Supplementary Information

Diversity-oriented synthesis of pyrazolo[4,3-*b*]indoles by gold-catalysed three-component annulation: application to the development of a new class of CK2 inhibitors

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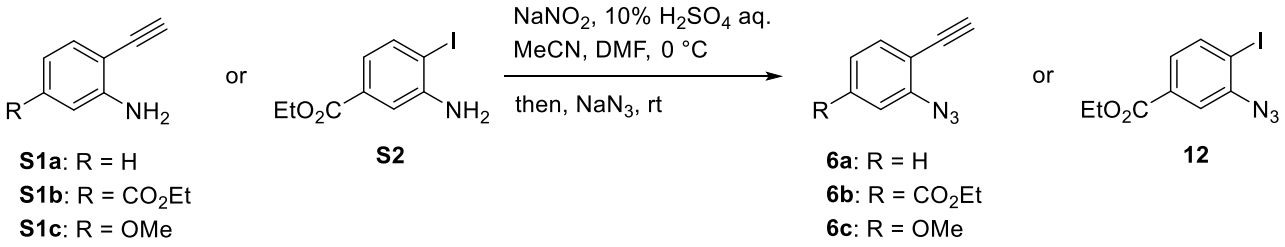
Experimental section

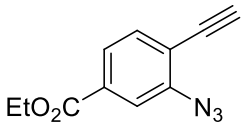
Synthesis of aryl azides 6a–c and 12



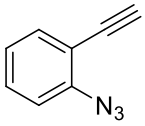
S1a: R = H
S1b: R = CO_2Et
S1c: R = OMe

6a: R = H
6b: R = CO_2Et
6c: R = OMe

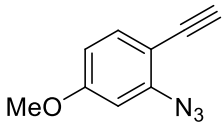
Compounds **S1a**,[1] **S1b**,[2] **S1c**,[3] and **S2**[4] were prepared according to the literature.



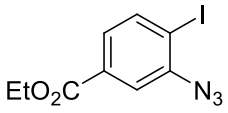
Representative procedure: synthesis of ethyl 3-azido-4-ethynylbenzoate (6b). To a solution of **S1b** (1286 mg, 6.8 mmol) in MeCN (24 mL), DMF (4 mL) and 10% aqueous H_2SO_4 (8 mL) was added dropwise a solution of $NaNO_2$ (563 mg, 8.2 mmol) in H_2O (2 mL) at 0 °C. The reaction mixture was stirred at the same temperature for 30 min. Then, a solution of NaN_3 (530 mg, 8.2 mmol) in H_2O (2 mL) was added dropwise to the mixture at 0 °C. The mixture was allowed to warm to room temperature and stirred for further 30 min. The resulting mixture was diluted with H_2O and extracted with EtOAc twice. The combined extracts were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was chromatographed on silica gel (hexane/EtOAc = 8/1) followed by recrystallization from EtOAc–hexane to afford the title compound **6b** (1.20 g, 82%) as light yellow crystals: mp 75 °C; IR (neat): ν_{max}/cm^{-1} 3236 (C≡CH), 2111 (N_3), 1699 (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.41 (t, *J* = 7.2 Hz, 3H), 3.53 (s, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.80 (s, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 14.2, 61.6, 78.7, 85.4, 118.1, 119.4, 125.4, 132.0, 134.2, 142.1, 165.1; HRMS (FAB$^+$) calcd for $C_{11}H_{10}N_3O_2$ [*M*+H]$^+$: 216.0773, found: 216.0765.



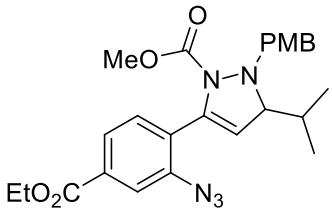
1-Azido-2-ethynylbenzene (6a). By use of the procedure for the synthesis of **6b**, **S1a** (1.02 g, 8.7 mmol) was converted to the title compound **6a** (1.02 mg, 82%) as a yellow oil: IR (neat): ν_{max}/cm^{-1} 3295 (C≡CH), 2106 (N_3); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 3.38 (s, 1H), 7.08–7.15 (m, 2H), 7.36–7.39 (m, 1H), 7.47–7.49 (m, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 79.3, 82.9, 114.1, 118.5, 124.6, 130.1, 134.3, 141.7; HRMS (FAB$^+$) calcd for $C_8H_6N_3$ [*M*+H]$^+$: 144.0562, found: 144.0553.



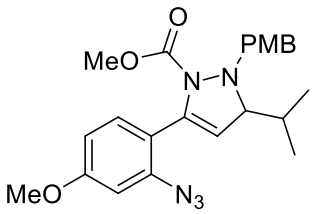
2-Azido-1-ethynyl-4-methoxybenzene (6c). By use of the procedure for the synthesis of **6b**, **S1c** (900 mg, 6.1 mmol) was converted to the title compound **6c** (656 mg, 62%) as yellow crystals: mp 52 °C; IR (neat): ν_{max}/cm^{-1} 3281 (C≡CH), 2114 (N_3); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 3.30 (s, 1H), 3.82 (s, 3H), 6.61–6.64 (m, 2H), 7.38 (d, *J* = 8.0 Hz, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 55.5, 79.3, 81.3, 104.3, 106.5, 110.7, 135.2, 142.9, 161.0; HRMS (FAB$^+$) calcd for $C_9H_8N_3O$ [*M*+H]$^+$: 174.0667, found: 174.0659.



Ethyl 3-azido-4-iodobenzoate (12). By use of the procedure for the synthesis of **6b**, **S2** (3.30 g, 11.3 mmol) was converted to the title compound **12** (2.48 g, 69%) as colourless crystals: mp 43 °C; IR (neat): ν_{max}/cm^{-1} 2110 (N_3), 1706 (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.41 (t, *J* = 7.2 Hz, 3H), 4.40 (q, *J* = 7.2 Hz, 2H), 7.48–7.51 (m, 1H), 7.76–7.77 (m, 1H), 7.87 (d, *J* = 8.0 Hz, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 14.3, 61.6, 93.8, 118.8, 126.8, 132.1, 140.2, 142.3, 165.3; HRMS (FAB$^+$) calcd for $C_9H_9IN_3O_2$ [*M*+H]$^+$: 317.9740, found: 317.9746.

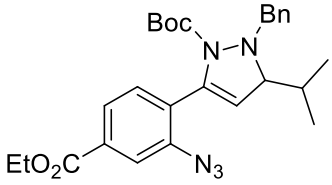


Methyl 5-[2-azido-4-(ethoxycarbonyl)phenyl]-3-isopropyl-2-(4-methoxybenzyl)-2,3-dihydro-1*H*-pyrazole-1-carboxylate (9b). By use of the procedure for the synthesis of **9a**, **6b** (108 mg, 0.5 mmol), hydrazine **8a** (158 mg, 0.75 mmol) and isobutyraldehyde (68 μL, 0.75 mmol) were converted to the title compound **9b** (230 mg, 96%) as a yellow oil: IR (neat): ν_{max}/cm^{-1} 2116 (N_3), 1710 (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 0.75–0.77 (m, 6H), 1.40 (t, *J* = 6.9 Hz, 3H), 1.52–1.58 (m, 1H), 3.38 (dd, *J* = 6.0, 2.9 Hz, 1H), 3.59 (s, 3H), 3.77 (d, *J* = 12.0 Hz, 1H), 3.81 (s, 3H), 4.08 (d, *J* = 12.0 Hz, 1H), 4.38–4.43 (m, 2H), 5.54 (d, *J* = 2.9 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 7.37–7.39 (m, 3H), 7.77–7.79 (m, 1H), 7.85 (s, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 14.3, 18.1, 18.2, 32.8, 52.7, 55.2, 61.3, 61.7, 73.9, 113.3 (2C), 114.5, 119.4, 125.4, 128.5, 128.8, 130.1, 131.3, 131.5 (2C), 136.6, 138.1, 155.2, 159.1, 165.5; HRMS (FAB$^+$) calcd for $C_{25}H_{30}N_5O_5$ [*M*+H]$^+$: 480.2247, found: 480.2250.

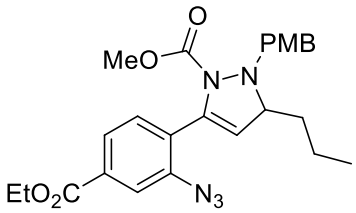


Methyl 5-(2-azido-4-methoxyphenyl)-3-isopropyl-2-(4-methoxybenzyl)-2,3-dihydro-1*H*-pyrazole-1-carboxylate (9c). By use of the procedure for the synthesis of **9a**, **6c** (43 mg, 0.25 mmol), hydrazine **8a** (79 mg, 0.38 mmol) and isobutyraldehyde (34 μL, 0.38 mmol) were converted to the title compound **9c** (100 mg, 91%) as a yellow oil: IR (neat): ν_{max}/cm^{-1} 2109 (N_3), 1712 (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 0.74–0.76 (m, 6H), 1.49–1.55 (m, 1H), 3.32 (dd, *J* = 5.7, 2.9 Hz, 1H), 3.60 (s, 3H), 3.76 (d, *J* = 12.0 Hz, 1H), 3.81 (s, 3H), 3.83 (s, 3H), 4.06 (d, *J* = 12.0 Hz, 1H), 5.35 (d, *J* = 2.9 Hz, 1H), 6.65–6.70 (m, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 1H), 7.37 (d, *J* = 8.6 Hz, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 18.0, 18.2, 32.8, 52.5, 55.2, 55.4, 61.6, 73.5, 104.3,

109.9, 111.8, 113.3 (2C), 117.5, 129.1, 131.2, 131.5 (2C), 137.0, 138.8, 155.0, 159.0, 160.4; HRMS (FAB$^+$) calcd for $C_{23}H_{28}N_5O_4$ [*M*+H]$^+$: 438.2142, found: 438.2134.

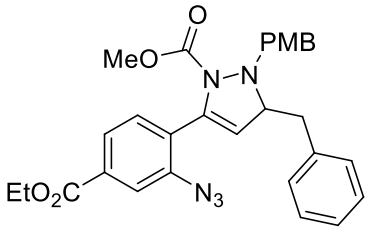


***tert*-Butyl 5-[2-azido-4-(ethoxycarbonyl)phenyl]-2-benzyl-3-isopropyl-2,3-dihydro-1*H*-pyrazole-1-carboxylate (9d).** By use of the procedure for the synthesis of **9a**, **6b** (54 mg, 0.25 mmol), hydrazine **8b** (83 mg, 0.38 mmol) and isobutyraldehyde (34 μL, 0.38 mmol) were converted to the title compound **9d** (98 mg, 80%) as a yellow oil: IR (neat): ν_{max}/cm^{-1} 2114 (N_3), 1712 (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 0.75–0.78 (m, 6H), 1.24 (s, 9H), 1.41 (t, *J* = 6.9 Hz, 3H), 1.50–1.56 (m, 1H), 3.31 (dd, *J* = 5.7, 2.9 Hz, 1H), 3.79 (d, *J* = 12.0 Hz, 1H), 4.16 (d, *J* = 12.0 Hz, 1H), 4.40 (q, *J* = 6.9 Hz, 2H), 5.52 (d, *J* = 2.9 Hz, 1H), 7.26–7.29 (m, 1H), 7.31–7.34 (m, 2H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.47–7.49 (m, 2H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.84 (s, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 14.3, 18.08, 18.10, 27.9 (3C), 32.7, 61.3, 62.3, 73.8, 80.6, 114.1, 119.5, 125.3, 127.3, 127.9 (2C), 129.6, 130.0, 130.4 (2C), 131.0, 136.85, 136.94, 137.9, 153.3, 165.5; HRMS (FAB$^+$) calcd for $C_{27}H_{34}N_5O_4$ [*M*+H]$^+$: 492.2611, found: 492.2609.

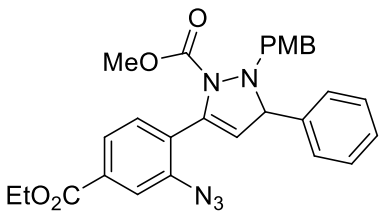


Methyl 5-[2-azido-4-(ethoxycarbonyl)phenyl]-2-(4-methoxybenzyl)-3-propyl-2,3-dihydro-1*H*-pyrazole-1-carboxylate (9e). By use of the procedure for the synthesis of **9a**, **6b** (54 mg, 0.25 mmol), hydrazine **8a** (79 mg, 0.38 mmol) and *n*-butyraldehyde (34 μL, 0.38 mmol) were converted to the title compound **9e** (94 mg, 78%) as a yellow oil. In this case, $AgNTf_2$ (2.9 mg, 0.0075 mmol) was used instead of AgOTf: IR (neat): ν_{max}/cm^{-1} 2112 (N_3), 1713 (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 0.77 (t, *J* = 7.2 Hz, 3H), 1.10–1.34 (m, 4H), 1.40 (t, *J* = 7.2 Hz, 3H), 3.57–3.60 (m, 4H), 3.78–3.81 (m, 4H), 4.09 (d, *J* = 12.0 Hz, 1H), 4.38–4.42 (m, 2H), 5.59 (d, *J* = 2.9 Hz, 1H), 6.87 (d, *J*

= 8.6 Hz, 2H), 7.37–7.39 (m, 3H), 7.77–7.79 (m, 1H), 7.85 (s, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 13.8, 14.3, 18.5, 37.0, 52.7, 55.2, 60.9, 61.3, 67.8, 113.4 (2C), 116.5, 119.4, 125.4, 128.7, 128.8, 130.1, 131.2 (2C), 131.3, 136.0, 138.0, 155.2, 159.0, 165.4; HRMS (FAB$^+$) calcd for $C_{25}H_{30}N_5O_5$ [*M*+H]$^+$: 480.2247, found: 480.2241.

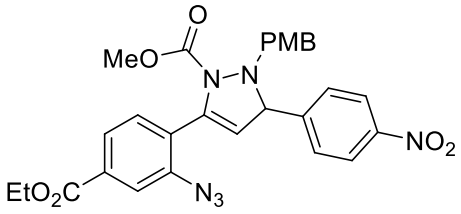


Methyl 5-[2-azido-4-(ethoxycarbonyl)phenyl]-3-benzyl-2-(4-methoxybenzyl)-2,3-dihydro-1*H*-pyrazole-1-carboxylate (9f). By use of the procedure for the synthesis of **9a**, **6b** (54 mg, 0.25 mmol), hydrazine **8a** (79 mg, 0.38 mmol) and 2-phenylacetaldehyde (49 μL, 0.38 mmol) were converted to the title compound **9f** (67 mg, 51%) as a yellow oil. In this case, $AgNTf_2$ (2.9 mg, 0.0075 mmol) was used instead of AgOTf: IR (neat): ν_{max}/cm^{-1} 2114 (N_3), 1714 (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.39 (t, *J* = 7.2 Hz, 3H), 2.61–2.70 (m, 2H), 3.58 (s, 3H), 3.77 (d, *J* = 12.0 Hz, 1H), 3.79–3.82 (m, 4H), 4.09 (d, *J* = 12.0 Hz, 1H), 4.37–4.42 (m, 2H), 5.49 (d, *J* = 2.9 Hz, 1H), 6.81 (d, *J* = 8.6 Hz, 2H), 7.13–7.14 (m, 2H), 7.17–7.19 (m, 1H), 7.21–7.25 (m, 2H), 7.28–7.31 (m, 3H), 7.75–7.77 (m, 1H), 7.83 (s, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 14.3, 41.5, 52.7, 55.2, 60.8, 61.3, 69.1, 113.5 (2C), 115.2, 119.4, 125.4, 126.2, 127.9 (2C), 128.50, 128.52, 129.7 (2C), 130.2, 130.9 (2C), 131.4, 136.9, 137.5, 138.1, 154.9, 158.9, 165.4; HRMS (FAB$^+$) calcd for $C_{29}H_{30}N_5O_5$ [*M*+H]$^+$: 528.2247, found: 528.2250.

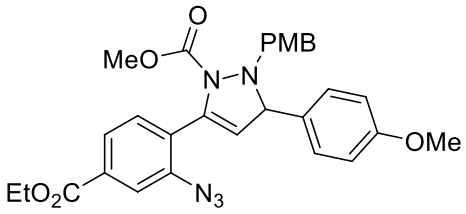


Methyl 5-[2-azido-4-(ethoxycarbonyl)phenyl]-2-(4-methoxybenzyl)-3-phenyl-2,3-dihydro-1*H*-pyrazole-1-carboxylate (9g). By use of the procedure for the synthesis of **9a**, **6b** (108 mg, 0.5 mmol), hydrazine **8a** (158 mg, 0.75 mmol) and benzaldehyde (76 μL, 0.75 mmol) were converted to

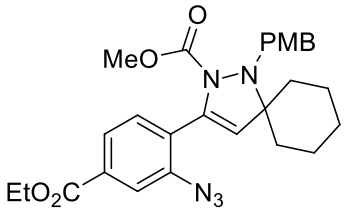
the title compound **9g** (134 mg, 52%) as a yellow oil. In this case, the reaction was carried out at room temperature using $AgNTf_2$ (5.8 mg, 0.015 mmol) instead of AgOTf: IR (neat): ν_{max}/cm^{-1} 2114 (N_3), 1714 (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.40 (t, *J* = 7.2 Hz, 3H), 3.59 (s, 3H), 3.81 (s, 3H), 4.02 (d, *J* = 12.0 Hz, 1H), 4.30 (d, *J* = 12.0 Hz, 1H), 4.37–4.44 (m, 2H), 4.70 (d, *J* = 3.4 Hz, 1H), 5.73 (d, *J* = 3.4 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 2H), 7.14–7.15 (m, 2H), 7.20–7.28 (m, 3H), 7.41–7.43 (m, 3H), 7.78–7.80 (m, 1H), 7.87 (s, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 14.3, 52.9, 55.2, 61.4, 61.5, 70.4, 113.6 (2C), 114.8, 119.4, 125.4, 126.7 (2C), 127.4, 128.2, 128.4, 128.6 (2C), 130.3, 131.2 (2C), 131.6, 136.8, 138.3, 140.4, 154.9, 159.2, 165.4; HRMS (FAB$^+$) calcd for $C_{28}H_{28}N_5O_5$ [*M*+H]$^+$: 514.2091, found: 514.2089.



Methyl 5-[2-azido-4-(ethoxycarbonyl)phenyl]-2-(4-methoxybenzyl)-3-(4-nitrophenyl)-2,3-dihydro-1*H*-pyrazole-1-carboxylate (9h). By use of the procedure for the synthesis of **9a**, **6b** (54 mg, 0.25 mmol), hydrazine **8a** (79 mg, 0.38 mmol) and 4-nitrobenzaldehyde (57 mg, 0.38 mmol) were converted to the title compound **9h** (82 mg, 59%) as a yellow oil. In this case, $AgNTf_2$ (2.9 mg, 0.0075 mmol) was used instead of AgOTf: IR (neat): ν_{max}/cm^{-1} 2115 (N_3), 1714 (C=O), 1514, 1346 (NO_2); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.41 (t, *J* = 6.9 Hz, 3H), 3.63 (s, 3H), 3.81 (s, 3H), 4.02 (d, *J* = 12.0 Hz, 1H), 4.36 (d, *J* = 12.0 Hz, 1H), 4.39–4.44 (m, 2H), 4.78 (d, *J* = 2.9 Hz, 1H), 5.73 (d, *J* = 2.9 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 9.2 Hz, 2H), 7.39–7.42 (m, 3H), 7.79–7.81 (m, 1H), 7.88 (s, 1H), 8.13 (d, *J* = 8.0 Hz, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 14.3, 53.1, 55.2, 61.3, 61.5, 69.2, 112.8, 113.8 (2C), 119.4, 123.9 (2C), 125.4, 127.4 (2C), 127.5, 127.8, 130.2, 131.1 (2C), 132.0, 137.8, 138.4, 147.3, 147.8, 154.5, 159.4, 165.3; HRMS (FAB$^+$) calcd for $C_{28}H_{27}N_6O_7$ [*M*+H]$^+$: 559.1941, found: 559.1939.

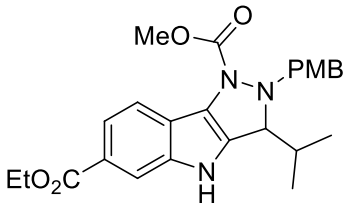


Methyl 5-[2-azido-4-(ethoxycarbonyl)phenyl]-2-(4-methoxybenzyl)-3-(4-methoxyphenyl)-2,3-dihydro-1*H*-pyrazole-1-carboxylate (9i). By use of the procedure for the synthesis of **9a**, **6b** (54 mg, 0.25 mmol), hydrazine **8a** (79 mg, 0.38 mmol) and *p*-anisaldehyde (46 μL, 0.38 mmol) were converted to the title compound **9i** (42 mg, 31%) as a yellow oil. In this case, $AgNTf_2$ (2.9 mg, 0.0075 mmol) was used instead of AgOTf: IR (neat): ν_{max}/cm^{-1} 2116 (N_3), 1716 (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.41 (t, *J* = 7.2 Hz, 3H), 3.58 (s, 3H), 3.76 (s, 3H), 3.82 (s, 3H), 3.99 (d, *J* = 12.0 Hz, 1H), 4.28 (d, *J* = 12.0 Hz, 1H), 4.38–4.45 (m, 2H), 4.65 (d, *J* = 2.9 Hz, 1H), 5.71 (d, *J* = 2.9 Hz, 1H), 6.80 (d, *J* = 9.2 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 7.03 (d, *J* = 9.2 Hz, 2H), 7.40–7.45 (m, 3H), 7.79–7.81 (m, 1H), 7.88 (s, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 14.3, 52.9, 55.2, 55.2, 61.4, 61.5, 70.0, 113.6 (2C), 114.0 (2C), 115.1, 119.4, 125.4, 128.0 (2C), 128.3, 128.5, 130.2, 131.2 (2C), 131.6, 132.5, 136.6, 138.3, 155.0, 159.0, 159.1, 165.4; HRMS (FAB$^+$) calcd for $C_{29}H_{30}N_5O_6$ [*M*+H]$^+$: 544.2196, found: 544.2194.

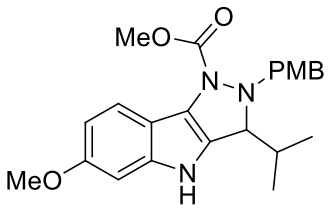


Methyl 3-[2-azido-4-(ethoxycarbonyl)phenyl]-1-(4-methoxybenzyl)-1,2-diazaspiro[4.5]dec-3-ene-2-carboxylate (9j). By use of the procedure for the synthesis of **9a**, **6b** (54 mg, 0.25 mmol), hydrazine **8a** (79 mg, 0.38 mmol) and cyclohexanone (39 μL, 0.38 mmol) were converted to the title compound **9j** (104 mg, 82%) as a yellow oil. In this case, $AgNTf_2$ (2.9 mg, 0.0075 mmol) was used instead of AgOTf: IR (neat): ν_{max}/cm^{-1} 2115 (N_3), 1715; (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.39 (t, *J* = 7.2 Hz, 3H), 1.48–1.77 (m, 10H), 3.37 (s, 3H), 3.81–3.82 (m, 5H), 4.39 (q, *J* = 7.2 Hz, 2H), 6.07 (s, 1H), 6.86 (d, *J* = 8.6 Hz, 2H), 7.32–7.33 (m, 1H), 7.39 (d, *J* = 8.6 Hz, 2H), 7.75–7.77 (m,

1H), 7.84 (s, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 14.3, 23.4 (2C), 25.6, 33.9 (2C), 52.5, 54.0, 55.2, 61.3, 72.2, 113.0 (2C), 119.6, 123.6, 125.3, 128.6, 130.2, 130.3, 131.0, 131.1 (2C), 136.1, 137.6, 156.6, 158.7, 165.4; HRMS (FAB$^+$) calcd for $C_{27}H_{32}N_5O_5$ [*M*+H]$^+$: 506.2403, found: 506.2409.

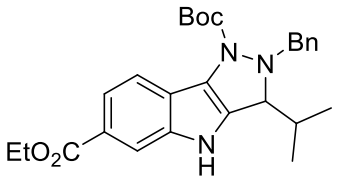


6-Ethyl 1-methyl 3-isopropyl-2-(4-methoxybenzyl)-1,2,3,4-tetrahydropyrazolo[4,3-*b*]indole-1,6-dicarboxylate (10b). By use of the procedure for the synthesis of **10a**, **9b** (210 mg, 0.44 mmol) was converted to the title compound **10b** (170 mg, 85%) as a colourless oil: IR (neat): ν_{max}/cm^{-1} 1707; (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 0.71–0.77 (m, 6H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.71–1.77 (m, 1H), 3.79–3.86 (m, 5H), 3.89 (s, 3H), 4.22 (d, *J* = 12.0 Hz, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 7.82–7.84 (m, 2H), 8.09–8.10 (m, 1H), 8.17 (s, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 14.4, 17.8, 18.4, 33.2, 53.0, 55.2, 60.8, 62.5, 69.8, 113.5 (2C), 114.2, 119.1, 120.0, 121.3, 123.6, 128.4, 131.4 (2C), 133.7, 139.4, 140.6, 151.8, 159.2, 167.6; HRMS (FAB$^+$) calcd for $C_{25}H_{30}N_3O_5$ [*M*+H]$^+$: 452.2185, found: 452.2179.

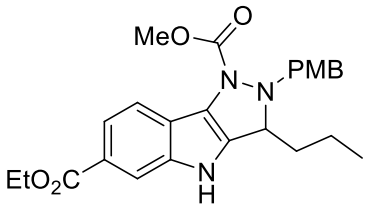


Methyl 3-isopropyl-6-methoxy-2-(4-methoxybenzyl)-1,2,3,4-tetrahydropyrazolo[4,3-*b*]indole-1-carboxylate (10c). By use of the procedure for the synthesis of **10a**, **9c** (100 mg, 0.23 mmol) was converted to the title compound **10c** (67 mg, 72%) as a yellow oil: IR (neat): ν_{max}/cm^{-1} 1698 (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 0.68–0.73 (m, 6H), 1.65–1.71 (m, 1H), 3.78–3.86 (m, 11H), 4.21 (d, *J* = 12.0 Hz, 1H), 6.80–6.84 (m, 4H), 7.34 (d, *J* = 8.6 Hz, 2H), 7.70–7.78 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 17.7, 18.3, 33.2, 52.9, 55.1, 55.8, 62.4, 70.0, 95.7, 110.0, 111.9, 113.3 (2C), 120.2,

123.6, 128.0, 128.8, 131.3 (2C), 140.9, 154.3, 156.2, 159.1; HRMS (FAB$^+$) calcd for $C_{23}H_{28}N_3O_4$ [*M*+H]$^+$: 410.2080, found: 410.2078.

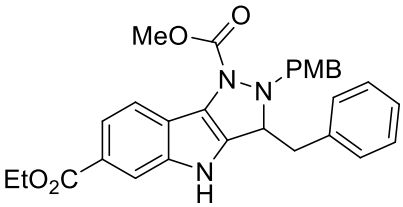


1-*tert*-Butyl 6-ethyl 2-benzyl-3-isopropyl-1,2,3,4-tetrahydropyrazolo[4,3-*b*]indole-1,6-dicarboxylate (10d). By use of the procedure for the synthesis of **10a**, **9d** (90 mg, 0.18 mmol) was converted to the title compound **10d** (70 mg, 84%) as a colourless oil: IR (neat): ν_{max}/cm^{-1} 1686 (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$) ^{1}H-NMR ($CDCl_3$) δ: 0.71–0.77 (m, 6H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.56 (s, 9H), 1.68–1.75 (m, 1H), 3.76 (d, *J* = 5.2 Hz, 1H), 3.82 (d, *J* = 12.0 Hz, 1H), 4.25 (d, *J* = 12.0 Hz, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 7.24–7.31 (m, 3H), 7.41–7.42 (m, 2H), 7.80 (d, *J* = 8.6 Hz, 1H), 7.88 (d, *J* = 8.6 Hz, 1H), 8.14 (s, 1H), 8.63 (s, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 14.4, 17.7, 18.2, 28.5 (3C), 33.1, 60.7, 63.4, 70.1, 81.2, 114.3, 119.3, 120.5, 120.9, 123.1, 124.6, 127.5, 128.1 (2C), 130.2 (2C), 134.2, 136.8, 139.4, 153.9, 167.9; HRMS (FAB$^+$) calcd for $C_{27}H_{34}N_3O_4$ [*M*+H]$^+$: 464.2549, found: 464.2551.

