Acid Catalyzed Activation of Peroxyketals: Tunable Radical Initiation at Ambient Temperature and Below

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Supporting Information

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1 Experimental details

1.1 General details

Unless otherwise indicated, all reagents and solvents were purchased from commercial distributors and used as received. For details concerning the peroxyketals, see below.

Solvents (pentane, hexanes, ethyl acetate, dichloromethane, methanol) used for column chromatography were of technical grade and used after distillation in a rotary evaporator.

Air sensitive reactions were performed using classical Schlenk line techniques under an atmosphere of argon (*Air Liquide*, >99.5%).

TLC was used to check the reactions for full conversion and was performed on Macherey-Nagel Polygram Sil G/UV_{254} thin layer plates. TLC spots were visualized by UV-light irradiation and/or staining with solutions of $KMnO_4$ or anisaldehyde.

Flash column chromatography was carried out using Merck Silica Gel 60 (40-63 μm). Yields refer to pure isolated compounds.

^{1}H and ^{13}C NMR spectra were measured with Bruker AV 600, AV 500 and AV 400 spectrometers. All chemical shifts are given in ppm downfield relative to TMS and were referenced to the solvent residual peaks.[1] ^{1}H NMR chemical shifts are designated using the following abbreviations as well as their combinations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal, app. = apparent. For ^{13}C NMR data the following abbreviations are used: p = primary (CH_3), s = secondary (CH_2), t = tertiary (CH), q = quaternary (C).

High resolution mass spectra were recorded with a Bruker APEX III FTICR-MS or a Finnigan SSQ 7000 quadrupole MS or a Finnigan MAT 95 double focusing sector field MS instrument.

Abbreviations: MsOH: methane sulfonic acid; pTsOH: *para*toluene sulfonic acid; Me: methyl; tBu: *tert*butyl; Ph: phenyl; DCM: dichloromethane; AcOEt: ethyl acetate; MeOH: methanol; MeCN: acetonitrile; NBS: N-bromosuccinimide; TMS: trimethylsilyl.

1.2 SAFETY PRECAUTIONS, working with peroxides

Although we never experienced any problems in the experiments as described in this work, precautions should be taken when working with peroxides. In particular, it should be avoided as much as possible to expose neat peroxides or even the commercial solutions to heat or to mix them undiluted with reactive compounds. Performing such reactions behind a blast shield is recommended. In this report, the peroxides were generally added to the reagents in solvent and the catalyst was added last; we did not encounter any problems using this approach. Pure peroxides were only synthesized on relatively small scale, as described below, and were stored in the dark in a fridge.

1.3 Use of commercial peroxyketals

Peroxide **1a** (Trigonox 22, 50 % solution in mineral oil) was purchased from Acros Organics (catalog n° 361310100)

Peroxide **3a** (Trigonox D, 50% solution in aromatic free mineral spirit) was purchased from Acros Organics (catalog n° 349830100)

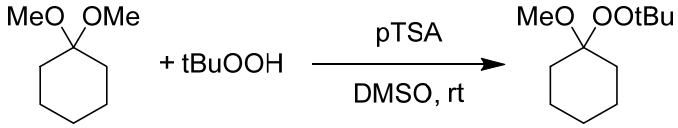
Peroxide **4** (Trigonox 301, 41% solution in aromatic free mineral spirit) was purchased from Acros Organics (catalog n° 349940050)

Peroxide **5** (Luperox DHD-9, 32% solution in phthalate-free plasticizer mixture) was purchased from Sigma-Aldrich (catalog n° 524670)

General note on using the commercial mineral oil solutions
Use of the commercial solutions of peroxides in mineral oil often leads to a biphasic system with the mineral oil floating on top, especially in acetonitrile. This can also happen in other solvents, especially when the peroxide solution is used in larger amounts. In our hands, this never seemed to cause problems: results with the pure peroxide **1a**, synthesized according to a literature procedure,[2] gave essentially identical results as with the use of the commercial solution of **1a**. Reactions with such biphasic systems were always stirred at high speed (~700 rpm) to ensure optimal mixing, just in case.

2 Synthesis of substrates

2.1 1-(tert-butylperoxy)-1-methoxycyclohexane (1b)

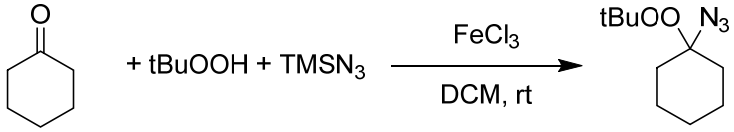


Synthesized according to the report of Matsuyama and Minoshima.[3]

In a 25mL round bottom flask, 1,1-dimethoxycyclohexane (1g, 6.94 mmol, 1eq) was dissolved in DMSO (5 mL) and tBuOOH (5.5M solution in decane, 1 eq) was added followed by *p*TsOH (400 mg, 0.3 eq) and the resulting mixture stirred at room temperature for 3 hours. Pentane (15 ml) was then added, followed by aqueous NaOH (2M, 10 mL). Phases were separated and the organic phase washed with distilled water (2 x 15 mL), dried over Na_2SO_4 and evaporated to dryness. The resulting clear oil was purified by flash chromatography on silica gel (prewashed with pentane containing 1% NEt_3) and pentane as eluant to afford **1b** as a clear oil (544 mg, 2.69 mmol, 39% yield)

^{1}H NMR (500 MHz, d6-DMSO): 3.15 (s, 3H); 1.63-1.56 (m, 4H); 1.52-1.31 (m, 6H); 1.20 (s, 9H)
^{13}C NMR (125 MHz, d6-DMSO): 102.77 (q); 78.23 (q); 47.36 (CH_3); 31.28 (CH_2); 26.40 (3x CH_3); 25.00 (CH_2); 22.31 (CH_2)
MS (EI): 197 (2); 145 (27); 129 (73); 113 (30); 97 (85); 87 (50); 69 (80); 57 (100); 41 (41)
HRMS (ESI): calculated for $C_{11}H_{22}O_3Na$: 225.1461; found: 225.1460

2.2 1-Azido-1-(*tert*-butylperoxy)cyclohexane (1c)



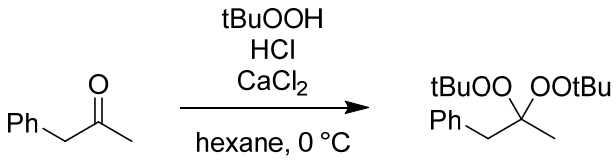
Synthesized according to the procedure of Ghorai.[4]

In a 25mL round bottom flask, cyclohexanone (103µL, 1 mmol) was dissolved in DCM (10 mL) and cooled to 0°C in an ice bath. *t*BuOOH (5.5M solution in decane, 182µL, 1 mmol) and $TMSN_3$ (330µL, 2.5 mmol) was added followed by $FeCl_3$ (16 mg, 0.1 mmol). The ice bath was removed and the reaction mixture stirred at room temperature for 30 minutes. The mixture was filtered over a pad of silica to remove the iron catalyst and the solvent removed under reduced pressure. The resulting clear oil was purified by flash chromatography on silica gel (hexanes as eluant) to afford **1c** as a clear oil (166 mg, 0.78 mmol, 78% yield)

^{1}H NMR (500 MHz, d6-DMSO): 1.75 (t, J=5.9 Hz, 4H); 1.60-1.50 (m, 2H); 1.48-1.34 (m, 4H); 1.24 (s, 9H)

^{13}C NMR (125 MHz, d6-DMSO):96.54 (C); 79.69 (C); 32.09 (CH_2); 26.03 (CH_3); 24.27 (CH_2); 21.99 (CH_2)
MS (ESI-pos): 409 (100); 320 (76); 236 (M+Na, 32); 213 (32)
HRMS (ESI-pos): calculated for $C_{10}H_{19}N_3O_2Na_1$: 236.1369; found: 236.1370

2.3 (2,2-bis(tert-butylperoxy)propyl)benzene (3b)

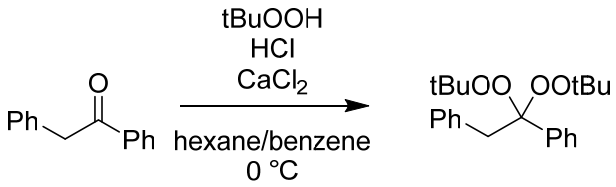


Synthesized according to a reported method. [5]

In a 50 mL round bottom flask, phenyl acetone (1g, 7.46 mmol) was dissolved in hexanes (6 mL) and cooled to 0°C (ice bath). Ground calcium chloride (500 mg) was added followed by tBuOOH (70% solution in water, 4 mL) and concentrated hydrochloric acid (0.5 mL), making sure the temperature does not exceed 5°C. The resulting mixture was vigorously stirred at 0°C for 4 hours. Hexane (30 mL) was added and the phases separated. The organic phase was then successively washed with an aqueous NaOH solution (2M, 15 mL) and distilled water (2x 15 mL), dried over Na_2SO_4 and evaporated to dryness. The resulting clear liquid was purified by flash chromatography on silica gel (prewashed with hexane containing 1% NEt_3) and hexane as eluant to afford **3b** as white solid (1.846 g, 6.23 mmol, 83% yield).

^{1}H NMR (500 MHz, d6-DMSO): 7.31-7.26 (m, 4H); 7.25-7.19 (m, 1H) 3.03 (s, 2H); 1.19 (s, 18H)
^{13}C NMR (125 MHz, d6-DMSO): 136.29 (Ar C); 130.62 (Ar CH); 127.74 (Ar CH); 126.34 (Ar CH); 107.95 (C); 79.13 (C); 40.73 (CH_2); 26.37 (CH_3); 18.99 (CH_3)
MS (EI): 207 (3); 91 (18); 73 (100); 57 (8); 43 (18)
HRMS (ESI): calculated for $C_{17}H_{28}O_4Na$: 319.1880; found: 319.1878

2.4 (1,1-bis(tert-butylperoxy)ethane-1,2-diyl)dibenzene (3c)



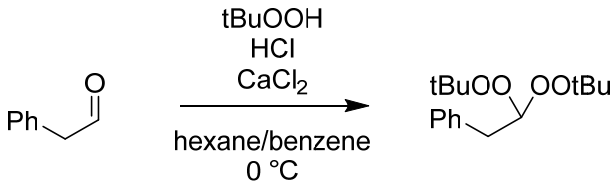
Synthesized in analogy to a reported method.[5]

In a 50 mL round bottom flask, deoxybenzoin (1g, 5.1 mmol) was dissolved in a 1:1 mixture of benzene and hexanes (6 mL in total) and cooled to 0°C (ice bath). Ground calcium chloride (500 mg) was added followed by tBuOOH (70% solution in water, 4 mL) and concentrated hydrochloric acid (0.5 mL), making sure the temperature did

not exceed 5°C. The resulting mixture was vigorously stirred at 0°C for 4 hours. Hexane (30 mL) was added and the phases separated. The organic phase was then successively washed with an aqueous NaOH solution (2M, 15 mL) and distilled water (2x 15 mL), dried over Na_2SO_4 and evaporated to dryness. The resulting clear liquid was purified by flash chromatography on silica gel (prewashed with hexane containing 1% NEt_3) and hexane as eluant to afford **3c** as white solid (217 mg, 0.60 mmol, 11% yield).

^{1}H NMR (500 MHz, d6-DMSO): 7.24-7.16 (m, 3H); 7.16-7.10 (m, 2H); 7.09-7.03 (m, 3H); 6.84-6.78 (m, 2H); 3.29 (s, 3H); 1.29 (s, 18H)
^{13}C NMR (125 MHz, d6-DMSO): 137.46 (Ar C); 135.08 (Ar C); 130.56 (Ar CH); 127.69 (Ar CH); 127.22 (Ar CH); 127.09 (Ar CH); 126.91 (Ar CH); 126.09 (Ar CH); 108.51 (C); 79.45 (C); 42.10 (CH_2); 26.55 (CH_3)
MS (EI): 269 (4); 197 (3); 105 (34); 91 (19); 73 (100)
HRMS (ESI): calculated for $C_{22}H_{30}O_4Na$: 381.2036; found: 381.2034

2.5 (2,2-bis(tert-butylperoxy)ethyl)benzene (3d)

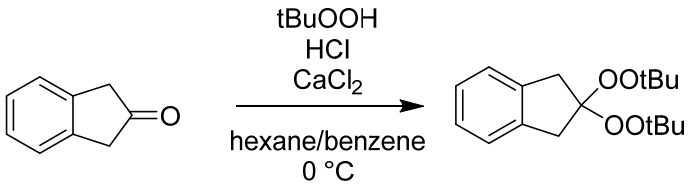


Synthesized according to a reported method. [5]

In a 50 mL round bottom flask, phenylacetaldehyde (1g, 8.33 mmol) was dissolved in a 1:1 mixture of benzene and hexanes (6 mL in total) and cooled to 0°C (ice bath). Ground calcium chloride (500 mg) was added followed by tBuOOH (70% solution in water, 4 mL) and concentrated hydrochloric acid (0.5 mL), making sure the temperature did not exceed 5°C. The resulting mixture was vigorously stirred at 0°C for 4 hours. Hexane (30 mL) was added and the phases separated. The organic phase was then successively washed with an aqueous NaOH solution (2M, 15 mL) and distilled water (2x 15 mL), dried over Na_2SO_4 and evaporated to dryness. The resulting clear liquid was purified by flash chromatography on silica gel (prewashed with hexane containing 1% NEt_3) and hexane as eluant to afford **3d** as clear oil (1.3 g, 4.60 mmol, 55% yield).

^{1}H NMR (500 MHz, d6-DMSO): 7.35-7.18 (m, 5H); 5.34 (t, J=6.2 Hz, 1H); 2.97 (d, J=6.2 Hz, 2H); 1.10 (s, 18H)
^{13}C NMR (125 MHz, d6-DMSO): 136.23 (Ar q); 129.58 (Ar CH); 128.13 (Ar CH); 126.48 (Ar CH); 108.39 (CH); 80.13 (C); 36.47 (CH_2); 26.07 (3x CH_3)
MS (EI): 193 (3); 91 (31); 73 (100); 57 (11); 43 (8)
HRMS (ESI): calculated for $C_{16}H_{26}O_4Na$: 305.1723; found: 305.1722

2.6 2,2-bis(tert-butylperoxy)-2,3-dihydro-1H-indene (6a)

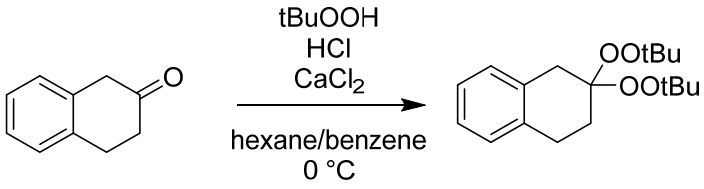


Synthesized according to the method by Colombo et al.[6]

In a 50 mL round bottom flask, 2-indanone (1g, 7.57 mmol) was dissolved in a 6:1 mixture of benzene and hexanes (6 mL in total) and cooled to 0°C (ice bath). Ground calcium chloride (500 mg) was added followed by tBuOOH (70% solution in water, 4 mL) and concentrated hydrochloric acid (0.5 mL), making sure the temperature did not exceed 5°C. The resulting mixture was vigorously stirred at 0°C for 5 hours. Hexane (30 mL) was added and the phases separated. The organic phase was then successively washed with an aqueous NaOH solution (2M, 15 mL) and distilled water (2x 15 mL), dried over Na_2SO_4 and evaporated to dryness. The resulting clear liquid was purified by flash chromatography on silica gel (prewashed with hexane containing 1% NEt_3) and hexane as eluant to afford **6a** as white solid (1.176 g, 4.055 mmol, 53% yield).

^{1}H NMR (500 MHz, d6-DMSO): 7.22-7.12 (m, 4H); 3.25 (s, 4H); 1.19 (s, 18H)
^{13}C NMR (125 MHz, d6-DMSO): 139.19 (Ar C); 126.57 (Ar CH); 124.55 (Ar CH); 116.45(C); 79.56 (C); 39.63 (CH_2); 26.36 (CH_3)
MS (EI): 205 (4); 104 (16); 73 (100); 57 (5); 43 (7)
HRMS (ESI): calculated for $C_{17}H_{26}O_4Na$: 317.1723; found: 317.1721

2.7 2,2-bis(tert-butylperoxy)-1,2,3,4-tetrahydronaphthalene (6b)



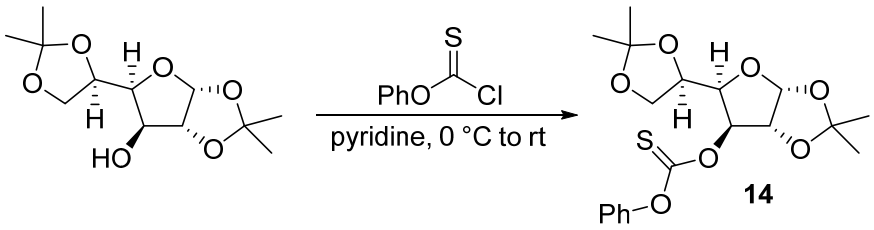
Synthesized according to the method by Colombo et al.[6]

In a 50 mL round bottom flask, 2-tetralone (1g, 6.85 mmol) was dissolved in a 2:4 mixture of benzene and hexanes (6 mL in total) and cooled to 0°C (ice bath). Ground calcium chloride (500 mg) was added followed by tBuOOH (70% solution in water, 4 mL) and concentrated hydrochloric acid (0.5 mL), making sure the temperature did not exceed 5°C. The resulting mixture was vigorously stirred at 0°C for 5 hours. Hexane (30 mL) was added and the phases separated. The organic phase was then successively washed with an aqueous NaOH solution (2M, 15 mL) and distilled water (2x 15 mL), dried over Na_2SO_4 and evaporated to dryness. The resulting clear liquid was purified by flash chromatography on silica gel (prewashed with hexane

containing 1% NEt_3) and hexane as eluant to afford **6b** as white solid (1.512 g, 4.909 mmol, 71% yield).

^{1}H NMR (500 MHz, d6-DMSO): 7.14-7.03 (m, 4H); 3.07 (s, 2H); 2.80 (t, J=6.7 Hz, 2H); 2.05 (t, J=6.7 Hz, 2H); 1.17 (s, 18H)
^{13}C NMR (125 MHz, d6-DMSO): 135.68 (Ar C); 133.42 (Ar C); 128.79 (Ar CH); 127.94 (Ar CH); 125.76 (Ar CH); 125.68 (Ar CH); 106.78 (C); 79.12 (C); 34.74 (CH_2): 27.62 (CH_2); 26.38 (CH_3); 26.31 (CH_2)
MS (EI): 219 (12); 104 (8); 73 (100)
HRMS (ESI): calculated for $C_{18}H_{28}O_4Na$: 331.1880; found: 331.1879

2.8 O-((3a*R*,6*S*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl) O-phenyl carbonothioate (14)



Synthesized according to the method by Roy et al.,[7] in 94% yield as a colorless solid.

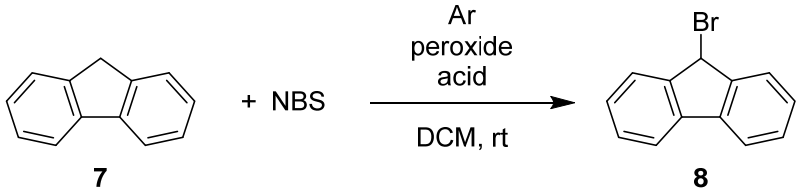
^{1}H NMR (500 MHz, d6-DMSO): 7.51-7.46 (m, 2H), 7.37-7.32 (m, 1H), 7.24-7.20 (m, 2H), 5.99(d, Hz=1.96, 1H), 5.48(d, Hz=1.50, 1H), 4.85(d, Hz=1.96, 1H), 4.28-4.20 (m, 2H), 4.05-4.00 (m, 1H), 3.86-3.84 (m, 1H), 1.46 (s, 3H), 1.35 (s, 3H), 1.29 (s,3H), 1.28 (s, 3H)

^{13}C NMR (125 MHz, d6-DMSO):193.15, 152.80, 129.82, 126.87, 121.63, 111.52, 108.54, 104.57, 85.10, 82.21, 78.72, 71.85, 65.89, 26.56, 26.28, 25.99, 29.10

HRMS (ESIpos): calculated for $C_{19}H_{24}O_7SNa$: 419.1135; found: 419.1134

3 Wohl-Ziegler bromination of fluorene.

3.1 Reaction at room temperature.



In an oven-dried Schlenk flask was fluorene **7** (83 mg, 0.5 mmol, 1 eq), *N*-bromosuccinimide (98 mg, 0.55 mmol, 1.1 eq) were dissolved in DCM (5 mL). The desired peroxide (0.025 mmol, 5 mol %) was introduced and the resulting mixture was degassed by the freeze-pump-thaw method (3 cycles). After warming to room temperature, the acid catalyst was added under a stream of argon and after the desired reaction time, the reaction mixture was quenched with NEt_3 (250 µL), CH_2Br_2 (0.5 mmol) added as a standard and an aliquot taken for direct ^1H NMR analysis. Yield was determined by integrating a reference peak of **8** (5.9 ppm, s, 1H; determined from an authentic sample) relative to the peak of CH_2Br_2.

Results are presented in table 1 of the main text.

3.2 Reaction at cryogenic temperatures.

Using the same experimental procedure, the reaction was evaluated at low temperature (Table S1).

Table S1: Wohl-Ziegler bromination of fluorene at cryogenic temperatures.

entry	temp. (°C)	peroxide	MsOH	additive	yield (%)
1	0	**1a** (5%)	5 mol %	/	30%
2	-10	**1a** (5%)	5 mol %	/	trace
3	-10	**1a** (1 equiv)	1 equiv	/	60
4	-10	*t*BuOOH (2 equiv)	1 equiv	cyclohexanone (1 equiv)	17
5	-10	*t*BuOOH (2 equiv)	1 equiv	/	0
6	-20	**1a** (1 equiv)	1 equiv	/	trace
7	-20	**6b** (1 equiv)	1 equiv	/	25
8	-30	**6b** (1 equiv)	1 equiv	/	trace

First the reaction was performed under the same reaction conditions than at room temperature (i.e. 5 mol % **1a** and MsOH) to give 30% of **8** after 24 hours (entry 1). Lowering the temperature to -10°C, only trace amount of **8** could be detected (entry2). Using stoichiometric amounts of **1a** and MsOH, a satisfying 60% yield of **2** was obtained after 24 hours (entry 3). This was directly compared with our previous method of generating radicals by using the ketone (cyclohexanone in this case) and tBuOOH. Although **8** was still obtained in 17% yield (entry 4), it was considerably less efficient than to use **1a** preformed (17% Vs 60%). A control experiment was

performed excluding cyclohexanone and no trace of **8** was detected after 24 hours, excluding any background reaction from the combination of tBuOOH and MsOH (entry 5). Lowering the temperature further to -20°C led to only traces of **2** after 24 hours (entry 6). Using **6b**, more reactive than **1a**, 25% of **8** was formed at -20°C (entry 7) but only traces if the temperature was further lowered to -30°C (entry 8).

Note: Care was taken to exclude light in order to avoid potential photochemical initiation. The reactions were carried out in a fume hood with the lights switched off and the Schlenk flask was wrapped in aluminium foil after the reaction mixture was degassed and warmed to the desired temperature.

