ASIAN JOURNAL
OF ORGANIC CHEMISTRY

Supporting Information

Recyclable Magnetic Nanoparticle-Supported Iodoarene Catalysts for Oxidation of 4-Alkoxyphenols to Quinones

Hisanori Nambu, Ikumi Shimokawa, Tomoya Fujiwara, and Takayuki Yakura*[a]

ajoc_201600036_sm_miscellaneous_information.pdf

Contents:

Experimental Section

General S2

I. Preparation of magnetic nanoparticle-supported iodoarene catalysts S3–S4

II. Preparation of phenols S4–S5

III. Oxidation of 4-alkoxyphenol **1a** to *p*-quinone **2a**

III-1. Typical procedure for the oxidation of *p*-alkoxyphenols **1** using magnetic nanoparticle-supported iodoarene catalyst S6

III-2. The recovered catalyst **4b** after 8 cycles S6

III-3. Recyclability of the catalyst **4b** with a reductive treatment S7

III-4. The catalyst **4b** after treatment with Oxone in the absence of substrate **1a** S7

IV. Oxidation of 4-alkoxyphenols **1** to *p*-quinones **2** S8–S10

References S10

IR spectra of Fe_3O_4 and silica-coated catalyst **4a** S11

IR spectra of azide **8** and phosphonic acid-coated catalyst **4b** S12

IR spectra of the recovered catalyst **4b** after 8 cycles and the catalyst **4b** after treatment with Oxone in the absence of substrate **1a** S13

^{1}H and ^{13}C NMR spectra of **1i**, **2a–g** S14–S21

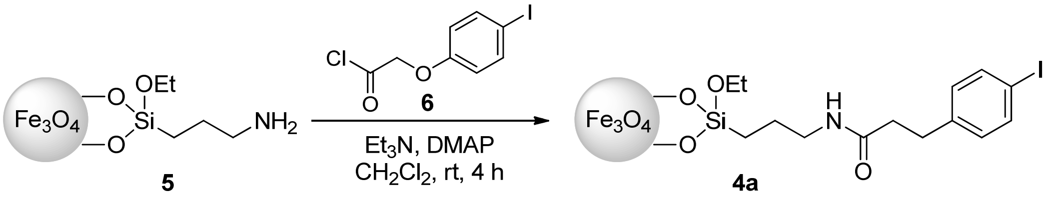
Experimental Section

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, 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. 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 hydroquinone (**1b**), 4-methoxyphenol (**1c**), 4-ethoxyphenol (**1d**), 3-*tert*-butyl-4-hydroxyanisole (**1e**), Oxone® and 0.1 M-phosphate buffer solution were 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. 2-Hydroxy-5-methoxybenzyl 2,2-dimethylpropanoate (**1a**)[1], 2-azidomethyl-4-methoxyphenol (**1f**)[1], 2-(*tert*-butyldiphenylsilyloxymethyl)-4-methoxyphenol (**1g**)[1] and ethyl 2-hydroxy-5-methoxyphenylpropanoate (**1h**)[2] were prepared according to literature procedures.

I. Preparation of magnetic nanoparticle-supported iodoarene catalysts

Silica-coated iodoarene catalyst 4a

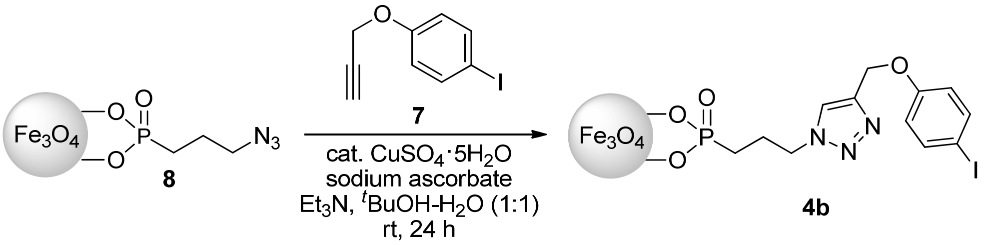


Magnetic nanoparticle-supported amine **5** was prepared according to literature procedure.[3] **5** (1.50 g) and 2-(4-iodophenoxy)acetyl chloride (249 mg, 0.84 mmol) were treated with Et_3N (255 mg, 2.52 mmol) in CH_2Cl_2 (8 mL). The reaction mixture was stirred at room temperature using mechanical stirrer for 4 h. The particles were collected at the bottom of the flask using an external magnet, and the supernatant carefully decanted. The catalyst was washed five times with EtOH. The particles were dried in vacuo to provide **4a** (1.51 g) as brown particles. The loading of **4a** was 0.087 mmol/g as determined by elemental analysis of iodine (1.11%).

Magnetite (Fe_3O_4): IR (KBr, cm^{-1}) ν 3444 (OH), 1633, 633 (Fe–O–Fe), 592 (Fe–O–Fe).

Silica-coated iodoarene catalyst **4a**: IR (KBr, cm^{-1}) ν 3339 (OH), 2980, 2952, 1488 (aryl), 1280 (NH_2), 1236 (Si–O–C, Si–C), 1056 (Si–O–C), 935 (Fe–O–Si), 847, 629 (Fe–O–Fe), 581(Fe–O–Fe).

Phosphonic acid-coated iodoarene catalyst 4b



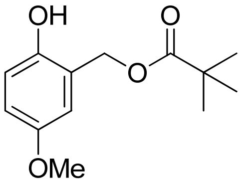
Magnetic nanoparticle-supported azide **8**[4] and 1-iodo-4-(prop-2-ynyloxy)benzene (**7**)[5] were prepared according to literature procedures. **8** (2.83 g) and **7** (924 mg, 3.58 mmol) were treated with $CuSO_4•5H_2O$ (41 mg, 5 mol%), sodium ascorbate (97 mg, 15 mol%) and Et_3N (0.9 mL, 6.50 mmol) in *t*-BuOH–H_2O (1:1, 14 mL). The reaction mixture was stirred at room temperature using mechanical stirrer for 24 h. The particles were collected at the bottom of the flask using an external magnet, and the supernatant carefully decanted. The catalyst was washed five times with EtOH, three times with acetone, and three times with Et_2O. After the particles were dried in vacuo, washed again three times with H_2O, three times with EtOH, three times with acetone, and three times with Et_2O. The particles were dried in vacuo to provide **4b** (2.38 g) as brown particles. The loading of **4b** was 0.33 mmol/g as determined by elemental analysis of iodine (4.2%).

Magnetic nanoparticle-supported azide **8**: IR (KBr, cm^{-1}) ν 3422 (OH), 2938, 2105 (N_3), 1629, 1445, 1410, 1348, 1303, 1285, 1248 (P=O), 1051 (Fe–O–P, P=O), 634 (Fe–O–Fe), 576 (Fe–O–Fe).

Phosphonic acid-coated iodoarene catalyst **4b**: IR (KBr, cm^{-1}) ν 3434 (OH), 2943, 2100 (N_3), 1627, 1583 (aryl), 1485 (aryl), 1462, 1404, 1281, 1239 (P=O), 1176, 1058 and 999 (Fe–O–P, P=O), 821, 631 (Fe–O–Fe), 591 (Fe–O–Fe).

II. Preparation of phenols

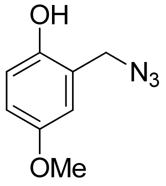
2-Hydroxy-5-methoxybenzyl 2,2-dimethylpropanoate (1a)[1] (Table 1, Table 2 and Table 3, entry 1)



1a

Mp 66.0–66.5 °C; IR (KBr, cm^{-1}) ν 3363, 2967, 1686, 1509, 1469, 1433, 1292, 1260, 1210, 1182, 1037, 948, 851, 830, 714; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 6.88 (d, J = 8.7 Hz, 1H), 6.85 (d, J = 2.8 Hz, 1H), 6.82 (dd, J = 8.7, 2.8 Hz, 1H), 5.07 (s, 2H), 3.77 (s, 3H), 1.91 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.9, 153.3, 149.3, 122.5, 118.6, 116.5, 63.4, 55.7, 38.9, 27.1.

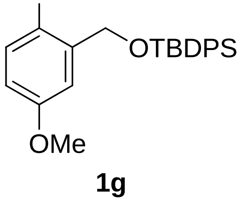
2-Azidomethyl-4-methoxyphenol (1f)[1] (Table 3, entry 6)



1f

Mp 35.0–37.0 °C; IR (KBr, cm^{-1}) ν 3330, 2998, 2120, 1513, 1435, 1343, 1271, 1216, 1198, 1161, 1048, 932, 863, 811, 719; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81–6.76 (m, 3H), 5.06 (br s, 1H), 4.39 (s, 2H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 148.1, 122.6, 116.9, 115.3, 114.9, 55.8, 51.0.

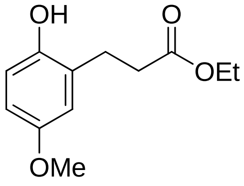
2-(*tert*-Butyldiphenylsilyloxymethyl)-4-methoxyphenol (1g)[1] (Table 3, entry 7)



1g

IR (film, cm^{-1}) ν 3395, 2932, 2857, 1499, 1465, 1428, 1377, 1241, 1154, 1114, 1041, 821, 742, 703, 611; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69–7.67 (m, 4H), 7.61 (br s, 1H), 7.46–7.38 (m, 6H), 6.85 (d, J = 8.7 Hz, 1H), 6.75 (dd, J = 8.7, 2.8 Hz, 1H), 6.34 (d, J = 2.8 Hz, 1H), 4.84 (s, 2H), 3.68 (s, 3H), 1.07 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 150.2, 135.5, 132.0, 130.1, 127.9, 124.5, 117.2, 114.1, 112.4, 66.5, 55.7, 26.7, 19.1.

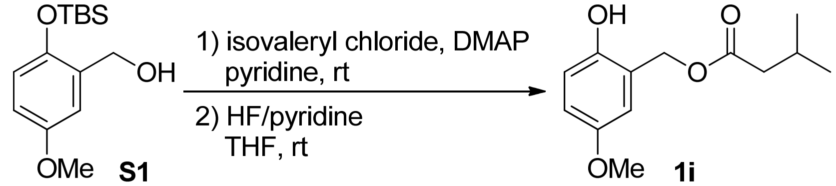
Ethyl 2-hydroxy-5-methoxyphenylpropanoate (1h)[1] (Table 3, entry 8)



1h

IR (film, cm^{-1}) ν 3714, 2939, 2834, 1710, 1509, 1433, 1375, 1209, 1111, 1042, 859, 810, 713; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (br s, 1H), 6.82 (d, *J* = 8.7 Hz, 1H), 6.68 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.64 (d, *J* = 2.7 Hz, 1H), 4.14 (q, *J* = 7.3 Hz, 2H), 3.75 (s, 3H), 2.87 (t, *J* = 6.9 Hz, 2H), 2.71 (t, *J* = 6.9 Hz, 2H), 1.23 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7, 153.7, 148.1, 128.3, 118.1, 115.7, 112.9, 61.3, 55.7, 35.3, 24.7, 14.1.

2-Hydroxy-5-methoxybenzyl 3-methylbutanoate (1i) (Table 3, entry 9)



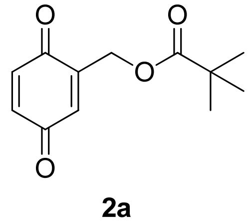
Isovaleryl chloride (0.23 mL, 1.88 mmol) and DMAP (7.7 mg, 0.063 mmol) were added to a solution of 2-(*tert*-butyldimethylsilanyloxy)-5-methoxybenzylalcohol (**S1**)[6] (336 mg, 1.253 mmol) in pyridine (1.9 mL). After stirring at room temperature for 2 h, the reaction was quenched by addition of aqueous 10% HCl (2 mL), and the resulting mixture was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with aqueous 10% HCl (20 mL), H_2O (20 mL) and brine (20 mL), and dried over anhydrous Na_2SO_4. Filtration was concentrated in vacuo to provide crude product (424 mg), which was used in the next step without further purification.

HF/pyridine (50 drops) was added to a solution of crude product in THF (12 mL). After stirring at room temperature for 19 h, the reaction was quenched by addition of saturated aqueous $NaHCO_3$ (15 mL), and the resulting mixture was extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with H_2O (20 mL) and brine (20 mL), and dried over anhydrous Na_2SO_4. Filtration was concentrated in vacuo, and the residue was purified by column chromatography (silica gel, 20% EtOAc in hexane) to provide **1i** (269 mg, 90%) as a colorless oil: IR (film, cm^{-1}) ν 3386, 2960, 2872, 2835, 1728, 1704, 1509, 1466, 1434, 1380, 1355, 1295, 1266, 1203, 1162, 1120, 1099, 1045, 1004, 981, 815, 742, 714; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (br s, 1H), δ 6.88 (d, *J* = 8.8 Hz, 1H), 6.84 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.80 (d, *J* = 2.8 Hz, 1H), 5.08 (s, 2H), 3.77 (s, 3H), 2.23 (d, *J* = 6.8 Hz, 2H), 2.09 (m, 1H), 0.92 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 153.3, 149.3, 122.4, 118.7, 116.8, 116.5, 63.0, 55.7, 43.1, 25.7, 22.3; HRMS (EI) *m/z* calcd for $C_{15}H_{12}O$ (M^+) 238.1205, found 238.1188.