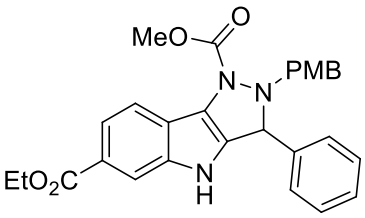


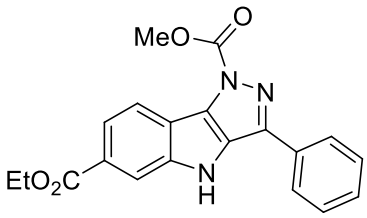
6-Ethyl 1-methyl 2-(4-methoxybenzyl)-3-propyl-1,2,3,4-tetrahydropyrazolo[4,3-*b*]indole-1,6-dicarboxylate (10e). By use of the procedure for the synthesis of **10a**, **9e** (80 mg, 0.17 mmol) was converted to the title compound **10e** (65 mg, 86%) as a colourless oil: IR (neat): ν_{max}/cm^{-1} 1701 (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 0.71 (t, *J* = 7.2 Hz, 3H), 1.14–1.22 (m, 2H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.46–1.58 (m, 2H), 3.79 (s, 3H), 3.85 (d, *J* = 12.0 Hz, 1H), 3.89 (s, 3H), 4.05 (t, *J* = 6.3 Hz, 1H), 4.24 (d, *J* = 12.0 Hz, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.81–7.87 (m, 2H), 8.11 (s, 1H), 8.51 (s, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 13.7, 14.4, 18.4, 37.6, 53.1, 55.2, 60.8, 61.9, 64.0, 113.6 (2C), 114.3, 119.0, 120.1, 121.2, 123.1, 123.4, 128.4, 131.1

(2C), 135.6, 139.4, 154.4, 159.2, 167.7; HRMS (FAB$^+$) calcd for $C_{25}H_{30}N_3O_5$ [*M*+H]$^+$: 452.2186, found: 452.2177.



6-Ethyl 1-methyl 3-benzyl-2-(4-methoxybenzyl)-1,2,3,4-tetrahydropyrazolo[4,3-*b*]indole-1,6-dicarboxylate (10f). By use of the procedure for the synthesis of **10a**, **9f** (48 mg, 0.09 mmol) was converted to the title compound **10f** (33 mg, 73%) as a light yellow oil: IR (neat): ν_{max}/cm^{-1} 1705 (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.40 (t, *J* = 7.2 Hz, 3H), 2.75–2.80 (m, 1H), 2.86–2.89 (m, 1H), 3.81 (s, 3H), 3.86 (d, *J* = 12.0 Hz, 1H), 3.90 (s, 3H), 4.28–4.34 (m, 2H), 4.37 (q, *J* = 7.2 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.90–6.92 (m, 2H), 7.21–7.22 (m, 3H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.50 (s, 1H), 7.80–7.85 (m, 2H), 7.95 (s, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 14.4, 42.4, 53.1, 55.2, 60.7, 61.9, 65.7, 113.7 (2C), 114.2, 119.1, 119.8, 121.2, 123.4, 123.7, 126.8, 128.1, 128.4 (2C), 129.4 (2C), 131.0 (2C), 134.2, 136.9, 139.1, 154.4, 159.2, 167.5; HRMS (FAB$^+$) calcd for $C_{29}H_{30}N_3O_5$ [*M*+H]$^+$: 500.2186, found: 500.2185.



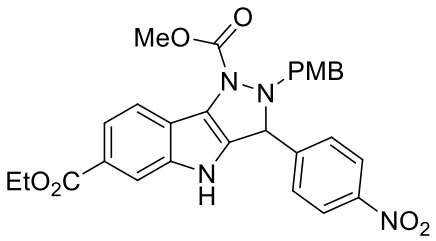


6-Ethyl 1-methyl 2-(4-methoxybenzyl)-3-phenyl-1,2,3,4-tetrahydropyrazolo[4,3-*b*]indole-1,6-dicarboxylate (10g) and 6-ethyl 1-methyl 3-phenyl-1,4-dihydropyrazolo[4,3-*b*]indole-1,6-dicarboxylate (11b). By use of the procedure for the synthesis of **10a**, **9g** (50 mg, 0.097 mmol) was converted to the compound **10g** (32 mg, 68%) as a yellow oil, together with the compound **11b** (12 mg, 27%) as colourless crystals.

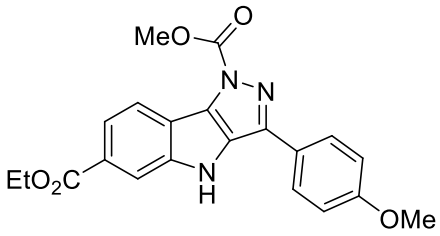
10g: IR (neat): ν_{max}/cm^{-1} 1697 (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.23 (t, *J* = 7.2 Hz, 3H), 3.62 (s, 3H), 3.70 (s, 3H), 3.90 (d, *J* = 12.0 Hz, 1H), 4.16–4.22 (m, 2H), 4.26 (d, *J* = 12.0 Hz, 1H), 4.99 (s,

1H), 6.67 (d, *J* = 8.6 Hz, 2H), 6.79–6.81 (m, 2H), 6.99–7.01 (m, 3H), 7.19 (d, *J* = 8.6 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.94 (s, 1H), 8.90 (s, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 14.3, 53.2, 55.1, 60.8, 65.8, 66.7, 113.7 (2C), 114.6, 119.2, 119.8, 121.1, 123.4, 123.6, 126.7 (2C), 127.9, 128.1, 128.7 (2C), 131.2 (2C), 134.1, 139.2, 139.7, 154.4, 159.2, 167.8; HRMS (FAB$^+$) calcd for $C_{28}H_{28}N_3O_5$ [*M*+H]$^+$: 486.2029, found: 486.2026.

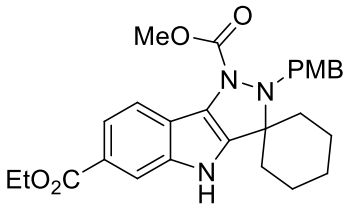
11b: mp 229 °C; IR (neat): ν_{max}/cm^{-1} 1737 (C=O), 1695 (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.43 (t, *J* = 7.2 Hz, 3H), 4.21 (s, 3H), 4.43 (q, *J* = 7.2 Hz, 2H), 7.42–7.45 (m, 1H), 7.49–7.52 (m, 2H), 7.94–7.98 (m, 3H), 8.25 (s, 1H), 8.31–8.35 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 14.4, 54.8, 61.1, 114.7, 117.6, 121.5, 121.6, 127.0 (2C), 127.8, 129.1 (2C), 129.5, 131.2, 131.7, 133.5, 139.9, 143.3, 150.7, 167.0; HRMS (FAB$^+$) calcd for $C_{20}H_{18}N_3O_4$ [*M*+H]$^+$: 364.1297, found: 364.1301.



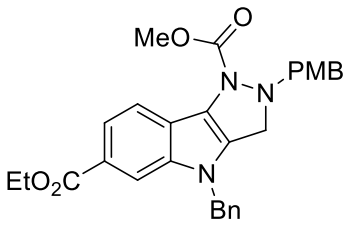
6-Ethyl 1-methyl 2-(4-methoxybenzyl)-3-(4-nitrophenyl)-1,2,3,4-tetrahydropyrazolo[4,3-*b*]indole-1,6-dicarboxylate (10h). By use of the procedure for the synthesis of **10a**, **9h** (38 mg, 0.068 mmol) was converted to the title compound **10h** (26 mg, 72%) as yellow needles: mp 167 °C; IR (neat): ν_{max}/cm^{-1} 1689 (C=O), 1514, 1347 (NO_2); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.40 (t, *J* = 7.1 Hz, 3H), 3.79 (s, 3H), 3.91 (s, 3H), 4.06 (d, *J* = 12.6 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 4.49 (d, *J* = 12.6 Hz, 1H), 5.23 (s, 1H), 6.84 (d, *J* = 8.6 Hz, 2H), 7.13 (d, *J* = 9.2 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.84 (d, *J* = 8.6 Hz, 1H), 7.90 (d, *J* = 8.6 Hz, 1H), 7.98 (d, *J* = 9.2 Hz, 2H), 8.08 (s, 1H), 8.70 (s, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 14.4, 53.4, 55.3, 61.0, 62.4, 65.8, 113.9 (2C), 114.6, 119.6, 119.8, 121.5, 123.9 (2C), 124.2, 124.4, 127.5 (2C), 127.6, 131.1 (2C), 131.8, 139.9, 146.3, 147.4, 154.3, 159.5, 167.6; HRMS (FAB$^+$) calcd for $C_{28}H_{27}N_4O_7$ [*M*+H]$^+$: 531.1880, found: 531.1873.



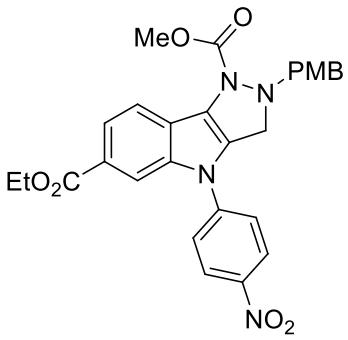
6-Ethyl 1-methyl 3-(4-methoxyphenyl)-1,4-dihydropyrazolo[4,3-*b*]indole-1,6-dicarboxylate (11c). By use of the procedure for the synthesis of **10a**, **9i** (38 mg, 0.07 mmol) was converted to the title compound **11c** (13 mg, 48%) as a white solid: mp 221 °C; IR (neat): ν_{max}/cm^{-1} 1696 (C=O); ^{1}H-NMR (500 MHz, DMSO-d_6) δ: 1.36 (t, *J* = 7.0 Hz, 3H), 3.85 (s, 3H), 4.12 (s, 3H), 4.34 (q, *J* = 7.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 2H), 8.14–8.18 (m, 2H), 12.04 (s, 1H); ^{13}C-NMR (125 MHz, DMSO-d_6) δ: 14.2, 54.6, 55.2, 60.6, 114.4, 114.5 (2C), 115.6, 119.6, 120.5, 122.9, 125.8, 127.9 (2C), 131.1, 131.3, 138.6, 142.9, 149.9, 160.2, 166.0; HRMS (FAB$^+$) calcd for $C_{21}H_{20}N_3O_5$ [*M*+H]$^+$: 394.1403, found: 394.1400.



6'-Ethyl 1'-methyl 2'-(4-methoxybenzyl)-1',2',3',4'-tetrahydrospiro[cyclohexane-1,3'-pyrazolo[4,3-*b*]indole]-1',6'-dicarboxylate (10i). Under argon atmosphere, a solution of **9j** (50 mg, 0.1 mmol) in *o*-dichlorobenzene (1 mL) was stirred at 150 °C for 2 h. After being cooled to room temperature, the resulting mixture was chromatographed on silica gel (hexane/EtOAc = 3/1) to afford the title compound **10i** (29 mg, 62%) as a yellow oil: IR (neat): ν_{max}/cm^{-1} 1704 (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.41 (t, *J* = 7.2 Hz, 3H), 1.46–1.62 (m, 4H), 1.85–1.89 (m, 4H), 1.95–2.01 (m, 2H), 3.52 (br s, 3H), 3.79 (s, 3H), 3.88 (s, 2H), 4.41 (q, *J* = 7.2 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.81–7.85 (m, 2H), 8.20 (s, 1H), 8.82 (s, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 14.4, 23.7 (2C), 25.2, 34.1 (2C), 52.8, 55.1, 55.2, 60.7, 70.4, 113.2 (2C), 114.6, 118.8, 120.9, 121.4, 123.1, 123.2, 129.7, 131.3 (2C), 138.7, 141.8, 155.4, 158.8, 167.8; HRMS (FAB$^+$) calcd for $C_{27}H_{32}N_3O_5$ [*M*+H]$^+$: 478.2342, found: 478.2350.

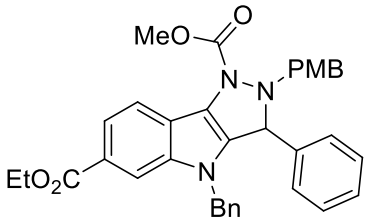


6-Ethyl 1-methyl 4-benzyl-2-(4-methoxybenzyl)-1,2,3,4-tetrahydropyrazolo[4,3-*b*]indole-1,6-dicarboxylate (15a). By use of the procedure for the synthesis of **15c**, **10j** (50 mg, 0.12 mmol) was converted to the title compound **15a** (43 mg, 71%) as a yellow oil: IR (neat): ν_{max}/cm^{-1} 1700 (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.41 (t, *J* = 7.2 Hz, 3H), 3.78 (s, 3H), 3.87 (s, 3H), 3.93 (br s, 2H), 3.97 (br s, 2H), 4.39 (q, *J* = 7.2 Hz, 2H), 5.23 (s, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 7.03–7.05 (m, 2H), 7.18 (d, *J* = 8.6 Hz, 2H), 7.30–7.32 (m, 3H), 7.83–7.88 (m, 2H), 8.09 (s, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 14.4, 48.7, 51.7, 53.1, 55.2, 60.8, 62.3, 112.3, 113.6 (2C), 119.1, 119.6, 121.1, 122.6, 123.4, 127.1 (2C), 127.8, 128.2, 129.0 (2C), 131.0 (2C), 133.9, 136.1, 139.7, 154.4, 159.2, 167.5; HRMS (FAB$^+$) calcd for $C_{29}H_{30}N_3O_5$ [*M*+H]$^+$: 500.2186, found: 500.2181.

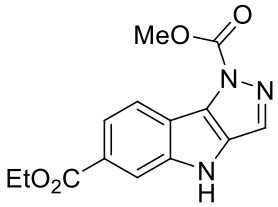


6-Ethyl 1-methyl 2-(4-methoxybenzyl)-4-(4-nitrophenyl)-1,2,3,4-tetrahydropyrazolo[4,3-*b*]indole-1,6-dicarboxylate (15b). By use of the procedure for the synthesis of **15c**, **10j** (50 mg, 0.12 mmol) was converted to the title compound **15b** (45 mg, 70%) as a yellow oil. In this case, 1-fluoro-4-nitrobenzene (16 μL, 0.15 mmol) was used: IR (neat): ν_{max}/cm^{-1} 1705 (C=O), 1513, 1343 (NO_2); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.41 (t, *J* = 7.1 Hz, 3H), 3.77 (s, 3H), 3.91 (s, 3H), 4.13 (s, 2H), 4.34 (br s, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.93–7.98 (m, 2H), 8.22 (s, 1H), 8.40 (d, *J* = 8.6 Hz, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 14.4, 52.7, 53.3, 55.3, 61.1, 62.8, 113.2, 113.7 (2C), 120.1, 121.4 (2C), 123.0, 123.6, 125.4 (2C),

125.9, 126.4, 127.6, 130.8 (2C), 132.1, 139.0, 142.7, 145.6, 154.5, 159.4, 166.9; HRMS (FAB$^+$) calcd for $C_{28}H_{27}N_4O_7$ [*M*+H]$^+$: 531.1880, found: 531.1884.

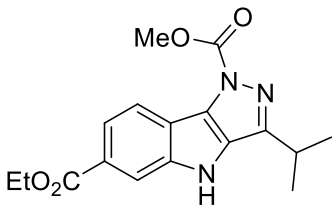


6-Ethyl 1-methyl 4-benzyl-2-(4-methoxybenzyl)-3-phenyl-1,2,3,4-tetrahydropyrazolo[4,3-*b*]indole-1,6-dicarboxylate (15d). By use of the procedure for the synthesis of **15c**, **10g** (60 mg, 0.12 mmol) was converted to the title compound **15d** (58 mg, 82%) as a yellow oil: IR (neat): ν_{max}/cm^{-1} 1703 (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.40 (t, *J* = 7.2 Hz, 3H), 3.79 (s, 3H), 3.88 (s, 3H), 3.90 (d, *J* = 12.0 Hz, 1H), 4.31 (d, *J* = 12.0 Hz, 1H), 4.36–4.41 (m, 2H), 4.72 (d, *J* = 15.5 Hz, 1H), 4.75 (s, 1H), 5.30 (d, *J* = 15.5 Hz, 1H), 6.69–6.70 (m, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 6.84–6.85 (m, 2H), 7.13–7.18 (m, 5H), 7.22–7.27 (m, 3H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 8.06 (s, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 14.5, 48.2, 53.3, 55.1, 60.8, 62.2, 66.3, 112.6, 113.8 (2C), 119.4, 121.0, 123.1, 123.8, 126.8, 127.1 (2C), 127.3, 127.8 (2C), 128.1, 128.6 (2C), 129.0 (2C), 131.2 (2C), 131.5, 135.7, 136.3, 138.9, 140.0, 154.2, 159.2, 167.4; HRMS (FAB$^+$) calcd for $C_{35}H_{34}N_3O_5$ [*M*+H]$^+$: 576.2498, found: 576.2504.

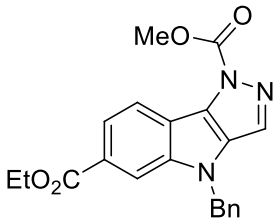


6-Ethyl 1-methyl 1,4-dihydropyrazolo[4,3-*b*]indole-1,6-dicarboxylate (11d). By use of the procedure for the synthesis of **11a**, **10j** (60 mg, 0.15 mmol) was converted to the title compound **11d** (48 mg, 95%) as a white solid: mp 215 °C; IR (neat): ν_{max}/cm^{-1} 1749 (C=O), 1708 (C=O); ^{1}H-NMR (500 MHz, DMSO-d_6) δ: 1.35 (t, *J* = 7.2 Hz, 3H), 4.11 (s, 3H), 4.34 (q, *J* = 7.2 Hz, 2H), 7.74 (d, *J* = 8.6 Hz, 1H), 8.13–8.17 (m, 3H), 11.52 (s, 1H); ^{13}C-NMR (125 MHz, DMSO-d_6) δ: 14.2, 54.7, 60.7,

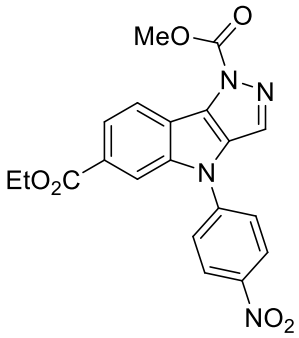
114.7, 115.5, 119.5, 120.4, 125.7, 128.9, 129.9, 134.2, 142.5, 149.9, 166.1; HRMS (FAB$^+$) calcd for $C_{14}H_{14}N_3O_4$ [*M*+H]$^+$: 288.0984, found: 288.0987.



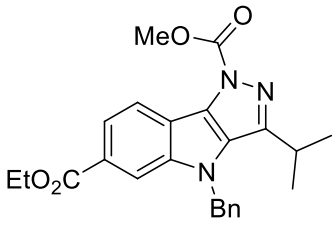
6-Ethyl 1-methyl 3-isopropyl-1,4-dihydropyrazolo[4,3-*b*]indole-1,6-dicarboxylate (11e). By use of the procedure for the synthesis of **11a**, **10b** (49 mg, 0.11 mmol) was converted to the title compound **11e** (25 mg, 70%) as a white solid: mp 201 °C; IR (neat): ν_{max}/cm^{-1} 1737 (C=O), 1685 (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.44 (t, *J* = 7.2 Hz, 3H), 1.48 (d, *J* = 6.9 Hz, 6H), 3.29–3.38 (m, 1H), 4.17 (s, 3H), 4.45 (q, *J* = 7.2 Hz, 2H), 7.91–7.93 (m, 1H), 8.30–8.33 (m, 2H), 8.99 (s, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 14.3, 21.5 (2C), 27.9, 54.6, 61.2, 114.7, 117.1, 120.8, 121.2, 126.8, 131.8, 132.3, 142.8, 147.6, 150.6, 167.5; HRMS (FAB$^+$) calcd for $C_{17}H_{20}N_3O_4$ [*M*+H]$^+$: 330.1454, found: 330.1451.



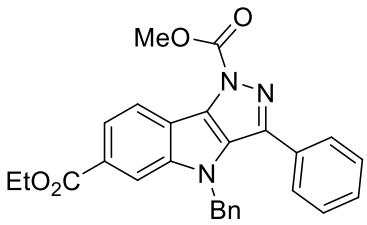
6-Ethyl 1-methyl 4-benzyl-1,4-dihydropyrazolo[4,3-*b*]indole-1,6-dicarboxylate (11f). By use of the procedure for the synthesis of **11a**, **15a** (40 mg, 0.08 mmol) was converted to the title compound **11f** (28 mg, 93%) as a white solid: mp 142 °C; IR (neat): ν_{max}/cm^{-1} 1735 (C=O), 1703 (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.43 (t, *J* = 7.2 Hz, 3H), 4.18 (s, 3H), 4.43 (q, *J* = 7.2 Hz, 2H), 5.41 (s, 2H), 7.20–7.22 (m, 2H), 7.31–7.34 (m, 4H), 7.92–7.94 (m, 1H), 8.20 (s, 1H), 8.32–8.33 (m, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 14.4, 49.0, 54.8, 61.1, 112.4, 113.8, 116.4, 120.6, 121.4, 127.1, 127.4, 127.5 (2C), 128.3, 129.0 (2C), 135.5, 135.6, 143.1, 150.3, 166.9; HRMS (FAB$^+$) calcd for $C_{21}H_{20}N_3O_4$ [*M*+H]$^+$: 378.1454, found: 378.1449.



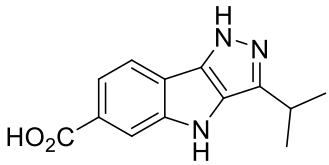
6-Ethyl 1-methyl 4-(4-nitrophenyl)-1,4-dihydropyrazolo[4,3-*b*]indole-1,6-dicarboxylate (11g). By use of the procedure for the synthesis of **11a**, **15b** (120 mg, 0.23 mmol) was converted to the title compound **11g** (80 mg, 87%) as a yellow solid: mp 228 °C; IR (neat): ν_{max}/cm^{-1} 1754 (C=O), 1731 (C=O), 1523, 1348 (NO_2); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.43 (t, *J* = 6.9 Hz, 3H), 4.23 (s, 3H), 4.44 (q, *J* = 6.9 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.90 (s, 1H), 8.03 (d, *J* = 8.6 Hz, 1H), 8.41 (s, 1H), 8.43 (d, *J* = 8.6 Hz, 1H), 8.48 (d, *J* = 8.0 Hz, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 14.4, 55.1, 61.4, 113.4, 118.5, 122.3, 123.0, 123.4 (2C), 126.0 (2C), 127.2, 128.8, 133.0, 134.6, 142.1, 143.4, 145.8, 150.2, 166.4; HRMS (FAB$^+$) calcd for $C_{20}H_{17}N_4O_6$ [*M*+H]$^+$: 409.1148, found: 409.1148.



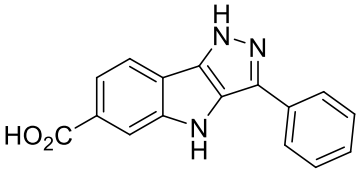
6-Ethyl 1-methyl 4-benzyl-3-isopropyl-1,4-dihydropyrazolo[4,3-*b*]indole-1,6-dicarboxylate (11h). By use of the procedure for the synthesis of **11a**, **15c** (60 mg, 0.11 mmol) was converted to the title compound **11h** (39 mg, 84%) as a yellow oil: IR (neat): ν_{max}/cm^{-1} 1740 (C=O), 1709 (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.31 (d, *J* = 6.9 Hz, 6H), 1.40 (t, *J* = 7.2 Hz, 3H), 3.10–3.18 (m, 1H), 4.18 (s, 3H), 4.39 (q, *J* = 7.2 Hz, 2H), 5.58 (s, 2H), 6.97–6.99 (m, 2H), 7.24–7.29 (m, 3H), 7.90–7.92 (m, 1H), 8.09 (s, 1H), 8.36 (br s, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 14.3, 21.8 (2C), 27.6, 48.2, 54.7, 61.0, 112.5, 116.6, 120.7, 121.5, 125.7 (2C), 127.0, 127.8, 128.9 (2C), 131.4, 133.4, 136.9, 143.3, 147.3, 150.5, 167.0; HRMS (FAB$^+$) calcd for $C_{24}H_{26}N_3O_4$ [*M*+H]$^+$: 420.1923, found: 420.1921.



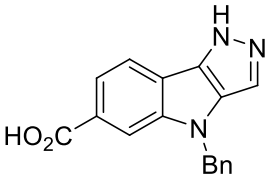
6-Ethyl 1-methyl 4-benzyl-3-phenyl-1,4-dihydropyrazolo[4,3-*b*]indole-1,6-dicarboxylate (11i). By use of the procedure for the synthesis of **11a**, **15d** (50 mg, 0.09 mmol) was converted to the title compound **11i** (27 mg, 69%) as a white solid: mp 185 °C; IR (neat): ν_{max}/cm^{-1} 1742 (C=O), 1710 (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.41 (t, *J* = 7.2 Hz, 3H), 4.21 (s, 3H), 4.40 (q, *J* = 7.2 Hz, 2H), 5.46 (s, 2H), 6.84–6.90 (m, 2H), 7.18–7.23 (m, 3H), 7.36–7.42 (m, 3H), 7.57–7.58 (m, 2H), 7.95 (d, *J* = 8.0 Hz, 1H), 8.11 (s, 1H), 8.41–8.42 (m, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 14.5, 48.1, 54.8, 61.1, 113.0, 116.6, 120.8, 121.7, 126.2 (2C), 127.4, 127.9, 128.5, 128.6 (2C), 128.8 (2C), 129.0 (2C), 129.4, 130.9, 133.2, 136.6, 141.1, 143.8, 150.6, 166.9; HRMS (FAB$^+$) calcd for $C_{27}H_{24}N_3O_4$ [*M*+H]$^+$: 454.1767, found: 454.1761.



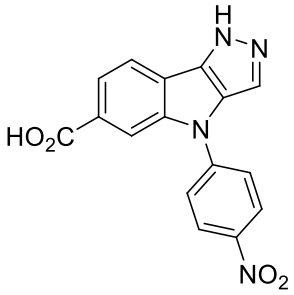
3-Isopropyl-1,4-dihydropyrazolo[4,3-*b*]indole-6-carboxylic acid (5b). By use of the procedure for the synthesis of **5a**, **11e** (43 mg, 0.13 mmol) was converted to the title compound **5b** (26 mg, 82%) as a white solid: mp >300 °C; IR (neat): ν_{max}/cm^{-1} 1663 (C=O); ^{1}H-NMR (500 MHz, DMSO-d_6) δ: 1.37 (d, *J* = 6.9 Hz, 6H), 3.14–3.20 (m, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.98 (s, 1H), 10.67 (s, 1H), 12.55–12.64 (m, 2H); ^{13}C-NMR (125 MHz, DMSO-d_6) δ: 22.3 (2C), 26.4, 113.6, 114.6, 117.1, 119.7, 128.6, 135.7, 144.6, 147.4, 168.4, 171.2; HRMS (FAB$^+$) calcd for $C_{13}H_{14}N_3O_2$ [*M*+H]$^+$: 244.1086, found: 244.1094; t_R (method A): 22.64 min.



