Electronic Supplementary Information for

Ring-opening cyclization of spirocyclopropanes with stabilized sulfonium ylides for the construction of a chromane skeleton

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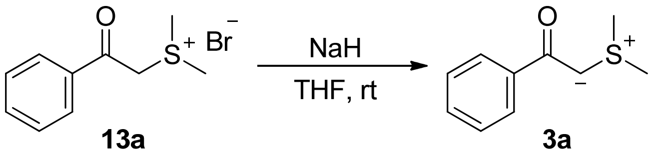
General. Melting points are uncorrected. IR spectra were recorded on a JASCO FT/IR-460 Plus spectrophotometer and absorbance bands are reported in wavenumber (cm^{-1}). ^{1}H NMR spectra were recorded on JEOL JNM-ECX400P (400 MHz) spectrometer. Chemical shifts are reported relative to internal standard (tetramethylsilane at δ_H 0.00 or $CDCl_3$ at δ_H 7.26). Data are presented as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broad), coupling constant and integration. ^{13}C NMR spectra were recorded on JEOL JNM-ECX400P (100 MHz) spectrometer. The following internal reference was used ($CDCl_3$ at δ 77.0). All ^{13}C NMR spectra were determined with complete proton decoupling. High-resolution mass spectra were determined with JEOL JMS-GCmate II instrument. Column chromatography was performed on Silica Gel 60 PF_{254} (Nacalai Tesque) and Kanto silica gel 60 N (63–210 mesh) under pressure. Analytical thin layer chromatography (TLC) was carried out on Merck Kieselgel 60 F_{254} plates. Visualization was accomplished with UV light and phosphomolybdic acid stain solution followed by heating.

All reagents, such as methyl sulfide, tetrahydrothiophene, iodine, lithium iodide, lithium carbonate, and potassium carbonate are commercially available and were purchased from suppliers such as Sigma-Aldrich Co.; Wako Pure Chemical Industries, Ltd.; Tokyo Chemical Industry Co., Ltd.; Nacalai Tesque, INC. Dehydrated CH_2Cl_2, acetonitrile, tetrahydrofuran (THF), EtOAc, and *N*,*N*-dimethylformamide (DMF) were purchased from Wako Pure Chemical Industries, Ltd. and Tokyo Chemical Industry Co., Ltd. Sulfonium bromides **13a**–**f** were prepared from the corresponding α-bromocarbonyl compounds with methyl sulfide (for **13a**–**d**) or tetrahydrothiophene (for **13f**) according to the Ratts' procedure.[1] 1-Phenylspiro-[2.5]octane-4,8-dione (**1a**),[2] 1-(4-methylphenyl)spiro[2.5]octane-4,8-dione (**1b**),[2] 1-(4-bromophenyl)spiro[2.5]octane-4,8-dione (**1c**),[2] spiro[2.5]octane-4,8-dione (**1d**),[3] 1-butylspiro[2.5]octane-4,8-dione (**1e**),[4] 6,6-dimethyl-1-phenylspiro[2.5]octane-4,8-dione (**1f**),[2] 1,1-diacetyl-2-phenylcyclopropane (**11a**),[2] and dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (**11b**)[5] were prepared according to literature procedures.

I. Preparation of stabilized sulfonium ylides

Typical procedure for preparation of sulfonium ylides with sodium hydride:

Dimethylsulfonium benzoylmethylide (3a).[1]

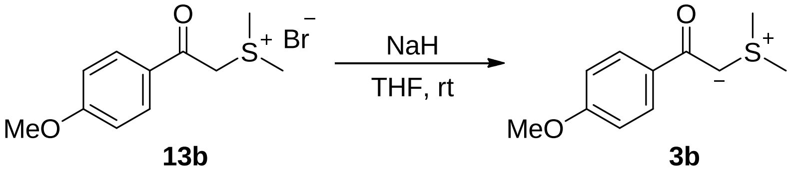


According to the Ratts' procedure,[1] **3a** was prepared from (benzoylmethyl)dimethylsulfonium bromide (**13a**).

NaH (60% dispersion in mineral oil) was washed with two portions of dry hexane to remove the mineral oil and the remaining NaH was dried in vacuo.

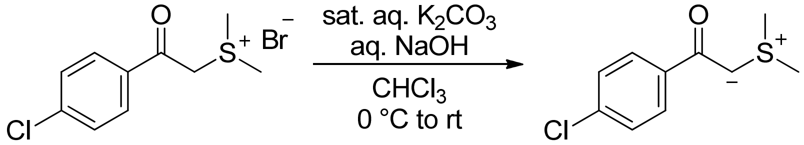
Sulfonium salt **13a** (522 mg, 2.00 mmol) was added to a suspension of NaH (53.0 mg, 2.20 mmol) in THF (10 mL) at room temperature. After stirring at this temperature for 12 h, the reaction mixture was filtered through a Celite pad and the filter cake was rinsed with CH_2Cl_2 (20 mL). The filtrate was concentrated in vacuo, and the crude solid was purified by recrystallization from acetone/hexane to provide **3a** (293 mg, 81%) as a pale yellow solid: mp 55.0–56.0 °C [lit.,[1] mp 56–57 °C]; IR (KBr, cm^{-1}) ν 3072, 2929, 1581, 1507, 1483, 1434, 985, 850, 707, 585; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.76 (m, 2 H), 7.35–7.34 (m, 3H), 4.34 (s, 1H), 2.96 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.0, 140.8, 129.5, 127.8, 126.3, 52.0, 28.5.

Dimethylsulfonium 4-methoxybenzoylmethylide (3b).



According to the typical procedure for the preparation of sulfonium ylides with sodium hydride, **3b** was prepared from (4-methoxybenzoylmethyl)dimethylsulfonium bromide (**13b**) (582 mg, 2.00 mmol). The crude product was purified by recrystallization from acetone/hexane to provide **3b** (283 mg, 67%) as a pale yellow solid: mp 96.5–97.5 °C; IR (KBr, cm^{-1}) ν 3010, 2928, 1601, 1582, 1515, 1494, 1417, 1392, 1254, 1174, 849, 754, 582; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.0 Hz, 2H), 6.86 (dt, J = 9.6, 2.4 Hz, 2H), 4.39 (brs, 1H), 3.82 (s, 3H), 3.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.5, 160.9, 132.9, 128.0, 113.0, 55.1, 51.2, 28.4; HRMS (FAB) m/z calcd for $C_{11}H_{15}O_2S$ $(M+H)^+$ 211.0793, found 211.0785.

Typical procedure for preparation of sulfonium ylides with potassium carbonate: Dimethylsulfonium 4-chlorobenzoylmethylide (3c).

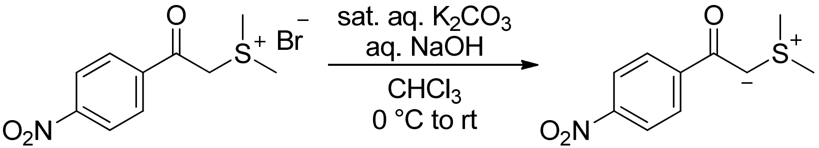


13c **3c**

According to the Payne's procedure,[6] **3c** was prepared from (4-chlorobenzoylmethyl)-dimethylsulfonium bromide **13c**.

Saturated aqueous K_2CO_3 (1.0 mL) and aqueous NaOH (12.5 M, 0.21 mL) were added to a solution of sulfonium salt **13c** (591 mg, 2.00 mmol) in $CHCl_3$ (2.0 mL) at 0 °C. After stirring at this temperature for 10 min, the reaction mixture was warmed to room temperature and stirred for an additional 30 min. The mixture was diluted with CH_2Cl_2 (5 mL) and filtered through a Celite pad, and the filter cake was rinsed with CH_2Cl_2 (20 mL). The filtrate was concentrated in vacuo, and the residue was purified by recrystallization from acetone/hexane to provide **3c** (351 mg, 82%) as a white solid: mp 117.5–118.5 °C; IR (KBr, cm^{-1}) ν 2993, 2916, 1578, 1508, 1480, 1379, 1192, 1087, 1039, 994, 963, 856, 846, 828, 744, 569; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 4.28 (s, 1H), 2.98 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.6, 139.3, 135.2, 127.9, 127.7, 51.1, 28.3; HRMS (FAB) *m/z* calcd for $C_{10}H_{12}OClS$ $(M+H)^+$: 215.0297, found 215.0300.

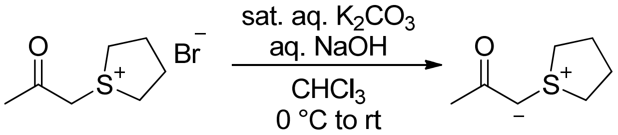
Dimethylsulfonium 4-nitrobenzoylmethylide (3d).[1]



13d **3d**

According to the typical procedure for the preparation of sulfonium ylides with potassium carbonate, **3d** was prepared from dimethyl(4-nitrobenzoylmethyl)sulfonium bromide (**13d**) (612 mg, 2.00 mmol). The crude product was purified by recrystallization from acetone/hexane to provide **3d** (304 mg, 67%) as a brown solid: mp 112.0 °C (decomp.) [lit.,[1] mp 105 °C (decomp.)]; IR (KBr, cm^{-1}) ν 3055, 2923, 1537, 1506, 1404, 1344, 1093, 874, 837, 717; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.2 Hz, 2 H), 7.90 (d, *J* = 7.2 Hz, 2H), 4.40 (s, 1H), 3.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.9, 148.2, 146.7, 127.1, 123.1, 53.7, 28.0.

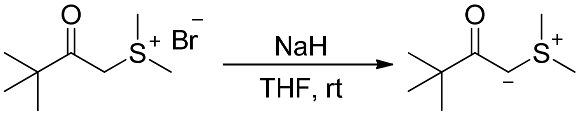
Tetrahydrothiophenium acetylmethylide (3e).



13e **3e**

According to the typical procedure for the preparation of sulfonium ylides with potassium carbonate, **3e** was prepared from (acetylmethyl)tetrahydrothiophenium bromide (**13e**) (450 mg, 2.00 mmol). The crude product **3d** (282 mg, ca. 98%), which was used in the next step without further purification, was obtained as a yellow oil: IR (film, cm^{-1}) ν 2950, 1660, 1530, 1433, 1385, 1175, 985, 835, 577; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.68 (s, 1H), 3.34–3.28 (m, 2H), 3.12–3.06 (m, 2H), 2.64–2.54 (m, 2H), 2.04–1.92 (m, 2H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.8, 54.0, 44.0, 27.9, 26.8; HRMS (FAB) *m/z* calcd for $C_7H_{13}OS$ $(M+H)^+$: 145.0687, found 145.0687.

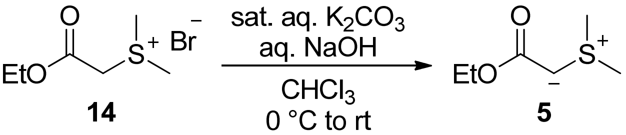
Dimethylsulfonium pivaloylmethylide (3f).[7]



13f **3f**

According to the typical procedure for the preparation of sulfonium ylides with sodium hydride, **3f** was prepared from dimethyl(pivaloylmethyl)sulfonium bromide (**13f**) (482 mg, 2.00 mmol). The crude product was purified by recrystallization from acetone/hexane to provide **3f** (248 mg, 77%) as a white solid: mp 116.0–117.0 °C [lit.,[7] mp 115.5–116 °C]; IR (KBr, cm^{-1}) ν 2952, 1681, 1493, 1427, 1352, 1220, 1137, 1037, 990, 847, 605; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 1H), 2.86 (s, 6H), 1.10 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 47.8, 40.4, 28.6, 28.3.

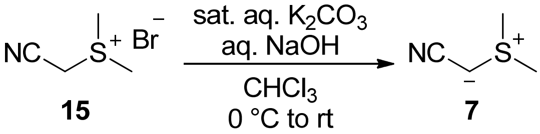
Dimethylsulfonium ethoxycarbonylmethylide (5).[6]



14 **5**

According to the typical procedure for the preparation of sulfonium ylides with potassium carbonate, **5** was prepared from (ethoxycarbonylmethyl)dimethylsulfonium bromide (**14**)[8] (458 mg, 2.00 mmol). The crude product **5** (263 mg, ca. 89%), which was used in the next step without further purification, was obtained as a yellow oil: IR (film, cm^{-1}) ν 2978, 1605, 1371, 1330, 1138, 1065, 998, 883, 757, 554; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.05 (q, *J* = 6.8 Hz, 2H), 2.92 (s, 1H), 2.77 (s, 6H), 1.23 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 57.8, 31.5, 30.3, 14.8.

Dimethylsulfonium cyanomethylide (7).

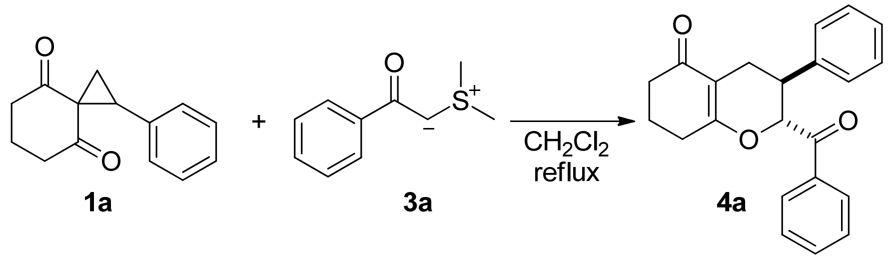


According to the typical procedure for the preparation of sulfonium ylides with potassium carbonate, **7** was prepared from (cyanomethyl)dimethylsulfonium bromide (**15**)[9] (364 mg, 2.00 mmol). The crude product **7** (185 mg, ca. 92%), which was immediately used in the next step without further purification, was obtained as an orange oil. The spectroscopic data of **7** could not be obtained due to an unstable compound.

II. Ring-opening cyclization of spirocyclopropanes with sulfonium ylides

Typical procedure for the ring-opening cyclization of spirocyclopropane 1a with sulfonium ylide 3a (Table 1, entry 3):

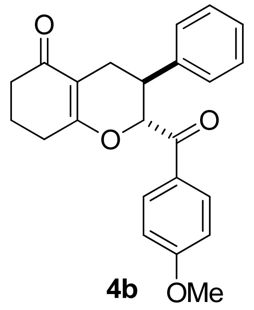
rac-(2*R*,3*S*)-2-Benzoyl-3-phenyl-2,3,4,6,7,8-hexahydro-5*H*-1-benzopyran-5-one (4a).



1-Phenylspiro[2.5]octane-4,8-dione (**1a**)[2] (64 mg, 0.30 mmol) was added to a solution of **3a** (81 mg, 0.45 mmol) in CH_2Cl_2 (0.75 mL) at room temperature. After stirring at reflux for 7 h, the reaction was cooled to room temperature and quenched by addition of water (3 mL), and the resulting mixture was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine (10 mL) and dried over anhydrous $MgSO_4$. Filtration and evaporation in vacuo furnished the crude product, which was purified by column chromatography (silica gel, 40% EtOAc in hexane) to provide **4a** (95 mg, 95%) as a white solid: mp 109.0–110.0 °C; IR (KBr, cm^{-1}) ν 2942, 1686, 1650, 1628, 1597, 1450, 1393, 1224, 1187, 975, 757, 699; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.6 Hz, 2 H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.24–7.15 (m, 5H), 5.53 (d, *J* = 6.8 Hz, 1H), 3.50 (q, *J* = 6.8 Hz, 1H), 2.58–2.45 (m, 4H), 2.44–2.37 (m, 2H), 2.07–1.97 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 195.1, 170.2, 140.1, 134.9, 133.6, 128.7, 128.6, 128.5, 127.6, 127.2, 111.0, 80.2, 39.2, 36.6, 28.2, 22.9, 20.8; HRMS (FAB) *m/z* calcd for $C_{22}H_{21}O_3$ $(M+H)^+$ 333.1491, found 333.1501.

rac-(2*R*,3*S*)-2-(4-Methoxyphenyl)-3-phenyl-2,3,4,6,7,8-hexahydro-5*H*-1-benzopyran-5-one (4b) (Table 2, entry 1).

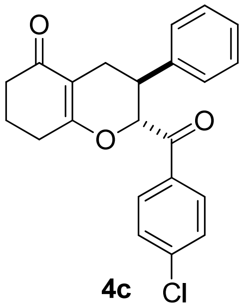
According to the typical procedure for the ring-opening cyclization of **1a** with **3a**, **4b** was prepared from **1a** (64 mg, 0.30 mmol) with **3b** (95 mg, 0.45 mmol) for 4.5 h. The crude product was purified by column chromatography (silica gel, 4:3.5:2.5 EtOAc/hexane/CH_2Cl_2) to provide **4b** (102 mg, 94%) as a white solid: mp 75.0–76.5 °C; IR (KBr, cm^{-1}) ν 2936, 1686, 1634, 1603, 1575, 1383, 1262, 1173, 1023, 975, 749; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.26–7.14 (m, 5H), 6.89 (dt, *J* = 8.8, 2.0 Hz, 2H), 5.49 (d, *J* = 6.4 Hz, 1H), 3.85 (s, 3H), 3.49 (q, *J* = 6.4 Hz, 1H), 2.61–2.47 (m, 4H), 2.42 (td, *J* = 6.4, 3.2 Hz, 2H),



4b

2.05–1.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 193.3, 170.3, 163.9, 140.2, 131.0, 128.7, 127.8, 127.6, 127.2, 113.9, 111.0, 79.9, 55.5, 39.3, 36.7, 28.3, 23.1, 20.8; HRMS (FAB) *m/z* calcd for $C_{23}H_{23}O_4$ $(M+H)^+$ 363.1596, found 363.1599.

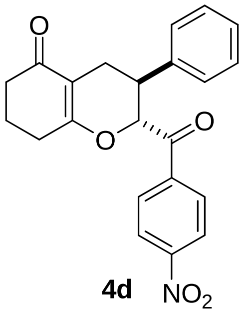
rac-(2_R_,3_S_)-2-(4-Chlorophenyl)-3-phenyl-2,3,4,6,7,8-hexahydro-5_H_-1-benzopyran-5-one (4c) (Table 2, entry 2).



4c

According to the typical procedure for the ring-opening cyclization of **1a** with **3a**, **4c** was prepared from **1a** (64 mg, 0.30 mmol) with **3c** (97 mg, 0.45 mmol) for 9.5 h. The crude product was purified by column chromatography (silica gel, 40% EtOAc in hexane) to provide **4c** (102 mg, 93%) as a white solid: mp 118.5–120.0 °C; IR (KBr, cm^{-1}) ν 2939, 1683, 1651, 1629, 1591, 1390, 1224, 1190, 1092, 977, 762, 700; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.23 (t, J = 7.2 Hz, 2H), 7.16 (t, J = 7.2 Hz, 3H), 5.42 (d, J = 6.8 Hz, 1H), 3,45 (q, J = 6.8 Hz, 1H), 2.65–2.47 (m, 4H), 2.42 (dd, J = 6.4, 4.8 Hz, 2H), 2.02 (quint, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 194.1, 169.9, 140.2, 139.7, 133.3, 130.0, 128.9, 128.8, 127.7, 127.4, 111.2, 80.2, 39.5, 36.6, 28.2, 23.3, 20.7; HRMS (FAB) *m/z* calcd for $C_{22}H_{20}O_3Cl$ $(M+H)^+$ 367.1101, found 367.1105.

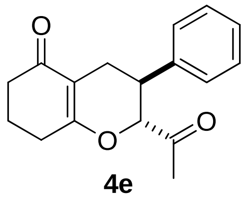
rac-(2_R_,3_S_)-2-(4-Nitrophenyl)-3-phenyl-2,3,4,6,7,8-hexahydro-5_H_-1-benzopyran-5-one (4d) (Table 2, entry 4).



4d

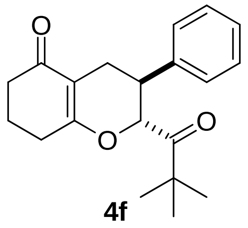
According to the typical procedure for the ring-opening cyclization of **1a** with **3a**, **4d** was prepared from **1a** (64 mg, 0.30 mmol) with **3d** (203 mg, 0.90 mmol) for 48 h. The crude product was purified by column chromatography (silica gel, 40% EtOAc in hexane) to provide **4d** (93 mg, 82%) as a pale yellow solid: mp 165.0–166.5 °C; IR (KBr, cm^{-1}) ν 2935, 1705, 1634, 1604, 1523, 1395, 1350, 1212, 1098, 843, 693; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.8 Hz, 2H), 7.92 (d, J = 8.8 Hz, 2H), 7.22 (t, J = 7.2 Hz, 2H), 7.18–7.13 (m, 3H), 5.40 (d, J = 8.0 Hz, 1H), 3.43 (q, J = 8.0 Hz, 1H), 2.69 (dd, J = 17.2, 6.0 Hz, 1H), 2.59–2.51 (m, 3H), 2.43 (t, J = 6.8 Hz, 2H), 2.03 (quint, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 194.5, 169.5, 150.3, 139.8, 139.0, 129.6, 128.9, 127.7, 127.6, 123.7, 111.6, 80.6, 39.9, 36.6, 28.2, 23.7, 20.7; HRMS (FAB) *m/z* calcd for $C_{22}H_{20}O_5N$ $(M+H)^+$ 378.1341, found 378.1347.

rac-(2*R*,3*S*)-2-Acetyl-3-phenyl-2,3,4,6,7,8-hexahydro-5*H*-1-benzopyran-5-one (4e) (Table 2, entry 5).


4e

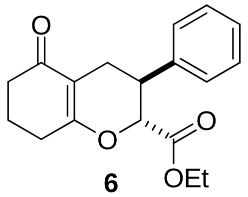
According to the typical procedure for the ring-opening cyclization of **1a** with **3a**, **4e** was prepared from **1a** (64 mg, 0.30 mmol) with **3e** (65 mg, 0.45 mmol) for 24 h. The crude product was purified by column chromatography (silica gel, 40% EtOAc in hexane) to provide **4e** (72 mg, 89%) as a white solid: mp 88.0–89.0 °C; IR (KBr, cm^{-1}) ν 2935, 1719, 1652, 1631, 1604, 1385, 1351, 1212, 1182, 1134, 1014, 764, 707; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.2 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 7.17 (d, *J* = 7.2 Hz, 2H), 4.56 (d, *J* = 7.2 Hz, 1H), 3.25 (q, *J* = 7.2 Hz, 1H), 2.62–2.46 (m, 4H), 2.41 (t, *J* = 6.4 Hz, 2H), 2.05 (s, 3H), 2.03–1.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.5, 197.6, 169.5, 139.5, 128.8, 127.5, 127.4, 111.4, 84.5, 39.4, 36.5, 28.1, 26.8, 23.8, 20.7; HRMS (FAB) *m/z* calcd for $C_{17}H_{19}O_3$ $(M+H)^+$ 271.1334, found 271.1339.

rac-(2*R*,3*S*)-2-Pivaloyl-3-phenyl-2,3,4,6,7,8-hexahydro-5*H*-1-benzopyran-5-one (4f) (Table 2, entry 6).


4f

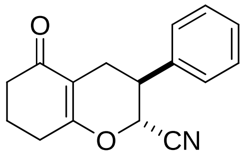
According to the typical procedure for the ring-opening cyclization of **1a** with **3a**, **4f** was prepared from **1a** (64 mg, 0.30 mmol) with **3f** (72 mg, 0.45 mmol) for 2 h. The crude product was purified by column chromatography (silica gel, 40% EtOAc in hexane) to provide **4f** (79 mg, 84%) as a colorless oil: IR (film, cm^{-1}) ν 2969, 1717, 1654, 1631, 1388, 1187, 976, 755, 701; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.2 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 7.2 Hz, 2H), 4.85 (d, *J* = 9.6 Hz, 1H), 3.31 (td, *J* = 9.6, 5.6 Hz, 1H), 2.72 (dd, *J* = 16.4, 5.6 Hz, 1H), 2.52–2.35 (m, 5H), 2.00 (quint, *J* = 6.0 Hz, 2H), 0.87 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5, 197.8, 170.2, 146.5, 139.0, 128.6, 127.4, 111.4, 77.4, 44.1, 39.0, 36.6, 28.2, 25.2, 23.5, 20.8; HRMS (FAB) *m/z* calcd for $C_{20}H_{25}O_3$ $(M+H)^+$: 313.1804, found 313.1811.

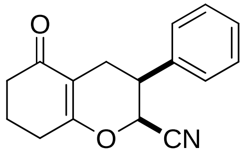
rac-(2*R*,3*S*)-2-Ethoxycarbonyl-3-phenyl-2,3,4,6,7,8-hexahydro-5*H*-1-benzopyran-5-one (6) (Scheme 2).


6

According to the typical procedure for the ring-opening cyclization of **1a** with **3a**, **6** was prepared from **1a** (64 mg, 0.30 mmol) with **5** (67 mg, 0.45 mmol) for 1 h. The crude product was purified by column chromatography (silica gel, 40% EtOAc in hexane) to provide **6** (87 mg, 97%) as a white solid: mp 76.5–77.5 °C; IR (KBr, cm^{-1}) ν 2937, 1746, 1649, 1626, 1388, 1210, 1188, 1069, 1034, 765, 743, 705; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.2 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 7.19 (d, *J* = 7.2 Hz, 2H), 4.59 (d, *J* = 7.6 Hz, 1H), 4.02 (q, *J* = 7.2 Hz, 2H), 3.27 (q, *J* = 7.6 Hz, 1H), 2.62 (dd, *J* = 17.6, 5.6 Hz, 1H), 2.55–2.46 (m, 3H), 2.41 (td, *J* = 6.4, 2.8 Hz, 2H), 2.01 (quint, *J* = 6.4 Hz, 2H), 1.00 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 169.7, 168.8, 139.3, 128.5, 127.6, 127.3, 111.3, 79.0, 61.3, 40.2, 36.5, 28.0, 23.7, 20.6, 13.6; HRMS (FAB) *m/z* calcd for $C_{18}H_{21}O_4$ $(M+H)^+$: 301.1440, found 301.1448.

***rac*-(2*R*,3*S*)-2-Cyano-3-phenyl-2,3,4,6,7,8-hexahydro-5*H*-1-benzopyran-5-one (8) and *rac*-(2*R*,3*R*)-isomer 8' (Scheme 2).**


8

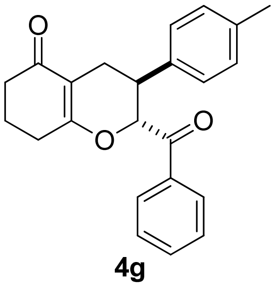

8'

According to the typical procedure for the ring-opening cyclization of **1a** with **3a**, **8** and **8'** was prepared from **1a** (64 mg, 0.30 mmol) with **7** (46 mg, 0.45 mmol) for 4.5 h. The crude product was purified by column chromatography (silica gel, 30% EtOAc in hexane) to provide **8** (53 mg, 70%) as a white solid and **8'** (16 mg, 21%) as a colorless oil.

8: mp 159.0–160.0 °C; IR (KBr, cm^{-1}) ν 2923, 2363, 1698, 1657, 1636, 1456, 1385, 1239, 1213, 1184, 1133, 1065, 1036, 762, 702; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.32 (m, 3H), 7.22 (d, *J* = 6.8 Hz, 2H), 4.77 (d, *J* = 8.8 Hz, 1H), 3.23 (td, *J* = 8.8 Hz, 6.0 Hz, 1H), 2.84 (m, 1H), 2.56–2.37 (m, 5H), 2.03 (quint, *J* = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 168.1, 137.4, 129.2, 128.4, 127.6, 115.8, 111.9, 68.9, 41.3, 36.4, 27.8, 23.9, 20.6; HRMS (FAB) *m/z* calcd for $C_{16}H_{16}O_2N$ $(M+H)^+$ 254.1181, found 254.1179.

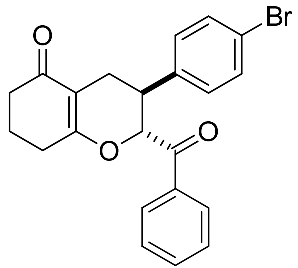
8': IR (film, cm^{-1}) ν 2928, 2360, 1661, 1638, 1385, 1266, 1184, 1068, 1027, 739, 704; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.34 (m, 5H), 5.08 (dd, *J* = 4.0, 1.6 Hz, 1H), 3.29 (ddd, *J* = 10.4, 6.4, 4.0 Hz, 1H), 2.82–2.69 (m, 2H), 2.57–2.43 (m, 4H), 2.17–1.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 167.3, 135.8, 129.2, 128.5, 127.8, 112.5, 99.9, 68.8, 39.9, 36.5, 27.8, 20.6, 20.3; HRMS (FAB) *m/z* calcd for $C_{16}H_{16}O_2N$ $(M+H)^+$ 254.1181, found 254.1177.