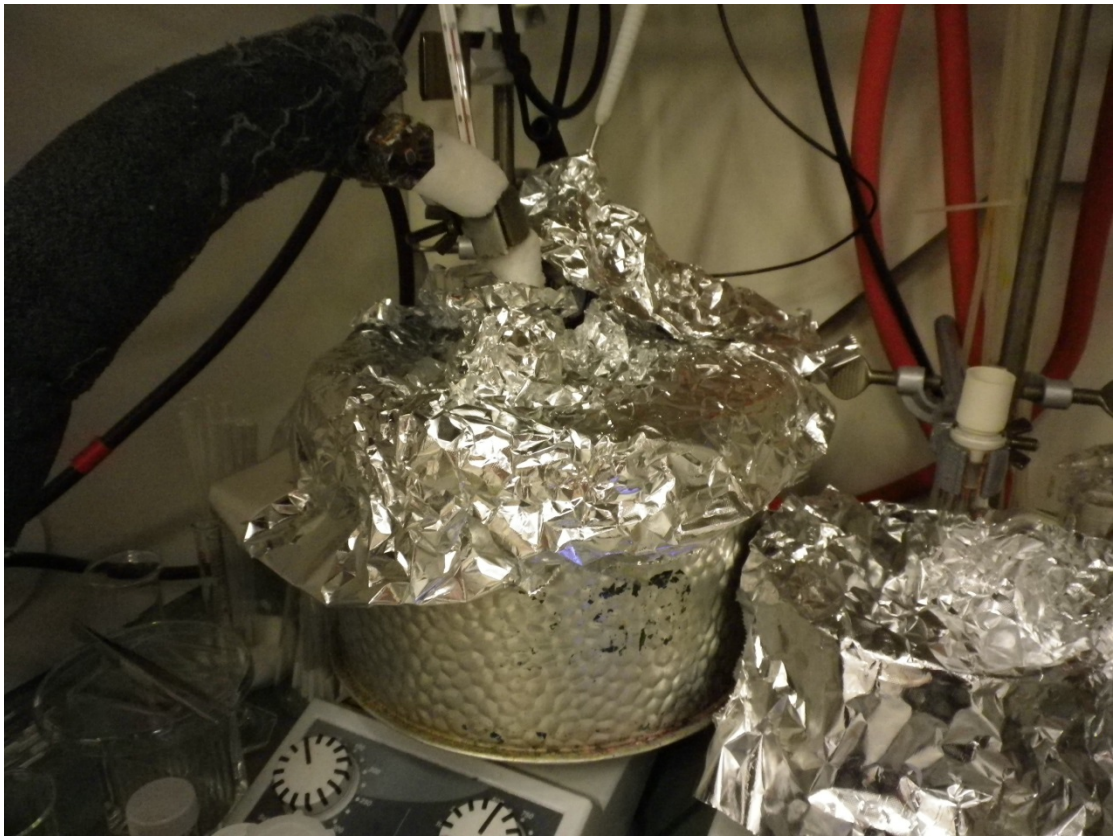
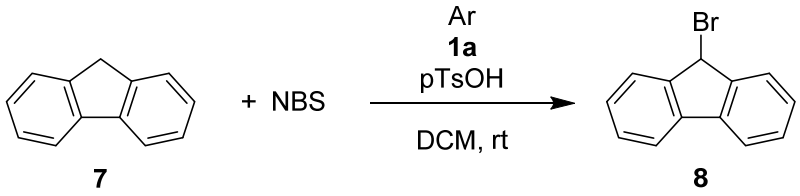


Figure S1: picture of the experimental set-up used. Left stirring plate: reaction performed at cryogenic temperature using a cryostat and an ethanol bath. Right stirring plate: reaction performed at room temperature (22-23°C) using an oil bath as temperature regulator.

4 Synthesis of products.

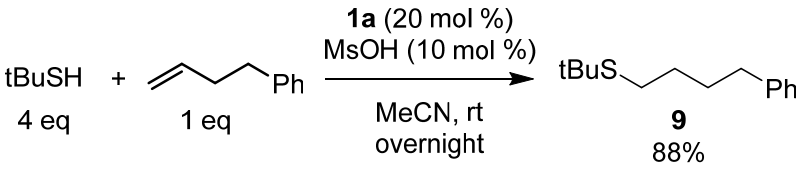
4.1 9-bromo-9H-fluorene (8)



In an oven-dried Schlenk flask was fluorene **7** (166 mg, 1 mmol, 1 eq), N-bromosuccinimide (195 mg, 1.1 mmol, 1.1 eq) were dissolved in DCM (10 mL). **1a** (50% solution, 52 mg, 0.05 mmol) was introduced and the resulting mixture was degassed by the freeze-pump-thaw method (3 cycles). After warming to room temperature, *para*-toluenesulfonic acid (9.5 mg; 0.05 mmol) was added under a stream of argon and after three hours, a small amount of silica was added, the solvent was removed under vacuo and the resulting white powder was purified by flash chromatography on silica gel (Hex/AcOEt 99:1 as eluent) to afford **2** as a white solid (237mg, 96% yield). Analytical data was in accordance with reported values.[8]

^{1}H NMR (500 MHz, CDCl3): 7.68 (br t, J=7.5 Hz, 4H); 7.41 (td, J=7.5 and 1 Hz; 2H); 7.35 (td, J=7.5 and 1 Hz, 2H); 6.01 (s, 1H)
^{13}C NMR (125 MHz, CDCl3): 144.17 (Ar C); 139.80 (Ar C); 129.24 (Ar CH); 128.11 (Ar CH); 126.38 (Ar CH); 120.30 (Ar CH); 46.08 (CH)
MS (EI): 246 (7); 244 (7); 165 (100)
HRMS (ESI): calculated for $C_{13}H_9Br$: 243.9888; found: 243.9889

4.2 tert-butyl(4-phenylbutyl)sulfane (9)

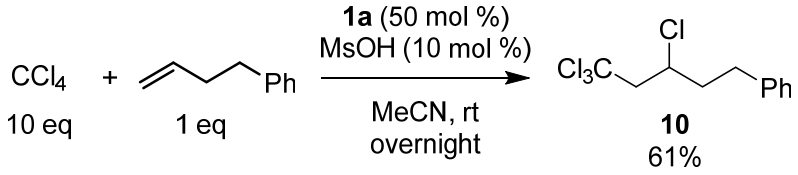


In an oven dried Schlenk tube, tBuSH (225µL, 2 mmol), 4-phenyl butane (75µL, 0.5 mmol) and **1a** (50% solution, 52 mg, 0.1 mmol) were dissolved in acetonitrile (5 mL). The resulting mixture was degassed (Freeze-Pump-Thaw technique, 3 cycles), brought to room temperature and methane sulfonic acid (3.5 µL, 0.05 mmol) was added and the mixture left to react overnight. The mixture was transferred to an extraction funnel, diluted with ethyl acetate (20 mL) and washed with NaOH (2M, 2x 10 mL) and distilled water (2x 10 mL). The organic phase was dried over Na2SO4, evaporated to dryness and the resulting oil was purified by flash chromatography on silica gel (Hex/AcOEt 99:1 as eluent) to afford **9** as a clear oil (98mg, 88% yield)

^{1}H NMR (500 MHz, CDCl3): 7.31-7.25 (m, 2H); 7.21-7.15 (m, 2H); 2.64 (t, J=7.6 Hz, 2H); 2.55 (t, J=7.4 Hz, 2H); 1.78-1.70 (m, 2H); 1.67-1.59 (m, 2H); 1.32 (s, 9H)

^{13}C NMR (125 MHz, CDCl3): 142.30 (Ar C); 128.43 (Ar CH); 128.31 (Ar CH); 125.74 (Ar CH); 41.83 (C); 35.60 (CH_2); 31.01 (CH_3); 29.46 (CH_2); 29.44 (CH_2); 28.15 (CH_2)
MS (EI): 222 (32); 166 (29); 165 (33); 164 (21); 131 (25); 104 (36); 91 (63); 87 (22); 57 (100)
HRMS (ESI): calculated for $C_{14}H_{22}S$: 222.1442; found: 222.1444

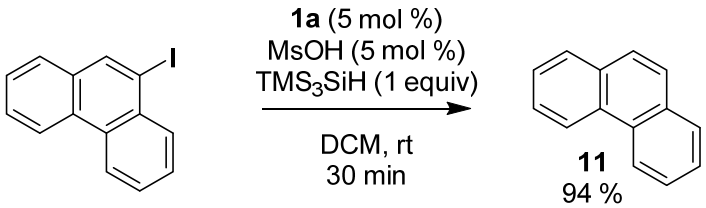
4.3 (3,5,5,5-tetrachloropentyl)benzene (10)



In an oven dried Schlenk tube, CCl_4 (962µL, 10 mmol), 4-phenyl butane (150µL, 1 mmol) and **1a** (50% solution, 260 mg, 0.5 mmol) were dissolved in acetonitrile (1 mL). The resulting mixture was degassed (Freeze-Pump-Thaw technique, 3 cycles), brought to room temperature and methane sulfonic acid (7 µL, 0.1 mmol) was added and the mixture left to react overnight. The mixture was evaporated to dryness and the resulting oil was purified by flash chromatography on silica gel (hexane as eluent) to afford **10** as a clear oil (172 mg, 60% yield). Analytical data of ^{13}C-NMR was in accordance with reported values.[9]

^{1}H NMR (500 MHz, CDCl3): 7.25-7.19 (m, 2 H); 7.16-7.11 (m, 3 H); 4.20-4.14 (m, 1H); 3.23 (dd, J=5.5 and 15.6 Hz, 1H); 3.06 (dd, J=4.6 and 15.6 Hz, 1H); 2.86 (ddd, J=4.8, 9.6 and 14 Hz, 1H); 2.72 (ddd, J=6.8, 9.5 and 13.8 Hz, 1H); 2.24-2.16 (m, 1H); 2.10-2.01 (m, 1H)
^{13}C NMR (125 MHz, CDCl3): 140.29 (Ar C); 128.62 (Ar CH); 128.52 (Ar CH); 126.35 (Ar CH); 96.76 (C); 62.26 (CH_2); 57.11 (CH); 40.57 (CH_2); 32.33 (CH_2)
MS (EI): 286 (10); 284 (8); 92 (60); 91 (100); 65 (11)
HRMS (ESI): calculated for $C_{11}H_{12}Cl_4$: 283.9693; found: 283.9695

4.4 Phenanthrene (11)

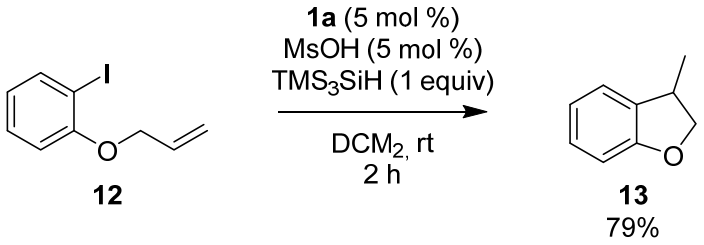


In an oven dried Schlenk tube, 9-iodophenanthrene (304 mg, 1 mmol), was dissolved in dichloromethane (10 mL). The resulting solution was degassed (Freeze-Pump-Thaw technique, 3 cycles), brought to room temperature and **1a** (50% solution, 26 mg, 0.05 mmol) and TMS_3SiH (308 µL, 1 mmol) were added. The mixture was degassed once more and after being brought back to room temperature, methane sulfonic acid (3.5 µL, 0.05 mmol) was added and the mixture left to react for 30

minutes. The mixture was evaporated to dryness and the resulting slightly yellow oil was purified by flash chromatography on silica gel (hexane as eluent) to afford **11** as a white solid (168 mg, 94% yield).

^{1}H NMR (500 MHz, CDCl3): 8.75 (br d, J=8.1 Hz, 2H); 7.96 (dd, J=1 and 7.8 Hz, 2H); 7.80 (s, 2H); 7.74-7.64 (m, 4H);
^{13}C NMR (125 MHz, CDCl3): 132.16 (C); 130.41 (C); 128.68 (CH); 127.03 (CH); 126.67 (CH); 122.78 (CH)
MS (EI): 178 (100)
HRMS (ESI): calculated for $C_{14}H_{10}$: 178.0783; found: 178.0781

4.5 3-methyl-2,3-dihydrobenzofuran (13)

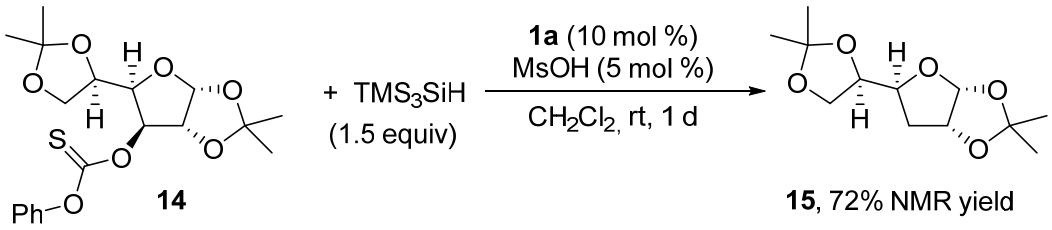


Note: 12 was synthesized according to a reported procedure.[10]

In an oven dried Schlenk tube, **12** (259 mg, 1 mmol), was dissolved in dichloromethane (10 mL). The resulting solution was degassed (Freeze-Pump-Thaw technique, 3 cycles), brought to room temperature and **1a** (50% solution, 26 mg, 0.05 mmol) and TMS_3SiH (308 µL, 1 mmol) were added. The mixture was degassed once more and after being brought back to room temperature, methane sulfonic acid (3.5 µL, 0.05 mmol) was added and the mixture left to react for 2 hours. The mixture was evaporated to dryness and the resulting slightly yellow oil was purified by flash chromatography on silica gel (pentane as eluent) to afford **13** as a clear oil (106 mg, 79% yield). Analytical data was in accordance with reported values.[11]

^{1}H NMR (500 MHz, $CDCl_3$): 7.16 (br d, J=7.5 Hz, 1H); 7.12 (br t, J=7.8 Hz, 1H); 6.88 (td, J=7.5 and 1 Hz, 1H); 6.79 (br d, H=7.8 Hz, 1H); 4.68 (t, J=8.8 Hz, 1H); 4.07 (dd, J=7.5 and 8.8 Hz, 1H); 3.55 (m, 1H); 1.34 (d, J=7 Hz, 3H)
^{13}C NMR (125 MHz, $CDCl_3$): 159.82 (Ar C); 132.38 (Ar C); 128.11 (Ar CH); 123.93 (Ar CH); 120.55 (Ar CH); 109.58 (Ar CH); 78.47 (CH_2); 36.60 (CH); 19.33 (CH_3)
MS (EI): 134 (72); 119 (100); 91 (94)
HRMS (ESI): calculated for $C_9H_{10}ONa$: 157.0624; found: 157.0624

4.6 Barton-McCombie deoxygenation



Representative procedure, used for initial isolation and characterization of **15**, on the basis of a reported method:[12]

In an oven dried Schlenk tube, **14** (198.23 mg, 0.5 mmol), was dissolved in CH_2Cl_2 (5 mL). The resulting solution was degassed (Freeze-Pump-Thaw technique, 3 cycles), brought to room temperature and **1a** (50% solution, 13 mg, 0.05 mmol) and TMS_3SiH (153.49 µL, 1 mmol) were added. The mixture was degassed once more and after being brought back to room temperature, methane sulfonic acid (1.62 µL, 0.05 mmol) was added and the mixture left to react for 2 days. The mixture was evaporated to dryness and the resulting slightly yellow oil was purified by flash chromatography on silica gel (pentane as eluent) to afford 13 3aR,6aR)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxole (**15**) as a clear oil (34.2 mg, 28% yield). The analytical data was in accordance with literature data.[12]

^{1}H NMR (500 MHz, d6-DMSO): 5.74 (d, ^3J = 1.83 Hz, 1H), 4.75-4.72 (m, 1H), 4.07-3.98 (m, 3H), 3.69-3.65 (m, 1H), 2.03-1.98 (m, 1H), 1.68-1.60 (m, 1H), 1.39 (s, 3H), 1.32 (s, 3H), 1.26 (s, 3H), 1.23 (s, 3H)
^{13}C NMR (125 MHz, d6-DMSO):110.23, 108.61, 105.07, 79.85, 77.92, 76.18, 66.09, 34.64, 26.63, 26.30, 26.05, 25.16
HRMS (ESIpos): calculated for $C_{12}H_{20}O_5Na$: 267.1203; found: 267.1200

The reaction conditions were then varied to improve the product yield and study the effect of acid and peroxide loading. For this purpose, 1.0 equivalents (relative to **14**) of internal standard 1,4-dimethoxybenzene were added to the reaction before addition of dichloromethane. Aliquots of 0.1 mL were then taken at the time indicated in the table below, mixed with 0.4 mL of DMSO-d_6, which was found to effectively quench the reaction, and analyzed by ^{1}H-NMR.

entry	TMS_3SiH	peroxide	MsOH	solvent	yield SM/P (%)[a]	time
1a	1 equiv	**1a** (5%)	5 mol %	DCM	61.3 / 32.4	2 h
1b	1 equiv	**1a** (5%)	5 mol %	DCM	54.8 / 42.9	1 d
2a	1 equiv	**1a** (10%)	10 mol %	DCM	52.5 / 41.1	2 h
2b	1 equiv	**1a** (10%)	10 mol %	DCM	53.4 / 15.8	1 d
3	1 equiv	**1a** (5%)	5 mol %	toluene	-	1 d
4	1 equiv	**1a** (5%)	5 mol %	acetonitrile	-	1 d
5a	1 equiv	**1a** (10%)	5 mol %	DCM	57.7 / 43.5	2 h
5b	1 equiv	**1a** (10%)	5 mol %	DCM	54.9 / 45.1	1 d
6a	1.5 equiv	**1a** (10%)	5 mol %	DCM	27.6 / 72.1	1 d
6b	1.5 equiv	**1a** (10%)	5 mol %	DCM	19.5 / 66.6	2 d

[a] NMR yields relative to internal standard 1,4-dimethoxybenzene.

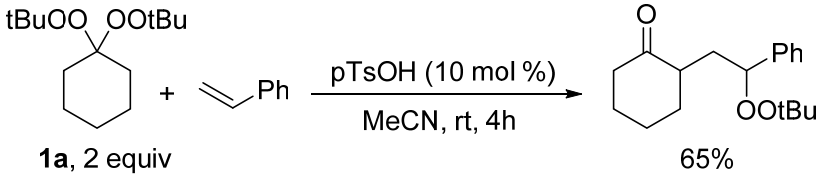
Common entry numbers indicate a single experiment from which two samples (a, b) were taken for analysis.

An increased amount of acid catalyst doesn't increase conversion of substrate significantly while it enhances decomposition of the product over time (cf. entries 1a, 1b and entries 2a, 2b). Similarly, the product yield goes down if the reaction is allowed to take place for too long, most likely by acid-catalyzed cleavage of the ketal groups (entries 6a, 6b).

An increase of the amount of peroxide initiator leads to a small increase in conversion and product yield (cf. entries 1a and 5a). Excess of silane (1.5 equiv vs. 1.0 equiv) leads to an increase of conversion as well as of product yield (cf. entries 5a and 6a).

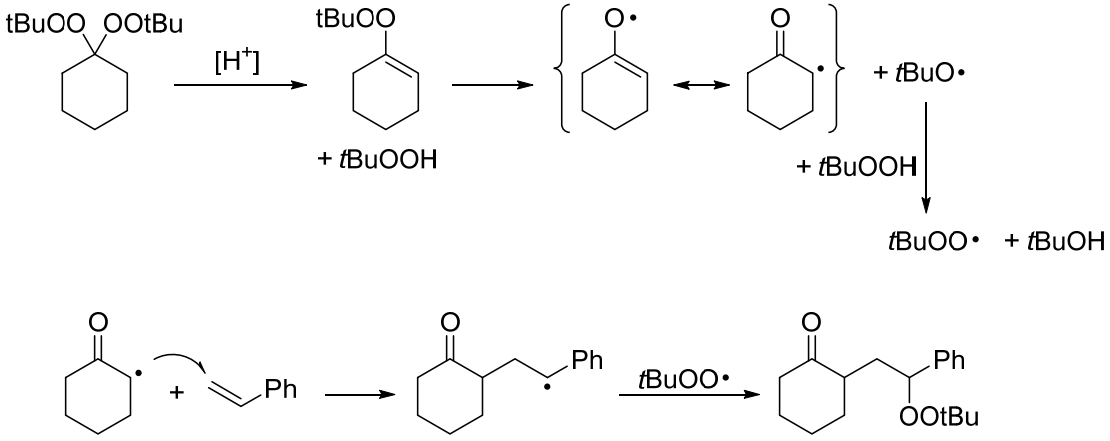
5 Trapping of generated radicals with styrene

In order to support the presumed structure of the radicals generated, the acid-mediated decomposition of perketal **1a** was performed in the presence of styrene:



The resulting γ-peroxyketone (2-(2-(tert-butylperoxy)-2-phenylethyl)cyclohexan-1-one) was received in 65% isolated yield after 4 hours of reaction time at ambient temperature. The product was found to be identical with the one previously synthesized from cyclohexanone, *tert*-butylhydroperoxide and styrene,[13] according to the characterization data. In contrast to this three-component reaction, the reaction time was shorter and the required reaction temperature lower.