III. Oxidation of 4-alkoxyphenol 1a to *p*-quinone 2a

III-1. Typical procedure for the oxidation of *p*-alkoxyphenols 1 using magnetic nanoparticle-supported iodoarene catalyst:

3,6-Dioxocyclohexa-1,4-dienylmethyl 2,2-dimethylpranoate (2a)[1] (Table 2, cycle 1 and Table 3, entry 1)



2a

Magnetic nanoparticle-supported iodoarene catalyst **4b** (121 mg, 0.04 mmol, 10 mol%) was added to a solution of 2-hydroxy-5-methoxybenzyl 2,2-dimethylpropanoate (**1a**) (95 mg, 0.40 mmol) and Oxone (246 mg, 0.40 mmol) in CF_3CH_2OH–0.1 M phosphate buffer (2.0 mL, 1:2). The reaction mixture was stirred at room temperature using mechanical stirrer for 4 h. The catalyst **4b** was collected at the bottom of the flask using an external magnet, and the supernatant carefully decanted. The catalyst **4b** was washed three times with EtOAc, three times with H_2O, three times with acetone, two times with Et_2O, and dried in vacuo. Then, the recovered catalyst **4b** was reused in the next reaction cycle. The organic layer was washed with H_2O and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (silica gel, 10% EtOAc in hexane) to provide **2a** (71 mg, 80%) as a yellow crystals: mp 70.0–72.0 °C; IR (KBr, cm^{-1}) ν 3060, 2987, 2946, 2878, 1735, 1658, 1484, 1440, 1328, 1278, 1085, 1038, 924; ^1H NMR (400 MHz, $CDCl_3$) δ 6.80 (d, J = 10.0 Hz, 1H), 6.77 (dd, J = 10.0 , 2.3 Hz, 1H), 6.65 (q, J = 2.3 Hz, 1H), 4.99 (d, J = 2.3 Hz, 2H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.0, 186.1, 177.5, 143.6, 136.6, 136.5, 131.1, 59.4, 38.9, 27.2.

III-2. The recovered catalyst 4b after 8 cycles

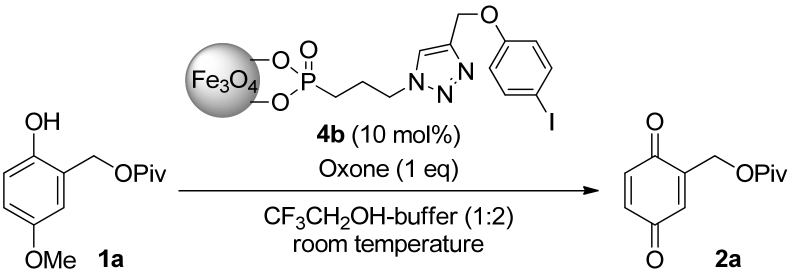
The loading of the catalyst **4b** after 8 cycles was 0.043 mmol/g as determined by elemental analysis of nitrogen (0.18%). [Elemental analysis of iodine could not be performed.]

The recovered catalyst **4b** was also analyzed by using IR spectroscopy. The bands that are characteristic of the catalyst **4b** were much weaker than those obtained from the original catalyst **4b**. Therefore, the loading of the recovered catalyst **4b** is very low.

IR (KBr, cm^{-1}) ν 3400 (OH), 2963, 1634, 1262 (P=O), 1042 (Fe–O–P, P=O), 804, 628 (Fe–O–Fe), 563 (Fe–O–Fe)

III-3. Recyclability of the catalyst 4b with a reductive treatment

Table S1.



With a reductive treatment using sat. $Na_2S_2O_3$ solution

Cycle	Time (h)	Yield (%)	Recovery of **4b** (%)
1	3.5	79	95
2	5.5	85	97
3	7.5	84	99
4	7.5	78	96
5	11.5	82	99

Without a reductive treatment

Cycle	Time (h)	Yield (%)	Recovery of **4b** (%)
1	4	80	98
2	4	81	97
3	5.5	80	98
4	7.5	82	96
5	8	82	96

The reactivity of the recovered catalyst **4b** with a reductive treatment using sat. $Na_2S_2O_3$ solution was almost the same as that of **4b** without a reductive treatment. Therefore, a reductive treatment after the reaction is not necessary.

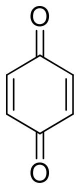
III-4. The catalyst 4b after treatment with Oxone in the absence of substrate 1a

The IR spectrum of the recovered catalyst **4b** after treatment with Oxone in the absence of substrate **1a** for 4 h was almost the same as that of the original catalyst **4b**. This result indicated that the structure of the catalyst **4b** was almost unchanged by using Oxone.

IR (KBr, cm^{-1}) ν 3434 (OH), 2106 (N_3), 1632, 1574 (aryl), 1486 (aryl), 1405, 1302, 1248 (P=O), 1048 (Fe–O–P, P=O), 823, 634 (Fe–O–Fe), 592 (Fe–O–Fe).

IV. Oxidation of 4-alkoxyphenols 1 to *p*-quinones 2

1,4-Benzoquinone (2b) (Table 3, entry 2)



2b

According to the typical procedure for the oxidation of *p*-alkoxyphenols, hydroquinone (**1b**) (44 mg, 0.40 mmol) was treated with catalyst **4b** (121 mg, 0.04 mmol, 10 mol%) and Oxone (246 mg, 0.40 mmol) in CF_3CH_2OH–0.1 M phosphate buffer (2.0 mL, 1:2). After stirring at room temperature for 0.5 h, the product **2b** (35 mg, 81%) was provided as yellow crystals, which was directly identical to the commercial sample supplied by Nacalai Tesque, INC: IR (KBr, cm^{-1}) ν 3056, 1655, 1591, 1505, 1307, 1211, 1085, 943, 896; ^1H NMR (400 MHz, $CDCl_3$): δ 6.79 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.2 ,136.5.

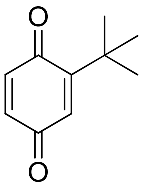
1,4-Benzoquinone (2b) (Table 3, entry 3)

According to the typical procedure for the oxidation of *p*-alkoxyphenols, 4-methoxyphenol (**1c**) (50 mg, 0.40 mmol) was treated with catalyst **4b** (121 mg, 0.04 mmol, 10 mol%) and Oxone (246 mg, 0.40 mmol) in CF_3CH_2OH–0.1 M phosphate buffer (2.0 mL, 1:2). After stirring at room temperature for 2 h, the product **2b** (41 mg, 95%) was provided as yellow crystals.

1,4-Benzoquinone (2b) (Table 3, entry 4)

According to the typical procedure for the oxidation of *p*-alkoxyphenols, 4-ethoxyphenol (**1d**) (55 mg, 0.40 mmol) was treated with catalyst **4b** (121 mg, 0.04 mmol, 10 mol%) and Oxone (246 mg, 0.40 mmol) in CF_3CH_2OH–0.1 M phosphate buffer (2.0 mL, 1:2). After stirring at room temperature for 3 h, the product **2b** (40 mg, 93%) was provided as yellow crystals.

2-*tert*-Butyl-1,4-benzoquinone (2c) (Table 3, entry 5)

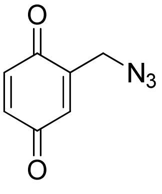


2c

According to the typical procedure for the oxidation of *p*-alkoxyphenols, 3-*tert*-butyl-4-hydroxyanisole (**1e**) (72 mg, 0.40 mmol) was treated with catalyst **4b** (121 mg, 0.04 mmol, 10 mol%) and Oxone (246 mg, 0.40 mmol) in CF_3CH_2OH–0.1 M phosphate buffer (2.0 mL, 1:2). After stirring at room temperature for 2.5 h, the crude product was purified by column chromatography (silica gel, 5% EtOAc in hexane) to provide **2c** (48 mg, 73%) as yellow crystals, which was directly identical to the commercial sample supplied by Tokyo Chemical Industry Co., Ltd.: mp 53.0–54.5 °C; IR (KBr, cm^{-1}) ν 3060, 2999, 2961, 2872, 1656, 1590, 1485, 1462, 1367, 1339, 1289, 1108, 1013, 934, 923, 834; ^1H NMR (400 MHz, $CDCl_3$): δ 6.68 (s, 2H), 6.60 (s, 1H), 1.29

(s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.4, 187.4, 156.0, 138.7, 134.9, 131.5, 35.2, 29.1.

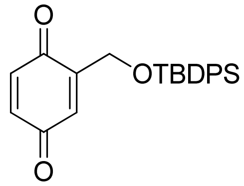
2-Azidomethyl-1,4-benzoquinone (2d)[1] (Table 3, entry 6)



2d

According to the typical procedure for the oxidation of *p*-alkoxyphenols, 2-azidomethyl-4-methoxyphenol (**1f**) (72 mg, 0.40 mmol) was treated with catalyst **4b** (121 mg, 0.04 mmol, 10 mol%) and Oxone (246 mg, 0.40 mmol) in CF_3CH_2OH–0.1 M phosphate buffer (2.0 mL, 1:2). After stirring at room temperature for 2.5 h, the crude product was purified by column chromatography (silica gel, 10% EtOAc in hexane) to provide **2d** (44 mg, 68%) as yellow crystals: mp 63.0–64.5 °C; IR (KBr, cm^{-1}) ν 2103, 1661, 1602, 1316, 1292, 1271, 1129, 1070, 934, 911; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83–6.77 (m ,3H), 4.29 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.9, 186.3, 142.8, 136.8, 136.4, 132.7, 48.5.

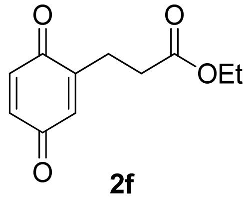
2-(*tert*-Butyldiphenylsilyloxymethyl)-1,4-benzoquinone (2e)[1] (Table 3, entry 7)



2e

According to the typical procedure for the oxidation of *p*-alkoxyphenols, 2-(*tert*-butyldiphenylsilyloxymethyl)-4-methoxyphenol (**1g**) (157 mg, 0.40 mmol) was treated with catalyst **4b** (121 mg, 0.04 mmol, 10 mol%) and Oxone (246 mg, 0.40 mmol) in CF_3CH_2OH–0.1 M phosphate buffer (2.0 mL, 3:1). After stirring at room temperature for 4 h, the crude product was purified by column chromatography (silica gel, 10% EtOAc in hexane) to provide **2e** (119 mg, 79%) as yellow crystals: mp 79.0–80.0 °C; IR (KBr, cm^{-1}) ν 3040, 2947, 2887, 2858, 1656, 1470, 1429, 1324, 1281, 1137, 1110, 1043, 920, 834, 705, 617, 501; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65–7.63 (m ,4H), 7.44–7.37 (m ,6H), 7.04 (td, J = 2.8, 2.4 Hz, 1H), 6.74 (dd, J = 10.4, 2.8 Hz, 1H), 6.69 (d, J = 10.4 Hz, 1H), 4.58 (d, J = 2.4 Hz, 2H), 1.10 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.7, 187.1, 148.0, 136.6, 136.4, 135.4, 132.5, 130.6, 130.0, 127.9, 59.8, 26.8, 19.3.

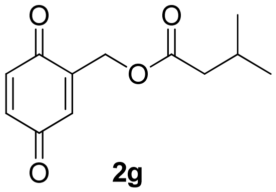
Ethyl 3-(3,6-dioxocyclohexa-1,4-dienyl)propanoate (2f) (Table 3, entry 8)



2f

According to the typical procedure for the oxidation of *p*-alkoxyphenols, ethyl 2-hydroxy-5-methoxyphenylpropanoate (**1h**) (90 mg, 0.40 mmol) was treated with catalyst **4b** (121 mg, 0.04 mmol, 10 mol%) and Oxone (246 mg, 0.40 mmol) in CF_3CH_2OH–0.1 M phosphate buffer (2.0 mL, 1:2). After stirring at room temperature for 3 h, the crude product was purified by column chromatography (silica gel, 20% EtOAc in hexane) to provide **2f** (62 mg, 75%) as yellow oil: IR (film, cm^{-1}) ν 2983, 2934, 1734, 1657, 1601, 1374, 1295, 1188, 1084, 1039, 909; ^1H NMR (400 MHz, $CDCl_3$): δ 6.78 (d, *J* = 10.1 Hz, 1H), 6.73 (dd, *J* = 10.1, 2.3 Hz, 1H), 6.60 (dt, *J* = 2.3, 1.4 Hz, 1H), 4.14 (q, *J* = 7.3 Hz, 2H), 2.77 (td, *J* = 7.3, 1.4 Hz, 2H), 2.57 (t, *J* = 7.3 Hz, 2H), 1.25 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.4, 187.1, 171.9, 147.5, 136.8, 136.4, 133.0, 60.8, 32.0, 24.6, 14.2; HRMS (EI) *m/z* calcd for $C_{15}H_{12}O$ (M^+) 208.0888, found 208.0888.