***rac*-(2*R*,3*S*)-2-Benzoyl-3-(4-methylphenyl)-2,3,4,6,7,8-hexahydro-5*H*-1-benzopyran-5-one (4g) (Table 3, entry 1).**


4g

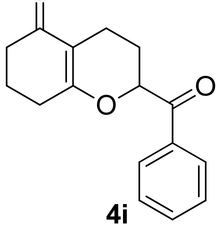
According to the typical procedure for the ring-opening cyclization of **1a** with **3a**, **4g** was prepared from **1b**[2] (68 mg, 0.30 mmol) with **3a** (81 mg, 0.45 mmol) for 6 h. The crude product was purified by column chromatography (silica gel, 30% EtOAc in hexane) to provide **4g** (92 mg, 89%) as a white solid: mp 98.0–99.0 °C; IR (KBr, cm^{-1}) ν 2945, 1694, 1652, 1632, 1597, 1516, 1448, 1387, 1215, 1185, 1098, 974, 691; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.08–7.03 (m, 4H), 5.51 (d, *J* = 6.0 Hz, 1H), 3.47 (q, *J* = 6.0 Hz, 1H), 2.59–2.46 (m, 4H), 2.41 (td, *J* = 6.4, 2.8 Hz, 2H), 2.25 (s, 3H), 2.00 (quint, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 195.2, 170.2, 137.0, 136.8, 134.9, 133.6, 129.4, 128.7, 128.6, 127.4, 111.0, 80.5, 38.7, 36.6, 28.2, 22.9, 20.9, 20.8; HRMS (FAB) *m/z* calcd for $C_{23}H_{23}O_3$ $(M+H)^+$: 347.1647, found 347.1648.

rac-(2*R*,3*S*)-2-Benzoyl-3-(4-bromophenyl)-2,3,4,6,7,8-hexahydro-5*H*-1-benzopyran-5-one (4h) (Table 3, entry 2).


4h

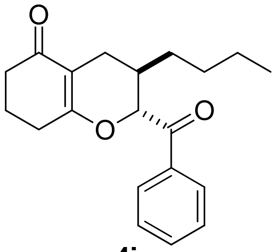
According to the typical procedure for the ring-opening cyclization of **1a** with **3a**, **4h** was prepared from **1c**^{2} (88 mg, 0.30 mmol) with **3a** (81 mg, 0.45 mmol) for 13 h. The crude product was purified by column chromatography (silica gel, 30% EtOAc in hexane) to provide **4h** (114 mg, 93%) as a colorless oil: IR (film, cm^{-1}) ν 2946, 1695, 1652, 1632, 1597, 1489, 1448, 1388, 1215, 1185, 1097, 1009, 975, 756; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dt, *J* = 7.2, 1.6 Hz, 2H), 7.58 (tt, *J* = 7.2, 1.6 Hz, 1H), 7.45 (m, 2H), 7.36 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.06 (dt, *J* = 8.8, 2.0 Hz, 2H), 5.47 (d, *J* = 6.4 Hz, 1H), 3.48 (q, *J* = 6.4 Hz, 1H), 2.60–2.46 (m, 4H), 2.42 (td, *J* = 6.4, 1.6 Hz, 2H), 2.01 (quint, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 194.7, 170.1, 139.2, 134.7, 133.8, 131.8, 129.3, 128.8, 128.6, 121.1, 110.8, 79.9, 38.5, 36.6, 28.2, 22.9, 20.7; HRMS (FAB) *m/z* calcd for $C_{22}H_{20}O_3Br$ $(M+H)^+$: 411.0596, found 411.0590.

2-Benzoyl-2,3,4,6,7,8-hexahydro-5*H*-1-benzopyran-5-one (4i) (Table 3, entry 4).


4i

According to the typical procedure for the ring-opening cyclization of **1a** with **3a**, **4i** was prepared from **1d**^{3} (41 mg, 0.30 mmol) with **3a** (81 mg, 0.45 mmol) in refluxing CH_3CN (0.75 mL) for 8 h. The crude product was purified by column chromatography (silica gel, 35% EtOAc in hexane) to provide **4i** (70 mg, 91%) as a white solid: mp 84.0–85.0 °C; IR (KBr, cm^{-1}) ν 2939, 1698, 1648, 1621, 1597, 1400, 1232, 1189, 1101, 1003, 778, 702; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.91 (m, 2H), 7.62 (tt, *J* = 7.2, 1.6 Hz, 1H), 7.53–7.48 (m, 2H), 5.47 (dd, *J* = 6.8, 3.6 Hz, 1H), 2.58–2.30 (m, 5H), 2.26–2.17 (m, 2H), 2.09 (m, 1H), 1.99 (quint, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 195.4, 170.5, 134.1, 133.8, 128.8, 128.5, 111.4, 77.4, 36.6, 28.4, 24.1, 20.8, 16.0; HRMS (FAB) *m/z* calcd for $C_{16}H_{17}O_3$ $(M+H)^+$: 257.1178, found 257.1177.

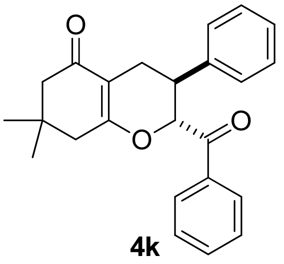
***rac*-(2*R*,3*S*)-2-Benzoyl-3-butyl-2,3,4,6,7,8-hexahydro-5*H*-1-benzopyran-5-one (4j) (Table 3, entry 5).**



4j

According to the typical procedure for the ring-opening cyclization of **1a** with **3a**, **4j** was prepared from **1e**^{4} (58 mg, 0.30 mmol) with **3a** (81 mg, 0.45 mmol) for 24 h. The crude product was purified by column chromatography (silica gel, 35% EtOAc in hexane) to provide **4j** (21 mg, 22%) as a colorless oil and starting material **1e** (37 mg, 64%) was recovered. **4j**: IR (film, cm^{-1}) ν 2930, 1697, 1652, 1628, 1597, 1448, 1393, 1216, 1131, 1086, 971, 755, 695; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 7.2, 1.2 Hz, 2H), 7.62 (tt, *J* = 7.2, 1.2 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 2H), 5.31 (d, *J* = 4.0 Hz, 1H), 2.58–2.38 (m, 4H), 2.27 (m, 1H), 2.11 (d, *J* = 5.2 Hz, 2H), 2.04–1.96 (m, 2H), 1.47–1.28 (m, 6H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 195.7, 170.0, 134.5, 133.7, 128.9, 128.5, 109.9, 80.7, 36.7, 33.0, 31.6, 29.1, 28.2, 22.6, 20.8, 20.4, 13.9; HRMS (FAB) *m/z* calcd for $C_{20}H_{25}O_3$ $(M+H)^+$: 313.1804, found 313.1813.

***rac*-(2*R*,3*S*)-2-Benzoyl-7,7-dimethyl-3-phenyl-2,3,4,6,7,8-hexahydro-5*H*-1-benzopyran-5-one (4k) (Table 3, entry 7).**



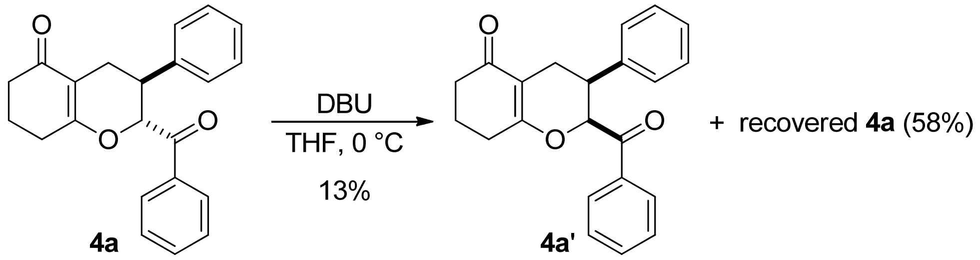
4k

According to the typical procedure for the ring-opening cyclization of **1a** with **3a**, **4k** was prepared from **1f**^{2} (73 mg, 0.30 mmol) with **3a** (81 mg, 0.45 mmol) for 9.5 h. The crude product was purified by column chromatography (silica gel, 30% EtOAc in hexane) to provide **4k** (98 mg, 91%) as a white solid: mp 124.5–125.5 °C; IR (KBr, cm^{-1}) ν 2952, 1698, 1646, 1597, 1448, 1384, 1205, 1163, 1111, 1040, 984, 765, 702; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.27–7.17 (m, 5H), 5.60 (d, *J* = 5.6 Hz, 1H), 3.55 (q, *J* = 5.6 Hz, 1H), 2.55 (qd, *J* = 16.8, 6.4 Hz, 2H), 2.46–2.24 (m, 4H), 1.10 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 195.1, 168.6, 140.4, 134.7, 133.7, 128.8, 128.7, 128.6, 127.5, 127.2, 109.4, 80.5, 50.6, 42.0, 38.5, 32.2, 28.4, 22.1 ; HRMS (FAB) *m/z* calcd for $C_{24}H_{25}O_3$ $(M+H)^+$: 361.1804, found 361.1804.

III. Determination of the stereochemistry of 4a

In order to assign the stereochemistry of **4a**, stereoisomer **4a'** was prepared under basic conditions and ^{1}H NOE experiments of these compounds **4a** and **4a'** were conducted.

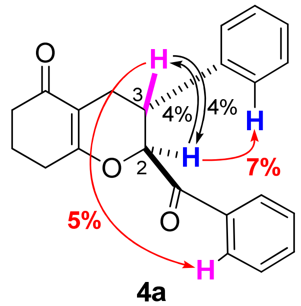
rac-(2*R*,3*R*)-2-Benzoyl-3-phenyl-2,3,4,6,7,8-hexahydro-5*H*-1-benzopyran-5-one (4a').



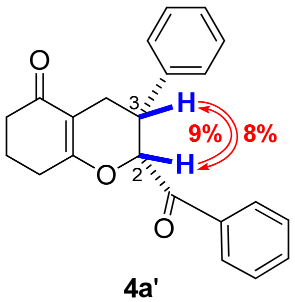
1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 62 mg, 0.30 mmol) was added to a solution of **4a** (136 mg, 0.41 mmol) in THF (4.1 mL) at 0 °C. After stirring at this temperature for 3 h, the reaction was quenched by addition of saturated aqueous NH_4Cl (3 mL), and the resulting mixture was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with water (10 mL) and brine (10 mL), and dried over anhydrous $MgSO_4$. Filtration and evaporation in vacuo furnished the crude product, which was purified by column chromatography (silica gel, 40% EtOAc in hexane) to provide **4a'** (18 mg, 13%) as a colorless oil and starting material **4a** (79 mg, 58%) was recovered.

4a': IR (film, cm^{-1}) ν 2925, 1687, 1652, 1626, 1600, 1450, 1391, 1215, 1189, 1077, 755, 696, 593; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.2 Hz, 2H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.26 (t, *J* = 7.2 Hz, 2H), 7.14–7.08 (m, 3H), 7.04–7.02 (m, 2H), 5.71 (d, *J* = 4.0 Hz, 1H), 3.62 (m, 1H), 2.79 (dd, *J* = 16.4, 6.0 Hz, 1H), 2.66–2.52 (m, 3H), 2.47 (q, *J* = 6.0 Hz, 2H), 2.13–1.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 195.6, 170.4, 138.1, 135.9, 133.2, 128.4, 128.3, 128.2, 128.0, 127.3, 111.8, 79.7, 40.3, 36.7, 28.3, 21.6, 20.9; HRMS (FAB) *m/z* calcd for $C_{22}H_{21}O_3$ $(M+H)^+$ 333.1491, found 333.1491.

^{1}H NOE experiments:



4a
trans
$J_{2H,3H}$ = 6.8 Hz



4a'
cis
$J_{2H,3H}$ = 4.0 Hz

^{1}H NOE interaction

4a: C2-H → 3-phenyl-H (7%); C3-H → 2-benzoyl-H (5%)

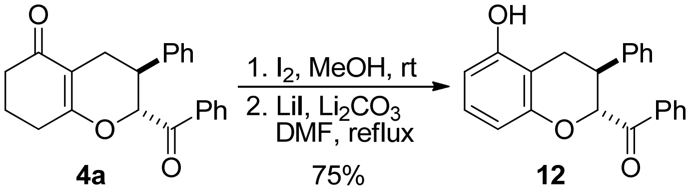
[a less significant interaction: C2-H → C3-H (4%); C3-H → C2-H (4%)]

4a': C2-H → C3-H (9%); C3-H → C2-H (8%);

These data reveal that these stereochemistries of **4a** and **4a'** are 2,3-*trans* and 2,3-*cis*, respectively.

IV. Synthesis of 5-hydroxychromane 12

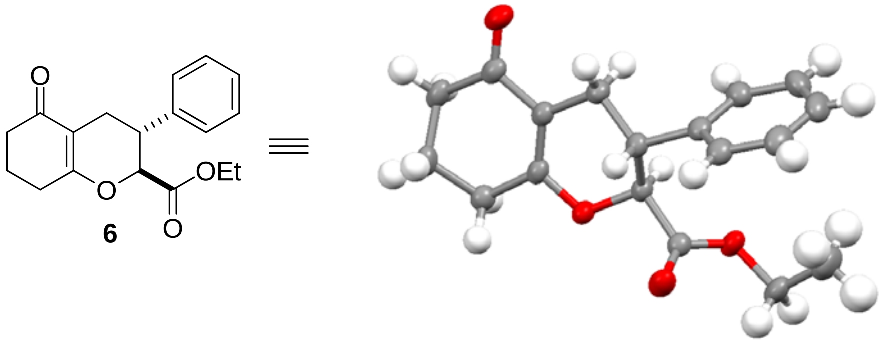
rac-(2*R*,3*S*)-2-Benzoyl-5-hydroxy-3-phenyl-3,4-dihydro-2*H*-1-benzopyran (12) (Scheme 5).



Iodine (137 mg, 0.54 mmol,) was added to a solution of **4a** (60 mg, 0.18 mmol) in MeOH (0.90 mL) at room temperature. After stirring at this temperature for 24 h, the reaction mixture was quenched by addition of saturated aqueous $Na_2S_2O_3$ (3 mL), and the resulting mixture was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with water (10 mL) and brine (10 mL), and dried over anhydrous $MgSO_4$. Filtration and evaporation in vacuo furnished the crude product (103 mg), which was used in the next step without further purification.

LiI (27 mg, 0.20 mmol) and Li_2CO_3 (15 mg, 0.20 mmol) were added to a solution of crude product in DMF (1.8 mL). After stirring at reflux for 1.5 h, the reaction was cooled to room temperature and diluted with 20% EtOAc in hexane (3 mL). The reaction mixture was quenched by addition of saturated aqueous NH_4Cl (3 mL), and the resulting mixture was extracted with 20% EtOAc in hexane (3 x 10 mL). The combined organic layers were washed with water (10 mL) and brine (10 mL), and dried over anhydrous $MgSO_4$. Filtration was concentrated in vacuo, and the residue was purified by column chromatography (silica gel, 30% EtOAc in hexane) to provide **12** (44 mg, 75%) as a colorless oil: IR (film, cm^{-1}) ν 2925, 1684, 1617, 1597, 1497, 1466, 1448, 1283, 1225, 1069, 1002, 757, 695; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 7.2 Hz, 1H), 7.54 (t, J = 7.2 Hz, 1H), 7.40 (t, J = 7.2 Hz, 1H). 7.26–7.15 (m, 5H), 7.00 (t, J = 8.0 Hz, 1H), 6.56 (d, J = 8.0 Hz, 1H), 6.41 (d, J = 8.0 Hz, 1H), 5.46 (d, J = 7.2 Hz, 1H), 5.05 (s, 1H), 3.66 (q, J = 7.2 Hz, 1H), 3.11 (dd, J = 16.8, 7.2 Hz, 1H), 2.95 (dd, J = 16.8 Hz, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 154.5, 153.8, 140.7, 135.4, 133.4, 129.0, 128.7, 128.5, 127.9, 127.3, 127.1, 109.2, 109.1, 107.4, 80.0, 39.6, 25.4; HRMS (FAB) *m/z* calcd for $C_{22}H_{19}O_3$ $(M+H)^+$ 331.1334, found 331.1333.

V. X-ray crystallographic data of 6



X-ray of **6** (CCDC 1915566)

A. Crystal Data

Empirical Formula	$C_{18}H_{20}O_4$
Formula Weight	300.35
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.250 X 0.250 X 0.150 mm
Crystal System	orthorhombic
Lattice Type	A-centered
Lattice Parameters	a = 8.05576(16) Å
	b = 24.7866(5) Å
	c = 15.4543(3) Å
	V = 3085.84(11) $Å^3$
Space Group	Aea2 (#41)
Z value	8
D_{calc}	1.293 g/cm^3
F_{000}	1280.00
μ(CuKα)	7.399 cm^{-1}

B. Intensity Measurements

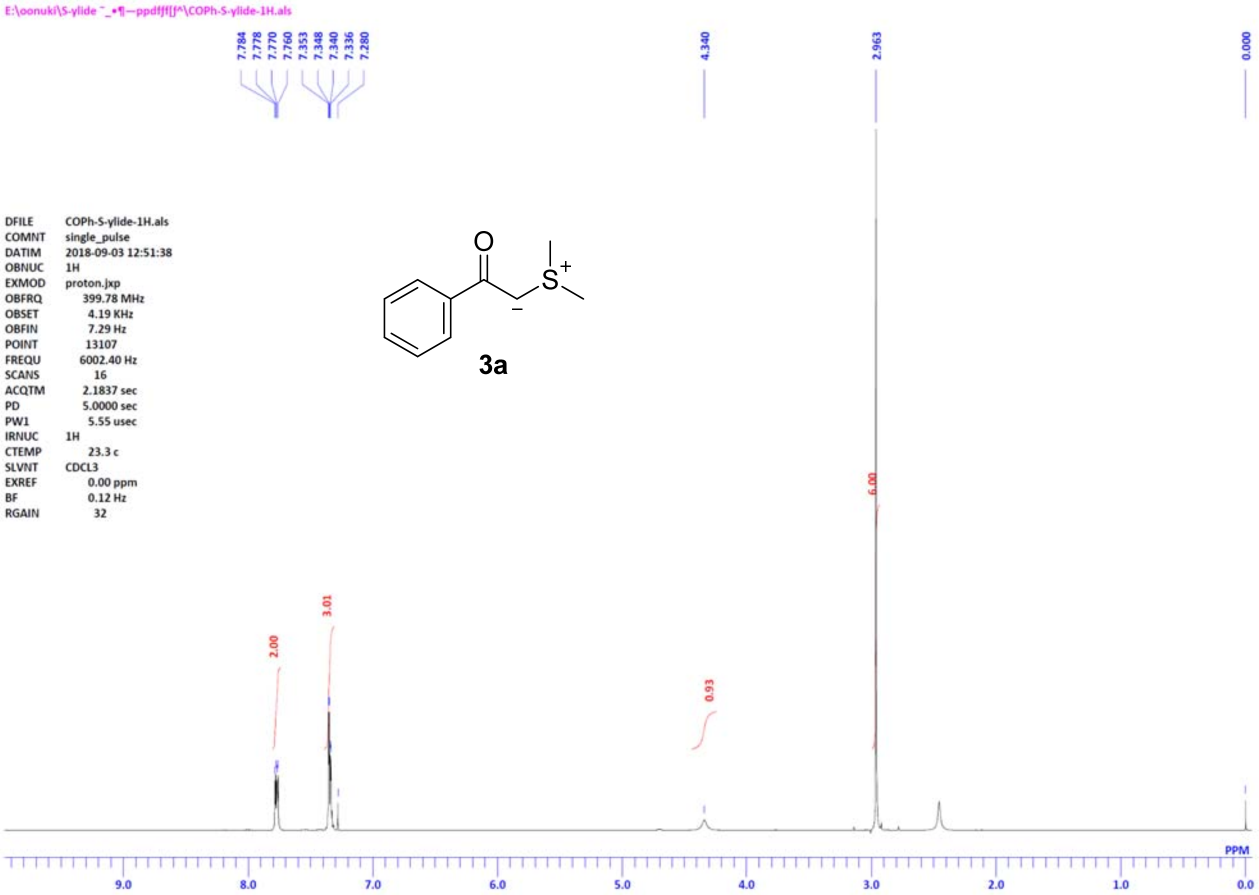
Diffractometer	R-AXIS RAPID
Radiation	CuKα (λ = 1.54187 Å) multi-layer mirror monochromated
Voltage, Current	40kV, 30mA
Temperature	-100.0°C
Detector Aperture	460.0 x 256.0 mm
Data Images	180 exposures
ω oscillation Range (χ=54.0, ϕ=0.0)	80.0 - 260.0°
Exposure Rate	5.0 sec./$^{\circ}$
ω oscillation Range (χ=54.0, ϕ=90.0)	80.0 - 260.0°
Exposure Rate	5.0 sec./$^{\circ}$
ω oscillation Range (χ=54.0, ϕ=180.0)	80.0 - 260.0°
Exposure Rate	5.0 sec./$^{\circ}$
ω oscillation Range (χ=54.0, ϕ=270.0)	80.0 - 260.0°
Exposure Rate	5.0 sec./$^{\circ}$
ω oscillation Range (χ=0.0, ϕ=0.0)	80.0 - 260.0°
Exposure Rate	5.0 sec./$^{\circ}$
Detector Position	127.00 mm
Pixel Size	0.100 mm
$2\theta_{max}$	136.3°
No. of Reflections Measured	Total: 16768 Unique: 2780 (R_{int} = 0.0329) Parsons quotients (Flack x parameter): 1197
Corrections	Lorentz-polarization Absorption (trans. factors: 0.728 - 0.895)

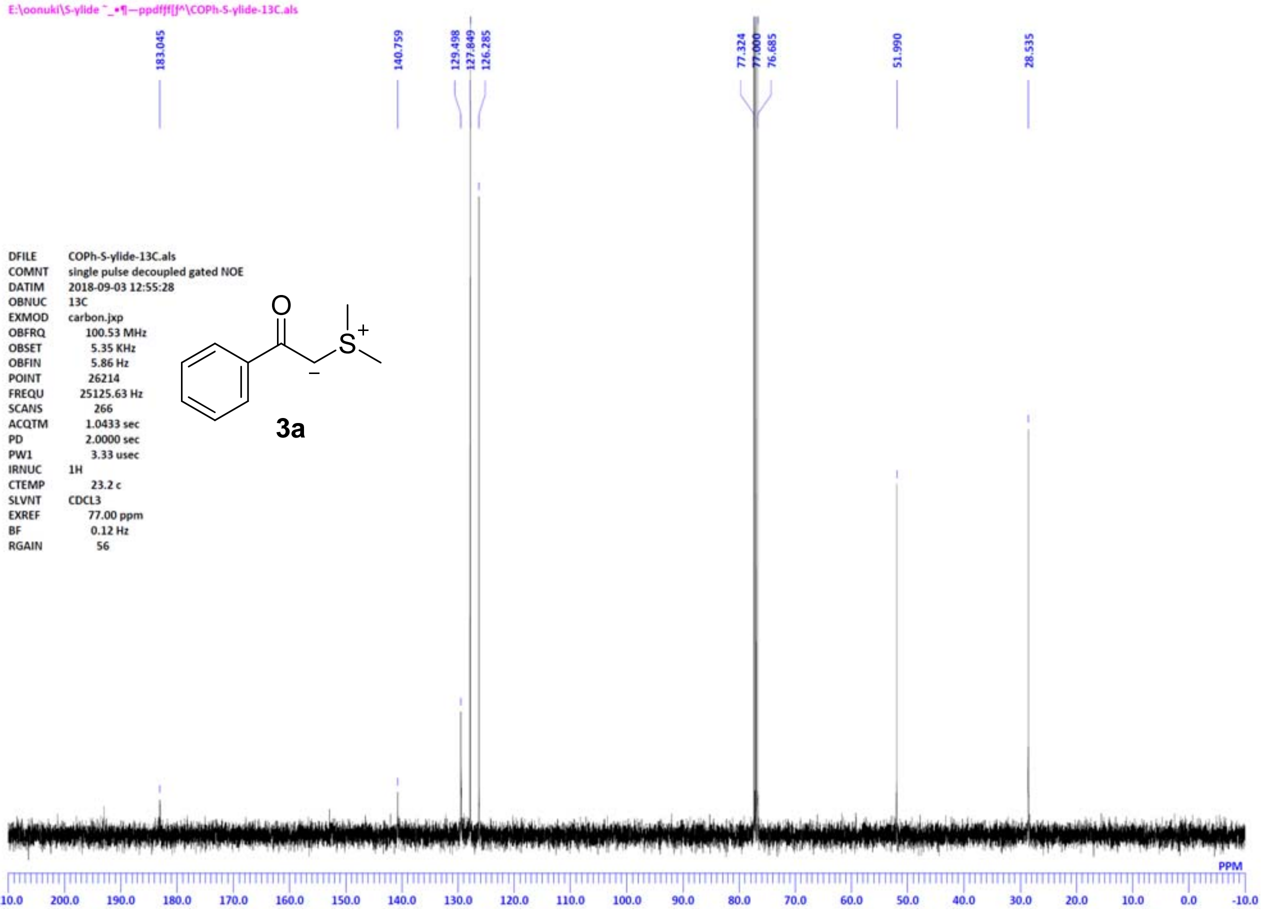
C. Structure Solution and Refinement

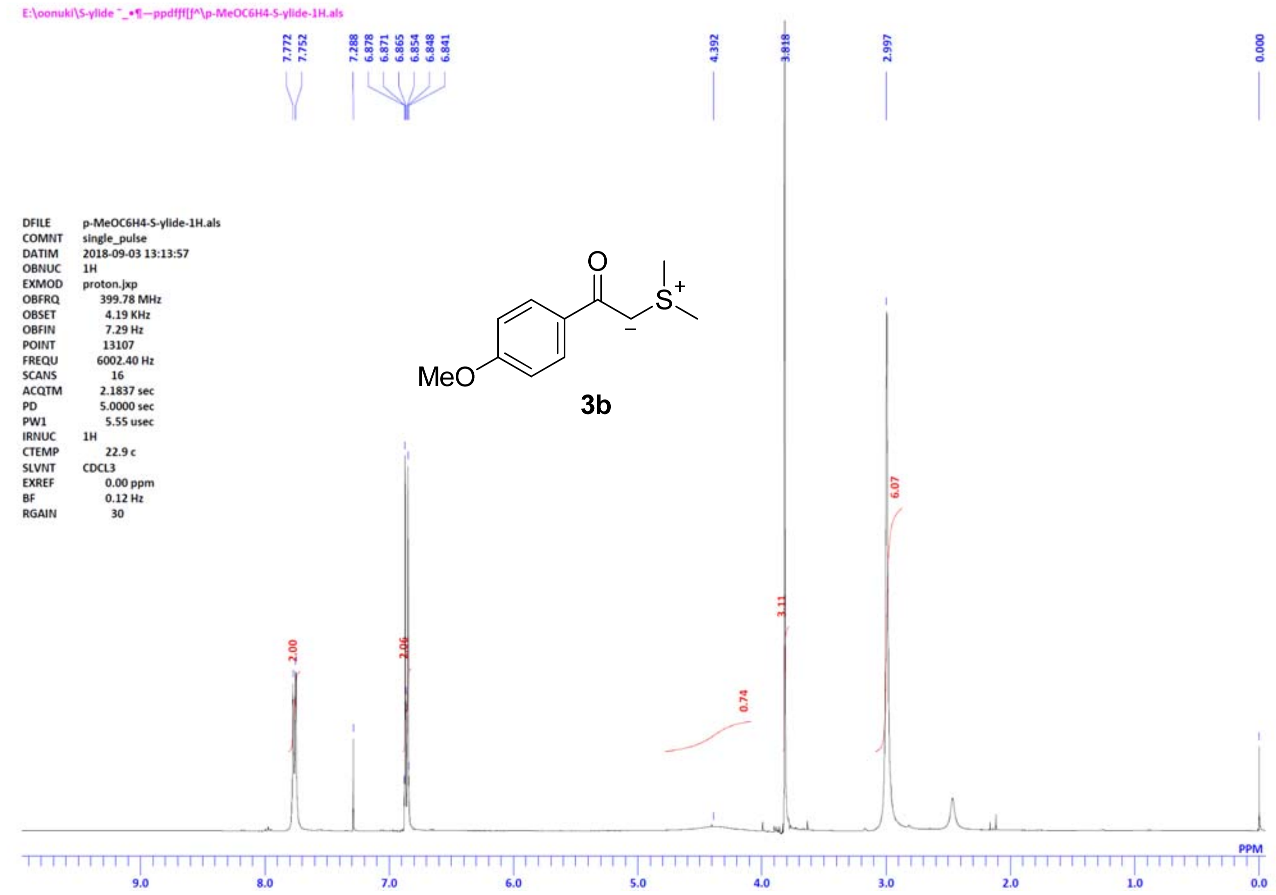
Structure Solution	Direct Methods (SHELXT Version 2018/2)
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w (Fo^2 - Fc^2)^2
Least Squares Weights	w = 1/ [$\sigma^2(Fo^2)$ + (0.0339 · P)^2 + 0.6254 · P] where P = (Max(Fo^2,0) + 2Fc^2)/3
$2\theta_{max}$ cutoff	136.3°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	2780
No. Variables	200
Reflection/Parameter Ratio	13.90
Residuals: R1 (I>2.00σ(I))	0.0248
Residuals: R (All reflections)	0.0259
Residuals: wR2 (All reflections)	0.0636
Goodness of Fit Indicator	1.033
Flack parameter (Parsons' quotients = 1197)	0.03(4)
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.14 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.13 $e^-/Å^3$