This supports the proposed in situ generation of alkenyl peroxides and the corresponding radicals generated thereof by homolytic O-O bond cleavage. The formation of the peroxyl radical is explained by a fast hydrogen atom transfer between the initially formed oxyl radical and *tert*-butylhydroperoxide:[13-14]



Synthetic procedure:

In an oven dried Schlenk tube, **1a** (50% solution, 520 mg, 1 mmol) and styrene (58 μL, 0.5 mmol) were dissolved in acetonitrile (2 mL). The resulting solution was degassed (Freeze-Pump-Thaw technique, 3 cycles), brought to room temperature and paratoluene sulfonic acid (9.5 mg, 0.05 mmol) was added and the mixture left to react for 2 hours. The mixture was diluted, a small amount of silica added and evaporated to dryness and the resulting slightly yellow powder was purified by flash chromatography on silica gel (hexane/AcOEt 95/5 as eluent) to afford 2-(2-(tert-butylperoxy)-2-phenylethyl)cyclohexan-1-one as a clear oil (94 mg, 65% yield). Analytical data was found to be consistent with previously reported data.[13]

^{1}H NMR: ($CDCl_3$; 500 MHz, 2 diastereoisomers): 7.42-7.22 (m, 5H); 5.02-4.96 (m, 1H); 2.62-2.53 (m, 1H, major); 2.51-2.43 (m, 1H, minor); 2.44-2.38 (m, 1H); 2.38-2.14 (m, 3H); 2.12-2.01 (m, 1H); 1.91-1.81 (m, 1H); 1.74-1.57 (m, 3H); 1.53-1.35 (m, 2H); 1.21 (s, 9H, minor); 1.18 (s, 9H, major)

^{13}C NMR: ($CDCl_3$; 125 MHz; 2 diastereoisomers): 212.63 (C); 141.83 (Ar q, major); 141.48 (Ar q, minor); 128.21 (Ar CH, major); 128.17 (Ar CH, minor); 127.63 (Ar CH, minor); 127.53 (Ar CH; major); 126.94 (Ar CH, major); 126.72 (Ar CH; minor); 84.01 (CH, major); 83.05 (CH, minor); 80.08 (C); 47.65 (CH, minor); 47.26 (CH, major); 42.28 (CH_2, major); 42.11 (CH_2, minor); 35.60 (CH_2, minor); 35.06 (CH_2, major); 34.93 (CH_2, major); 34.41 (CH_2, minor); 28.26 (CH_2, minor); 28.08 (CH_2, major); 26.50 (3x CH_3, major); 26.49 (3x CH_3, minor); 25.33 (CH_2, major); 25.00 (CH_2, minor)
MS (EI): 217 (3.8); 201 (100); 105 (16); 91 (26)
HRMS (ESI): Calculated for $[C_{18}H_{26}O_3Na]^+$ ($M+Na^+$): 313.1774; found: 313.1775

6 NMR-spectra

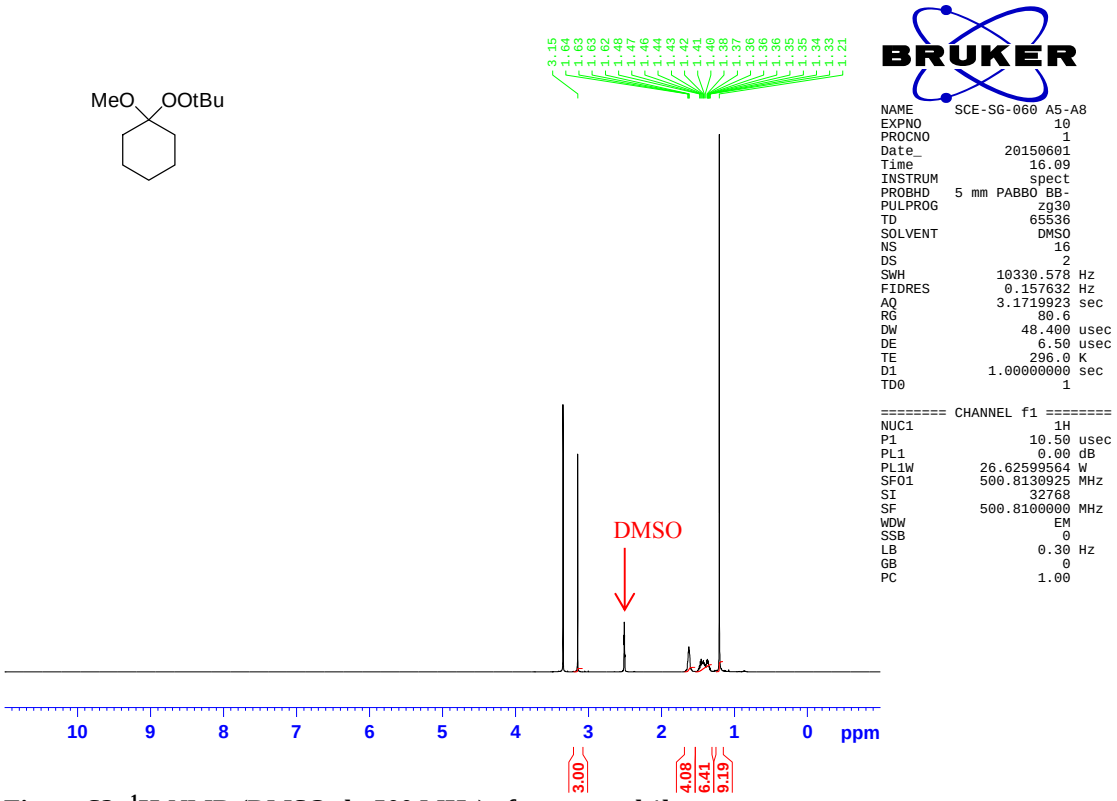


Figure S2: ^{1}H-NMR (DMSO-d$_6$, 500 MHz) of compound 1b.

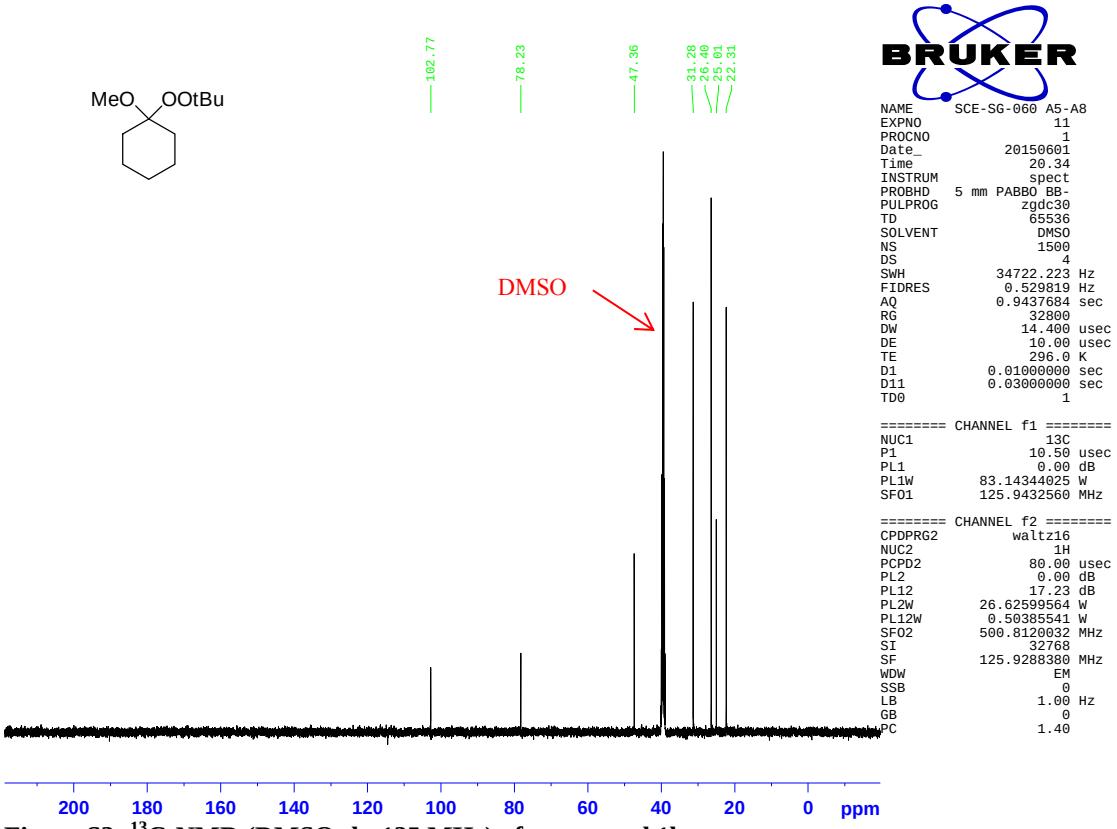


Figure S3: ^{13}C-NMR (DMSO-d$_6$, 125 MHz) of compound 1b.

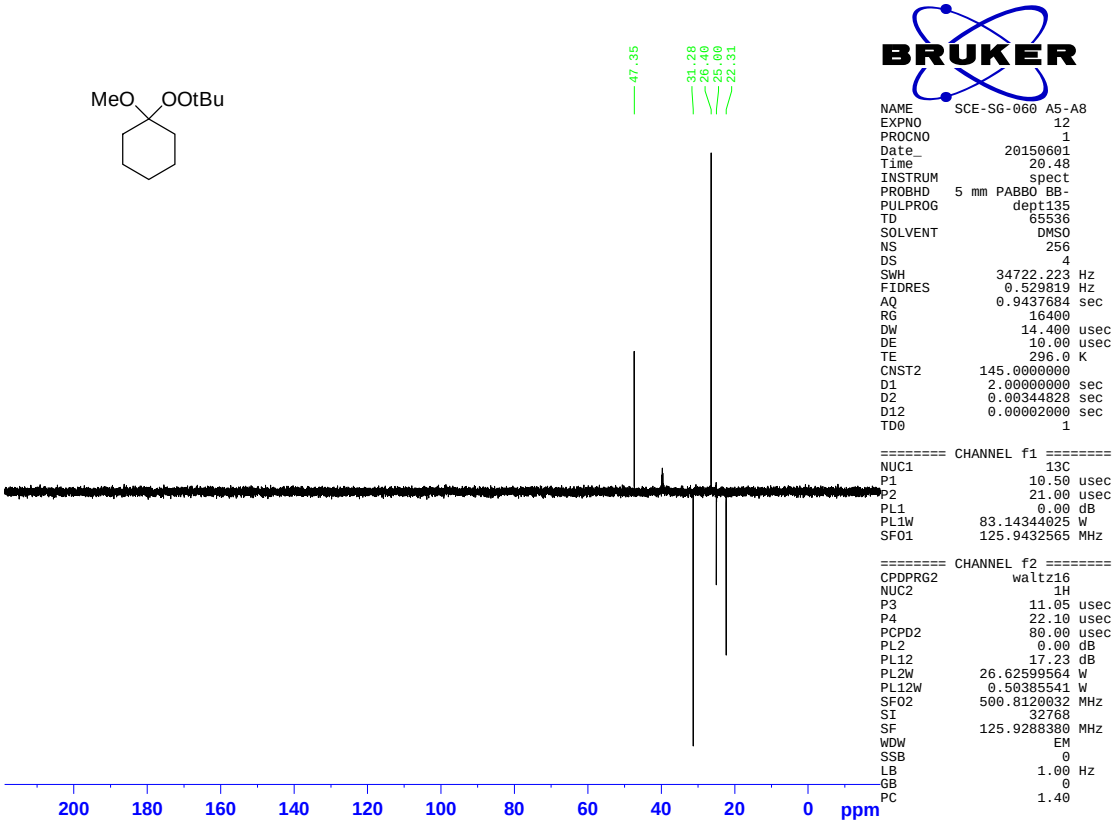


Figure S4: DEPT 135-NMR (DMSO-d_6, 125 MHz) of compound 1b.

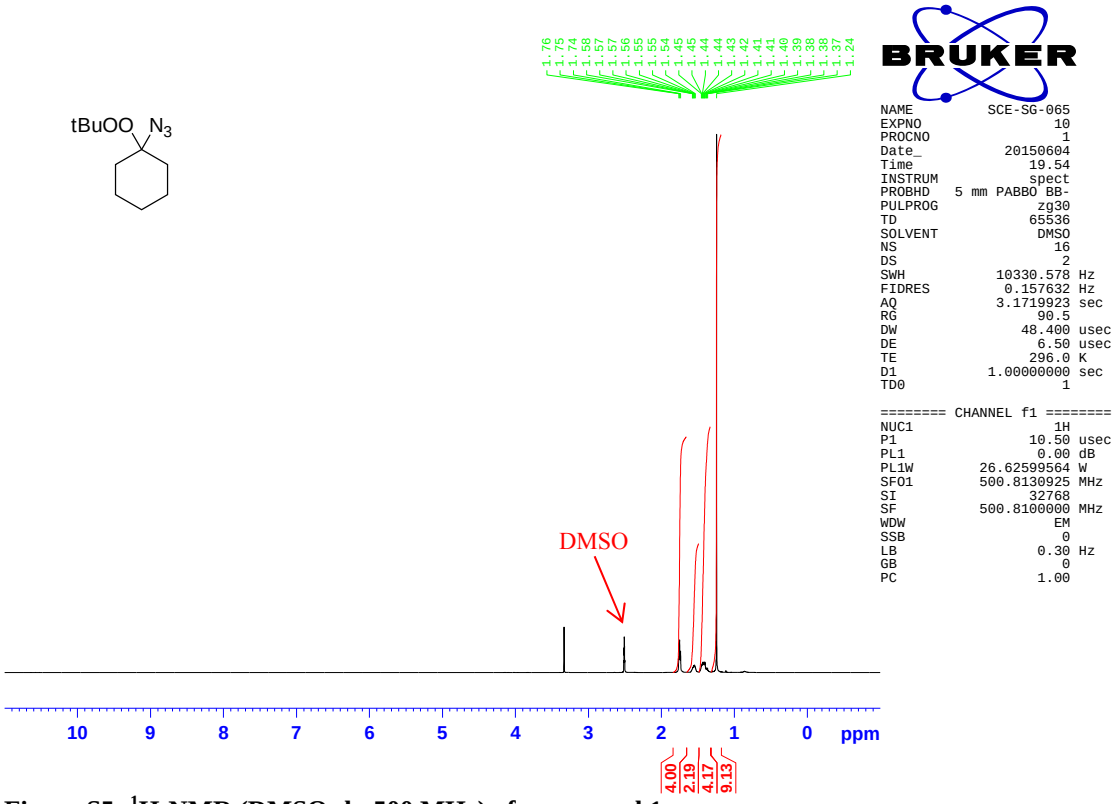


Figure S5: ^{1}H-NMR (DMSO-d_6, 500 MHz) of compound 1c.

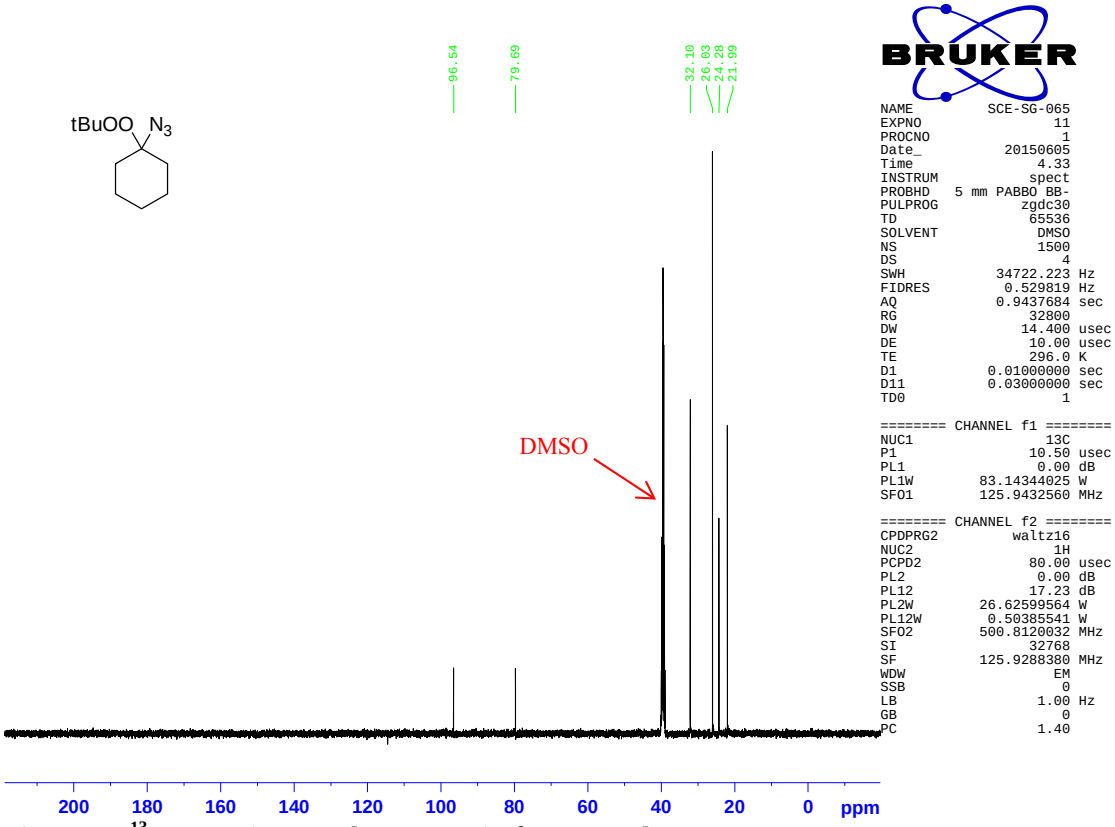


Figure S6: ^{13}C-NMR (DMSO-d$_6$, 125 MHz) of compound 1c.

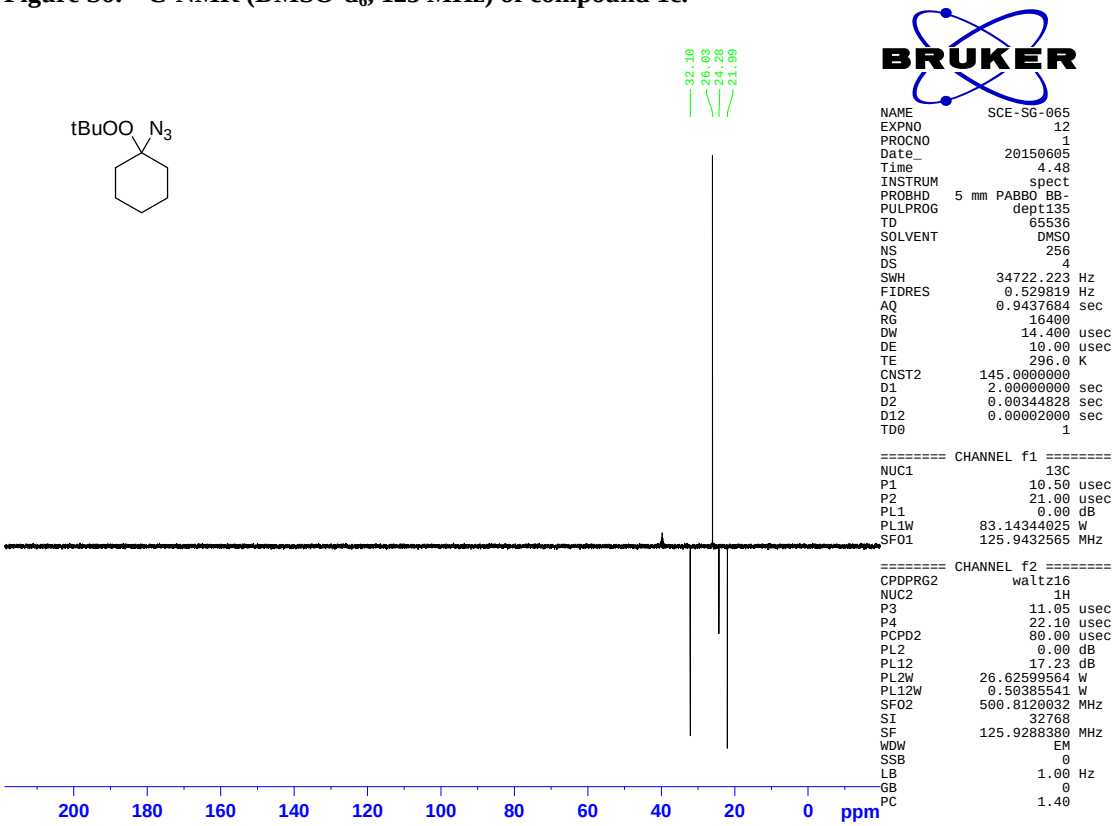


Figure S7: DEPT 135-NMR (DMSO-d$_6$, 125 MHz) of compound 1c.

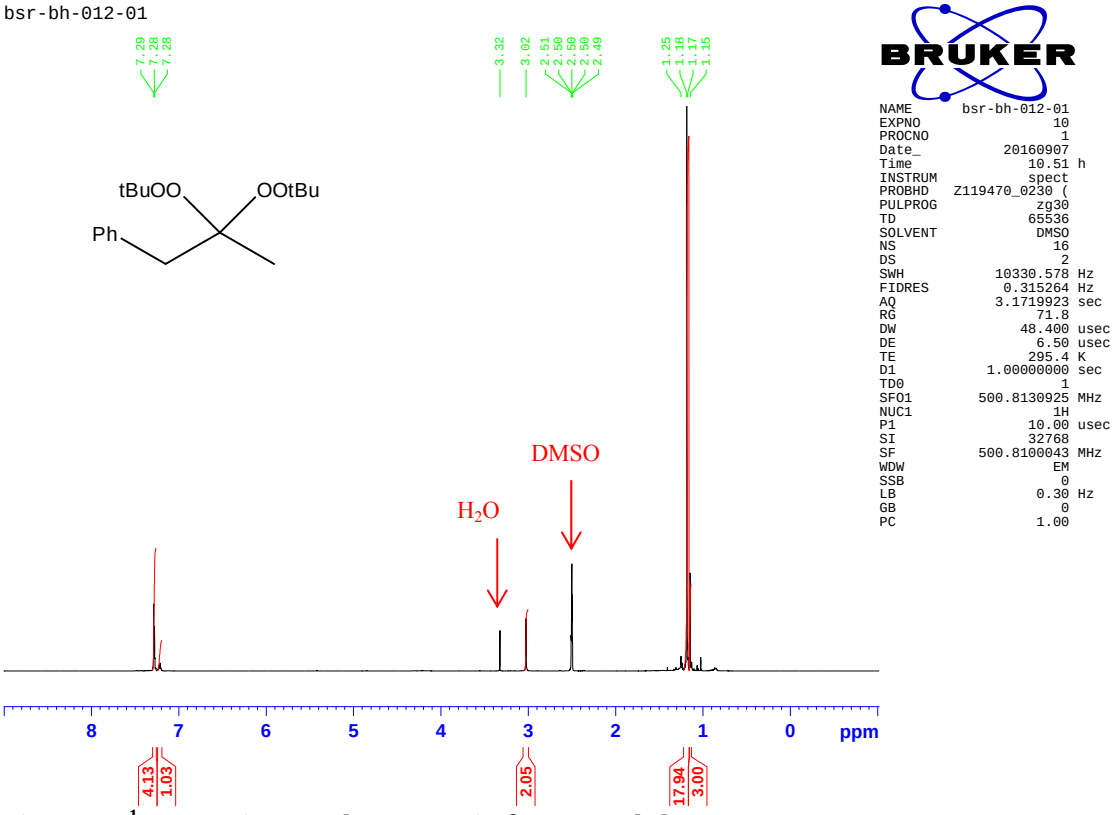


Figure S8: ^{1}H-NMR (DMSO-d$_6$, 500 MHz) of compound 3b.

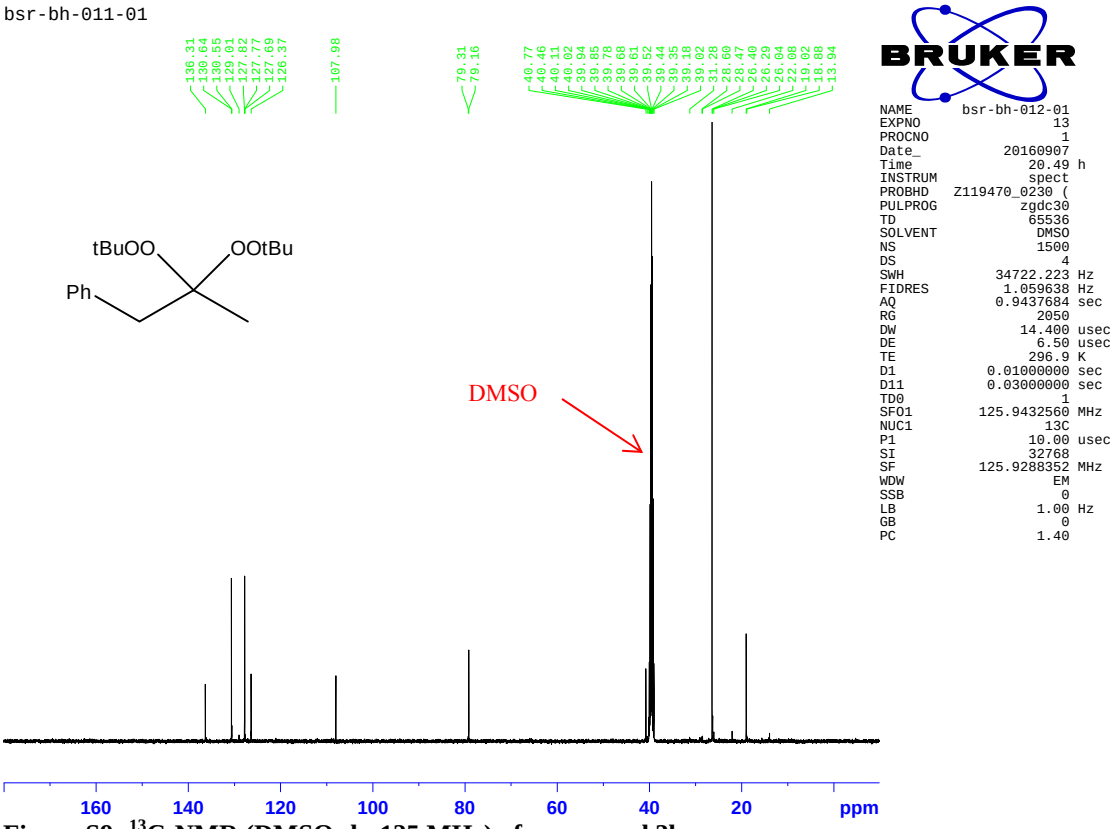


Figure S9: ^{13}C-NMR (DMSO-d$_6$, 125 MHz) of compound 3b.