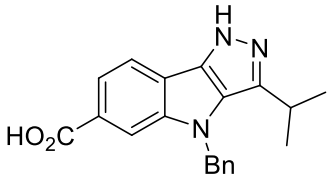
3-Phenyl-1,4-dihydropyrazolo[4,3-*b*]indole-6-carboxylic acid (5c). By use of the procedure for the synthesis of **5a**, **11b** (12 mg, 0.03 mmol) was converted to the title compound **5c** (8 mg, 87%) as a light yellow solid. In this case, compound **5c** precipitated after the neutralization, which was collected by filtration: mp >300 °C; IR (neat): ν_{max}/cm^{-1} 1688 (C=O); ^{1}H-NMR (500 MHz, DMSO-d_6) δ: 7.31–7.34 (m, 1H), 7.49–7.52 (m, 2H), 7.71 (d, J = 7.6 Hz, 1H), 7.84 (d, J = 7.6 Hz, 1H), 7.95–7.99 (m, 2H), 8.06 (s, 1H), 11.27 (s, 1H), 12.81–13.22 (m, 2H); ^{13}C-NMR (125 MHz, DMSO-d_6) δ: 113.9, 118.5, 119.5, 124.7, 124.9 (2C), 126.3, 126.7, 127.0, 128.8, 129.0 (2C), 129.5, 131.9, 144.3, 167.9; HRMS (FAB$^+$) calcd for $C_{16}H_{12}N_3O_2$ [M+H]$^+$: 278.0929, found: 278.0935; t_R (method B): 13.07 min.



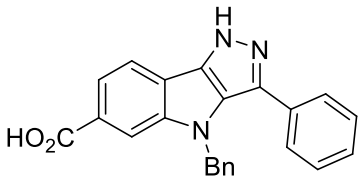
4-Benzyl-1,4-dihydropyrazolo[4,3-*b*]indole-6-carboxylic acid (5d). By use of the procedure for the synthesis of **5a**, **11f** (40 mg, 0.11 mmol) was converted to the title compound **5d** (25 mg, 81%) as a white solid: mp >300 °C; IR (neat): ν_{max}/cm^{-1} 1683 (C=O); ^{1}H-NMR (500 MHz, DMSO-d_6) δ: 5.47 (s, 2H), 7.22–7.31 (m, 5H), 7.54 (s, 1H), 7.71 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 8.11 (s, 1H), 12.79–13.09 (m, 2H); ^{13}C-NMR (125 MHz, DMSO-d_6) δ: 48.1, 111.8, 114.2, 117.4, 118.9, 119.4, 126.3, 127.2 (2C), 127.4, 128.6 (2C), 134.3, 135.9, 137.5, 143.8, 167.9; HRMS (FAB$^+$) calcd for $C_{17}H_{14}N_3O_2$ [M+H]$^+$: 292.1086, found: 292.1085; t_R (method B): 13.08 min.



4-(4-Nitrophenyl)-1,4-dihydropyrazolo[4,3-*b*]indole-6-carboxylic acid (5e). By use of the procedure for the synthesis of **5a**, **11g** (37 mg, 0.09 mmol) was converted to the title compound **5e** (23 mg, 79%) as a yellow solid. In this case, compound **5e** precipitated after the neutralization, which was collected by filtration: mp >300 °C; IR (neat): ν_{max}/cm^{-1} 1683 (C=O), 1503, 1308 (NO_2); ^{1}H-NMR (500 MHz, DMSO-d_6) δ: 7.92 (d, J = 7.6 Hz, 1H), 7.98–8.03 (m, 3H), 8.09 (s, 1H), 8.42 (s, 1H), 8.46 (d, J = 8.4 Hz, 2H), 12.76–13.83 (m, 2H); ^{13}C-NMR (125 MHz, DMSO-d_6) δ: 113.1, 119.7, 120.8, 121.4 (2C), 122.6, 125.6, 125.9 (2C), 127.8, 131.6, 138.8, 142.0, 143.3, 144.5, 167.4; HRMS (FAB$^+$) calcd for $C_{16}H_{11}N_4O_4$ $[M+H]^+$: 323.0780, found: 323.0774; t_R (method B): 17.46 min.



4-Benzyl-3-isopropyl-1,4-dihydropyrazolo[4,3-*b*]indole-6-carboxylic acid (5f). By use of the procedure for the synthesis of **5a**, **11h** (35 mg, 0.08 mmol) was converted to the title compound **5f** (20 mg, 72%) as a white solid: mp >300 °C; IR (neat): ν_{max}/cm^{-1} 1682 (C=O); ^{1}H-NMR (500 MHz, DMSO-d_6) δ: 1.15 (d, J = 6.9 Hz, 6H), 3.13–3.19 (m, 1H), 5.58 (s, 2H), 6.98–6.99 (m, 2H), 7.19–7.22 (m, 1H), 7.25–7.28 (m, 2H), 7.69 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 8.02 (s, 1H), 12.69–12.85 (m, 2H); ^{13}C-NMR (125 MHz, DMSO-d_6) δ: 22.9 (2C), 25.7, 47.4, 111.7, 117.0, 118.8, 119.4, 125.9 (2C), 126.2, 127.2, 128.6 (2C), 130.5, 134.3, 136.5, 138.4, 144.1, 167.9; HRMS (FAB$^+$) calcd for $C_{20}H_{20}N_3O_2$ $[M+H]^+$: 334.1555, found: 334.1559; t_R (method B): 18.82 min.



4-Benzyl-3-phenyl-1,4-dihydropyrazolo[4,3-*b*]indole-6-carboxylic acid (5g). By use of the procedure for the synthesis of **5a**, **11i** (25 mg, 0.06 mmol) was converted to the title compound **5g** (18 mg, 89%) as a white solid: mp >300 °C; IR (neat): ν_{max}/cm^{-1} 1687 (C=O); ^{1}H-NMR (500 MHz, DMSO-d_6) δ: 5.57 (s, 2H), 6.88–6.90 (m, 2H), 7.16–7.20 (m, 3H), 7.35–7.45 (m, 3H), 7.60–7.62 (m, 2H), 7.77 (d, J = 7.6 Hz, 1H), 7.93 (d, J = 7.6 Hz, 1H), 8.09 (s, 1H), 12.79–13.42 (m, 2H); ^{13}C-NMR (125 MHz, DMSO-d_6) δ: 47.6, 112.2, 117.2, 119.1, 120.0, 125.9 (2C), 126.2 (2C), 126.8, 127.0, 127.5, 127.9 (2C), 128.4, 128.6, 128.8 (2C), 130.8, 131.5, 137.7, 144.5, 167.8; HRMS (FAB$^+$) calcd for $C_{23}H_{18}N_3O_2$ $[M+H]^+$: 368.1399, found: 368.1409; t_R (method B): 15.32 min.

References

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2. A. Varela-Fernández, J. A. Varela and C. Saá, *Adv. Synth. Catal.*, 2011, **353**, 1933–1937.
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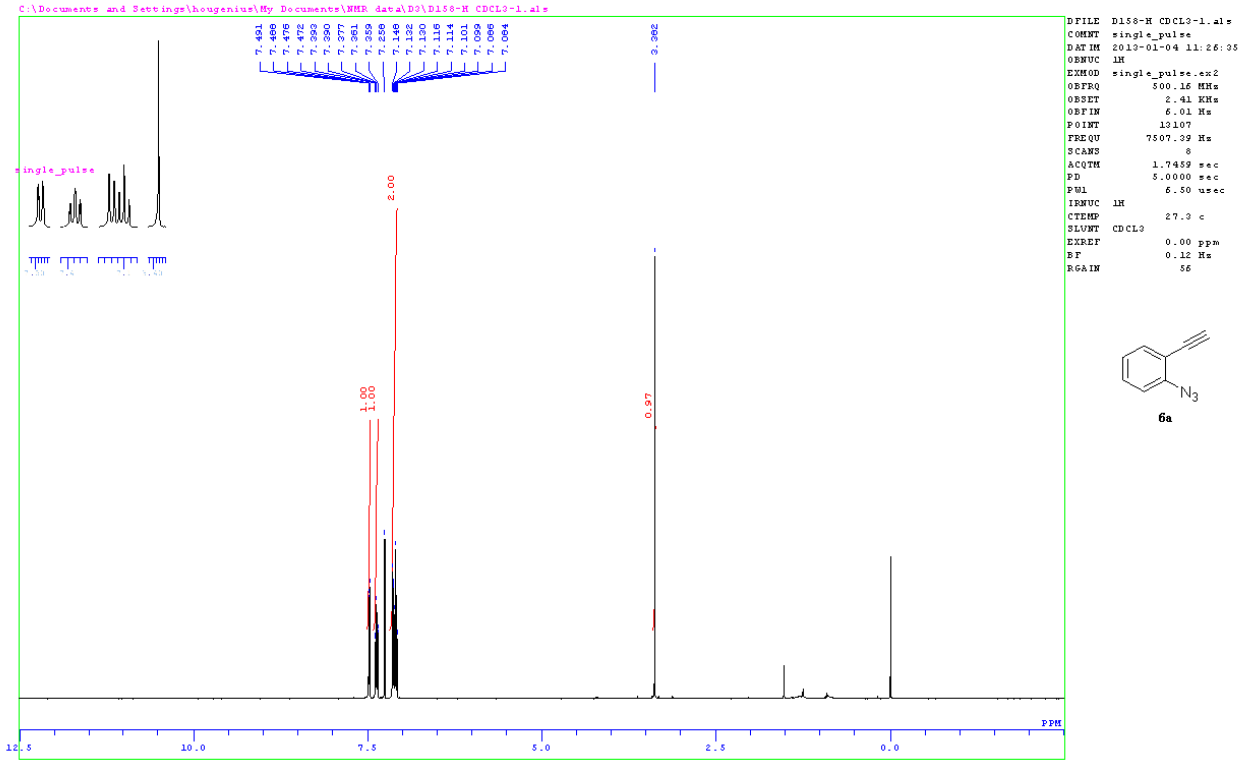
4. F. Roschangar, J. Liu, E. Estanove, M. Dufour, S. Rodríguez, V. Farina, E. Hickey, A. Hossain, P. Jones, H. Lee, B. Z. Lu, R. Varsolona, J. Schröder, P. Beaulieu, J. Gillard and C. H. Senanayake, *Tetrahedron Lett.*, 2008, **49**, 363–366.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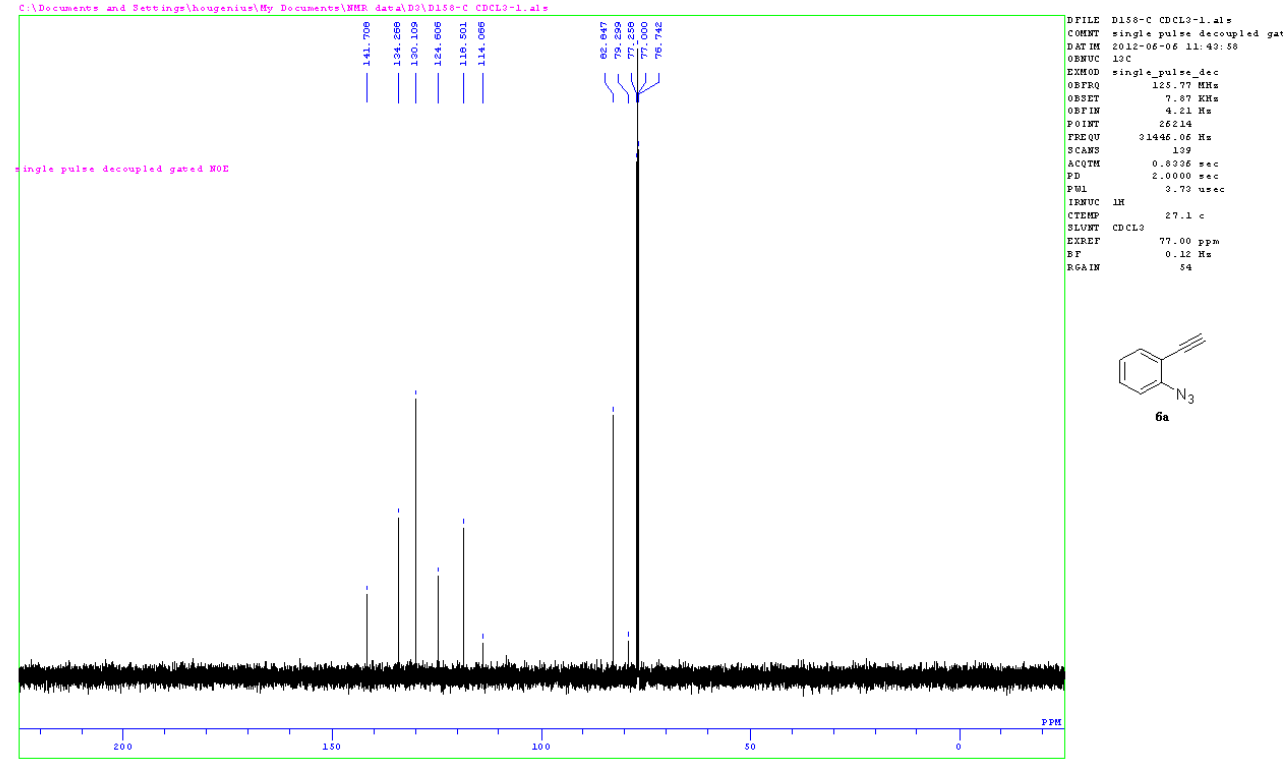
7.486
7.476
7.472
7.392
7.390
7.377
7.361
7.359
7.256
7.148
7.132
7.130
7.116
7.114
7.101
7.099
7.066
7.064
3.982
single_pulse
2.00
1.00
1.00
0.97
PPM
12.5
10.0
7.5
5.0
2.5
0.0
DFILE D158-H CDCL3-1.als
COMNT single_pulse
DATIM 2012-01-04 11:26:35
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.15 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 12107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 27.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 56
N3
6a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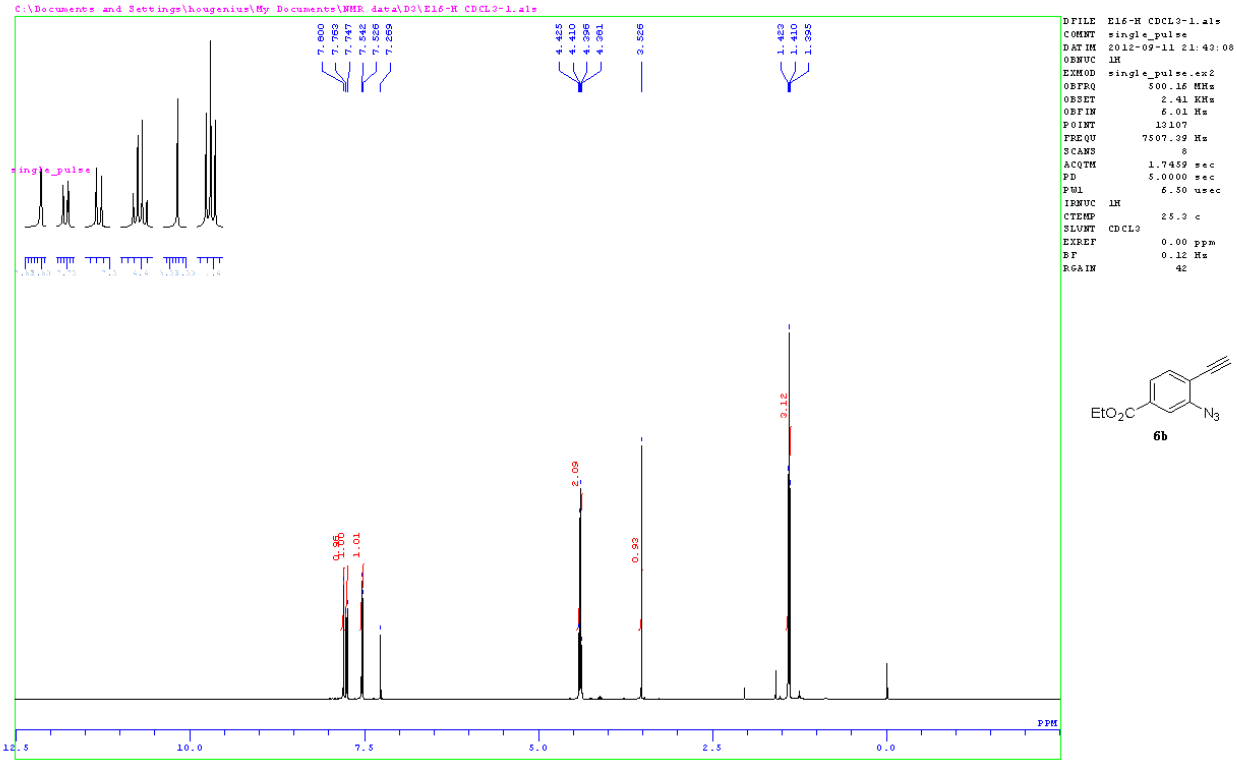
134.266
130.109
124.606
118.501
114.066
82.647
79.299
77.259
77.000
76.742
single pulse decoupled gated NOE
PPM
200
150
100
50
0
DFILE D158-C CDCL3-1.als
COMNT single pulse decoupled gat
DATIM 2012-06-06 11:40:58
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 139
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.73 usec
IRNUC 1H
CTEMP 27.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 54
N3
6a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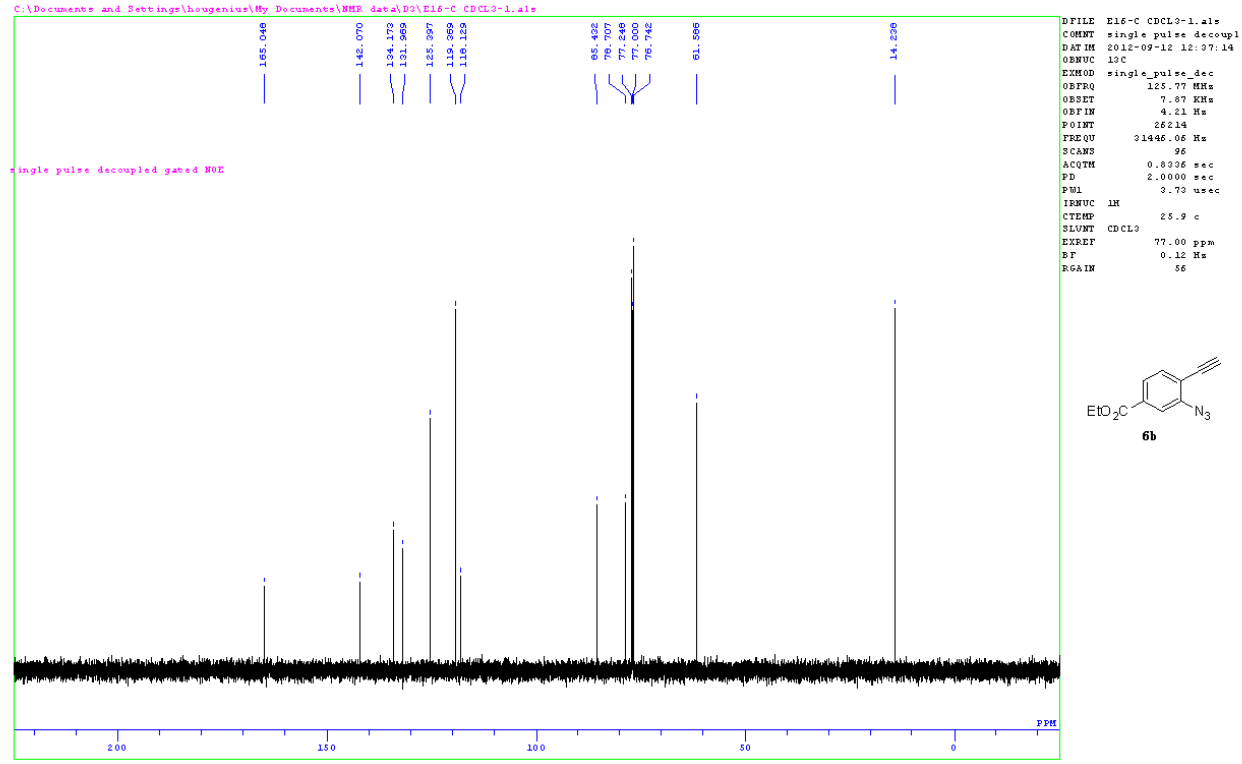
7.800
7.783
7.747
7.542
7.526
7.269
4.425
4.410
4.396
4.381
3.526
1.423
1.410
1.395
single_pulse
0.96
1.01
2.09
0.93
3.12
PPM
12.5
10.0
7.5
5.0
2.5
0.0
DFILE E16-H CDCL3-1.als
COMNT single_pulse
DATIM 2012-09-11 21:43:08
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 12107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 25.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 42
EtO2C
N3
6b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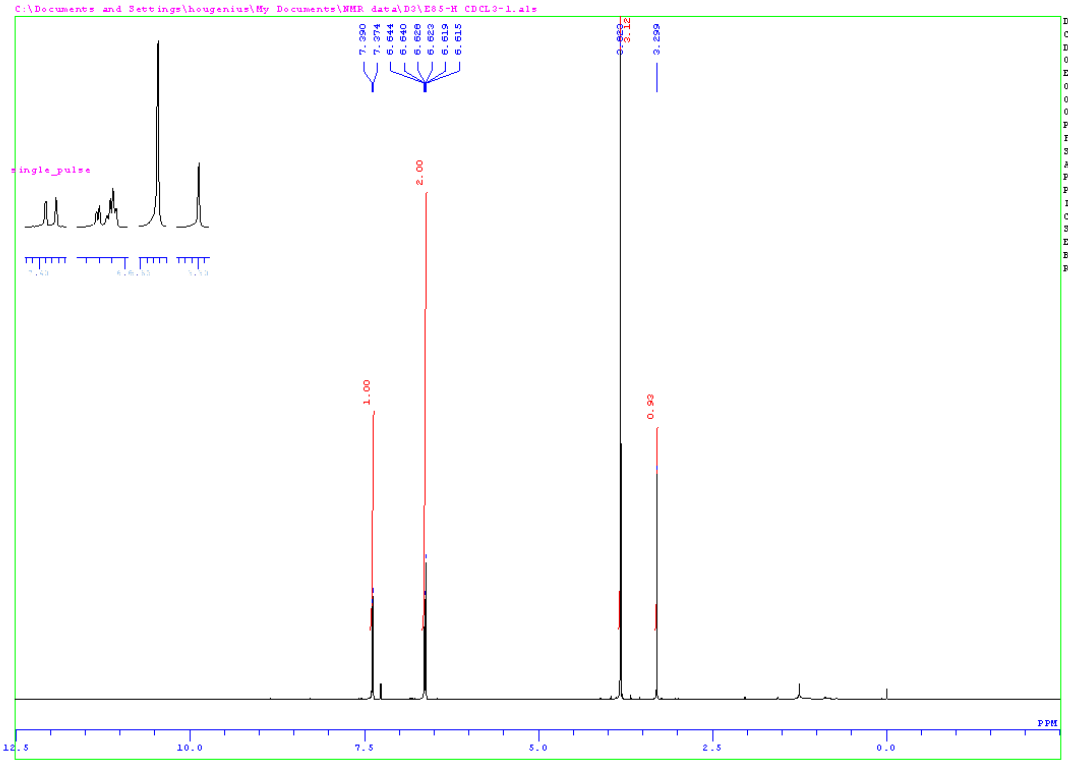
142.070
134.178
131.969
125.397
119.269
118.128
65.432
76.707
77.248
77.000
76.742
61.586
14.236
single pulse decoupled gated NOE
PPM
200
150
100
50
0
DFILE E16-C CDCL3-1.als
COMNT single pulse decoupled gat
DATIM 2012-09-12 12:37:14
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 96
ACQTM 0.8326 sec
PD 2.0000 sec
PW1 3.73 usec
IRNUC 1H
CTEMP 25.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 56
EtO2C
N3
6b

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OBNUC  1H
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OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         12107
FREQU       7507.39 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1           6.50 usec
IRNUC  1H
CTEMP         27.2 c
SLVNT  CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           38
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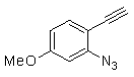

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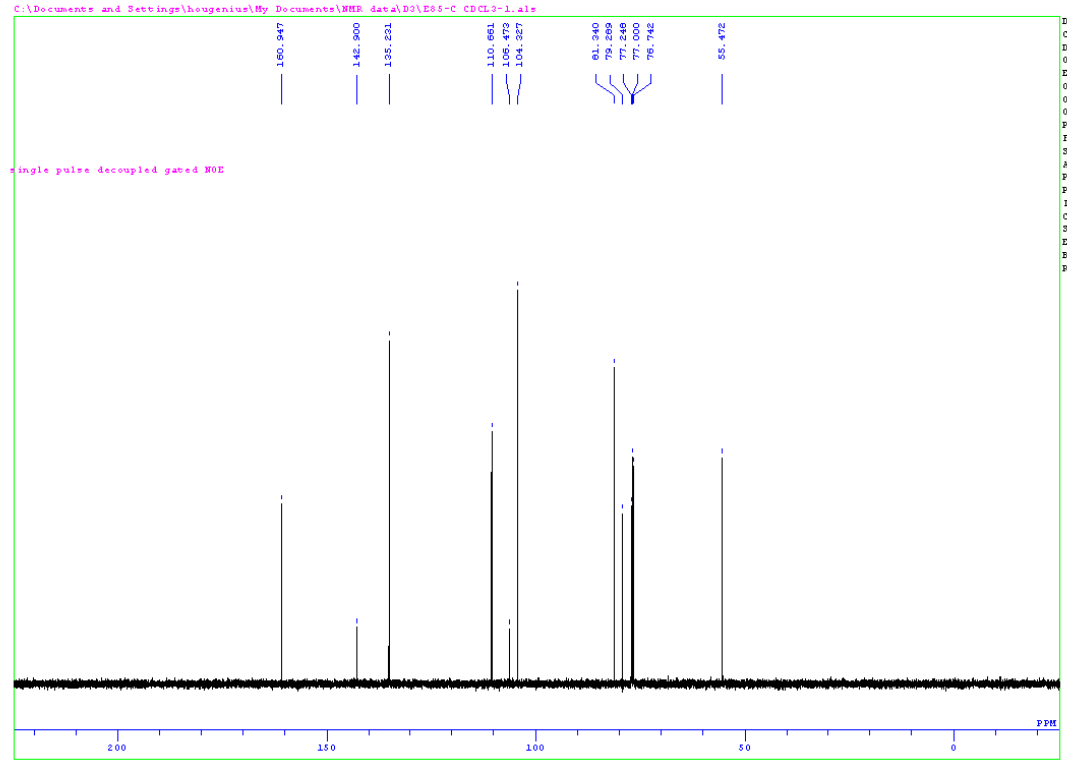


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EXMOD  single_pulse_dec
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OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS           152
ACQTM         0.8336 sec
PD            2.0000 sec
PW1           3.73 usec
IRNUC  1H
CTEMP         27.6 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF            0.12 Hz
RGAIN           54
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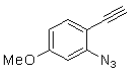