3,6-Dioxocyclohexa-1,4-dienylmethyl 3-methylbutanoate (blattellaquinone) (2g)[7] (Table 3, entry 9)


2g

According to the typical procedure for the oxidation of *p*-alkoxyphenols, ethyl 2-hydroxy-5-methoxyphenylpropanoate (**1i**) (90 mg, 0.40 mmol) was treated with catalyst **4b** (121 mg, 0.04 mmol, 10 mol%) and Oxone (246 mg, 0.40 mmol) in CF_3CH_2OH–0.1 M phosphate buffer (2.0 mL, 1:2). After stirring at room temperature for 4 h, the crude product was purified by column chromatography (silica gel, 10% EtOAc in hexane) to provide **2g** (68 mg, 76%) as yellow crystal: IR (film, cm^{-1}) ν 3059, 2961, 2873, 1744, 1649, 1602, 1470, 1422, 1359, 1326, 1286, 1181, 1168, 1135, 1086, 1011, 927; ^1H NMR (400 MHz, $CDCl_3$): δ 6.80 (d, *J* = 10.8 Hz, 1H), 6.77 (dd, *J* = 10.8, 2.0 Hz, 1H), 6.69 (br q, *J* = 2.0 Hz, 1H), 5.00 (d, *J* = 2.0 Hz, 2H), 2.30 (d, *J* = 6.8 Hz, 2H), 2.14 (m, 1H), 0.99 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.0, 186.1, 172.1, 143.3, 136.6, 136.5, 131.5, 59.2, 43.0, 25.6, 22.4.

References

[1] T. Yakura, Y. Tian, Y. Yamauchi, M. Omoto, T. Konishi, *Chem. Pharm. Bull.* **2009**, *57*, 252–256.

[2] C. D. Gutsche, B. A. M. Oude-Alink, *J. Am. Chem. Soc.* **1968**, *90*, 5855–5861.

[3] K. Fujita, S. Umeki, H. Yasuda, *Synlett* **2013**, *24*, 947–950.

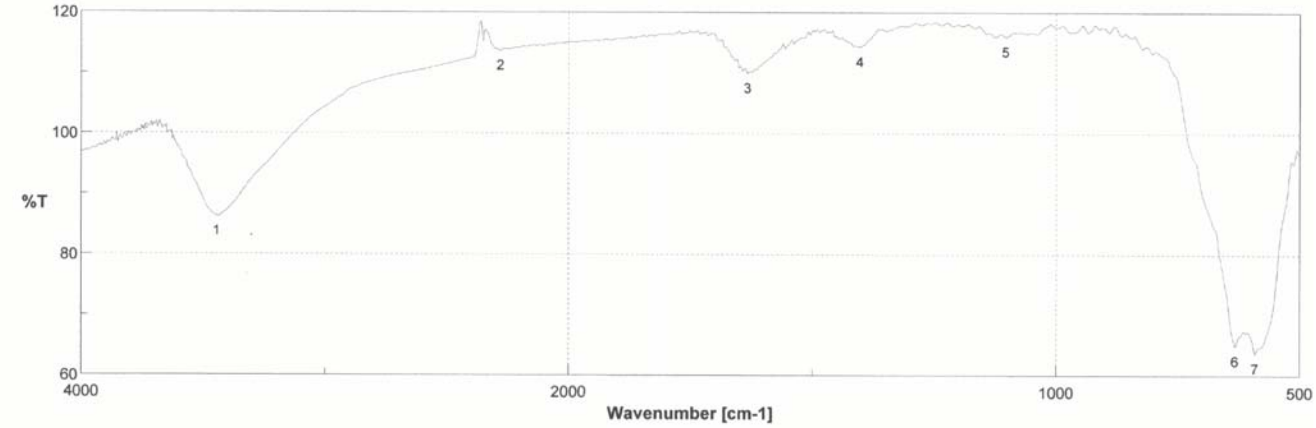
[4] A. K. Tucker-Schwartz, R. L. Garrell, *Chem. Eur. J.* **2010**, *16*, 12718–12726.

[5] a) M. Pal, K. Parasuraman, K. R. Yeleswarapu, *Org. Lett.* **2003**, *5*, 349–352; b) D. James, J.-M. Escudier, E. Amigues, J. Schulz, C. Vitry, T. Bordenave, M. Szlosek-Pinaud, E. Fouquet, *Tetrahedron Lett.* **2010**, *51*, 1230–1232.

[6] R. Manetsch, L. Zheng, M. T. Reymond, W.-D. Woggon, J.-L. Reymond, *Chem. Eur. J.* **2004**, *10*, 2487–2506.

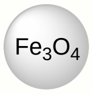
[7] a) S. Nojima, C. Schal, F. X. Webster, R. G. Santangelo, W. L. Roelofs, *Science* **2005**, *307*, 1104–1106; b) T. Yakura, M. Omoto, Y. Yamauchi, Y. Tian, A. Ozono, *Tetrahedron* **2010**, *66*, 5833–5840.

IR spectrum of Fe_3O_4



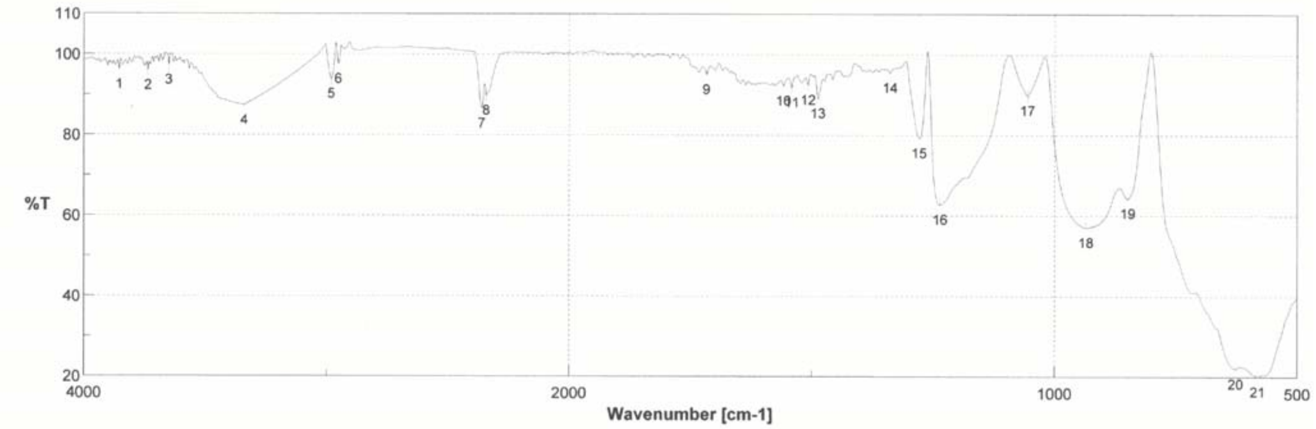
積算回数	32
ゼロフィリング	ON
ゲイン	Auto (8)
スキャンスピード	Auto (2 mm/sec)
測定日時	2016/01/28 16:50
測定者	
ファイル名	Fe304
サンプル名	Fe304
コメント	KBr

分解	4 cm-1
アポダイゼーション	Cosine
アパーチャー	Auto (7.1 mm)
更新日時	2016/01/28 16:52



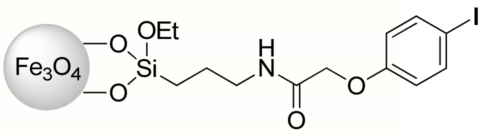
No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T
1	3444	86	2	2279	114	3	1633	110	4	1403	114	5	1104	116
6	633	65	7	592	64									

IR spectrum of silica-coated catalyst 4a



積算回数	Auto (162)
ゼロフィリング	ON
ゲイン	Auto (16)
スキャンスピード	Auto (2 mm/sec)
測定日時	2015/10/30 15:01
測定者	
ファイル名	341110
サンプル名	341110
コメント	KBr

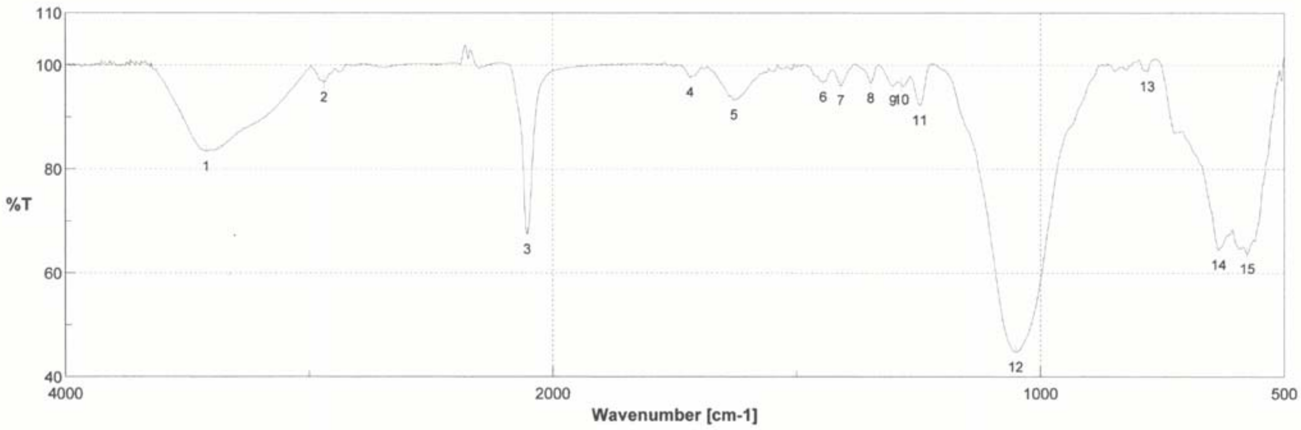
分解	4 cm-1
アポダイゼーション	Cosine
アパーチャー	Auto (7.1 mm)
更新日時	2016/02/01 15:09



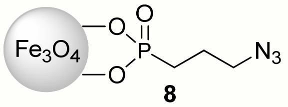
4a

No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T
1	3854	96	2	3735	96	3	3650	97	4	3339	87	5	2980	94
6	2952	98	7	2360	87	8	2342	90	9	1717	95	10	1559	92
11	1542	92	12	1508	92	13	1488	89	14	1339	96	15	1280	79
16	1236	63	17	1056	90	18	935	57	19	849	64	20	627	22
21	581	20												

IR spectrum of azide 8



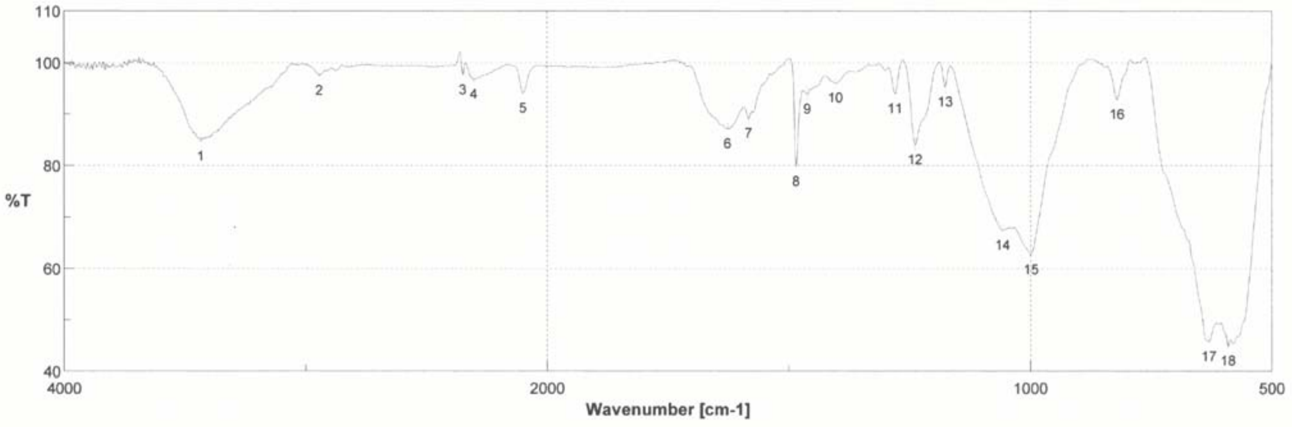
積算回数	32
ゼロフィリング	ON
ゲイン	Auto (16)
スキャンスピード	Auto (2 mm/sec)
測定日時	2016/01/28 17:23
測定者	
ファイル名	Memory#2
サンプル名	343082
コメント	KBr
分解	4 cm-1
アポダイゼーション	Cosine
アパーチャー	Auto (7.1 mm)
更新日時	2016/01/28 17:25



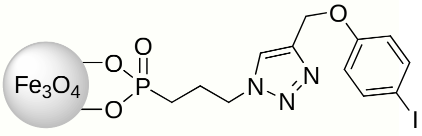
8

No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T
1	3422	83	2	2938	97	3	2105	67	4	1718	98	5	1629	93
6	1445	97	7	1410	96	8	1348	97	9	1303	96	10	1285	96
11	1248	92	12	1051	45	13	781	99	14	634	64	15	576	64