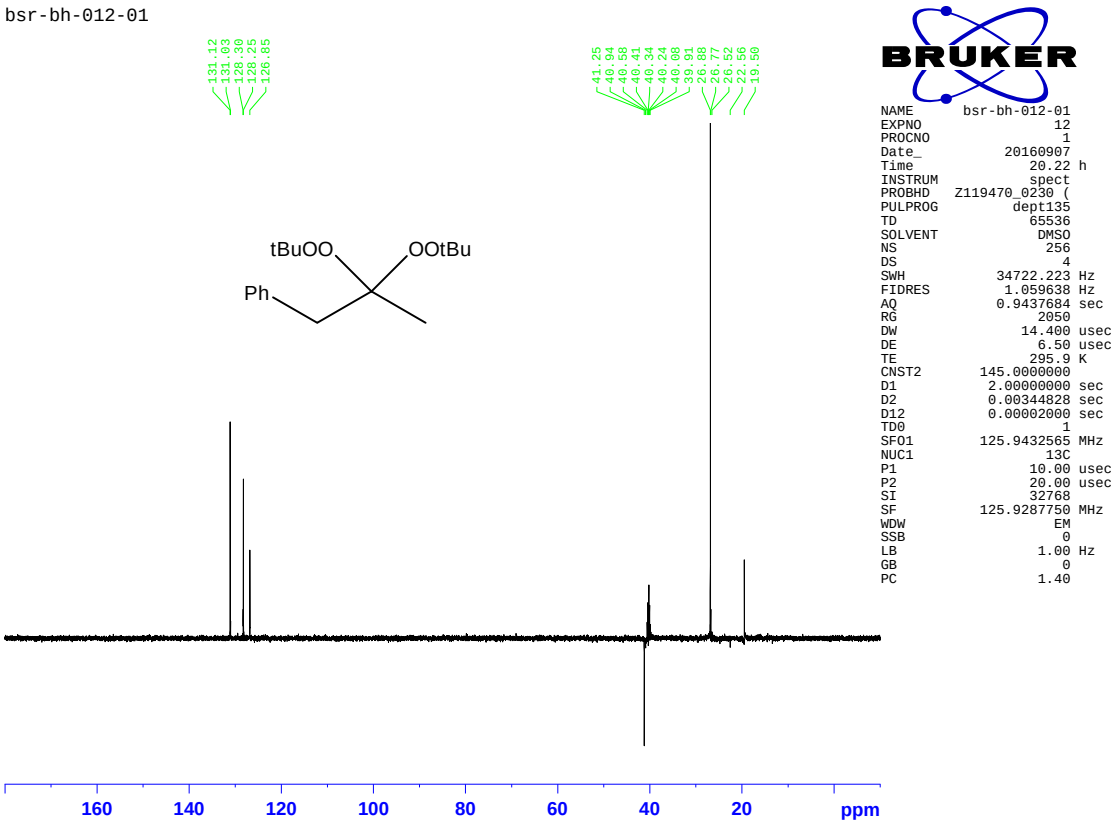


Figure S10: DEPT 135-NMR (DMSO-d_6, 125 MHz) of compound 3b.

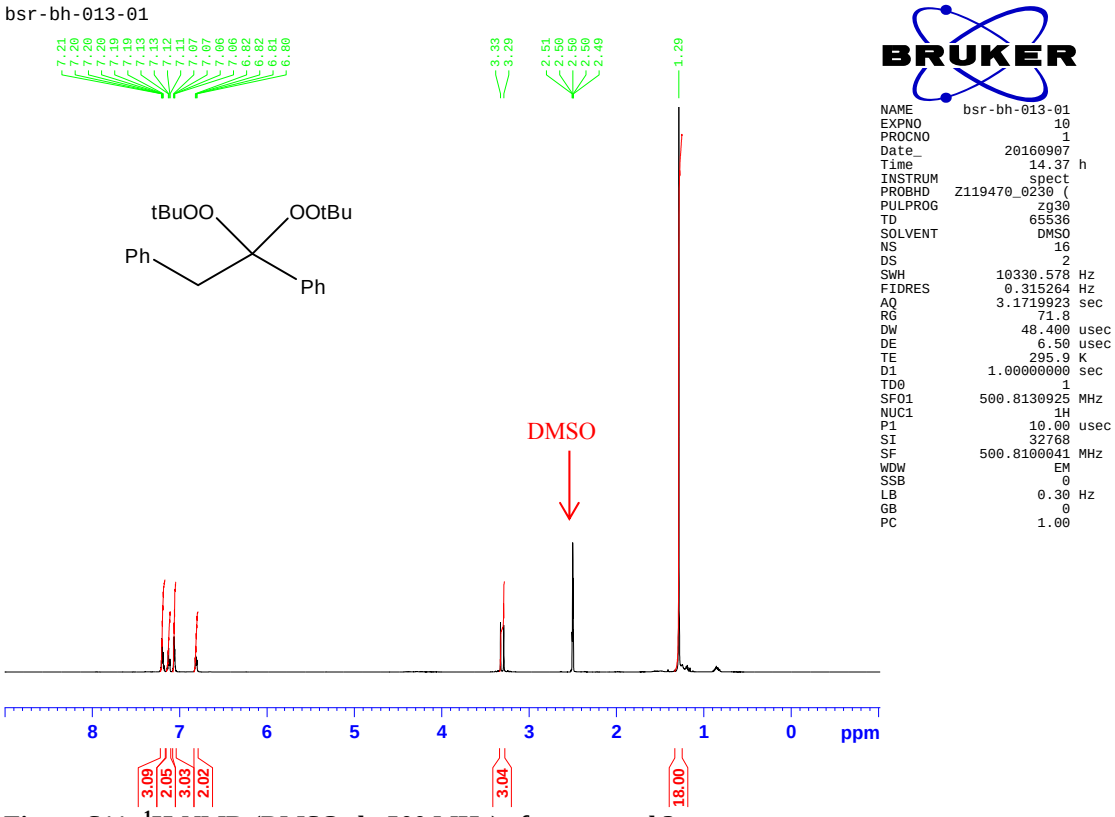


Figure S11: ^{1}H-NMR (DMSO-d_6, 500 MHz) of compound 3c.

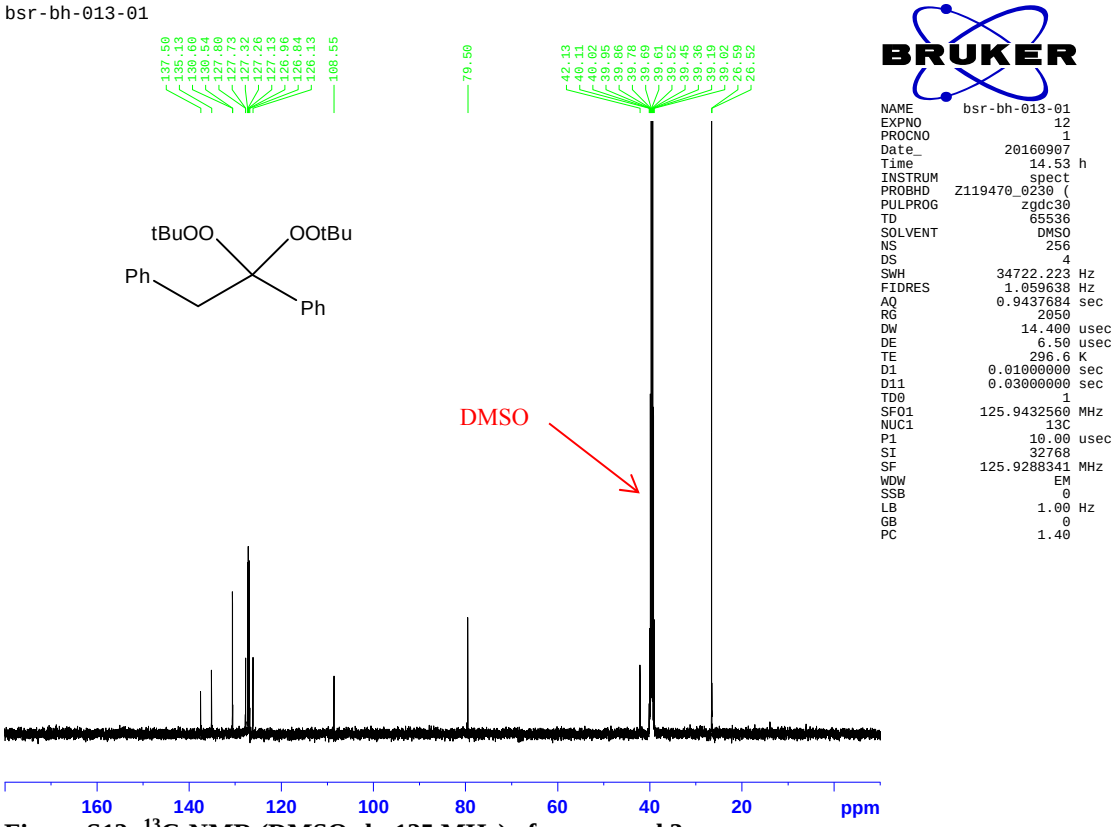


Figure S12: ^{13}C-NMR (DMSO-d$_6$, 125 MHz) of compound 3c.

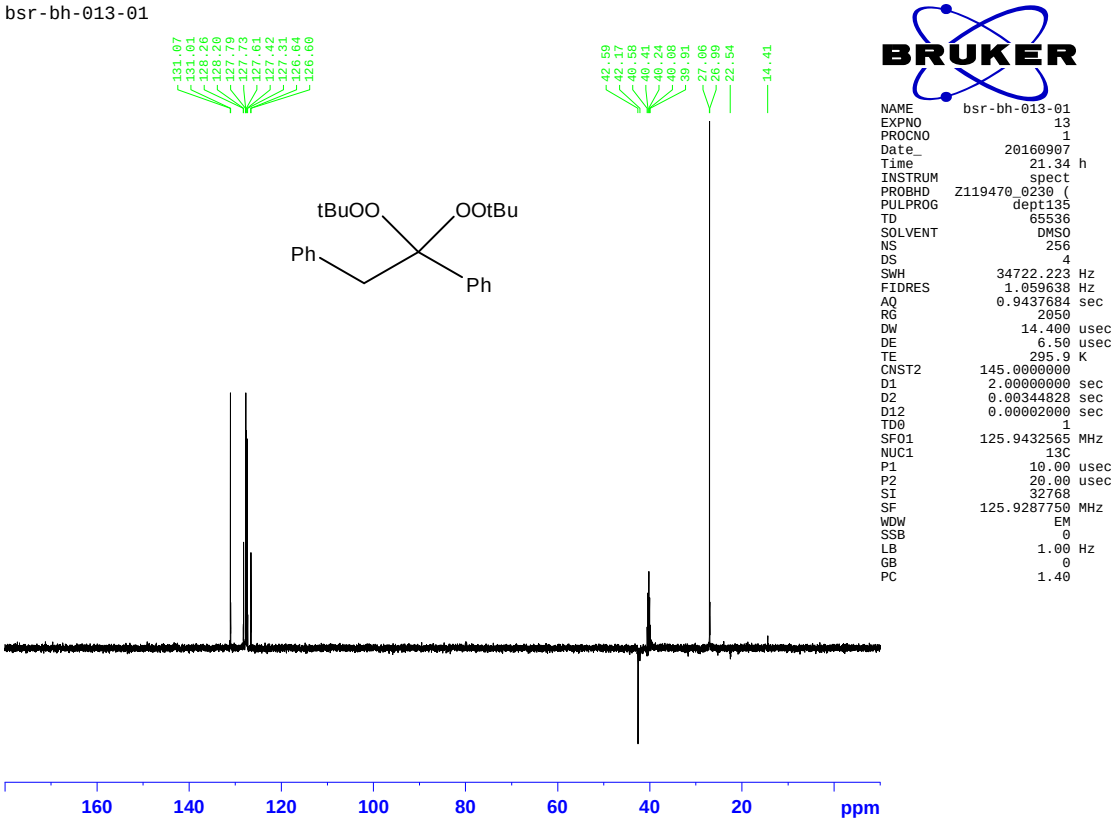


Figure S13: DEPT 135-NMR (DMSO-d$_6$, 125 MHz) of compound 3c.

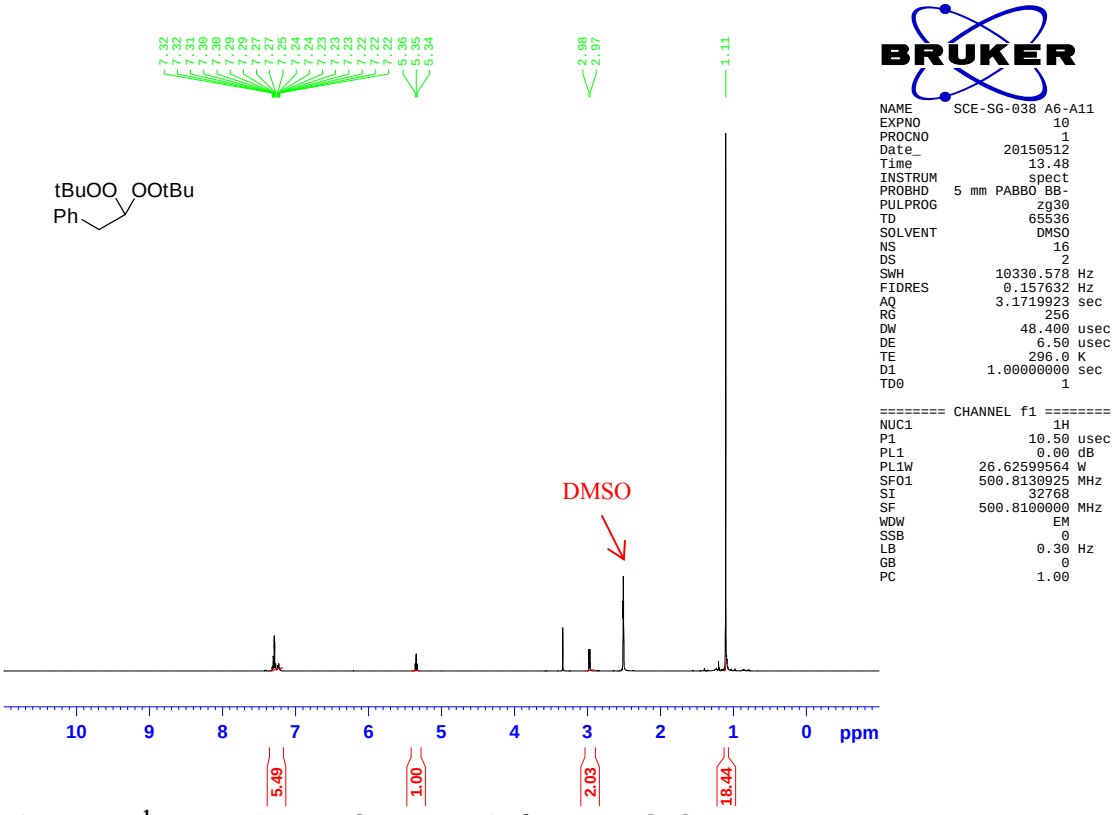


Figure S14: ^{1}H-NMR (DMSO-d$_6$, 500 MHz) of compound 3d.

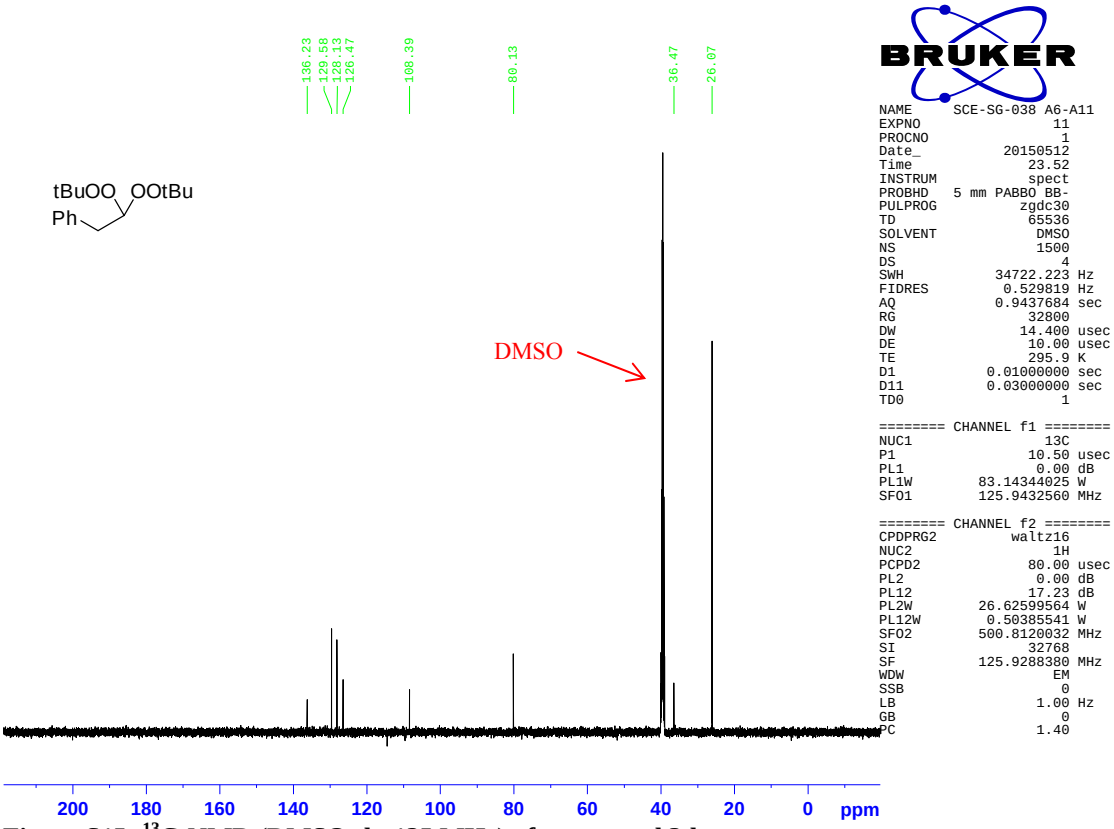


Figure S15: ^{13}C-NMR (DMSO-d$_6$, 125 MHz) of compound 3d.

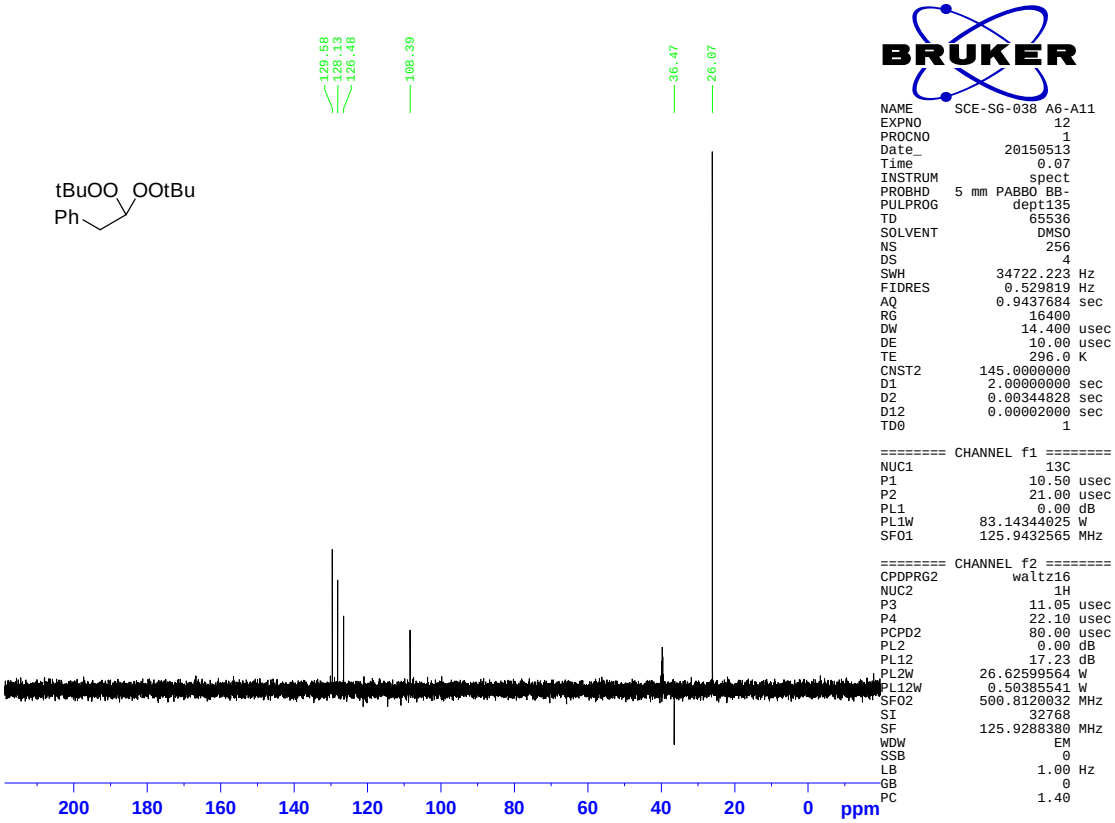


Figure S16: DEPT 135-NMR (DMSO-d_6, 125 MHz) of compound 3d.

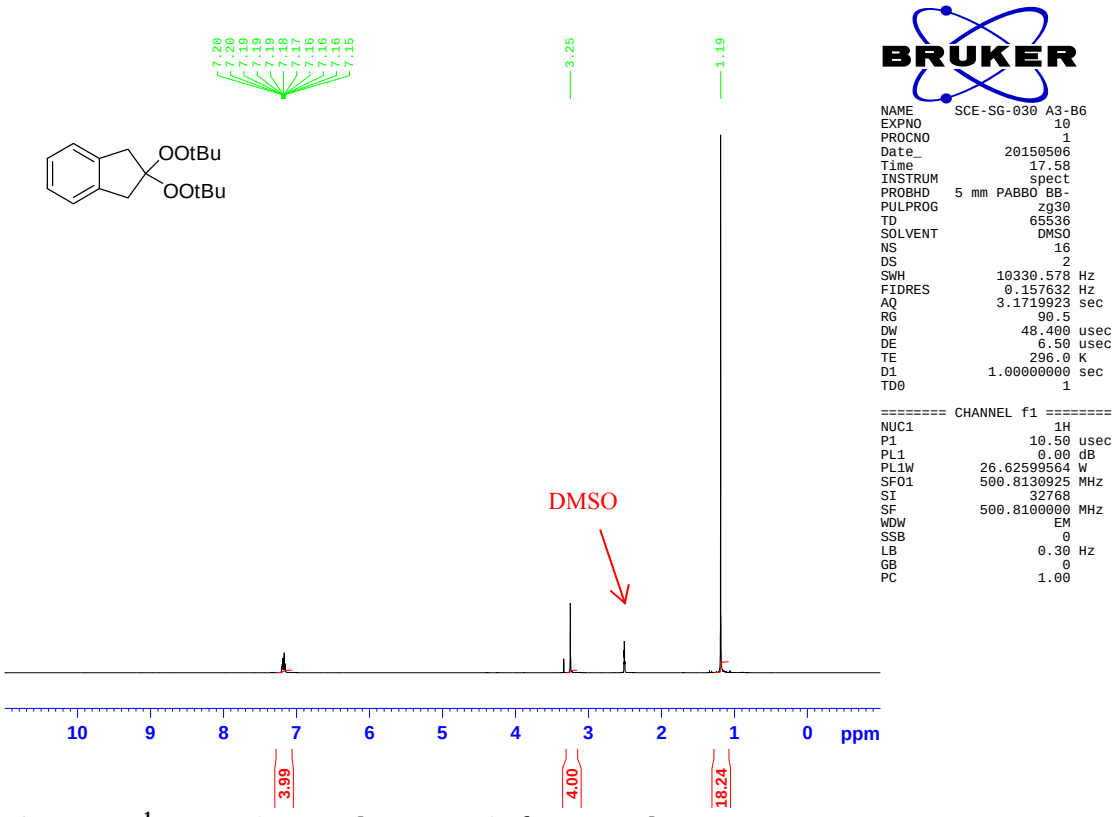


Figure S17: ^{1}H-NMR (DMSO-d_6, 500 MHz) of compound 6a.