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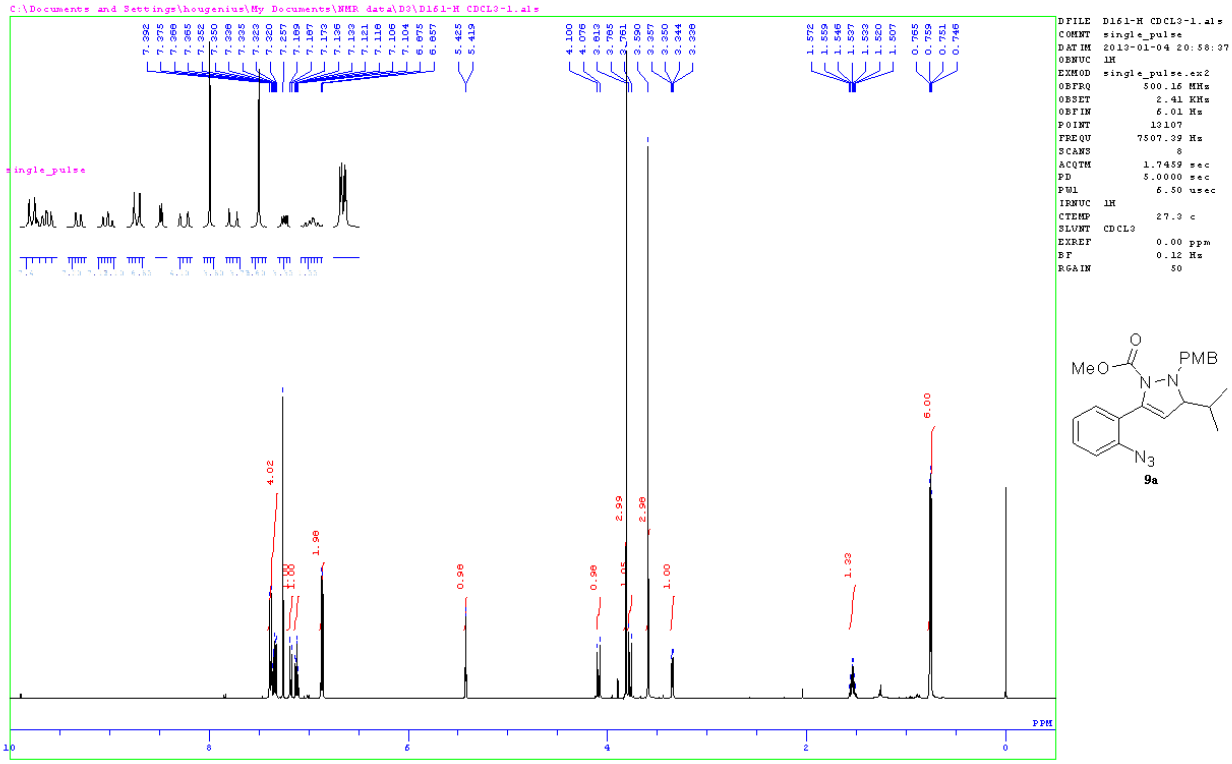
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EXMOD single_pulse.ex2
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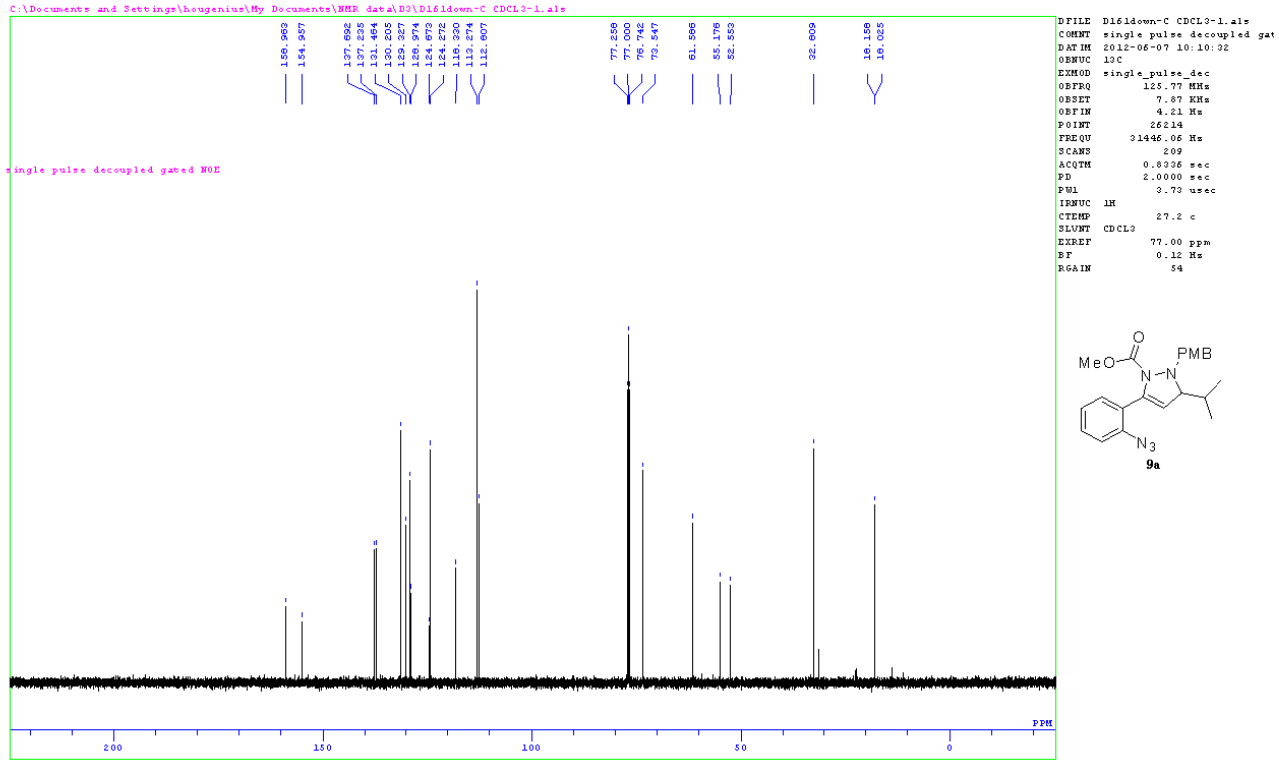
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 12107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 27.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 50
MeO
PMB
N
N
N3
9a
PPM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DFILE D161down-C CDCL3-1.als
COMNT single pulse decoupled gat
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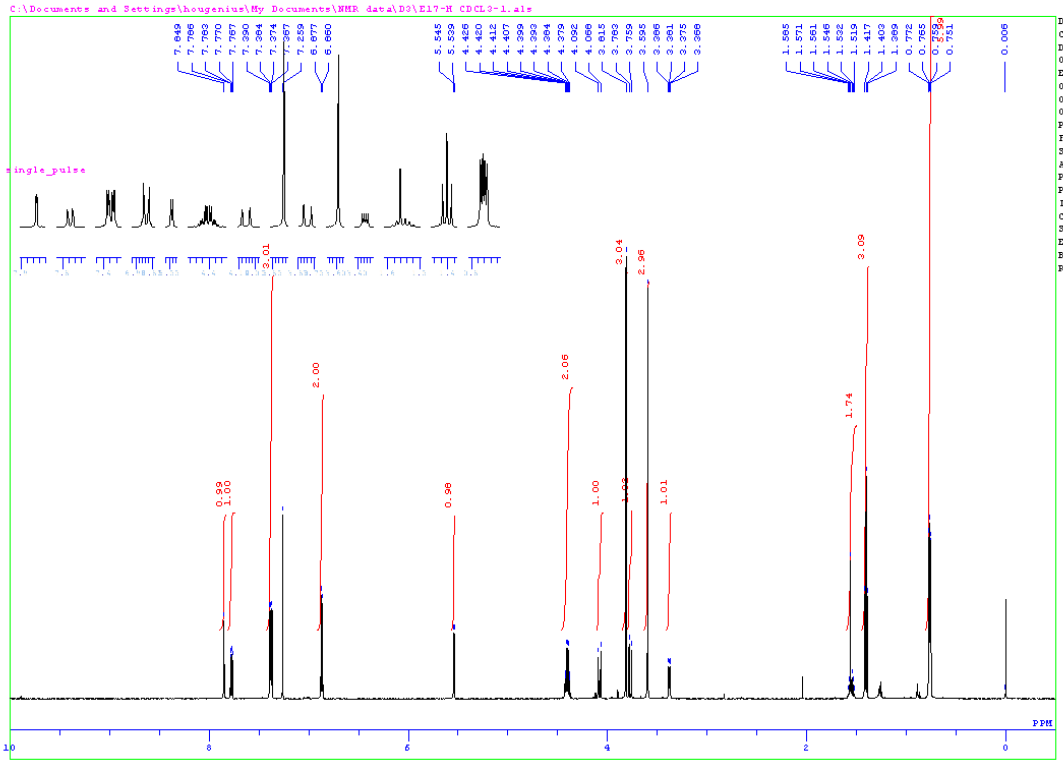
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 209
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.73 usec
IRNUC 1H
CTEMP 27.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 54
MeO
PMB
N
N
N3
9a
PPM



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OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 12107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
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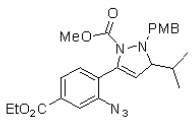
IRNUC 1H
CTEMP 25.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 46



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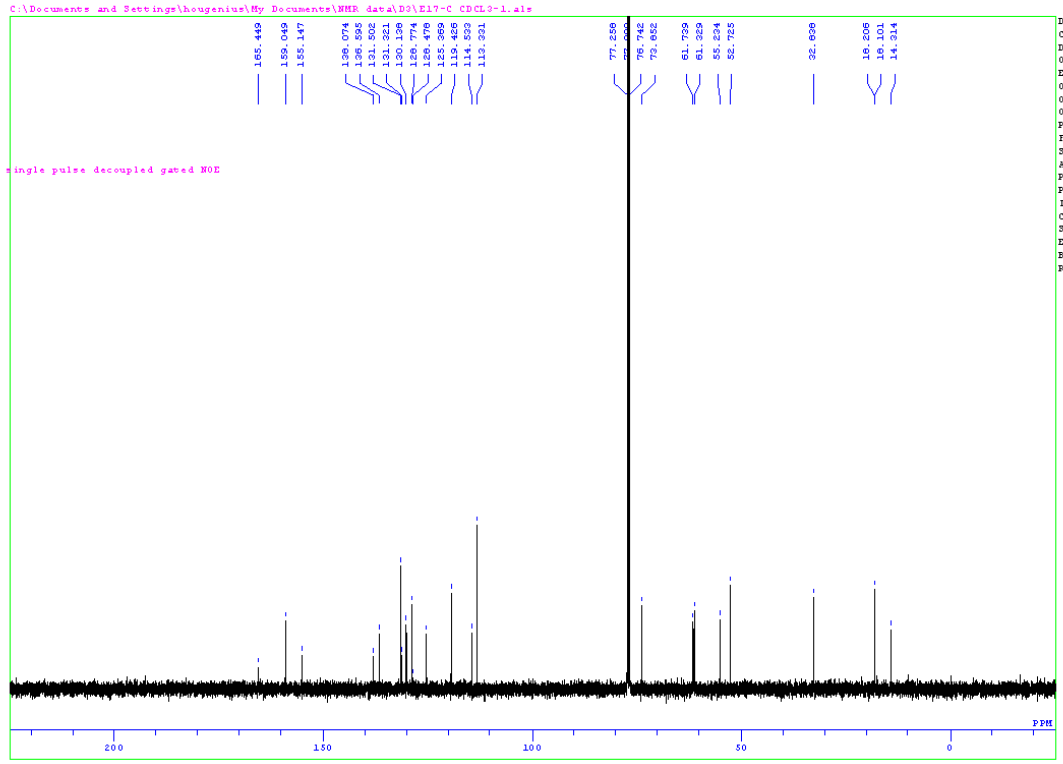

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OBFIN 4.21 Hz
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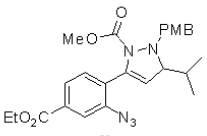

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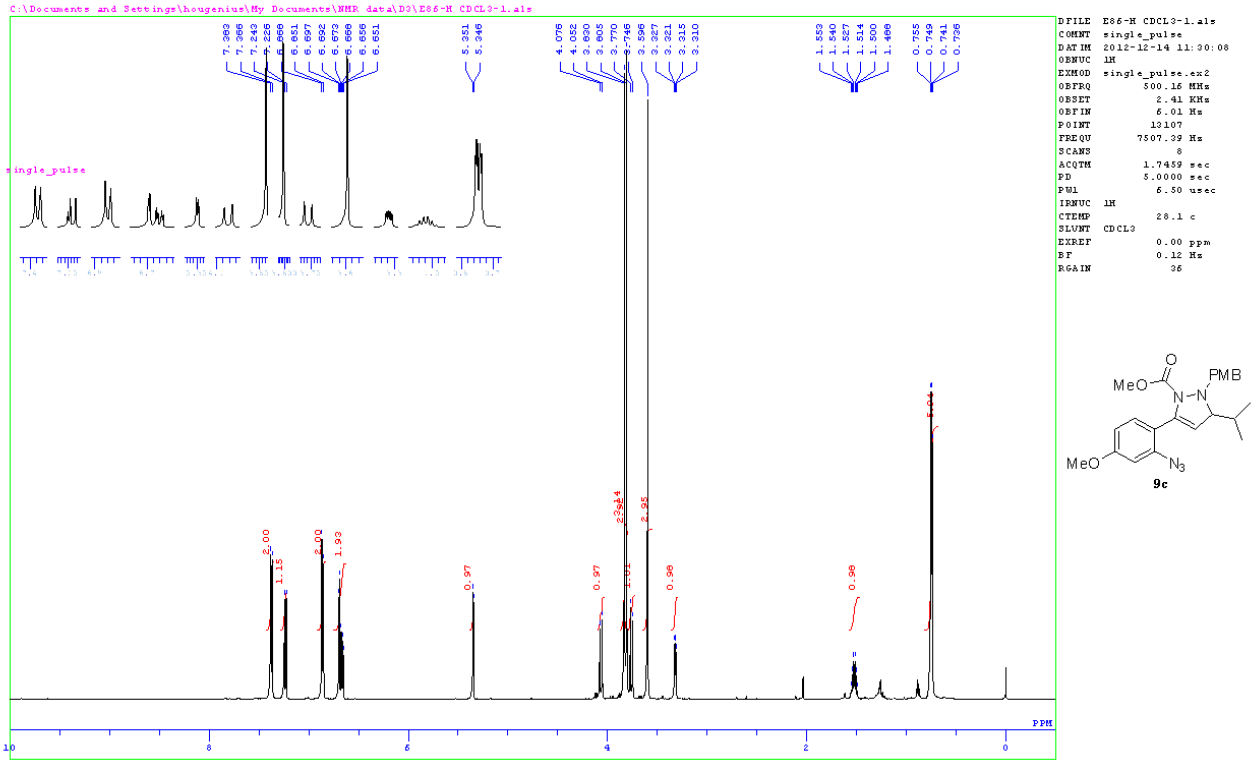