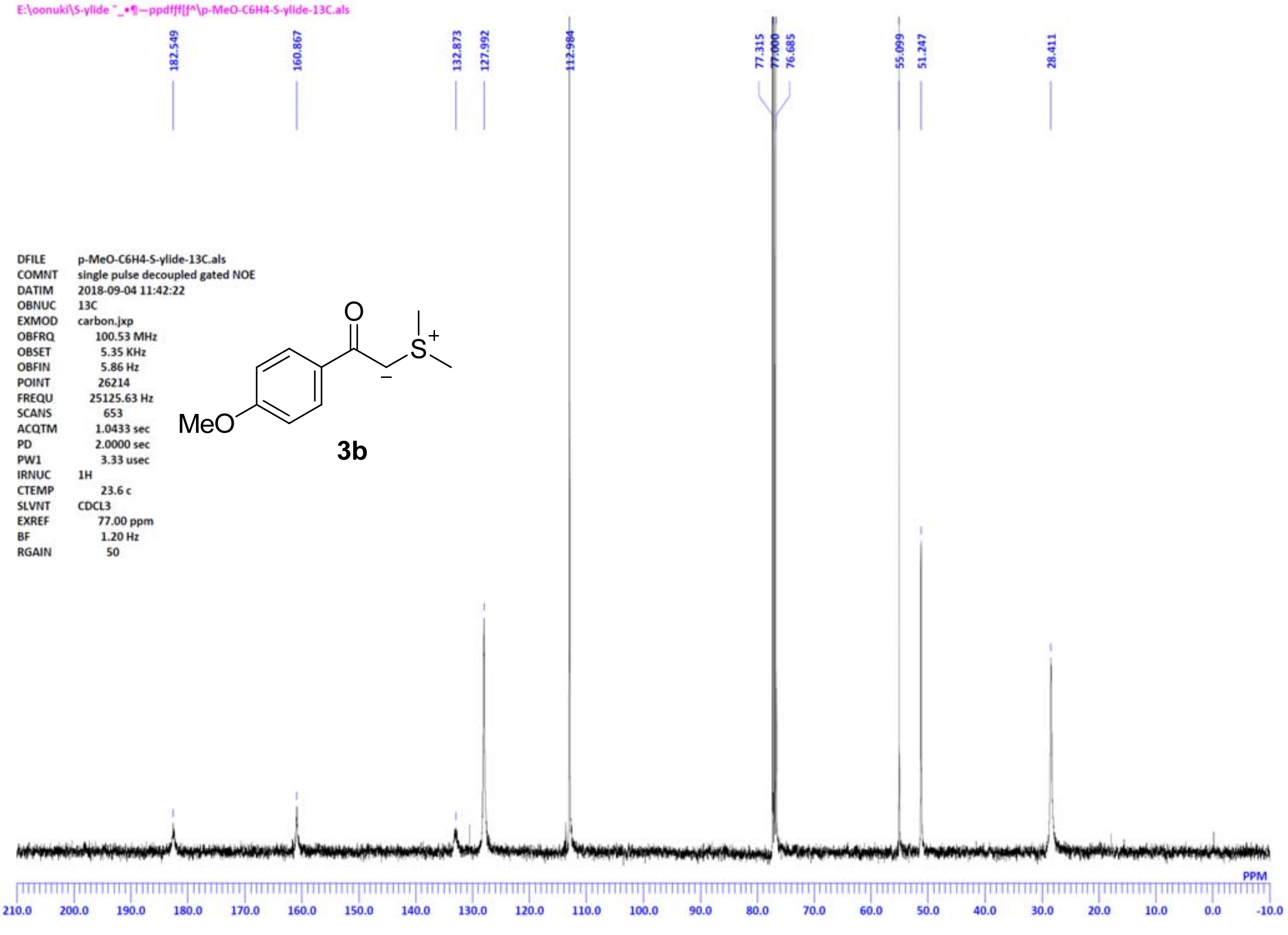
References

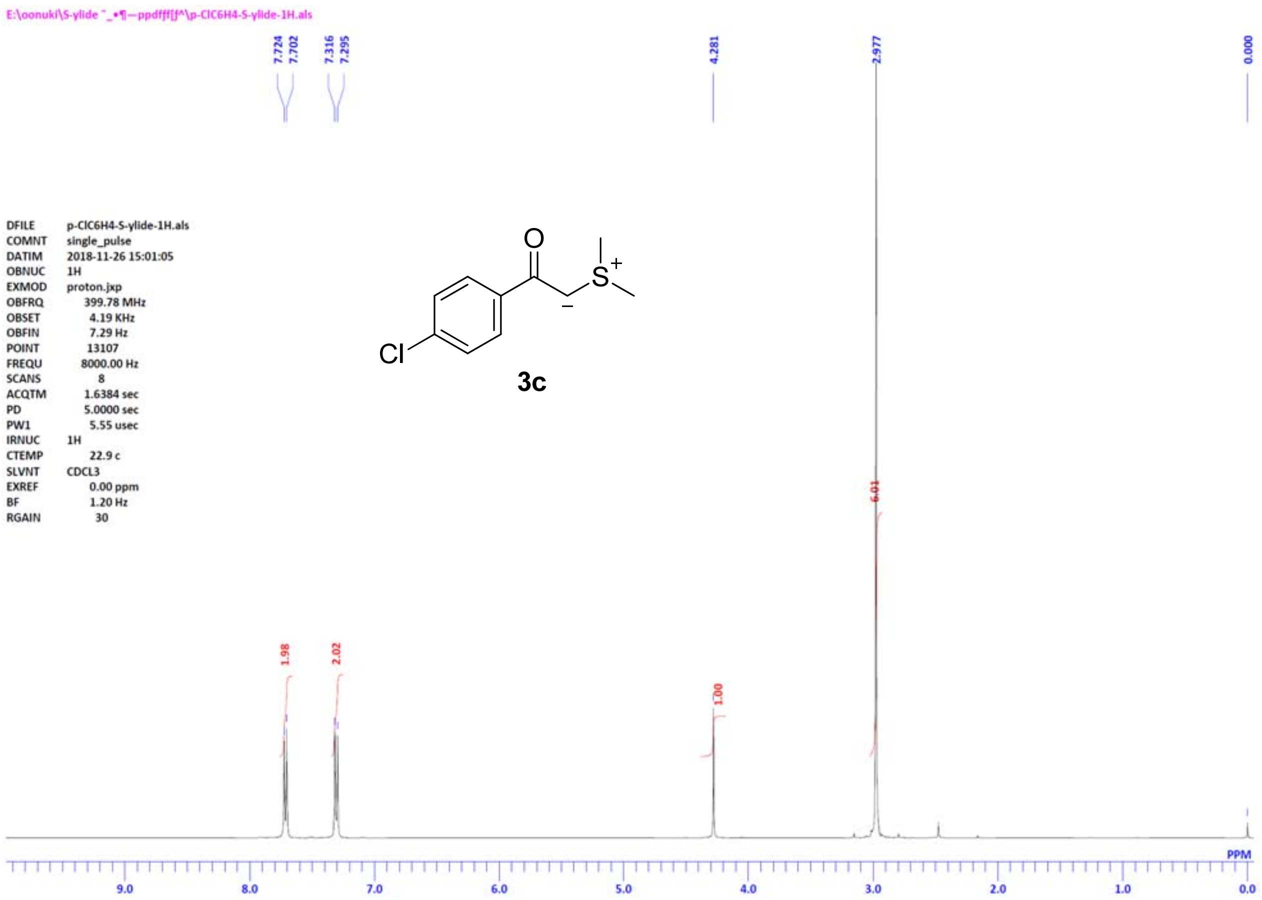
1. K. W. Ratts and A. N. Yao, *J. Org. Chem.*, 1966, **31**, 1185–1188.
2. H. Nambu, M. Fukumoto, W. Hirota, N. Ono and T. Yakura, *Tetrahedron Lett.*, 2015, **56**, 4312–4315.
3. H. Nambu, N. Ono, W. Hirota, M. Fukumoto and T. Yakura, *Chem. Pharm. Bull.*, 2016, **64**, 1763–1768.
4. H. Nambu, N. Ono and T. Yakura, *Synthesis*, 2016, **48**, 1892–1901.
5. E. Richmond, V. D. Vuković and J. Moran, *Org. Lett.*, 2018, **16**, 1626–1629.
6. G. B. Payne, *J. Org. Chem.*, 1967, **32**, 3351–3355.
7. J. Quintana, M. Torres and F. Serratosa, *Tetrahedron*, 1973, **29**, 2065–2076.
8. E. T. Ledingham, C. J. Merritt, C. J. Sumby, M. K. Taylor and B. W. Greatrex, *Synthesis*, 2017, **49**, 2652–2662.
9. K. J. Bruemmer, S. Merrikhihaghi, C. T. Lollar, S. N. S. Morris, J. H. Bauer and A. R. Lippert, *Chem. Commun.*, 2014, **50**, 12311–12314.


E:\oonuki\S-ylide ˜_•¶—ppdfff[ƒ^\COPh-S-ylide-1H.als
7.784
7.778
7.770
7.760
7.353
7.348
7.340
7.336
7.280
4.340
2.963
0.000
DFILE COPh-S-ylide-1H.als
COMNT single_pulse
DATIM 2018-09-03 12:51:38
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 16
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.55 usec
IRNUC 1H
CTEMP 23.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 32
O
S+
–
3a
2.00
3.01
0.93
6.00
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


E:\oonuki\S-ylide ˜_•¶—ppdfff[ƒ^\COPh-S-ylide-13C.als
183.045
140.759
129.498
127.849
126.285
77.324
77.000
76.685
51.990
28.535
DFILE COPh-S-ylide-13C.als
COMNT single pulse decoupled gated NOE
DATIM 2018-09-03 12:55:28
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 266
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.33 usec
IRNUC 1H
CTEMP 23.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 56
O
S+
–
3a
PPM
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
-10.0

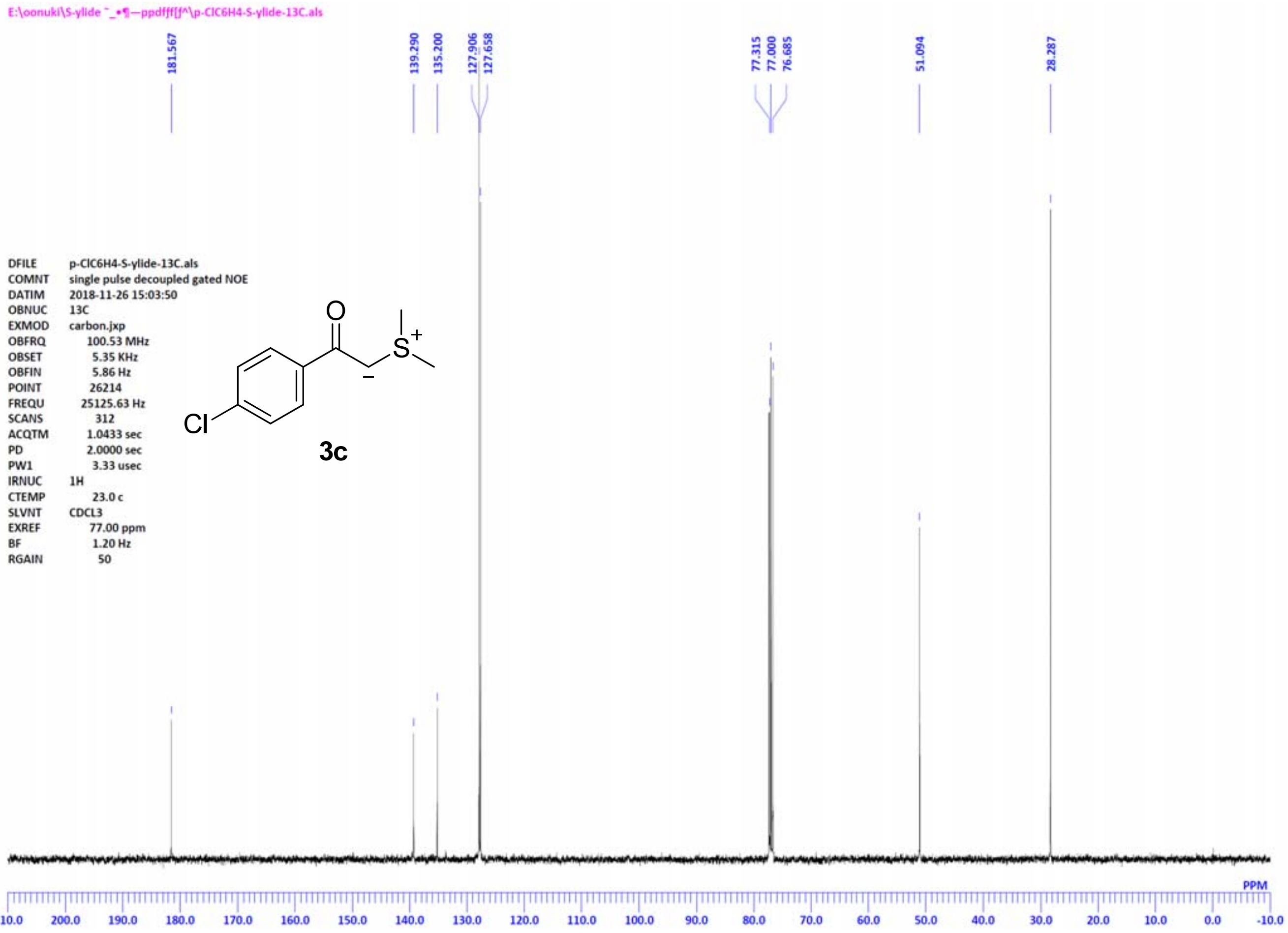

E:\oonuki\S-ylide ˜_•¶—ppdfff[f^\p-MeOC6H4-S-ylide-1H.als
7.772
7.752
7.288
6.878
6.871
6.865
6.854
6.848
6.841
4.392
3.818
2.997
0.000
DFILE p-MeOC6H4-S-ylide-1H.als
COMNT single_pulse
DATIM 2018-09-03 13:13:57
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 16
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.55 usec
IRNUC 1H
CTEMP 22.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 30
O
S
+
–
MeO
3b
2.00
2.06
0.74
3.11
6.07
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


E:\oonuki\S-ylide ˜_•¶—ppdfff[f^\p-MeO-C6H4-S-ylide-13C.als
182.549
160.867
132.873
127.992
112.984
77.315
77.000
76.685
55.099
51.247
28.411
DFILE p-MeO-C6H4-S-ylide-13C.als
COMNT single pulse decoupled gated NOE
DATIM 2018-09-04 11:42:22
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 653
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.33 usec
IRNUC 1H
CTEMP 23.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 50
O
S
+
–
MeO
3b
PPM
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
-10.0



E:\oonuki\S-ylide ˜_•¶–ppdfff[f^\p-ClC6H4-S-ylide-1H.als

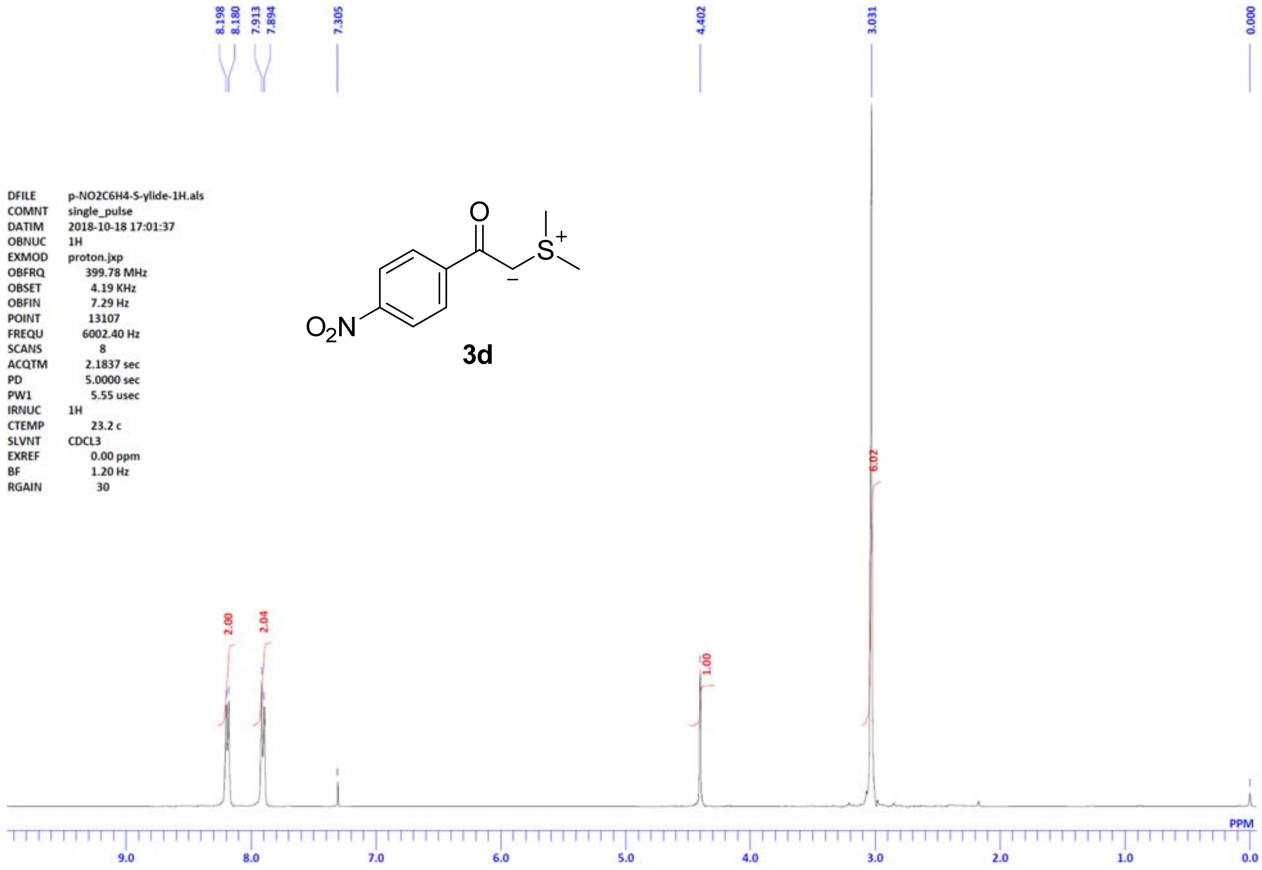
```
DFILE    p-ClC6H4-S-ylide-1H.als
COMNT    single_pulse
DATIM    2018-11-26 15:01:05
OBNUC    1H
EXMOD    proton.jxp
OBFRQ       399.78 MHz
OBSET         4.19 KHz
OBFIN         7.29 Hz
POINT        13107
FREQU      8000.00 Hz
SCANS            8
ACQTM       1.6384 sec
PD          5.0000 sec
PW1           5.55 usec
IRNUC    1H
CTEMP         22.9 c
SLVNT    CDCL3
EXREF         0.00 ppm
BF            1.20 Hz
RGAIN           30
```



E:\oonuki\S-ylide ˜_•¶–ppdfff[f^\p-ClC6H4-S-ylide-13C.als

```
DFILE    p-ClC6H4-S-ylide-13C.als
COMNT    single pulse decoupled gated NOE
DATIM    2018-11-26 15:03:50
OBNUC    13C
EXMOD    carbon.jxp
OBFRQ       100.53 MHz
OBSET         5.35 KHz
OBFIN         5.86 Hz
POINT        26214
FREQU     25125.63 Hz
SCANS          312
ACQTM       1.0433 sec
PD          2.0000 sec
PW1           3.33 usec
IRNUC    1H
CTEMP         23.0 c
SLVNT    CDCL3
EXREF        77.00 ppm
BF            1.20 Hz
RGAIN           50
```

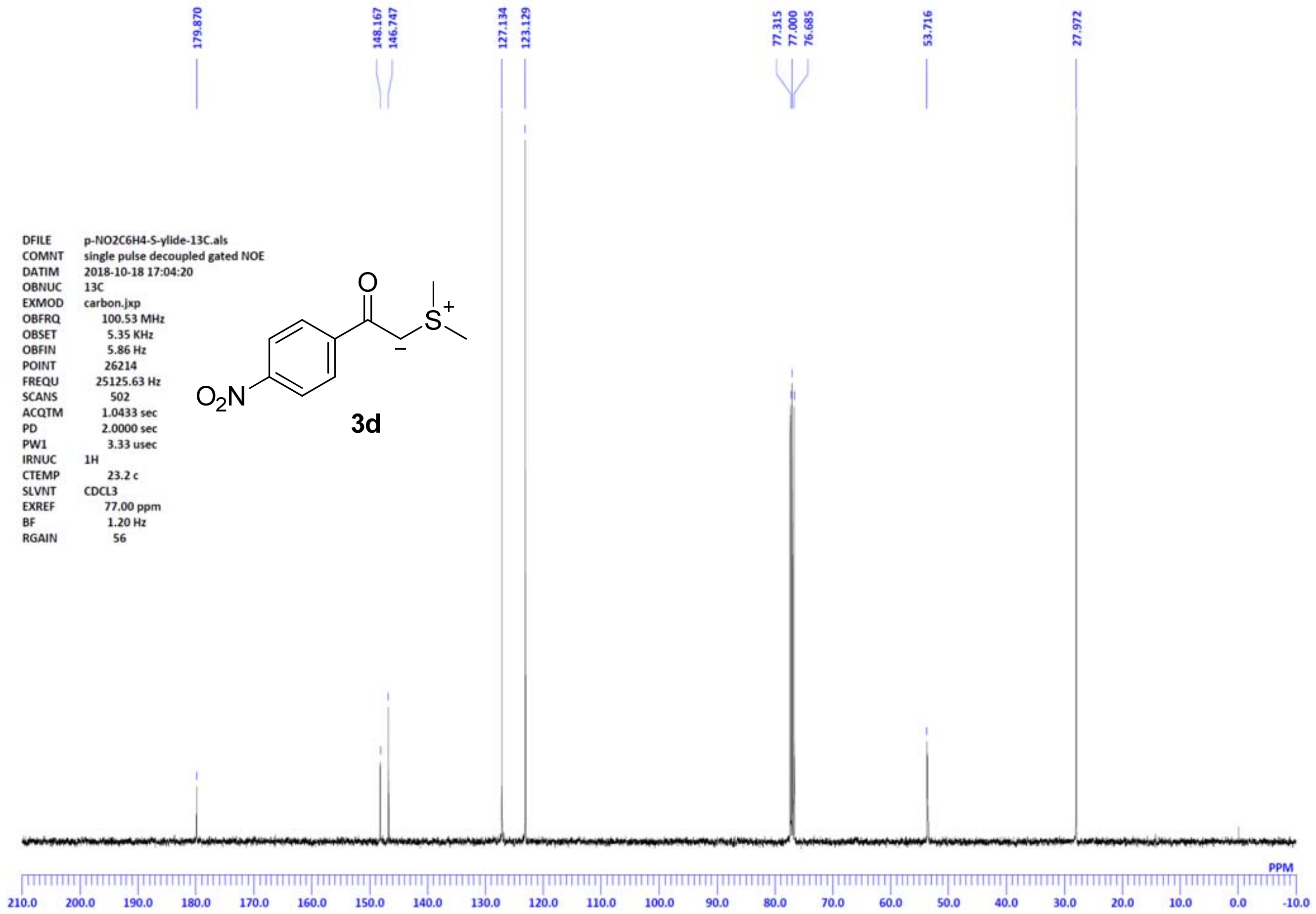
E:\oonuki\S-ylide ˜_•¶—ppdfff[f^\p-NO2C6H4-S-ylide-1H.als



3d

DFILE	p-NO2C6H4-S-ylide-1H.als
COMNT	single_pulse
DATIM	2018-10-18 17:01:37
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.40 Hz
SCANS	8
ACQTM	2.1837 sec
PD	5.0000 sec
PW1	5.55 usec
IRNUC	1H
CTEMP	23.2 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	1.20 Hz
RGAIN	30

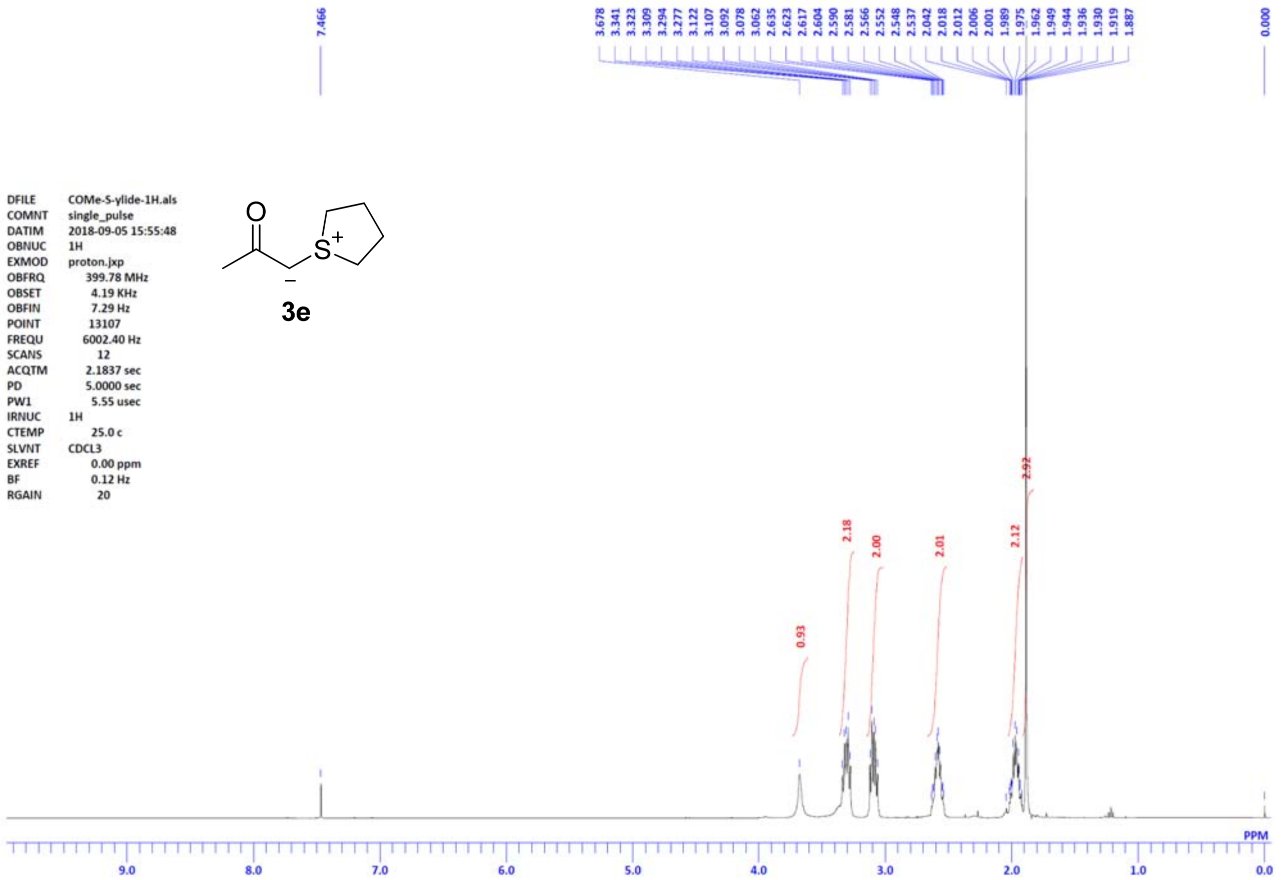
E:\oonuki\S-ylide ˜_•¶—ppdfff[f^\p-NO2C6H4-S-ylide-13C.als