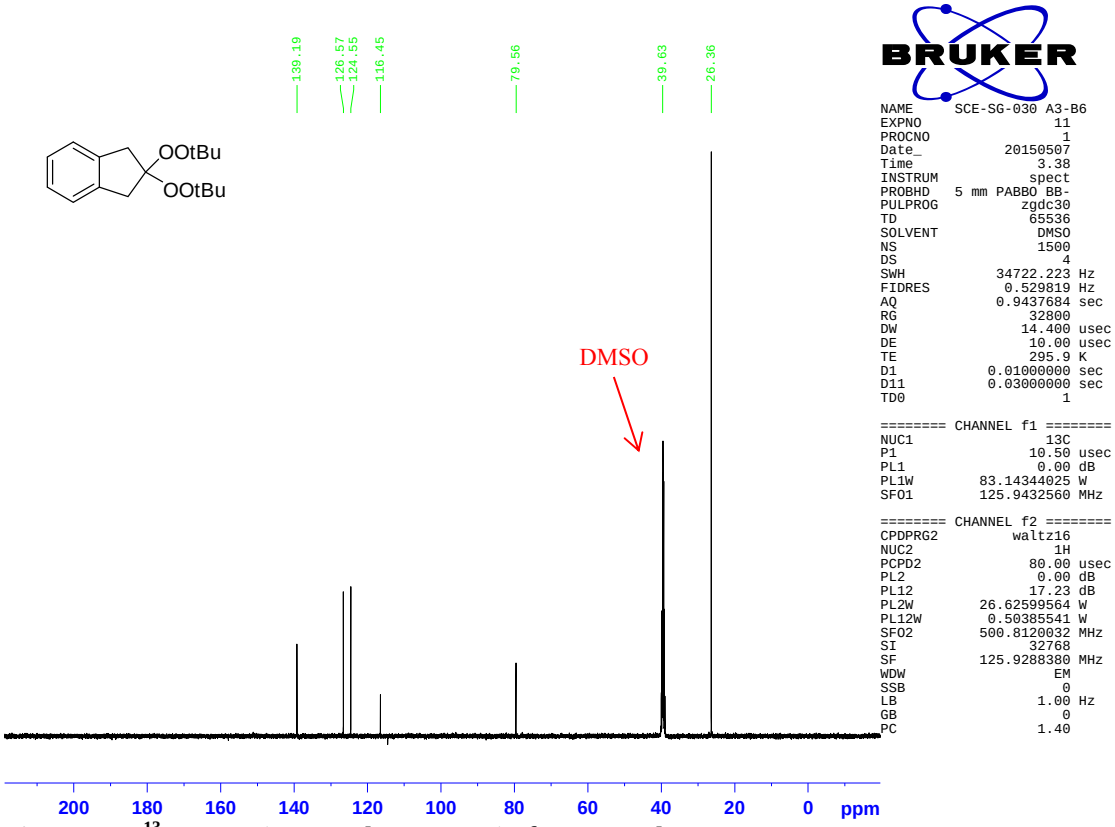


Figure S18: ^{13}C-NMR (DMSO-d$_6$, 125 MHz) of compound 6a.

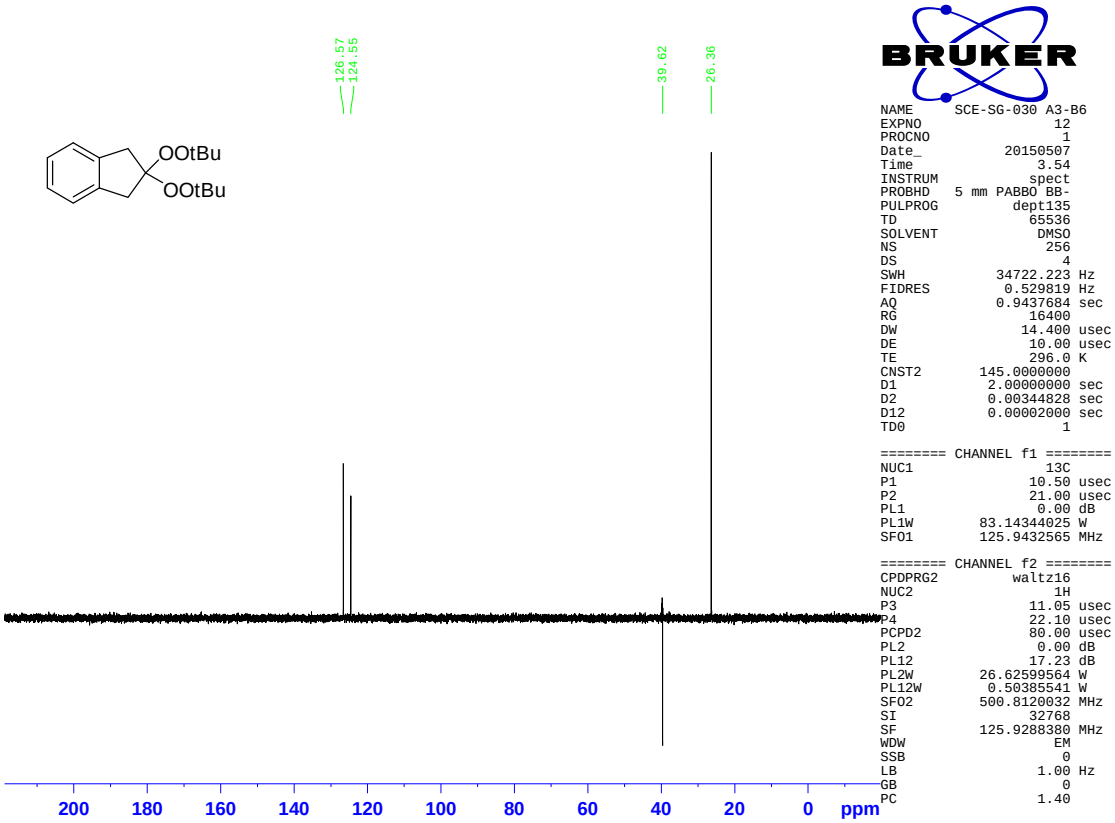


Figure S19: DEPT 135-NMR (DMSO-d$_6$, 125 MHz) of compound 6a.

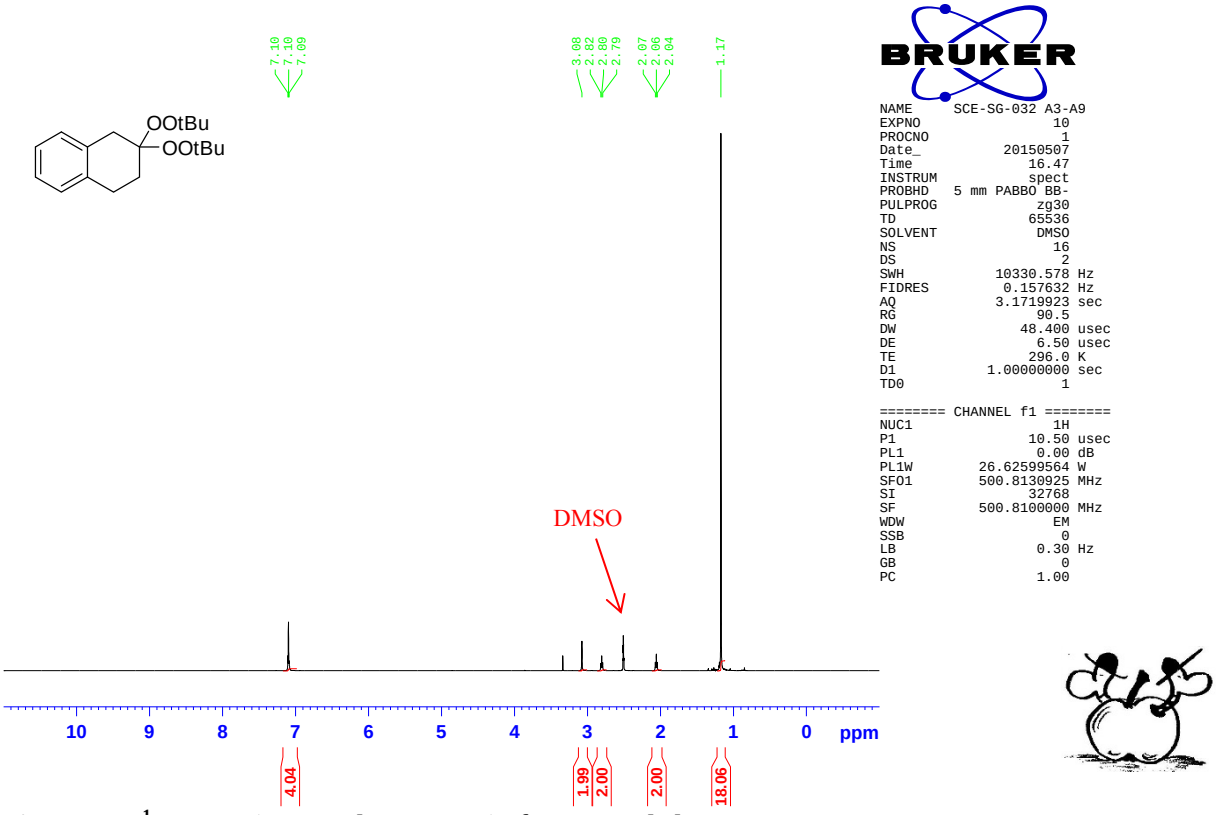


Figure S20: ^{1}H-NMR (DMSO-d$_6$, 500 MHz) of compound 6b.

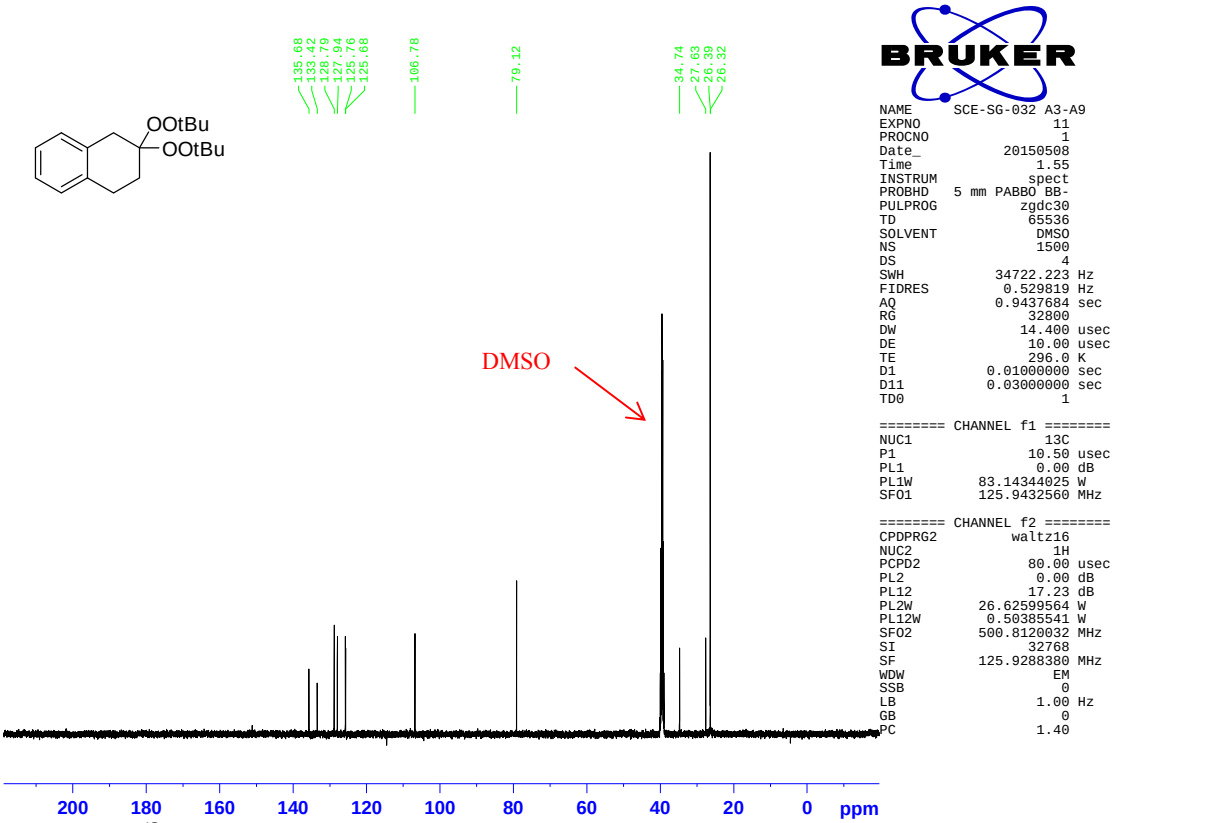
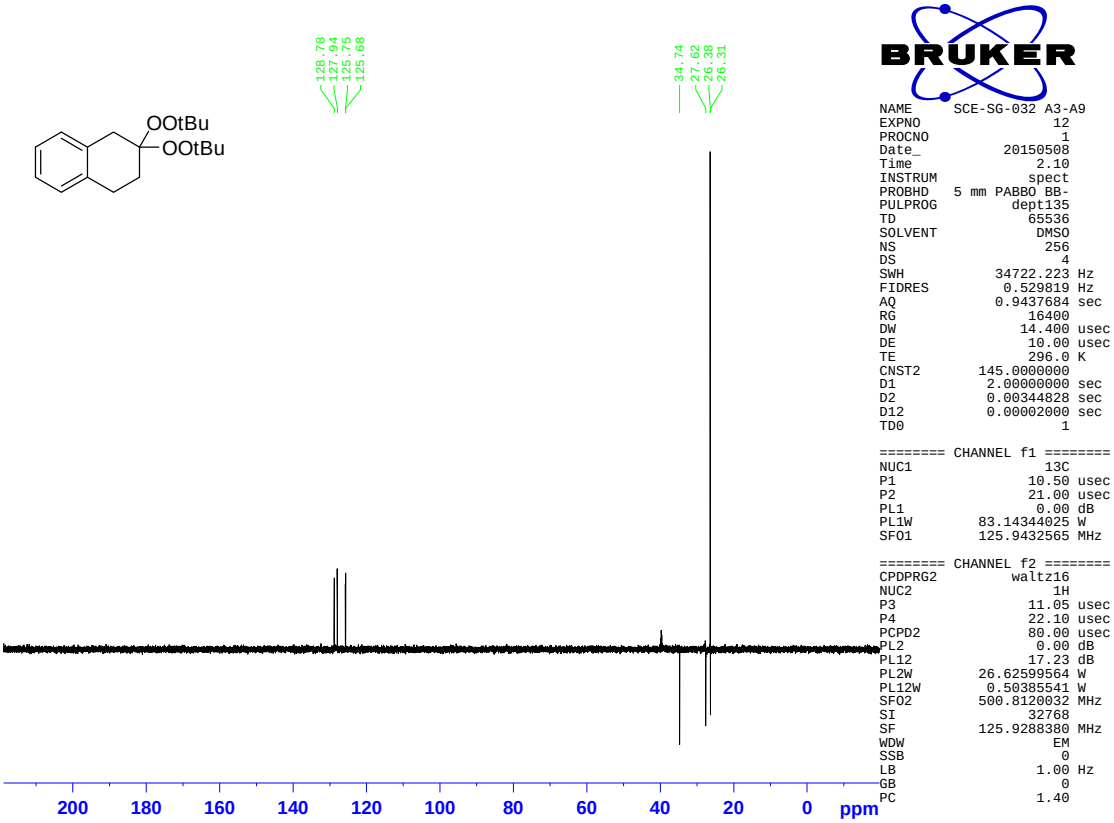


Figure S21: ^{13}C-NMR (DMSO-d$_6$, 125 MHz) of compound 6b.

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NS                      256
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FIDRES            0.529819 Hz
AQ               0.9437684 sec
RG                    16400
DW                 14.400 usec
DE                 10.00 usec
TE                   296.0 K
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D2                0.00344828 sec
D12               0.00002000 sec
TD0                       1

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NUC1                    13C
P1                  10.50 usec
P2                  21.00 usec
PL1                  0.00 dB
PL1W           83.14344025 W
SFO1           125.9432565 MHz

======== CHANNEL f2 ========
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NUC2                    1H
P3                  11.05 usec
P4                  22.10 usec
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                17.23 dB
PL2W           26.62599564 W
PL12W           0.50385541 W
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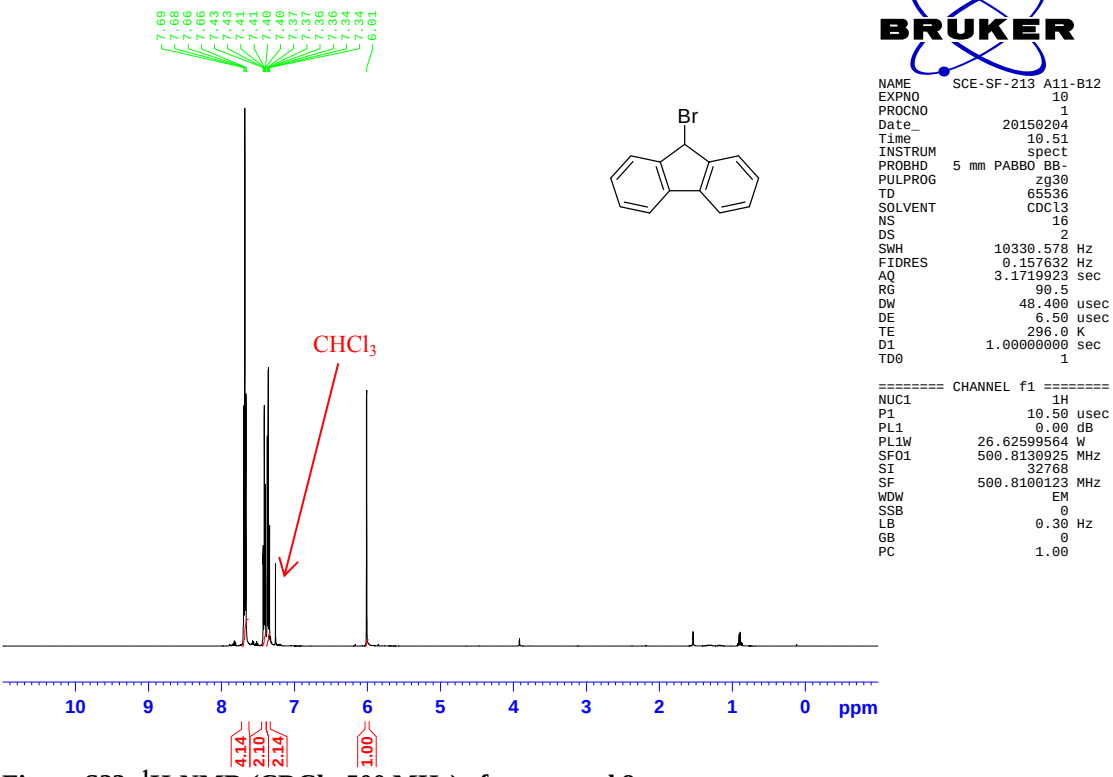
PC                     1.40
```

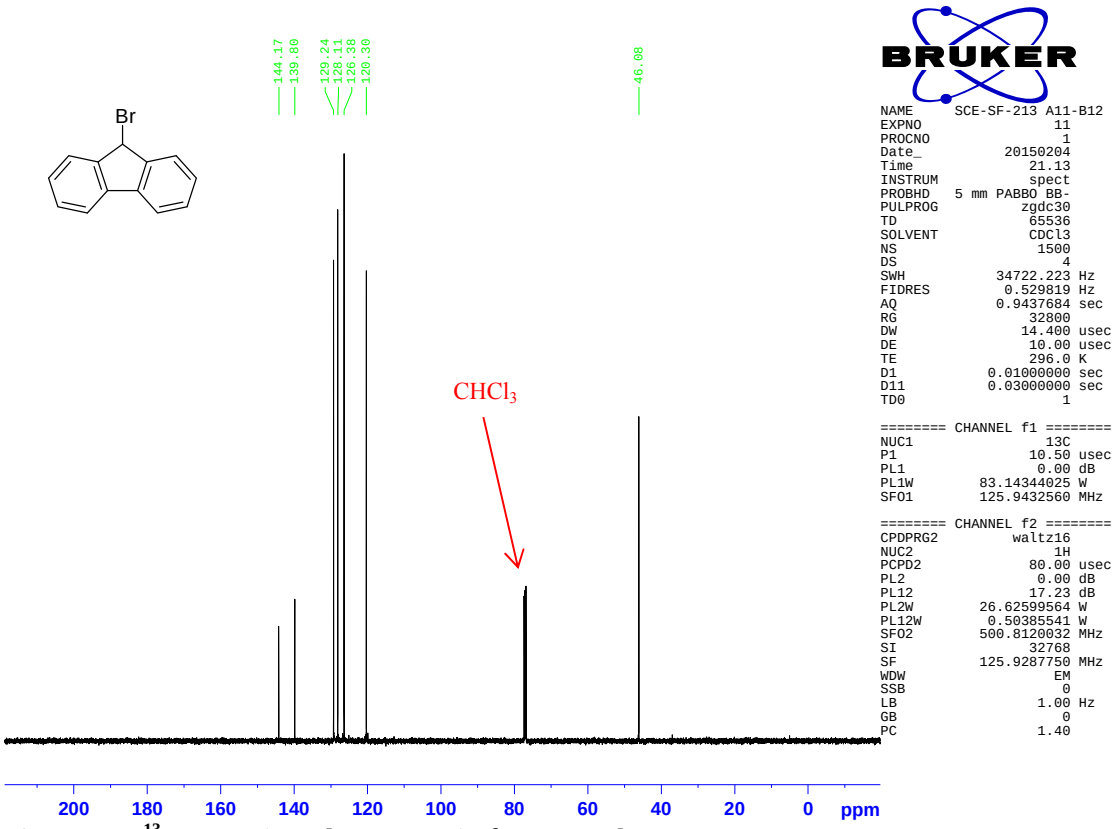
Figure S22: DEPT 135-NMR (DMSO-d_6, 125 MHz) of compound 6b.




```
NAME        SCE-SF-213 A11-B12
EXPNO                    10
PROCNO                    1
Date_              20150204
Time                  10.51
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH              10330.578 Hz
FIDRES            0.157632 Hz
AQ               3.1719923 sec
RG                     90.5
DW                 48.400 usec
DE                  6.50 usec
TE                   296.0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    1H
P1                  10.50 usec
PL1                  0.00 dB
PL1W           26.62599564 W
SFO1           500.8130925 MHz
SI                    32768
SF             500.8100123 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

Figure S23: ^{1}H-NMR ($CDCl_3$, 500 MHz) of compound 8.