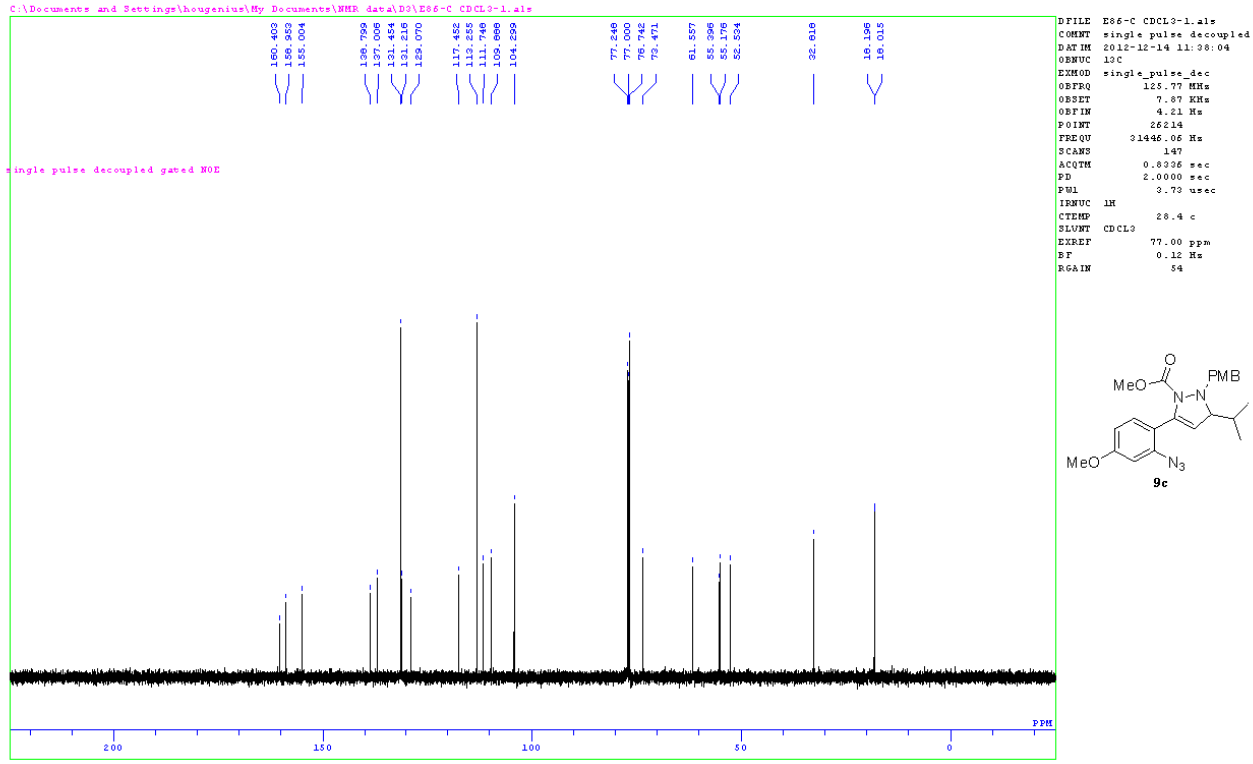

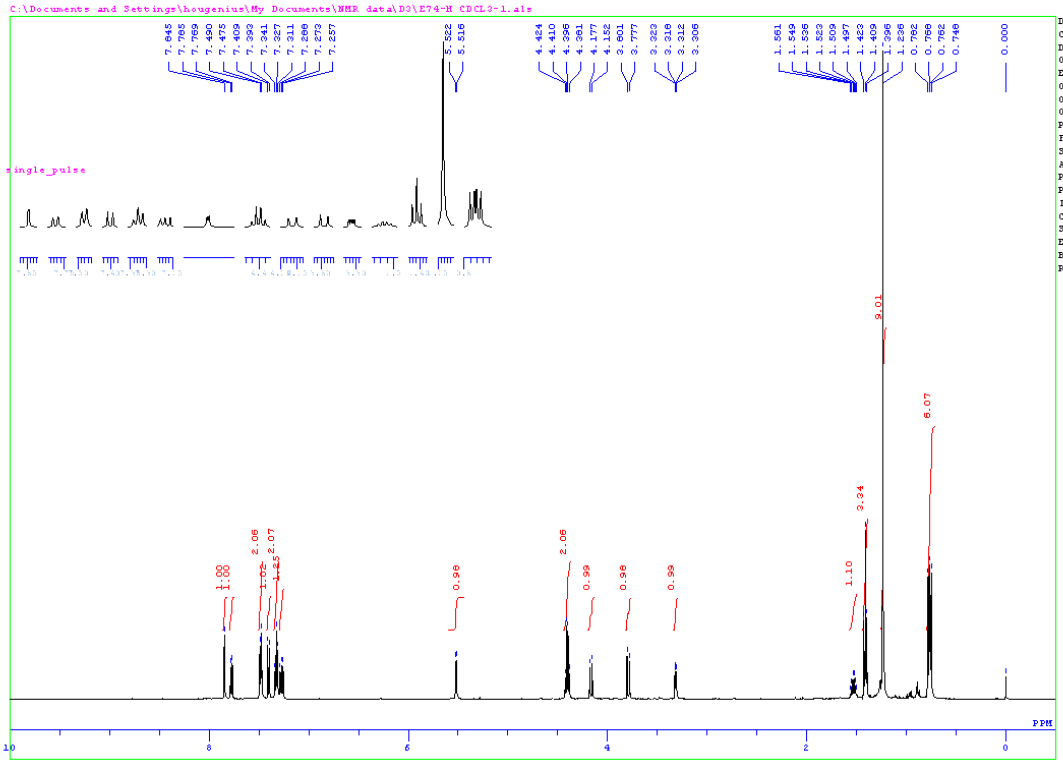
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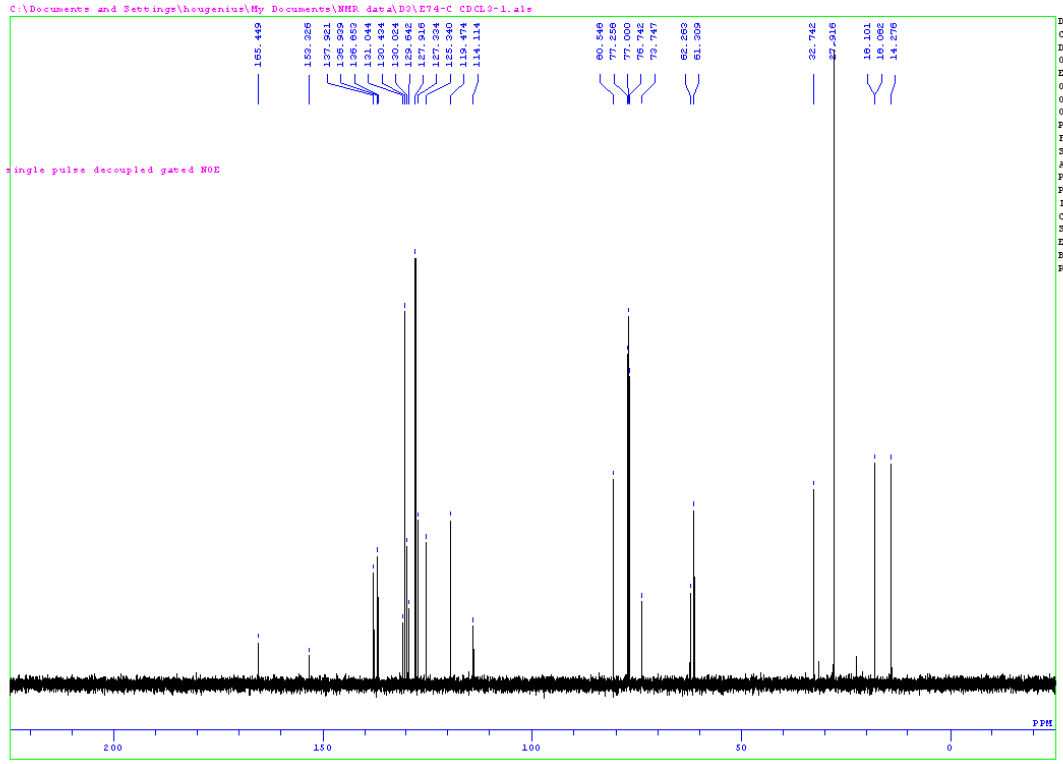
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 27.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 38
PPM
Boc
Bn
EtO2C
N3
9d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OBFIN 4.21 Hz
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FREQU 31446.06 Hz
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PD 2.0000 sec
PW1 3.73 usec
IRNUC 1H
CTEMP 27.8 c
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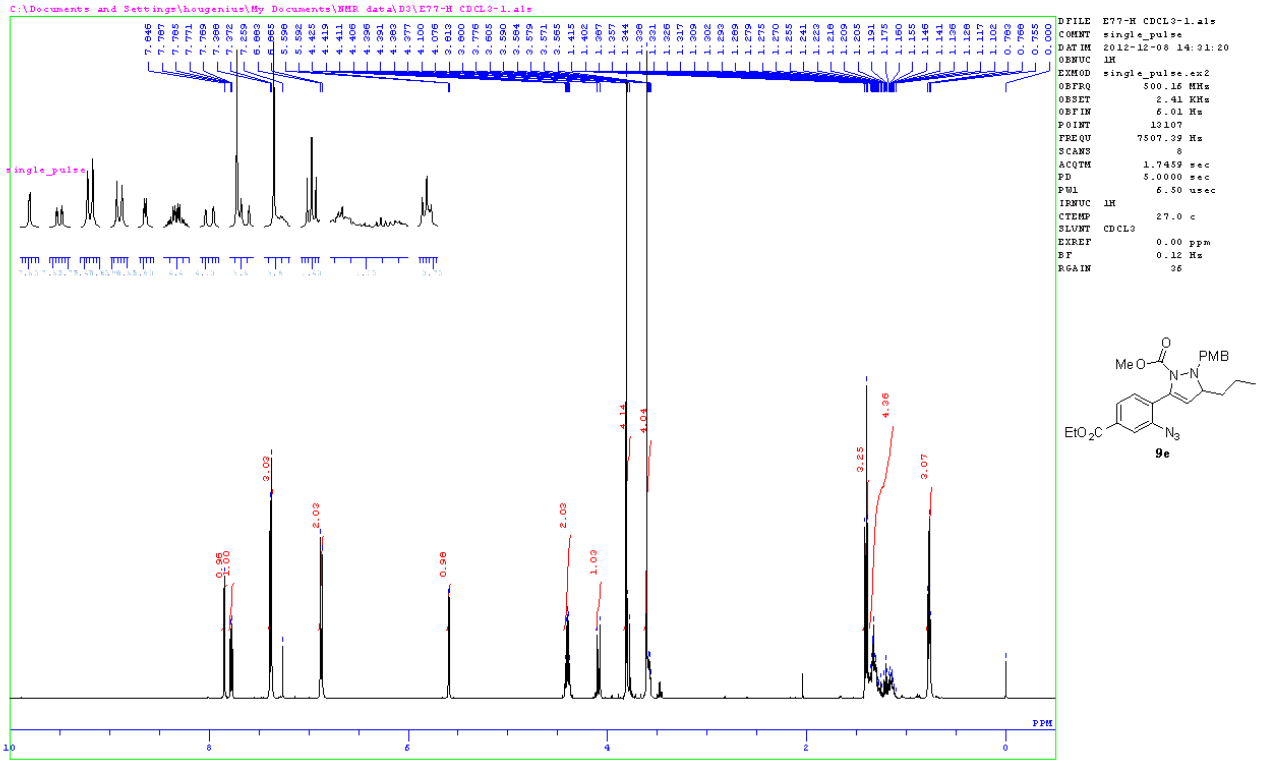
PPM
Boc
Bn
EtO2C
N3
9d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ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 27.0 c
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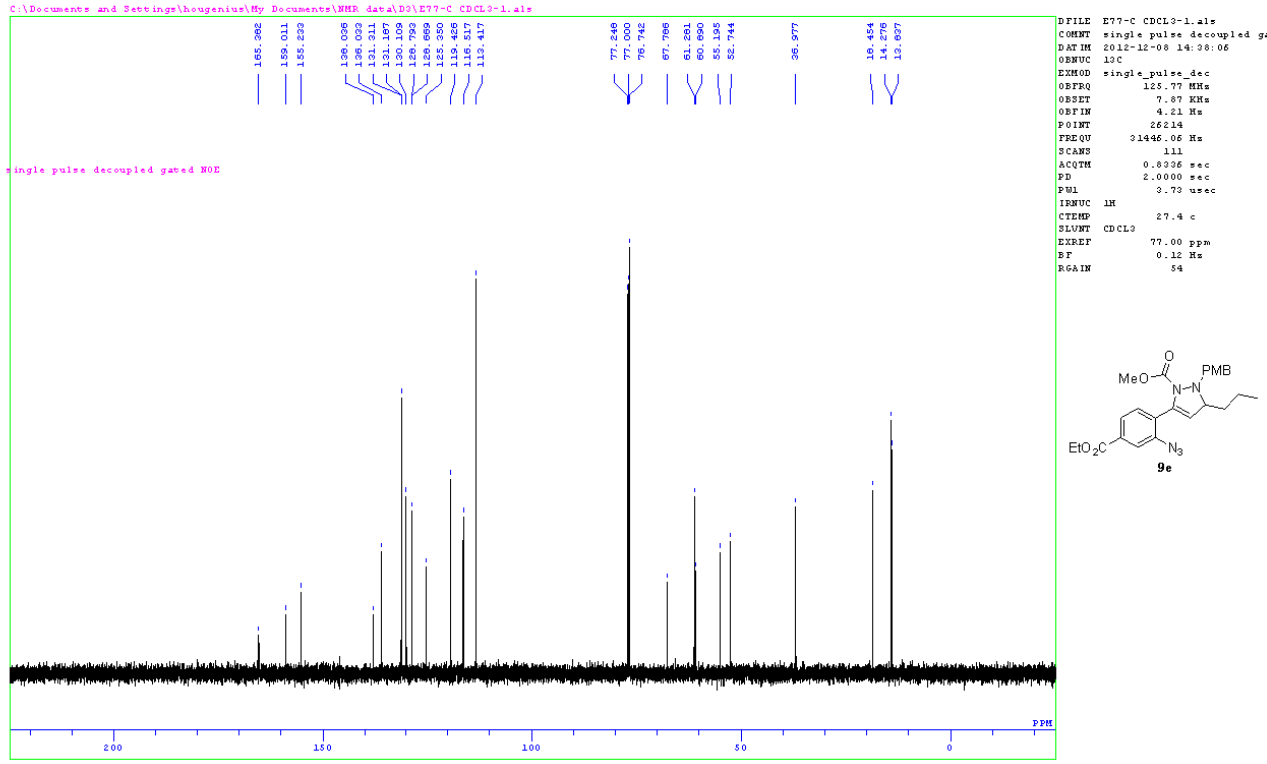
RGAIN 36
PPM
MeO
PMB
EtO2C
N3
9e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DFILE E77-C CDCL3-1.als
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EXMOD single_pulse_dec
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OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 111
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.73 usec
IRNUC 1H
CTEMP 27.4 c
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EXREF 77.00 ppm
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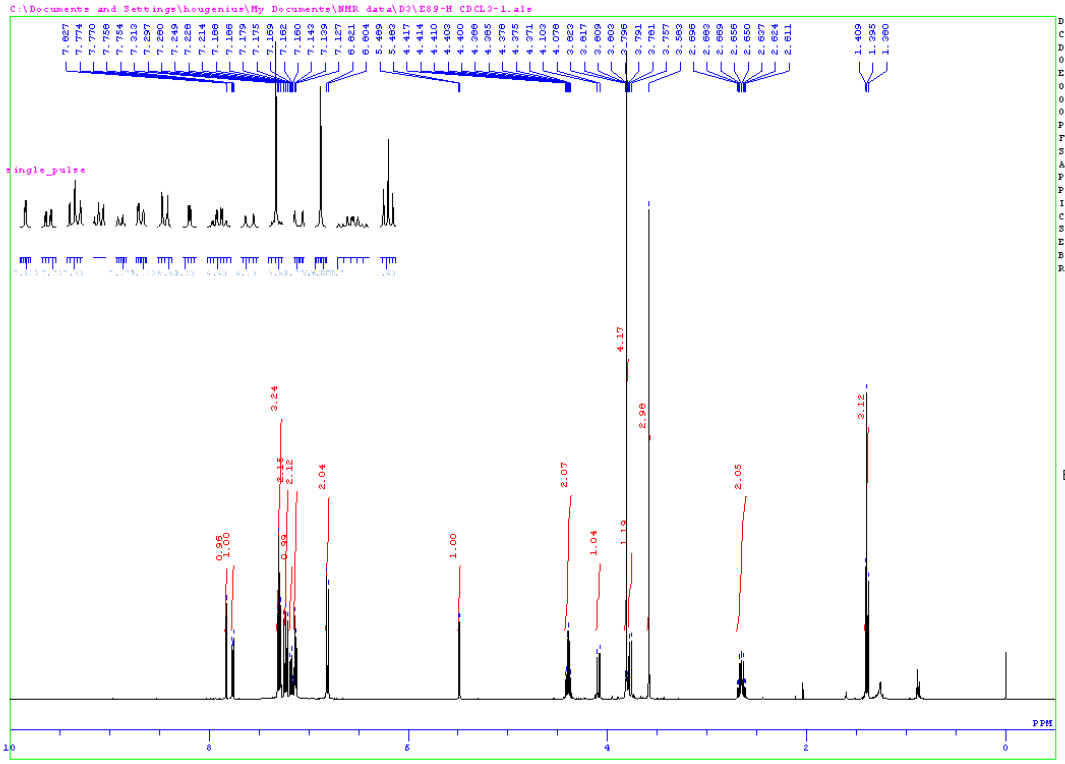
RGAIN 54
PPM
MeO
PMB
EtO2C
N3
9e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PPM
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OBFRQ 500.15 MHz
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OBFIN 6.01 Hz
POINT 12107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 27.4 c
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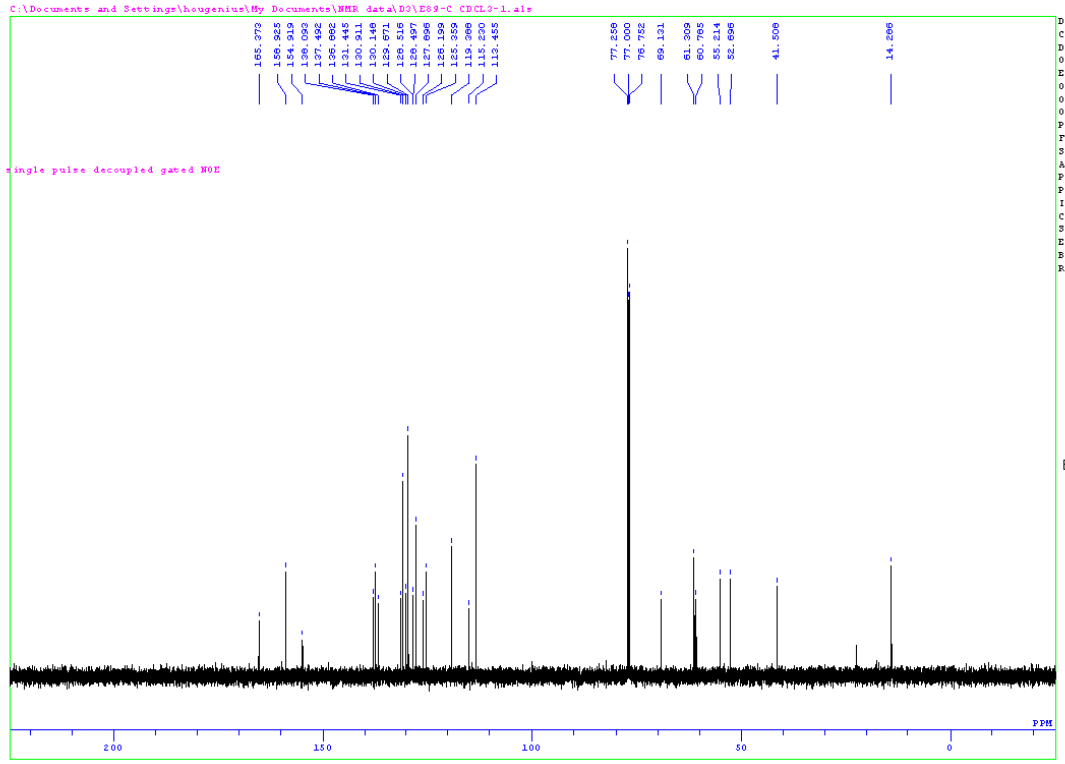
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 38
MeO
PMB
EtO2C
N3
9f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PPM
DFILE E89-C CDCL3-1.als
COMNT single pulse decoupled gat
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OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 86
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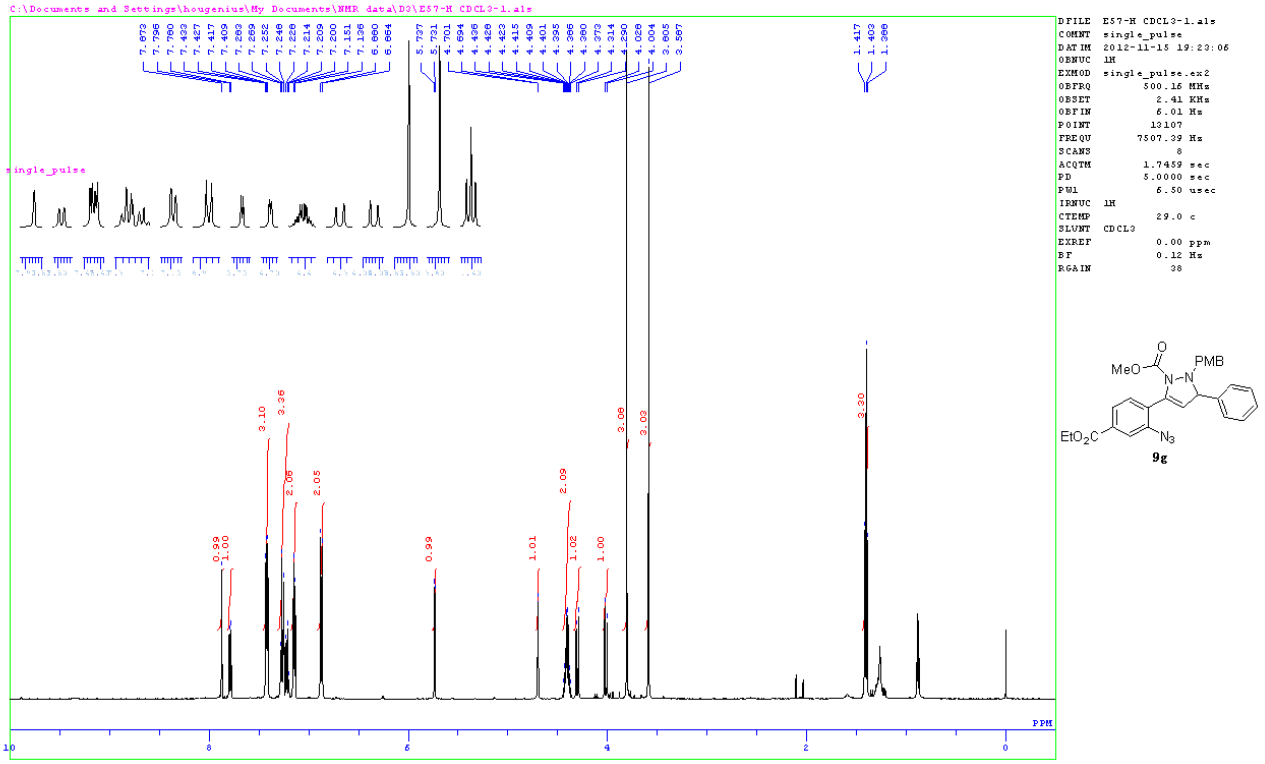
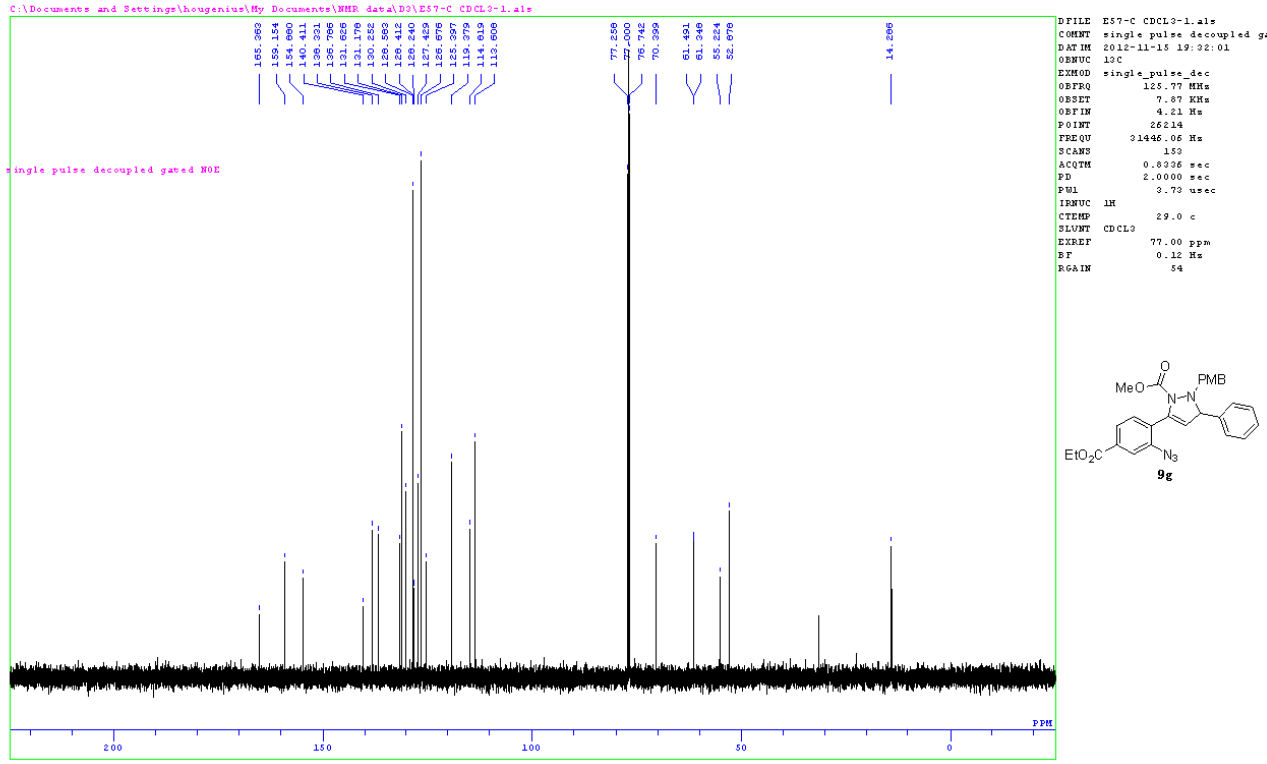
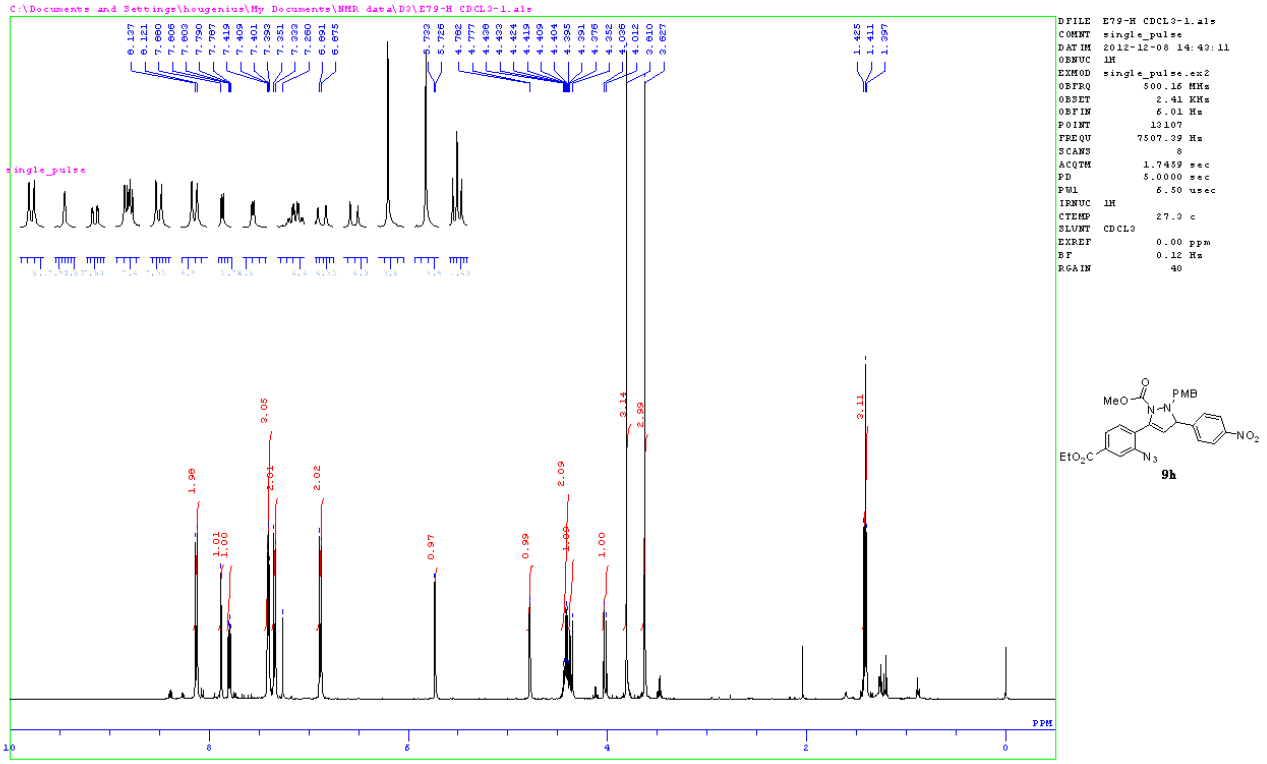
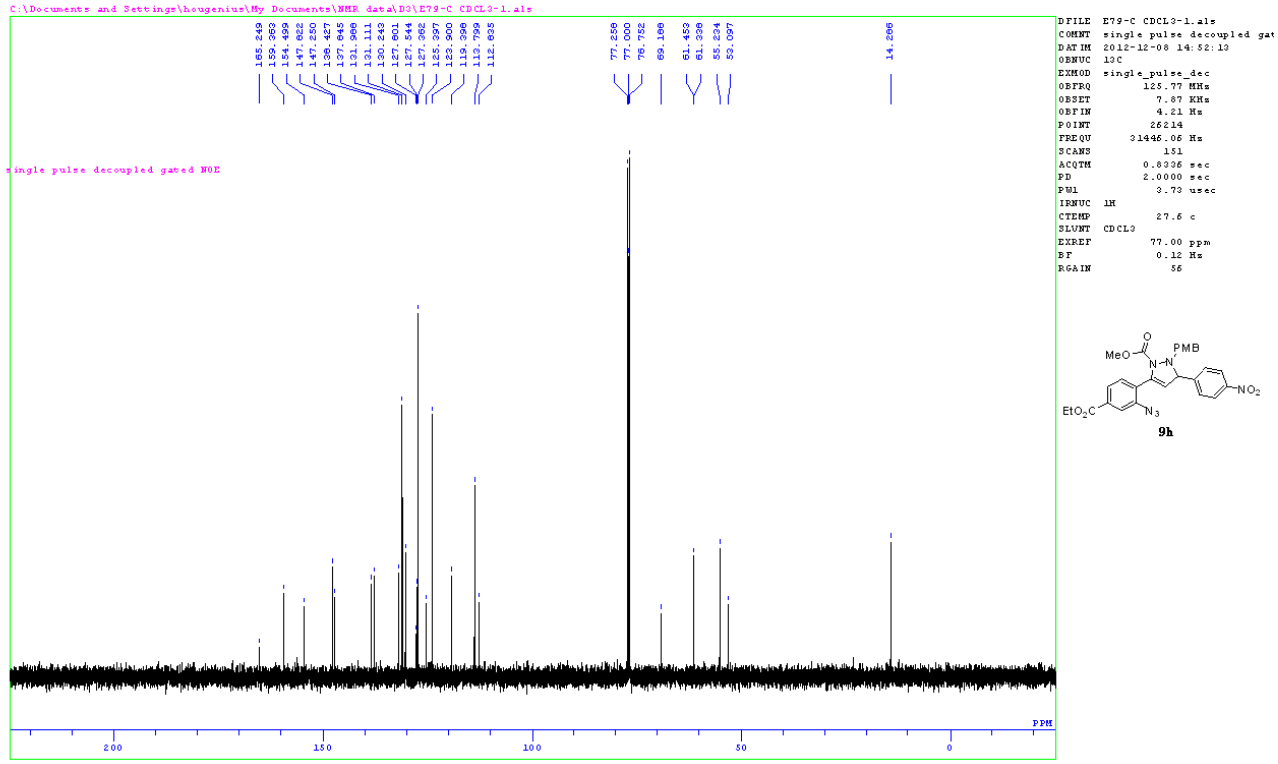
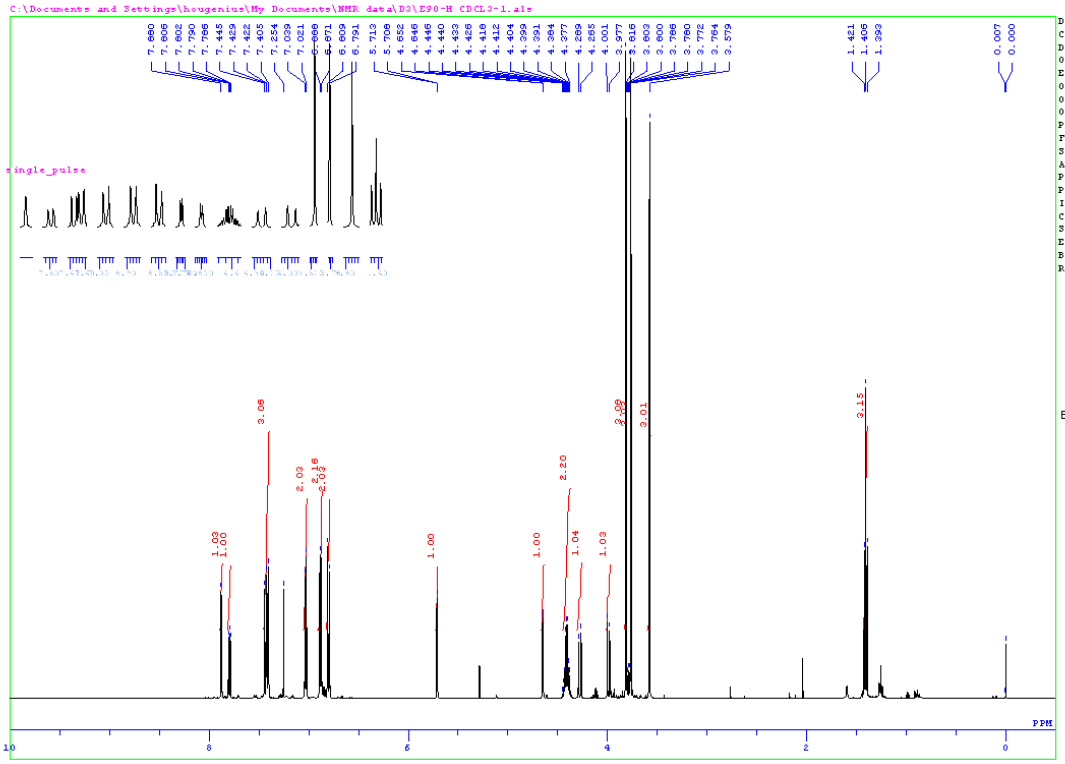
PD 2.0000 sec
PW1 3.73 usec
IRNUC 1H
CTEMP 27.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 56
MeO
PMB
EtO2C
N3
9f


C:\Documents and Settings\hougenius\My Documents\NMR data\D3\E57-H CDCL3-1.als
single_pulse
DFILE E57-H CDCL3-1.als
COMNT single_pulse
DATIM 2012-11-15 19:23:06
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 12107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 29.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 38
MeO
PMB
EtO2C
N3
9g
PPM

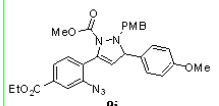

C:\Documents and Settings\hougenius\My Documents\NMR data\D3\E57-C CDCL3-1.als
single pulse decoupled gated NOE
DFILE E57-C CDCL3-1.als
COMNT single pulse decoupled gat
DATIM 2012-11-15 19:32:01
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 153
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.73 usec
IRNUC 1H
CTEMP 29.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 54
MeO
PMB
EtO2C
N3
9g
PPM







DFILE E90-H CDCL3-1.als
COMNT single_pulse
DATIM 2012-12-19 20:40:33
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 12107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 27.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 38



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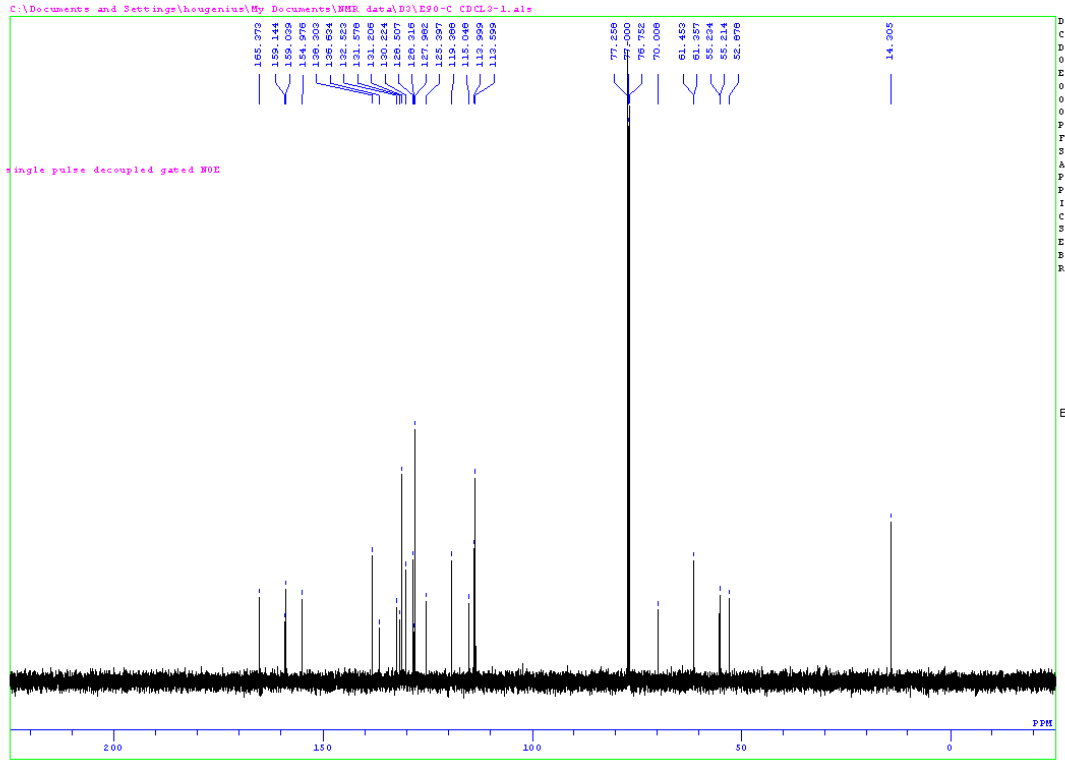
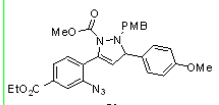
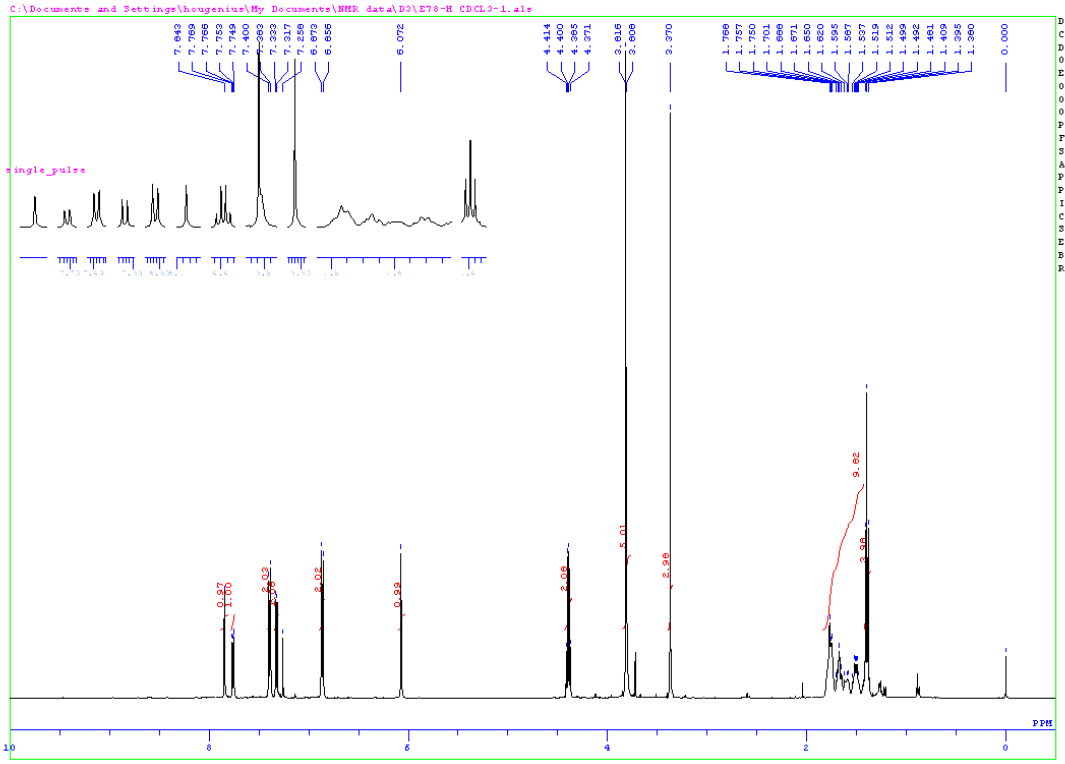
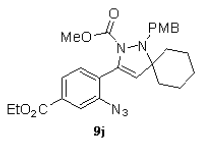


DFILE E90-C CDCL3-1.als
COMNT single pulse decoupled gat
DATIM 2012-12-19 20:48:43
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 157
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.73 usec
IRNUC 1H
CTEMP 27.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 54