3d

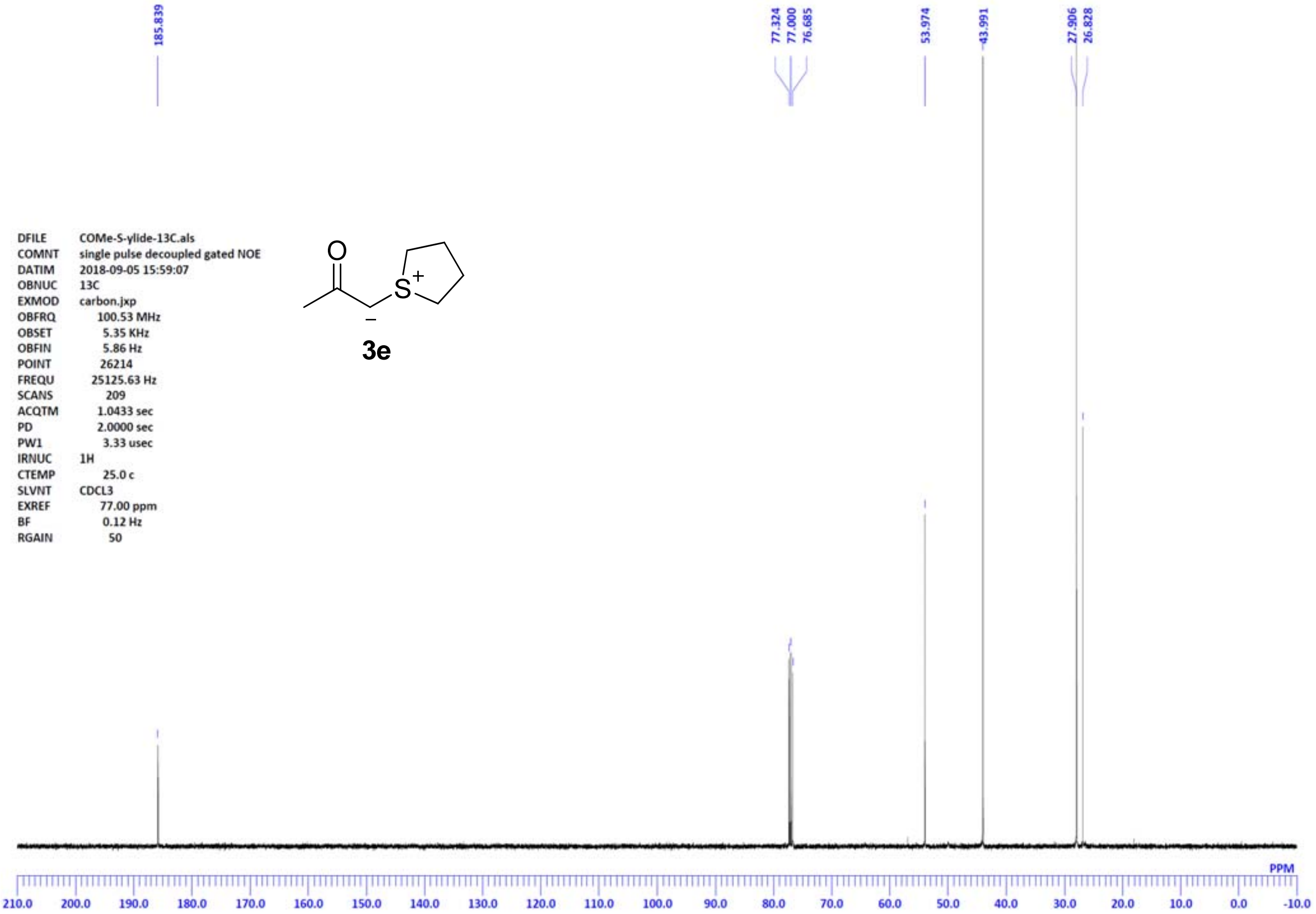
DFILE	p-NO2C6H4-S-ylide-13C.als
COMNT	single pulse decoupled gated NOE
DATIM	2018-10-18 17:04:20
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.63 Hz
SCANS	502
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.33 usec
IRNUC	1H
CTEMP	23.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	56

E:\oonuki\S-ylide ˜_•¶—ppdfff[ƒ^\COMe-S-ylide-1H.als

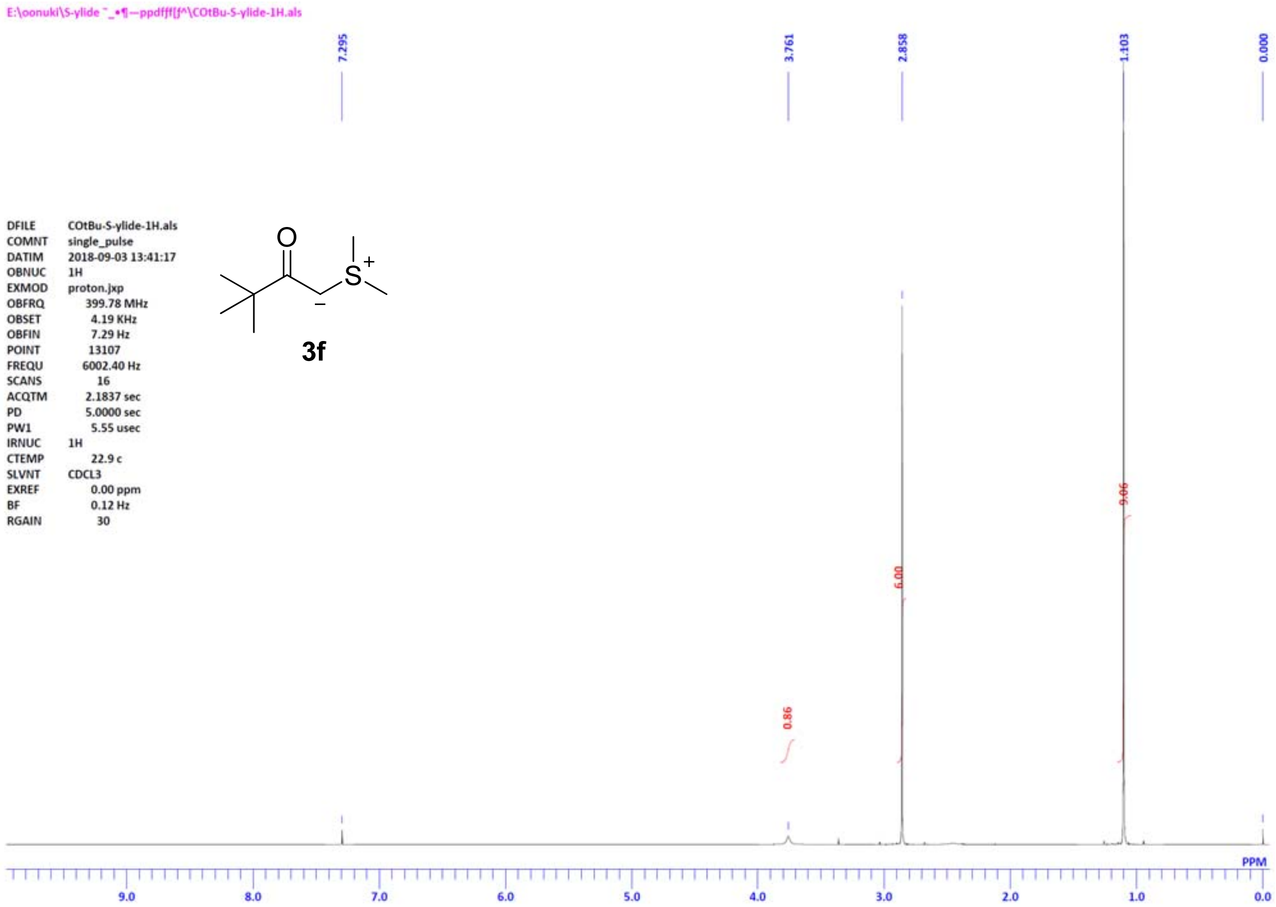


DFILE	COMe-S-ylide-1H.als
COMNT	single_pulse
DATIM	2018-09-05 15:55:48
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.40 Hz
SCANS	12
ACQTM	2.1837 sec
PD	5.0000 sec
PW1	5.55 usec
IRNUC	1H
CTEMP	25.0 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	20

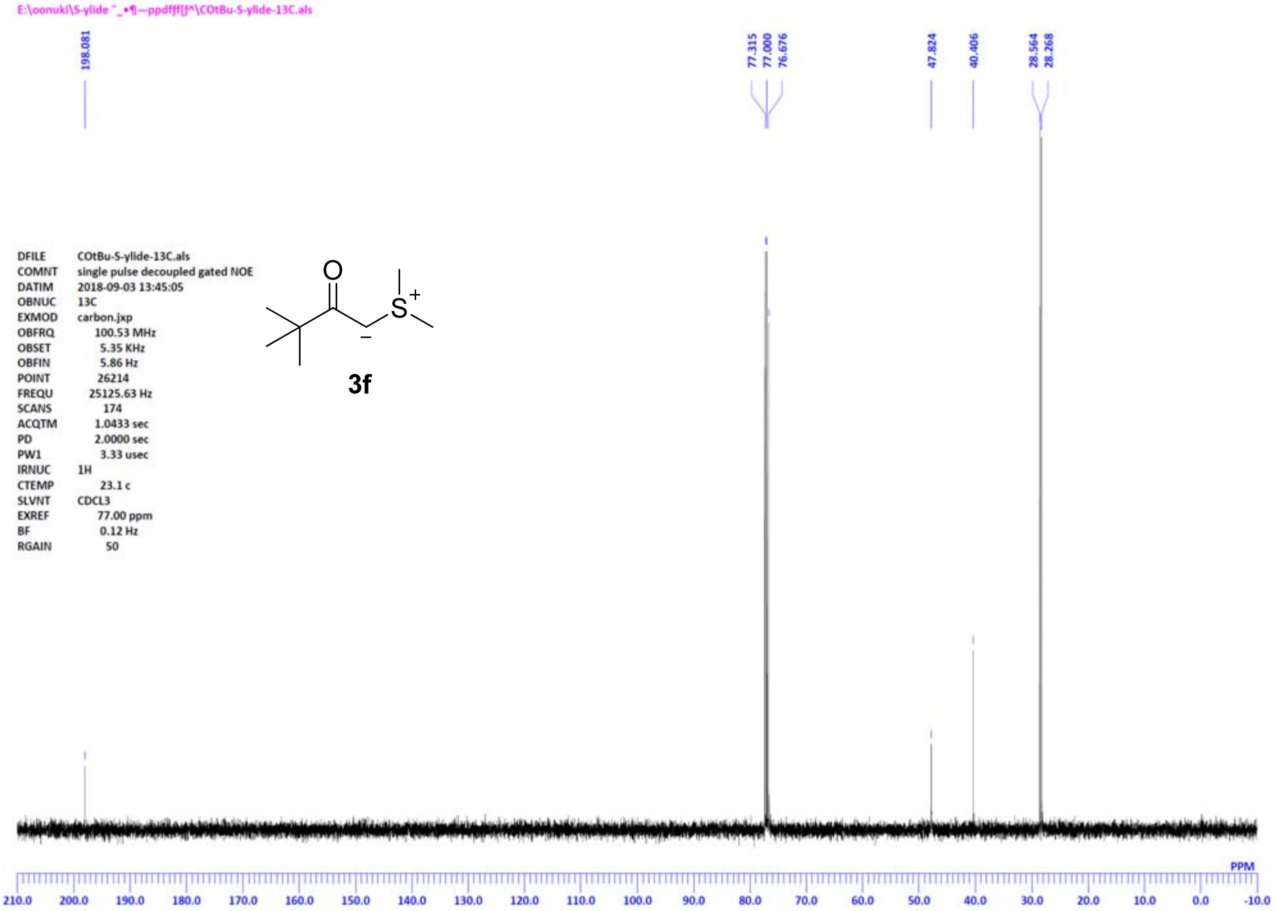
E:\oonuki\S-ylide ˜_•¶—ppdfff[ƒ^\COMe-S-ylide-13C.als



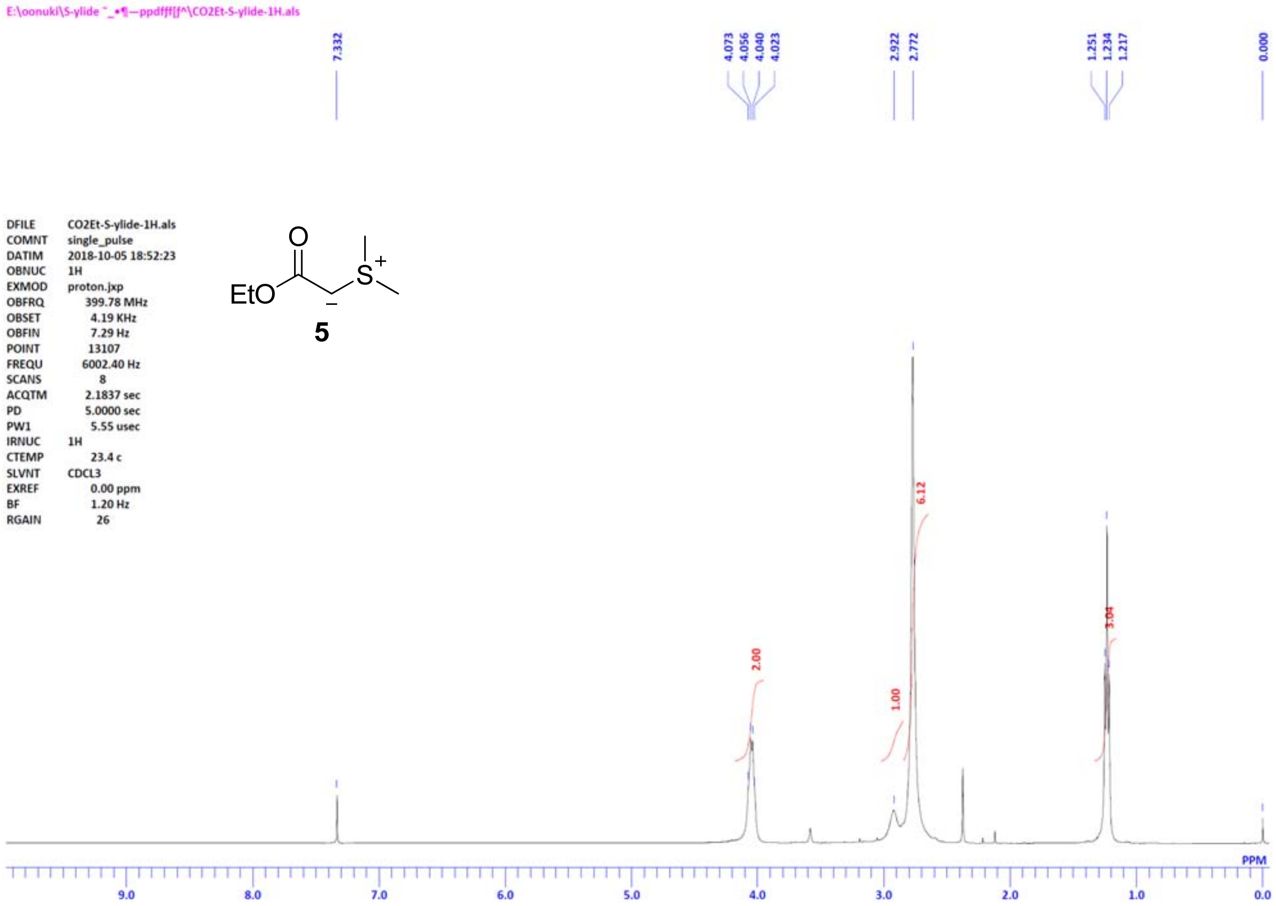
DFILE	COMe-S-ylide-13C.als
COMNT	single pulse decoupled gated NOE
DATIM	2018-09-05 15:59:07
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.63 Hz
SCANS	209
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.33 usec
IRNUC	1H
CTEMP	25.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	50



```
DFILE    COtBu-S-ylide-1H.als
COMNT    single_pulse
DATIM    2018-09-03 13:41:17
OBNUC    1H
EXMOD    proton.jxp
OBFRQ       399.78 MHz
OBSET         4.19 KHz
OBFIN         7.29 Hz
POINT        13107
FREQU      6002.40 Hz
SCANS           16
ACQTM       2.1837 sec
PD          5.0000 sec
PW1           5.55 usec
IRNUC    1H
CTEMP         22.9 c
SLVNT    CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           30
```



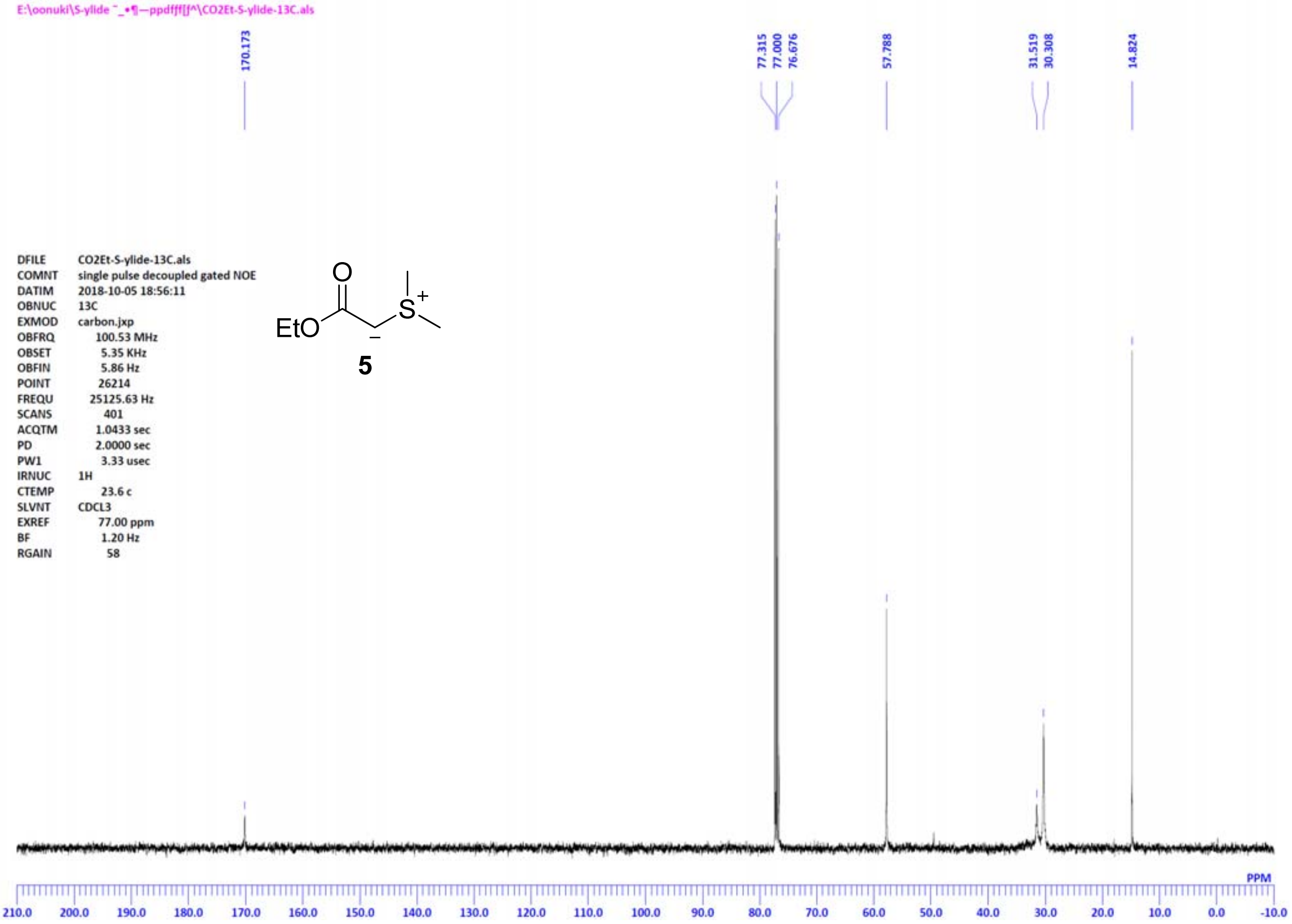
```
DFILE    COtBu-S-ylide-13C.als
COMNT    single pulse decoupled gated NOE
DATIM    2018-09-03 13:45:05
OBNUC    13C
EXMOD    carbon.jxp
OBFRQ       100.53 MHz
OBSET         5.35 KHz
OBFIN         5.86 Hz
POINT        26214
FREQU     25125.63 Hz
SCANS          174
ACQTM       1.0433 sec
PD          2.0000 sec
PW1           3.33 usec
IRNUC    1H
CTEMP         23.1 c
SLVNT    CDCL3
EXREF        77.00 ppm
BF            0.12 Hz
RGAIN           50
```



E:\oonuki\S-ylide ˜_•¶—ppdfff[f^\CO2Et-S-ylide-1H.als

```
DFILE    CO2Et-S-ylide-1H.als
COMNT    single_pulse
DATIM    2018-10-05 18:52:23
OBNUC    1H
EXMOD    proton.jxp
OBFRQ       399.78 MHz
OBSET         4.19 KHz
OBFIN         7.29 Hz
POINT        13107
FREQU      6002.40 Hz
SCANS            8
ACQTM       2.1837 sec
PD          5.0000 sec
PW1           5.55 usec
IRNUC    1H
CTEMP         23.4 c
SLVNT    CDCL3
EXREF         0.00 ppm
BF            1.20 Hz
RGAIN           26
```

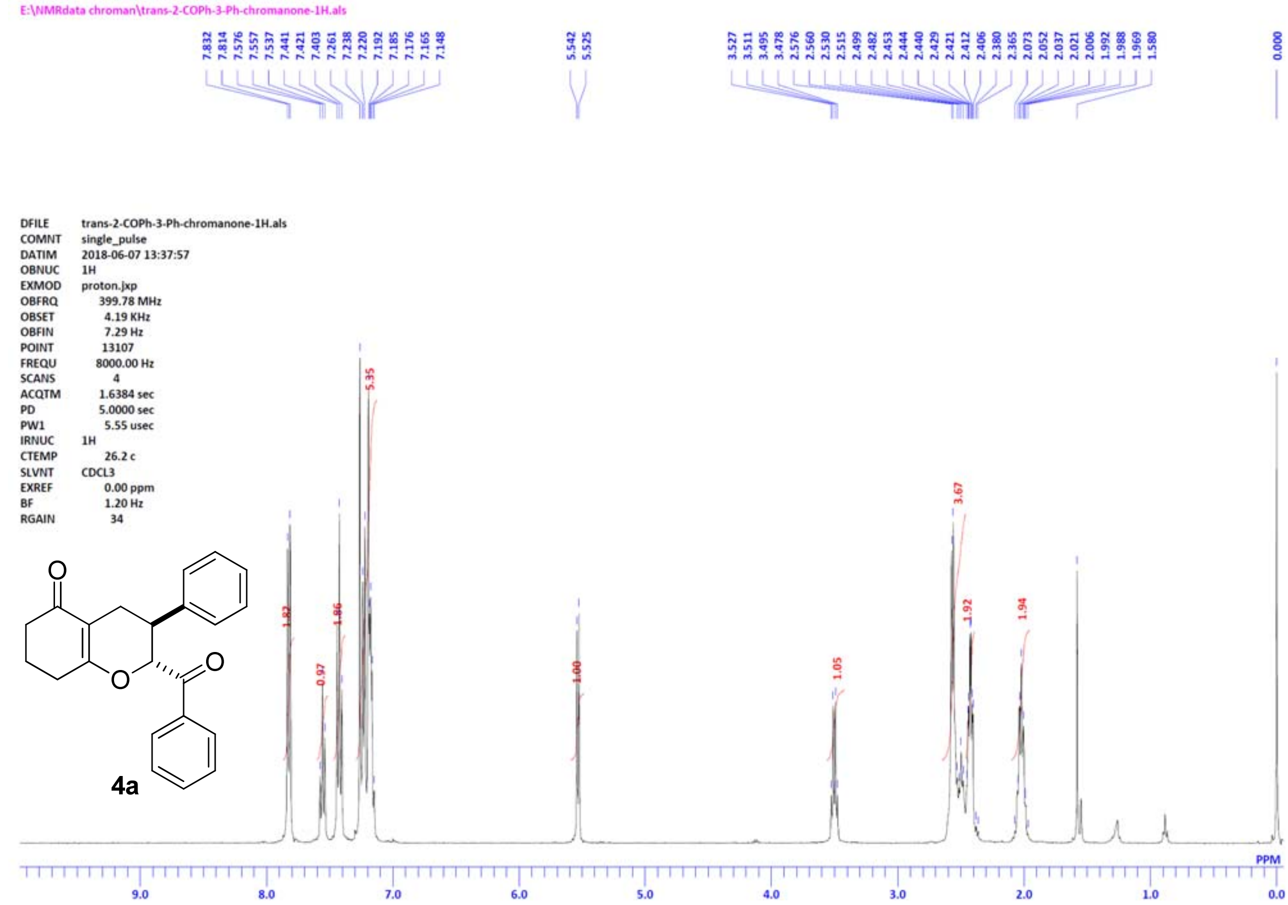
5



E:\oonuki\S-ylide ˜_•¶—ppdfff[f^\CO2Et-S-ylide-13C.als

```
DFILE    CO2Et-S-ylide-13C.als
COMNT    single pulse decoupled gated NOE
DATIM    2018-10-05 18:56:11
OBNUC    13C
EXMOD    carbon.jxp
OBFRQ       100.53 MHz
OBSET         5.35 KHz
OBFIN         5.86 Hz
POINT        26214
FREQU     25125.63 Hz
SCANS          401
ACQTM       1.0433 sec
PD          2.0000 sec
PW1           3.33 usec
IRNUC    1H
CTEMP         23.6 c
SLVNT    CDCL3
EXREF        77.00 ppm
BF            1.20 Hz
RGAIN           58
```

5



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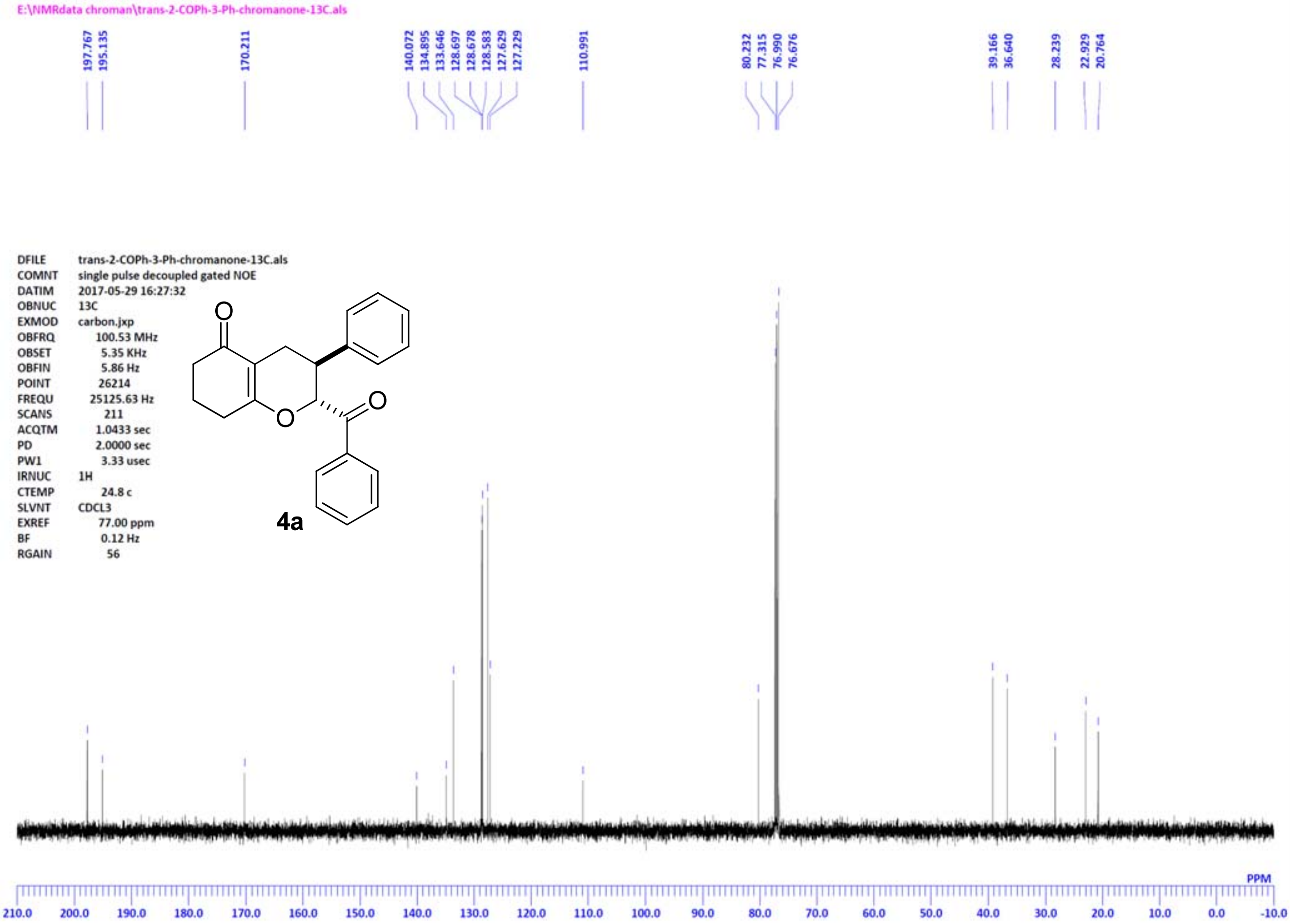
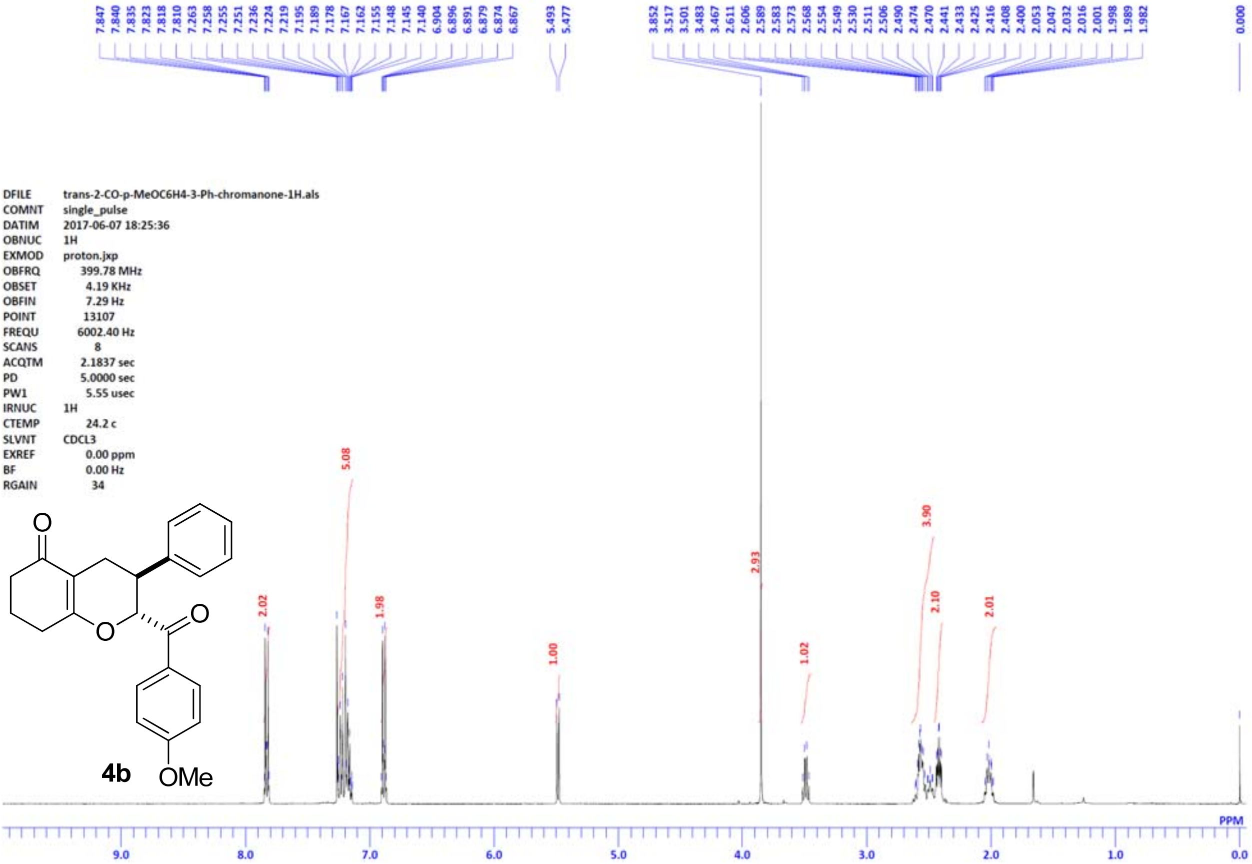
COMNT single_pulse
DATIM 2018-06-07 13:37:57
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 8000.00 Hz
SCANS 4
ACQTM 1.6384 sec
PD 5.0000 sec
PW1 5.55 usec
IRNUC 1H
CTEMP 26.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 34



