1.5 h at this temperature and quenched by addition of saturated NH_4Cl. The whole was extracted with EtOAc. The extract was washed with H_2O and brine, and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (3:1) to give **S5** as a pale yellow oil (485 mg, 99% yield): IR (neat): 3410 (NH), 3403 (OH), 2254 (C≡C), 1720 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.24 (t, J = 7.2 Hz, 6H), 1.97 (s, 1H), 2.80 (s, 2H), 3.51 (s, 2H), 4.11-4.25 (m, 4H), 4.31 (s, 2H), 6.90 (ddd, J = 8.9, 8.9, 2.5 Hz, 1H), 7.08 (d, J = 2.3 Hz, 1H), 7.22 (dd, J = 8.9, 4.4 Hz, 1H), 7.29 (dd, J = 10.0, 2.5 Hz, 1H), 8.19 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9 (2C), 23.1, 27.3, 51.2, 58.0, 61.7 (2C), 81.4, 82.2, 103.7 (d, J = 23.0 Hz), 109.7 (d,

J = 4.8 Hz), 110.4 (d, *J* = 25.9 Hz), 111.7 (d, *J* = 10.5 Hz), 125.4, 128.5 (d, *J* = 11.5 Hz), 132.3, 157.9 (d, *J* = 235 Hz), 170.2 (2C). HRMS (FAB) calcd $C_{20}H_{22}FNO_5$: [M^+], 375.1482; found: [M^+], 375.1478.

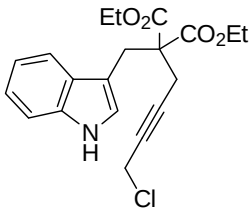
General procedure for the synthesis of propargyl chloride 1a and 1f-h.



S6 (X = H)
S5 (X = F)
S7 (X = Br)
S8 (X = OMe)

1a (X = H)
1f (X = F)
1g (X = Br)
1h (X = OMe)

To a stirred mixture of a propargyl alcohol (1.0 equiv) and PPh_3 (1.5 equiv) in CH_2Cl_2 was added NCS (1.2 equiv) in CH_2Cl_2 at room temperature. The mixture was stirred for 1.5-3 h at this temperature and quenched by addition of H_2O. The whole was extracted with EtOAc. The extract was washed with H_2O, brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel to give the corresponding propargyl chloride.

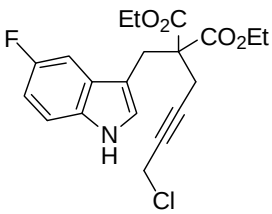


1a

Diethyl 2-[(1*H*-Indol-3-yl)methyl]-2-(4-chlorobut-2-yn-1-yl)malonate (1a).

Brown oil. Flash chromatography: *n*-hexane–EtOAc = 4:1. Yield = 90%.

IR (neat): 3409 (NH), 2242 (C≡C), 1729 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.23 (t, *J* = 7.3 Hz, 6H), 2.83 (t, *J* = 2.2 Hz, 2H), 3.57 (s, 2H), 4.10-4.25 (m, 6H), 7.03 (d, *J* = 2.4 Hz, 1H), 7.09 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 7.16 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 7.32 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.66 (dd, *J* = 8.0, 1.0 Hz, 1H), 8.08 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0 (2C), 23.1, 27.3, 30.8, 58.2, 61.7 (2C), 78.3, 82.9, 109.6, 111.0, 118.9, 119.5, 122.0, 123.4, 128.1, 135.8, 170.1 (2C). HRMS (FAB) calcd $C_{20}H_{21}ClNO_4$: [M – H]$^-$, 374.1165; found: [M – H]$^-$, 374.1168.

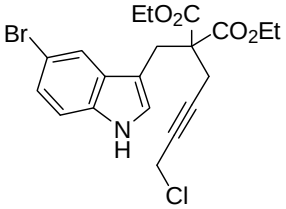


1f

Diethyl 2-(4-Chlorobut-2-yn-1-yl)-2-[(5-fluoro-1*H*-indol-3-yl)methyl]malonate (1f).

Brown oil. Flash chromatography: *n*-hexane–EtOAc = 5:1. Yield = 87%.

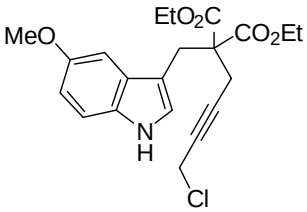
IR (neat): 3407 (NH), 2238 (C≡C), 1727 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.25 (t, *J* = 7.4 Hz, 6H), 2.82 (t, *J* = 2.3 Hz, 2H), 3.51 (s, 2H), 4.13-4.24 (m, 6H), 6.90 (ddd, *J* = 9.0, 9.0, 2.5 Hz, 1H), 7.07 (d, *J* = 2.3 Hz, 1H), 7.21 (dd, *J* = 9.0, 4.3 Hz, 1H), 7.29 (dd, *J* = 9.0, 2.5 Hz, 1H), 8.17 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9 (2C), 23.1, 27.4, 30.7, 58.0, 61.8 (2C), 78.6, 82.7, 103.8 (d, *J* = 24.0 Hz), 109.7 (d, *J* = 4.8 Hz), 110.5 (d, *J* = 26.4 Hz), 111.7 (d, *J* = 9.6 Hz), 125.3, 128.5 (d, *J* = 9.6 Hz), 132.3, 157.9 (d, *J* = 235 Hz), 170.0 (2C). HRMS (FAB) calcd $C_{20}H_{21}ClFNO_4$: [M^+], 393.1143; found: [M^+], 393.1147.



1g

Diethyl 2-[(5-Bromo-1*H*-indol-3-yl)methyl]-2-(4-chlorobut-2-yn-1-yl)malonate (1g). Brown oil. Flash chromatography: *n*-hexane–EtOAc = 4:1. Yield = 73%.

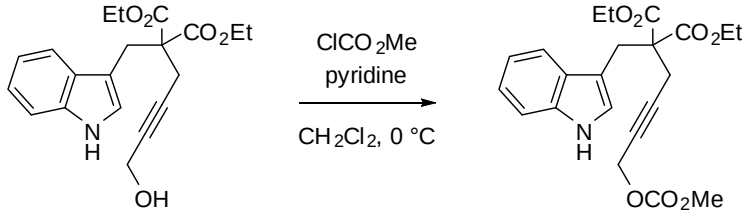
IR (neat): 3384 (NH), 2238 (C≡C), 1727 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.27 (t, J = 7.2 Hz, 6H), 2.80 (t, J = 2.3 Hz, 2H), 3.52 (s, 2H), 4.15-4.25 (m, 6H), 7.06 (d, J = 2.4 Hz, 1H), 7.18 (d, J = 8.6 Hz, 1H), 7.23 (dd, J = 8.6, 1.9 Hz, 1H), 7.75 (d, J = 1.9 Hz, 1H), 8.17 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0 (2C), 23.1, 27.2, 30.7, 57.8, 61.9 (2C), 78.7, 82.6, 109.3, 112.5, 112.9, 121.5, 124.8, 124.9, 129.7, 134.4, 169.9 (2C). HRMS (FAB) calcd $C_{20}H_{21}BrClNO_4$: [M^+], 453.0342; found: [M^+], 453.0345.



1h

Diethyl 2-(4-Chlorobut-2-yn-1-yl)-2-[(5-methoxy-1*H*-indol-3-yl)methyl]malonate (1h). Brown oil. Flash chromatography: *n*-hexane–EtOAc = 4:1. Yield = 70%.

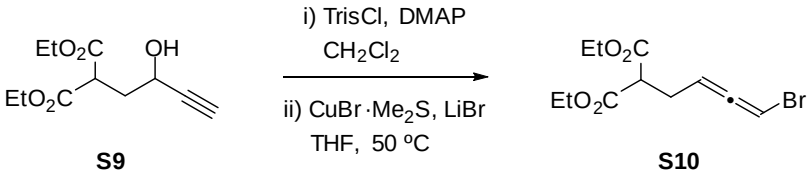
IR (neat): 3417 (NH), 2239 (C≡C), 1732 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.23 (t, J = 7.0 Hz, 6H), 2.85 (t, J = 2.0 Hz, 2H), 3.53 (s, 2H), 3.86 (s, 3H), 4.14-4.24 (m, 6H), 6.83 (dd, J = 8.9, 2.5 Hz, 1H), 6.97 (d, J = 2.5 Hz, 1H), 7.15 (d, J = 2.5 Hz, 1H), 7.20 (d, J = 8.9 Hz, 1H), 8.00 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0 (2C), 23.1, 27.4, 30.7, 55.9, 58.5, 61.7 (2C), 78.3, 83.1, 100.5, 109.4, 111.8, 112.6, 124.1, 128.6, 131.0, 154.2, 170.0 (2C). HRMS (FAB) calcd $C_{21}H_{24}ClNO_5$: [M^+], 405.1343; found: [M^+], 405.1345.



S6 **1b**

Diethyl 2-[(1*H*-Indol-3-yl)methyl]-2-{4-[(methoxycarbonyl)oxy]but-2-yn-1-yl}malonate (1b).

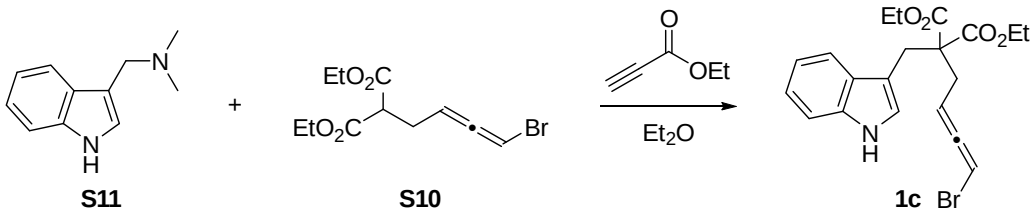
To a stirred mixture of **S6** (50 mg, 0.135 mmol), pyridine (33 μL, 0.41 mmol) in CH_2Cl_2 (675 μL) was added $ClCO_2Me$ (14 μL, 0.20 mmol) at 0 °C. The mixture was stirred for 30 min at this temperature and quenched by addition of saturated NH_4Cl. The whole was extracted with Et_2O. The extract was washed with H_2O, 1N HCl, brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (4:1) to give **1b** as a brown oil (47.5 mg, 82% yield): IR (neat): 3407 (NH), 2252 (C≡C), 1731 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22 (t, J = 6.8 Hz, 6H), 2.82 (t, J = 2.3 Hz, 2H), 3.56 (s, 2H), 3.82 (s, 3H), 4.10-4.23 (m, 4H), 4.78 (t, J = 2.3 Hz, 2H), 7.01 (d, J = 2.3 Hz, 1H), 7.09 (ddd, J = 8.0, 8.0, 1.0 Hz, 1H), 7.15 (ddd, J = 8.0, 8.0, 1.0 Hz, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 8.14 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9 (2C), 23.0, 27.3, 55.1, 55.9, 58.1, 61.6 (2C), 77.3, 83.7, 109.5, 110.0, 118.8, 119.4, 122.0, 123.5, 128.1, 135.8, 155.2, 170.0 (2C). HRMS (FAB) calcd $C_{22}H_{25}NO_7$: [M – H]$^-$, 414.1558; found: [M – H]$^-$, 414.1564.



S9 **S10**

Diethyl 2-(4-Bromobuta-2,3-dien-1-yl)malonate (S10)

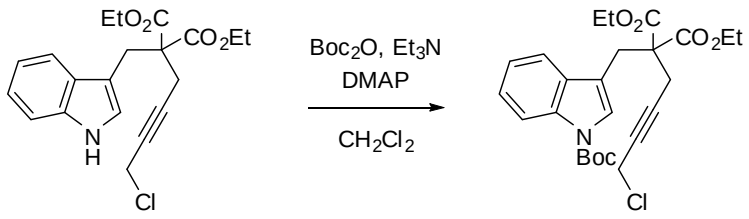
To a stirred mixture of **S9** (410 mg, 1.8 mmol) and TrisCl (1.36 g, 4.5 mmol) in CH_2Cl_2 (41 mL) was added DMAP (770 mg, 6.3 mmol) at room temperature. The mixture was stirred for 3 h at this temperature. Concentration of the mixture under reduced pressure followed by rapid filtration through a short pad of silica gel with Et_2O to give a crude sulfonate, which was used without further purification. CuBr·Me_2S (1.10 g, 5.4 mmol) and LiBr (465 mg, 0.373 mmol) was dissolved in THF (18 mL) at room temperature under argon, and the mixture was stirred for 30 min at this temperature. To this mixture was added a solution of the above crude sulfonate in THF (26 mL) at room temperature. The mixture was allowed to warm to 50 °C and stirred at this temperature for 1.5 h, which was quenched by addition of saturated NH_4Cl and 28% NH_4OH. The whole was extracted with EtOAc. The extract was washed with H_2O and brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (30:1) to give **S10** as a colorless oil (330 mg, 63% yield): IR (neat): 1958 (C=C=C), 1732 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.26-1.31 (m, 6H), 2.73-2.78 (m, 2H), 3.52 (t, J = 7.4 Hz, 1H), 4.18-4.27 (m, 4H), 5.45 (dd, J = 12.6, 5.7 Hz, 1H), 6.00 (ddd, J = 5.7, 2.4, 2.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0 (2C), 21.2, 50.8, 61.7 (2C), 73.7, 97.3, 168.4, 168.5, 202.3; HRMS (FAB) calcd $C_{11}H_{16}BrNO_4$: $[M + H]^+$, 291.0232; found: $[M + H]^+$, 291.0227.



S11 **S10** **1c**

Diethyl 2-(4-Bromobuta-2,3-dien-1-yl)-2-[(1*H*-indol-3-yl)methyl]malonate (1c).

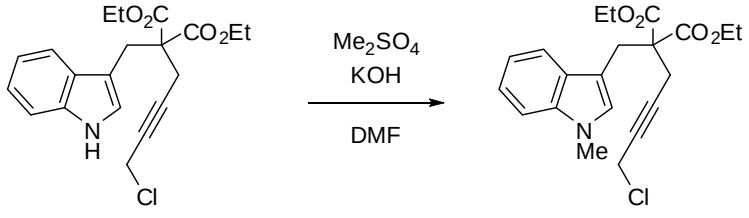
To a stirred mixture of **S11** (286 mg, 1.13 mmol) and **S10** (306 mg, 1.05 mmol) in Et_2O (1.1 mL) was added dropwise ethylpropiolate (115 μL, 1.13 mmol) at room temperature. The mixture was stirred for 5 h at this temperature, followed by quenching with H_2O. The whole was extracted with EtOAc. The extract was washed successively with H_2O and brine, and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (8:1 to 5:1) to give **1c** as a brown oil (285 mg, 64% yield): IR (neat): 3393 (NH), 1957 (C=C=C), 1720 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18-1.24 (m, 6H), 2.75-2.77 (m, 2H), 3.42-3.52 (m, 2H), 4.10-4.22 (m, 4H), 5.34-5.41 (m, 1H), 5.92-5.97 (m, 1H), 7.03 (d, J = 2.3 Hz, 1H), 7.10 (dd, J = 8.0, 8.0 Hz, 1H), 7.17 (dd, J = 8.0, 8.0 Hz, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 8.05 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9 (2C), 28.0, 31.9, 58.6, 61.5 (2C), 72.4, 95.7, 109.5, 111.1, 118.7, 119.4, 121.9, 123.4, 128.0, 135.7, 170.7 (2C), 203.6. HRMS (FAB) calcd $C_{20}H_{22}BrNO_4$: $[M^+]$, 419.0732; found: $[M^+]$, 419.0724.



1a **1d**

Diethyl 2-{[1-(*tert*-Butoxycarbony)-1*H*-indol-3-yl]methyl}-2-(4-chlorobut-2-yn-1-yl)malonate (1d).

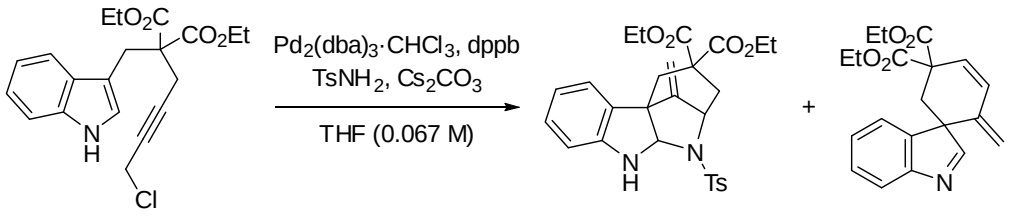
To a stirred mixture of **1a** (100 mg, 0.27 mmol), DMAP (3.2 mg, 0.027 mmol) and Et_3N (46 μL, 0.32 mmol) in CH_2Cl_2 (2.6 mL) was added Boc_2O (70 mg, 0.32 mmol) at room temperature. The mixture was stirred for 30 min at this temperature and quenched by addition of H_2O. The whole was extracted with EtOAc. The extract was washed with H_2O, brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (10:1) to give **1d** as a colorless oil (91.0 mg, 72% yield): IR (neat): 1733 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.26 (t, J = 7.3 Hz, 6H), 1.66 (s, 9H), 2.83 (t, J = 2.2 Hz, 2H), 3.49 (s, 2H), 4.14-4.25 (m, 6H), 7.22 (ddd, J = 7.6, 7.6, 1.0 Hz, 1H), 7.29 (ddd, J = 7.6, 7.6, 1.0 Hz, 1H), 7.41 (s, 1H), 7.63 (dd, J = 7.6, 1.0 Hz, 1H), 8.05-8.14 (br m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0 (2C), 23.2, 26.9, 28.2 (3C), 30.7, 57.9, 61.9 (2C), 78.7, 82.6, 83.7, 114.4, 115.2, 119.1, 122.5, 124.4, 124.9, 131.0, 135.1, 149.6, 169.7 (2C). HRMS (FAB) calcd $C_{25}H_{30}ClNO_6$: [M^+], 475.1762; found: [M^+], 475.1758.



1a **1e**

Diethyl 2-(4-Chlorobut-2-yn-1-yl)-2-[(1-methyl-1*H*-indol-3-yl)methyl]malonate (1e).

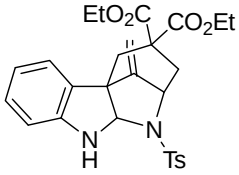
To a stirred mixture of **1a** (183 mg, 0.49 mmol) and KOH (64 mg, 0.97 mmol) in DMF (4.8 mL) was added Me_2SO_4 (92 μL, 0.32 mmol) at room temperature. The mixture was stirred for 3.5 h at this temperature and quenched by addition of H_2O. The whole was extracted with EtOAc. The extract was washed with H_2O, brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (6:1) to give **1e** as a pale yellow oil (100 mg, 53% yield): IR (neat): 2252 (C≡C), 1735 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.24 (t, J = 7.2 Hz, 6H), 2.83 (t, J = 2.3 Hz, 2H), 3.54 (s, 2H), 3.72 (s, 3H), 4.11-4.24 (m, 6H), 6.87 (s, 1H), 7.08 (ddd, J = 7.6, 7.6, 1.1 Hz, 1H), 7.18 (ddd, J = 7.6, 7.6, 1.1 Hz, 1H), 7.23-7.26 (m, 1H), 7.63 (d, J = 7.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0 (2C), 23.1, 27.3, 30.8, 32.7, 58.2, 61.6 (2C), 78.2, 83.0, 107.8, 109.1, 118.9 (2C), 121.5, 128.1, 128.6, 136.6, 169.7 (2C). HRMS (FAB) calcd $C_{21}H_{24}ClNO_4$: [M^+], 389.1394; found: [M^+], 389.1390.



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

General Procedure for the Palladium-Catalyzed Cascade Cyclization of Propargyl Chlorides.

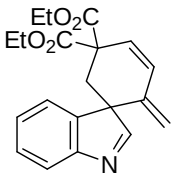
To a stirred mixture of **1a** (30 mg, 0.080 mmol) and $TsNH_2$ (20.5 mg, 0.16 mmol) were added $Pd_2(dba)_3{\cdot}CHCl_3$ (2.1 mg, 3.9 μmol, 2.5 mol %), dppf (3.4 mg, 8.0 μmol, 10 mol %), and Cs_2CO_3 (52 mg, 0.16 mmol) at room temperature under argon. The mixture was stirred for 3 h at this temperature, and H_2O was added to the mixture. The whole was extracted with EtOAc. The extract was washed with H_2O, brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over NH_2 silica gel with *n*-hexane–EtOAc (8:1) to give **2a** (29.3 mg, 72% yield) and **3a** (1.4 mg, 5.2% yield).



2a

Diethyl 11-Methylene-1-tosyl-2,3,10,10a-tetrahydro-1*H*-2,5a-methanoazepino[2,3-*b*]indole-4,4(5*H*)-dicarboxylate (2a).

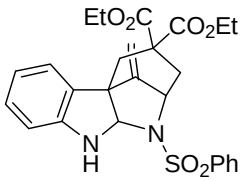
Colorless solid; mp 164–165 °C; IR (neat): 3361 (NH), 1729 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.24 (t, J = 7.1 Hz, 3H), 1.35 (t, J = 7.1 Hz, 3H), 2.38 (s, 3H), 2.40 (d, J = 13.7 Hz, 1H), 2.48 (d, J = 13.7 Hz, 1H), 3.22 (d, J = 13.7 Hz, 2H), 4.09-4.10 (m, 1H), 4.13-4.39 (m, 4H), 4.44 (s, 1H), 4.66 (d, J = 4.1 Hz, 1H), 4.76 (s, 1H), 6.05 (d, J = 4.6 Hz, 1H), 6.64 (d, J = 7.8 Hz, 1H), 6.82 (dd, J = 7.8, 7.8 Hz, 1H), 7.07-7.15 (m, 2H), 7.25 (d, J = 8.2 Hz, 2H), 7.86 (d, J = 8.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9 (2C), 21.4, 37.7, 39.9, 52.3, 57.7, 61.3, 62.1, 62.6, 84.0, 103.4, 110.7, 119.3, 122.9, 127.4 (3C), 129.0, 129.6 (2C), 137.6, 143.2, 148.8, 151.7, 170.9, 171.3. HRMS (FAB) calcd $C_{27}H_{30}N_2O_6S$: [M^+], 510.1825; found: [M^+], 510.1832.