IR spectrum of phosphonic acid-coated catalyst 4b



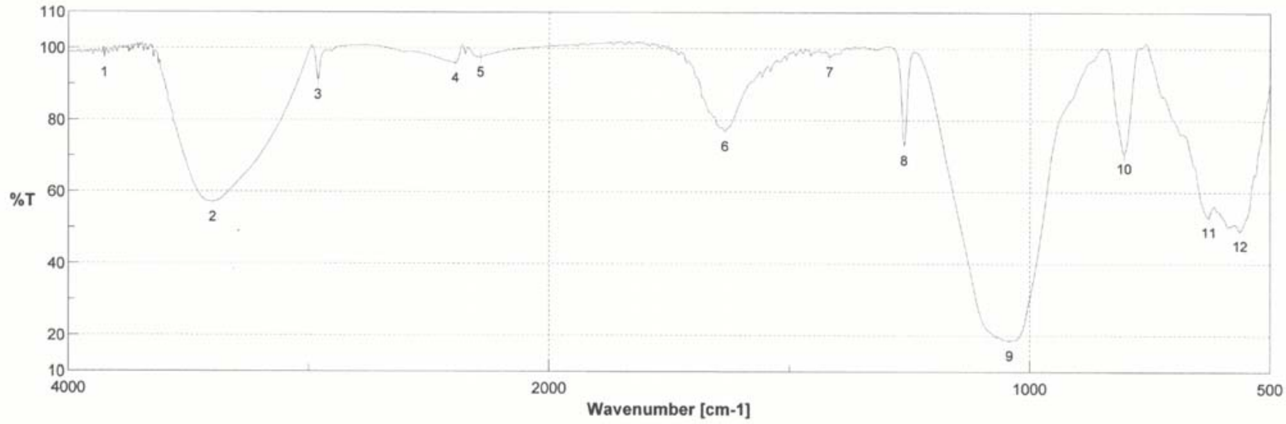
積算回数	32
ゼロフィリング	ON
ゲイン	Auto (32)
スキャンスピード	Auto (2 mm/sec)
測定日時	2016/01/28 17:10
測定者	
ファイル名	Memory#2
サンプル名	343043
コメント	KBr
分解	4 cm-1
アポダイゼーション	Cosine
アパーチャー	Auto (7.1 mm)
更新日時	2016/01/28 17:16



4b

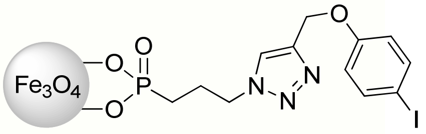
No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T
1	3434	85	2	2943	97	3	2349	98	4	2304	97	5	2100	94
6	1627	87	7	1583	89	8	1485	80	9	1462	94	10	1404	96
11	1281	94	12	1239	84	13	1176	95	14	1058	67	15	999	63
16	821	93	17	631	46	18	591	45						

IR spectrum of the recovered catalyst 4b after 8 cycles



積算回数 32
ゼロフィリング ON
ゲイン Auto (16)
スキャンスピード Auto (2 mm/sec)
測定日時 2016/01/19 13:35
測定者
ファイル名 343099
サンプル名 343099
コメント KBr

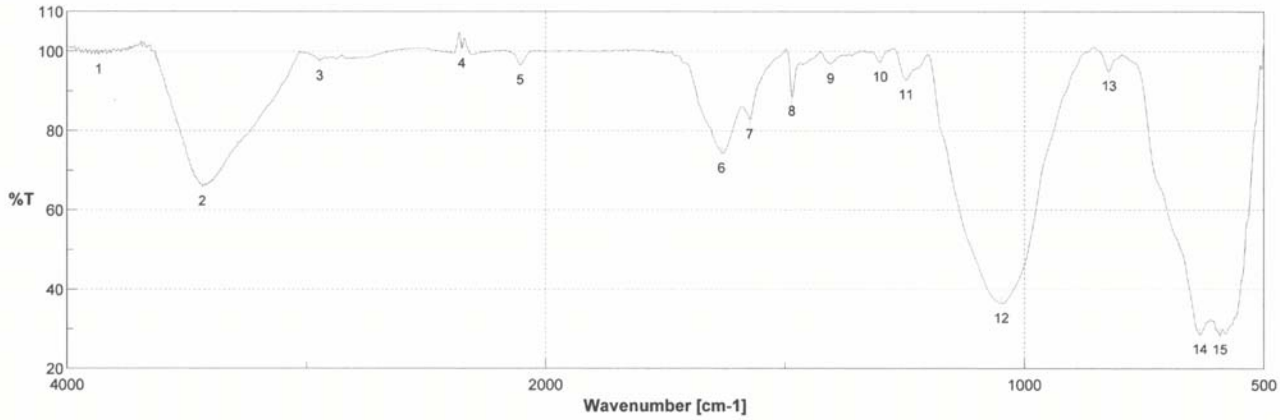
分解 4 cm-1
アポダイゼーション Cosine
アパーチャー Auto (7.1 mm)
更新日時 2016/01/28 17:30



4b after 8 cycles

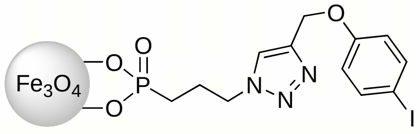
No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T
1	3852	97	2	3400	57	3	2963	91	4	2390	96	5	2286	97
6	1634	77	7	1417	98	8	1262	73	9	1042	19	10	804	71
11	628	53	12	563	49									

IR spectrum of the catalyst 4b after treatment with Oxone in the absence of substrate 1a



積算回数 32
ゼロフィリング ON
ゲイン Auto (16)
スキャンスピード Auto (2 mm/sec)
測定日時 2016/01/28 17:35
測定者
ファイル名 Memory#2
サンプル名 344110
コメント KBr

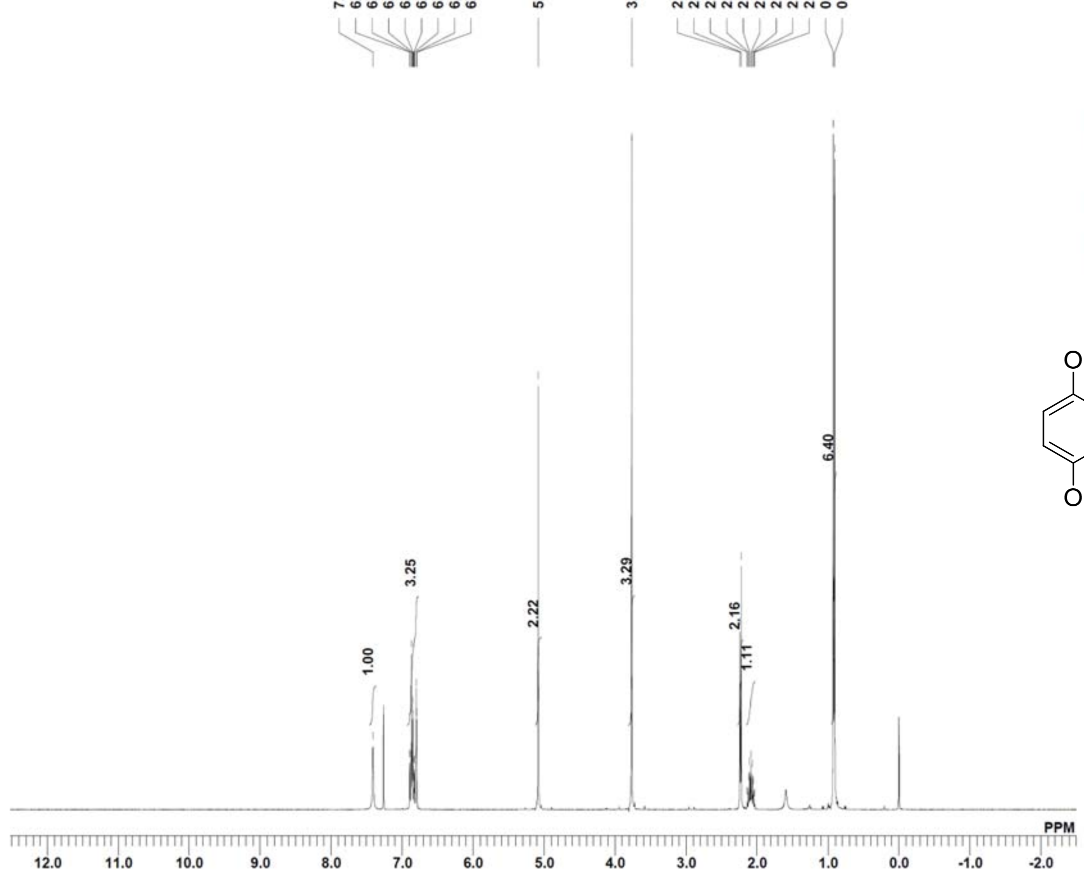
分解 4 cm-1
アポダイゼーション Cosine
アパーチャー Auto (7.1 mm)
更新日時 2016/01/28 17:38



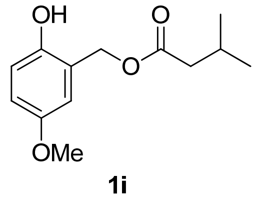
4b after treatment with Oxone

No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T
1	3868	99	2	3434	66	3	2944	98	4	2350	101	5	2106	97
6	1632	74	7	1574	83	8	1486	89	9	1405	97	10	1302	97
11	1248	93	12	1048	36	13	823	95	14	634	29	15	592	29

\\tsclient\F_344060 1H data.als
single_pulse

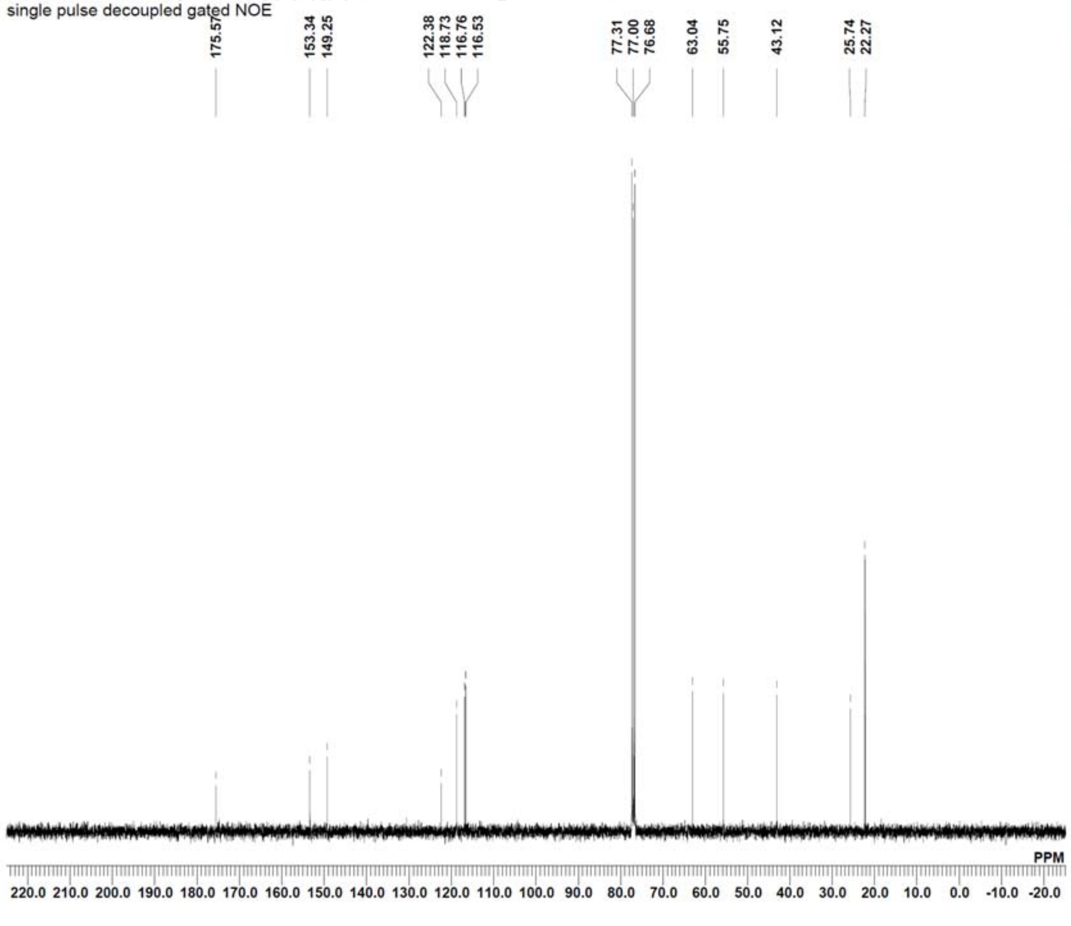


DFILE	_344060 1H data.als
COMNT	single_pulse
DATIM	2015-11-12 17:58:37
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.40 Hz
SCANS	8
ACQTM	2.1837 sec
PD	5.0000 sec
PW1	5.05 usec
IRNUC	1H
CTEMP	24.7 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	1.00 Hz
RGAIN	36