DFILE trans-2-COPh-3-Ph-chromanone-13C.als
COMNT single pulse decoupled gated NOE
DATIM 2017-05-29 16:27:32
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 211
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.33 usec
IRNUC 1H
CTEMP 24.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 56

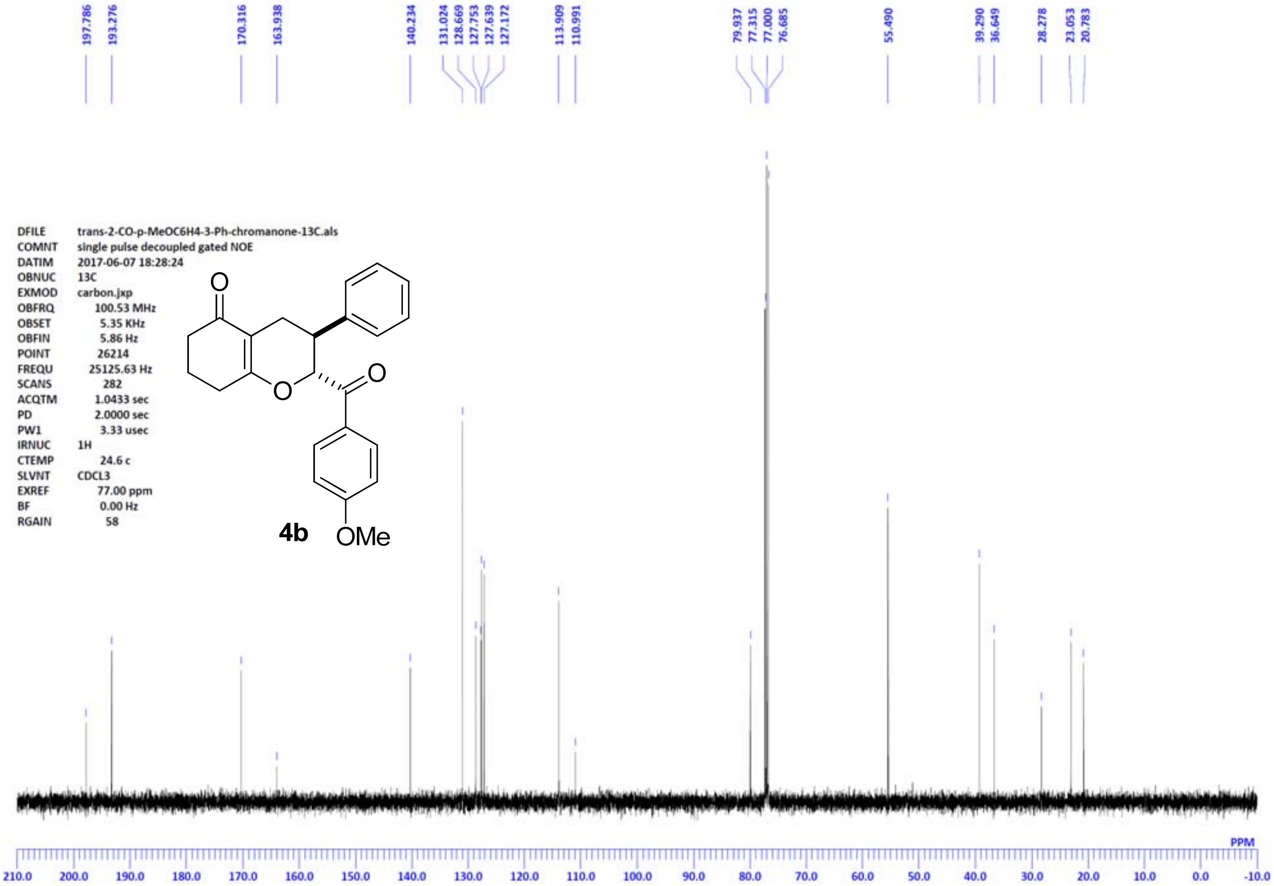
E:\NMRdata chroman\trans-2-CO-p-MeOC6H4-3-Ph-chromanone-1H.als



DFILE trans-2-CO-p-MeOC6H4-3-Ph-chromanone-1H.als
COMNT single_pulse
DATIM 2017-06-07 18:25:36
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.55 usec
IRNUC 1H
CTEMP 24.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.00 Hz
RGAIN 34

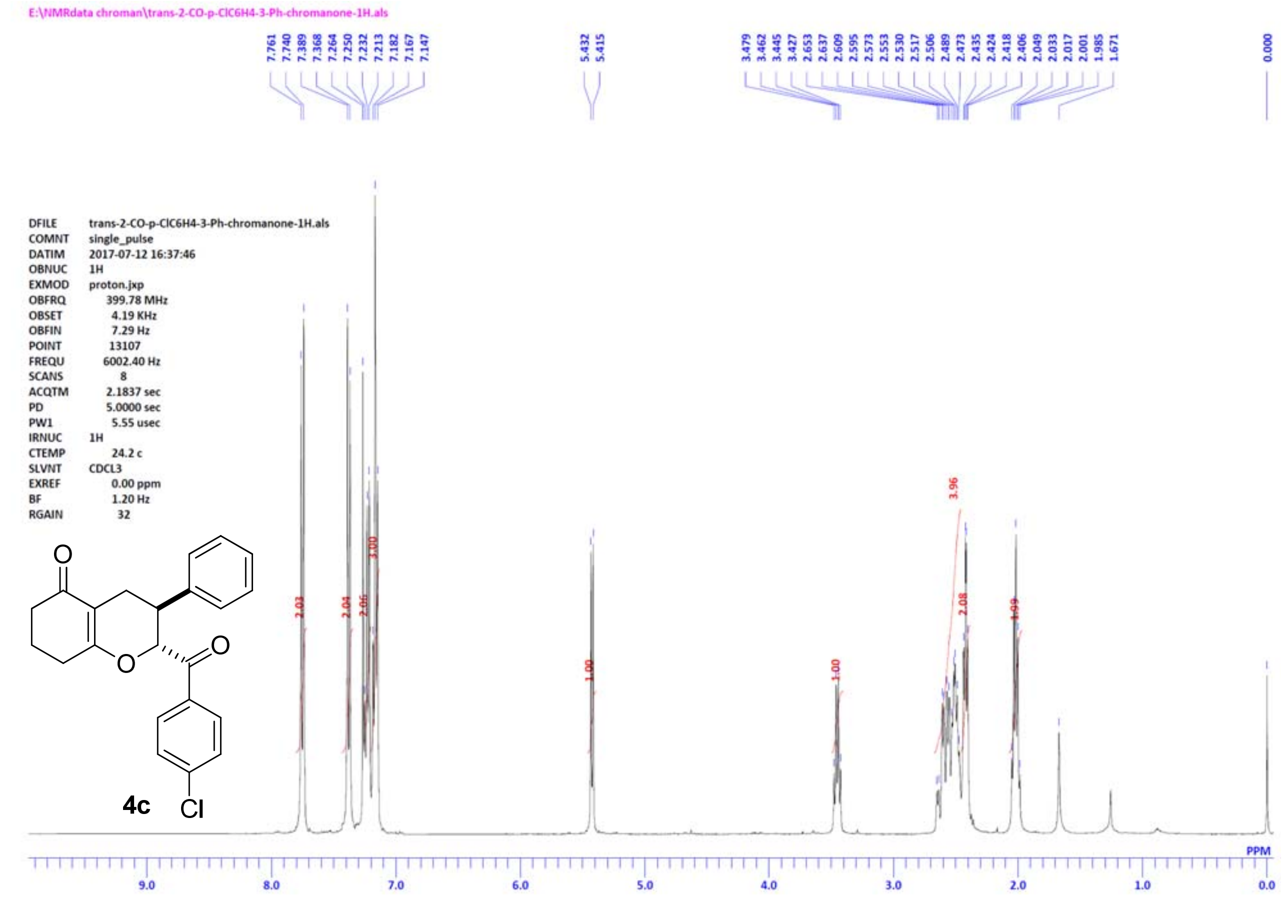
4b

E:\NMRdata chroman\trans-2-CO-p-MeOC6H4-3-Ph-chromanone-13C.als



DFILE trans-2-CO-p-MeOC6H4-3-Ph-chromanone-13C.als
COMNT single pulse decoupled gated NOE
DATIM 2017-06-07 18:28:24
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 282
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.33 usec
IRNUC 1H
CTEMP 24.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.00 Hz
RGAIN 58

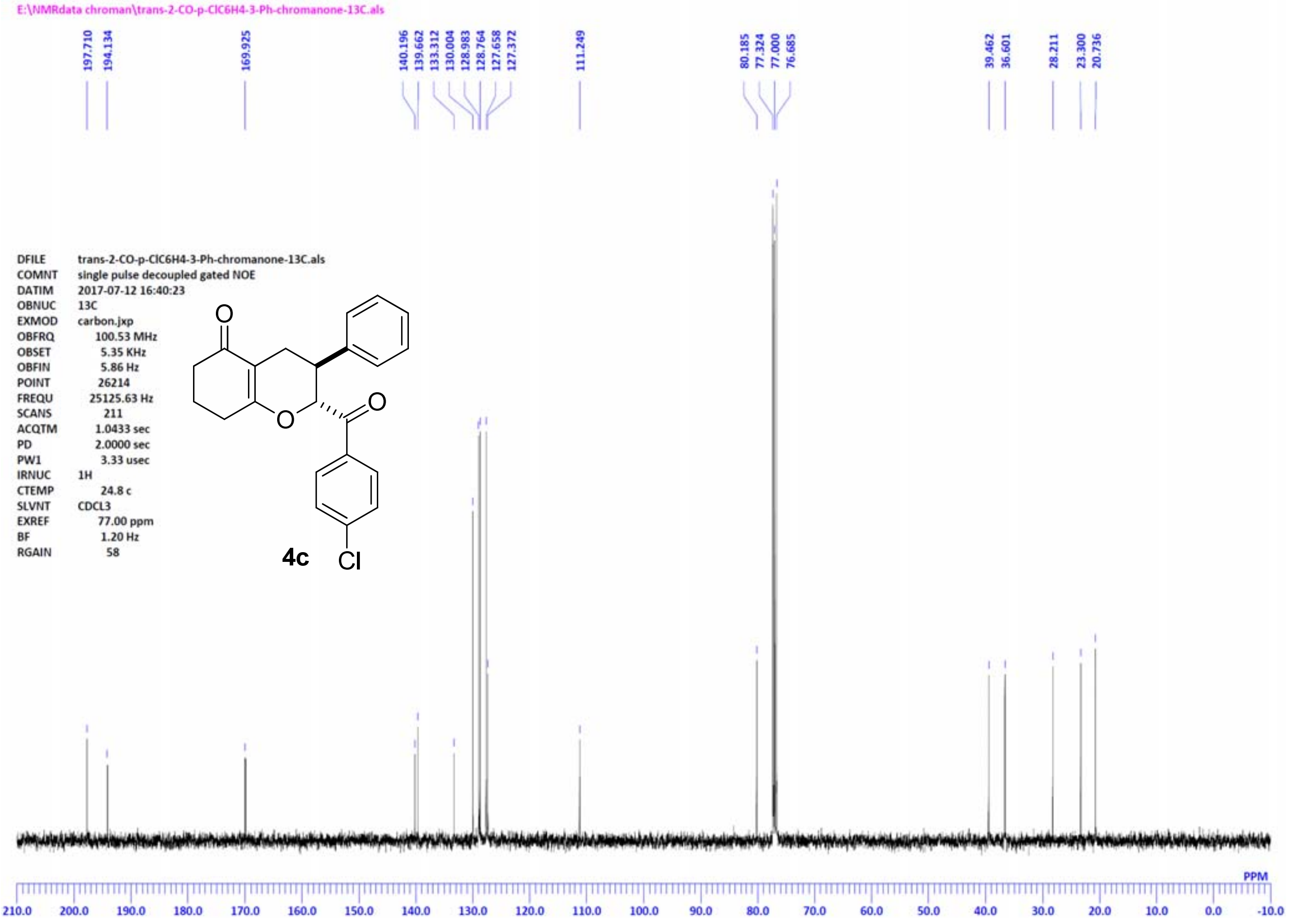
4b



E:\NMRdata chroman\trans-2-CO-p-ClC6H4-3-Ph-chromanone-1H.als

DFILE	trans-2-CO-p-ClC6H4-3-Ph-chromanone-1H.als
COMNT	single_pulse
DATIM	2017-07-12 16:37:46
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.40 Hz
SCANS	8
ACQTM	2.1837 sec
PD	5.0000 sec
PW1	5.55 usec
IRNUC	1H
CTEMP	24.2 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	1.20 Hz
RGAIN	32

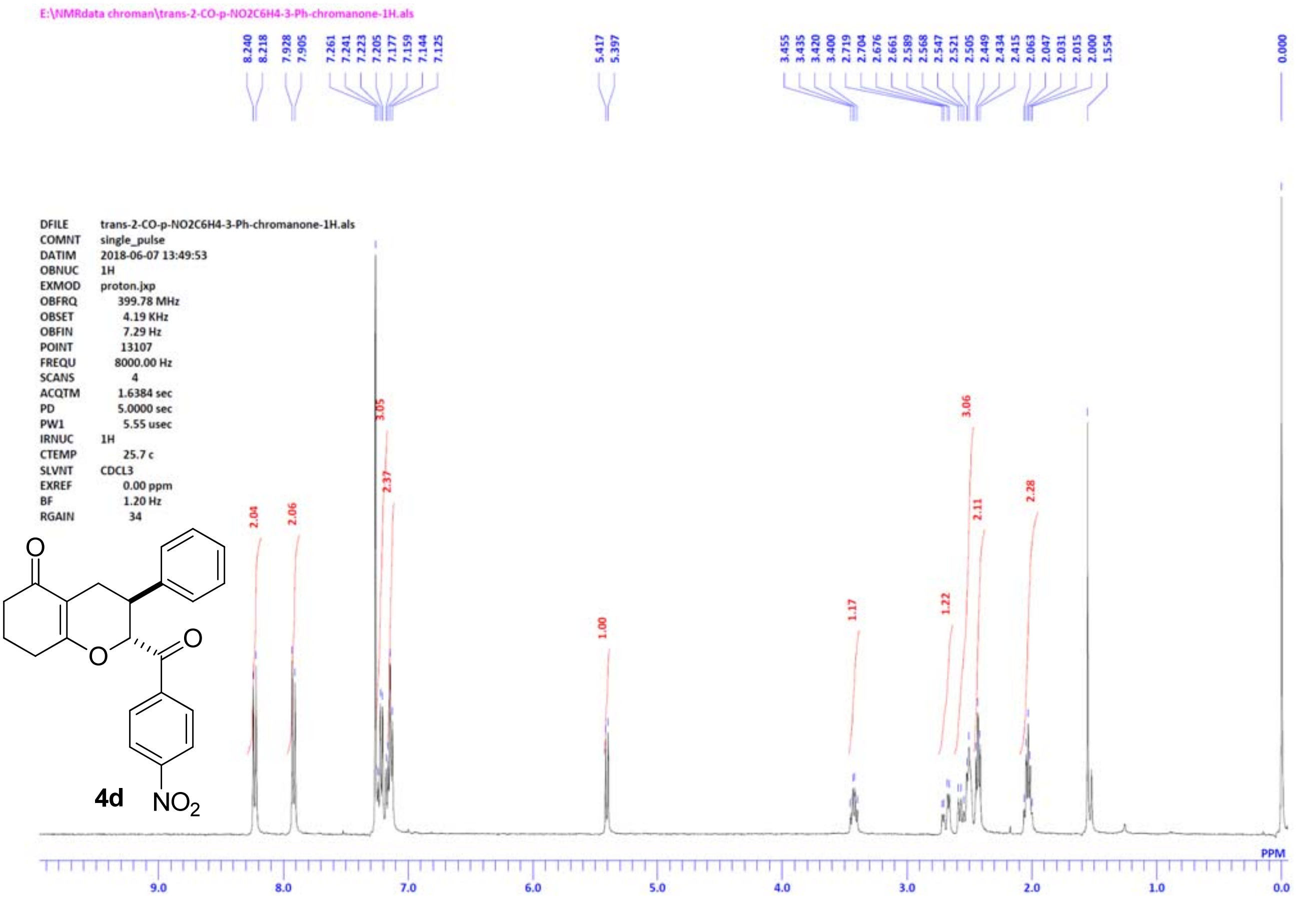
4c

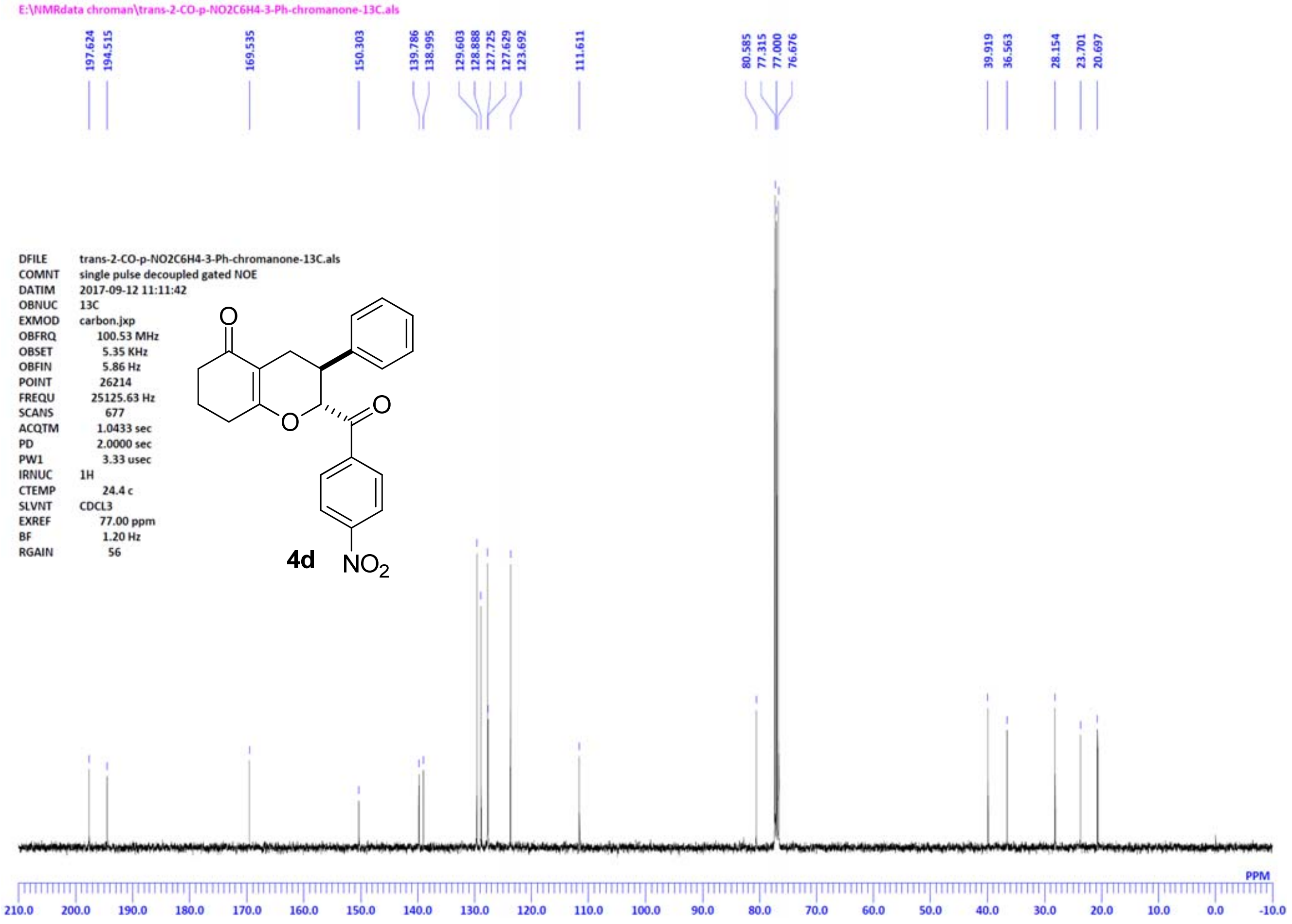


E:\NMRdata chroman\trans-2-CO-p-ClC6H4-3-Ph-chromanone-13C.als

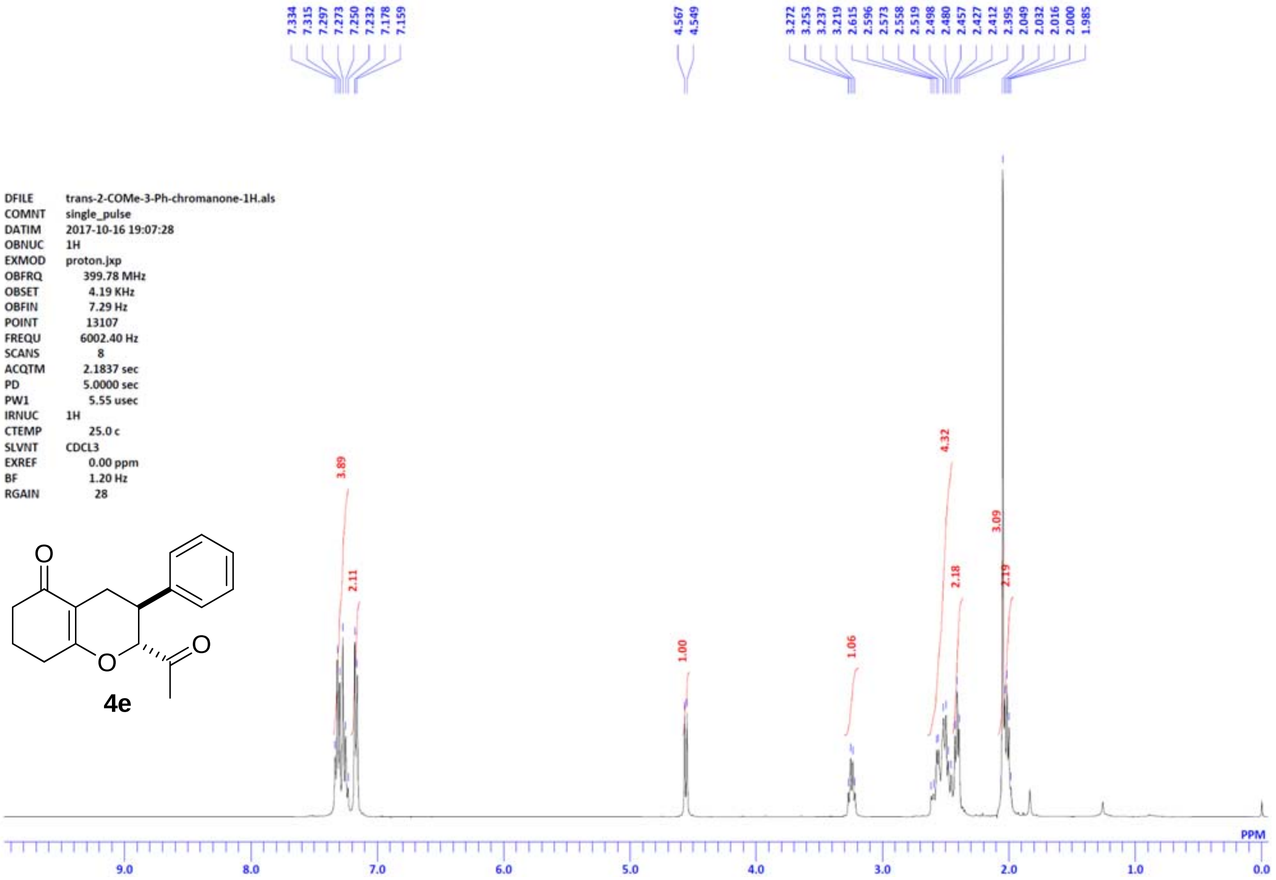
DFILE	trans-2-CO-p-ClC6H4-3-Ph-chromanone-13C.als
COMNT	single pulse decoupled gated NOE
DATIM	2017-07-12 16:40:23
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.63 Hz
SCANS	211
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.33 usec
IRNUC	1H
CTEMP	24.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	58

4c


E:\NMRdata chroman\trans-2-CO-p-NO2C6H4-3-Ph-chromanone-1H.als
8.240
8.218
7.928
7.905
7.261
7.241
7.223
7.205
7.177
7.159
7.144
7.125
5.417
5.397
3.455
3.435
3.420
3.400
2.719
2.704
2.676
2.661
2.589
2.568
2.547
2.521
2.505
2.449
2.434
2.415
2.063
2.047
2.031
2.015
2.000
1.554
0.000
DFILE trans-2-CO-p-NO2C6H4-3-Ph-chromanone-1H.als
COMNT single_pulse
DATIM 2018-06-07 13:49:53
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 8000.00 Hz
SCANS 4
ACQTM 1.6384 sec
PD 5.0000 sec
PW1 5.55 usec
IRNUC 1H
CTEMP 25.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 34
2.04
2.06
3.05
2.37
1.00
1.17
1.22
3.06
2.11
2.28
O
O
O
4d
NO2
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


E:\NMRdata chroman\trans-2-CO-p-NO2C6H4-3-Ph-chromanone-13C.als
197.624
194.515
169.535
150.303
139.786
138.995
129.603
128.888
127.725
127.629
123.692
111.611
80.585
77.315
77.000
76.676
39.919
36.563
28.154
23.701
20.697
DFILE trans-2-CO-p-NO2C6H4-3-Ph-chromanone-13C.als
COMNT single pulse decoupled gated NOE
DATIM 2017-09-12 11:11:42
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 677
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.33 usec
IRNUC 1H
CTEMP 24.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 56
O
O
O
4d
NO2
PPM
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
-10.0