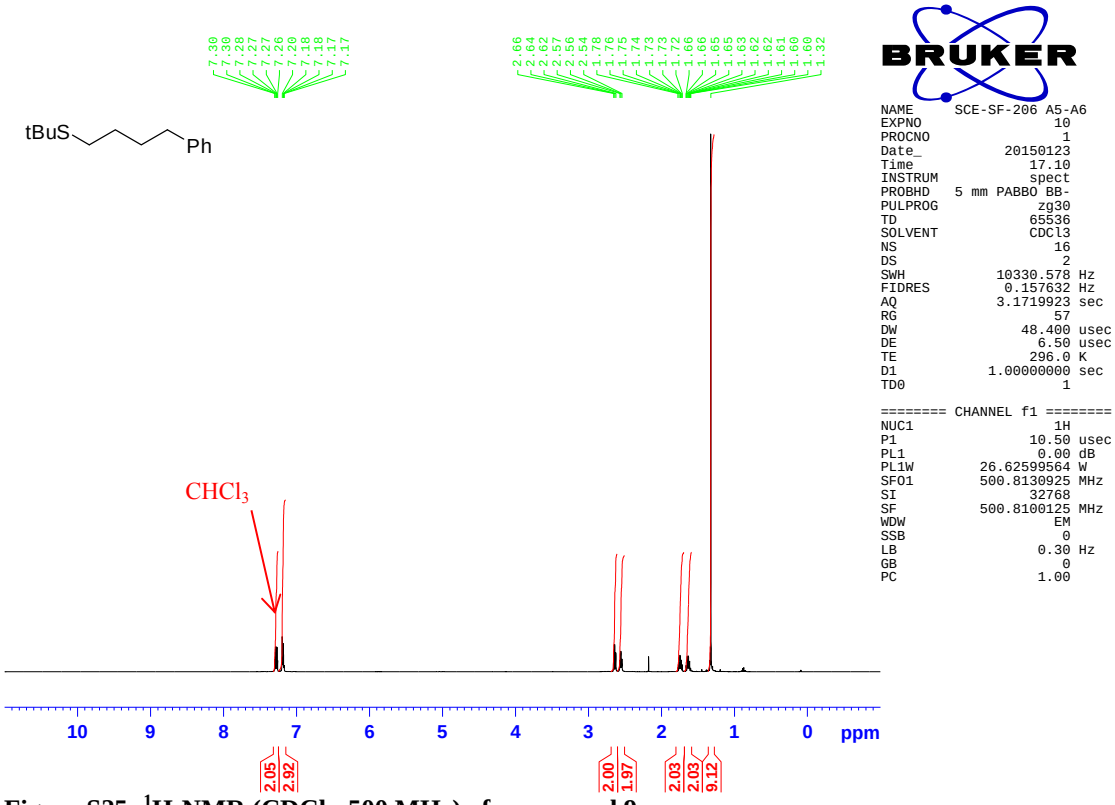



```
NAME        SCE-SF-213 A11-B12
EXPNO                       11
PROCNO                       1
Date_             20150204
Time                  21.13
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG             zgdc30
TD                   65536
SOLVENT              CDCl3
NS                    1500
DS                       4
SWH              34722.223 Hz
FIDRES            0.529819 Hz
AQ               0.9437684 sec
RG                   32800
DW                  14.400 usec
DE                  10.00 usec
TE                  296.0 K
D1              0.01000000 sec
D11             0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                      13C
P1                    10.50 usec
PL1                    0.00 dB
PL1W           83.14344025 W
SFO1          125.9432560 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                      1H
PCPD2                80.00 usec
PL2                    0.00 dB
PL12                  17.23 dB
PL2W           26.62599564 W
PL12W           0.50385541 W
SFO2          500.8120032 MHz
SI                    32768
SF            125.9287750 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

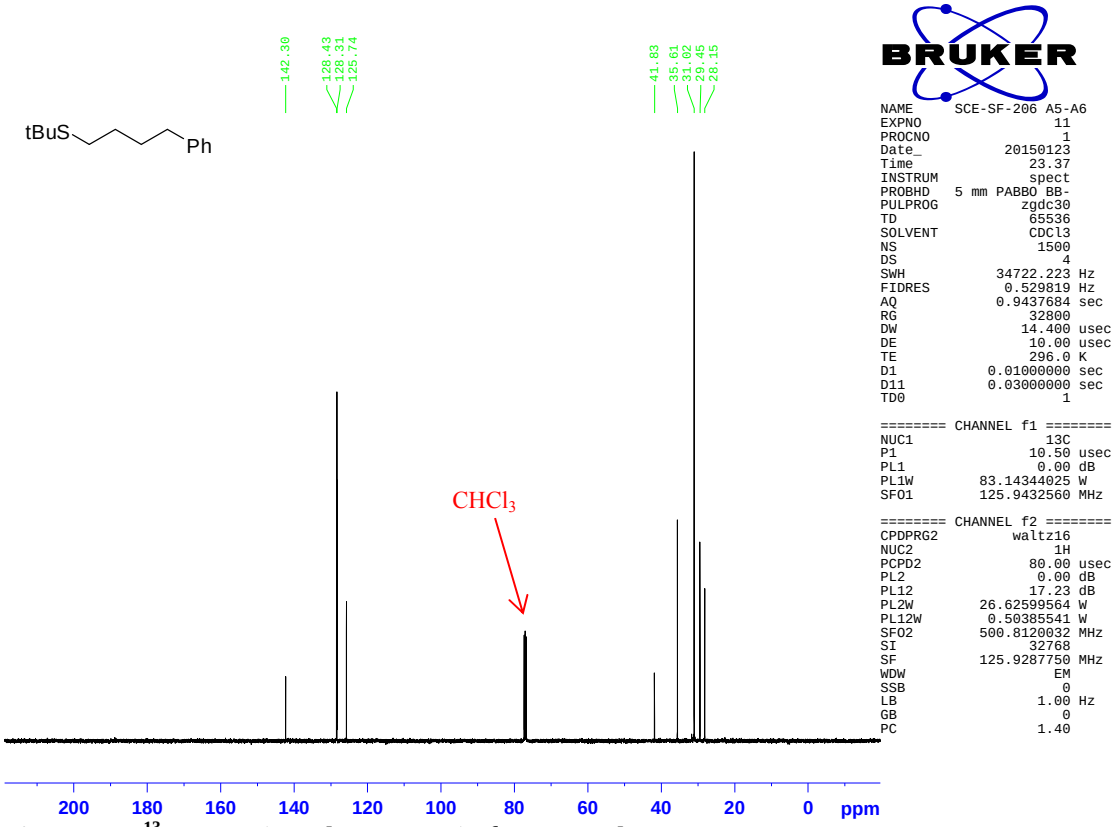
Figure S24: ^{13}C-NMR ($CDCl_3$, 125 MHz) of compound 8.




```
NAME        SCE-SF-206 A5-A6
EXPNO                       10
PROCNO                       1
Date_             20150123
Time                  17.10
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH              10330.578 Hz
FIDRES            0.157632 Hz
AQ               3.1719923 sec
RG                      57
DW                  48.400 usec
DE                   6.50 usec
TE                  296.0 K
D1              1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                      1H
P1                    10.50 usec
PL1                    0.00 dB
PL1W           26.62599564 W
SFO1          500.8130925 MHz
SI                    32768
SF            500.8100125 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

Figure S25: ^{1}H-NMR ($CDCl_3$, 500 MHz) of compound 9.

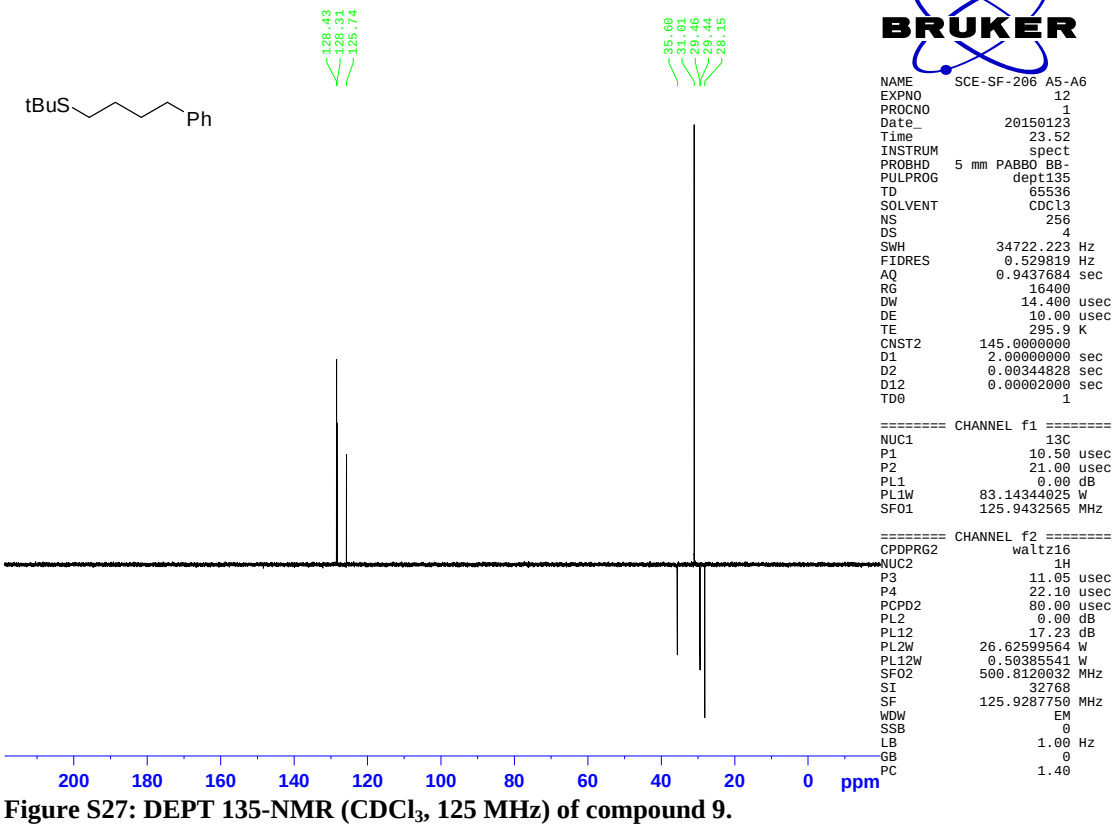



```
NAME        SCE-SF-206 A5-A6
EXPNO                    11
PROCNO                    1
Date_           20150123
Time               23.37
INSTRUM            spect
PROBHD    5 mm PABBO BB-
PULPROG          zgdc30
TD                 65536
SOLVENT            CDCl3
NS                  1500
DS                     4
SWH           34722.223 Hz
FIDRES         0.529819 Hz
AQ            0.9437684 sec
RG                 32800
DW                14.400 usec
DE                10.00 usec
TE                296.0 K
D1           0.01000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                10.50 usec
PL1                0.00 dB
PL1W        83.14344025 W
SFO1       125.9432560 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              17.23 dB
PL2W        26.62599564 W
PL12W        0.50385541 W
SFO2       500.8120032 MHz
SI                 32768
SF         125.9287750 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

Figure S26: ^{13}C-NMR ($CDCl_3$, 125 MHz) of compound 9.




```
NAME        SCE-SF-206 A5-A6
EXPNO                    12
PROCNO                    1
Date_           20150123
Time               23.52
INSTRUM            spect
PROBHD    5 mm PABBO BB-
PULPROG          dept135
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     4
SWH           34722.223 Hz
FIDRES         0.529819 Hz
AQ            0.9437684 sec
RG                 16400
DW                14.400 usec
DE                10.00 usec
TE                295.9 K
CNST2       145.0000000
D1           2.00000000 sec
D2           0.00344828 sec
D12          0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                10.50 usec
P2                21.00 usec
PL1                0.00 dB
PL1W        83.14344025 W
SFO1       125.9432565 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
P3                11.05 usec
P4                22.10 usec
PCPD2             80.00 usec
PL2                0.00 dB
PL12              17.23 dB
PL2W        26.62599564 W
PL12W        0.50385541 W
SFO2       500.8120032 MHz
SI                 32768
SF         125.9287750 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

Figure S27: DEPT 135-NMR ($CDCl_3$, 125 MHz) of compound 9.

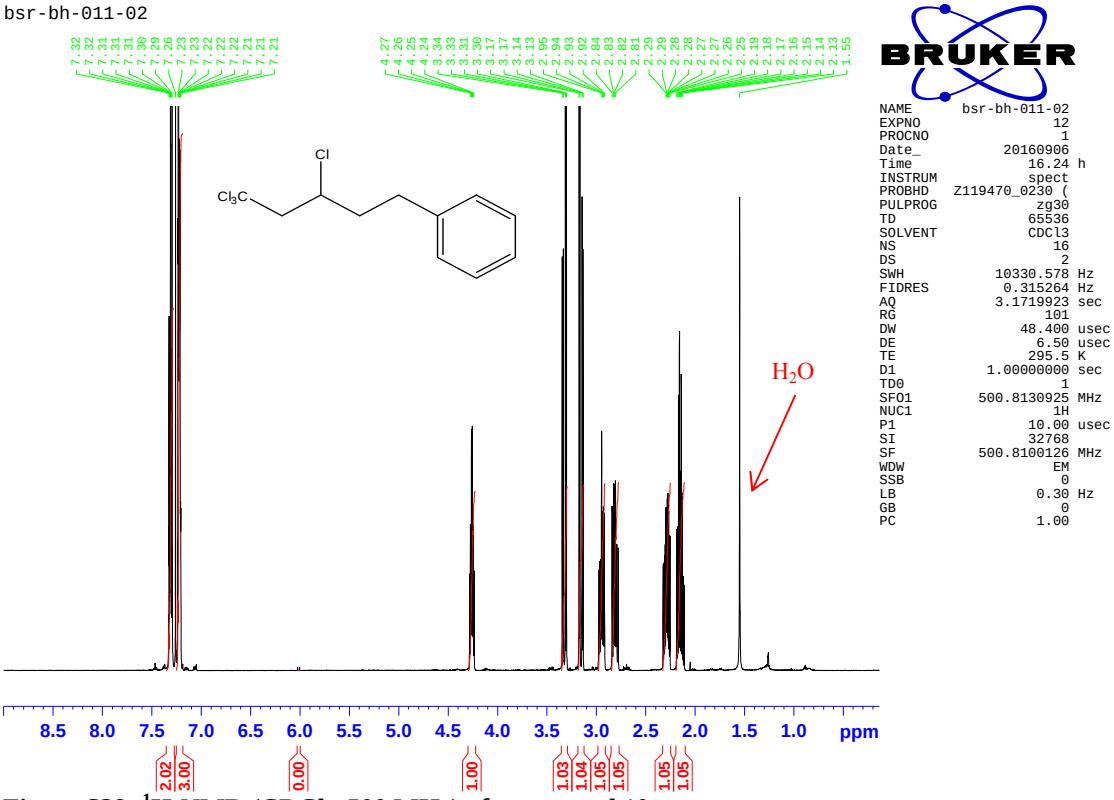


Figure S28: ^{1}H-NMR ($CDCl_3$, 500 MHz) of compound 10.

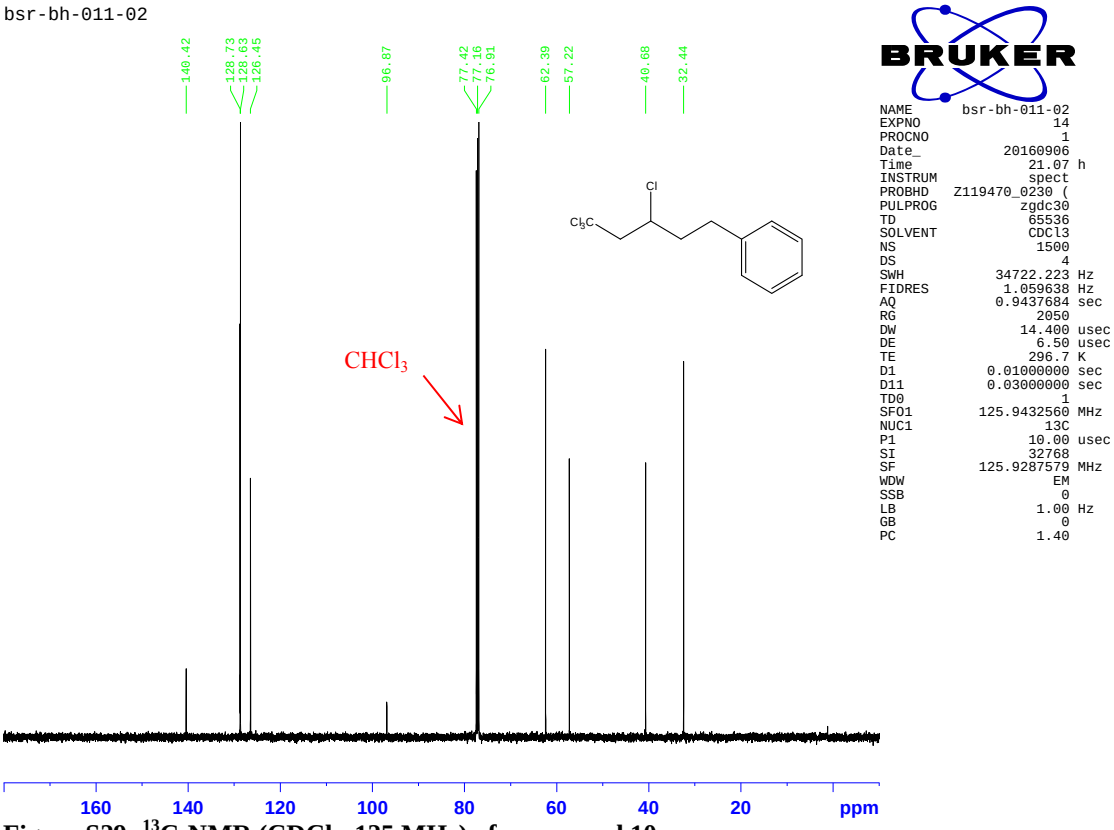


Figure S29: ^{13}C-NMR ($CDCl_3$, 125 MHz) of compound 10.

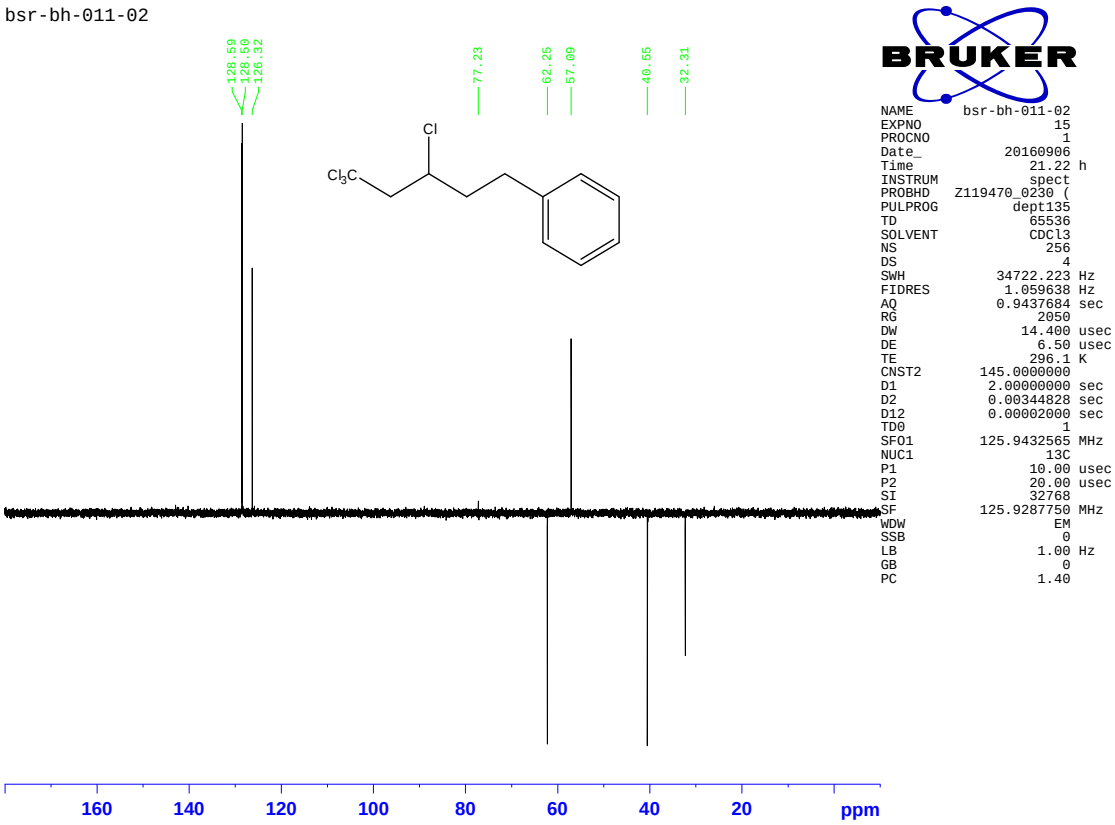


Figure S30: DEPT 135-NMR ($CDCl_3$, 125 MHz) of compound 10.