3a

Diethyl 2-Methylenespiro[cyclohexane-1,3'-indol]-3-ene-5,5-dicarboxylate (3a).

Yellow oil; IR (neat): 1732 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22-1.28 (m, 6H), 2.37 (d, J = 14.3 Hz, 1H), 2.72 (d, J = 14.3 Hz, 1H), 4.16-4.30 (m, 4H), 4.56 (s, 1H), 4.87 (s, 1H), 6.18 (d, J = 10.3 Hz, 1H), 6.57 (d, J = 10.3 Hz, 1H), 7.27-7.35 (m, 2H), 7.37-7.43 (m, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.95 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9 (2C), 35.0, 55.5, 60.8, 62.3 (2C), 114.8, 121.5, 122.9, 125.4, 126.5, 128.5, 131.6, 137.6, 141.3, 155.4, 169.8, 170.1, 173.9. HRMS (FAB) calcd $C_{20}H_{21}NO_4$: [M^+], 340.1549; found: [M^+], 340.1555.

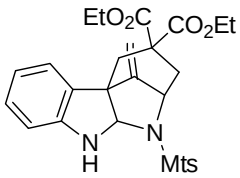


2b

Diethyl 11-Methylene-1-(phenylsulfonyl)-2,3,10,10a-tetrahydro-1*H*-2,5a-methano-azepino[2,3-*b*]indole-4,4(5*H*)-dicarboxylate (2b).

IR (neat): 3355 (NH), 1727 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.24 (t, J = 7.2 Hz, 3H), 1.35 (t, J = 7.2 Hz, 3H), 2.41 (d, J = 13.6 Hz, 1H), 2.49 (d, J = 13.6 Hz, 1H), 3.21-3.27 (m,

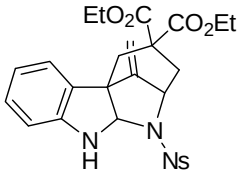
2H), 4.10-4.12 (m, 1H), 4.13-4.40 (m, 4H), 4.46 (s, 1H), 4.67 (d, *J* = 4.0 Hz, 1H), 4.77 (s, 1H), 6.07 (d, *J* = 4.0 Hz, 1H), 6.65 (d, *J* = 7.7 Hz, 1H), 6.83 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.09 (d, *J* = 7.7 Hz, 1H), 7.14 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.43-7.55 (m, 3H), 7.99 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9 (2C), 37.7, 39.9, 52.3, 57.7, 61.3, 62.1, 62.6, 84.0, 103.6, 110.8, 119.4, 122.9, 127.3 (2C), 127.4, 128.9 (2C), 129.0, 132.5, 140.5, 148.8, 151.6, 170.9, 171.2. HRMS (FAB) calcd $C_{26}H_{28}N_2O_6S$: [M^+], 496.1668; found: [M^+], 496.1668.



2c

Diethyl 1-(Mesitylsulfonyl)-11-methylene-2,3,10,10a-tetrahydro-1*H*-2,5a-methanoazepino[2,3-*b*]indole-4,4(5*H*)-dicarboxylate (2c).

IR (neat): 3377 (NH), 1728 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22-1.28 (m, 6H), 2.31 (s, 3H), 2.38 (d, *J* = 14.5 Hz, 1H), 2.64 (s, 6H), 2.73 (dd, *J* = 13.7, 2.9 Hz, 1H), 3.08 (dd, *J* = 14.5, 2.9 Hz, 1H), 3.21 (d, *J* = 13.7 Hz, 1H), 4.02 (d, *J* = 4.0 Hz, 1H), 4.10-4.33 (m, 4H), 4.37 (t, *J* = 2.9 Hz, 1H), 4.52 (s, 1H), 4.92 (s, 1H), 5.98 (d, *J* = 4.0 Hz, 1H), 6.46 (d, *J* = 8.0 Hz, 1H), 6.76 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.95 (s, 2H), 7.03-7.09 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.7, 13.9, 21.0, 23.1 (2C), 38.6, 39.4, 51.5, 58.0, 62.0, 62.3, 62.4, 82.8, 103.7, 109.9, 118.6, 122.8, 126.8, 128.9, 132.0 (2C), 133.9, 140.2 (2C), 142.6, 148.9, 151.4, 170.9, 171.5. HRMS (FAB) calcd $C_{29}H_{34}N_2O_6S$: [M^+], 538.2138; found: [M^+], 538.2142.

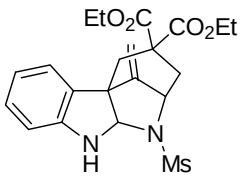


2d

Diethyl 11-Methylene-1-[(2-nitrophenyl)sulfonyl]-2,3,10,10a-tetrahydro-1*H*-2,5a-methanoazepino[2,3-*b*]indole-4,4(5*H*)-dicarboxylate (2d).

The reaction was performed for 2 h at 60 °C.

IR (neat): 3372 (NH), 1728 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.24 (t, *J* = 7.2 Hz, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 2.46-2.51 (m, 2H), 3.23-3.32 (m, 2H), 4.10-4.40 (m, 5H), 4.57 (s, 1H), 4.66 (d, *J* = 4.6 Hz, 1H), 4.95 (s, 1H), 6.07 (d, *J* = 4.6 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 6.86 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.12-7.17 (m, 2H), 7.59-7.71 (m, 3H), 8.18 (dd, *J* = 7.4, 1.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.8, 14.0, 37.8, 39.9, 52.3, 57.9, 62.3, 62.6, 62.8, 84.0, 104.3, 111.0, 119.8, 123.0, 124.4, 127.3, 129.1, 129.5, 132.1, 133.1, 134.6, 148.5, 148.9, 151.5, 170.8, 171.1. HRMS (FAB) calcd $C_{26}H_{27}N_3O_8S$: [M^+], 541.1519; found: [M^+], 541.1511.

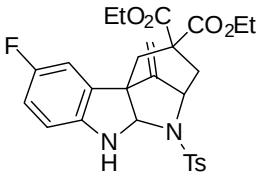


2e

Diethyl 11-Methylene-1-(methylsulfonyl)-2,3,10,10a-tetrahydro-1*H*-2,5a-methanoazepino[2,3-*b*]indole-4,4(5*H*)-dicarboxylate (2e).

The reaction was performed for 24 h at 60 °C.

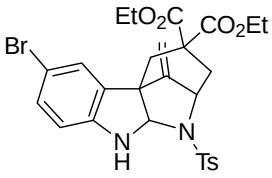
IR (neat): 3345 (NH), 1728 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.24 (t, *J* = 7.2 Hz, 3H), 1.33 (t, *J* = 7.2 Hz, 3H), 2.43-2.48 (m, 2H), 2.98 (s, 3H), 3.20-3.26 (m, 2H), 4.11-4.33 (m, 4H), 4.35-4.37 (m, 1H), 4.50 (s, 1H), 4.55 (d, *J* = 4.6 Hz, 1H), 4.96 (s, 1H), 5.78 (d, *J* = 4.6 Hz, 1H), 6.67 (d, *J* = 7.4 Hz, 1H), 6.87 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.10-7.17 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9, 14.0, 37.5, 40.5, 40.6, 52.6, 58.2, 61.8, 62.2, 62.6, 84.0, 103.4, 111.2, 119.8, 122.9, 127.8, 129.1, 148.6, 152.1, 170.7, 171.2. HRMS (FAB) calcd $C_{21}H_{26}N_2O_6S$: [M^+], 434.1512; found: [M^+], 434.1512.



2k

Diethyl 7-Fluoro-11-methylene-1-tosyl-2,3,10,10a-tetrahydro-1*H*-2,5a-methanoazepino[2,3-*b*]indole-4,4(5*H*)-dicarboxylate (2k).

IR (neat): 3345 (NH), 1730 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.24 (t, J = 7.7 Hz, 3H), 1.35 (t, J = 7.7 Hz, 3H), 2.32 (d, J = 13.7 Hz, 1H), 2.39 (s, 3H), 2.48 (d, J = 14.9 Hz, 1H), 3.20-3.23 (m, 2H), 4.09-4.11 (m, 1H), 4.13-4.41 (m, 4H), 4.46 (s, 1H), 4.55 (d, J = 4.0 Hz, 1H), 4.79 (s, 1H), 6.07 (d, J = 4.6 Hz, 1H), 6.55 (dd, J = 8.0, 4.3 Hz, 1H), 6.80-6.86 (m, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.85 (d, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.8, 14.0, 21.5, 37.6, 39.9, 52.2, 57.7, 61.2, 62.2, 62.7, 84.4, 103.6, 110.6 (d, J = 22.8 Hz), 111.2 (d, J = 8.4 Hz), 115.1 (d, J = 25.2 Hz), 127.4 (2C), 128.9 (d, J = 10.8 Hz), 129.6 (2C), 137.5, 143.3, 144.7, 151.3, 157.1 (d, J = 243.5 Hz), 170.9, 171.11. HRMS (FAB) calcd $C_{27}H_{29}FN_2O_6S$: [M^+], 528.1730; found: [M^+], 528.1724.

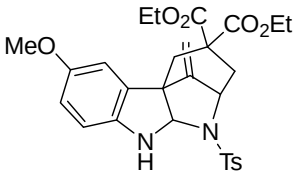


2l

Diethyl 7-Bromo-11-methylene-1-tosyl-2,3,10,10a-tetrahydro-1*H*-2,5a-methanoazepino[2,3-*b*]indole-4,4(5*H*)-dicarboxylate (2l).

The reaction was performed for 3 h at 60 °C.

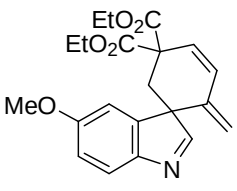
IR (neat): 3364 (NH), 1730 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.25 (t, J = 7.2 Hz, 3H), 1.34 (t, J = 7.2 Hz, 3H), 2.32 (d, J = 13.7 Hz, 1H), 2.39 (s, 3H), 2.48 (d, J = 12.6 Hz, 1H), 3.17-3.23 (m, 2H), 4.10 (s, 1H), 4.12-4.38 (m, 4H), 4.49 (s, 1H), 4.65 (d, J = 4.6 Hz, 1H), 4.79 (s, 1H), 6.06 (d, J = 4.6 Hz, 1H), 6.52 (d, J = 8.3 Hz, 1H), 7.18 (d, J = 2.0 Hz, 1H), 7.23 (dd, J = 8.3, 2.0 Hz, 1H), 7.26 (d, J = 8.0 Hz, 2H), 7.83 (d, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.8, 14.0, 21.5, 37.5, 39.8, 52.2, 57.6, 61.2, 62.2, 62.6, 84.1, 103.7, 111.0, 119.3, 126.0, 127.3 (2C), 129.0, 129.6 (2C), 129.7, 137.4, 143.3, 147.9, 151.1, 170.8, 171.0. HRMS (FAB) calcd $C_{27}H_{29}BrN_2O_6S$: [M^+], 588.0930; found: [M^+], 588.0926.



2m

Diethyl 7-Methoxy-11-methylene-1-tosyl-2,3,10,10a-tetrahydro-1*H*-2,5a-methanoazepino[2,3-*b*]indole-4,4(5*H*)-dicarboxylate (2m).

IR (neat): 3352 (NH), 1731 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.24 (t, J = 7.2 Hz, 3H), 1.35 (t, J = 7.2 Hz, 3H), 2.35 (d, J = 13.7 Hz, 1H), 2.38 (s, 3H), 2.46 (dd, J = 14.9, 1.7 Hz, 1H), 3.20-3.26 (m, 2H), 3.77 (s, 3H), 4.08-4.11 (m, 1H), 4.13-4.39 (m, 4H), 4.44 (d, J = 5.2 Hz, 1H), 4.47 (s, 1H), 4.77 (s, 1H), 6.03 (d, J = 5.2 Hz, 1H), 6.56 (d, J = 8.0 Hz, 1H), 6.67-6.71 (m, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.87 (d, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9, 14.0, 21.5, 37.7, 40.0, 52.3, 56.0, 57.9, 61.3, 62.1, 62.6, 84.3, 103.4, 110.1, 111.2, 113.6, 127.4 (2C), 128.8, 129.6 (2C), 137.6, 142.4, 143.1, 151.6, 153.7, 170.9, 171.3. HRMS (FAB) calcd $C_{28}H_{32}N_2O_7S$: [M^+], 540.1930; found: [M^+], 540.1935.

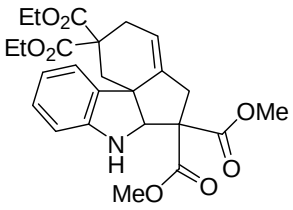


3d

Diethyl 5'-Methoxy-2-methylenespiro[cyclohexane-1,3'-indol]-3-ene-5,5-dicarboxylate (3d).

IR (neat): 1732 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22-1.30 (m, 6H), 2.38 (d, J = 14.3 Hz, 1H), 2.68 (d, J = 14.3 Hz, 1H), 3.84 (s, 3H), 4.19-4.27 (m, 4H), 4.58 (s, 1H), 4.89 (s, 1H), 6.17 (d, J = 10.3 Hz, 1H), 6.56 (d, J = 10.3 Hz, 1H), 6.86 (d, J = 2.6 Hz, 1H), 6.90 (dd,

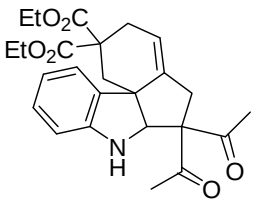
J = 8.6, 2.6 Hz, 1H), 7.56 (d, *J* = 8.6 Hz, 1H), 7.82 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9 (2C), 25.8, 35.2, 55.5, 55.7, 60.9, 62.3, 109.1, 113.6, 114.9, 121.9, 125.3, 131.6, 137.8, 143.0, 149.0, 158.9, 169.8, 170.1, 171.9. HRMS (FAB) calcd $C_{21}H_{23}NO_5$: $[M + H]^+$, 370.1654; found: $[M + H]^+$, 370.1653.



4a

2,2-Dimethyl 6,6-Dimethyl 3,5,6a,7-Tetrahydro-1*H*-indeno[1,7a-*b*]indole-2,2,6,6-tetracarboxylate (4a).

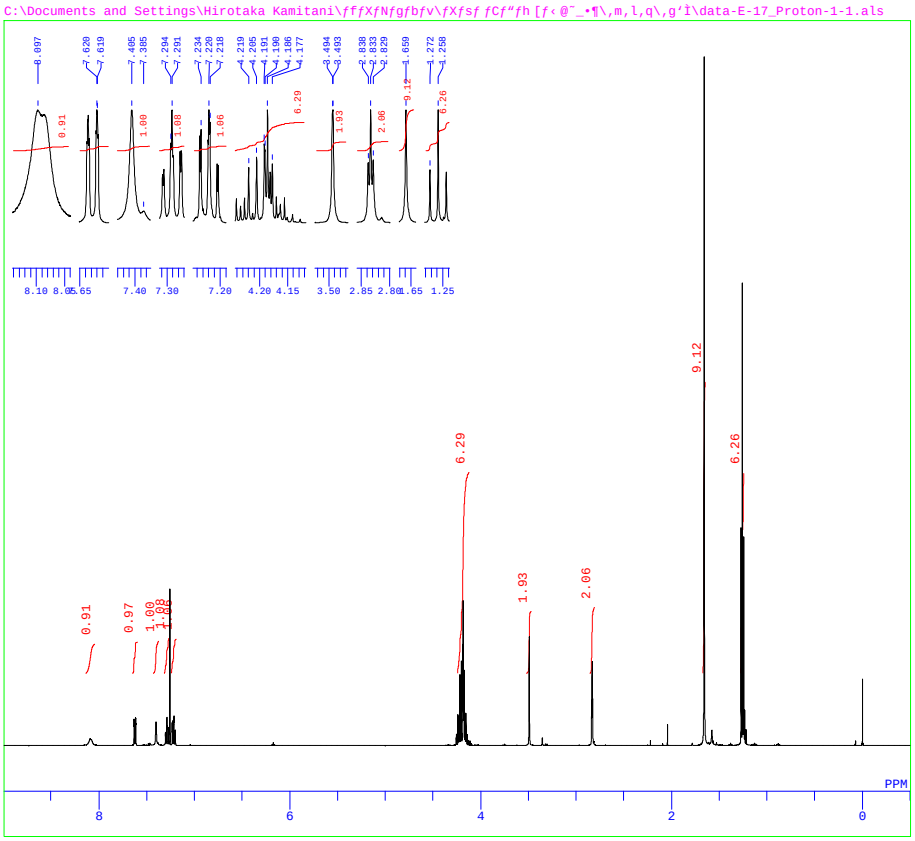
IR (neat): 1735 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.13 (t, *J* = 7.2 Hz, 3H), 1.23-1.28 (m, 3H), 2.53 (d, *J* = 14.9 Hz, 1H), 2.66-2.90 (m, 5H), 3.68 (s, 3H), 3.73 (s, 3H), 4.00-4.34 (m, 5H), 4.76 (s, 1H), 5.70-5.76 (m, 1H), 6.53 (d, *J* = 8.0 Hz, 1H), 6.67 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.99 (dd, *J* = 8.0, 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.8, 13.9, 29.6, 29.7, 38.6, 39.9, 52.6, 52.9, 53.9, 54.7, 61.5, 65.6., 74.2, 109.4, 118.0, 119.4, 123.6, 128.2, 135.0, 140.9, 149.6, 169.3, 170.6, 171.0, 171.8. HRMS (FAB) calcd $C_{25}H_{29}NO_8$: $[M^+]$, 471.1893; found: $[M^+]$, 471.1901.



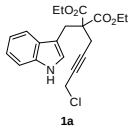
4b

Diethyl 6,6-Diacetyl 5,6,6a,7-tetrahydro-1*H*-indeno[1,7a-*b*]indole-2,2(3*H*)-dicarboxylate (4b).

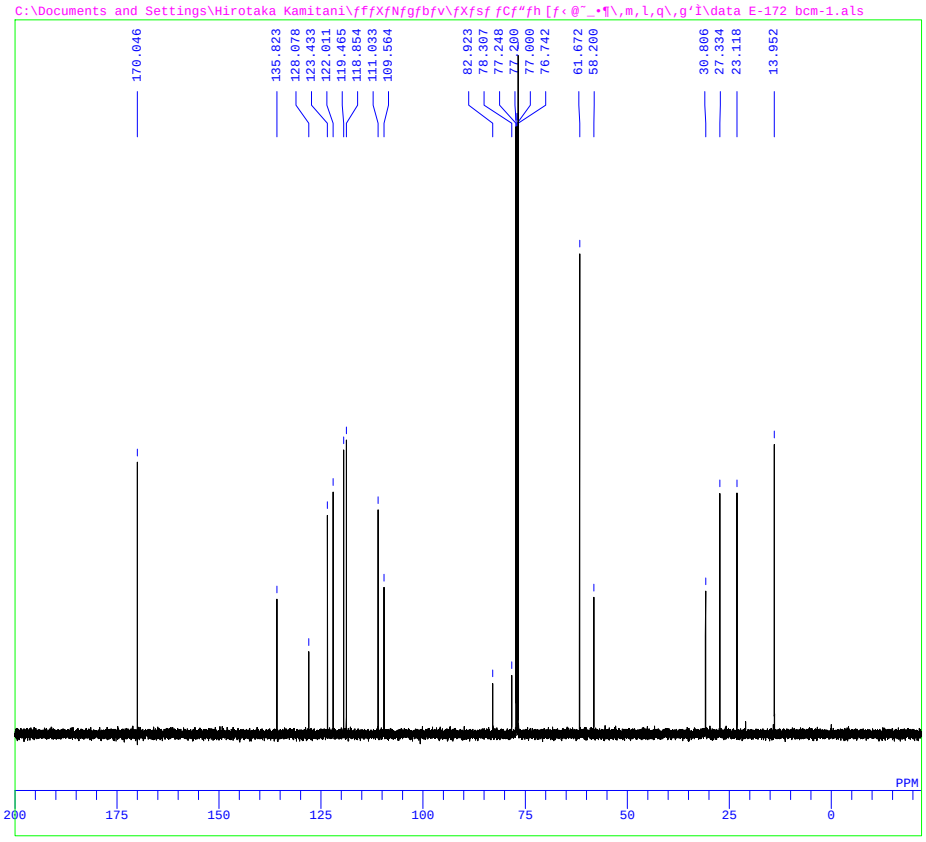
IR (neat): 3406 (NH), 1728 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.15 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 2.01 (s, 3H), 2.18 (s, 3H), 2.37 (d, *J* = 14.7 Hz, 1H), 2.64-2.73 (m, 3H), 2.84-2.91 (m, 2H), 4.04-4.20 (m, 4H), 4.43 (br s, 1H), 4.83 (s, 1H), 5.70-5.75 (m, 1H), 6.55 (d, *J* = 8.0 Hz, 1H), 6.70 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.91 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.00 (ddd, *J* = 8.0, 8.0, 1.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.8, 13.9, 26.3, 28.8, 29.5, 36.3, 40.4, 54.2, 55.0, 61.6 (2C), 73.3., 79.5, 110.2, 117.6, 119.8, 123.4, 128.3, 136.0, 141.1, 149.4, 170.8, 171.7, 203.1, 204.8. HRMS (FAB) calcd $C_{25}H_{29}NO_6$: $[M^+]$, 439.1995; found: $[M^+]$, 439.2000.