E:\NMRdata chroman\trans-2-COMe-3-Ph-chromanone-1H.als



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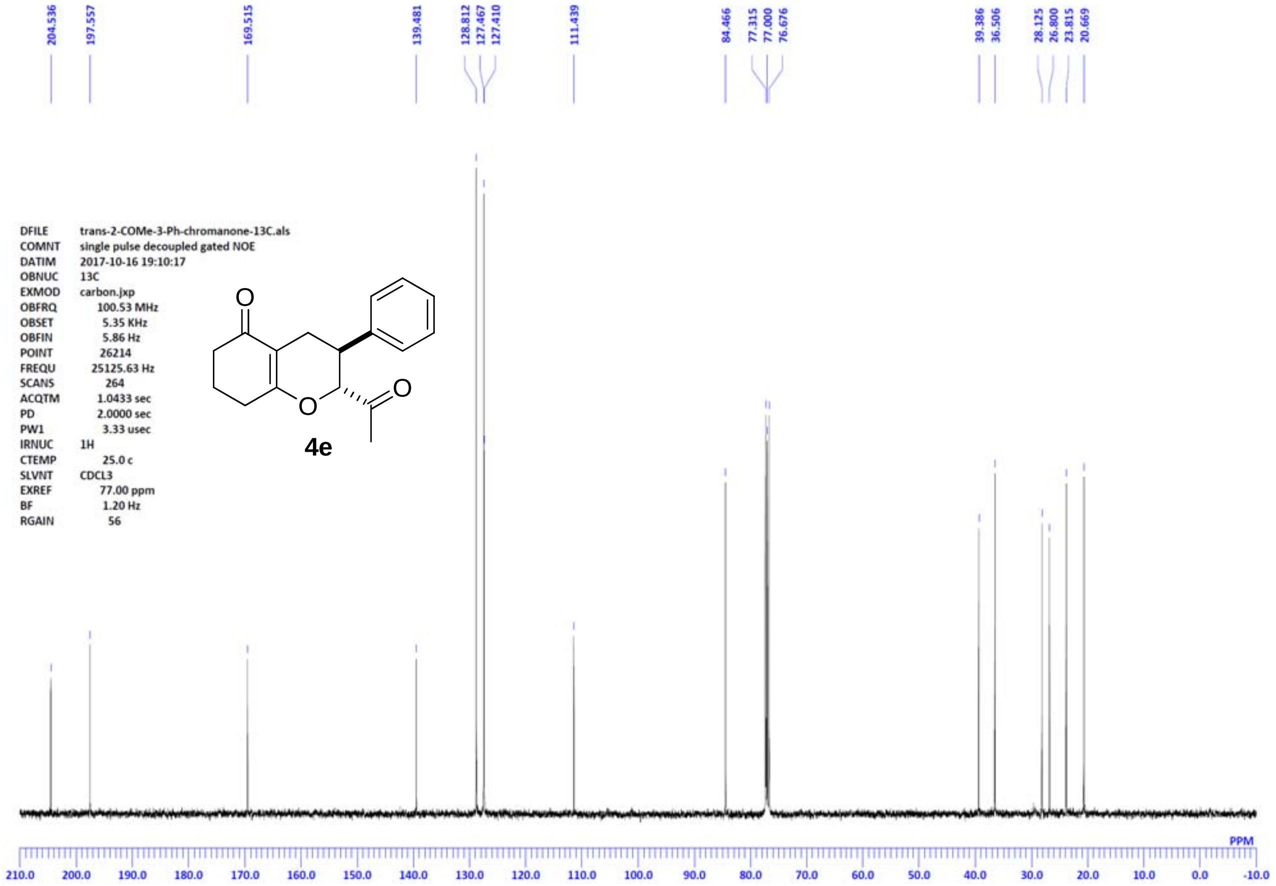
DFILE   trans-2-COMe-3-Ph-chromanone-1H.als
COMNT   single_pulse
DATIM   2017-10-16 19:07:28
OBNUC   1H
EXMOD   proton.jxp
OBFRQ      399.78 MHz
OBSET        4.19 KHz
OBFIN        7.29 Hz
POINT       13107
FREQU     6002.40 Hz
SCANS           8
ACQTM      2.1837 sec
PD         5.0000 sec
PW1          5.55 usec
IRNUC   1H
CTEMP        25.0 c
SLVNT   CDCL3
EXREF        0.00 ppm
BF           1.20 Hz
RGAIN          28
```

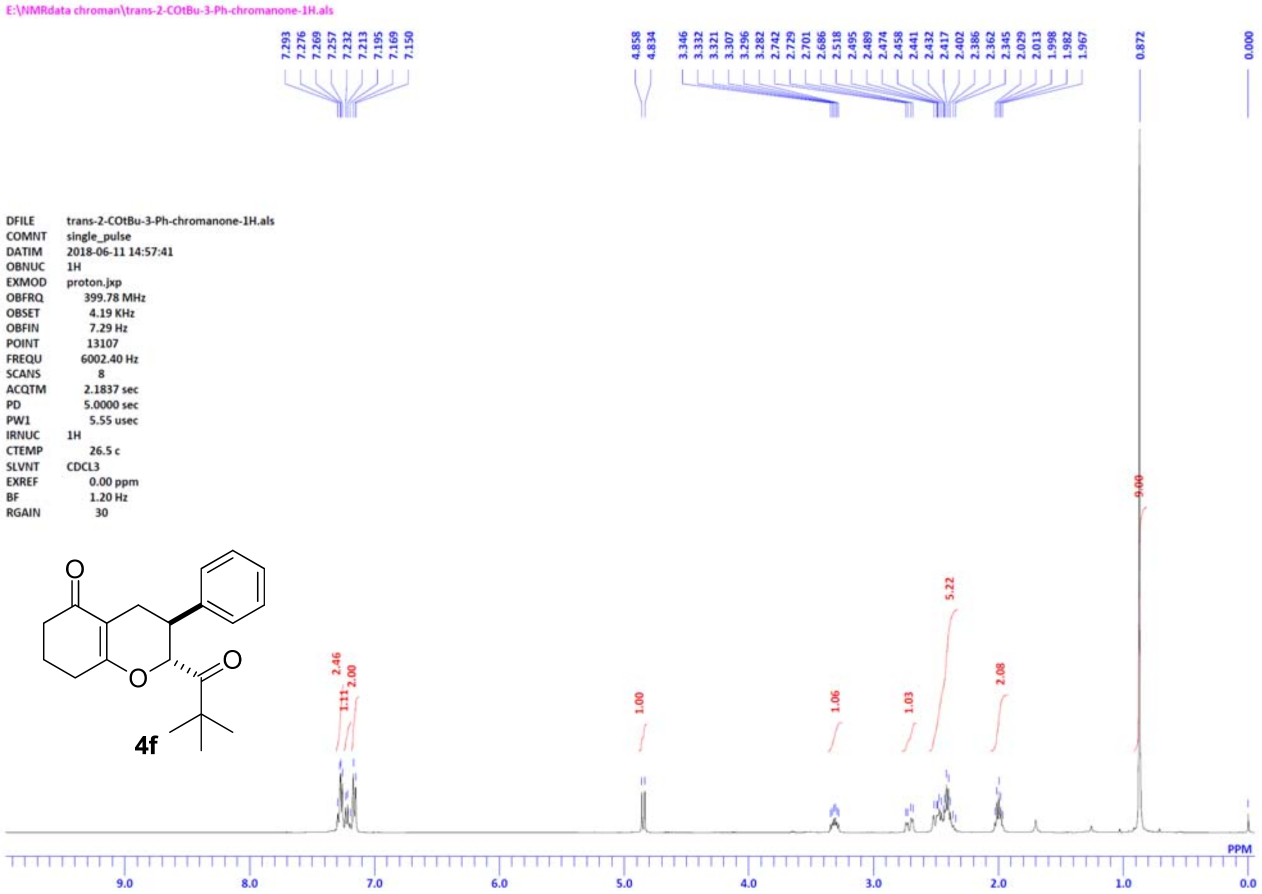
4e

E:\NMRdata chroman\trans-2-COMe-3-Ph-chromanone-13C.als

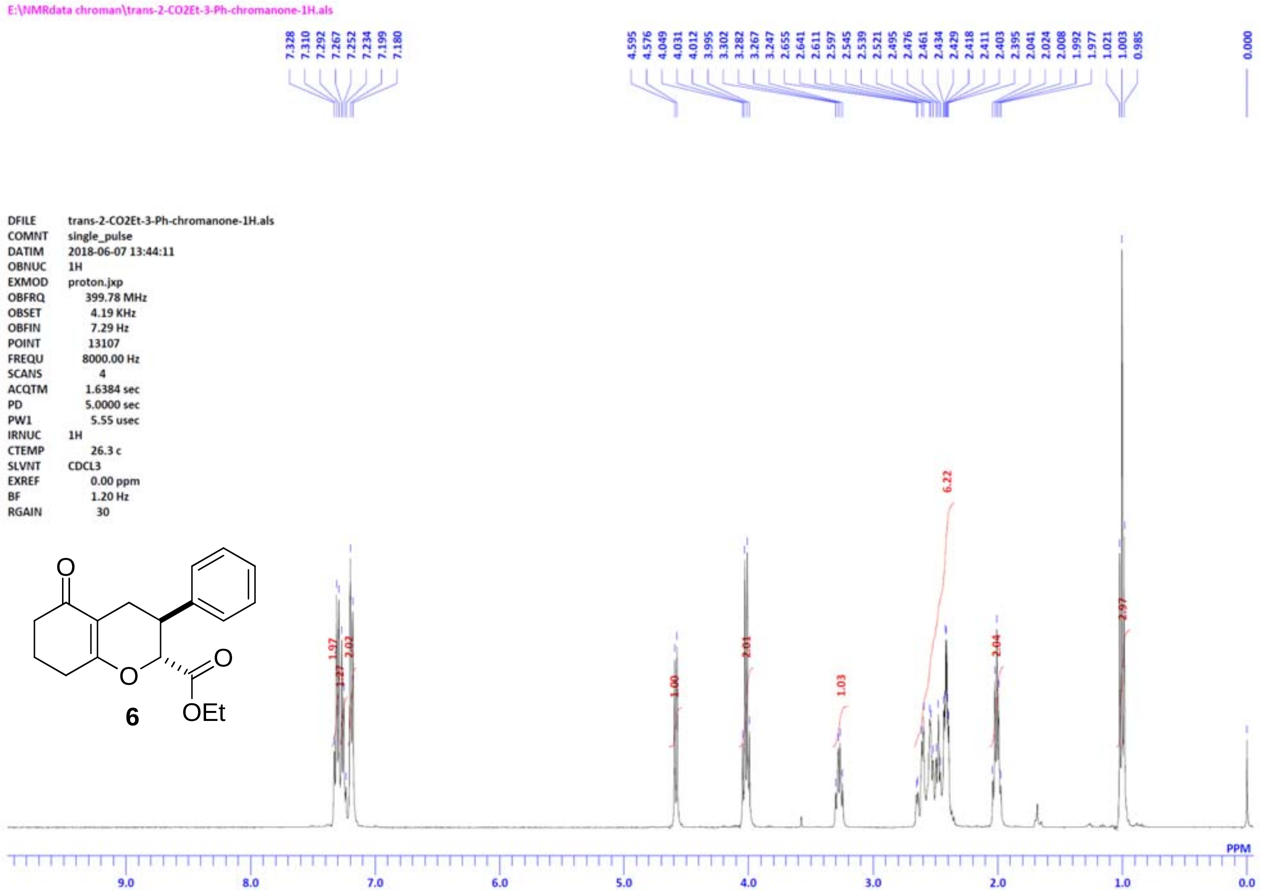


```
DFILE   trans-2-COMe-3-Ph-chromanone-13C.als
COMNT   single pulse decoupled gated NOE
DATIM   2017-10-16 19:10:17
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ      100.53 MHz
OBSET        5.35 KHz
OBFIN        5.86 Hz
POINT       26214
FREQU    25125.63 Hz
SCANS         264
ACQTM      1.0433 sec
PD         2.0000 sec
PW1          3.33 usec
IRNUC   1H
CTEMP        25.0 c
SLVNT   CDCL3
EXREF       77.00 ppm
BF           1.20 Hz
RGAIN          56
```

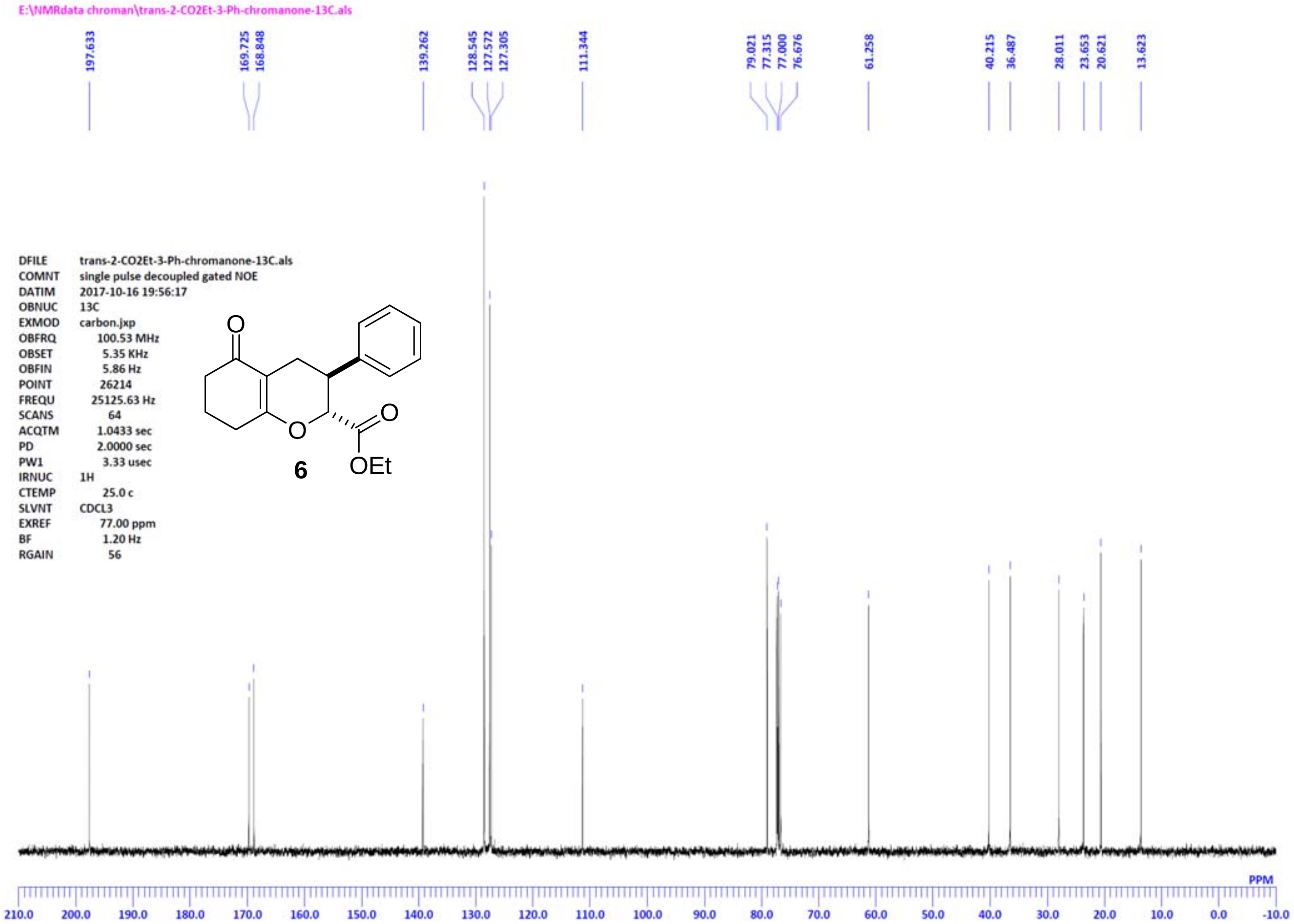
4e


E:\NMRdata chroman\trans-2-COtBu-3-Ph-chromanone-1H.als
7.293
7.276
7.269
7.257
7.232
7.213
7.195
7.169
7.150
4.858
4.834
3.346
3.332
3.321
3.307
3.296
3.282
2.742
2.729
2.701
2.686
2.518
2.495
2.489
2.474
2.458
2.441
2.432
2.417
2.402
2.386
2.362
2.345
2.029
2.013
1.998
1.982
1.967
0.872
0.000
DFILE trans-2-COtBu-3-Ph-chromanone-1H.als
COMNT single_pulse
DATIM 2018-06-11 14:57:41
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.55 usec
IRNUC 1H
CTEMP 26.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 30
4f
2.46
1.11
2.00
1.00
1.06
1.03
5.22
2.08
9.00
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


E:\NMRdata chroman\trans-2-COtBu-3-Ph-chromanone-13C.als
209.456
197.776
170.164
146.460
139.042
128.611
127.439
111.449
77.439
77.324
77.000
76.685
44.105
38.985
36.582
28.201
25.236
23.453
20.755
DFILE trans-2-COtBu-3-Ph-chromanone-13C.als
COMNT single pulse decoupled gated NOE
DATIM 2018-06-11 15:00:26
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 224
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.33 usec
IRNUC 1H
CTEMP 26.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 56
4f
PPM
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
-10.0

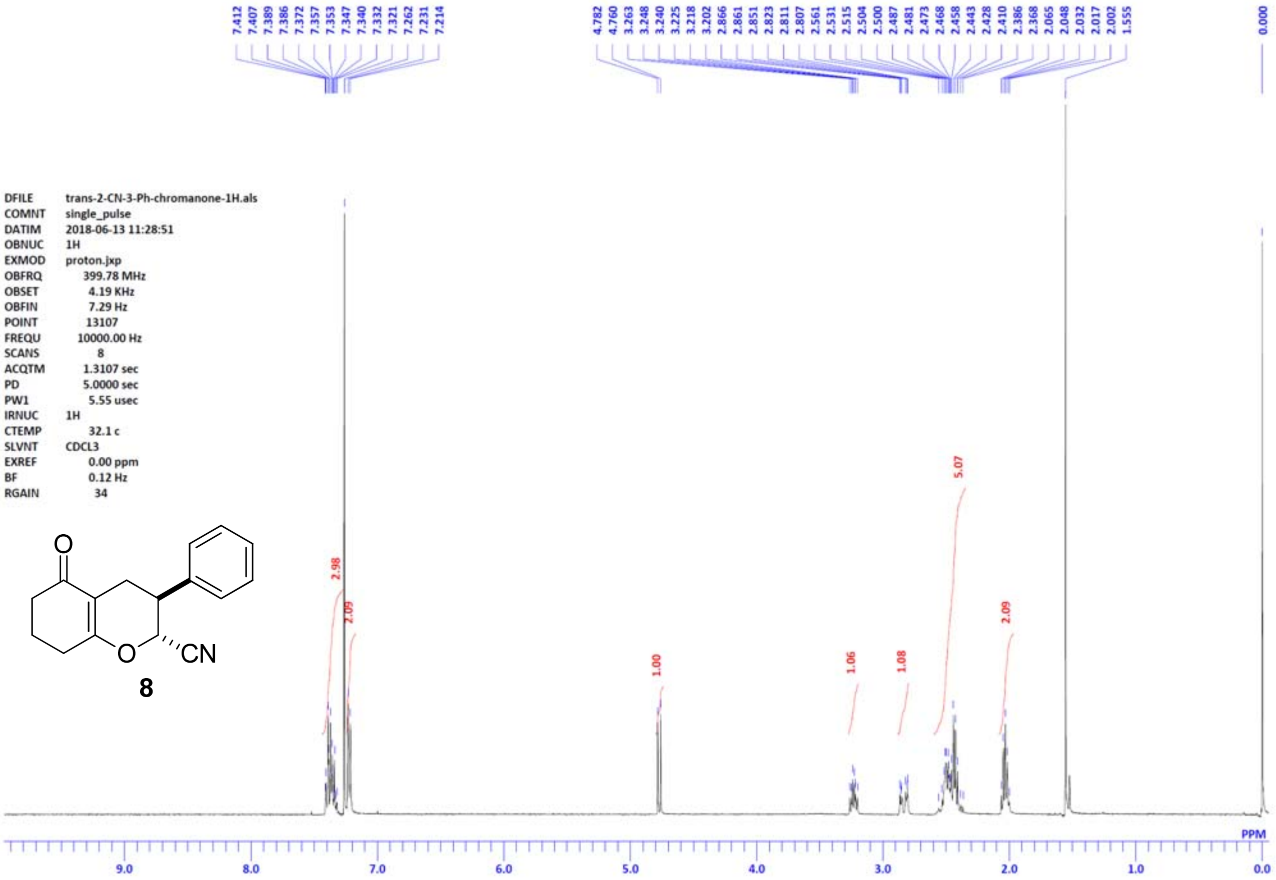