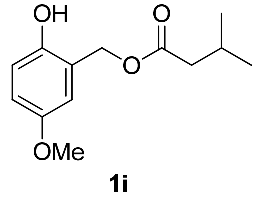


1i

C:\Documents and Settings\XPMUser\ƒƒXƒNƒgƒbƒv\NMR 13C 20151212_344060 13C-1 Full.als
single pulse decoupled gated NOE

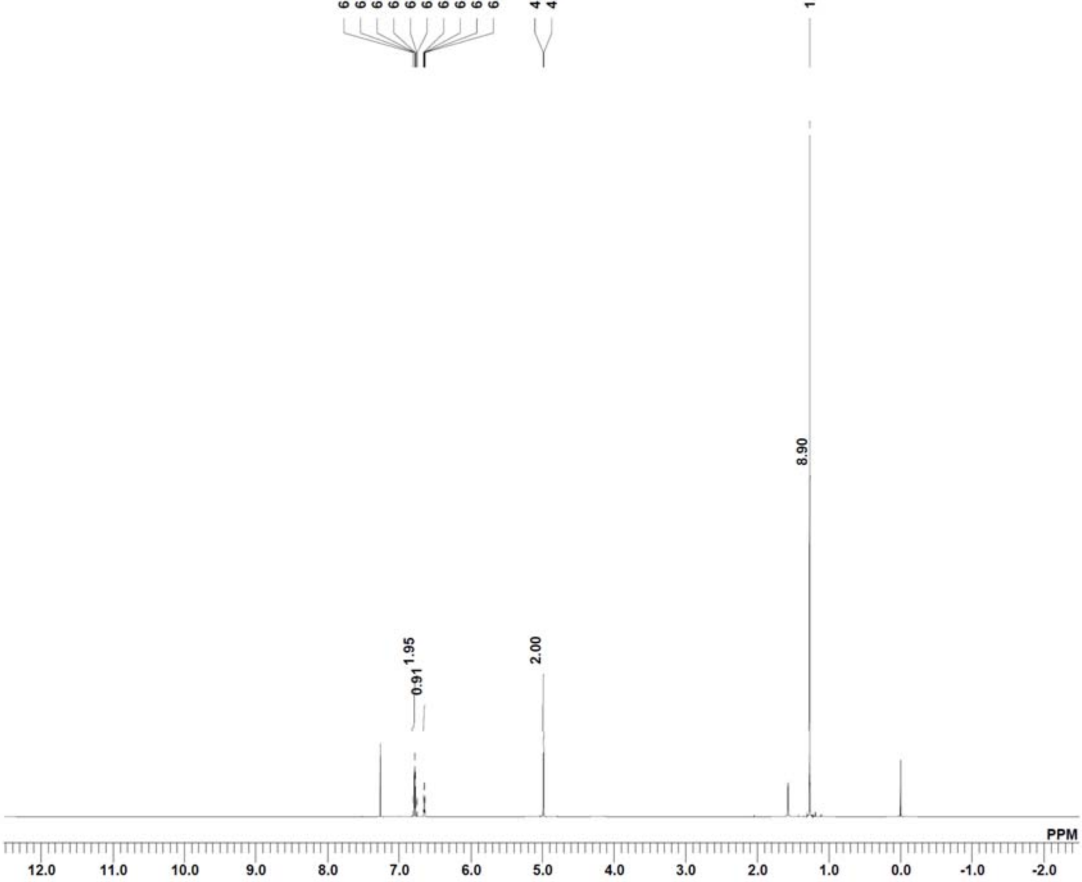


DFILE	_344060 13C-1 Full.als
COMNT	single pulse decoupled g
DATIM	2015-11-12 18:08:44
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.63 Hz
SCANS	219
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.22 usec
IRNUC	1H
CTEMP	24.9 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.00 Hz
RGAIN	56

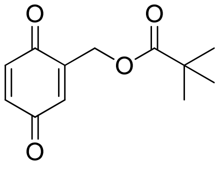


1i

C:\Documents and Settings\XPMUser\ƒƒXƒNƒgƒbƒv\NMR 20151211_343188 1H data.als
single_pulse

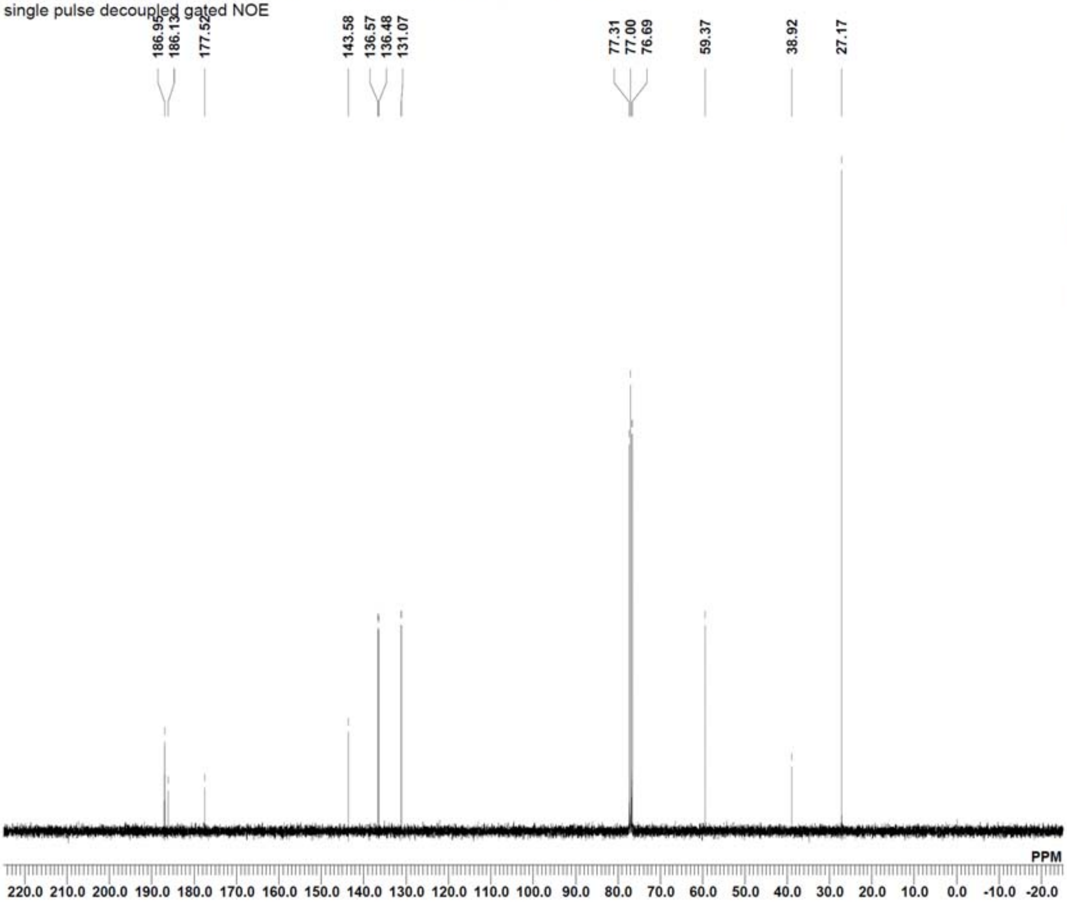


DFILE	_343188 1H data.als
COMNT	single_pulse
DATIM	2015-09-02 16:42:09
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.40 Hz
SCANS	8
ACQTM	2.1837 sec
PD	5.0000 sec
PW1	5.05 usec
IRNUC	1H
CTEMP	24.8 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	38

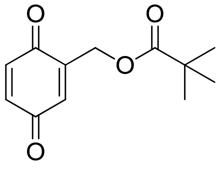


2a

C:\Documents and Settings\XPMUser\ƒƒXƒNƒgƒbƒv\NMR 13C 20151212_343188 13C-1 Full.als
single pulse decoupled gated NOE

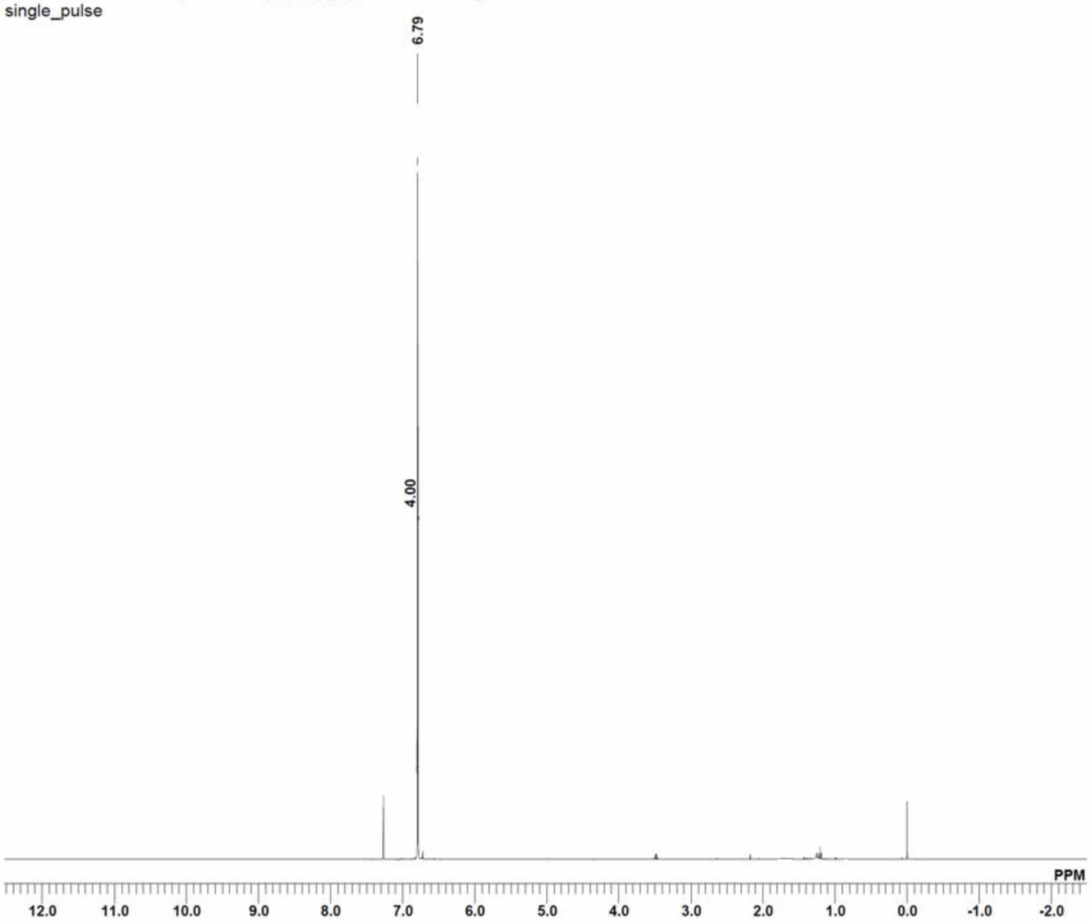


DFILE	_343188 13C-1 Full.als
COMNT	single pulse decoupled
DATIM	2015-12-10 14:23:36
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.63 Hz
SCANS	275
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.22 usec
IRNUC	1H
CTEMP	25.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	56

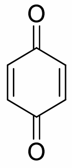


2a

C:\Documents and Settings\XPMUser\ƒƒXƒNƒgƒbƒv\NMR 20151211_344063 1H data.als
single_pulse