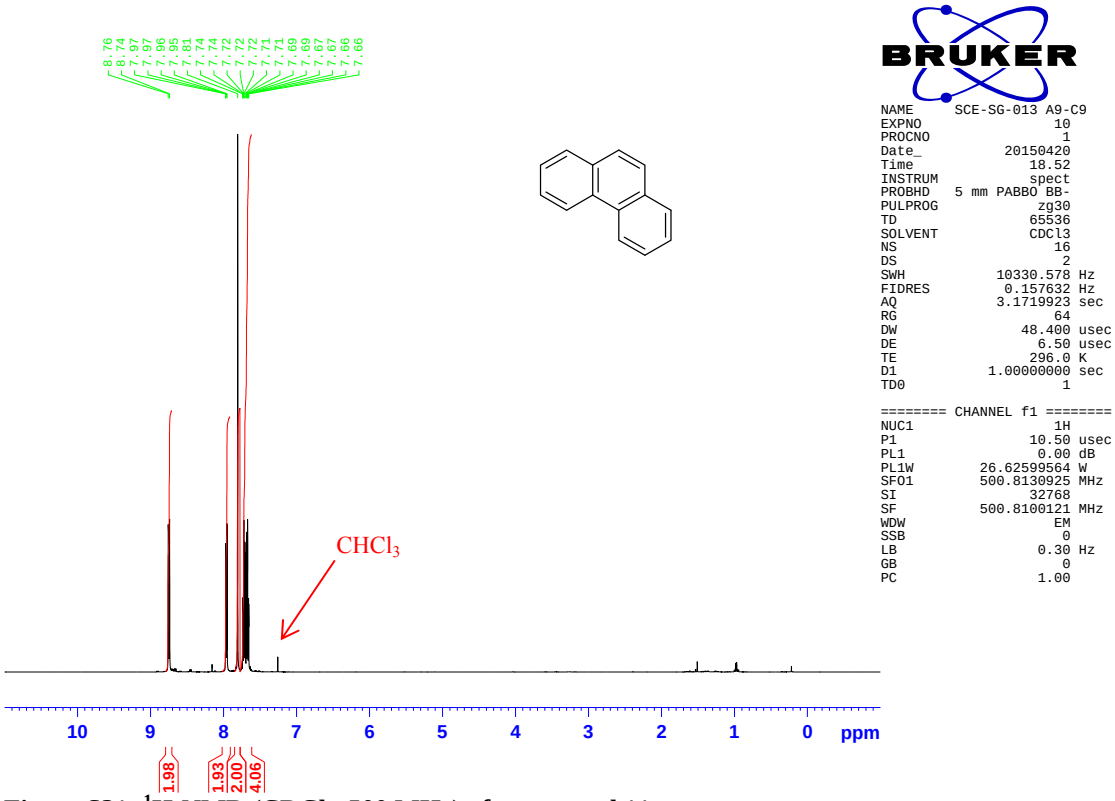
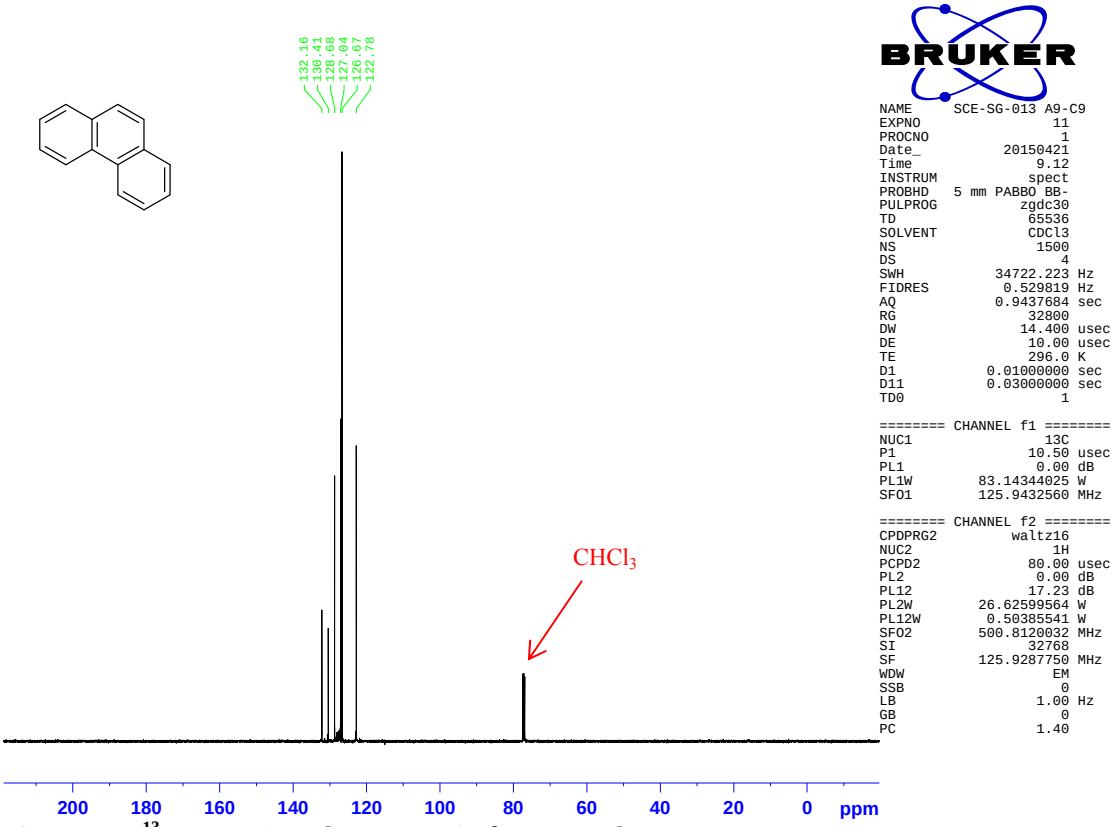


Figure S31: ^{1}H-NMR ($CDCl_3$, 500 MHz) of compound 11.

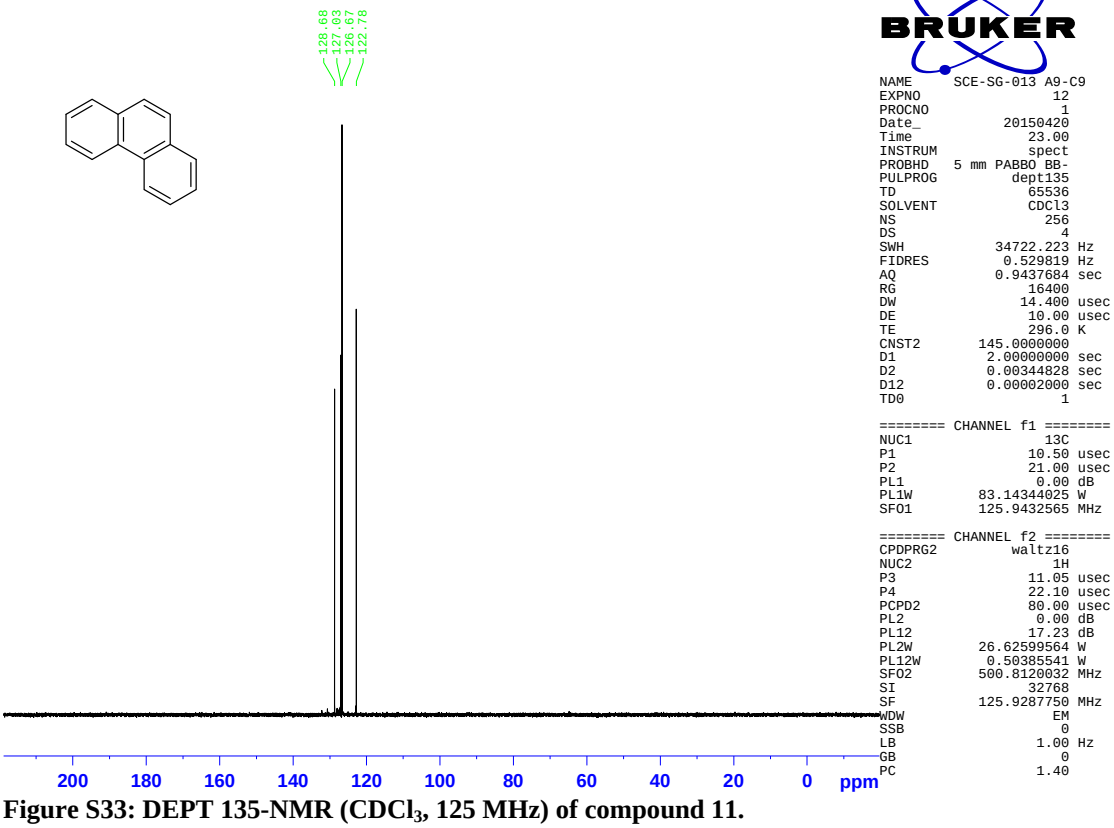



```
NAME        SCE-SG-013 A9-C9
EXPNO                    11
PROCNO                    1
Date_            20150421
Time                 9.12
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG           zgdc30
TD                 65536
SOLVENT            CDCl3
NS                  1500
DS                     4
SWH           34722.223 Hz
FIDRES         0.529819 Hz
AQ            0.9437684 sec
RG                 32800
DW                14.400 usec
DE                10.00 usec
TE                296.0 K
D1           0.01000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.50 usec
PL1                 0.00 dB
PL1W        83.14344025 W
SFO1       125.9432560 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               17.23 dB
PL2W        26.62599564 W
PL12W        0.50385541 W
SFO2       500.8120032 MHz
SI                 32768
SF         125.9287750 MHz
WDW                 EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

Figure S32: ^{13}C-NMR ($CDCl_3$, 125 MHz) of compound 11.

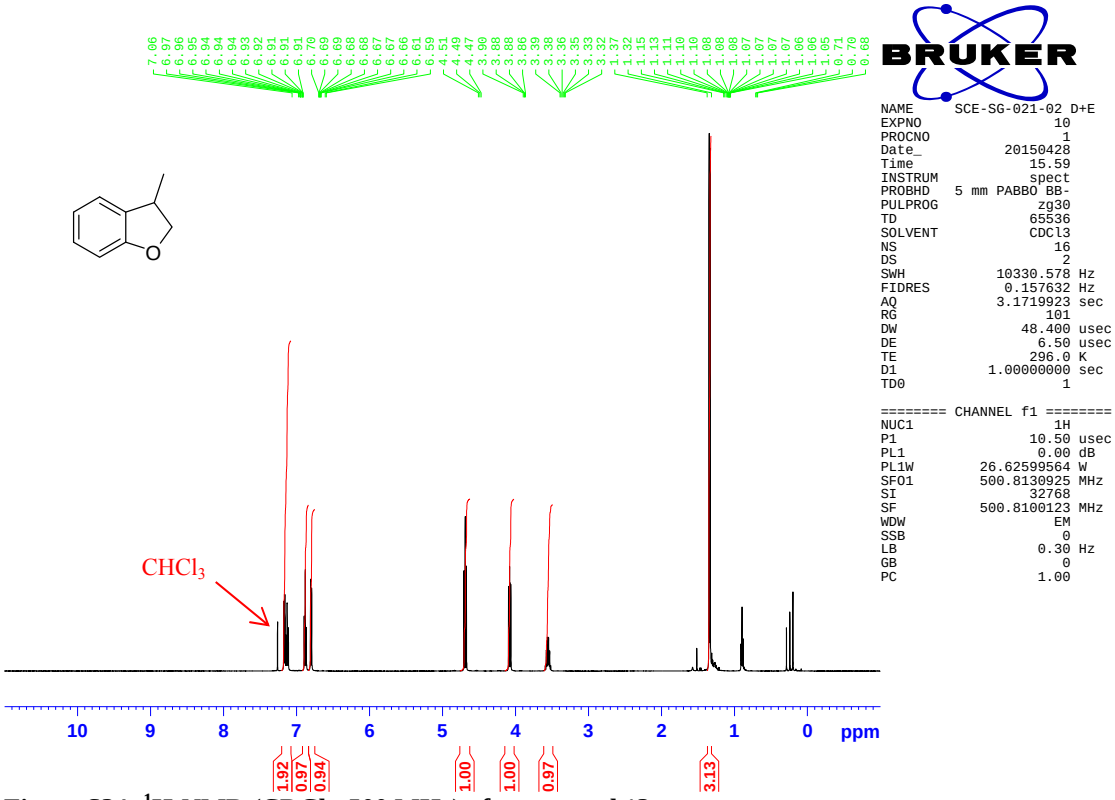



```
NAME        SCE-SG-013 A9-C9
EXPNO                    12
PROCNO                    1
Date_            20150420
Time                23.00
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG           dept135
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     4
SWH           34722.223 Hz
FIDRES         0.529819 Hz
AQ            0.9437684 sec
RG                 16400
DW                14.400 usec
DE                10.00 usec
TE                296.0 K
CNST2       145.0000000
D1           2.00000000 sec
D2           0.00344828 sec
D12          0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.50 usec
P2                 21.00 usec
PL1                 0.00 dB
PL1W        83.14344025 W
SFO1       125.9432565 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
P3                 11.05 usec
P4                 22.10 usec
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               17.23 dB
PL2W        26.62599564 W
PL12W        0.50385541 W
SFO2       500.8120032 MHz
SI                 32768
SF         125.9287750 MHz
WDW                 EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

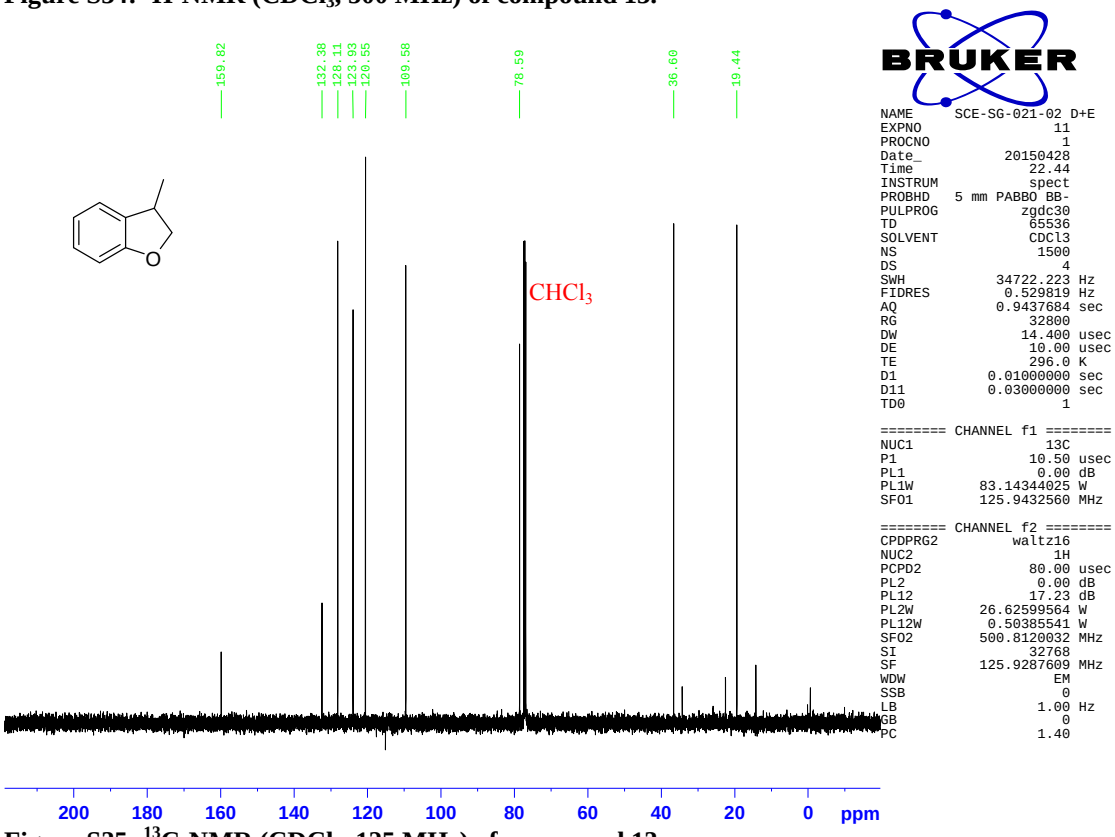
Figure S33: DEPT 135-NMR ($CDCl_3$, 125 MHz) of compound 11.




```
NAME        SCE-SG-021-02 D+E
EXPNO                    10
PROCNO                    1
Date_            20150428
Time                 15.59
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH             10330.578 Hz
FIDRES           0.157632 Hz
AQ               3.1719923 sec
RG                     101
DW                48.400 usec
DE                 6.50 usec
TE                 296.0 K
D1            1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   1H
P1                 10.50 usec
PL1                 0.00 dB
PL1W         26.62599564 W
SFO1         500.8130925 MHz
SI                   32768
SF           500.8100123 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                 1.00
```

Figure S34: ^{1}H-NMR ($CDCl_3$, 500 MHz) of compound 13.




```
NAME        SCE-SG-021-02 D+E
EXPNO                    11
PROCNO                    1
Date_            20150428
Time                 22.44
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG            zgdc30
TD                   65536
SOLVENT              CDCl3
NS                    1500
DS                       4
SWH             34722.223 Hz
FIDRES           0.529819 Hz
AQ               0.9437684 sec
RG                   32800
DW                14.400 usec
DE                 10.00 usec
TE                 296.0 K
D1            0.01000000 sec
D11           0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                  13C
P1                 10.50 usec
PL1                 0.00 dB
PL1W         83.14344025 W
SFO1         125.9432560 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                   1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               17.23 dB
PL2W         26.62599564 W
PL12W         0.50385541 W
SFO2         500.8120032 MHz
SI                   32768
SF           125.9287609 MHz
WDW                    EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                 1.40
```

Figure S35: ^{13}C-NMR ($CDCl_3$, 125 MHz) of compound 13.

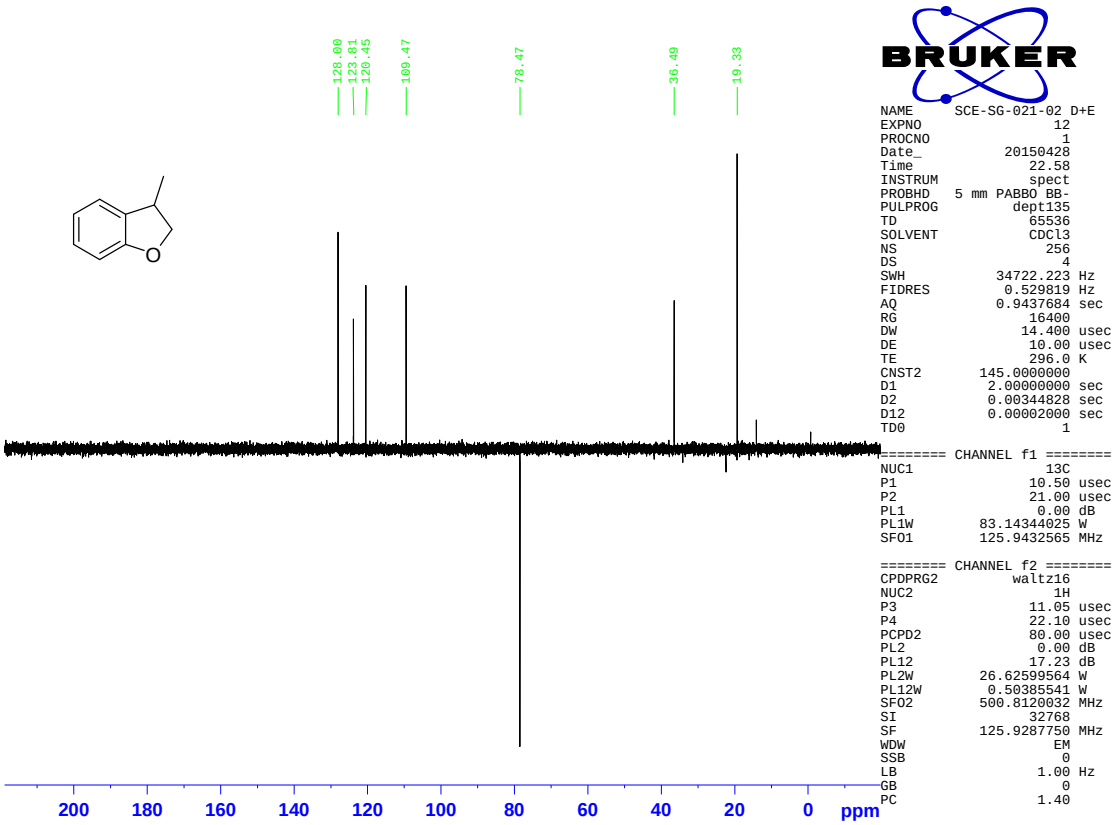


Figure S36: DEPT 135-NMR ($CDCl_3$, 125 MHz) of compound 13.

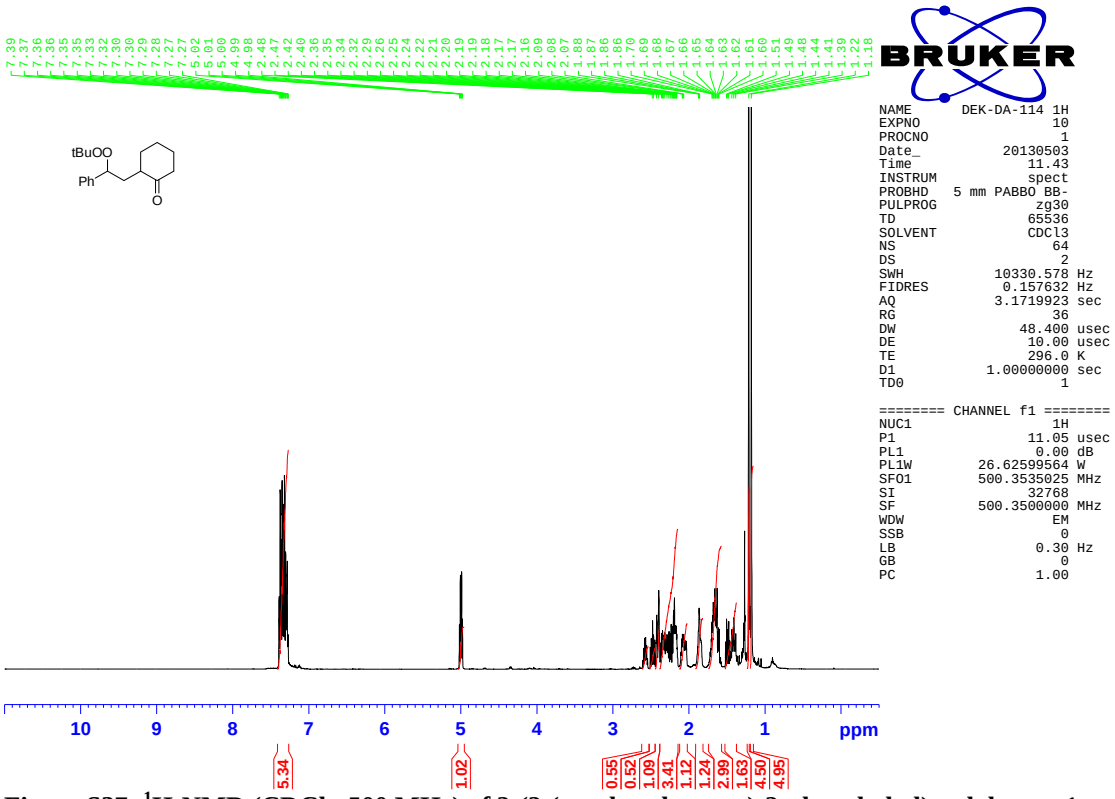
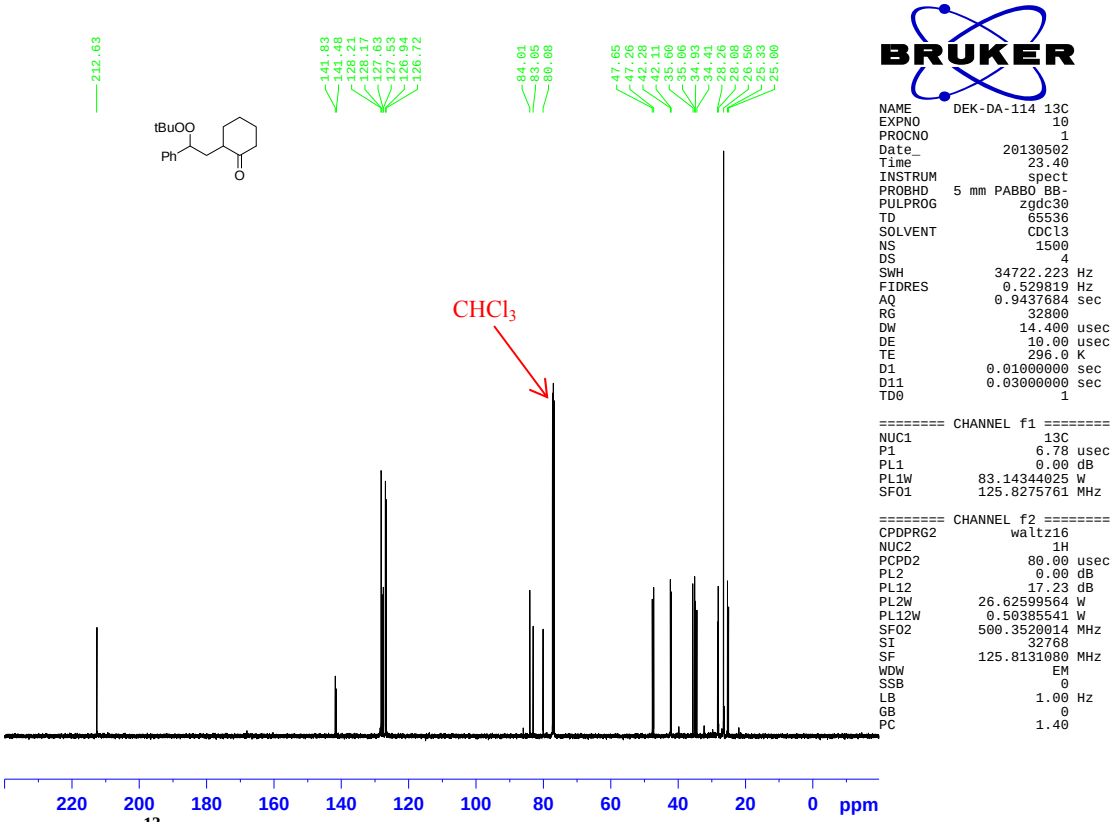


Figure S37: ^{1}H-NMR ($CDCl_3$, 500 MHz) of 2-(2-(tert-butylperoxy)-2-phenylethyl)cyclohexan-1-one.