```
DFILE    trans-2-CO2Et-3-Ph-chromanone-1H.als
COMNT    single_pulse
DATIM    2018-06-07 13:44:11
OBNUC    1H
EXMOD    proton.jxp
OBFRQ       399.78 MHz
OBSET         4.19 KHz
OBFIN         7.29 Hz
POINT        13107
FREQU      8000.00 Hz
SCANS            4
ACQTM       1.6384 sec
PD          5.0000 sec
PW1           5.55 usec
IRNUC    1H
CTEMP         26.3 c
SLVNT    CDCL3
EXREF         0.00 ppm
BF            1.20 Hz
RGAIN           30
```



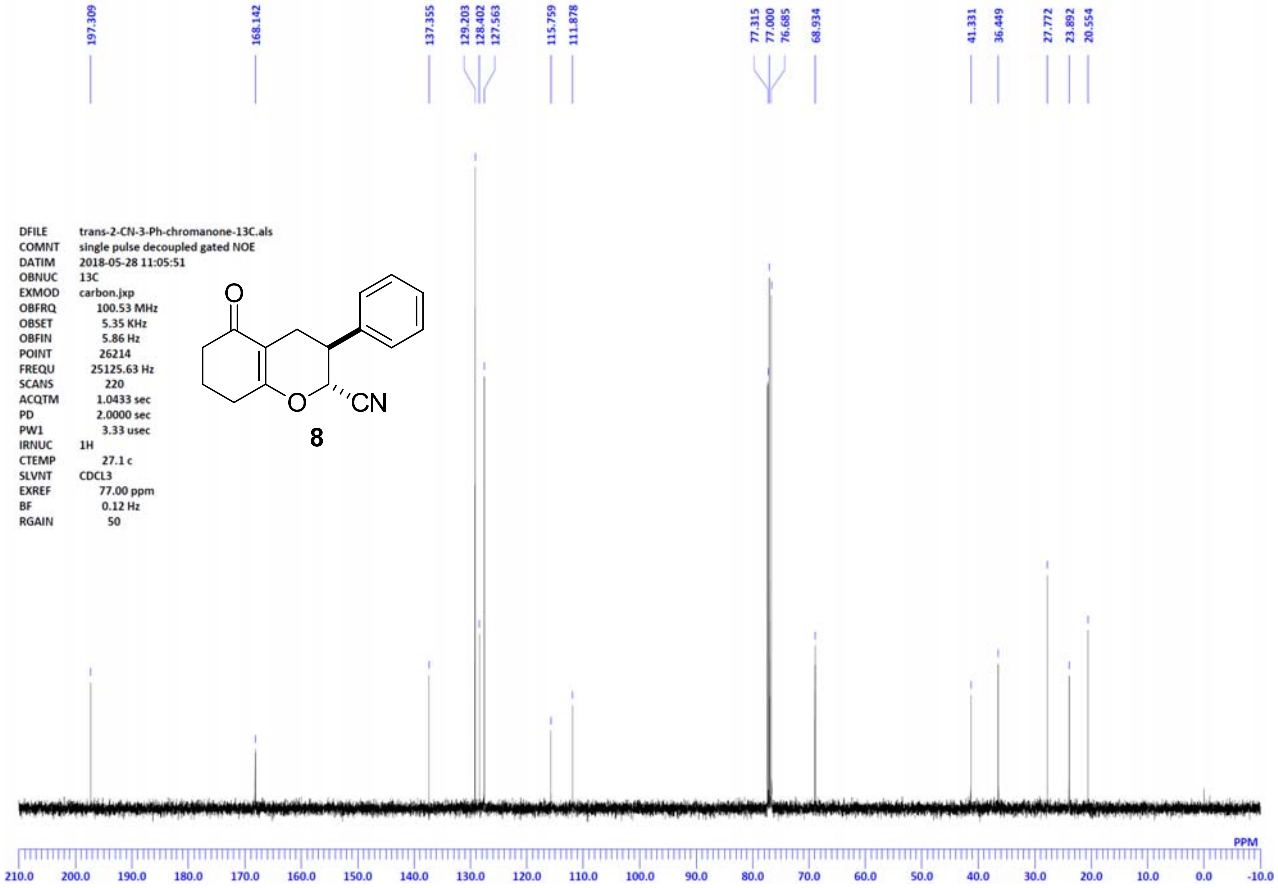
```
DFILE    trans-2-CO2Et-3-Ph-chromanone-13C.als
COMNT    single pulse decoupled gated NOE
DATIM    2017-10-16 19:56:17
OBNUC    13C
EXMOD    carbon.jxp
OBFRQ       100.53 MHz
OBSET         5.35 KHz
OBFIN         5.86 Hz
POINT        26214
FREQU     25125.63 Hz
SCANS           64
ACQTM       1.0433 sec
PD          2.0000 sec
PW1           3.33 usec
IRNUC    1H
CTEMP         25.0 c
SLVNT    CDCL3
EXREF        77.00 ppm
BF            1.20 Hz
RGAIN           56
```

E:\NMRdata chroman\trans-2-CN-3-Ph-chromanone-1H.als

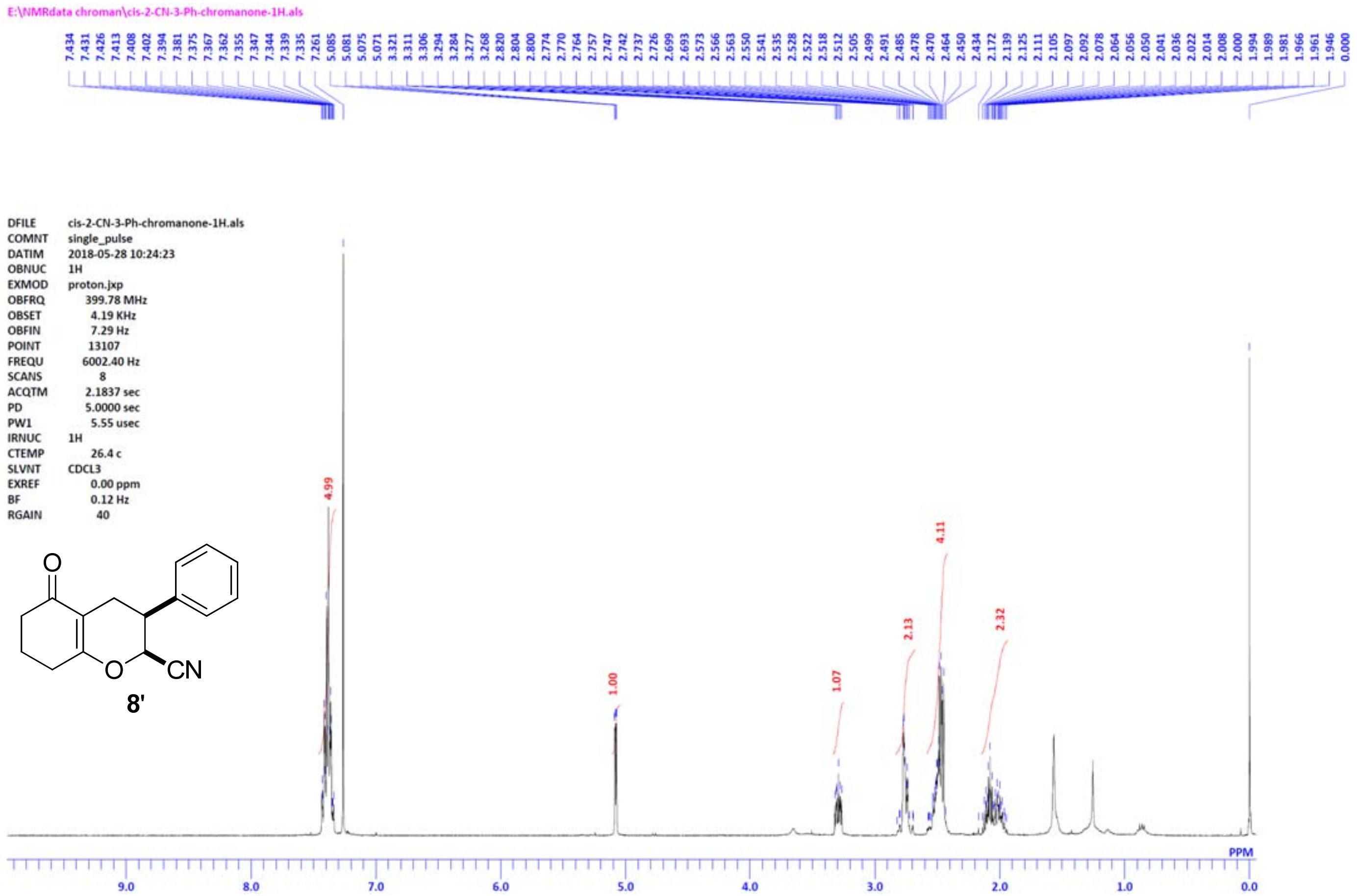


DFILE	trans-2-CN-3-Ph-chromanone-1H.als
COMNT	single_pulse
DATIM	2018-06-13 11:28:51
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	10000.00 Hz
SCANS	8
ACQTM	1.3107 sec
PD	5.0000 sec
PW1	5.55 usec
IRNUC	1H
CTEMP	32.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	34

E:\NMRdata chroman\trans-2-CN-3-Ph-chromanone-13C.als



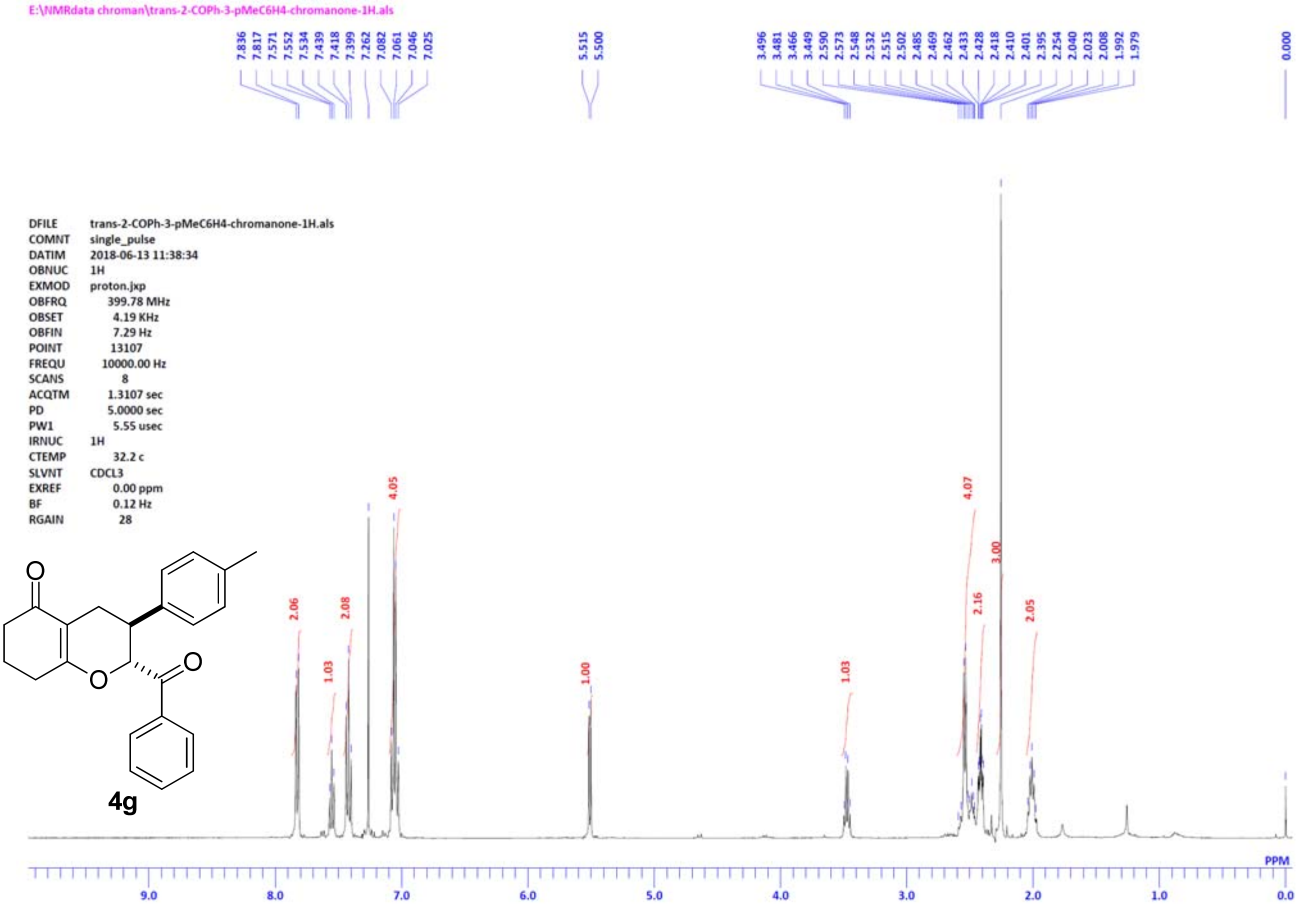
DFILE	trans-2-CN-3-Ph-chromanone-13C.als
COMNT	single pulse decoupled gated NOE
DATIM	2018-05-28 11:05:51
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.63 Hz
SCANS	220
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.33 usec
IRNUC	1H
CTEMP	27.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	50


E:\NMRdata chroman\cis-2-CN-3-Ph-chromanone-1H.als

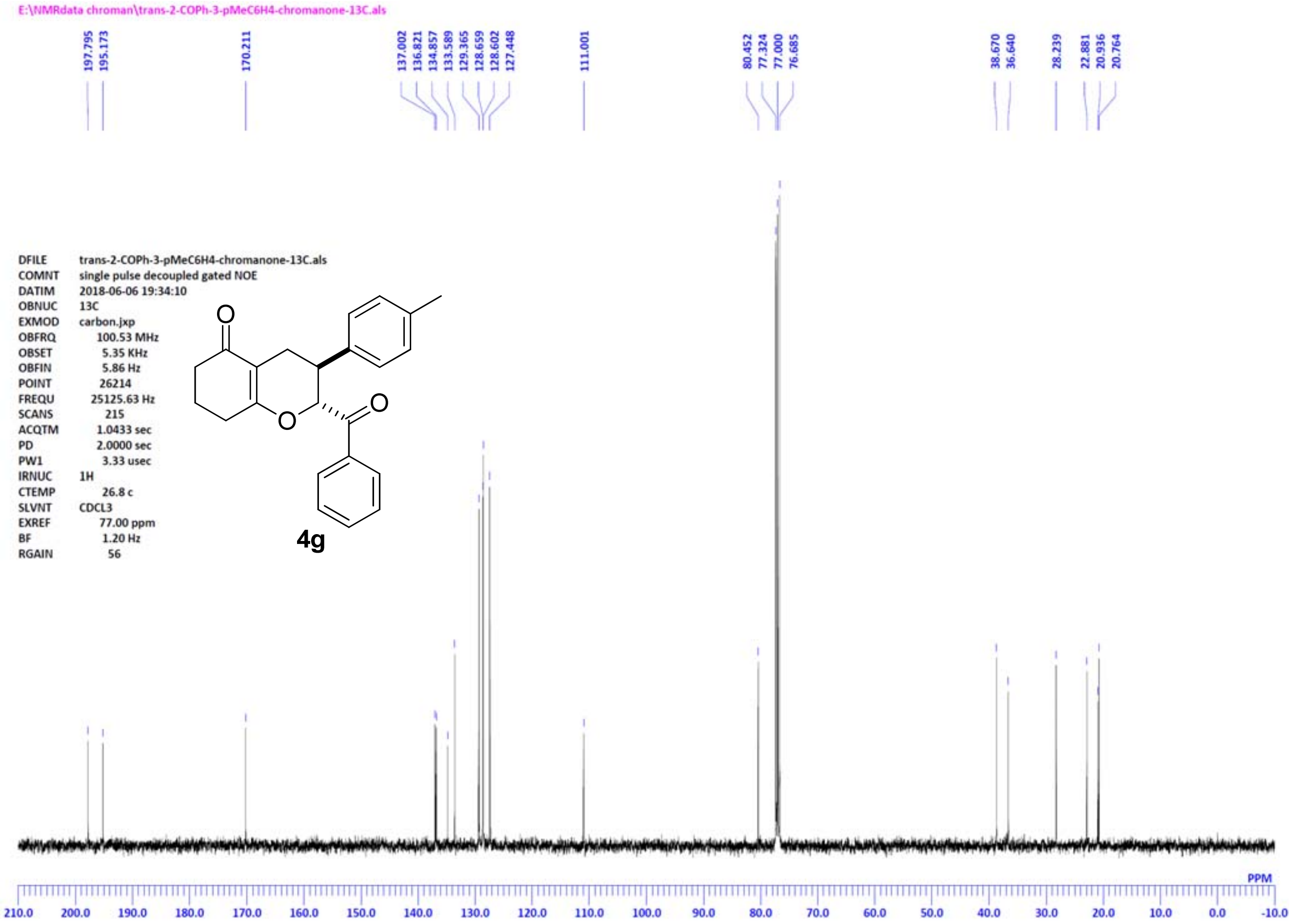
DFILE cis-2-CN-3-Ph-chromanone-1H.als
COMNT single_pulse
DATIM 2018-05-28 10:24:23
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.55 usec
IRNUC 1H
CTEMP 26.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 40


E:\NMRdata chroman\cis-2-CN-3-Ph-chromanone-13C.als

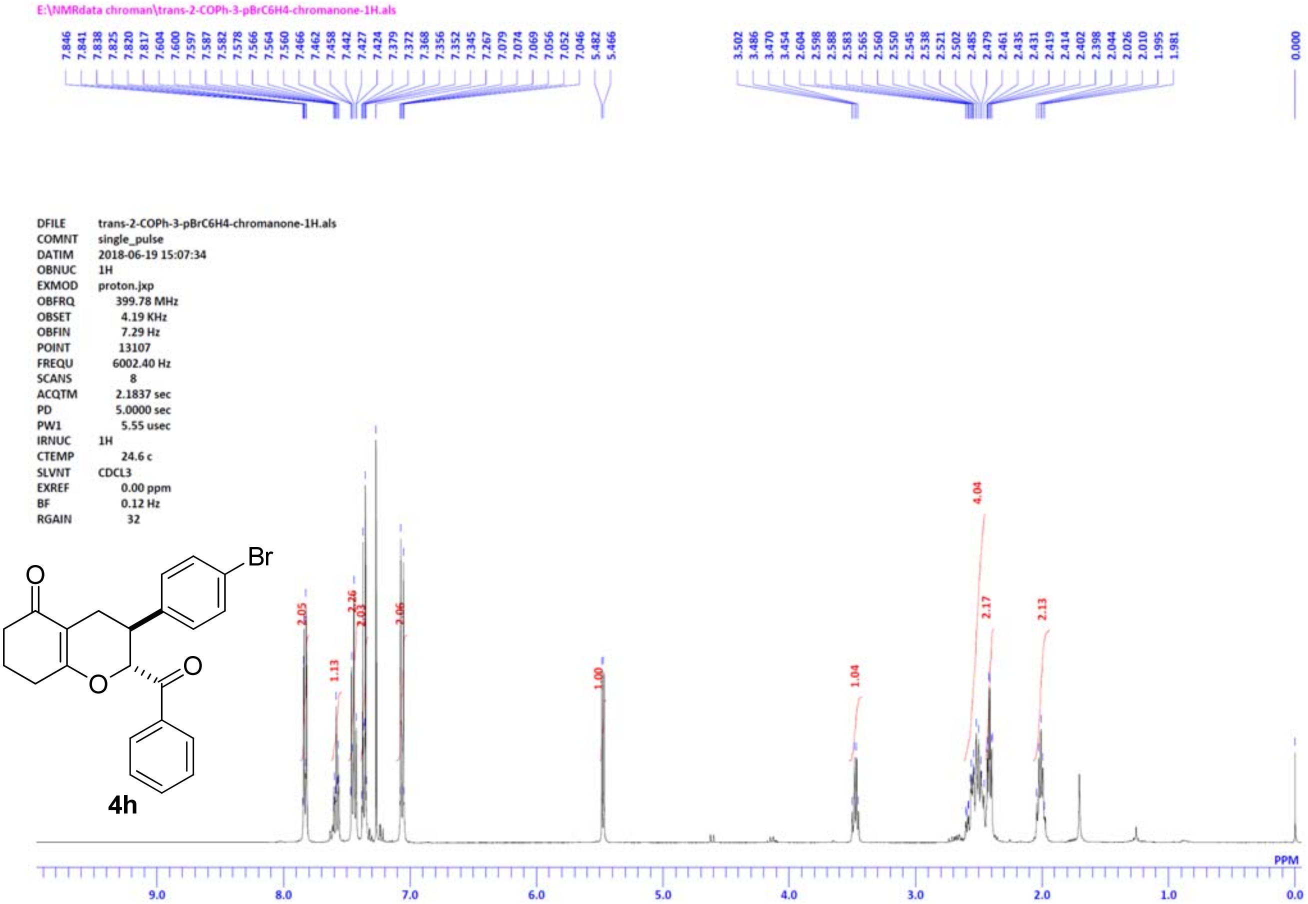
DFILE cis-2-CN-3-Ph-chromanone-13C.als
COMNT single pulse decoupled gated NOE
DATIM 2018-05-28 10:27:16
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 537
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.33 usec
IRNUC 1H
CTEMP 26.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 56

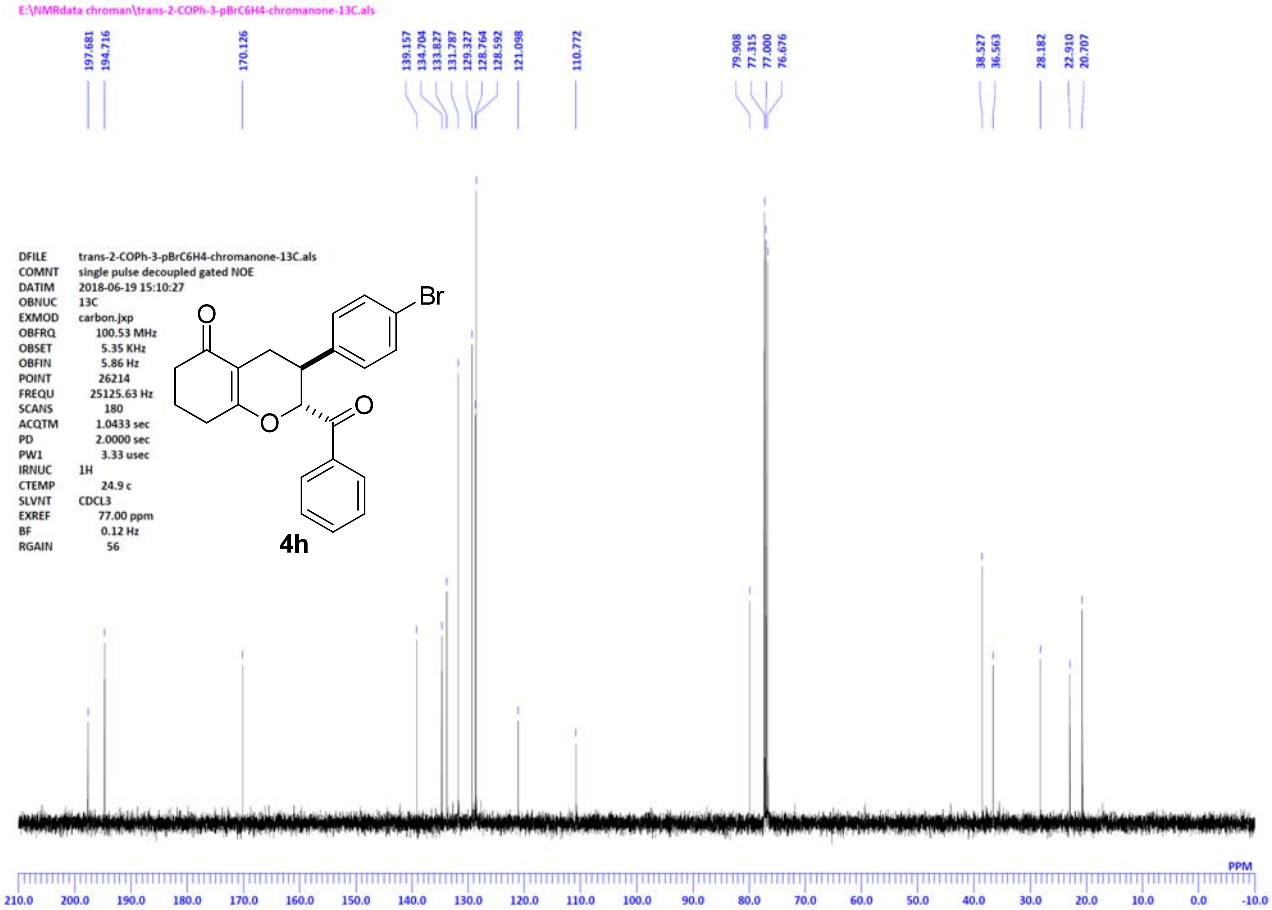


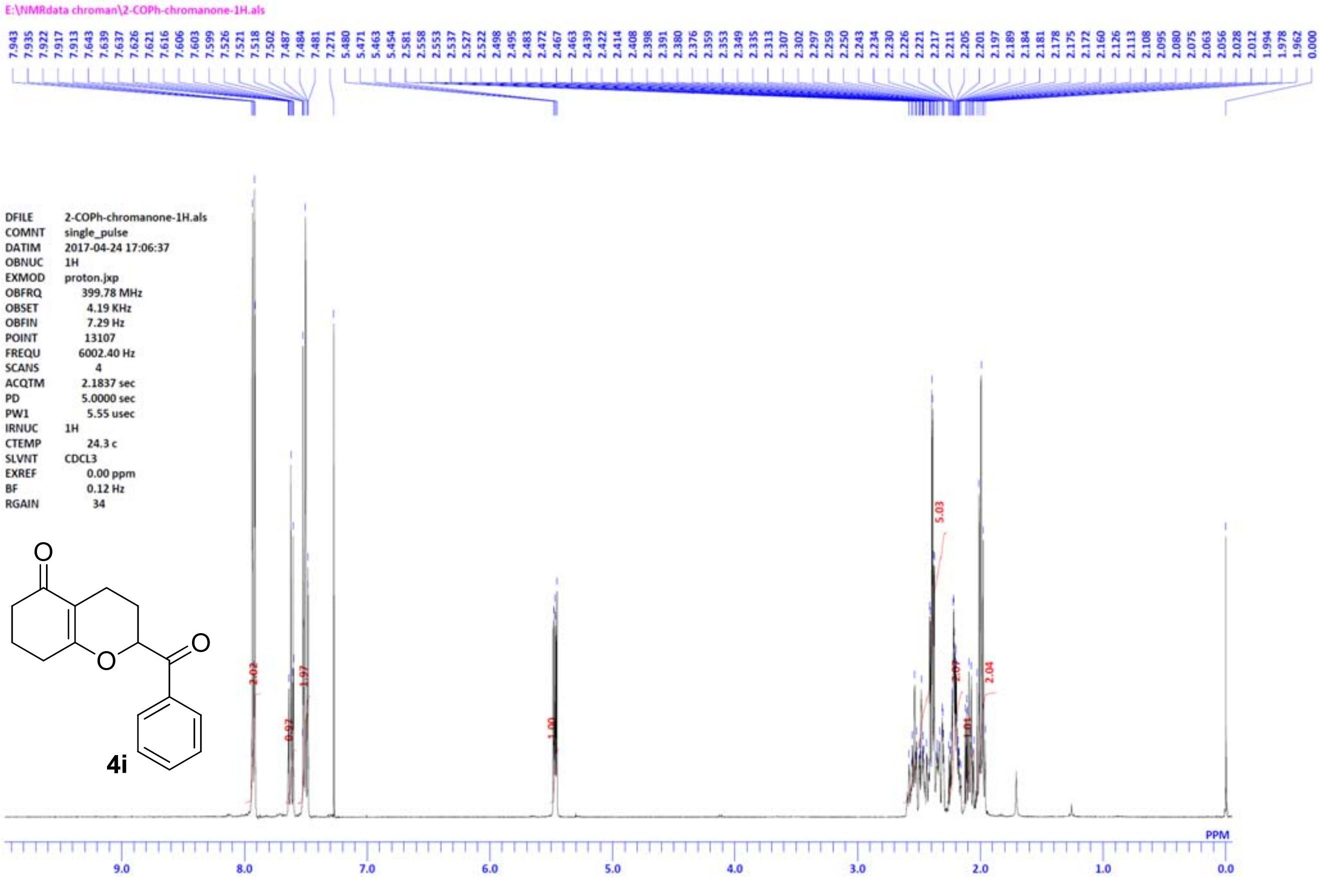
DFILE trans-2-COPh-3-pMeC6H4-chromanone-1H.als
COMNT single_pulse
DATIM 2018-06-13 11:38:34
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 10000.00 Hz
SCANS 8
ACQTM 1.3107 sec
PD 5.0000 sec
PW1 5.55 usec
IRNUC 1H
CTEMP 32.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 28

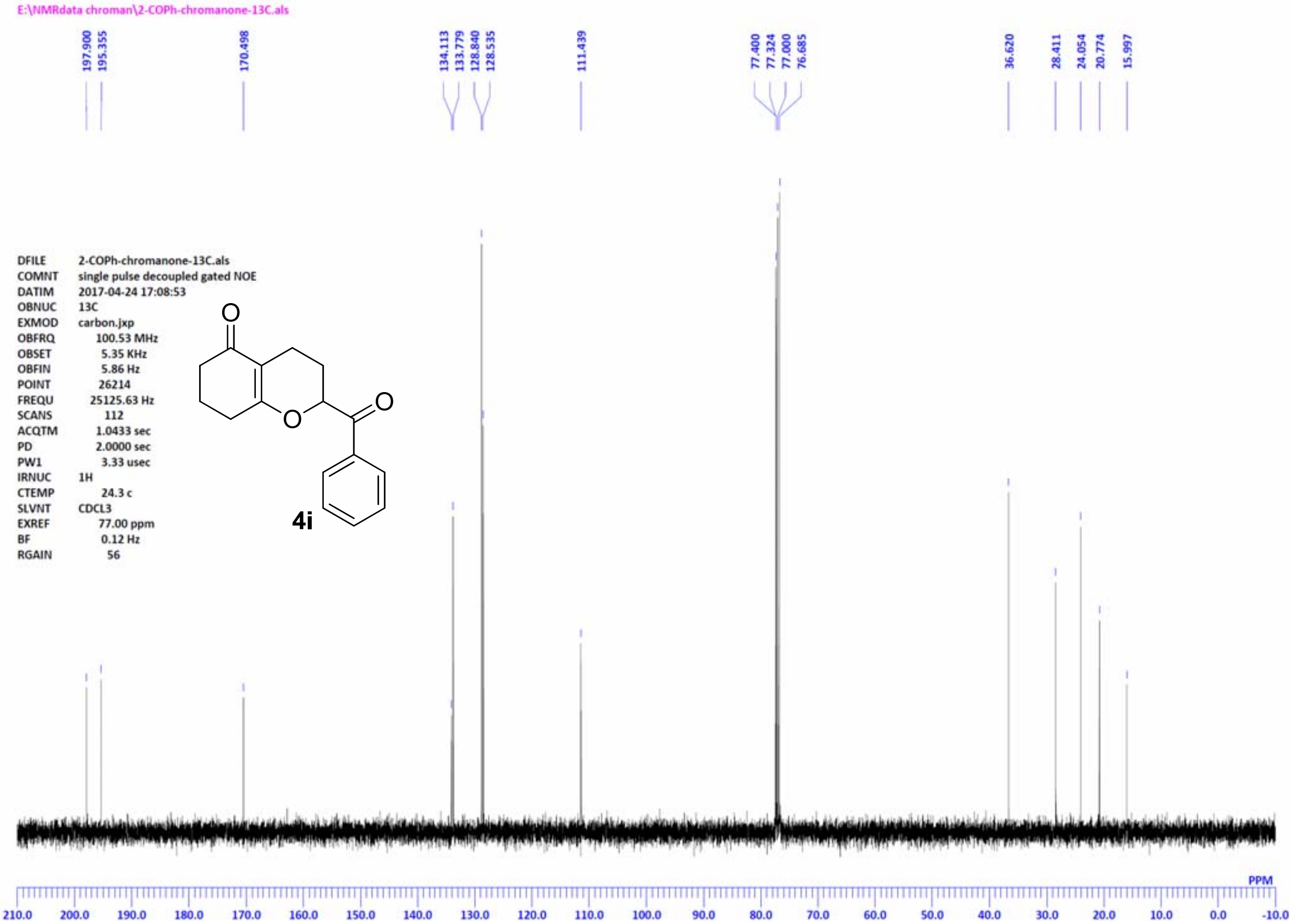


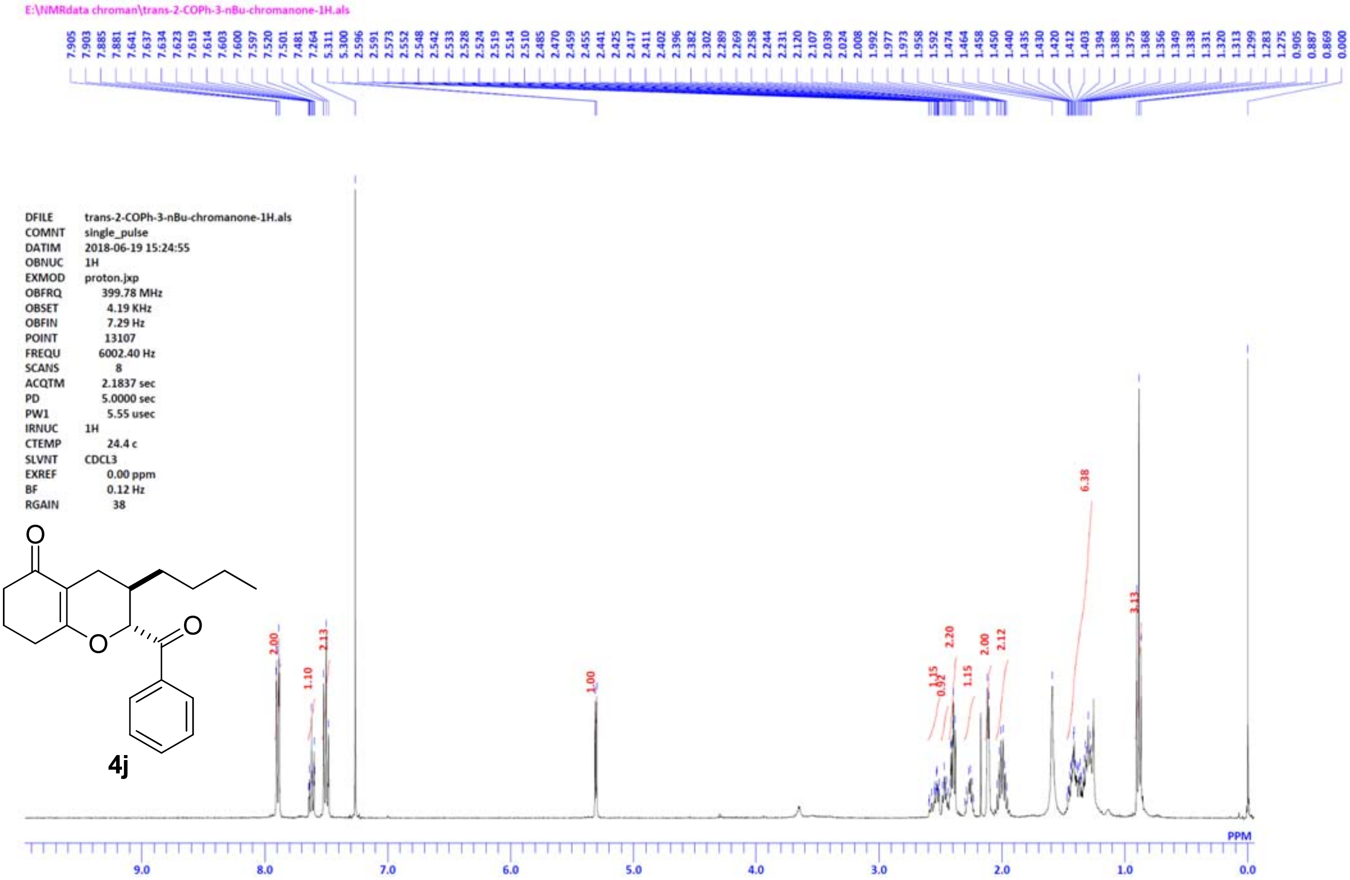
DFILE trans-2-COPh-3-pMeC6H4-chromanone-13C.als
COMNT single pulse decoupled gated NOE
DATIM 2018-06-06 19:34:10
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 215
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.33 usec
IRNUC 1H
CTEMP 26.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 56


E:\NMRdata chroman\trans-2-COPh-3-pBrC6H4-chromanone-1H.als
7.846 7.841 7.838 7.825 7.820 7.817 7.604 7.600 7.597 7.587 7.582 7.578 7.566 7.564 7.560 7.466 7.462 7.458 7.442 7.427 7.424 7.379 7.372 7.368 7.356 7.352 7.345 7.267 7.079 7.074 7.069 7.056 7.052 7.046 5.482 5.466
3.502 3.486 3.470 3.454 2.604 2.598 2.588 2.583 2.565 2.560 2.550 2.545 2.538 2.521 2.502 2.485 2.479 2.461 2.435 2.431 2.419 2.414 2.402 2.398 2.044 2.026 2.010 1.995 1.981
0.000
DFILE trans-2-COPh-3-pBrC6H4-chromanone-1H.als
COMNT single_pulse
DATIM 2018-06-19 15:07:34
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.55 usec
IRNUC 1H
CTEMP 24.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 32
O
Br
O
O
4h
2.05
1.13
2.26
2.03
2.06
1.00
1.04
4.04
2.17
2.13
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


E:\NMRdata chroman\trans-2-COPh-3-pBrC6H4-chromanone-13C.als
197.681 194.716 170.126 139.157 134.704 133.827 131.787 129.327 128.764 128.592 121.098 110.772 79.908 77.315 77.000 76.676 38.527 36.563 28.182 22.910 20.707
DFILE trans-2-COPh-3-pBrC6H4-chromanone-13C.als
COMNT single pulse decoupled gated NOE
DATIM 2018-06-19 15:10:27
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 180
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.33 usec
IRNUC 1H
CTEMP 24.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 56
O
Br
O
O
4h
PPM
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
-10.0

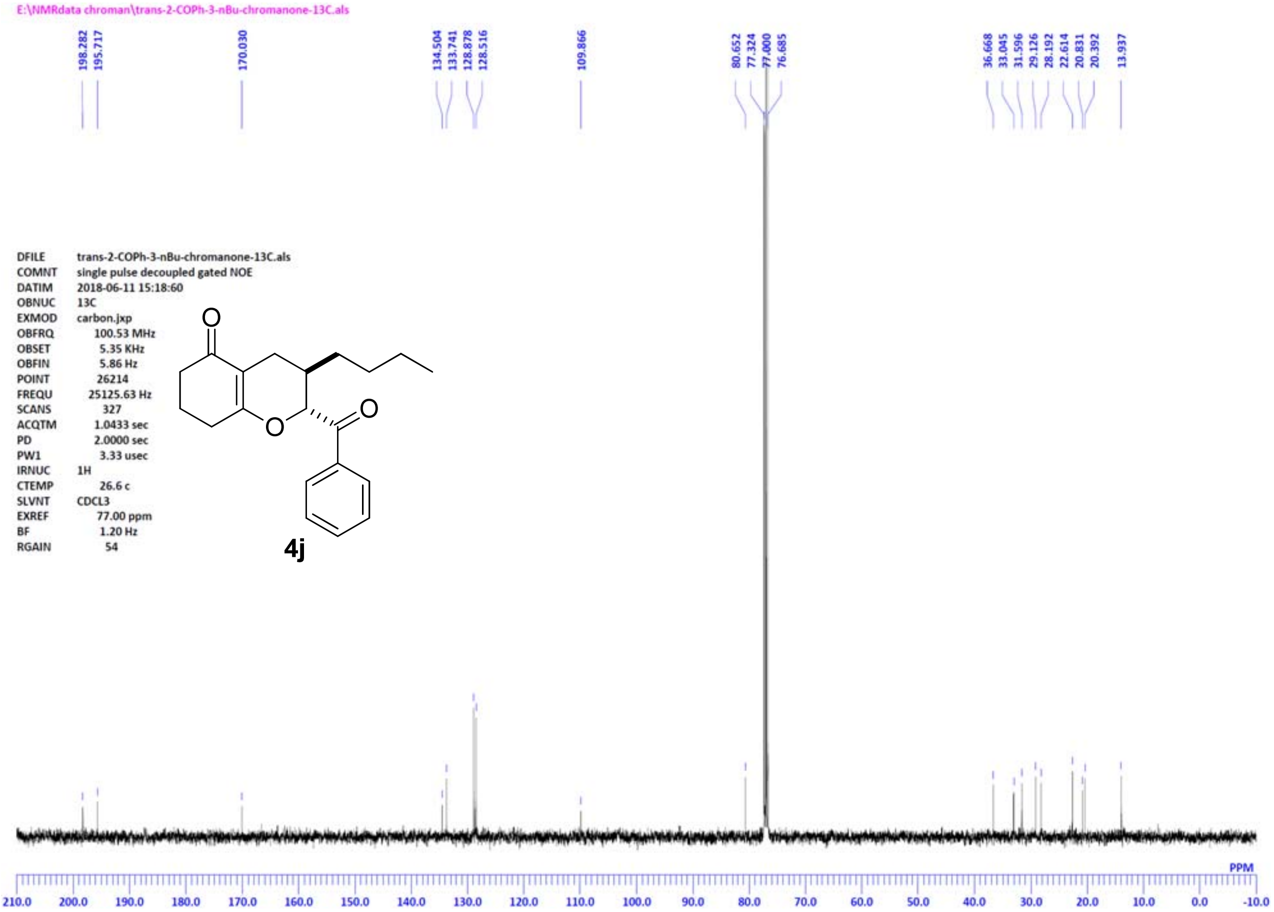

E:\NMRdata chroman\2-COPh-chromanone-1H.als
7.943 7.935 7.922 7.917 7.913 7.643 7.639 7.637 7.626 7.621 7.616 7.606 7.603 7.599 7.526 7.521 7.518 7.502 7.487 7.484 7.481 7.271 5.480 5.471 5.463 5.454 2.581 2.558 2.553 2.537 2.527 2.522 2.498 2.495 2.483 2.472 2.467 2.463 2.439 2.422 2.414 2.408 2.398 2.391 2.380 2.376 2.359 2.353 2.349 2.335 2.313 2.307 2.302 2.297 2.259 2.250 2.243 2.234 2.230 2.226 2.221 2.217 2.211 2.205 2.201 2.197 2.189 2.184 2.181 2.178 2.175 2.172 2.160 2.126 2.113 2.108 2.095 2.080 2.075 2.063 2.056 2.028 2.012 1.994 1.978 1.962 0.000