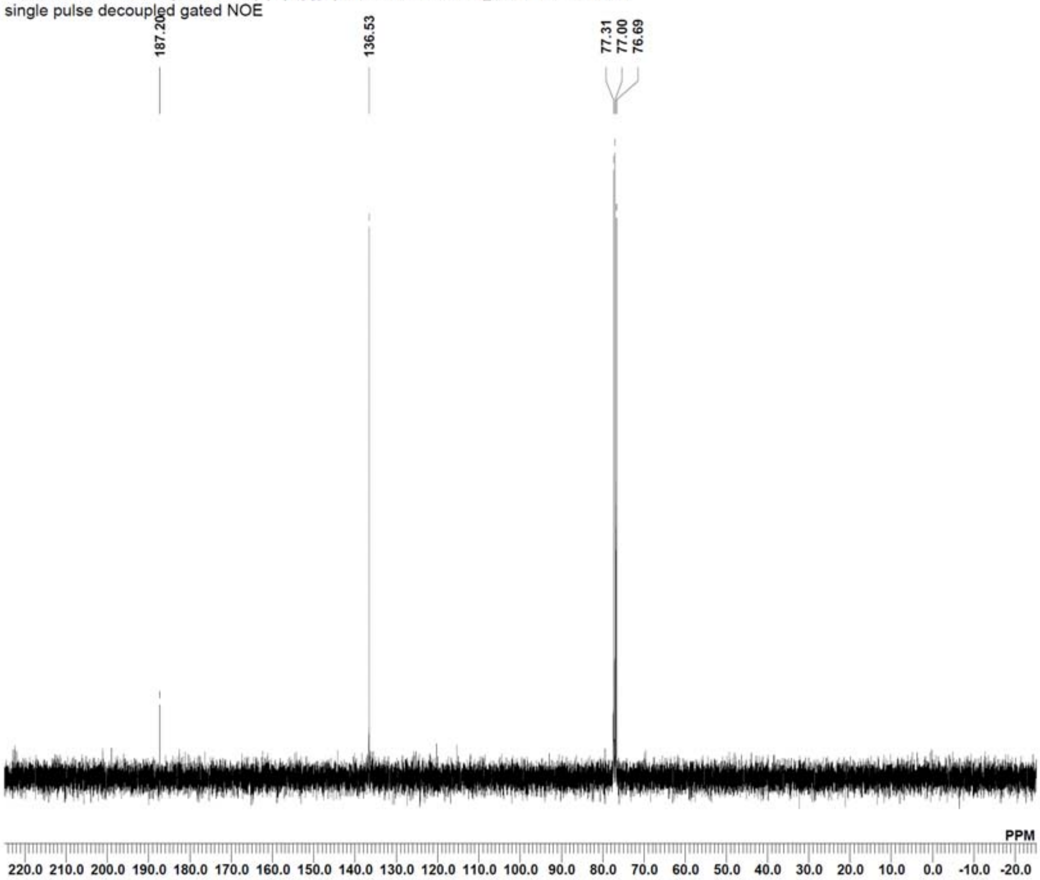


DFILE	_344063 1H data.als
COMNT	single_pulse
DATIM	2015-11-13 13:17:08
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.40 Hz
SCANS	8
ACQTM	2.1837 sec
PD	5.0000 sec
PW1	5.05 usec
IRNUC	1H
CTEMP	24.9 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	38

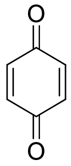


2b

C:\Documents and Settings\XPMUser\ƒƒXƒNƒgƒbƒv\NMR 13C 20151212_343197 13C-1 Full.als
single pulse decoupled gated NOE

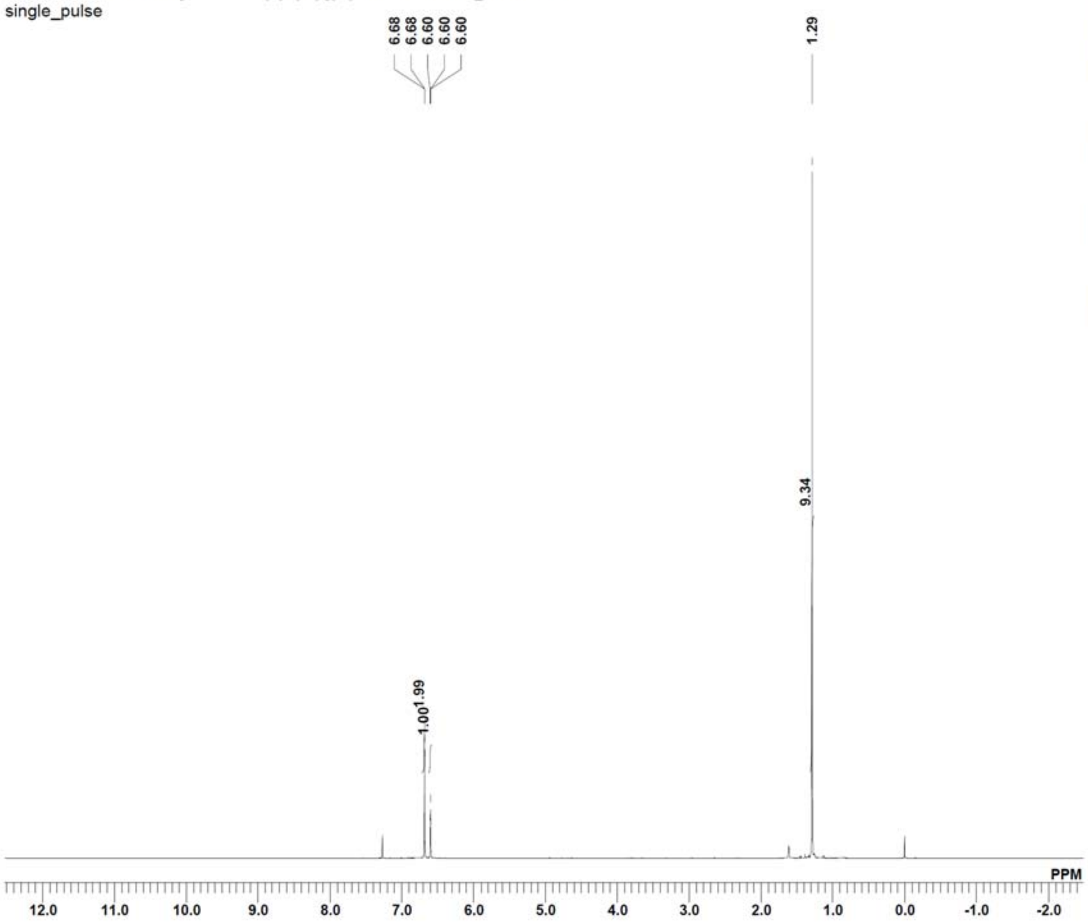


DFILE	_343197 13C-1 Full.als
COMNT	single pulse decouple
DATIM	2015-07-28 15:48:53
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.63 Hz
SCANS	347
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.22 usec
IRNUC	1H
CTEMP	25.5 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	58

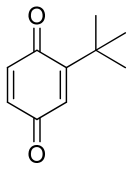


2b

C:\Documents and Settings\XPMUser\ƒƒXƒNƒgƒbƒv\NMR 20151211_344008 1H data.als
single_pulse

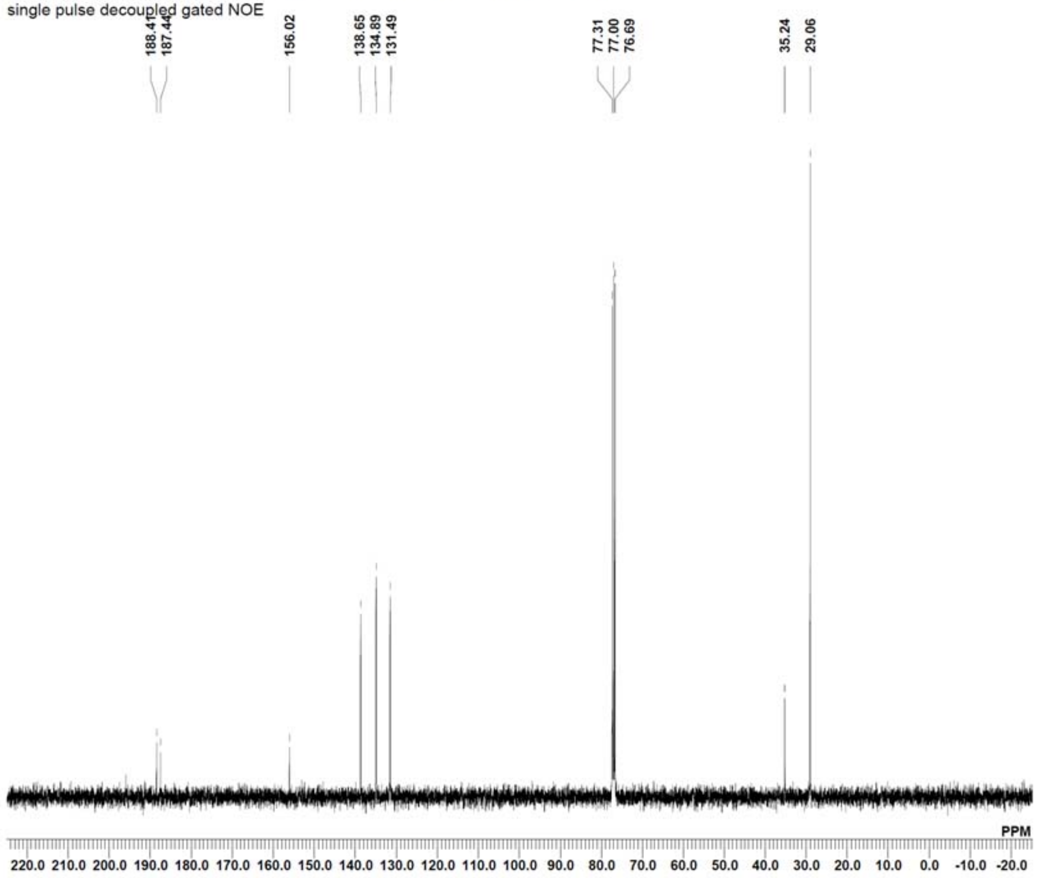


```
DFILE   _344008 1H data.als
COMNT   single_pulse
DATIM   2015-09-02 16:35:21
OBNUC   1H
EXMOD   proton.jxp
OBFRQ      399.78 MHz
OBSET        4.19 KHz
OBFIN        7.29 Hz
POINT       13107
FREQU     6002.40 Hz
SCANS           8
ACQTM      2.1837 sec
PD         5.0000 sec
PW1          5.05 usec
IRNUC   1H
CTEMP        24.9 c
SLVNT   CDCL3
EXREF        0.00 ppm
BF           0.12 Hz
RGAIN          34
```

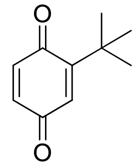


2c

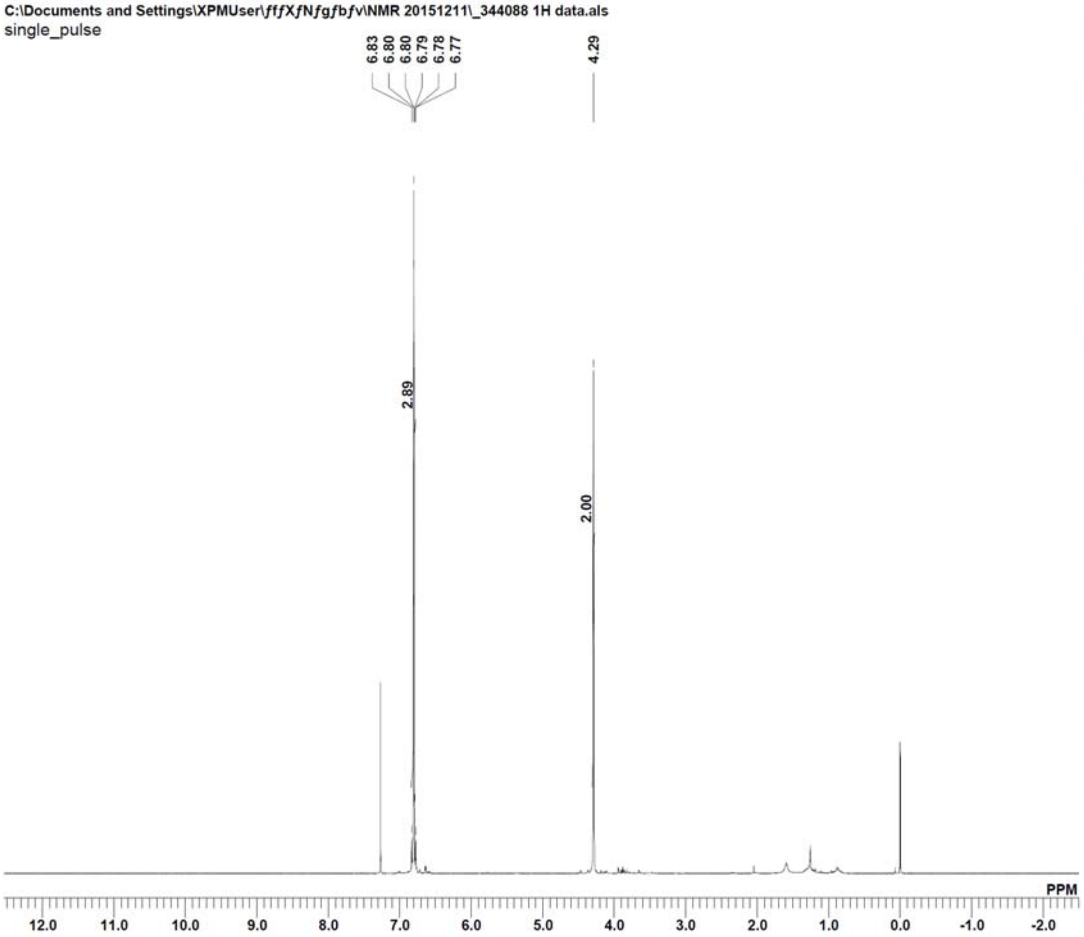
C:\Documents and Settings\XPMUser\ƒƒXƒNƒgƒbƒv\NMR 13C 20151212_343187 13C-1 Full.als
single pulse decoupled gated NOE