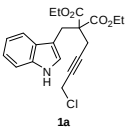

```
DFILE  data-E-17_Proton-1-1.als
COMNT  single_pulse
DATIM  2013-04-03 13:30:43
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         52428
FREQU       7507.39 Hz
SCANS             8
ACQTM        6.9835 sec
PD           5.0000 sec
PW1            6.50 usec
IRNUC  1H
CTEMP         24.8 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            40
```



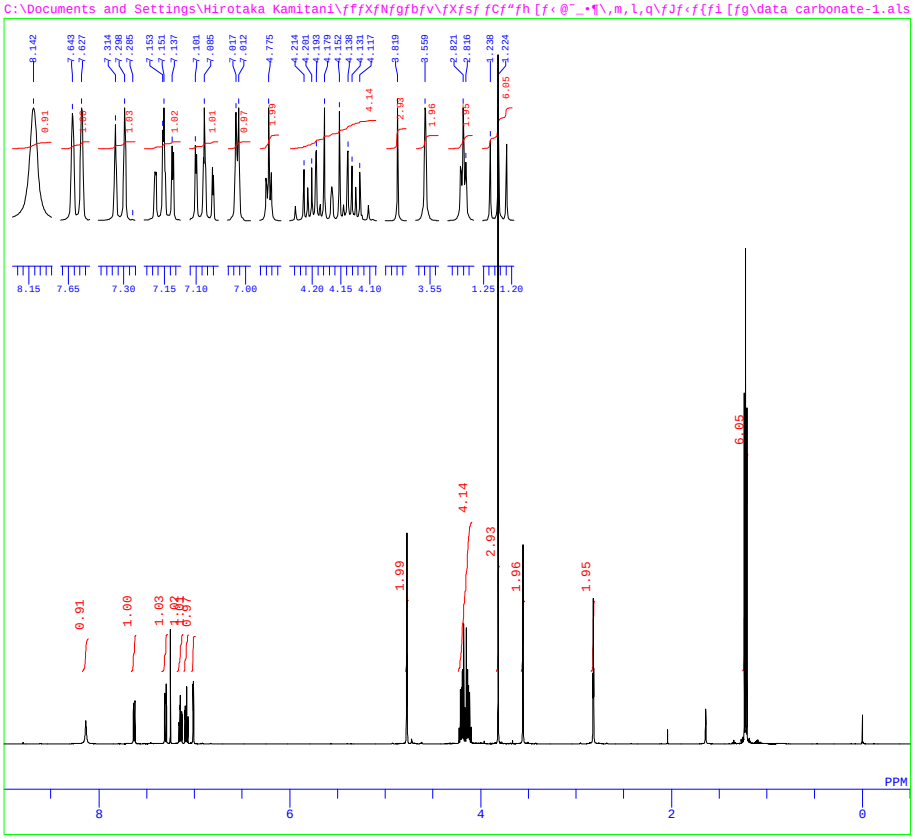
1a




```
DFILE  data E-172 bcm-1.als
COMNT  single pulse decoupled gated NOE
DATIM  2013-04-02 15:41:46
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS           883
ACQTM        0.8336 sec
PD           2.0000 sec
PW1            3.73 usec
IRNUC  1H
CTEMP          25.3 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            56
```



1a

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DFILE  data carbonate-1.als
COMNT  single_pulse
DATIM  2013-05-10 15:29:01
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         13107
FREQU       7507.39 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.50 usec
IRNUC  1H
CTEMP          25.5 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            38
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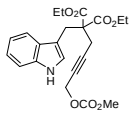
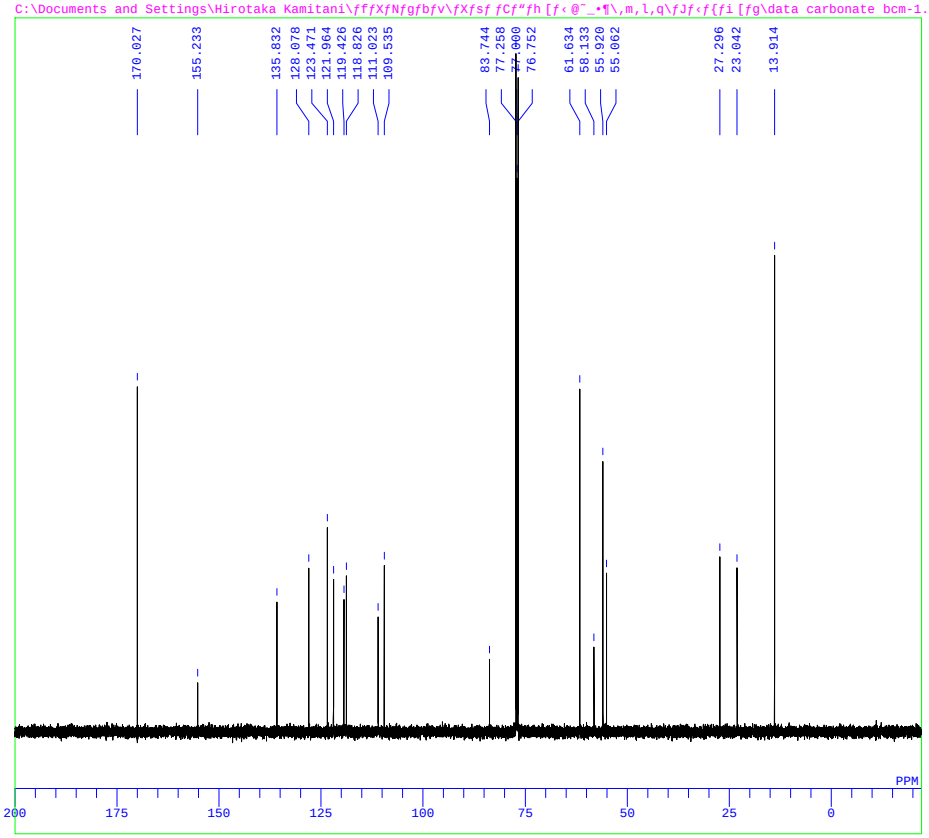
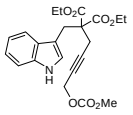


1b

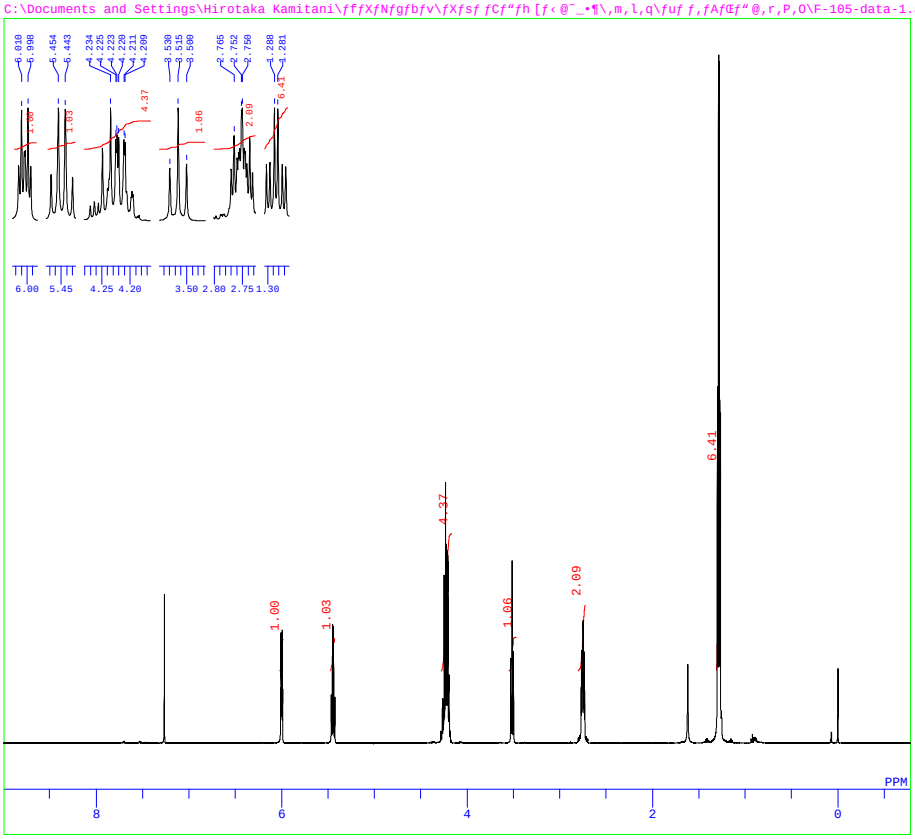



```
DFILE  data carbonate bcm-1.als
COMNT  single pulse decoupled gated NOE
DATIM  2013-05-10 15:58:49
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS           616
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.73 usec
IRNUC  1H
CTEMP          26.2 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            56
```

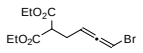


1b

C:\Documents and Settings\Hirotaka Kamitani\ƒfƒXƒfNƒgƒbƒv\ƒXƒsƒCƒ"ƒh[ƒ‹@˜_•¶\,m,l,q\ƒuƒ ƒ‚ƒfƒ‹"@,r,P,O\F-105-data-1.als

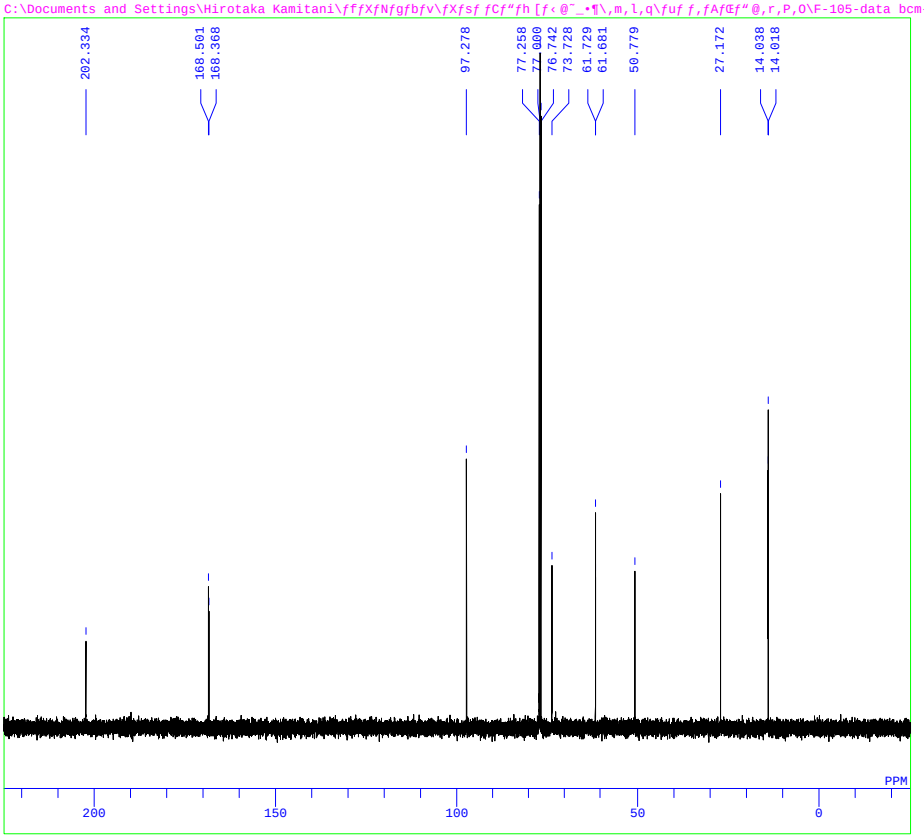


DFILE F-105-data-1.als
COMNT single_pulse
DATIM 2013-07-13 13:25:56
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 52428
FREQU 7507.39 Hz
SCANS 4
ACQTM 6.9835 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 25.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 40

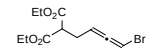


S10

C:\Documents and Settings\Hirotaka Kamitani\ƒfƒXƒfNƒgƒbƒv\ƒXƒsƒCƒ"ƒh[ƒ‹@˜_•¶\,m,l,q\ƒuƒ ƒ‚ƒfƒ‹"@,r,P,O\F-105-data bcm-1.als

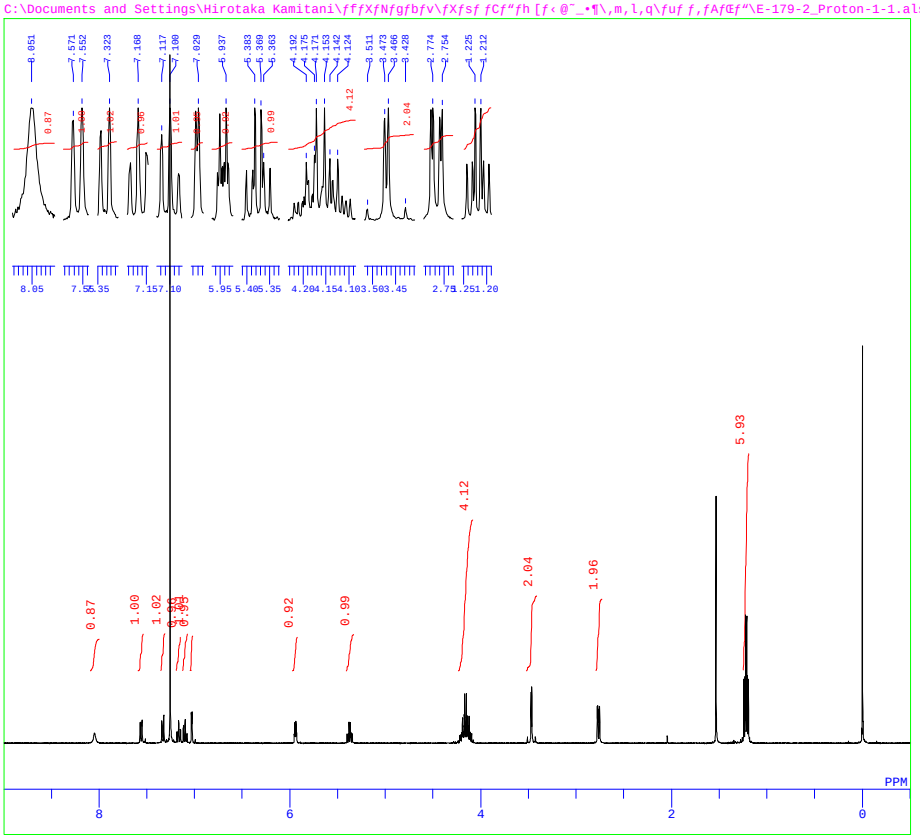


DFILE F-105-data bcm-1.als
COMNT single pulse decoupled gated NOE
DATIM 2013-07-13 13:42:20
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 333
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.73 usec
IRNUC 1H
CTEMP 25.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 52



S10

C:\Documents and Settings\Hirotaka Kamitani\ƒfƒXƒNƒgƒbƒv\ƒXƒsƒCƒ"ƒh [ƒ‹@˜_•¶\,m,l,q\ƒuƒ ƒ‚ƒfƒ‹"\E-179-2_Proton-1-1.als

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DFILE  E-179-2_Proton-1-1.als
COMNT  single_pulse
DATIM  2013-02-07 10:02:40
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         13107
FREQU       7598.78 Hz
SCANS            8
ACQTM        1.7249 sec
PD           5.0000 sec
PW1            4.65 usec
IRNUC  1H
CTEMP         25.2 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            52
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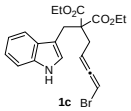
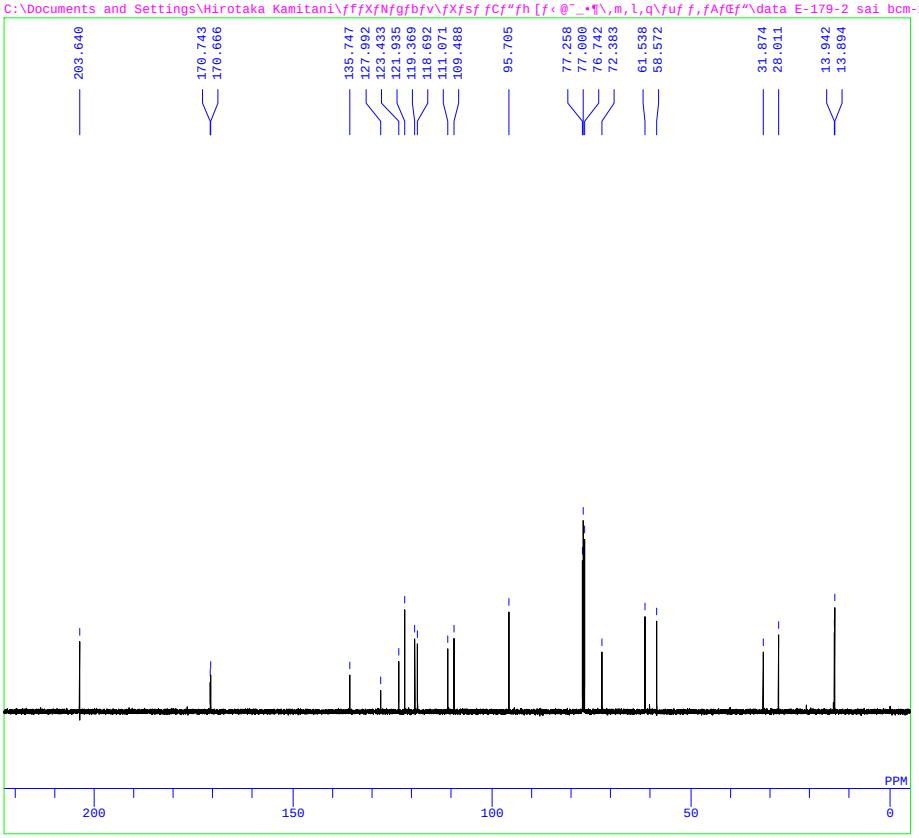
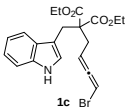
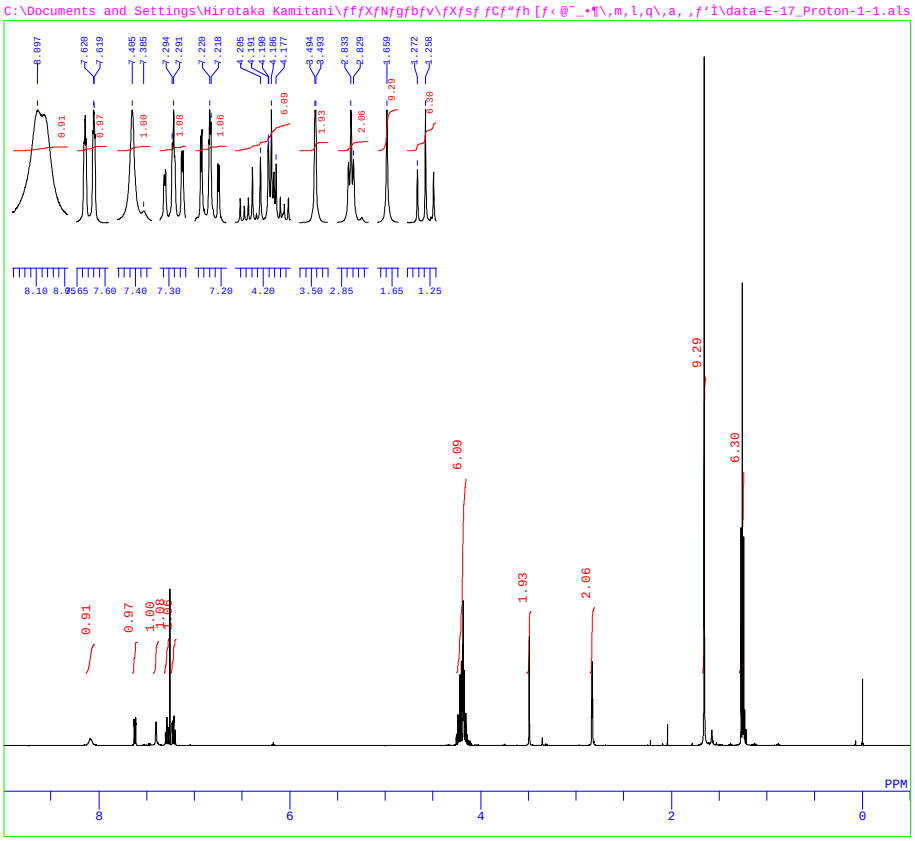


C:\Documents and Settings\Hirotaka Kamitani\ƒfƒXƒNƒgƒbƒv\ƒXƒsƒCƒ"ƒh [ƒ‹@˜_•¶\,m,l,q\ƒuƒ ƒ‚ƒfƒ‹"\data E-179-2 sai bcm-1.als

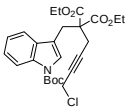



```
DFILE  data E-179-2 sai bcm-1.als
COMNT  single pulse decoupled gated NOE
DATIM  2013-05-11 14:08:34
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS           344
ACQTM        0.8336 sec
PD           2.0000 sec
PW1            3.73 usec
IRNUC  1H
CTEMP          25.8 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            56
```