9i





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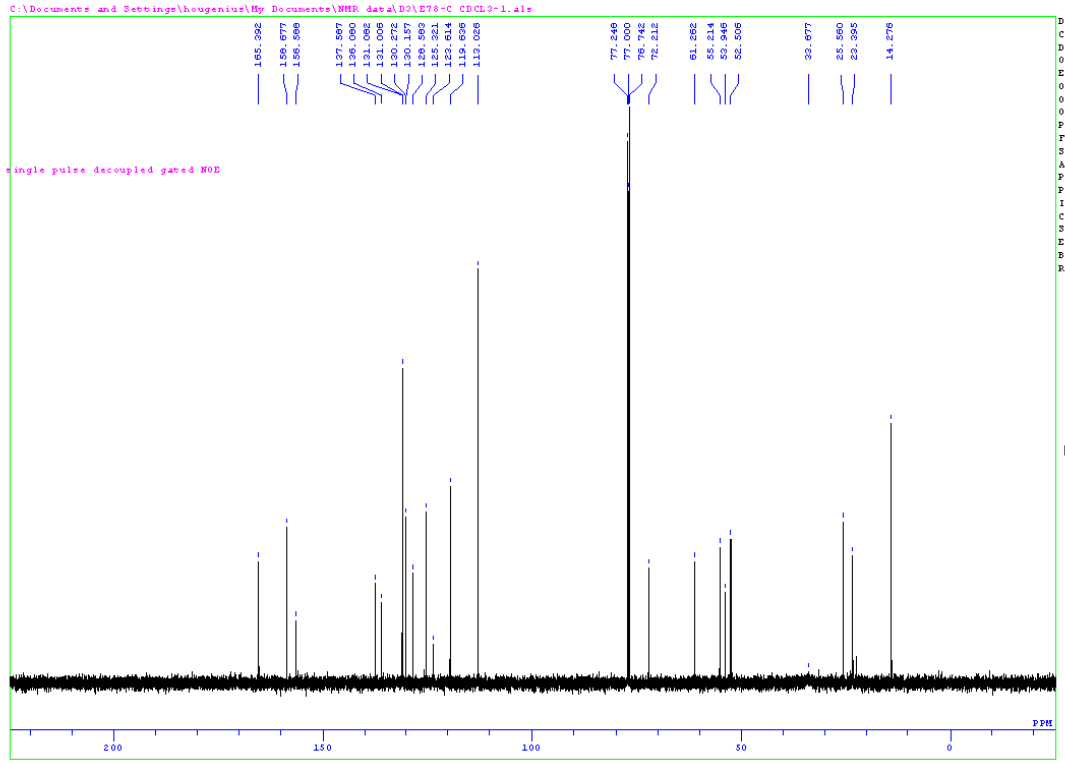
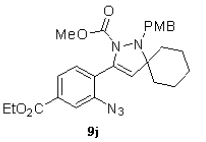
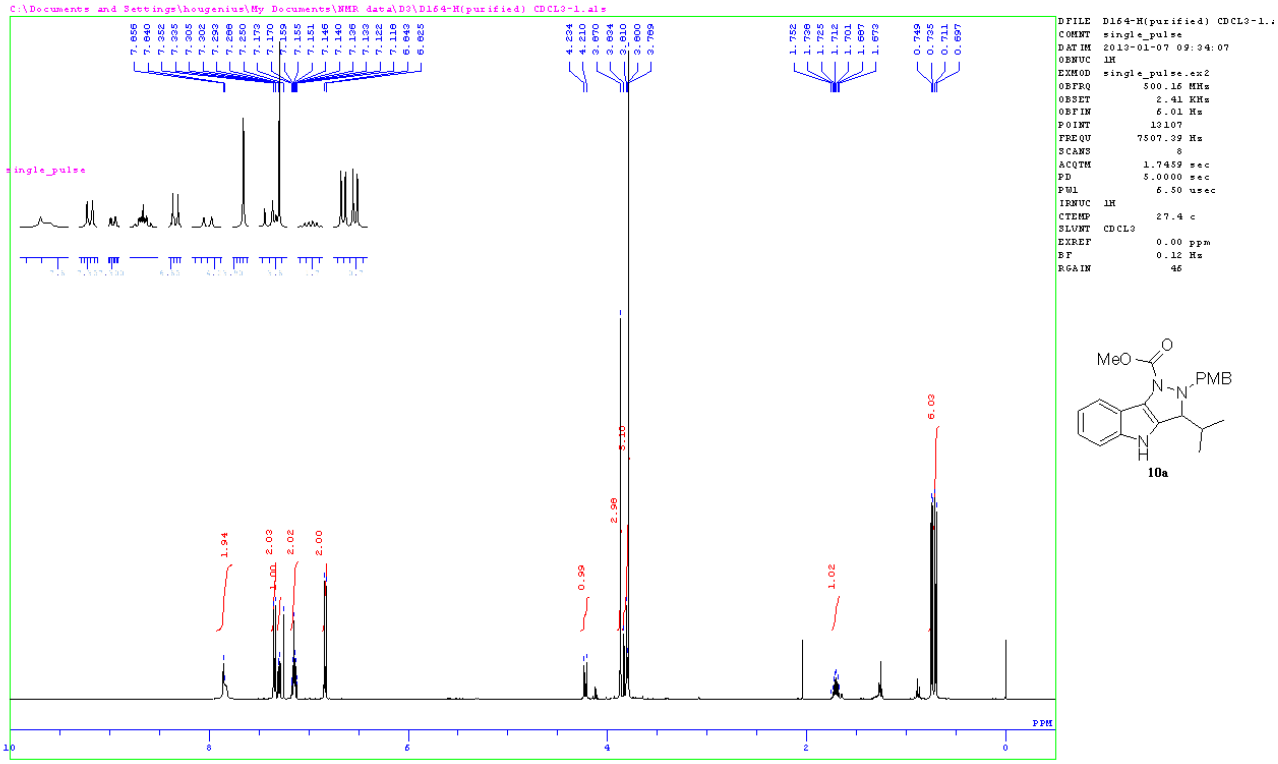
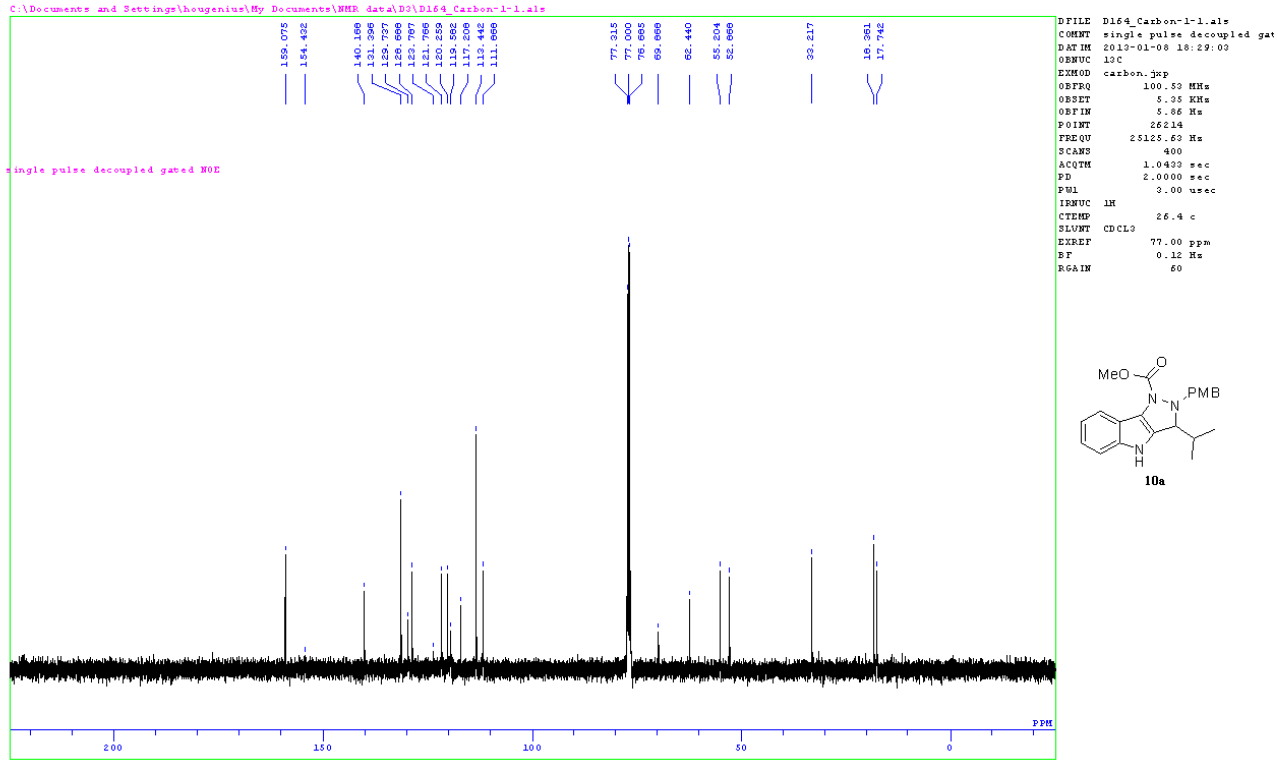
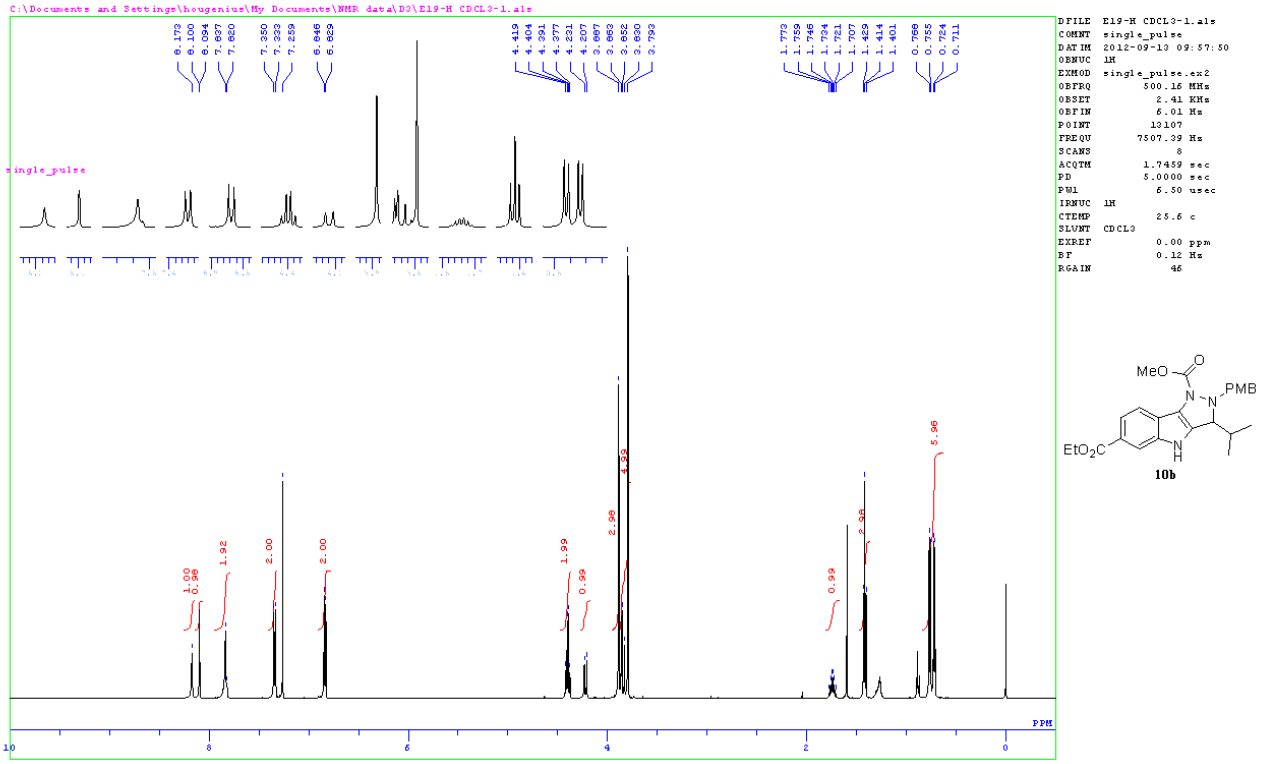




9j







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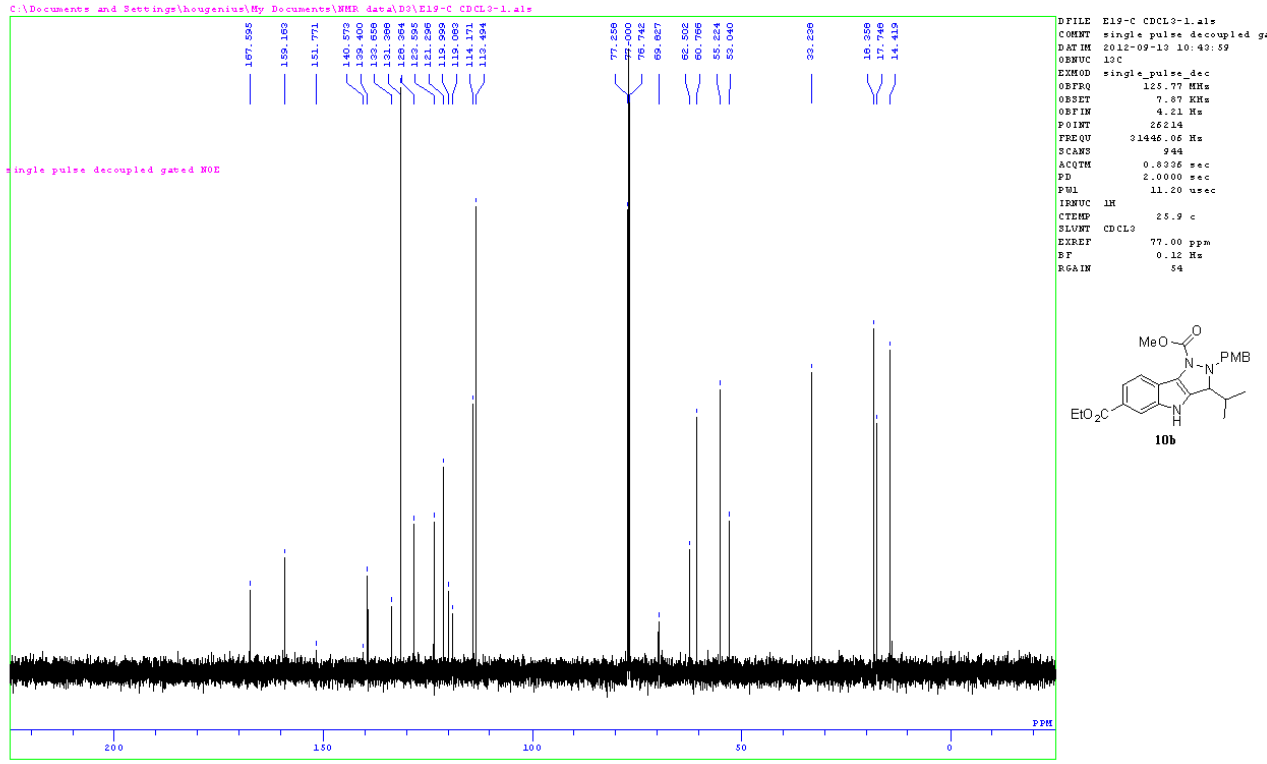
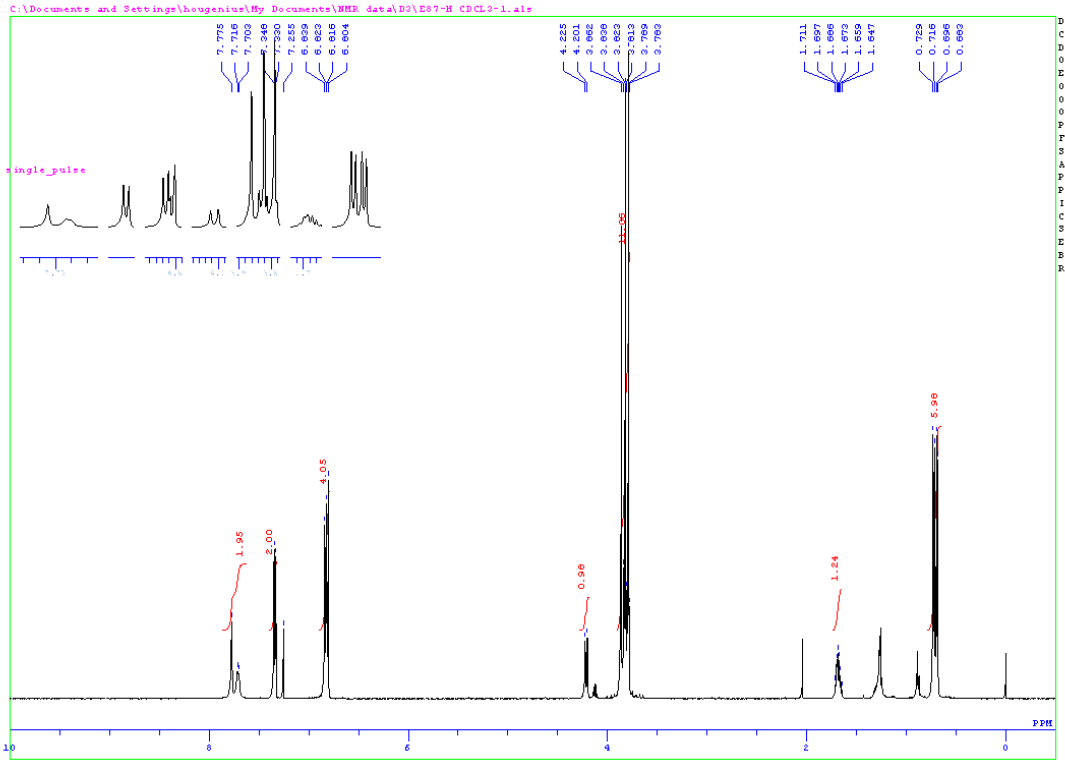
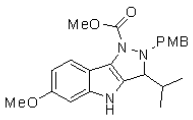


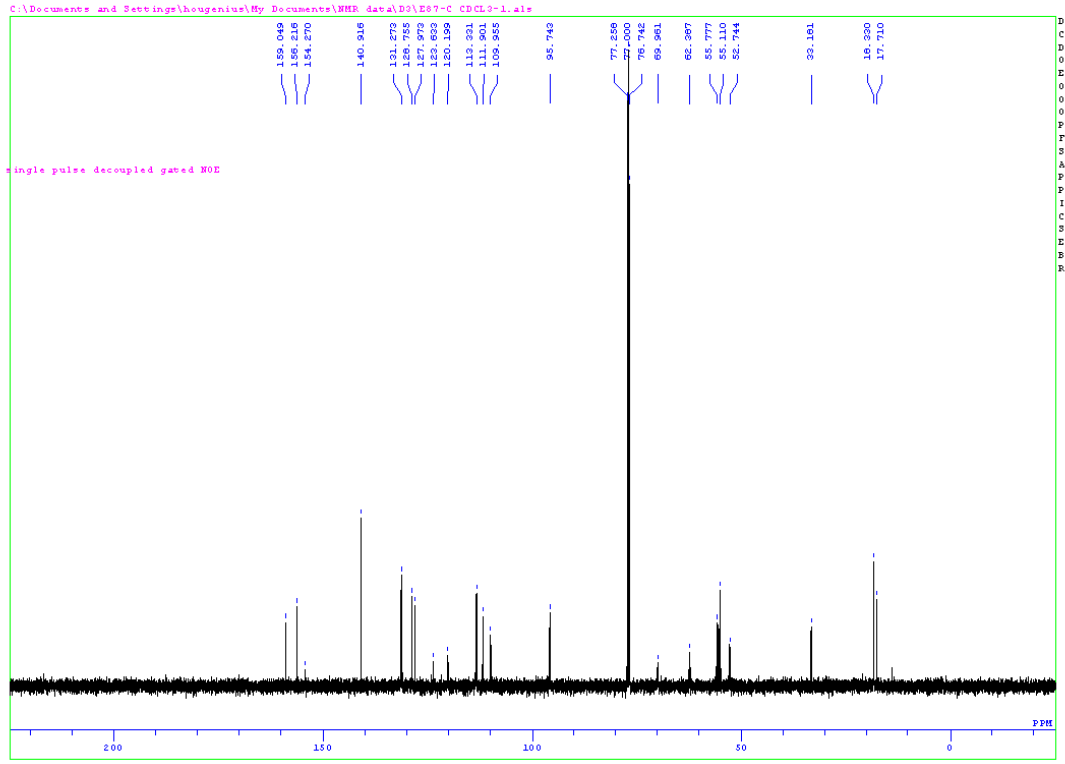
10b



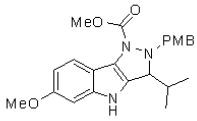
DFILE E87-H CDCL3-1.als
COMNT single_pulse
DATIM 2012-12-14 22:00:20
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 12107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 27.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 42



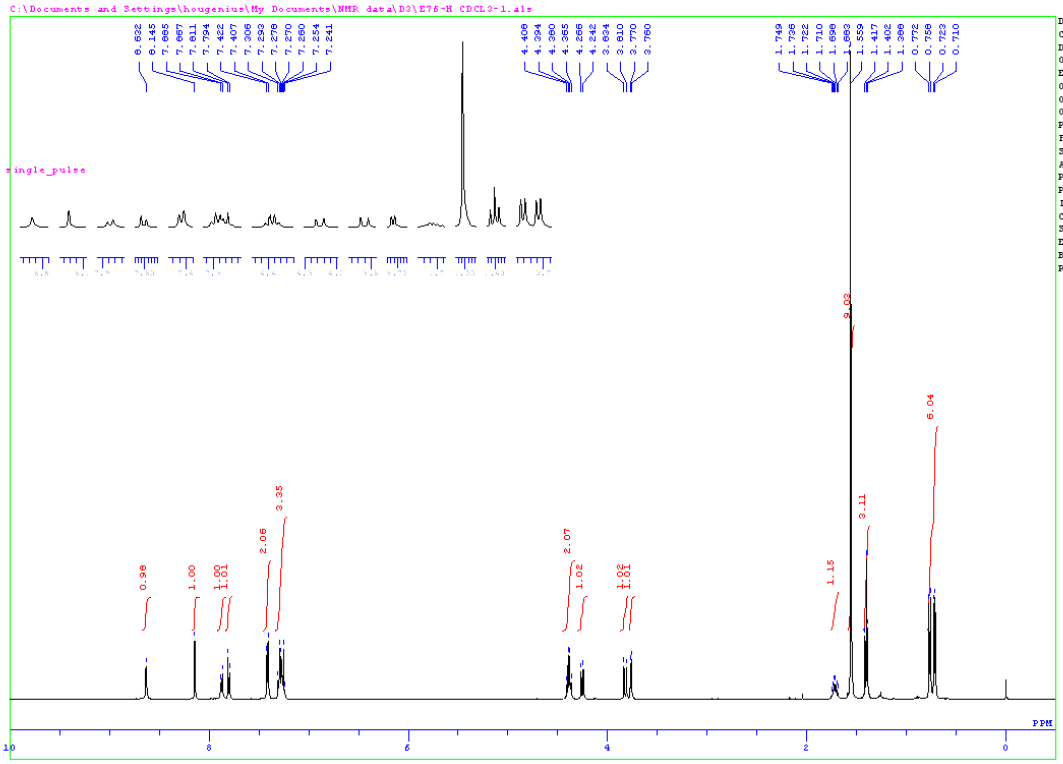
10c



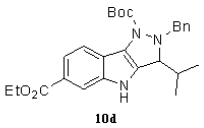
DFILE E87-C CDCL3-1.als
COMNT single pulse decoupled gat
DATIM 2012-12-15 12:58:21
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 882
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.73 usec
IRNUC 1H
CTEMP 26.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 52



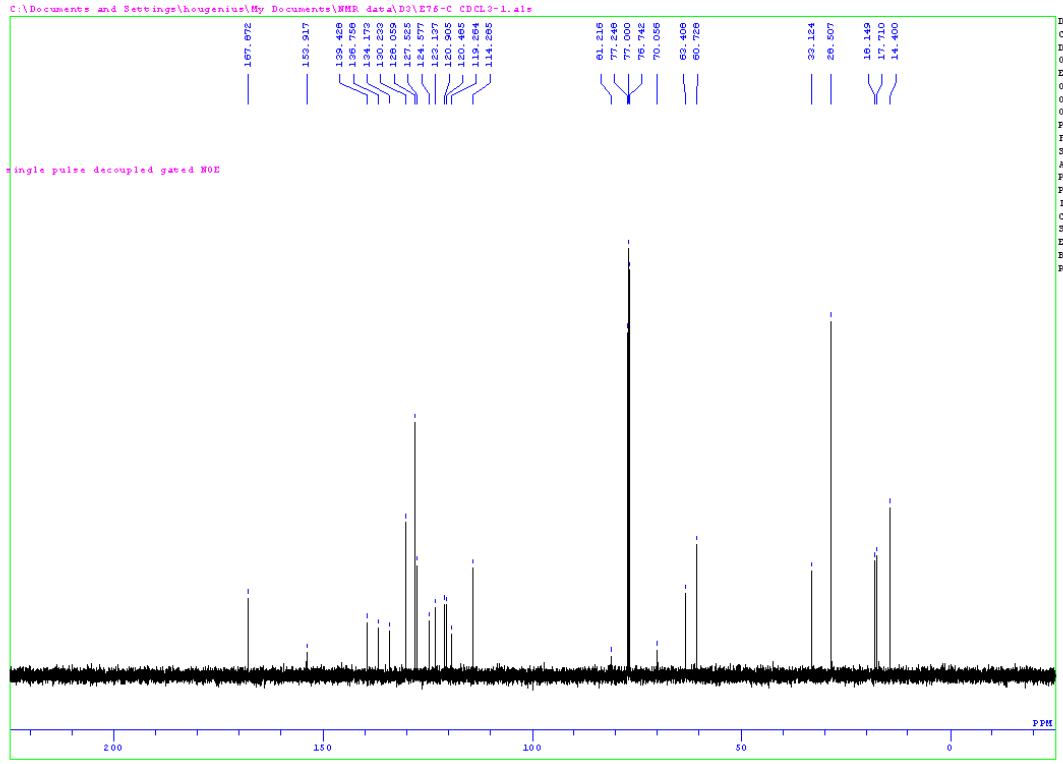
10c



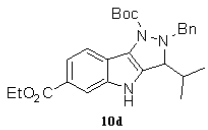

```
DFILE  E76-H CDCL3-1.als
COMNT  single_pulse
DATIM  2012-12-07 19:16:32
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         12107
FREQU       7507.39 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.50 usec
IRNUC  1H
CTEMP         27.9 c
SLVNT  CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           36
```