DFILE 2-COPh-chromanone-1H.als
COMNT single_pulse
DATIM 2017-04-24 17:06:37
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 4
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.55 usec
IRNUC 1H
CTEMP 24.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 34
O
O
O
4i
2.02
0.97
1.97
1.00
5.03
2.07
1.01
2.04
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


E:\NMRdata chroman\2-COPh-chromanone-13C.als
197.900 195.355 170.498 134.113 133.779 128.840 128.535 111.439 77.400 77.324 77.000 76.685 36.620 28.411 24.054 20.774 15.997
DFILE 2-COPh-chromanone-13C.als
COMNT single pulse decoupled gated NOE
DATIM 2017-04-24 17:08:53
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 112
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.33 usec
IRNUC 1H
CTEMP 24.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 56
O
O
O
4i
PPM
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
-10.0



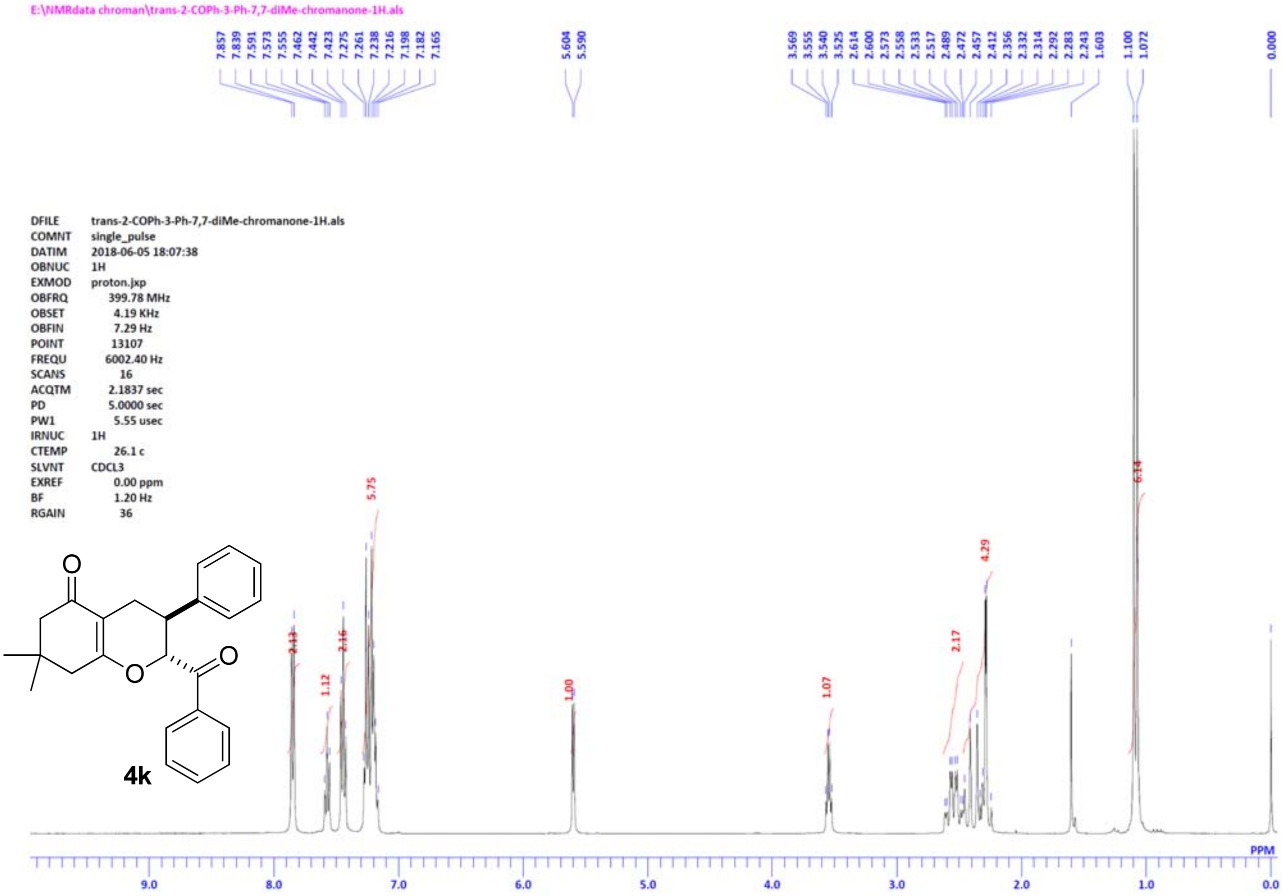
DFILE trans-2-COPh-3-nBu-chromanone-1H.als
COMNT single_pulse
DATIM 2018-06-19 15:24:55
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.55 usec
IRNUC 1H
CTEMP 24.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 38

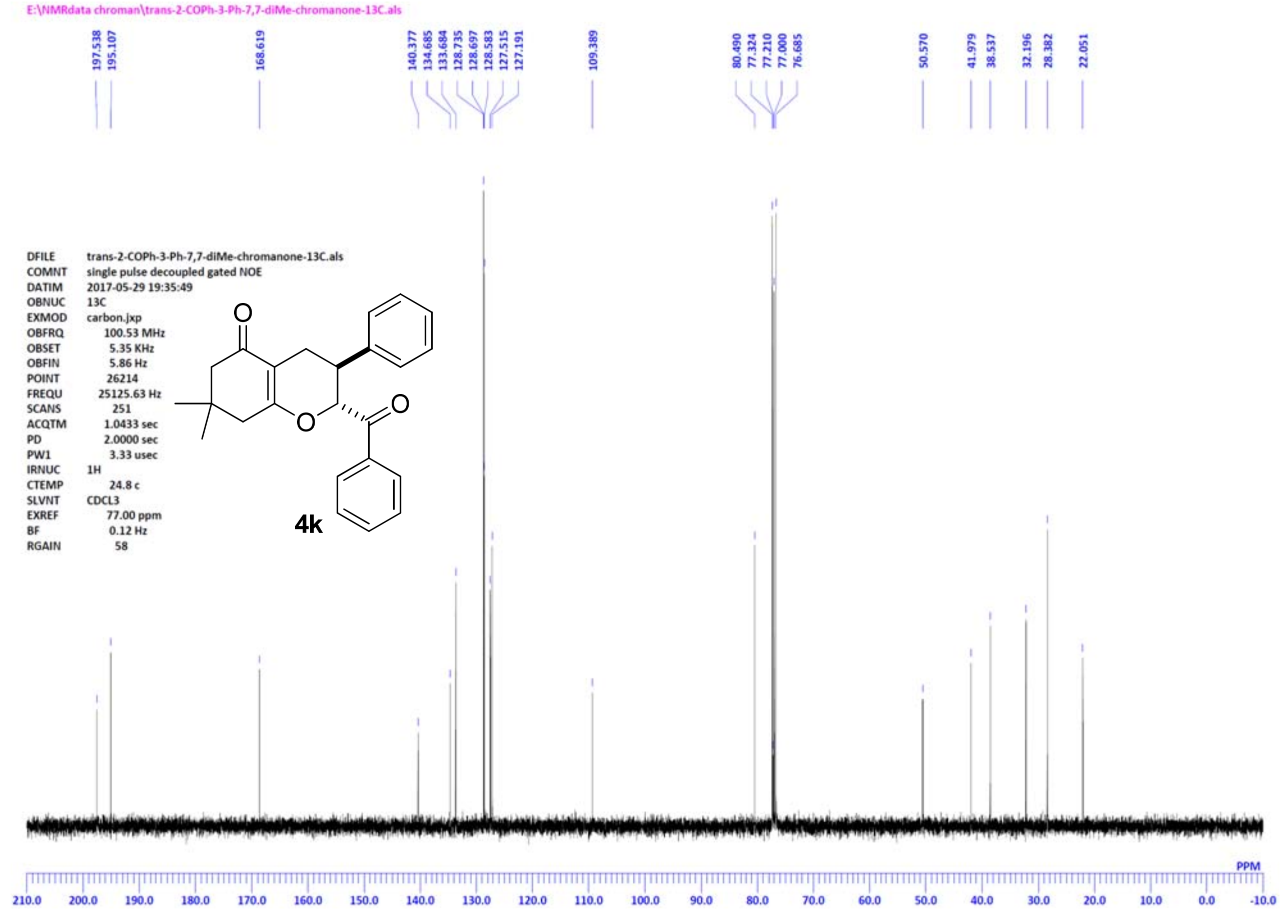
4j

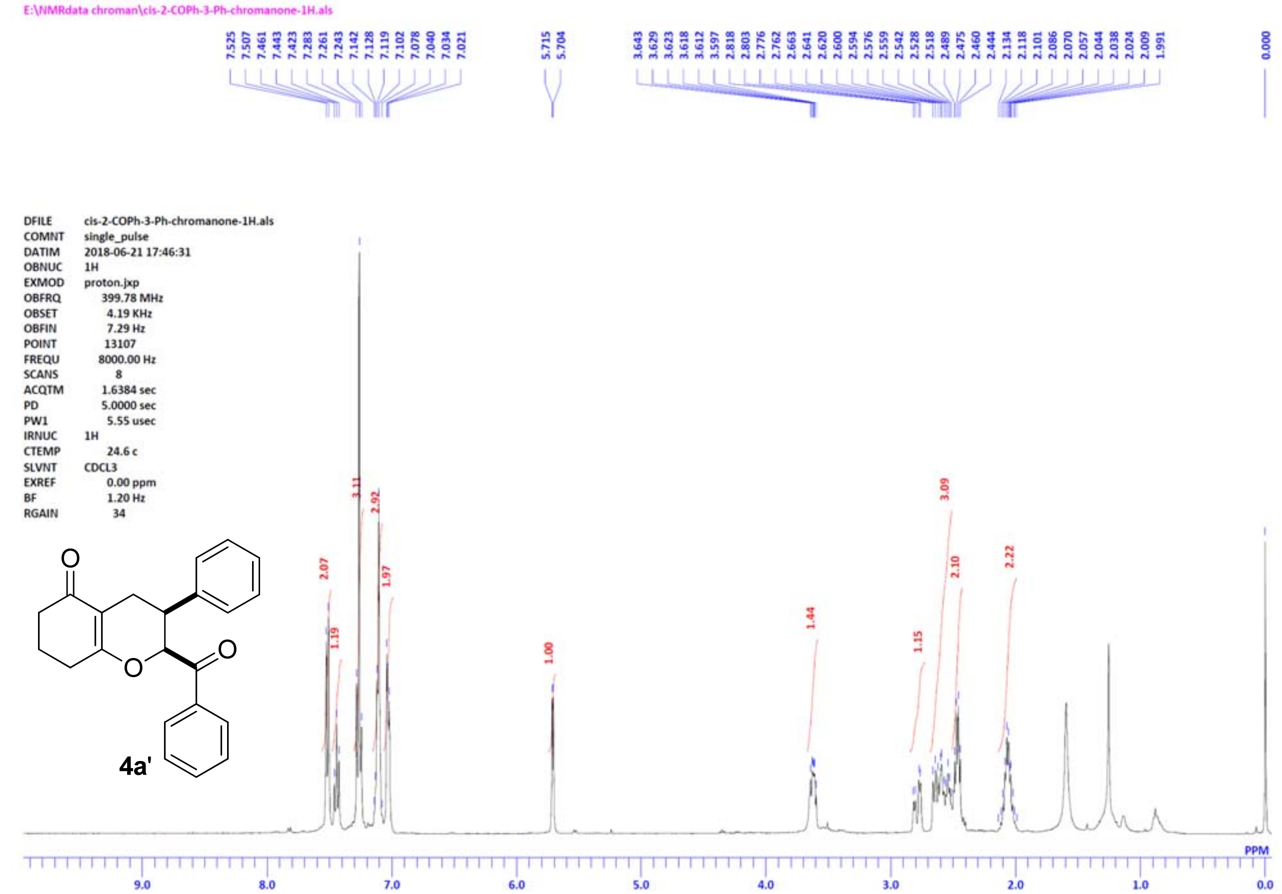


DFILE trans-2-COPh-3-nBu-chromanone-13C.als
COMNT single pulse decoupled gated NOE
DATIM 2018-06-11 15:18:60
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 327
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.33 usec
IRNUC 1H
CTEMP 26.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 54

4j


E:\NMRdata chroman\trans-2-COPh-3-Ph-7,7-diMe-chromanone-1H.als
7.857 7.839 7.591 7.573 7.555 7.462 7.442 7.423 7.275 7.261 7.238 7.216 7.198 7.182 7.165
5.604 5.590
3.569 3.555 3.540 3.525 2.614 2.600 2.573 2.558 2.533 2.517 2.489 2.472 2.457 2.412 2.356 2.332 2.314 2.292 2.283 2.243 1.603
1.100 1.072
0.000
DFILE trans-2-COPh-3-Ph-7,7-diMe-chromanone-1H.als
COMNT single_pulse
DATIM 2018-06-05 18:07:38
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 16
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.55 usec
IRNUC 1H
CTEMP 26.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 36
O
O
O
4k
2.13
1.12
2.16
5.75
1.00
1.07
2.17
4.29
6.14
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


E:\NMRdata chroman\trans-2-COPh-3-Ph-7,7-diMe-chromanone-13C.als
197.538 195.107
168.619
140.377 134.685 133.684 128.735 128.697 128.583 127.515 127.191
109.389
80.490 77.324 77.210 77.000 76.685
50.570
41.979 38.537
32.196 28.382
22.051
DFILE trans-2-COPh-3-Ph-7,7-diMe-chromanone-13C.als
COMNT single pulse decoupled gated NOE
DATIM 2017-05-29 19:35:49
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 251
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.33 usec
IRNUC 1H
CTEMP 24.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 58
O
O
O
4k
PPM
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
-10.0



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DFILE     cis-2-COPh-3-Ph-chromanone-1H.als
COMNT     single_pulse
DATIM     2018-06-21 17:46:31
OBNUC     1H
EXMOD     proton.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         13107
FREQU       8000.00 Hz
SCANS             8
ACQTM        1.6384 sec
PD           5.0000 sec
PW1            5.55 usec
IRNUC     1H
CTEMP          24.6 c
SLVNT     CDCL3
EXREF          0.00 ppm
BF             1.20 Hz
RGAIN            34
```

```
DFILE     cis-2-COPh-3-Ph-chromanone-13C.als
COMNT     single pulse decoupled gated NOE
DATIM     2018-06-21 17:49:26
OBNUC     13C
EXMOD     carbon.jxp
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         26214
FREQU      25125.63 Hz
SCANS           531
ACQTM        1.0433 sec
PD           2.0000 sec
PW1            3.33 usec
IRNUC     1H
CTEMP          24.9 c
SLVNT     CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            56
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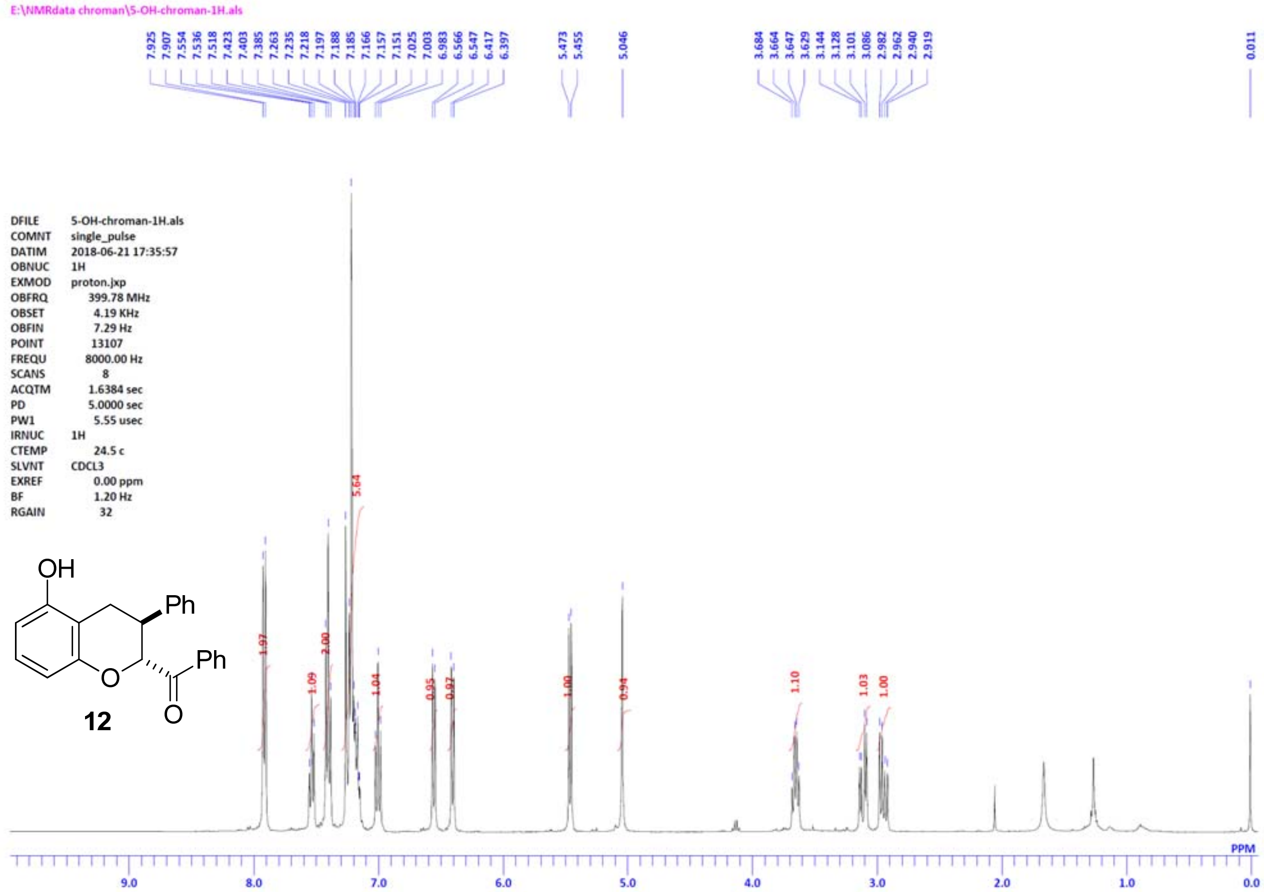
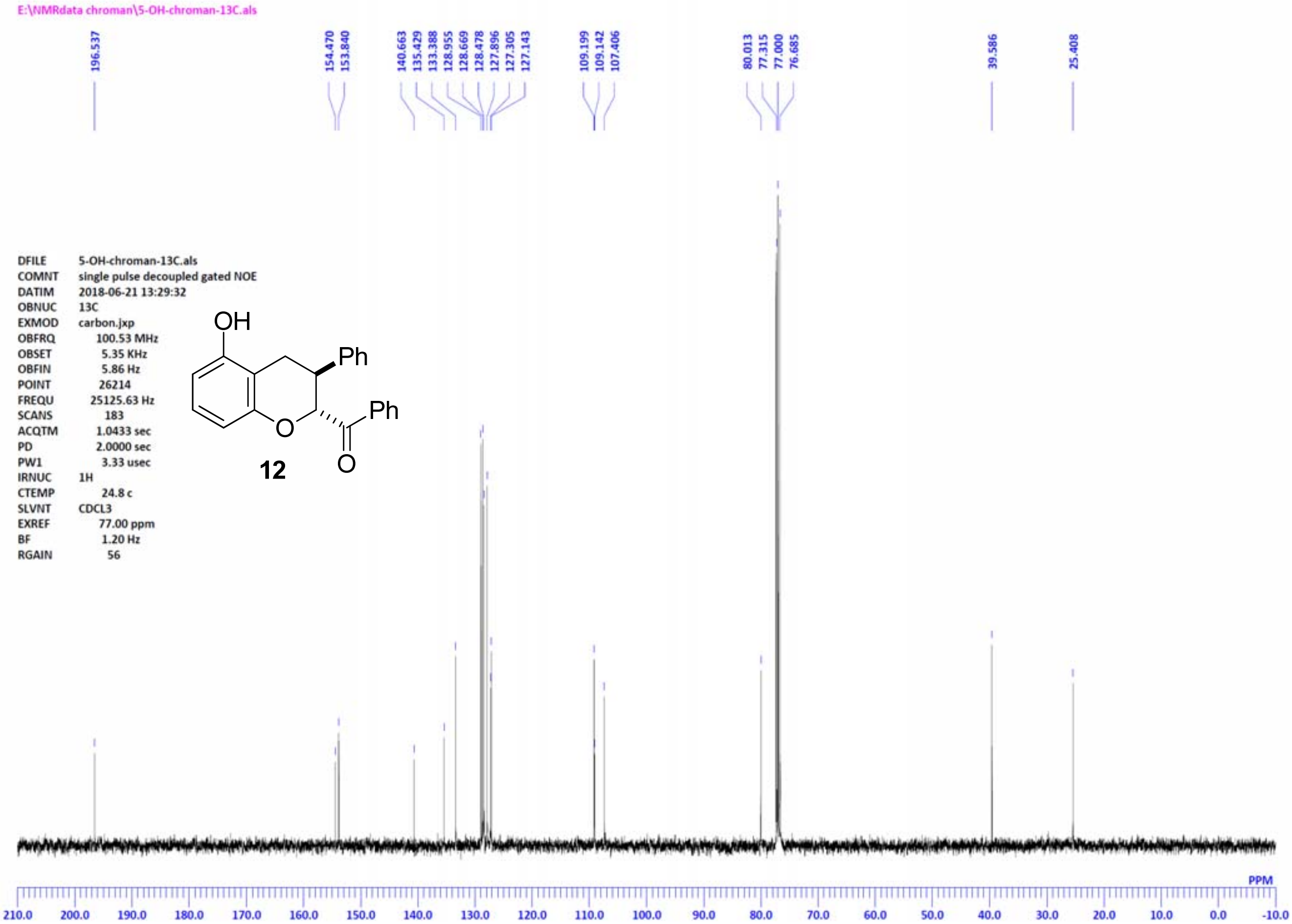

E:\NMRdata chroman\5-OH-chroman-1H.als
7.925
7.907
7.554
7.536
7.518
7.423
7.403
7.385
7.263
7.235
7.218
7.197
7.188
7.185
7.166
7.157
7.151
7.025
7.003
6.983
6.566
6.547
6.417
6.397
5.473
5.455
5.046
3.684
3.664
3.647
3.629
3.144
3.128
3.101
3.086
2.982
2.962
2.940
2.919
0.011
DFILE 5-OH-chroman-1H.als
COMNT single_pulse
DATIM 2018-06-21 17:35:57
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 8000.00 Hz
SCANS 8
ACQTM 1.6384 sec
PD 5.0000 sec
PW1 5.55 usec
IRNUC 1H
CTEMP 24.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 32
OH
Ph
O
Ph
O
12
1.97
1.09
2.00
5.64
1.04
0.95
0.97
1.00
0.94
1.10
1.03
1.00
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


E:\NMRdata chroman\5-OH-chroman-13C.als
196.537
154.470
153.840
140.663
135.429
133.388
128.955
128.669
128.478
127.896
127.305
127.143
109.199
109.142
107.406
80.013
77.315
77.000
76.685
39.586
25.408
DFILE 5-OH-chroman-13C.als
COMNT single pulse decoupled gated NOE
DATIM 2018-06-21 13:29:32
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 183
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.33 usec
IRNUC 1H
CTEMP 24.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 56
OH
Ph
O
Ph
O
12
PPM
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
-10.0