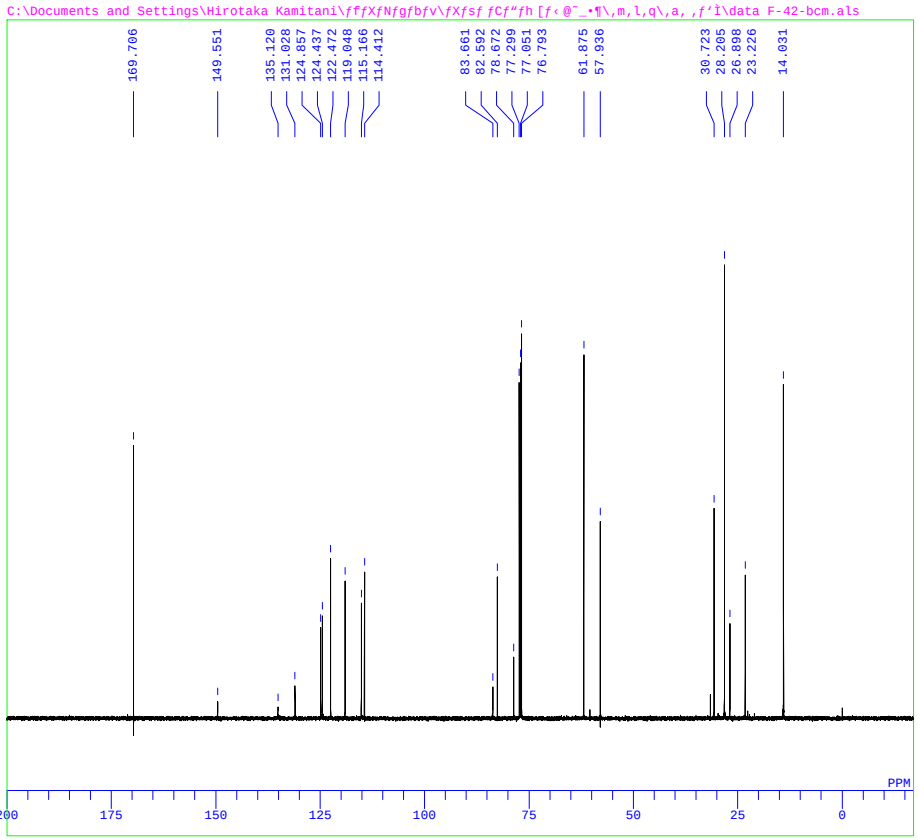





```
DFILE  data-E-17_Proton-1-1.als
COMNT  single_pulse
DATIM  2013-04-03 13:30:43
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         52428
FREQU       7507.39 Hz
SCANS             8
ACQTM        6.9835 sec
PD           5.0000 sec
PW1            6.50 usec
IRNUC  1H
CTEMP         24.8 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            40
```



1d

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DFILE  data F-42-bcm.als
COMNT  single pulse decoupled gated NOE
DATIM  2013-04-17 08:00:08
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS          2400
ACQTM        0.8336 sec
PD           2.0000 sec
PW1            3.73 usec
IRNUC  1H
CTEMP          25.7 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            60
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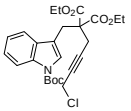
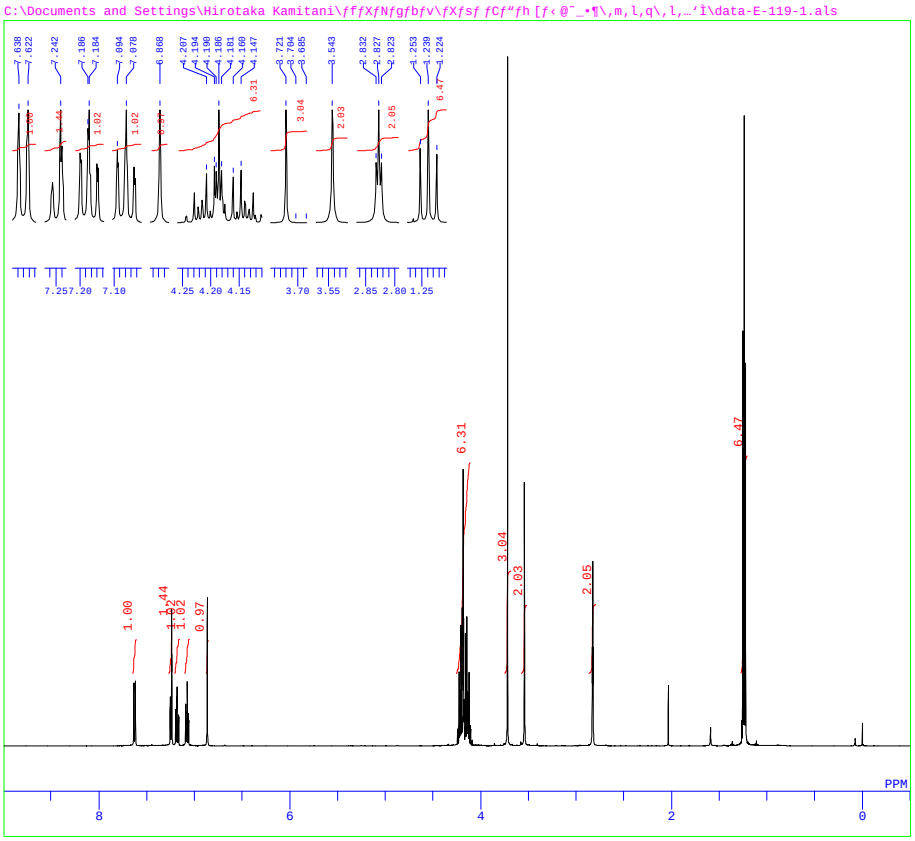
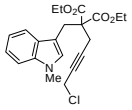


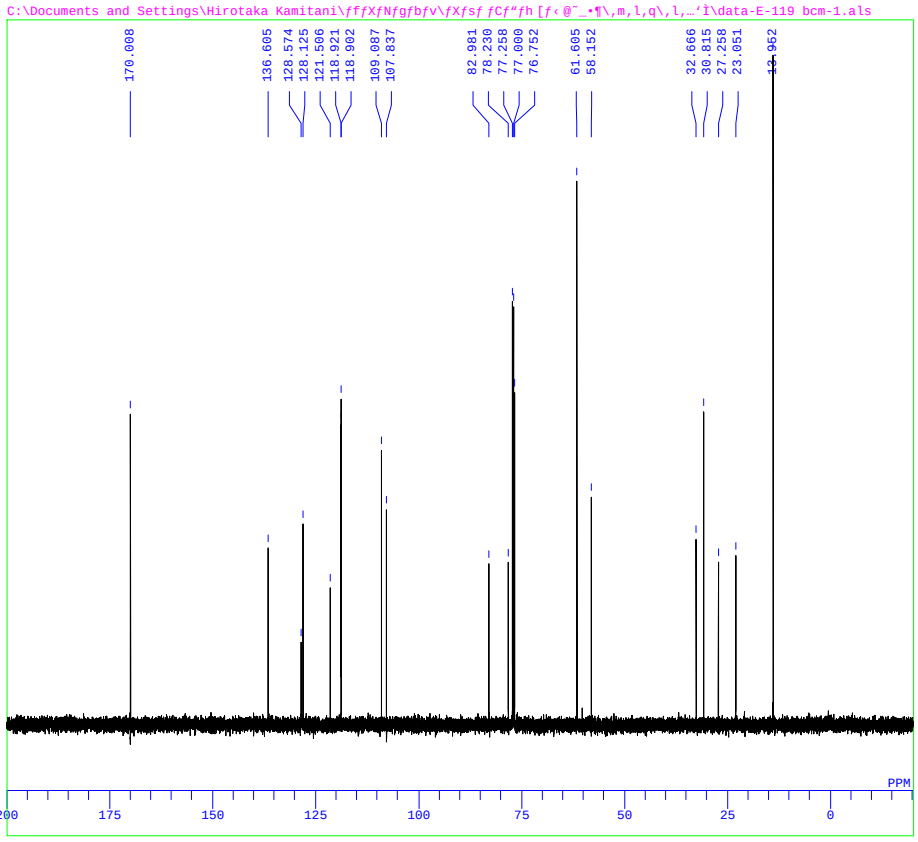
1d



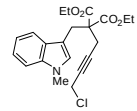
DFILE data-E-119-1.als
COMNT single_pulse
DATIM 2013-04-03 19:01:25
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 24.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 34



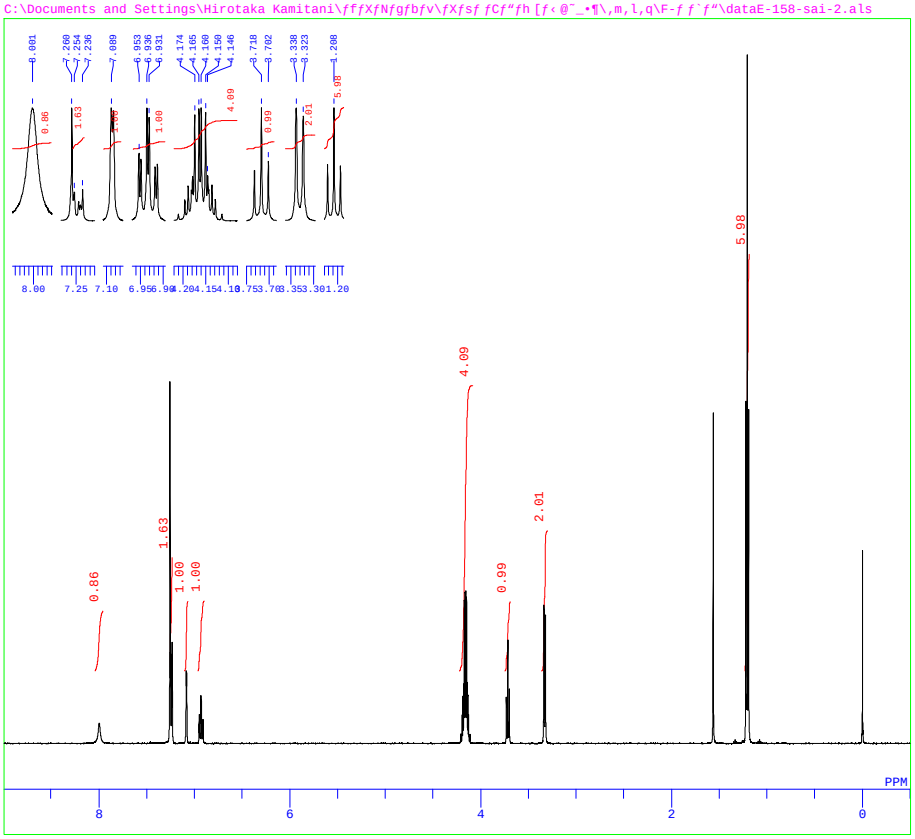
1e



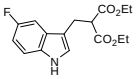
DFILE data-E-119 bcm-1.als
COMNT single pulse decoupled gated NOE
DATIM 2013-04-03 19:08:42
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 142
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.73 usec
IRNUC 1H
CTEMP 25.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 54



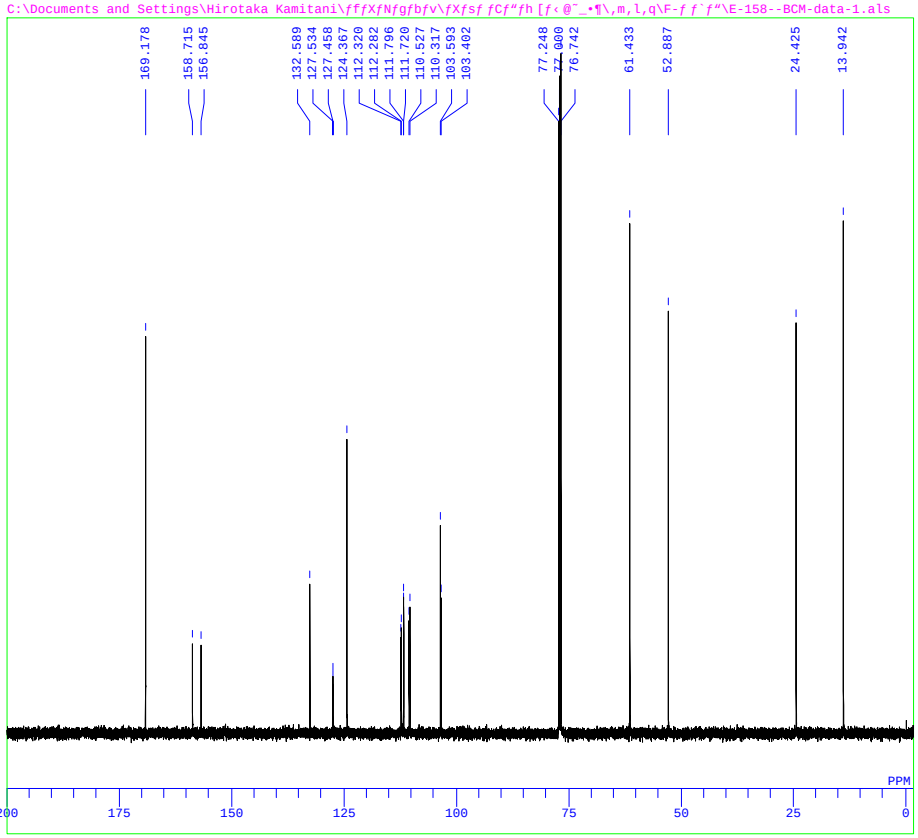
1e



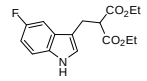

```
DFILE  dataE-158-sai-2.als
COMNT  single_pulse
DATIM  2013-06-21 13:18:46
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         52428
FREQU       7507.39 Hz
SCANS             8
ACQTM         6.9835 sec
PD            5.0000 sec
PW1           6.50 usec
IRNUC  1H
CTEMP          25.4 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            50
```



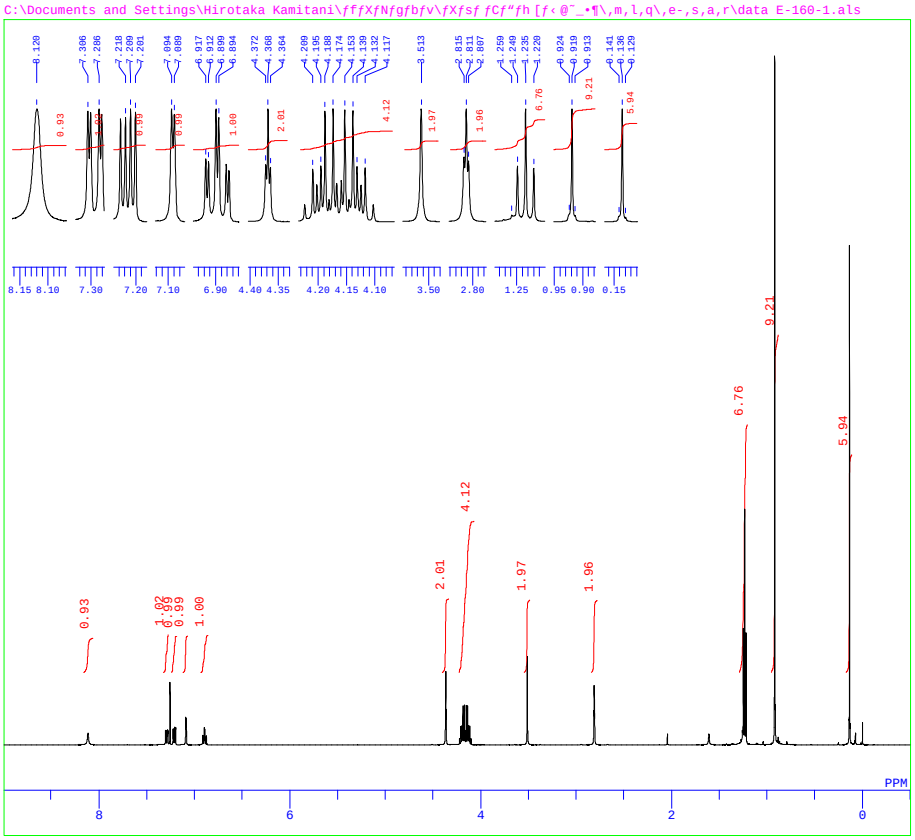
S2



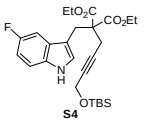

```
DFILE  E-158--BCM-data-1.als
COMNT  single pulse decoupled gated NOE
DATIM  2013-01-15 15:29:47
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS           688
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.73 usec
IRNUC  1H
CTEMP          26.2 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            58
```



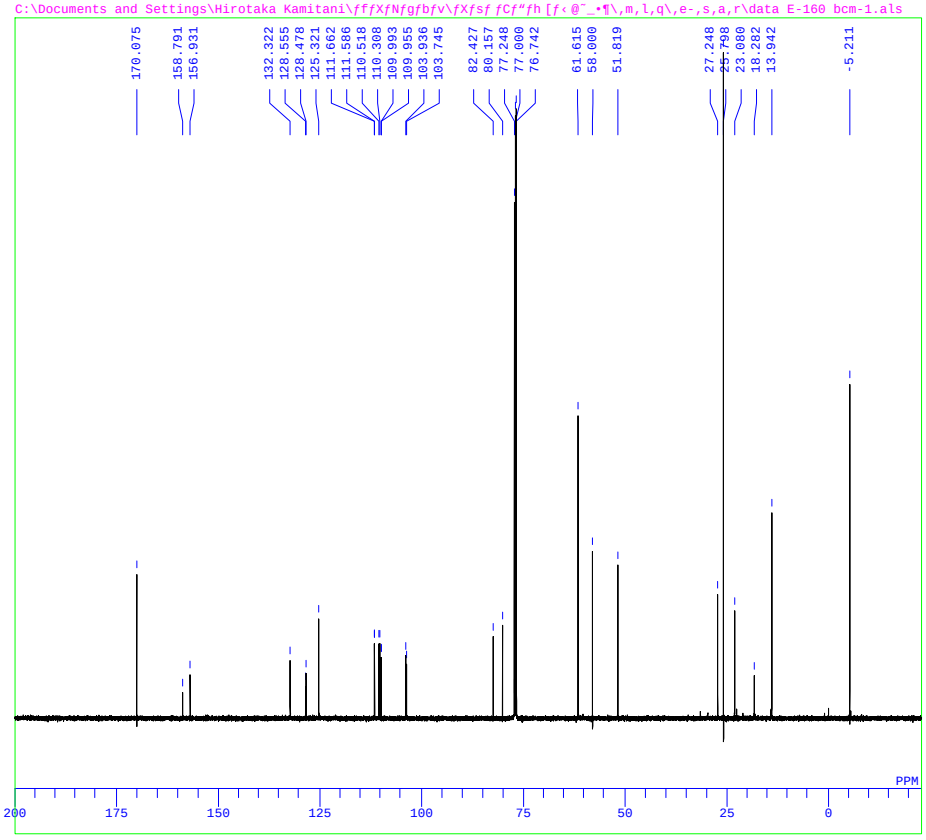
S2



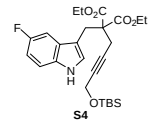

```
DFILE  data E-160-1.als
COMNT  single_pulse
DATIM  2013-04-04 23:52:33
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         52428
FREQU       7507.39 Hz
SCANS             8
ACQTM         6.9835 sec
PD            5.0000 sec
PW1           6.50 usec
IRNUC  1H
CTEMP          25.3 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            38
```



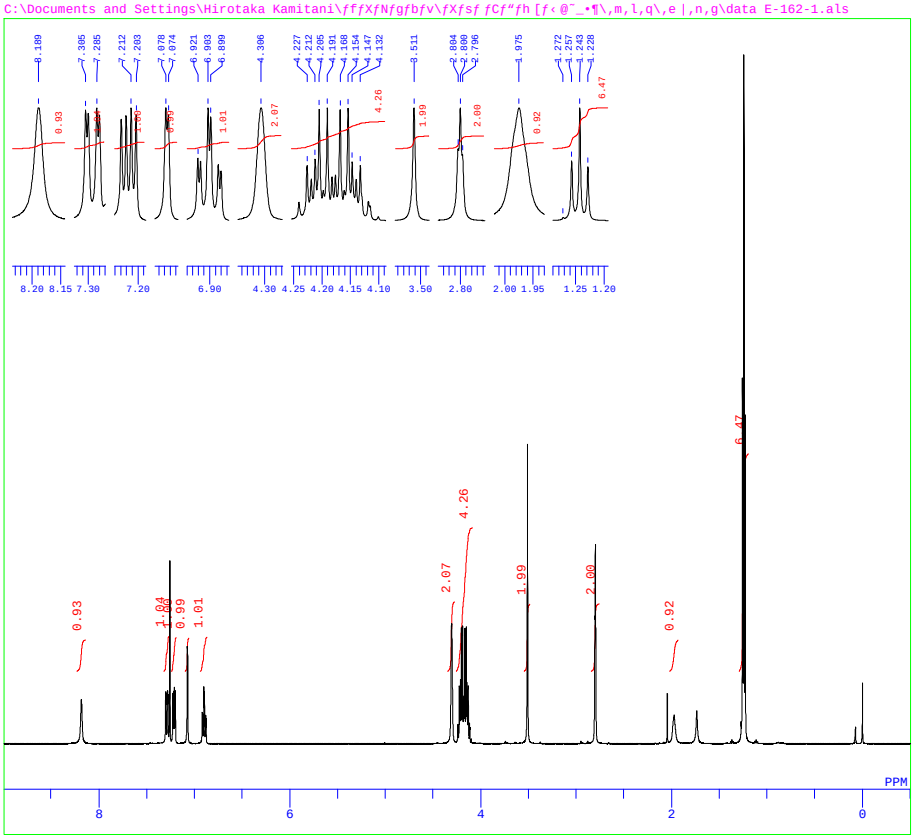
S4



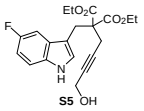

```
DFILE  data E-160 bcm-1.als
COMNT  single pulse decoupled gated NOE
DATIM  2013-04-05 03:04:19
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU       31446.06 Hz
SCANS          4048
ACQTM         0.8336 sec
PD            2.0000 sec
PW1           3.73 usec
IRNUC  1H
CTEMP          25.6 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            58
```