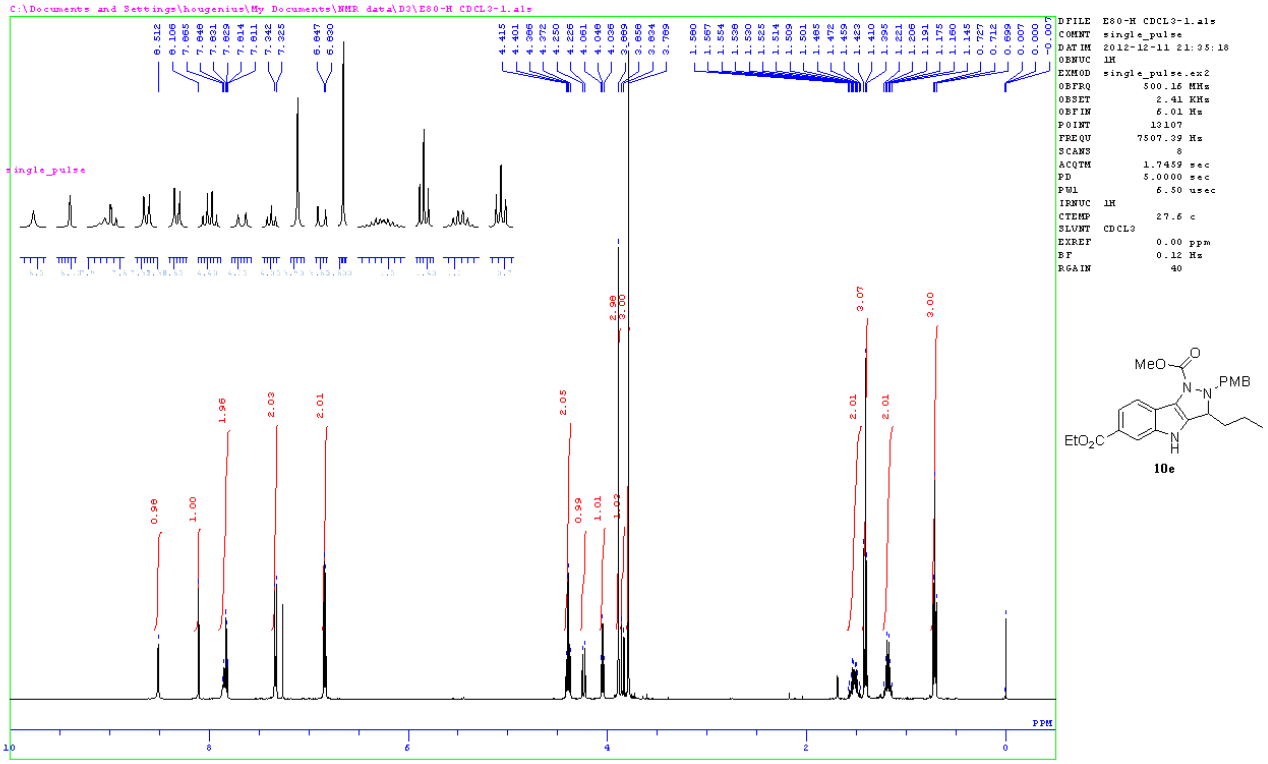
10d

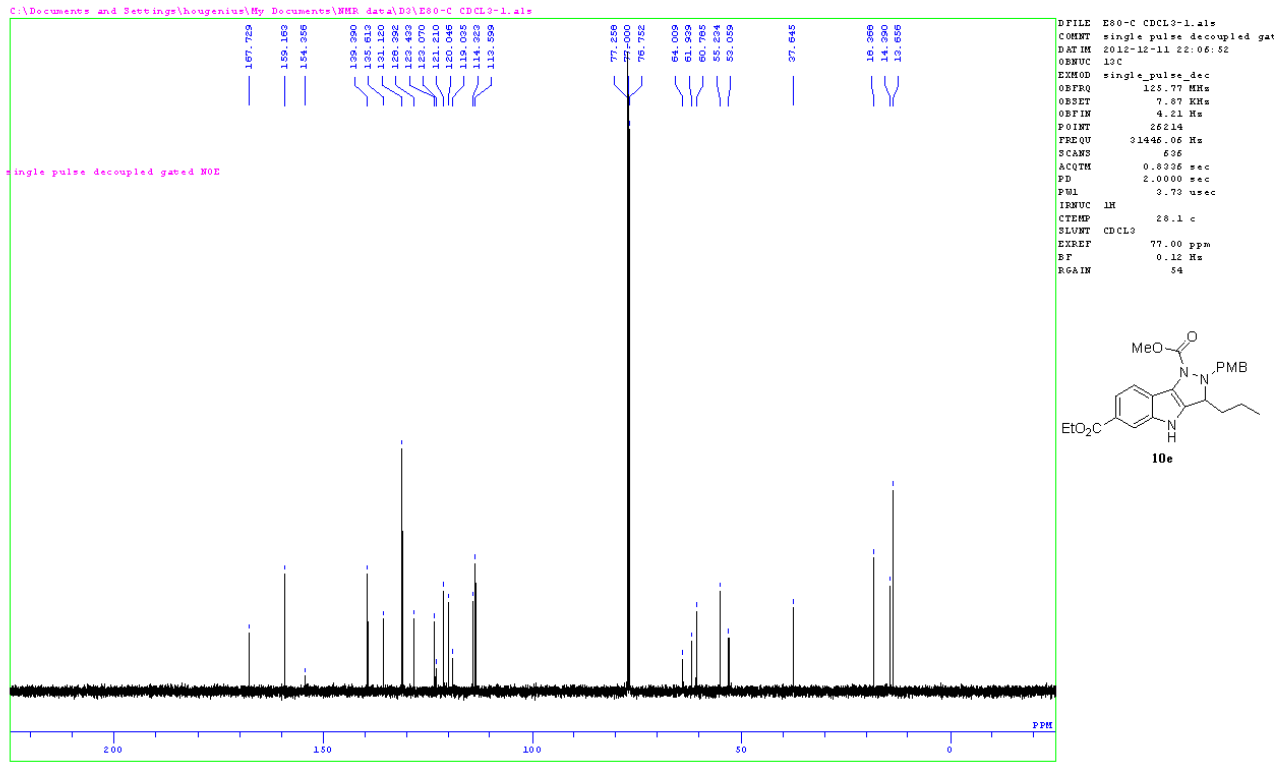


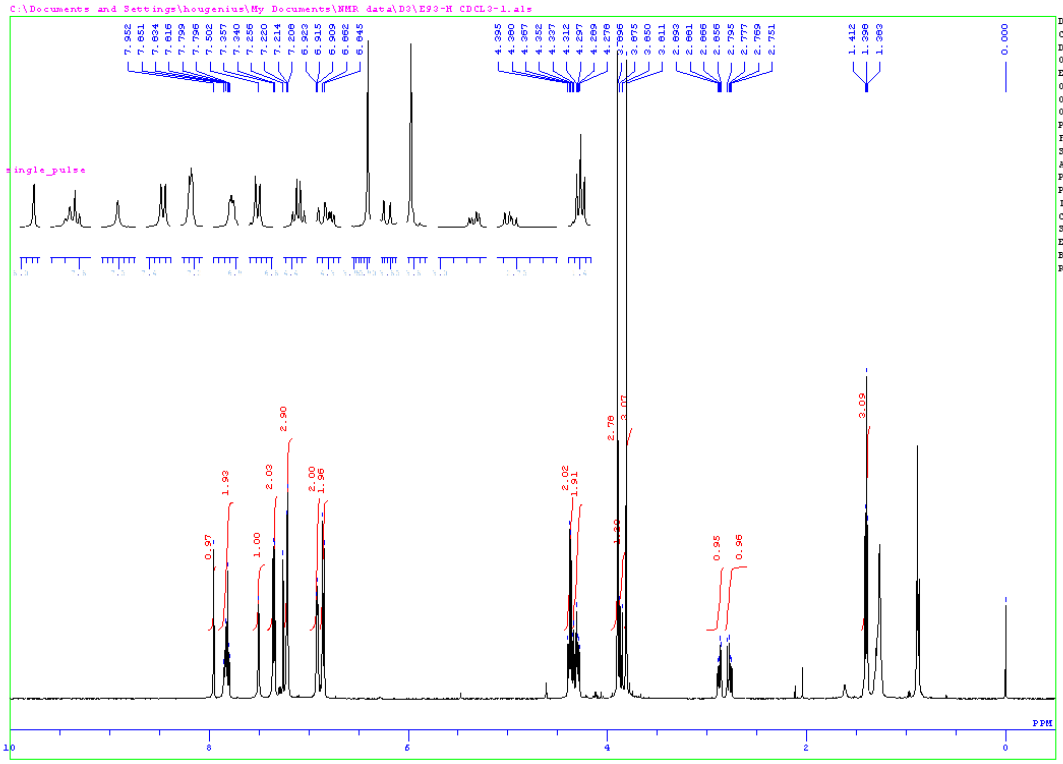

```
DFILE  E76-C CDCL3-1.als
COMNT  single pulse decoupled gat
DATIM  2012-12-07 19:27:49
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS           190
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.73 usec
IRNUC  1H
CTEMP         28.5 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            0.12 Hz
RGAIN           54
```



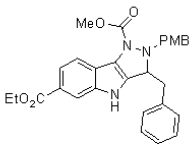
10d


C:\Documents and Settings\hougenius\My Documents\NMR data\D3\E80-H CDCL3-1.als
single_pulse
DFILE E80-H CDCL3-1.als
COMNT single_pulse
DATIM 2012-12-11 21:35:18
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 12107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 27.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 40
MeO
PMB
EtO2C
10e
PPM

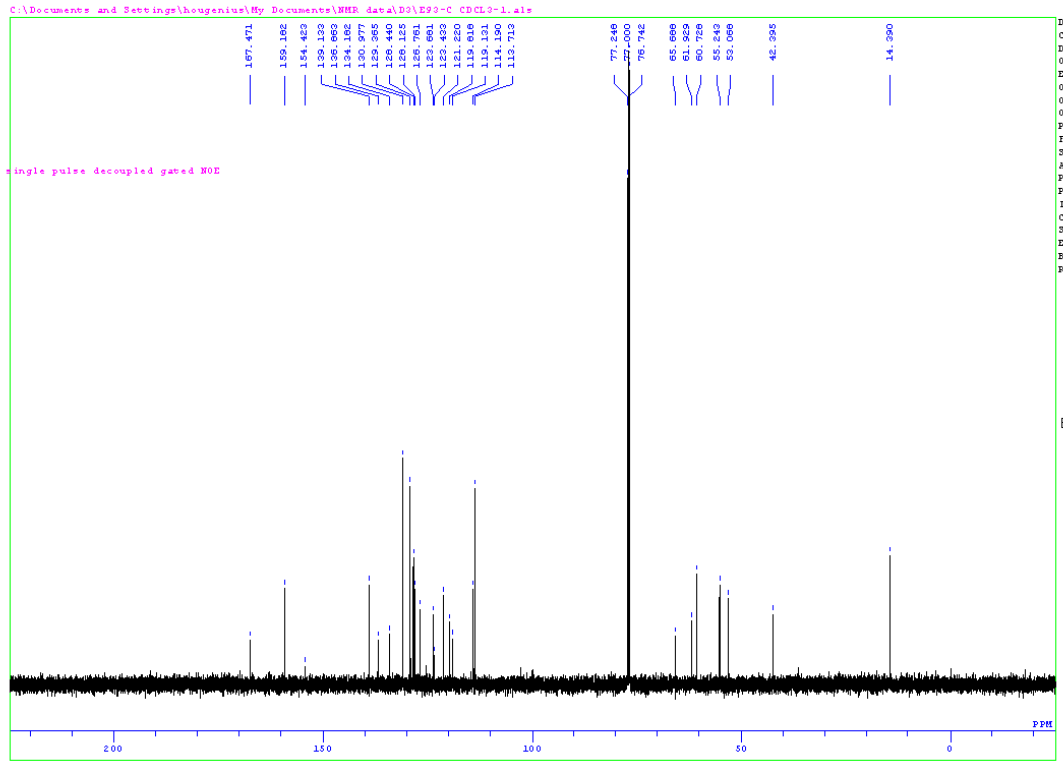

C:\Documents and Settings\hougenius\My Documents\NMR data\D3\E80-C CDCL3-1.als
single pulse decoupled gated NOE
DFILE E80-C CDCL3-1.als
COMNT single pulse decoupled gat
DATIM 2012-12-11 22:06:52
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 636
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.73 usec
IRNUC 1H
CTEMP 28.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 54
MeO
PMB
EtO2C
10e
PPM



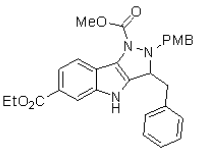

```
DFILE  E93-H CDCL3-1.als
COMNT  single_pulse
DATIM  2012-12-21 12:47:36
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         12107
FREQU       7507.39 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1           6.50 usec
IRNUC  1H
CTEMP        27.6 c
SLVNT  CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           40
```



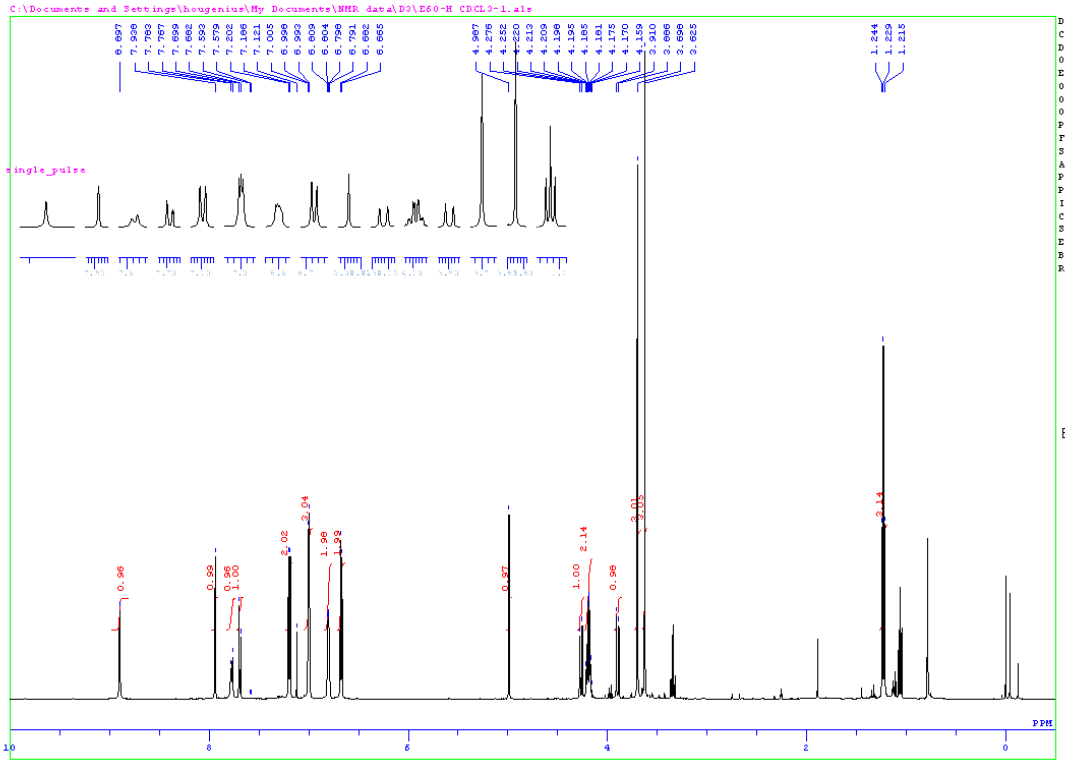
10f



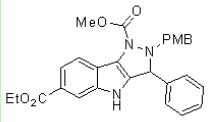

```
DFILE  E93-C CDCL3-1.als
COMNT  single pulse decoupled gat
DATIM  2012-12-22 11:08:34
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS          298
ACQTM         0.8336 sec
PD            2.0000 sec
PW1           3.73 usec
IRNUC  1H
CTEMP        27.4 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF            0.12 Hz
RGAIN           54
```



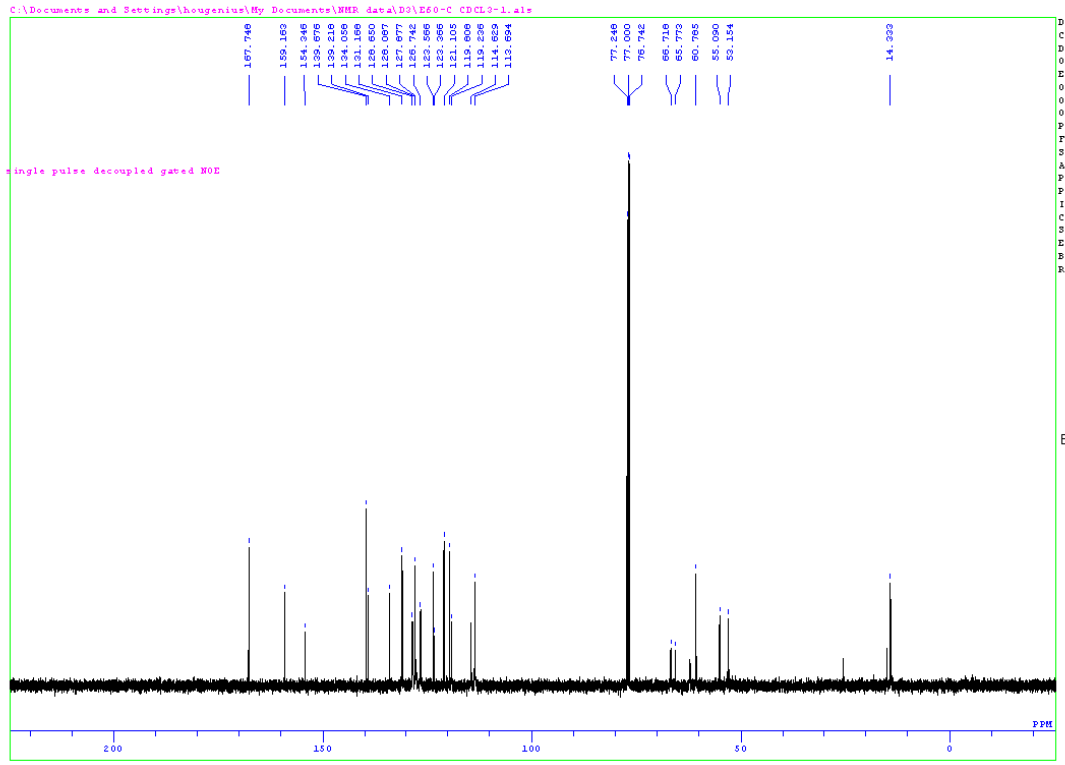
10f



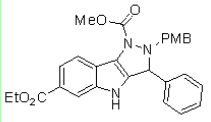

```
DFILE  E60-H CDCL3-1.als
COMNT  single_pulse
DATIM  2012-11-29 10:50:10
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         12107
FREQU       7507.39 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1           6.50 usec
IRNUC  1H
CTEMP        28.8 c
SLVNT  CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           38
```



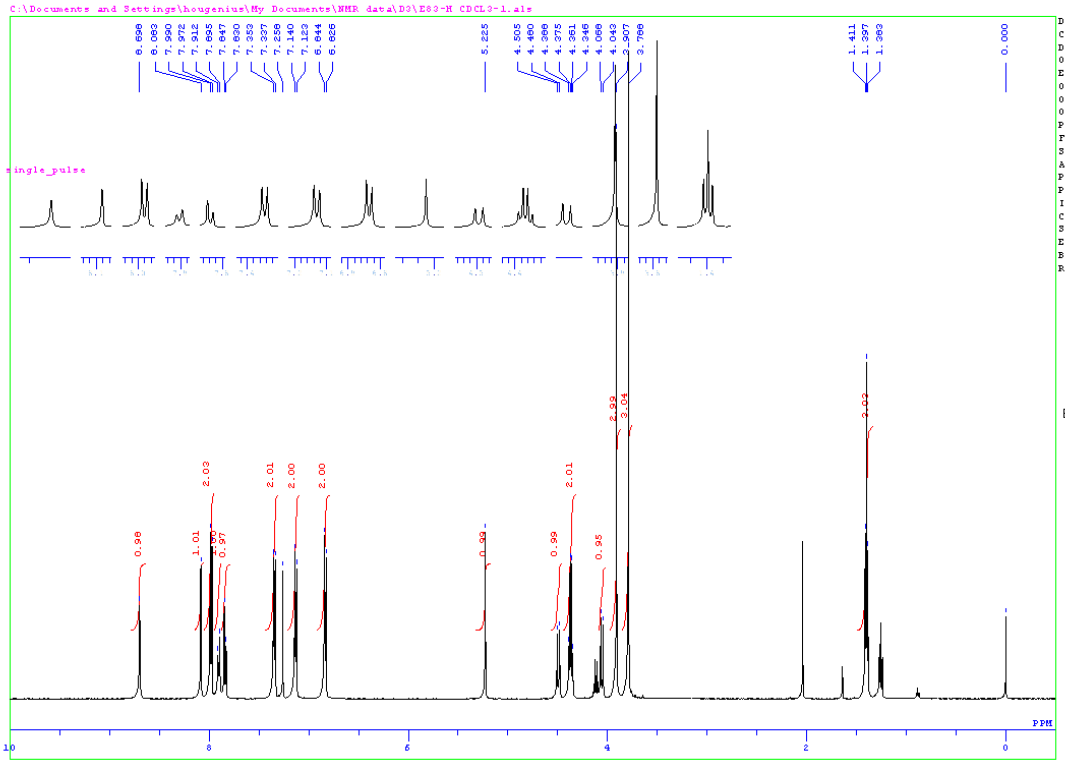
10g



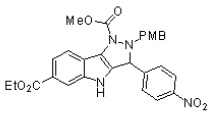

```
DFILE  E60-C CDCL3-1.als
COMNT  single pulse decoupled gat
DATIM  2012-11-29 11:32:18
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS          692
ACQTM         0.8336 sec
PD            2.0000 sec
PW1           3.73 usec
IRNUC  1H
CTEMP        28.8 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            0.12 Hz
RGAIN           56
```



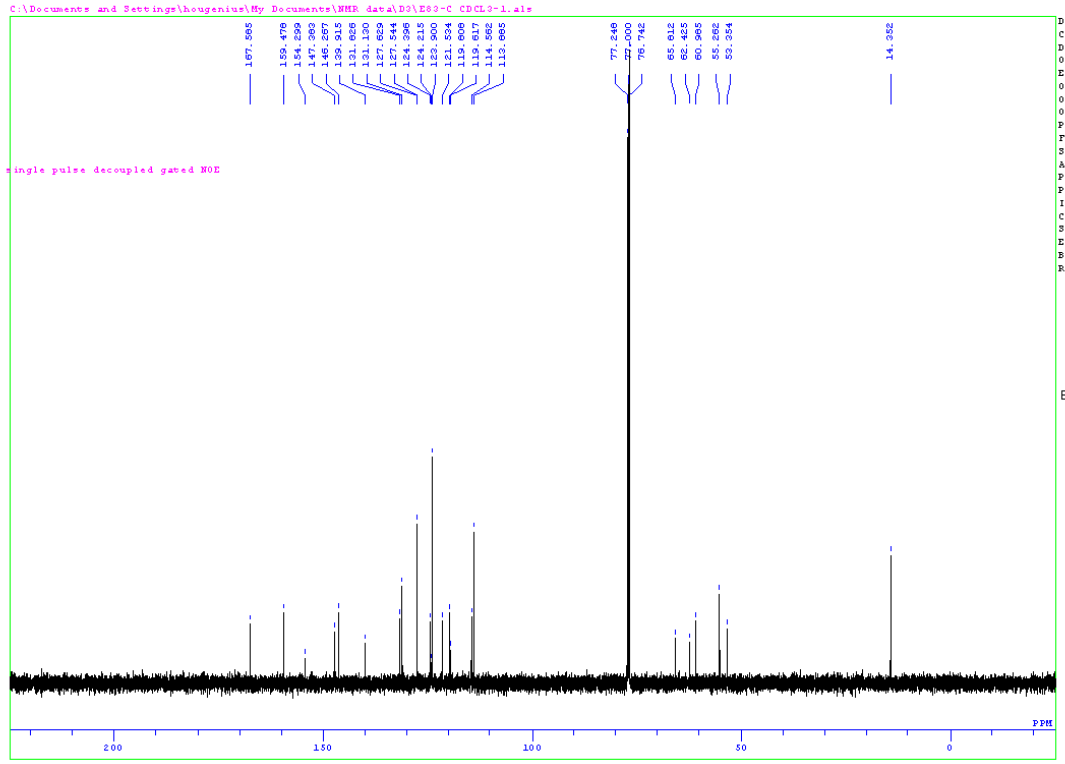
10g



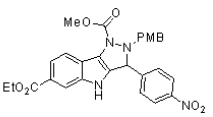

```
DFILE  E83-H CDCL3-1.als
COMNT  single_pulse
DATIM  2012-12-14 09:50:21
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         12107
FREQU       7507.39 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1           6.50 usec
IRNUC  1H
CTEMP         27.5 c
SLVNT  CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           46
```



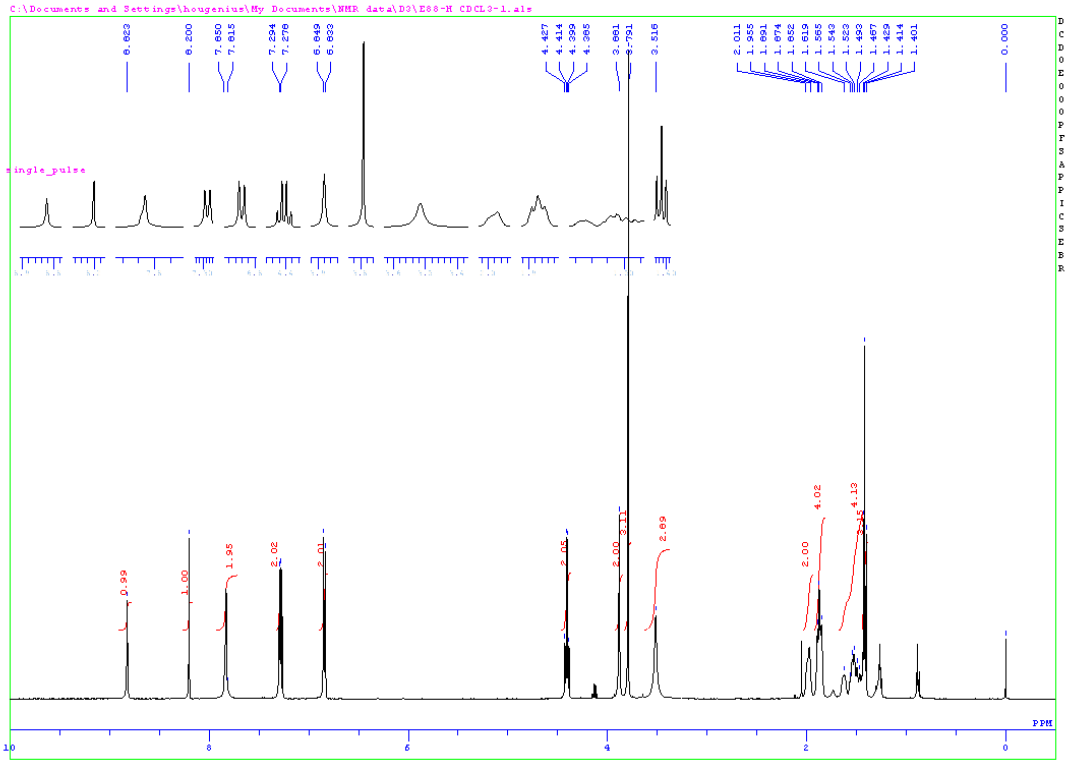
10h



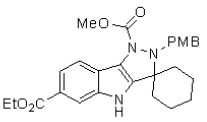

```
DFILE  E83-C CDCL3-1.als
COMNT  single pulse decoupled gat
DATIM  2012-12-14 10:12:05
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS           442
ACQTM         0.8336 sec
PD            2.0000 sec
PW1           3.73 usec
IRNUC  1H
CTEMP         27.5 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            0.12 Hz
RGAIN           58
```



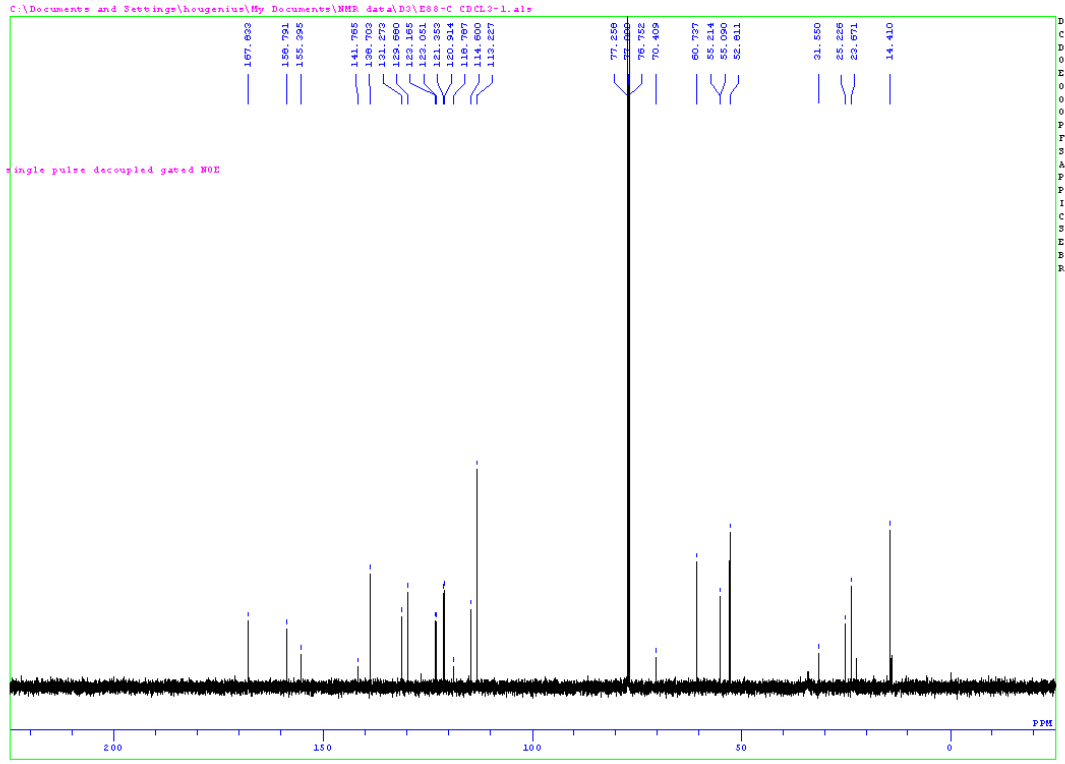
10h



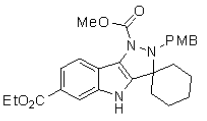
DFILE E88-H CDCL3-1.als
COMNT single_pulse
DATIM 2012-12-18 17:03:50
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 12107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 26.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 38