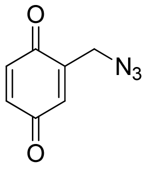
```
DFILE   _343187 13C-1 Full.als
COMNT   single pulse decoupled
DATIM   2015-07-16 16:37:09
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ      100.53 MHz
OBSET        5.35 KHz
OBFIN        5.86 Hz
POINT       26214
FREQU    25125.63 Hz
SCANS         293
ACQTM      1.0433 sec
PD         2.0000 sec
PW1          3.22 usec
IRNUC   1H
CTEMP        26.2 c
SLVNT   CDCL3
EXREF       77.00 ppm
BF           1.00 Hz
RGAIN          58
```



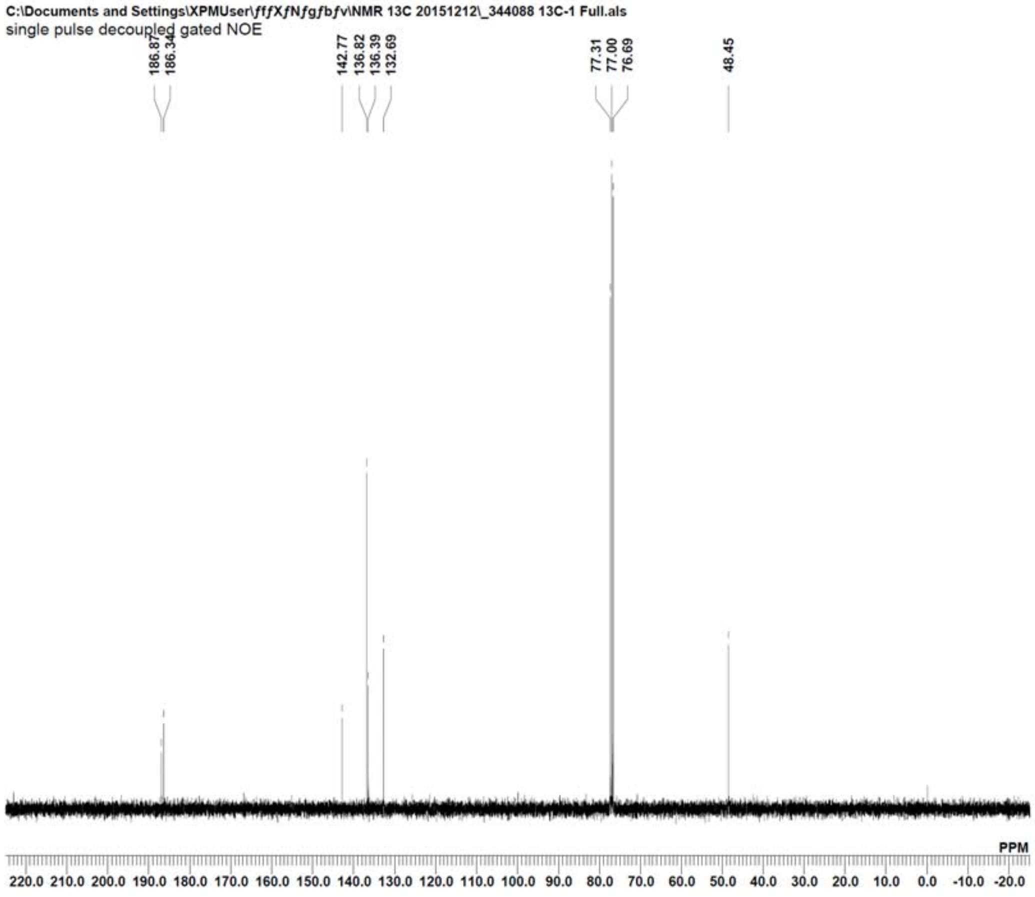
2c



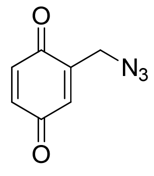
```
DFILE     _344088 1H data.als
COMNT     single_pulse
DATIM     2015-12-10 20:04:06
OBNUC     1H
EXMOD     proton.jxp
OBFRQ       399.78 MHz
OBSET         4.19 KHz
OBFIN         7.29 Hz
POINT        13107
FREQU      6009.62 Hz
SCANS            8
ACQTM       2.1810 sec
PD          5.0000 sec
PW1           5.05 usec
IRNUC     1H
CTEMP         24.7 c
SLVNT     CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           32
```



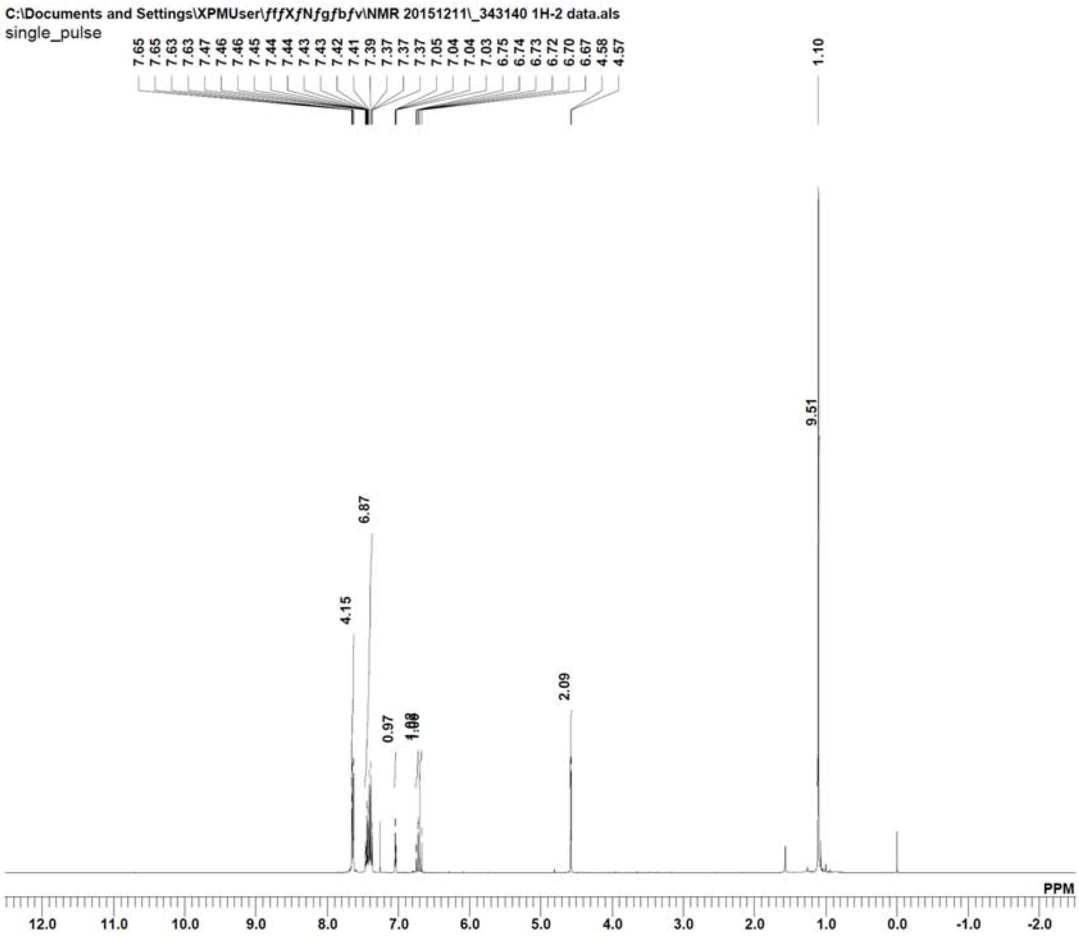
2d



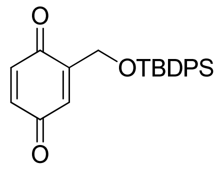
```
DFILE     _344088 13C-1 Full.als
COMNT     single pulse decoupled
DATIM     2015-12-10 20:06:27
OBNUC     13C
EXMOD     carbon.jxp
OBFRQ       100.53 MHz
OBSET         5.35 KHz
OBFIN         5.86 Hz
POINT        26214
FREQU     25125.63 Hz
SCANS          287
ACQTM       1.0433 sec
PD          2.0000 sec
PW1           3.22 usec
IRNUC     1H
CTEMP         25.3 c
SLVNT     CDCL3
EXREF        77.00 ppm
BF            0.12 Hz
RGAIN           56
```



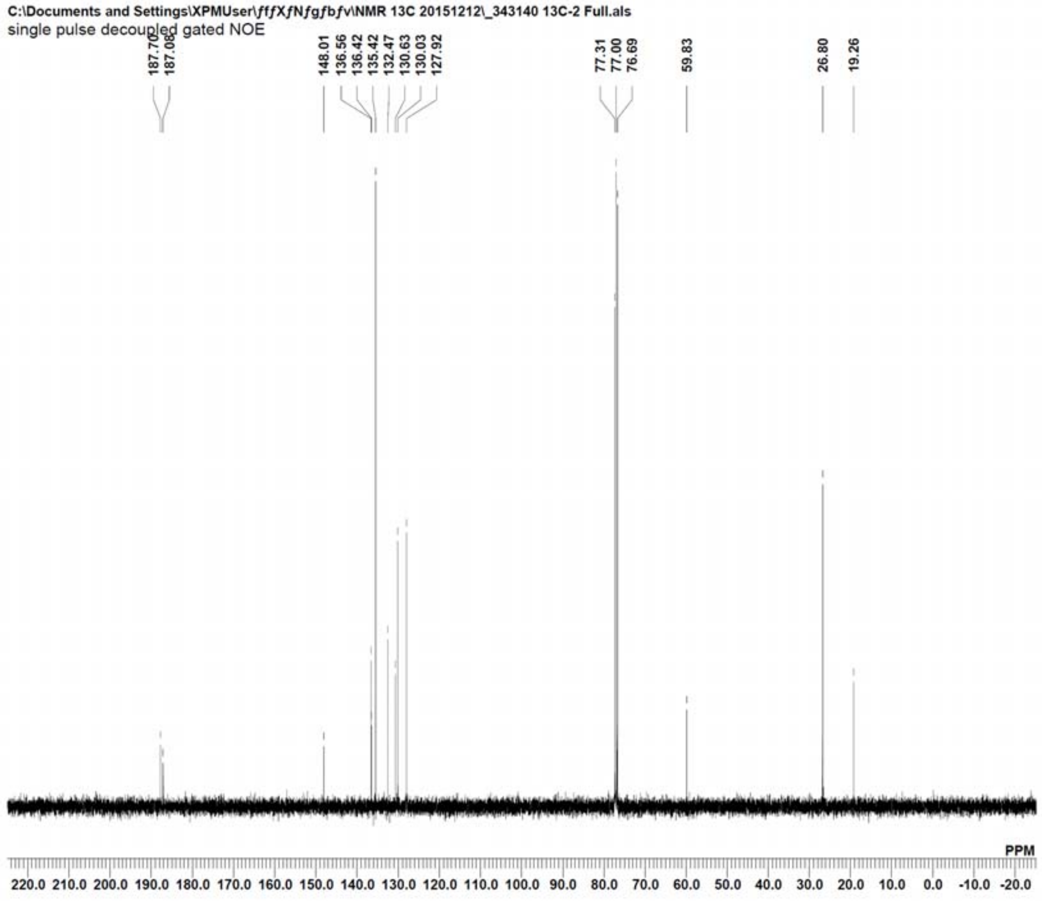
2d



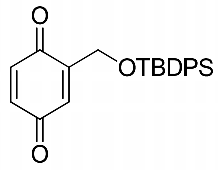
DFILE	_343140 1H-2 data.als
COMNT	single_pulse
DATIM	2015-12-11 19:32:33
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6009.62 Hz
SCANS	8
ACQTM	2.1810 sec
PD	5.0000 sec
PW1	5.05 usec
IRNUC	1H
CTEMP	24.6 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	30