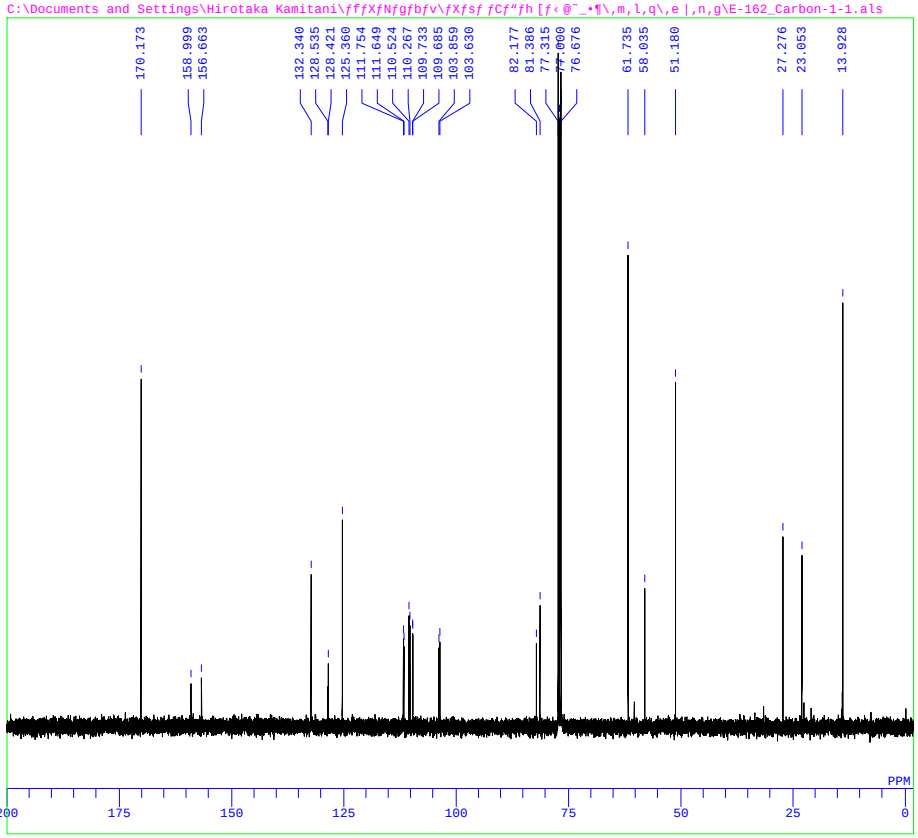


S4

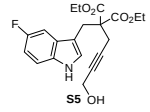



```
DFILE  data E-162-1.als
COMNT  single_pulse
DATIM  2013-04-04 09:27:30
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         52428
FREQU       7507.39 Hz
SCANS             8
ACQTM         6.9835 sec
PD            5.0000 sec
PW1           6.50 usec
IRNUC  1H
CTEMP         25.2 c
SLVNT  CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           42
```






```
DFILE  E-162_Carbon-1-1.als
COMNT  single pulse decoupled gated NOE
DATIM  2013-01-17 10:23:53
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         26214
FREQU       25125.63 Hz
SCANS           400
ACQTM         1.0433 sec
PD            2.0000 sec
PW1           3.00 usec
IRNUC  1H
CTEMP         26.3 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF            0.12 Hz
RGAIN           60
```



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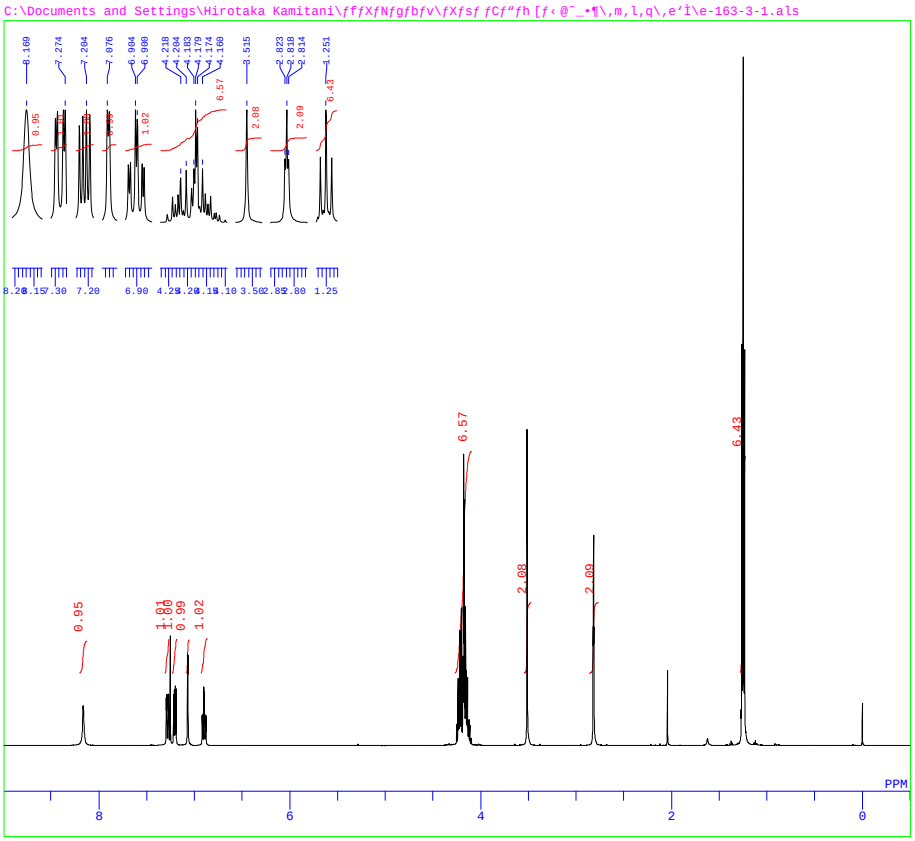
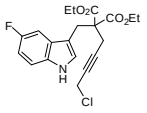
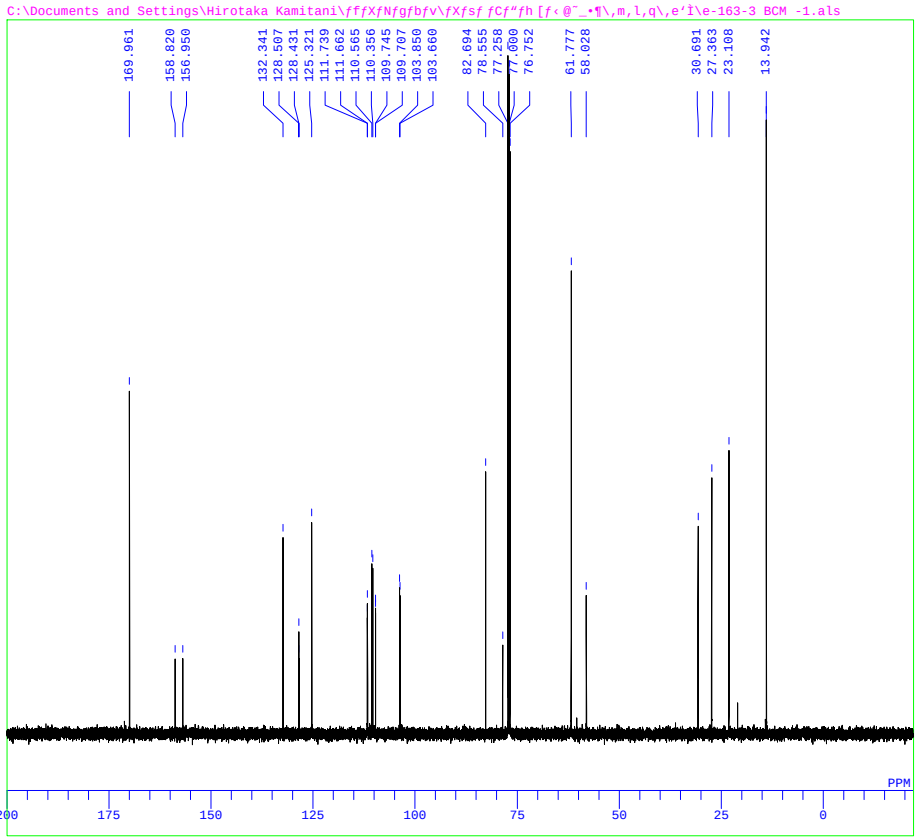


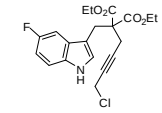

```
DFILE  e-163-3-1.als
COMNT  single_pulse
DATIM  2013-01-23 15:50:46
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         13107
FREQU       7507.39 Hz
SCANS            8
ACQTM        1.7459 sec
PD           5.0000 sec
PW1            6.90 usec
IRNUC  1H
CTEMP         27.3 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            30
```



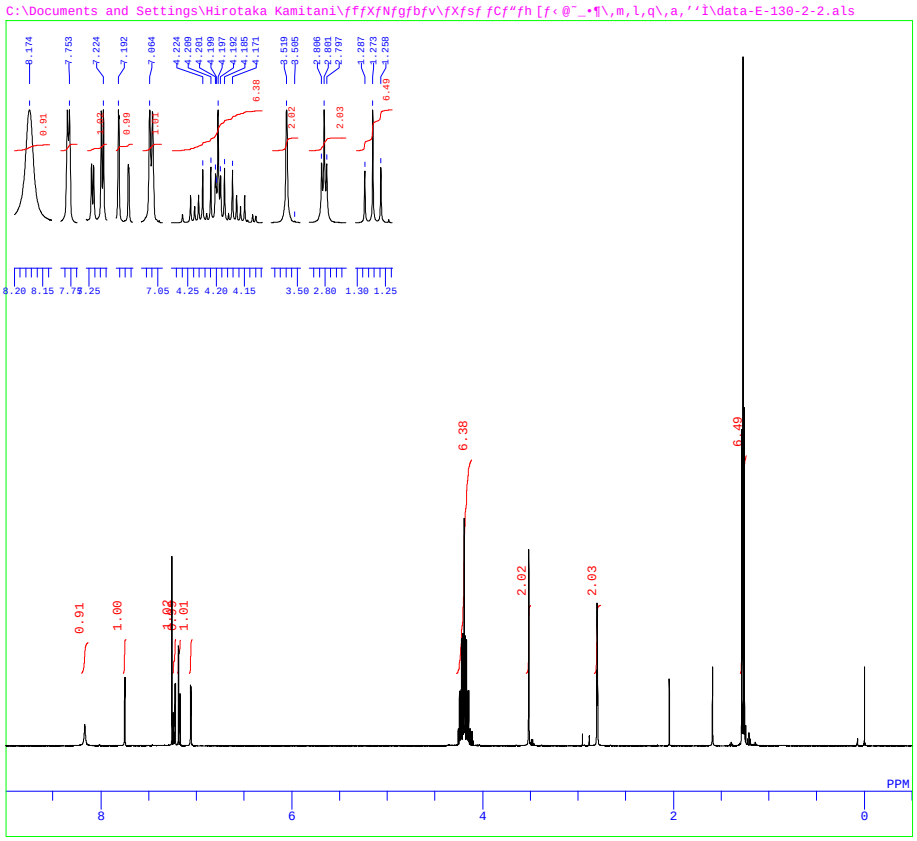
1f



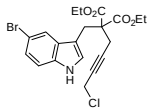

```
DFILE  e-163-3 BCM -1.als
COMNT  single pulse decoupled gated NOE
DATIM  2013-01-23 16:13:22
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS           466
ACQTM        0.8336 sec
PD           2.0000 sec
PW1            3.73 usec
IRNUC  1H
CTEMP          27.7 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            54
```



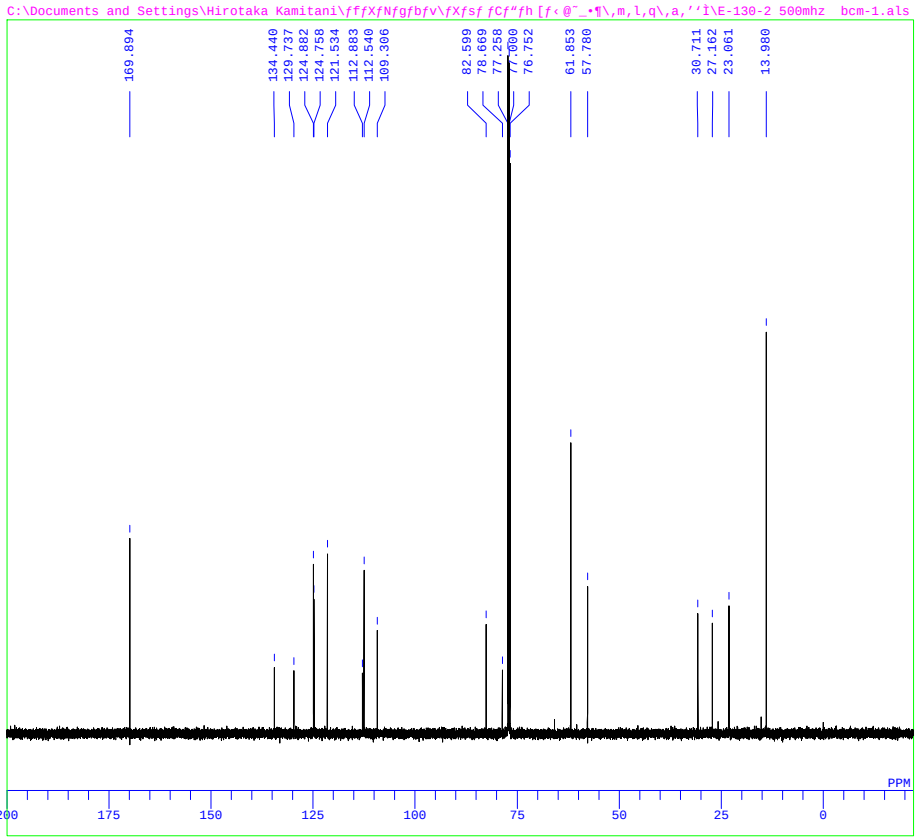
1f



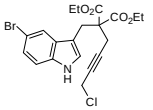

```
DFILE  data-E-130-2-2.als
COMNT  single_pulse
DATIM  2013-04-03 10:19:53
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         52428
FREQU       7507.39 Hz
SCANS             8
ACQTM         6.9835 sec
PD            5.0000 sec
PW1           6.50 usec
IRNUC  1H
CTEMP          25.1 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            42
```



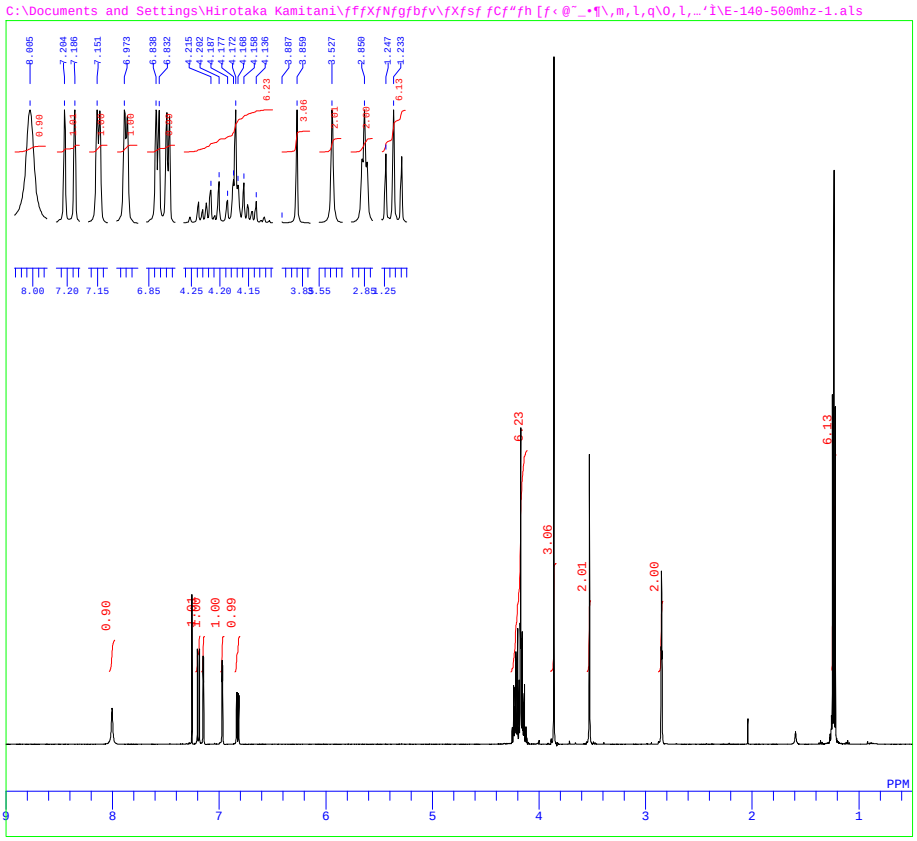
1g



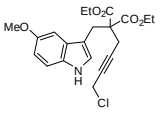

```
DFILE  E-130-2 500mhz  bcm-1.als
COMNT  single pulse decoupled gated NOE
DATIM  2012-12-03 19:23:44
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS          1024
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.73 usec
IRNUC  1H
CTEMP          27.7 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            54
```



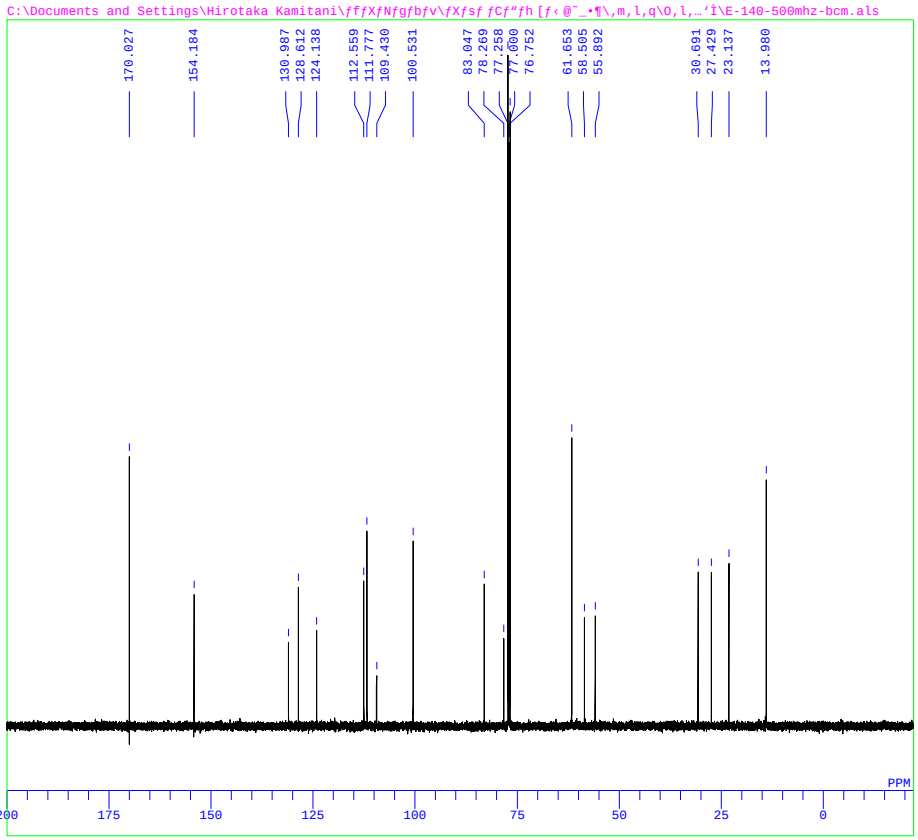
1g



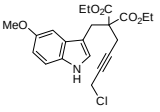

```
DFILE  E-140-500mhz-1.als
COMNT  single_pulse
DATIM  2012-12-10 09:49:60
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         13107
FREQU       7507.39 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.50 usec
IRNUC  1H
CTEMP          28.0 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            40
```



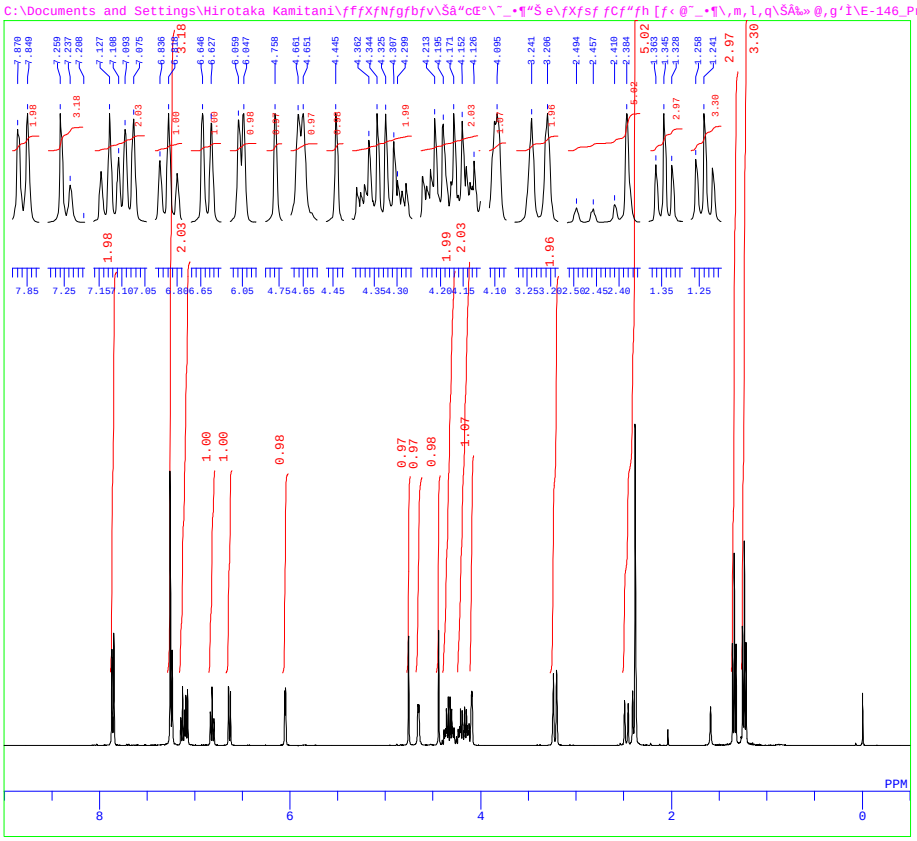
1h



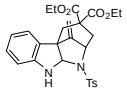

```
DFILE  E-140-500mhz-bcm.als
COMNT  single pulse decoupled gated NOE
DATIM  2012-12-10 10:39:54
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS          1024
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.73 usec
IRNUC  1H
CTEMP          28.3 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            56
```