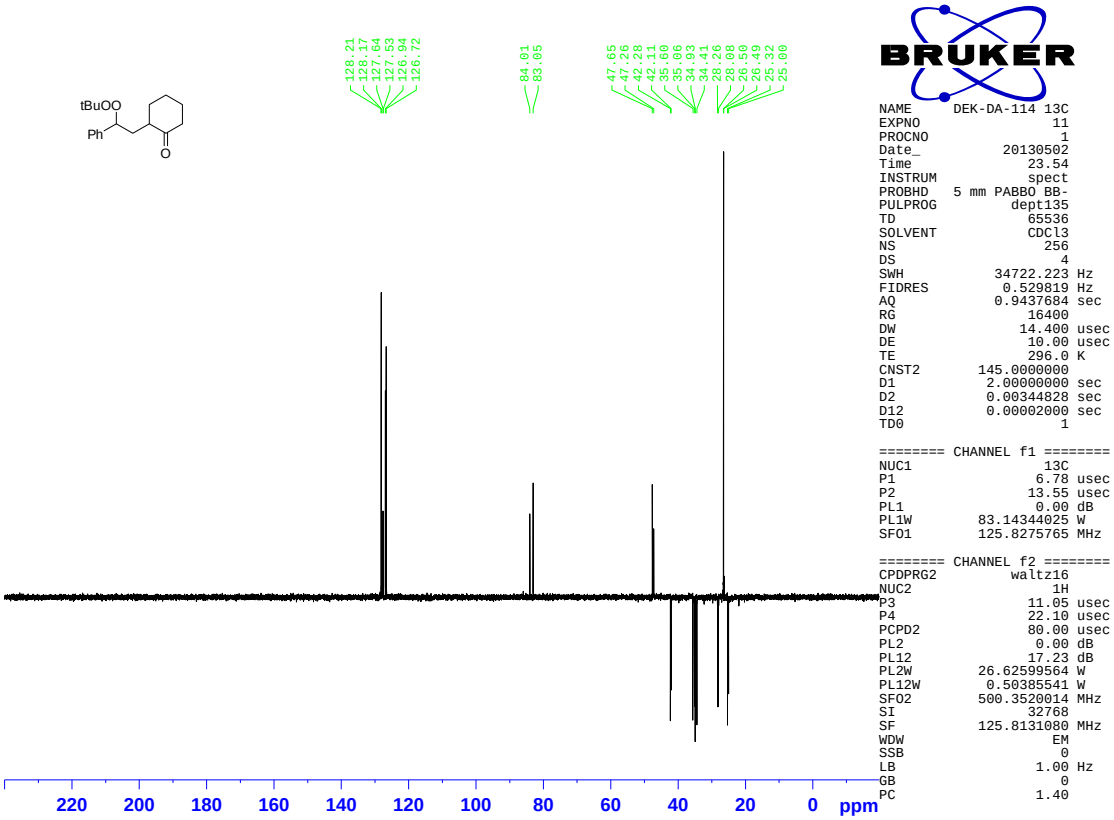



```
NAME        DEK-DA-114 13C
EXPNO                  10
PROCNO                  1
Date_           20130502
Time               23.40
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgdc30
TD                65536
SOLVENT           CDCl3
NS                 1500
DS                    4
SWH           34722.223 Hz
FIDRES        0.529819 Hz
AQ            0.9437684 sec
RG                32800
DW               14.400 usec
DE               10.00 usec
TE                296.0 K
D1           0.01000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                13C
P1                 6.78 usec
PL1                0.00 dB
PL1W        83.14344025 W
SFO1       125.8275761 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2           80.00 usec
PL2                0.00 dB
PL12              17.23 dB
PL2W        26.62599564 W
PL12W        0.50385541 W
SFO2       500.3520014 MHz
SI                 32768
SF         125.8131080 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC                1.40
```

Figure S38: ^{13}C-NMR ($CDCl_3$, 125 MHz) of 2-(2-(tert-butylperoxy)-2-phenylethyl)cyclohexan-1-one.

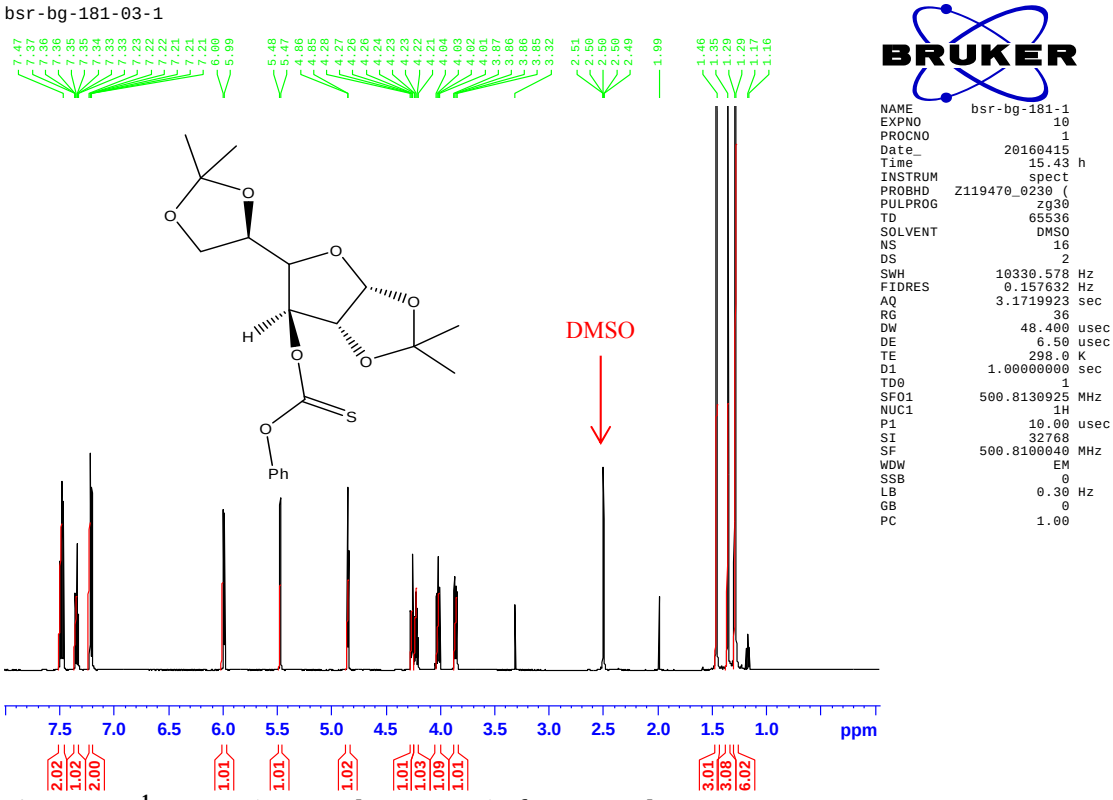



```
NAME        DEK-DA-114 13C
EXPNO                  11
PROCNO                  1
Date_           20130502
Time               23.54
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          dept135
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           34722.223 Hz
FIDRES        0.529819 Hz
AQ            0.9437684 sec
RG                16400
DW               14.400 usec
DE               10.00 usec
TE                296.0 K
CNST2       145.0000000
D1           2.00000000 sec
D2           0.00344828 sec
D12          0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                13C
P1                 6.78 usec
P2                13.55 usec
PL1                0.00 dB
PL1W        83.14344025 W
SFO1       125.8275765 MHz

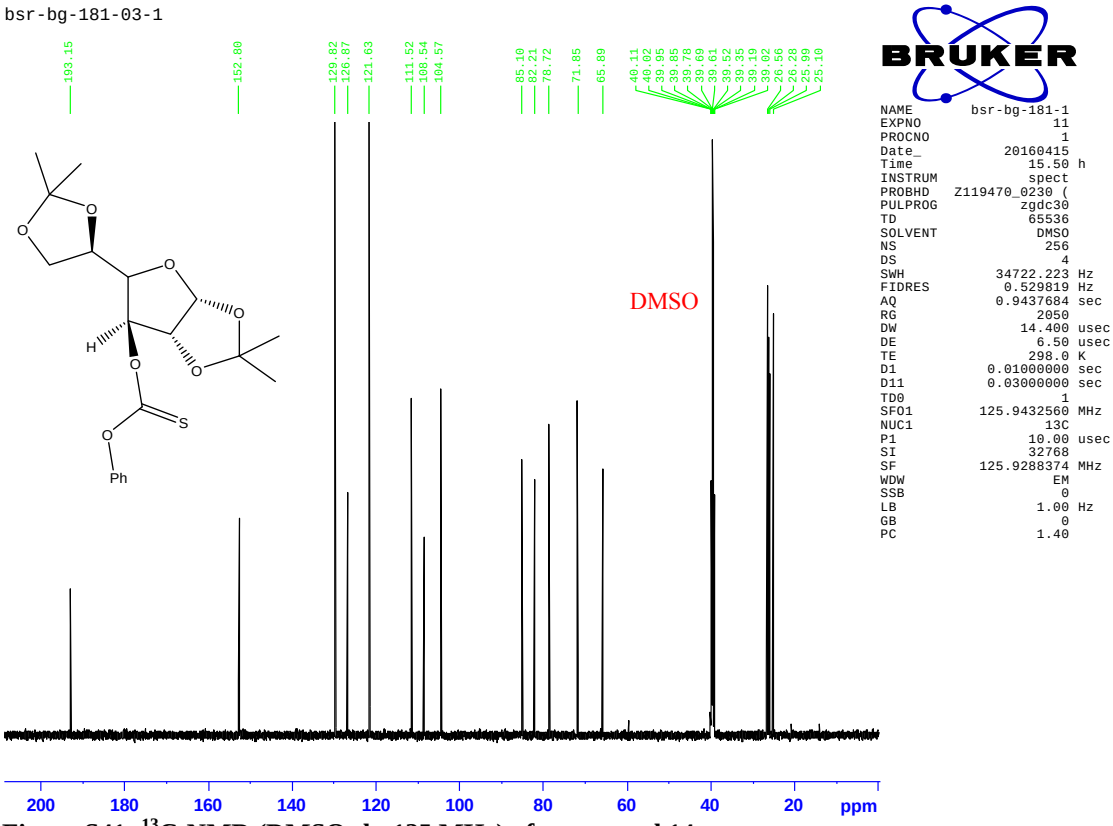
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
P3                11.05 usec
P4                22.10 usec
PCPD2           80.00 usec
PL2                0.00 dB
PL12              17.23 dB
PL2W        26.62599564 W
PL12W        0.50385541 W
SFO2       500.3520014 MHz
SI                 32768
SF         125.8131080 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC                1.40
```

Figure S39: DEPT 135-NMR ($CDCl_3$, 125 MHz) of 2-(2-(tert-butylperoxy)-2-phenylethyl)cyclohexan-1-one.



NAME bsr-bg-181-1
EXPNO 10
PROCNO 1
Date_ 20160415
Time 15.43 h
INSTRUM spect
PROBHD Z119470_0230 (
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 36
DW 48.400 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
SFO1 500.8130925 MHz
NUC1 1H
P1 10.00 usec
SI 32768
SF 500.8100040 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Figure S40: ^{1}H-NMR (DMSO-d$_6$, 500 MHz) of compound 14.



NAME bsr-bg-181-1
EXPNO 11
PROCNO 1
Date_ 20160415
Time 15.50 h
INSTRUM spect
PROBHD Z119470_0230 (
PULPROG zgdc30
TD 65536
SOLVENT DMSO
NS 256
DS 4
SWH 34722.223 Hz
FIDRES 0.529819 Hz
AQ 0.9437684 sec
RG 2050
DW 14.400 usec
DE 6.50 usec
TE 298.0 K
D1 0.01000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.9432560 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 125.9288374 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Figure S41: ^{13}C-NMR (DMSO-d$_6$, 125 MHz) of compound 14.

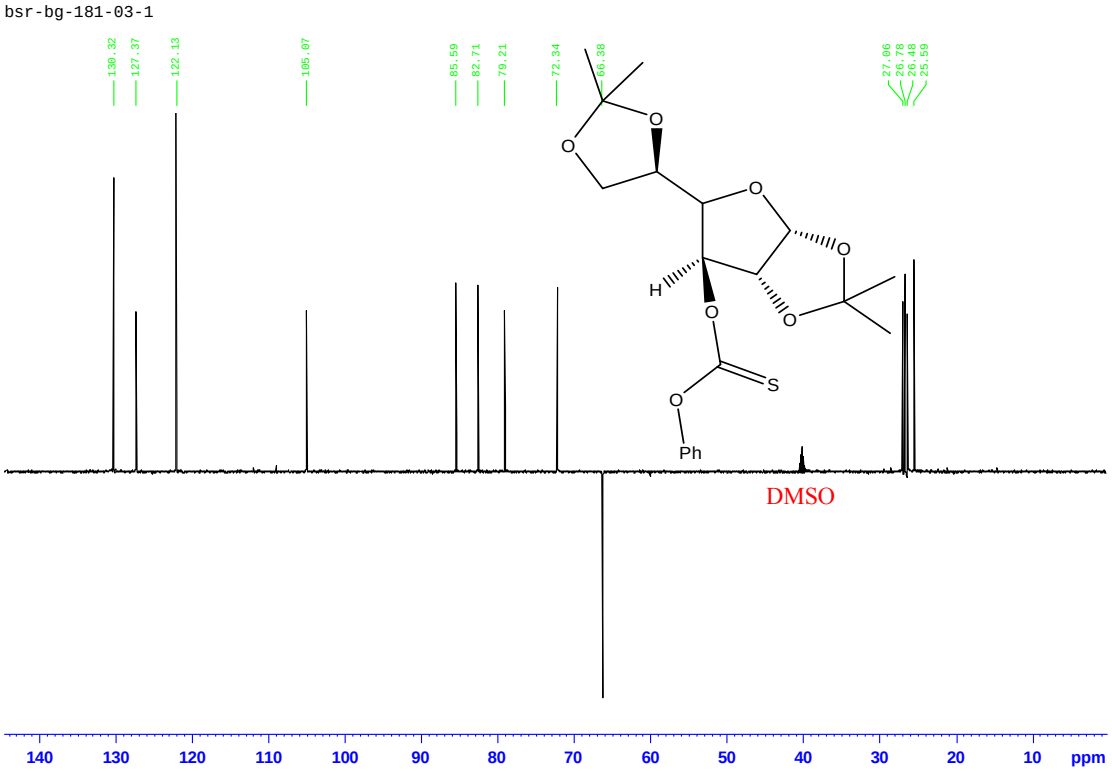


Figure S42: DEPT 135-NMR (DMSO-d_6, 125 MHz) of compound 14.

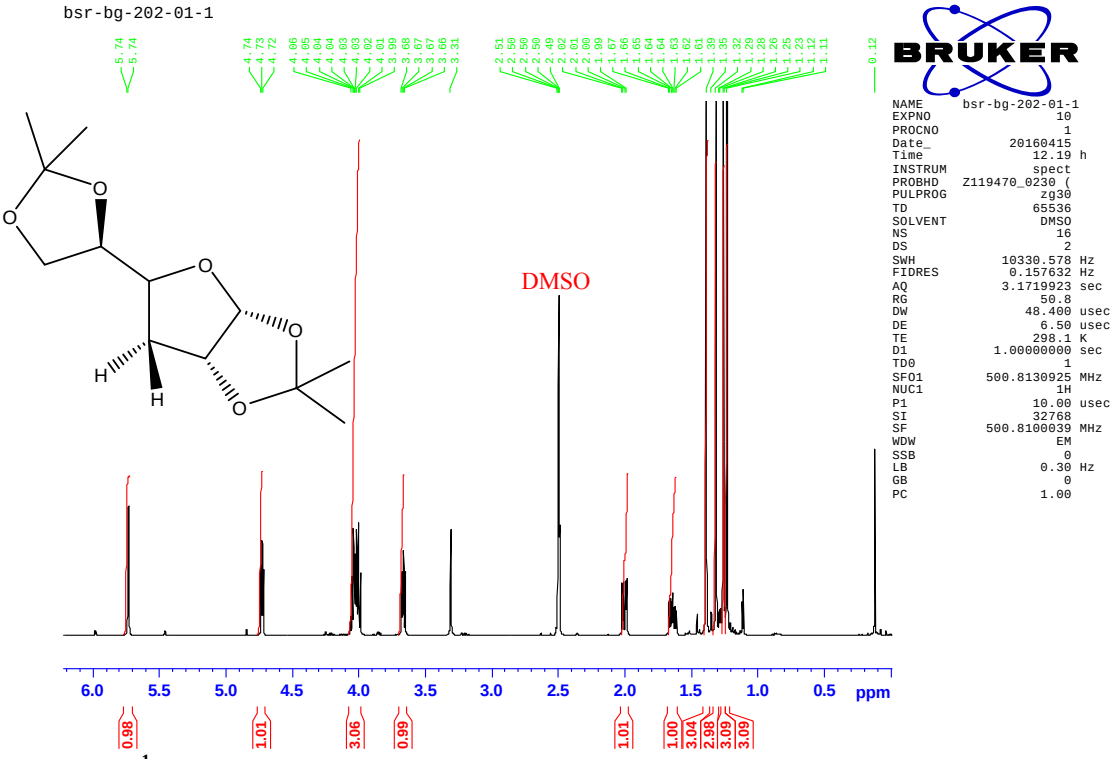


Figure S43: ^{1}H-NMR (DMSO-d_6, 500 MHz) of compound 15.

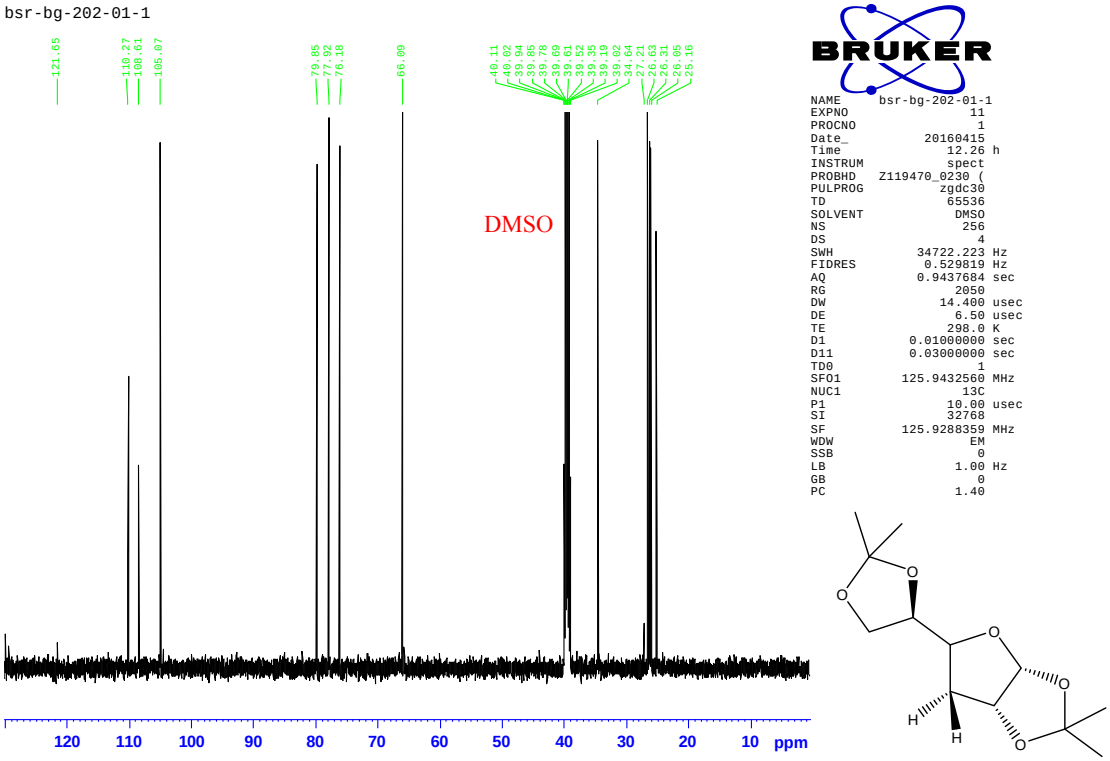


Figure S44: ^{13}C-NMR (DMSO-d$_6$, 125 MHz) of compound 15.

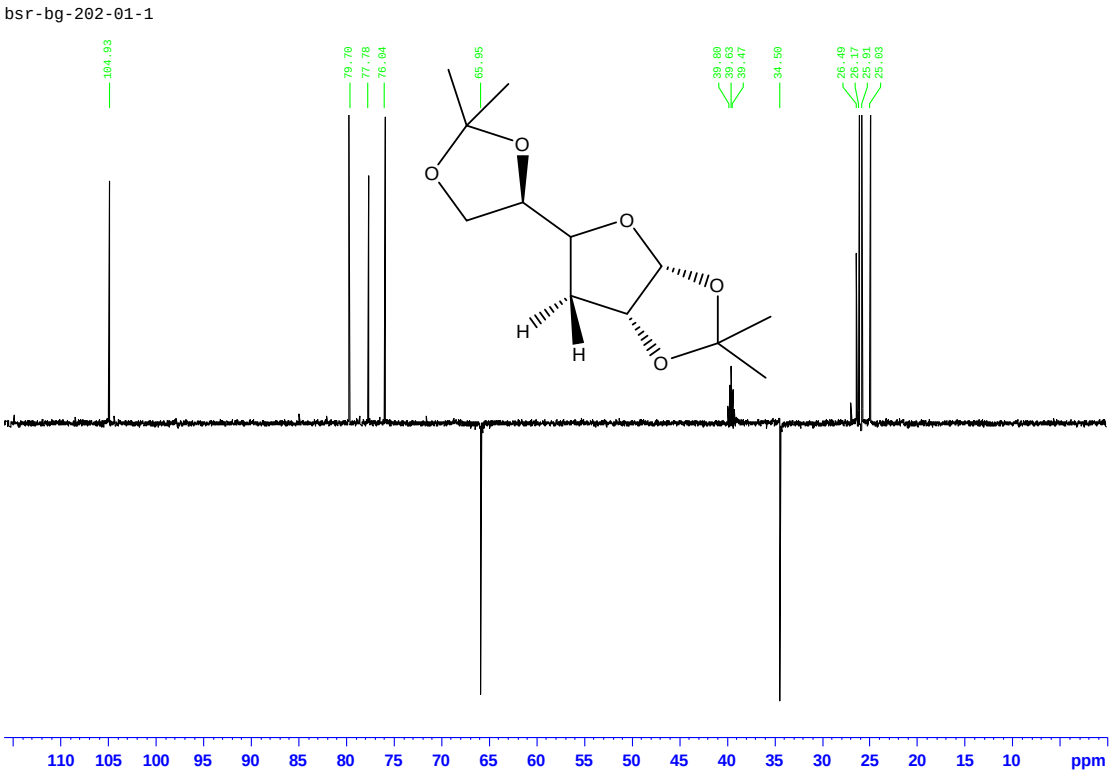


Figure S45: DEPT 135-NMR (DMSO-d$_6$, 125 MHz) of compound 15.

7 Supporting References

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