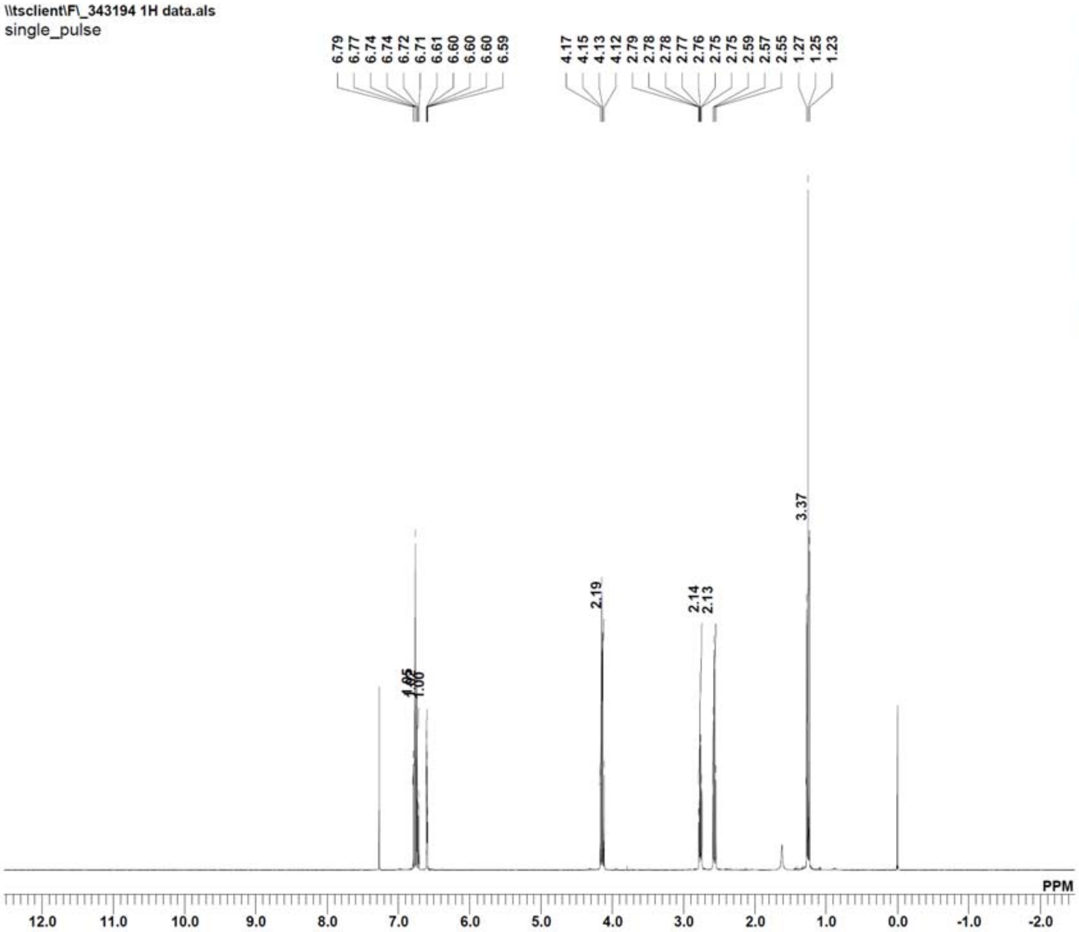
2e



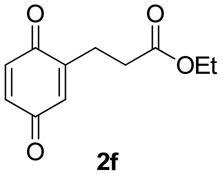
DFILE	_343140 13C-2 Full.als
COMNT	single pulse decoupled
DATIM	2015-12-11 19:35:35
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.63 Hz
SCANS	227
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.22 usec
IRNUC	1H
CTEMP	25.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	54



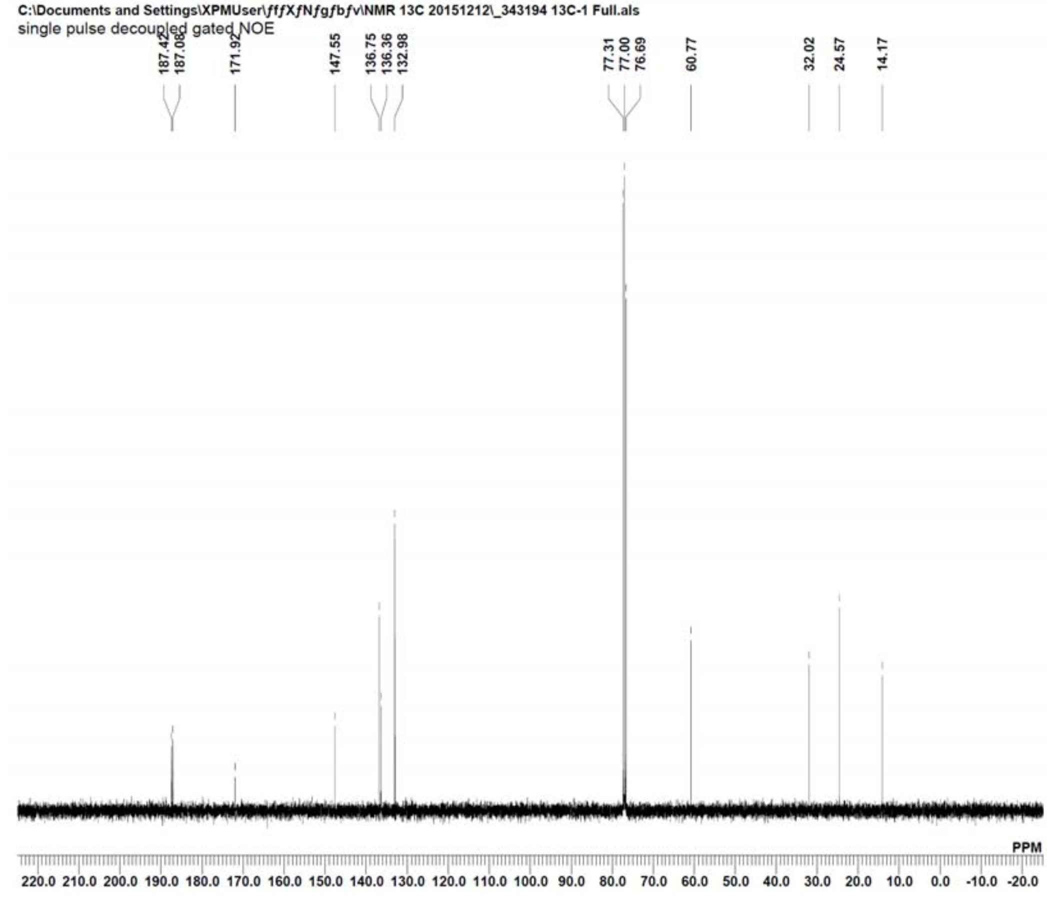
2e



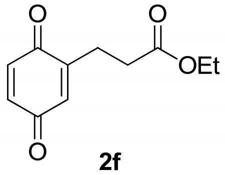
DFILE	_343194 1H data.als
COMNT	single_pulse
DATIM	2015-10-23 10:15:07
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.40 Hz
SCANS	8
ACQTM	2.1837 sec
PD	5.0000 sec
PW1	5.05 usec
IRNUC	1H
CTEMP	25.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	36



2f

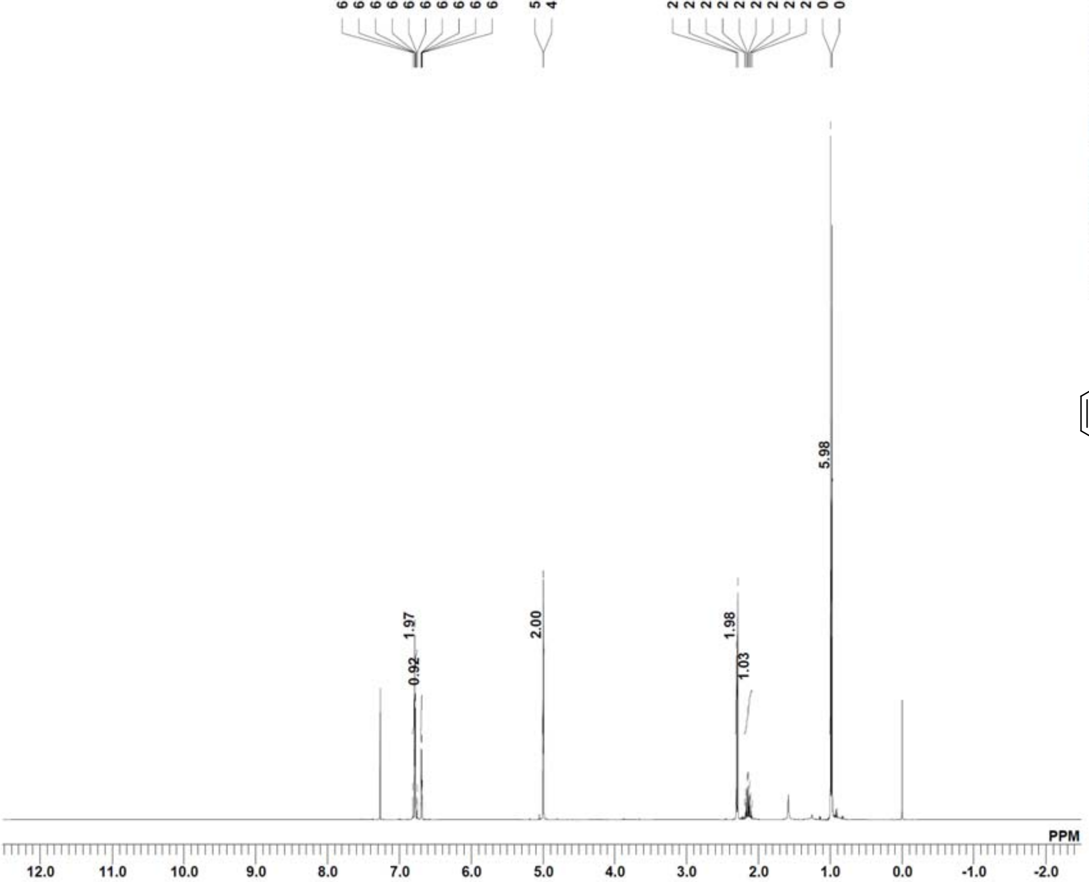


DFILE	_343194 13C-1 Full.als
COMNT	single pulse decoupled
DATIM	2015-10-23 10:18:14
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.63 Hz
SCANS	301
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.22 usec
IRNUC	1H
CTEMP	25.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	56

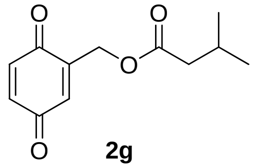


2f

\\tsclient\F_344062 1H data.als
single_pulse

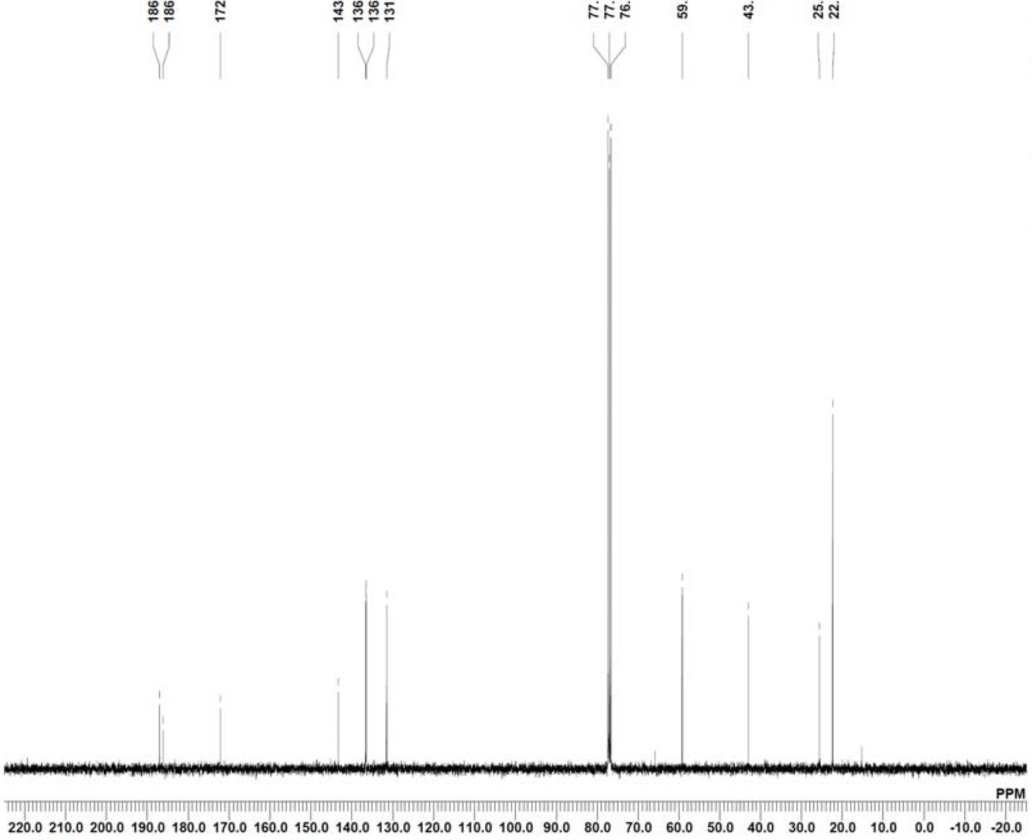


DFILE	_344062 1H data.als
COMNT	single_pulse
DATIM	2015-11-13 13:07:03
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.40 Hz
SCANS	8
ACQTM	2.1837 sec
PD	5.0000 sec
PW1	5.05 usec
IRNUC	1H
CTEMP	24.7 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	36

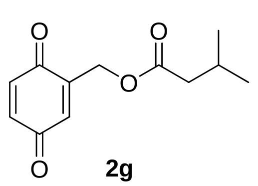


2g

C:\Documents and Settings\XPMUser\ƒƒXƒNƒgƒbƒv\NMR 13C 20151212_344062 13C-1 Full.als
single pulse decoupled gated NOE



DFILE	_344062 13C-1 Full.als
COMNT	single pulse decoupled
DATIM	2015-11-12 18:30:31
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.63 Hz
SCANS	360
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.22 usec
IRNUC	1H
CTEMP	25.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.00 Hz
RGAIN	50



2g