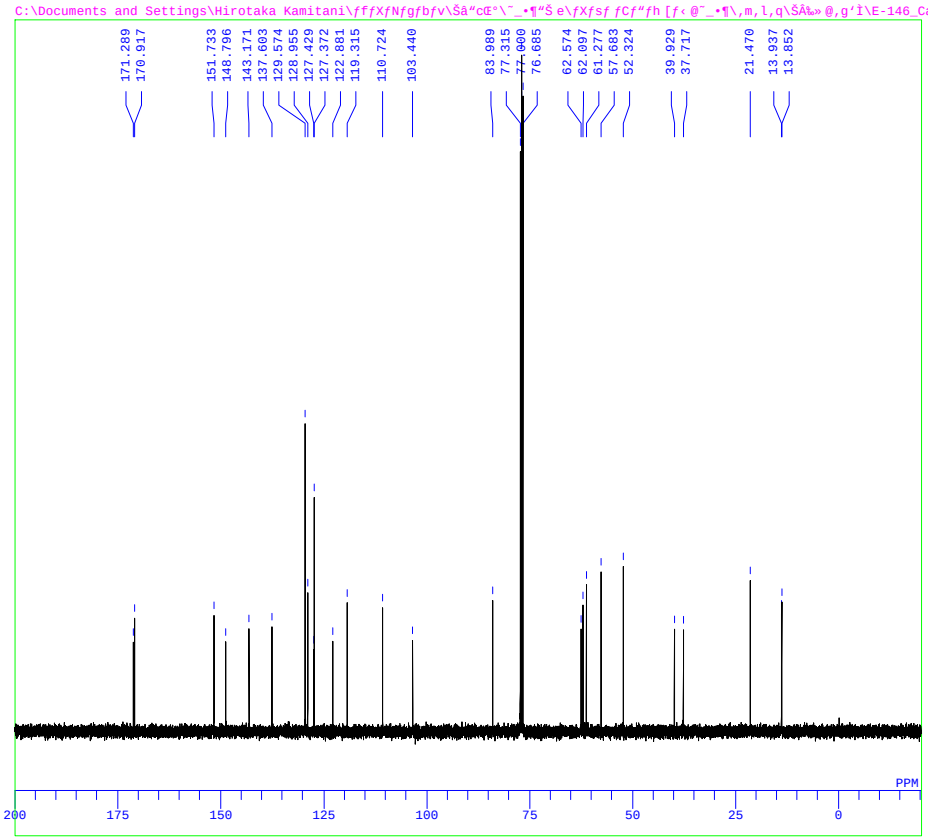
1h



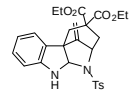

```
DFILE  E-146_Proton-1-1.als
COMNT  single_pulse
DATIM  2012-12-17 13:48:16
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         13107
FREQU       6002.40 Hz
SCANS             8
ACQTM         2.1837 sec
PD            5.0000 sec
PW1           4.65 usec
IRNUC  1H
CTEMP          25.4 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            38
```



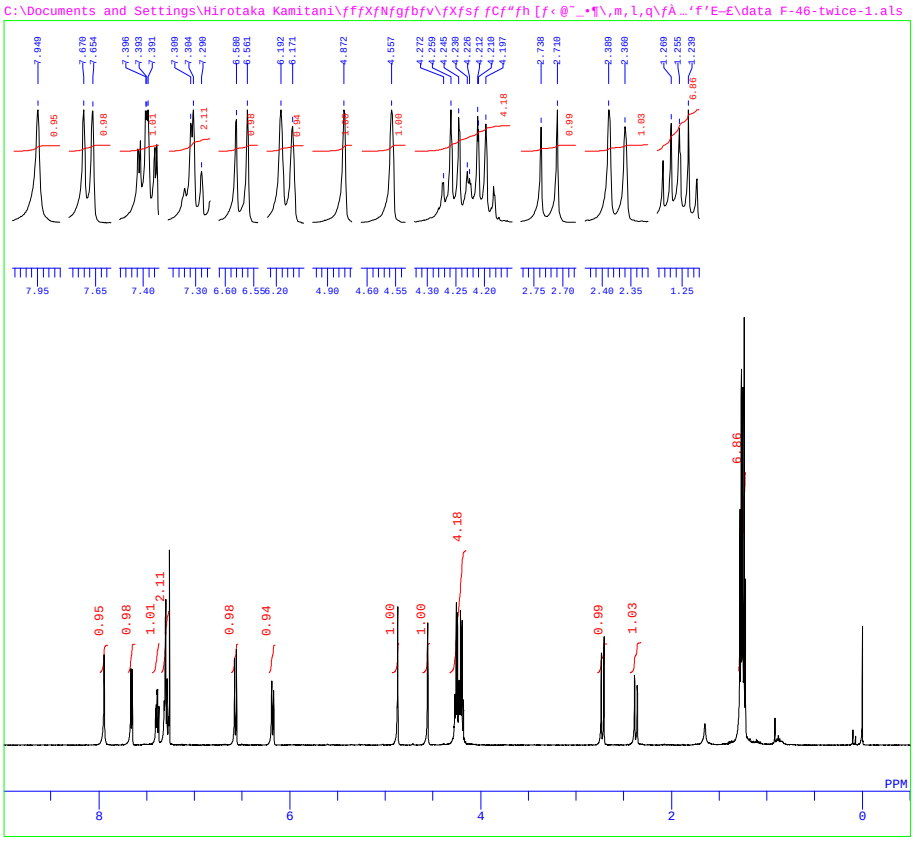
2a




```
DFILE  E-146_Carbon-1-1-400mhz.als
COMNT  single pulse decoupled gated NOE
DATIM  2012-12-17 13:50:00
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         26214
FREQU      25125.63 Hz
SCANS           512
ACQTM         1.0433 sec
PD            2.0000 sec
PW1           3.00 usec
IRNUC  1H
CTEMP          25.5 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            60
```

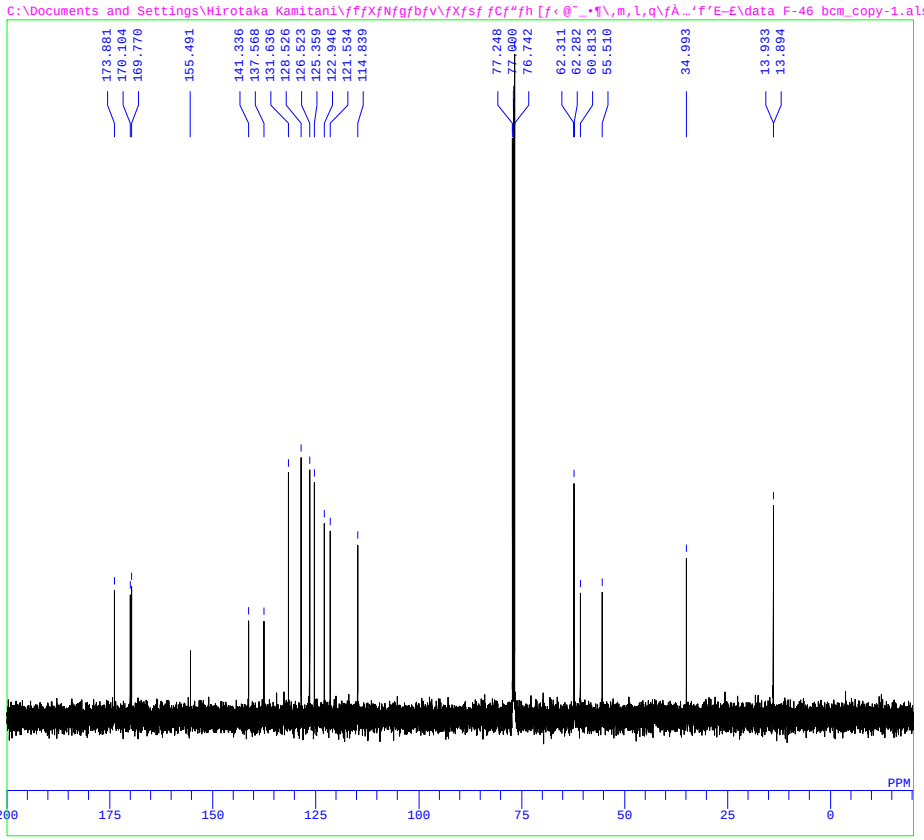


2a



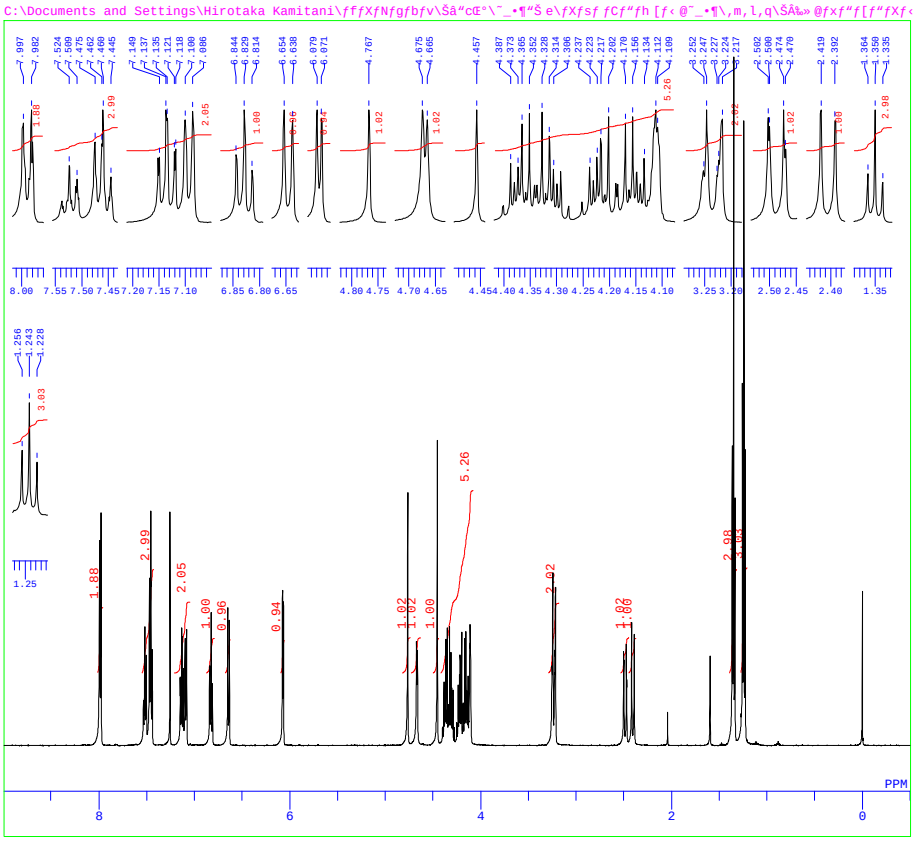

```
DFILE  data F-46-twice-1.als
COMNT  single_pulse
DATIM  2013-04-22 20:26:03
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         13107
FREQU       7507.39 Hz
SCANS            8
ACQTM        1.7459 sec
PD           5.0000 sec
PW1            6.50 usec
IRNUC  1H
CTEMP         25.7 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            46
```

3a

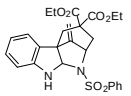



```
DFILE  data F-46 bcm_copy-1.als
COMNT  single pulse decoupled gated NOE
DATIM  2013-04-20 16:10:50
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS           417
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.73 usec
IRNUC  1H
CTEMP          25.8 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            54
```

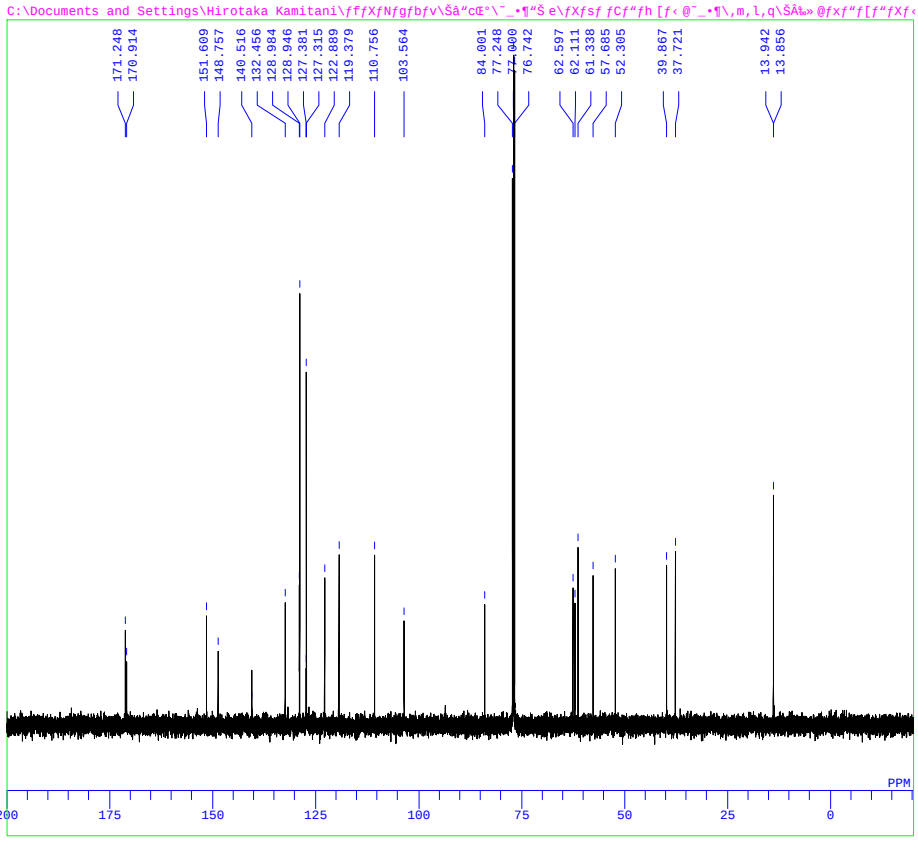
3a



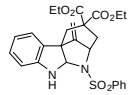

```
DFILE  data F-29-2 RECRYSTALIZATION-2.al
COMNT  single_pulse
DATIM  2013-04-09 16:22:05
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         13107
FREQU       7507.39 Hz
SCANS            8
ACQTM        1.7459 sec
PD           5.0000 sec
PW1            6.50 usec
IRNUC  1H
CTEMP          26.1 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            42
```



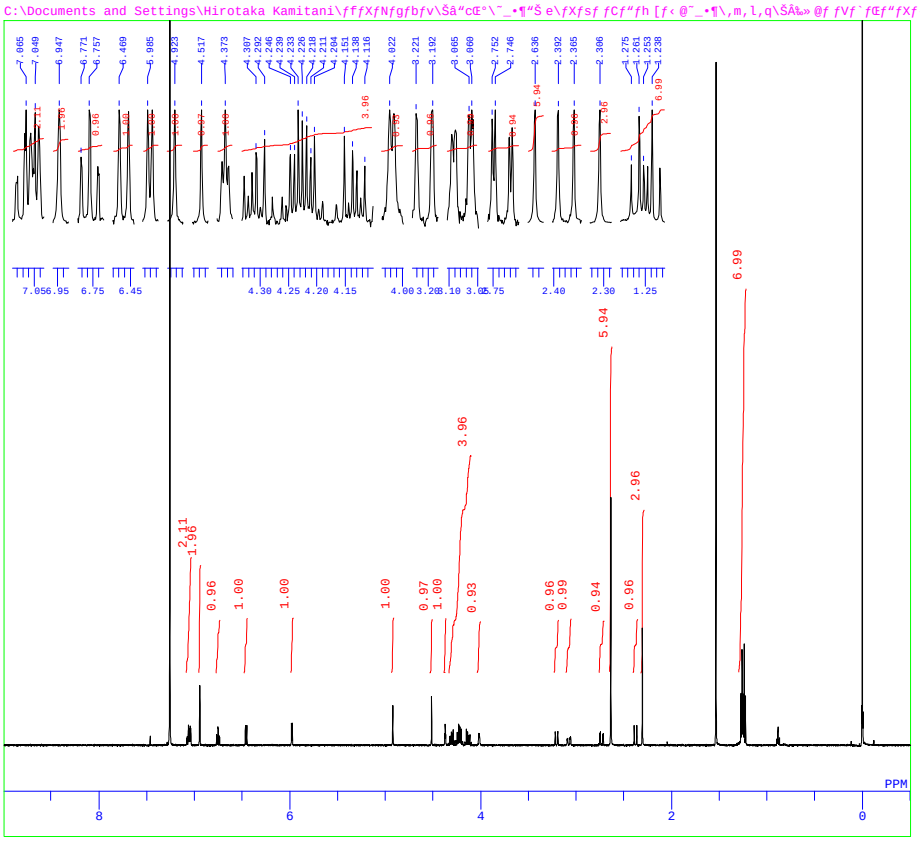
2b



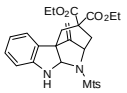

```
DFILE  data F-29-2 RECRYSTALIZATION BCM-
COMNT  single pulse decoupled gated NOE
DATIM  2013-04-09 17:00:06
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU       31446.06 Hz
SCANS            792
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.73 usec
IRNUC  1H
CTEMP          26.5 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            54
```



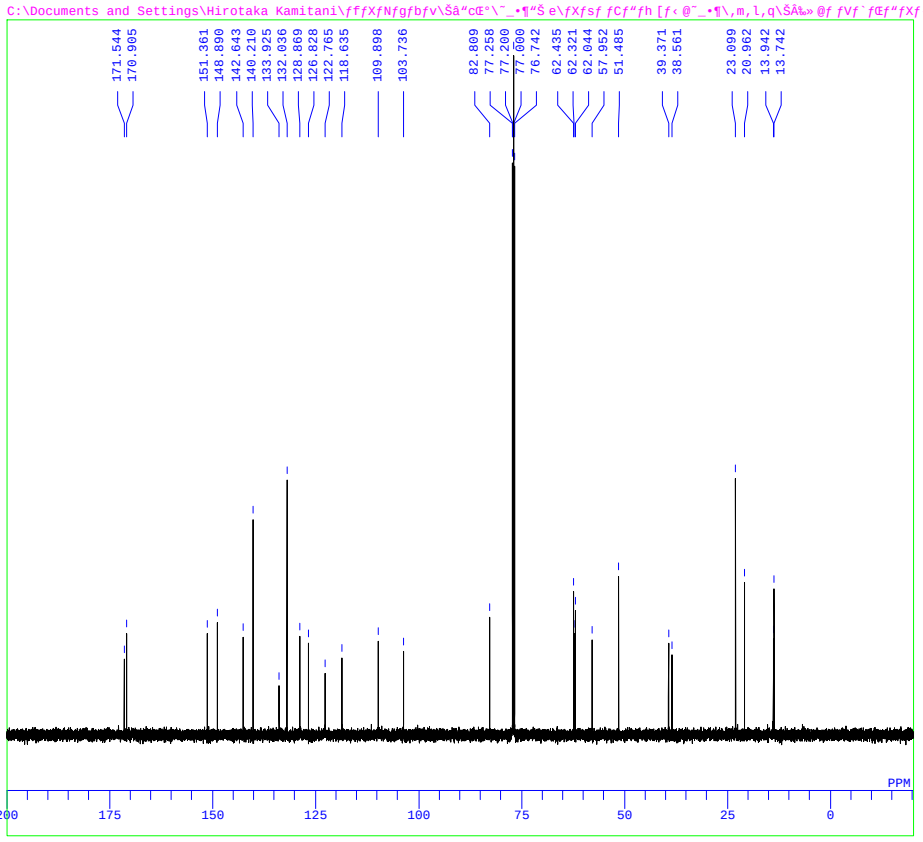
2b



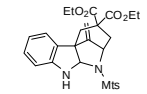

```
DFILE  data F-30-1-1.als
COMNT  single_pulse
DATIM  2013-04-16 22:45:43
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         13107
FREQU       7507.39 Hz
SCANS            8
ACQTM        1.7459 sec
PD           5.0000 sec
PW1            6.50 usec
IRNUC  1H
CTEMP         25.5 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            54
```



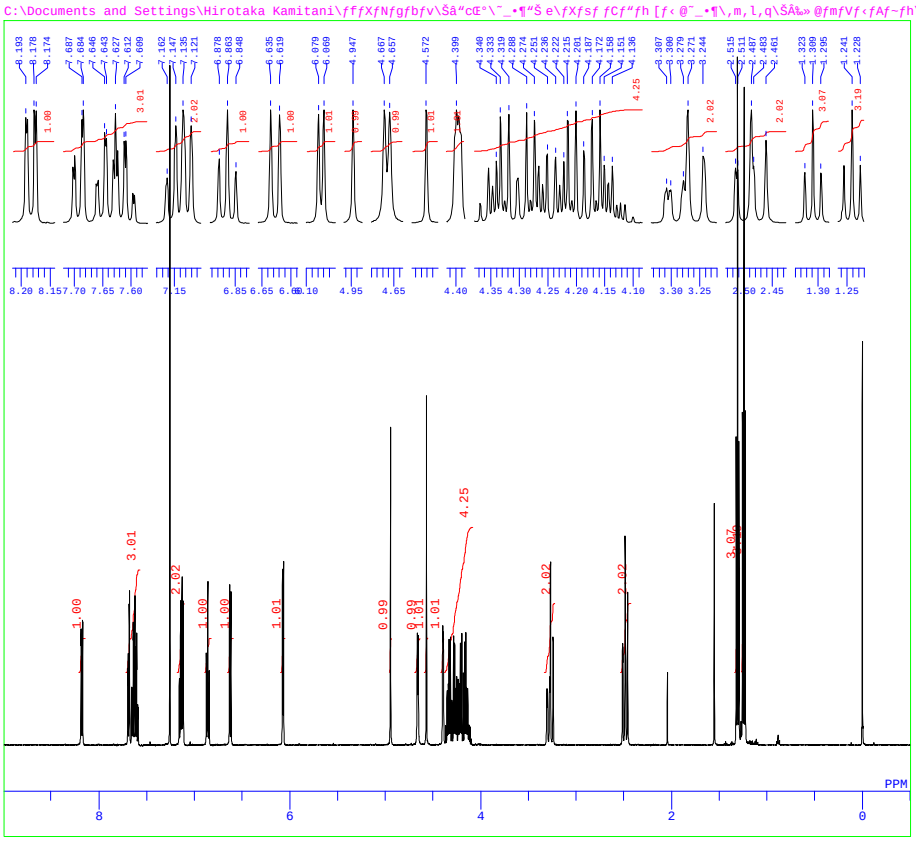
2c



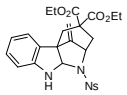

```
DFILE  F-30-bcm.als
COMNT  single pulse decoupled gated NOE
DATIM  2013-03-14 15:52:37
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU       31446.06 Hz
SCANS           570
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.73 usec
IRNUC  1H
CTEMP          26.2 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            54
```



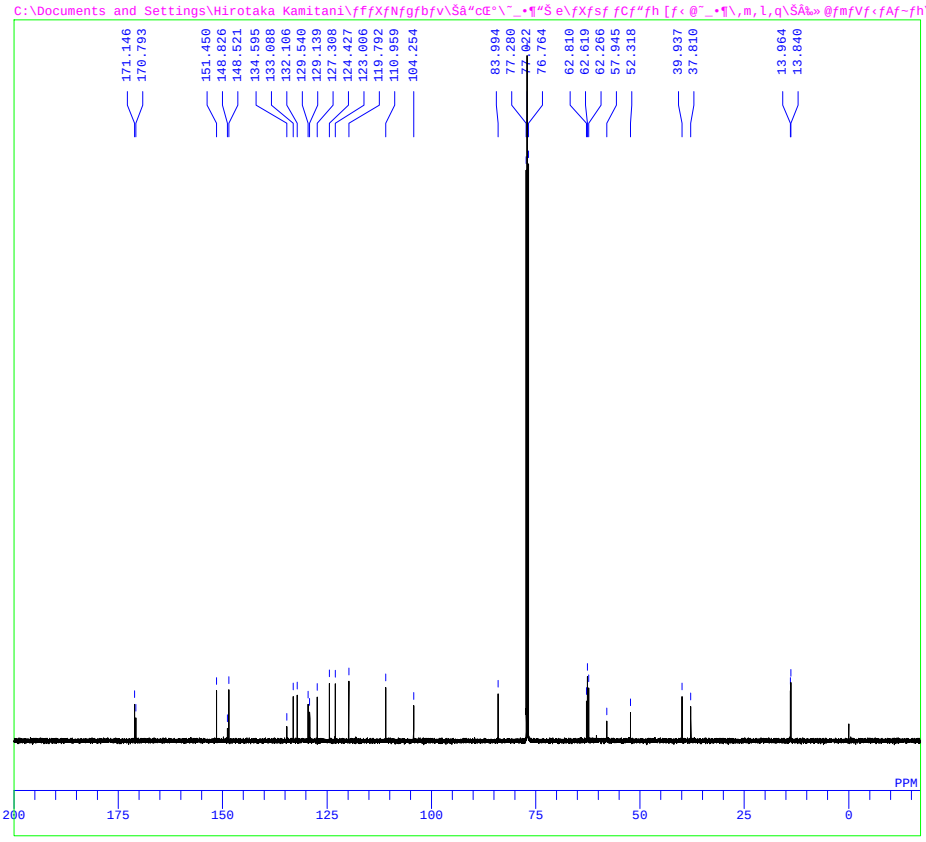
2c



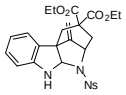

```
DFILE  data F-32-2-1.als
COMNT  single_pulse
DATIM  2013-04-17 02:30:45
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         13107
FREQU       7507.39 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.50 usec
IRNUC  1H
CTEMP          402.3 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            46
```



2d

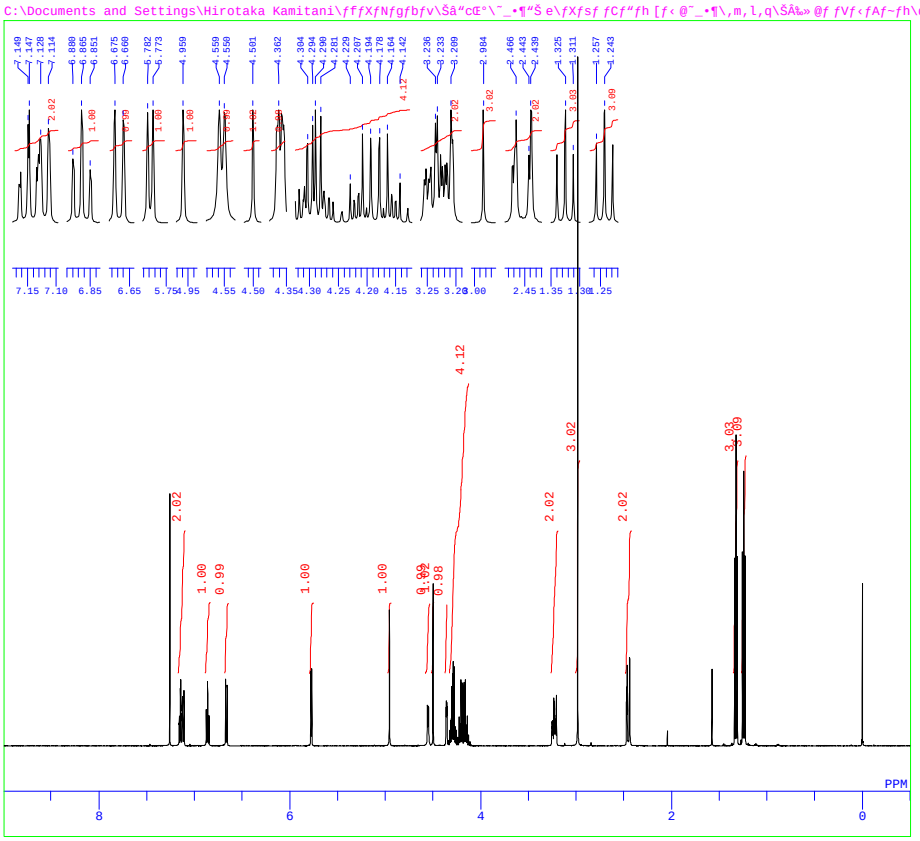



```
DFILE  data F-32-2-bcm.als
COMNT  single pulse decoupled gated NOE
DATIM  2013-04-17 05:59:09
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU       31446.06 Hz
SCANS          4400
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.73 usec
IRNUC  1H
CTEMP          25.5 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            60
```

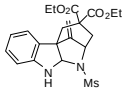


2d

C:\Documents and Settings\Hirotaka Kamitani\ƒfƒXƒNƒgƒbƒv\Šâ“cŒ°\˜_•¶\Še\ƒXƒsƒCƒ“ƒh[ƒ‹@˜_•¶\,m,l,q\ŠÄ‰»@ƒfƒVƒ‹ƒAƒ~ƒh\data F-31-2-1.als

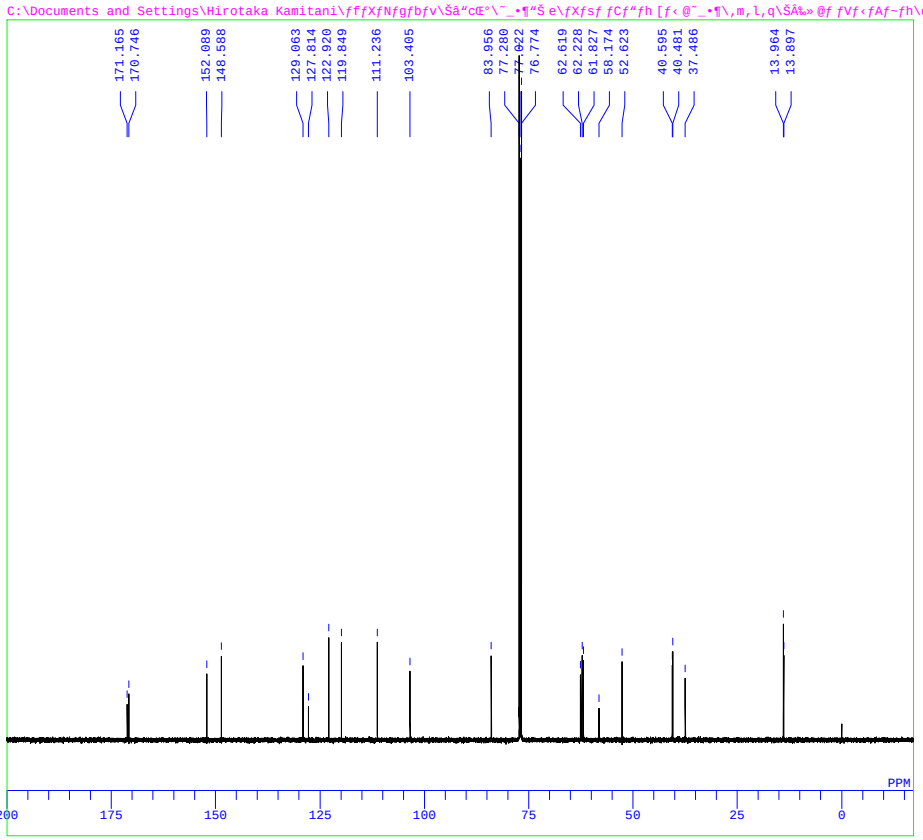


DFILE data F-31-2-1.als
COMNT single_pulse
DATIM 2013-04-16 22:53:32
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 402.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 44

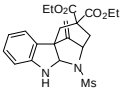


2e

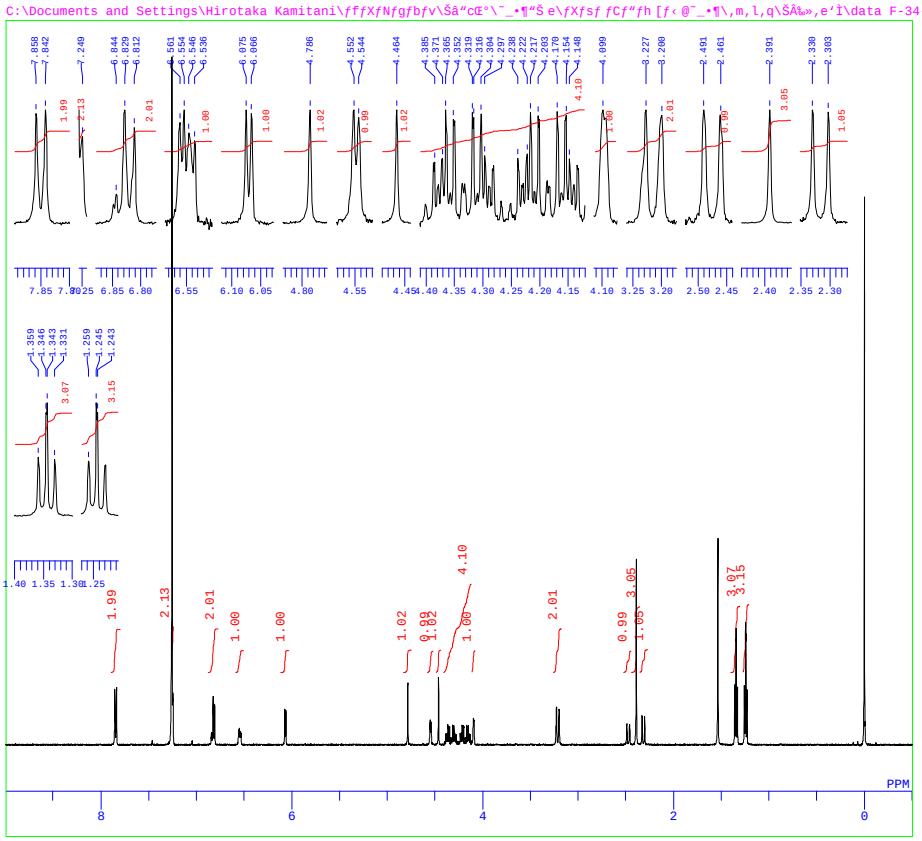
C:\Documents and Settings\Hirotaka Kamitani\ƒfƒXƒNƒgƒbƒv\Šâ“cŒ°\˜_•¶\Še\ƒXƒsƒCƒ“ƒh[ƒ‹@˜_•¶\,m,l,q\ŠÄ‰»@ƒfƒVƒ‹ƒAƒ~ƒh\data F-31-2-bcm.als



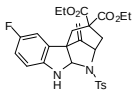
DFILE data F-31-2-bcm.als
COMNT single pulse decoupled gated NOE
DATIM 2013-04-17 02:21:55
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 4400
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.73 usec
IRNUC 1H
CTEMP 26.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 54



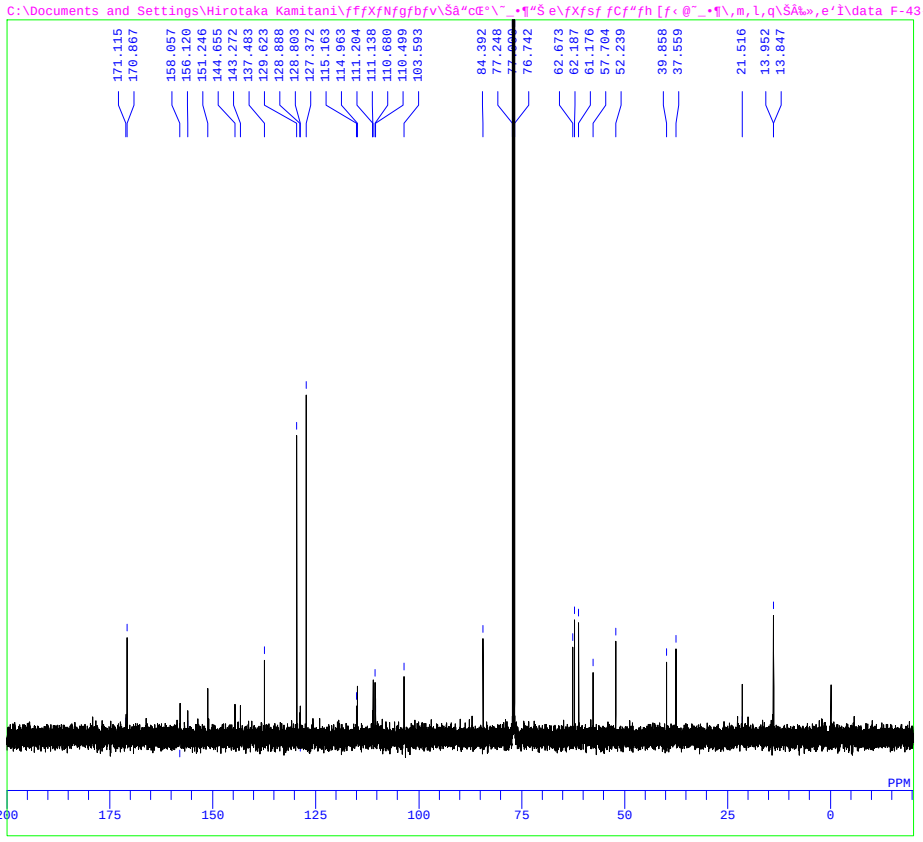
2e



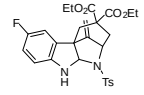

```
DFILE  data F-34-2.als
COMNT  single_pulse
DATIM  2013-04-09 16:16:58
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         13107
FREQU       7507.39 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.50 usec
IRNUC  1H
CTEMP          26.1 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            54
```



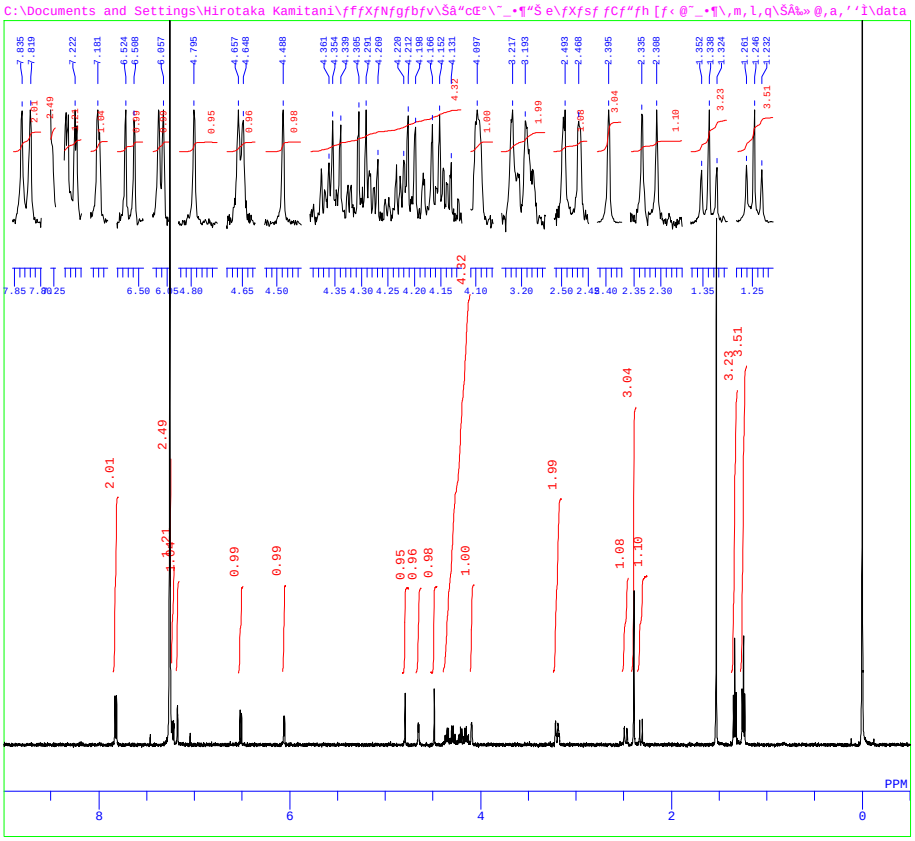
2k



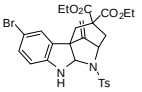

```
DFILE  data F-43-bcm twice-1.als
COMNT  single pulse decoupled gated NOE
DATIM  2013-04-18 16:33:00
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU       31446.06 Hz
SCANS             1024
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.73 usec
IRNUC  1H
CTEMP         401.8 c
SLVNT  CDCL3
EXREF          77.00 ppm
BF             0.12 Hz
RGAIN            56
```



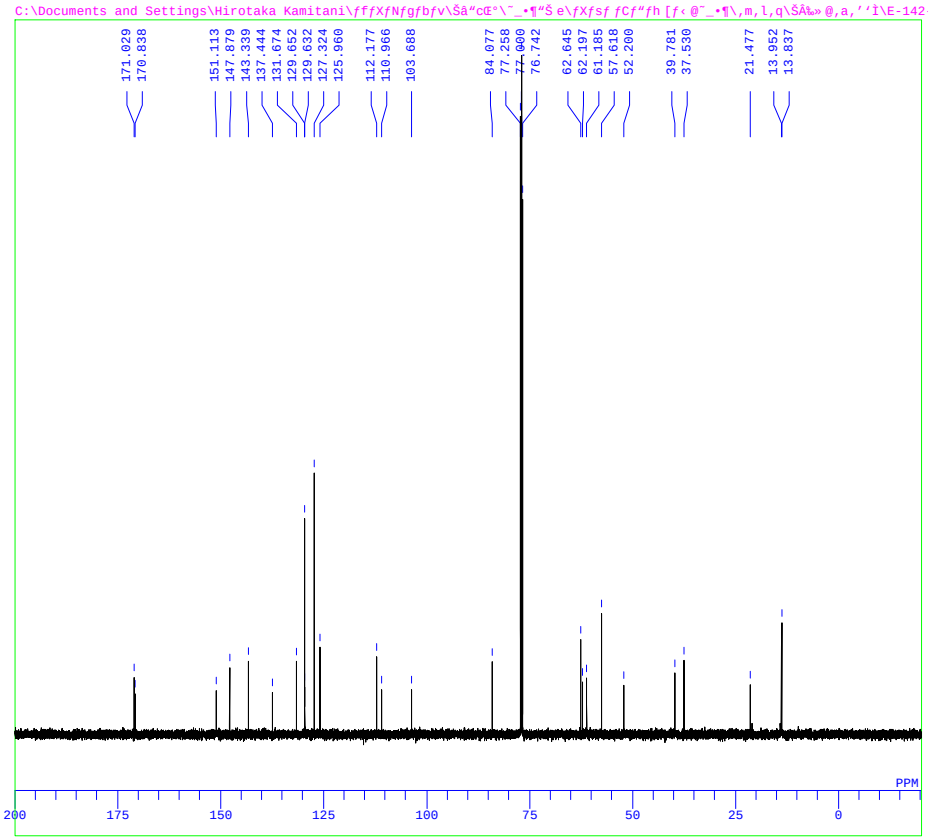
2k



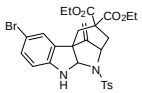

```
DFILE  data F-36-2-1.als
COMNT  single_pulse
DATIM  2013-04-12 11:19:40
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         13107
FREQU       7507.39 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.50 usec
IRNUC  1H
CTEMP          137.3 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             56
```



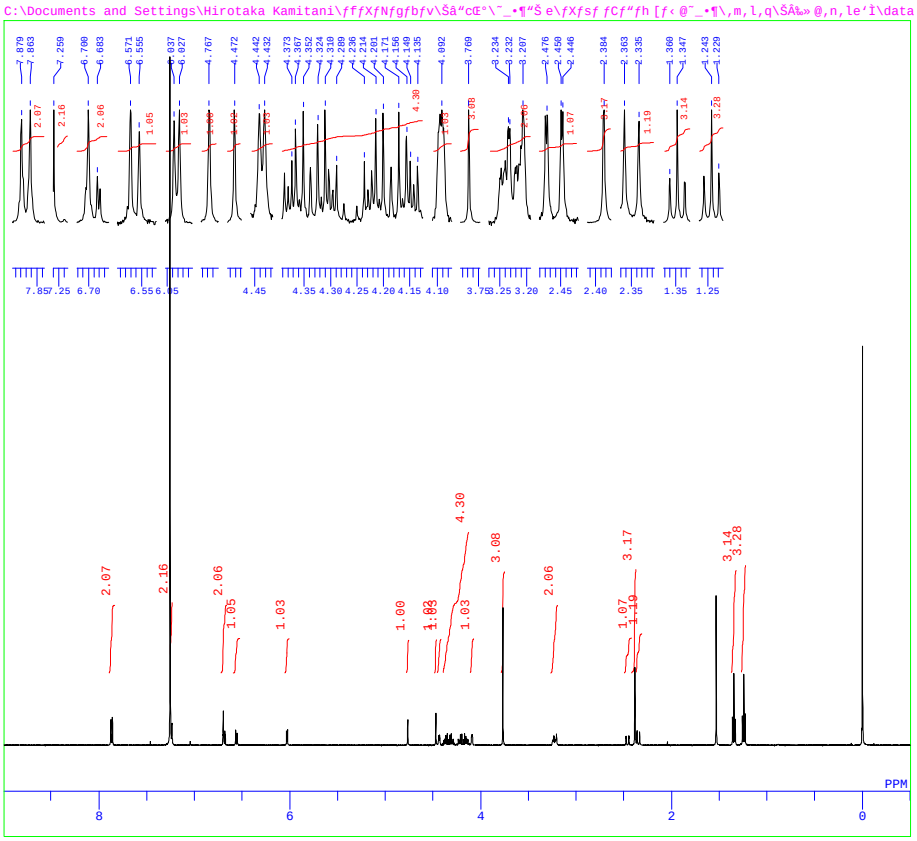
2l



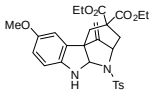

```
DFILE  E-142-1-500mhz BCM.als
COMNT  single pulse decoupled gated NOE
DATIM  2012-12-14 15:42:13
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS          1024
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.73 usec
IRNUC  1H
CTEMP          27.4 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            50
```



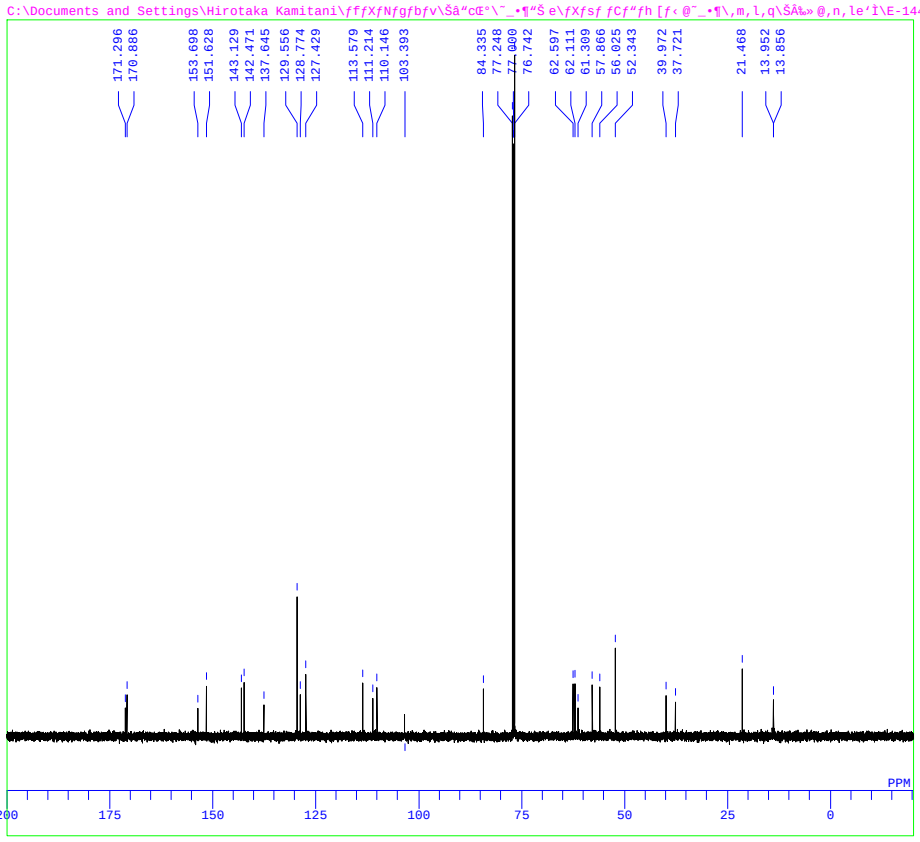
2l



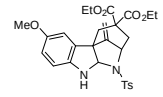

```
DFILE  data F-35-2-1.als
COMNT  single_pulse
DATIM  2013-04-12 11:15:53
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         13107
FREQU       7507.39 Hz
SCANS            8
ACQTM        1.7459 sec
PD           5.0000 sec
PW1            6.50 usec
IRNUC  1H
CTEMP         117.5 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            54
```



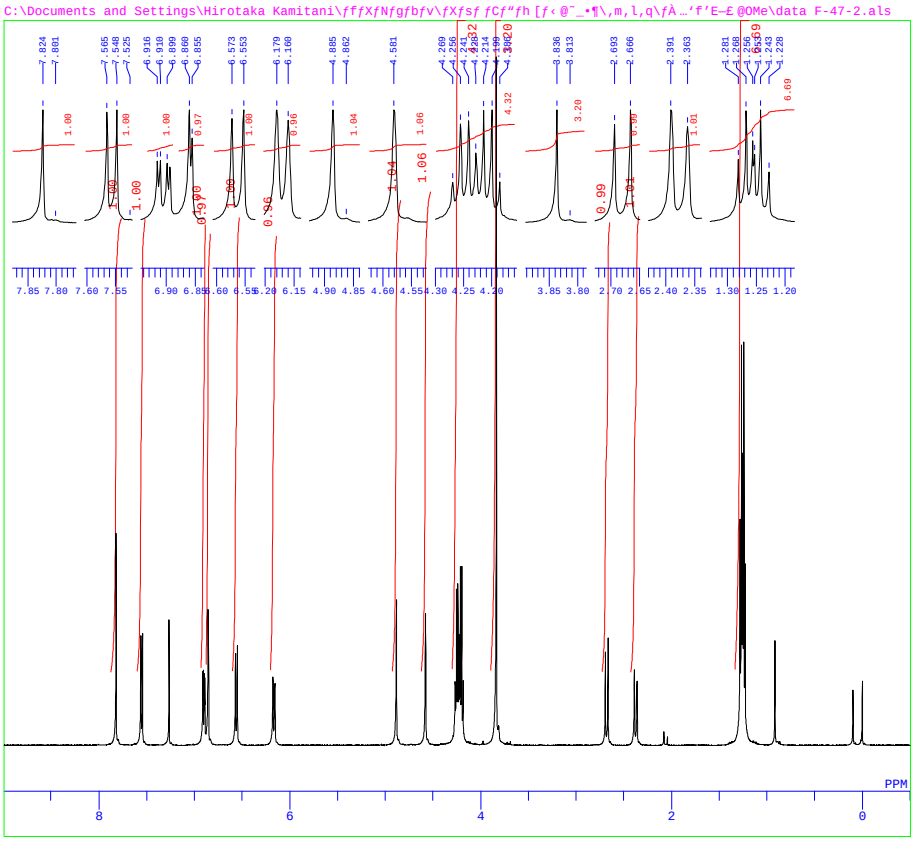
2m



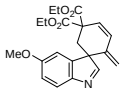

```
DFILE  E-144-1-500mhz bcm-1.als
COMNT  single pulse decoupled gated NOE
DATIM  2012-12-14 16:36:07
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS          1024
ACQTM        0.8336 sec
PD           2.0000 sec
PW1            3.73 usec
IRNUC  1H
CTEMP          27.5 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            58
```



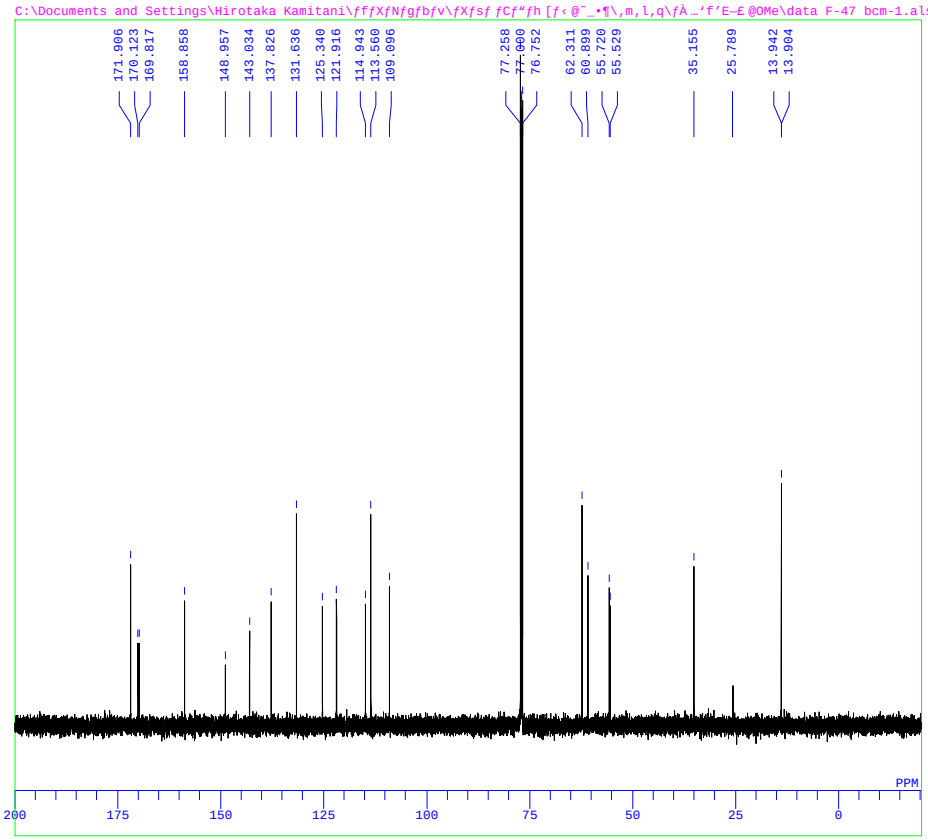
2m



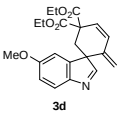

```
DFILE  data F-47-2.als
COMNT  single_pulse
DATIM  2013-04-20 14:35:47
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         13107
FREQU       7507.39 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1           6.50 usec
IRNUC  1H
CTEMP          25.6 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            42
```



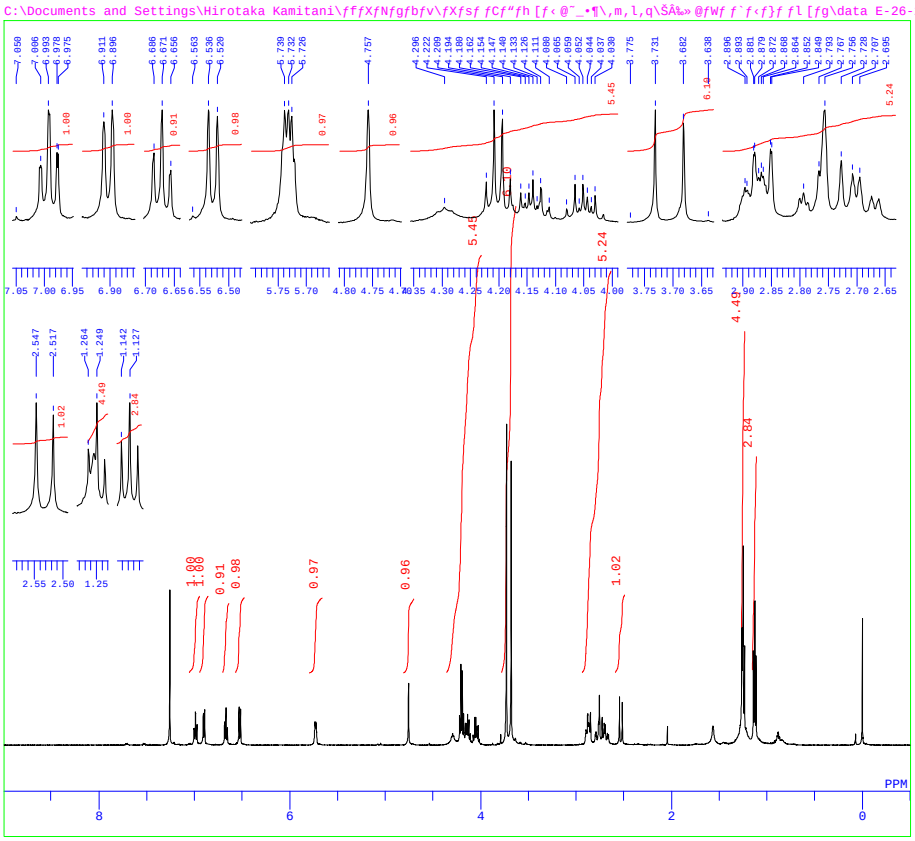
3d



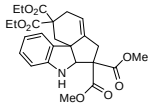

```
DFILE  data F-47 bcm-1.als
COMNT  single pulse decoupled gated NOE
DATIM  2013-04-20 14:32:47
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS           964
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.73 usec
IRNUC  1H
CTEMP          25.4 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            54
```



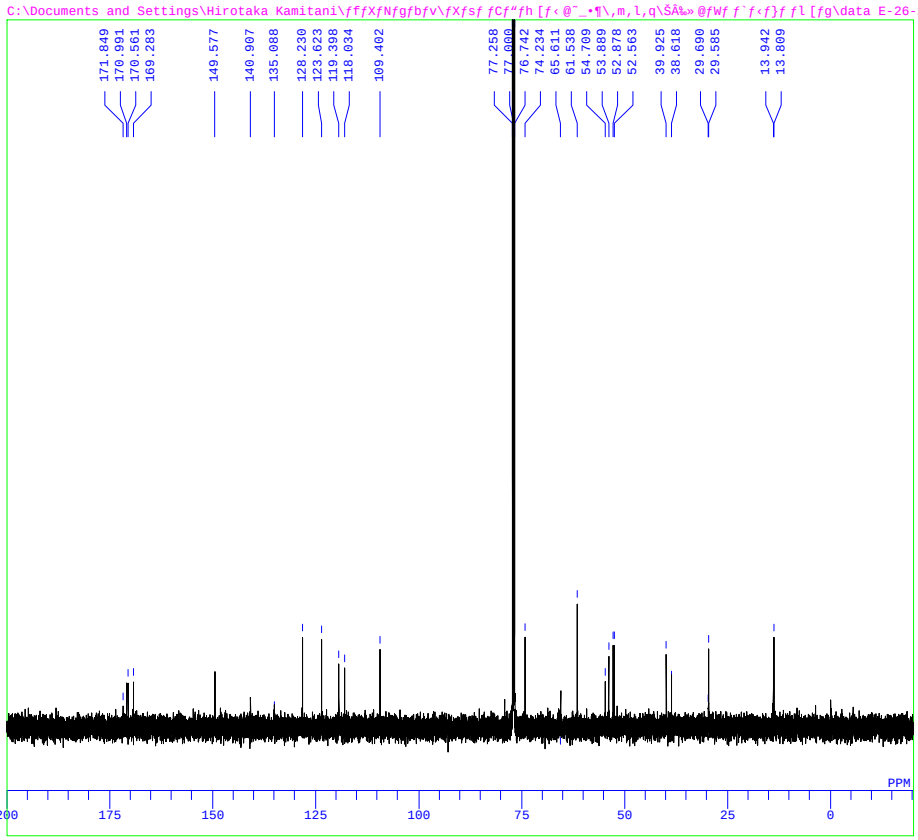
3d



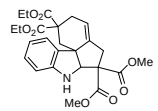

```
DFILE  data E-26-2-1.als
COMNT  single_pulse
DATIM  2013-04-23 09:43:28
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         13107
FREQU       7507.39 Hz
SCANS            8
ACQTM        1.7459 sec
PD           5.0000 sec
PW1            6.50 usec
IRNUC  1H
CTEMP         25.3 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            46
```



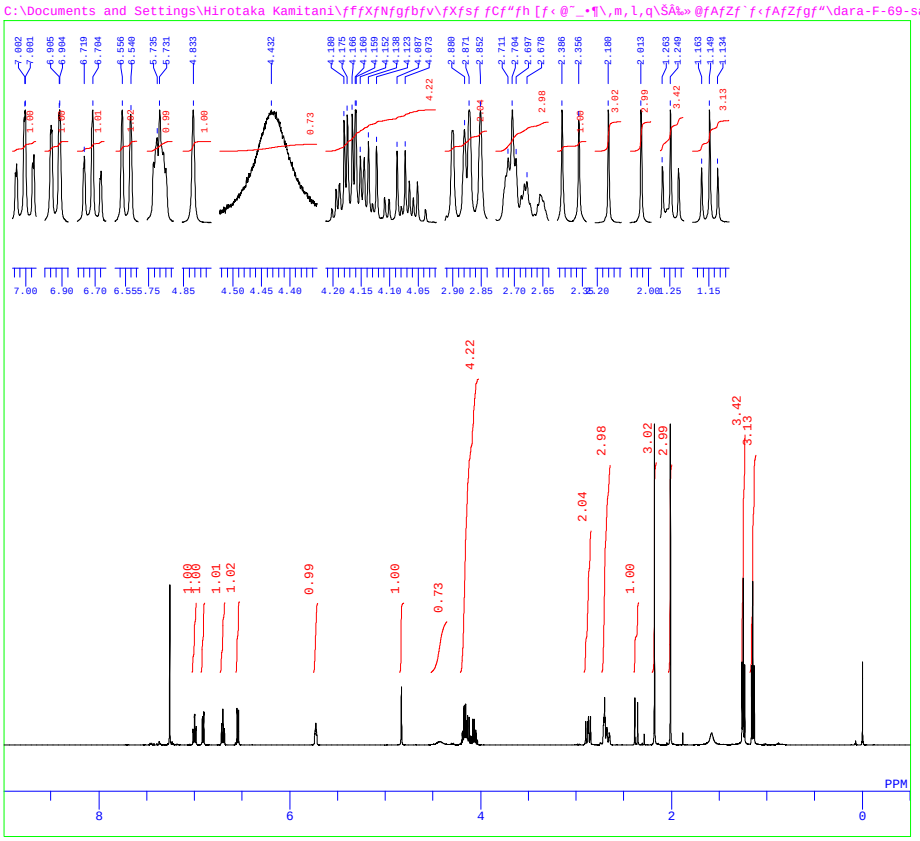
4a



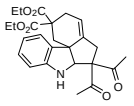

```
DFILE  data E-26-2 bcm-1.als
COMNT  single pulse decoupled gated NOE
DATIM  2013-04-23 10:33:34
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS          1024
ACQTM        0.8336 sec
PD           2.0000 sec
PW1            3.73 usec
IRNUC  1H
CTEMP         25.4 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            54
```



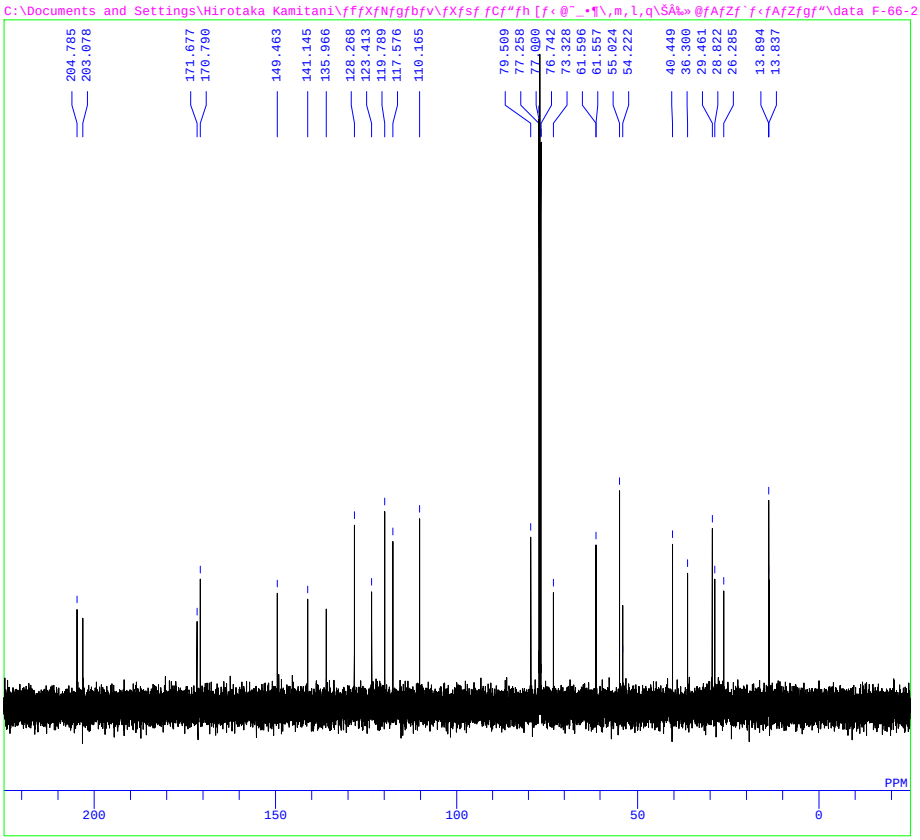
4a



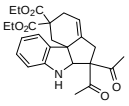

```
DFILE  dara-F-69-sai-2-1.als
COMNT  single_pulse
DATIM  2013-06-26 10:00:38
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         65536
FREQU       9384.38 Hz
SCANS            8
ACQTM        6.9835 sec
PD           5.0000 sec
PW1            6.50 usec
IRNUC  1H
CTEMP         26.4 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            46
```



4b




```
DFILE  data F-66-2 bcm_copy-1.als
COMNT  single pulse decoupled gated NOE
DATIM  2013-05-22 16:19:03
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS            92
ACQTM        0.8336 sec
PD           2.0000 sec
PW1            3.73 usec
IRNUC  1H
CTEMP          25.3 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            50
```



4b