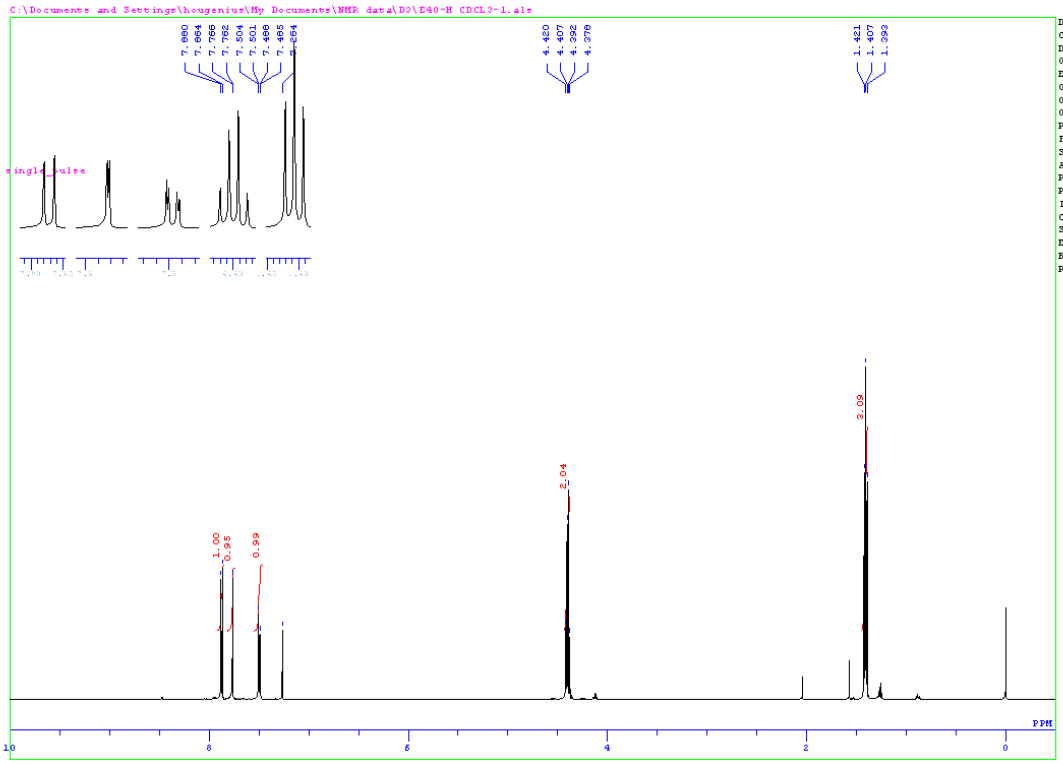
10i



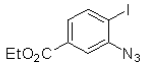
DFILE E88-C CDCL3-1.als
COMNT single pulse decoupled gat
DATIM 2012-12-17 21:19:48
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 370
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.73 usec
IRNUC 1H
CTEMP 27.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 54



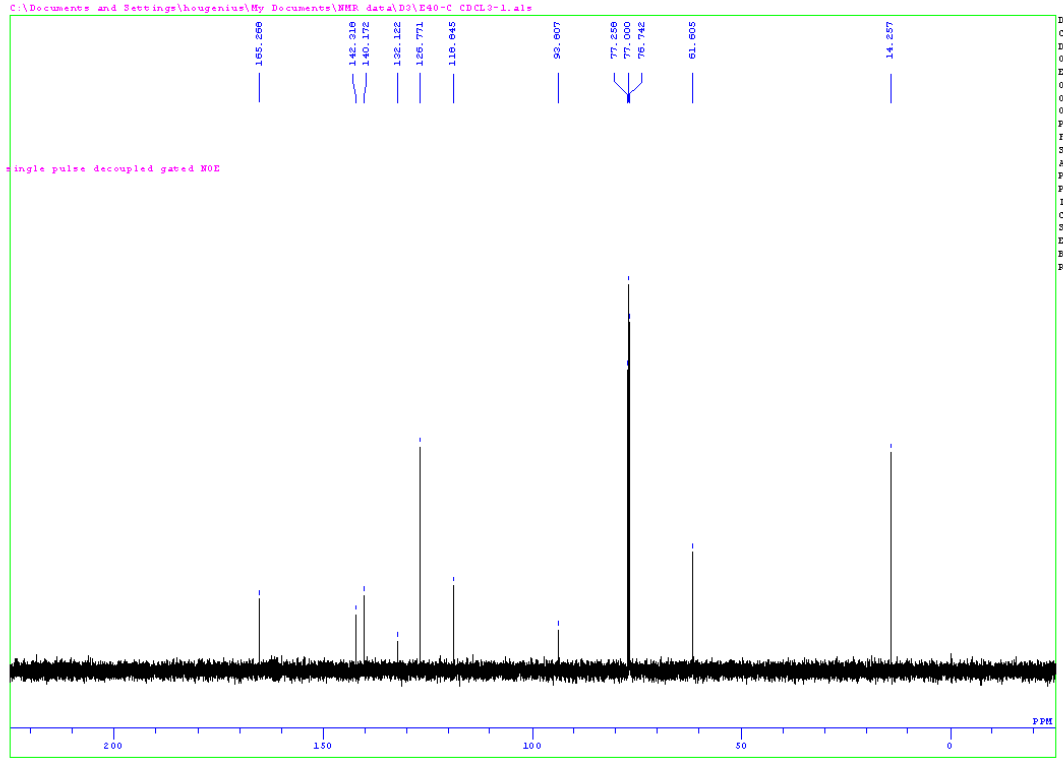
10i



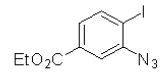
DFILE E40-H CDCL3-1.als
COMNT single_pulse
DATIM 2012-10-27 17:22:52
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 25.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 46



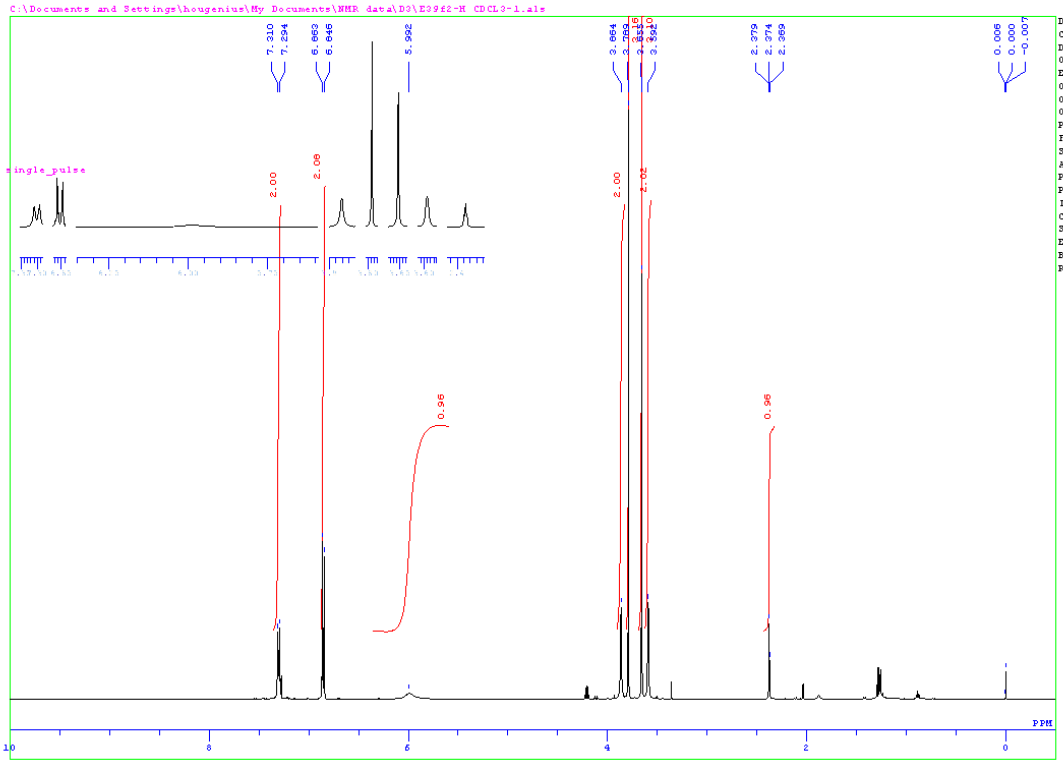
12



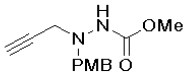
DFILE E40-C CDCL3-1.als
COMNT single pulse decoupled gat
DATIM 2012-10-27 17:28:50
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 94
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.73 usec
IRNUC 1H
CTEMP 25.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 54



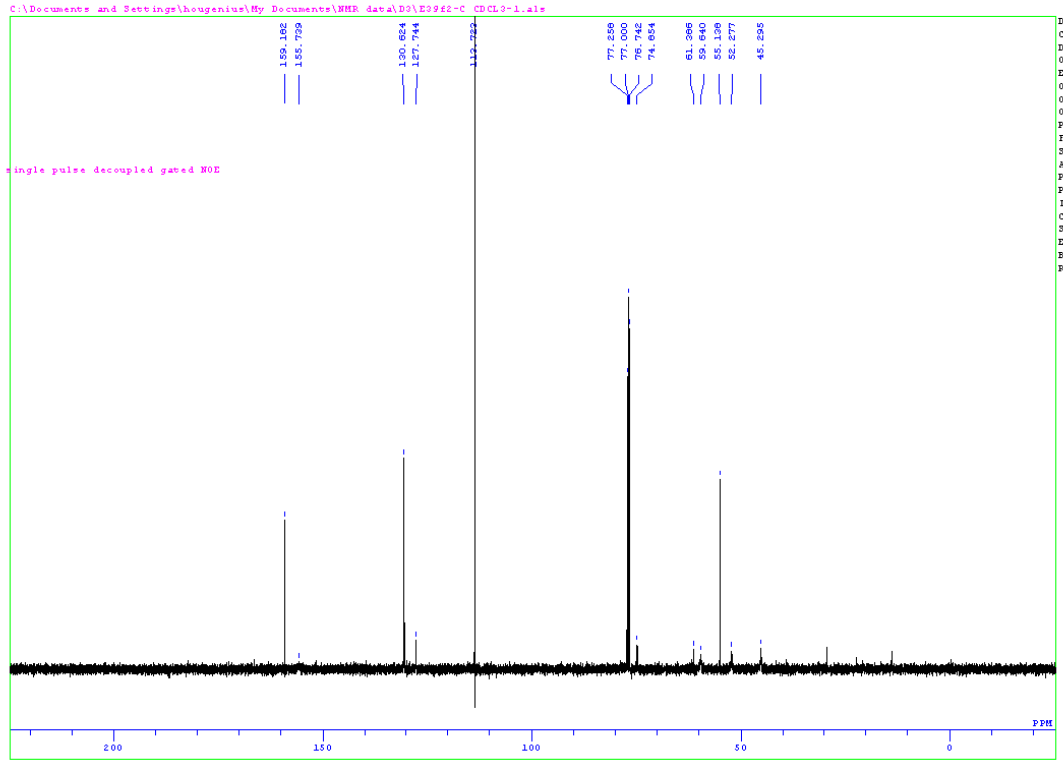
12



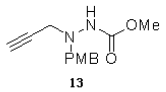
DFILE E39f2-H CDCL3-1.als
COMNT single_pulse
DATIM 2012-10-24 18:51:39
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 12107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 27.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 34



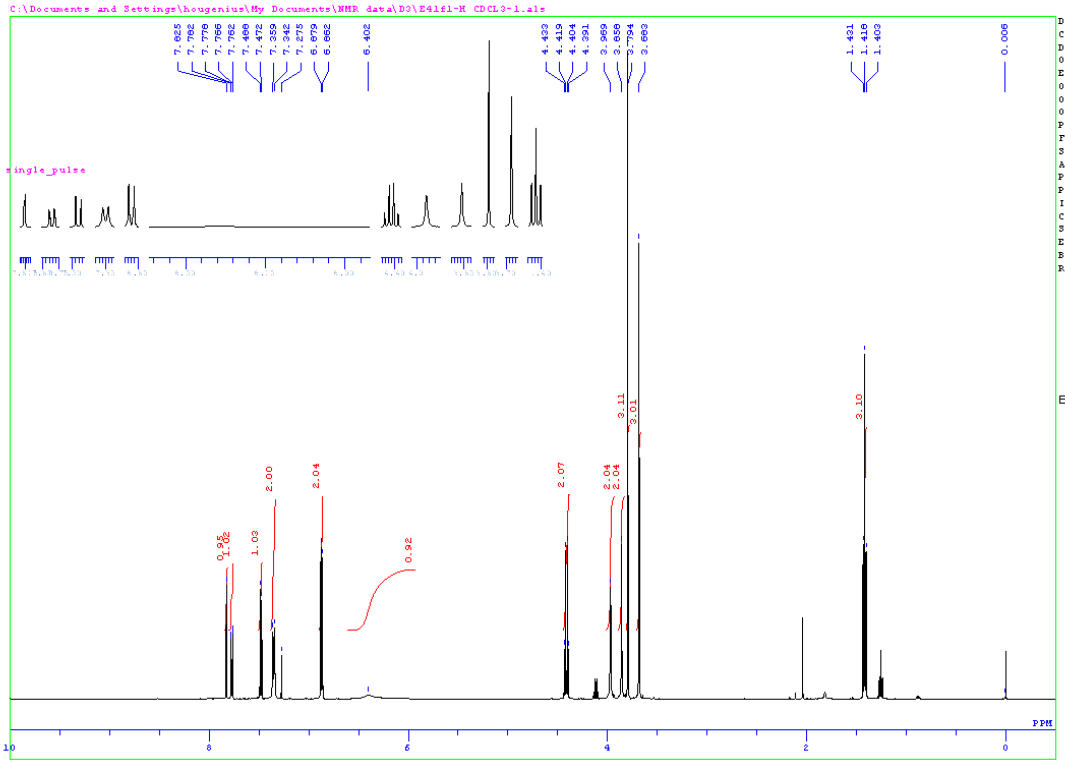
13

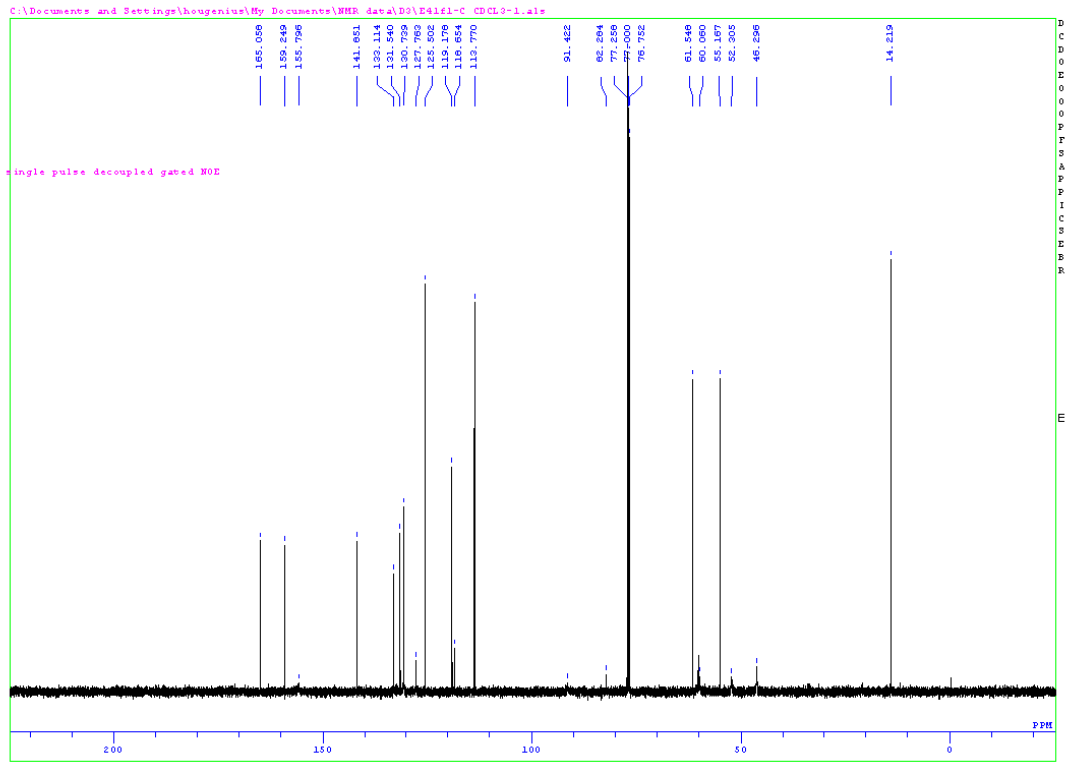


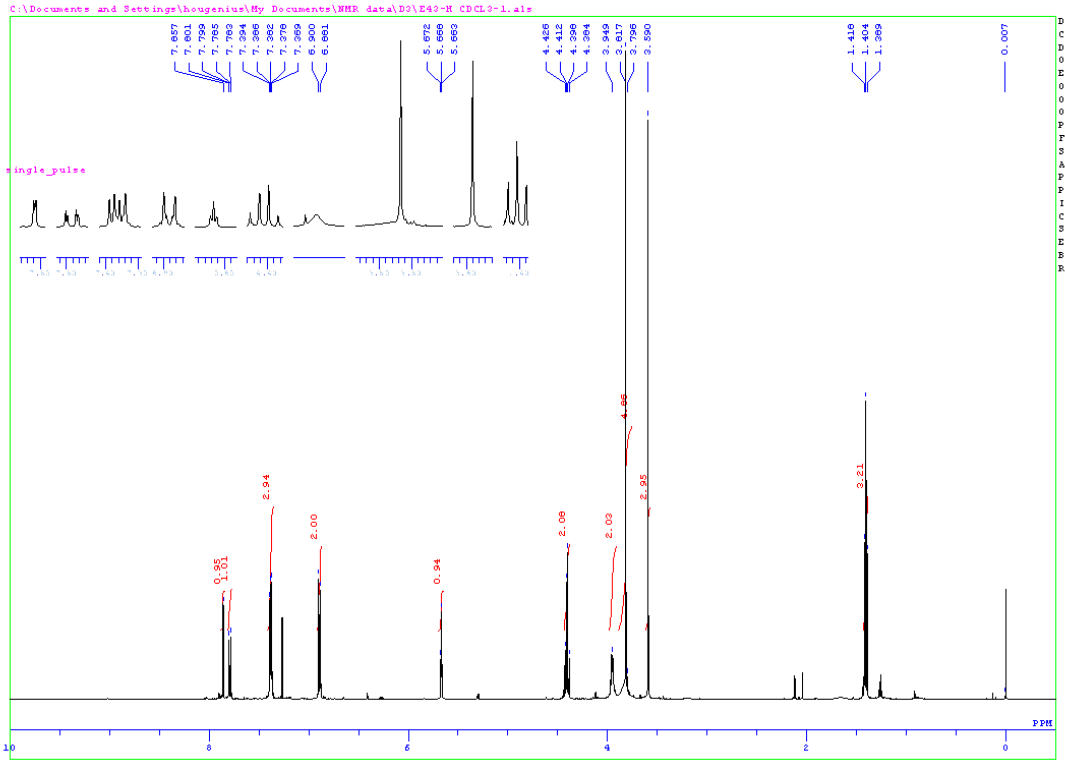
DFILE E39f2-C CDCL3-1.als
COMNT single pulse decoupled gat
DATIM 2012-10-24 19:04:12
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 208
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.73 usec
IRNUC 1H
CTEMP 27.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 54



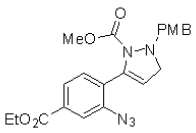
13


C:\Documents and Settings\hougenius\My Documents\NMR data\D3\E41f1-H CDCL3-1.als
single_pulse
7.625
7.782
7.778
7.766
7.762
7.466
7.472
7.359
7.342
7.275
6.879
6.862
6.402
4.423
4.419
4.404
4.391
3.869
3.856
3.794
3.663
1.431
1.418
1.403
0.006
0.95
1.02
1.03
2.00
2.04
0.92
2.07
2.04
2.04
3.11
3.01
3.10
PPM
10
8
6
4
2
0
DFILE E41f1-H CDCL3-1.als
COMNT single_pulse
DATIM 2012-10-25 22:08:41
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 12107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 26.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 38
OMe
PMB
EtO2C
N3
14

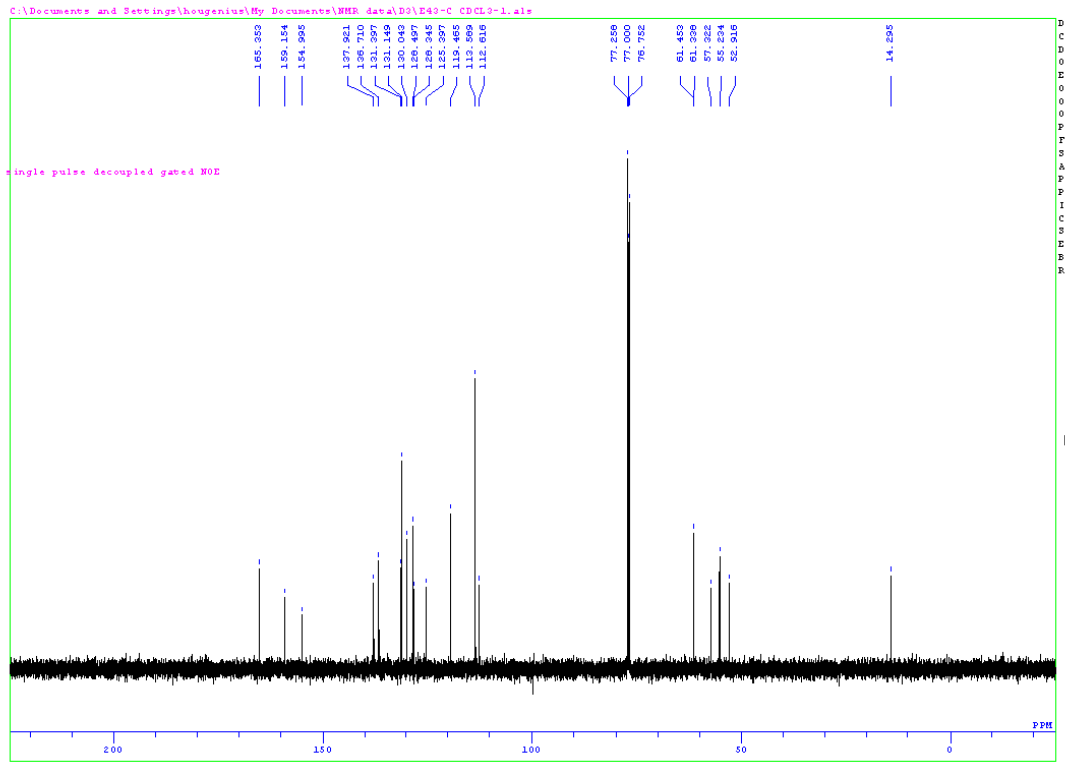

C:\Documents and Settings\hougenius\My Documents\NMR data\D3\E41f1-C CDCL3-1.als
single pulse decoupled gated NOE
165.058
159.249
155.796
141.851
132.114
131.540
130.799
127.760
125.502
119.176
118.654
112.770
91.422
82.284
77.258
77.000
76.752
61.548
60.060
55.167
52.305
46.296
14.219
PPM
200
150
100
50
0
DFILE E41f1-C CDCL3-1.als
COMNT single pulse decoupled gat
DATIM 2012-10-25 22:45:39
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 722
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.73 usec
IRNUC 1H
CTEMP 27.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 56
OMe
PMB
EtO2C
N3
14



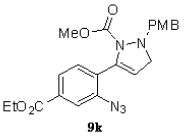
DFILE E43-H CDCL3-1.als
COMNT single_pulse
DATIM 2012-11-02 10:58:29
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 12107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 24.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 40



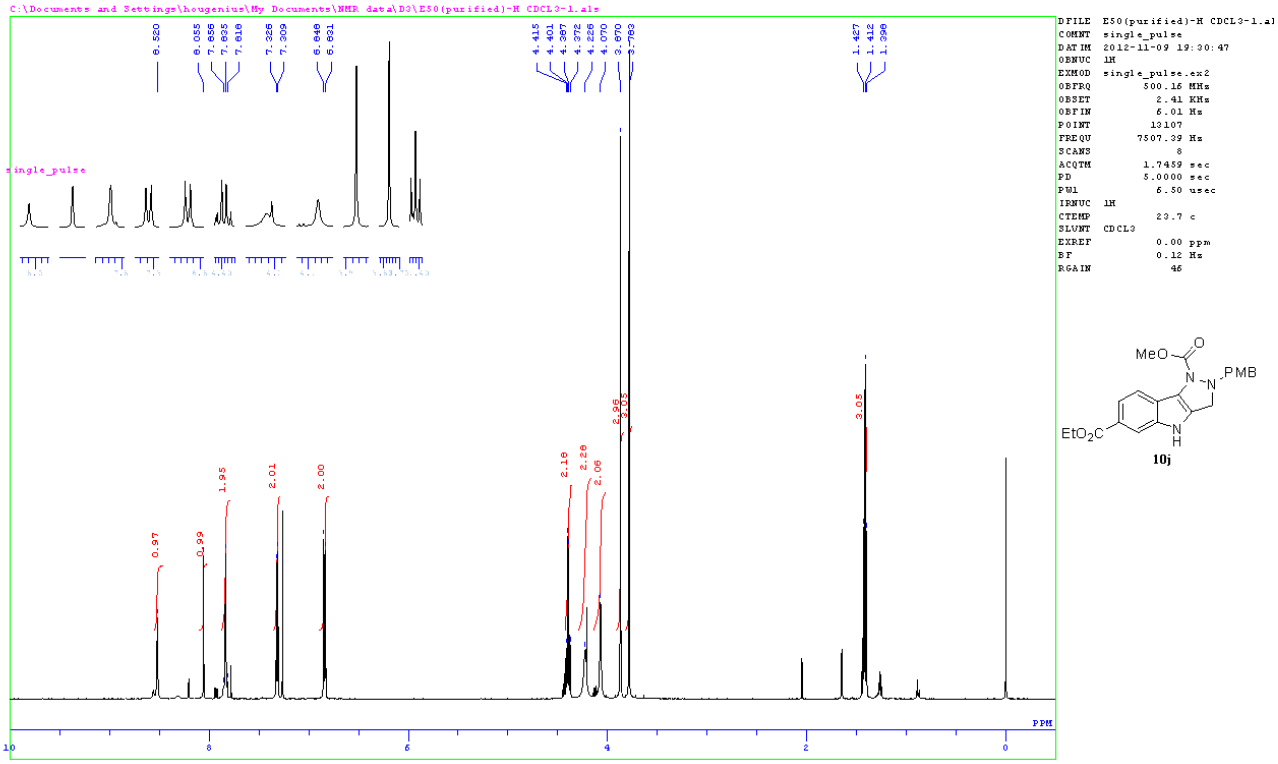
9k

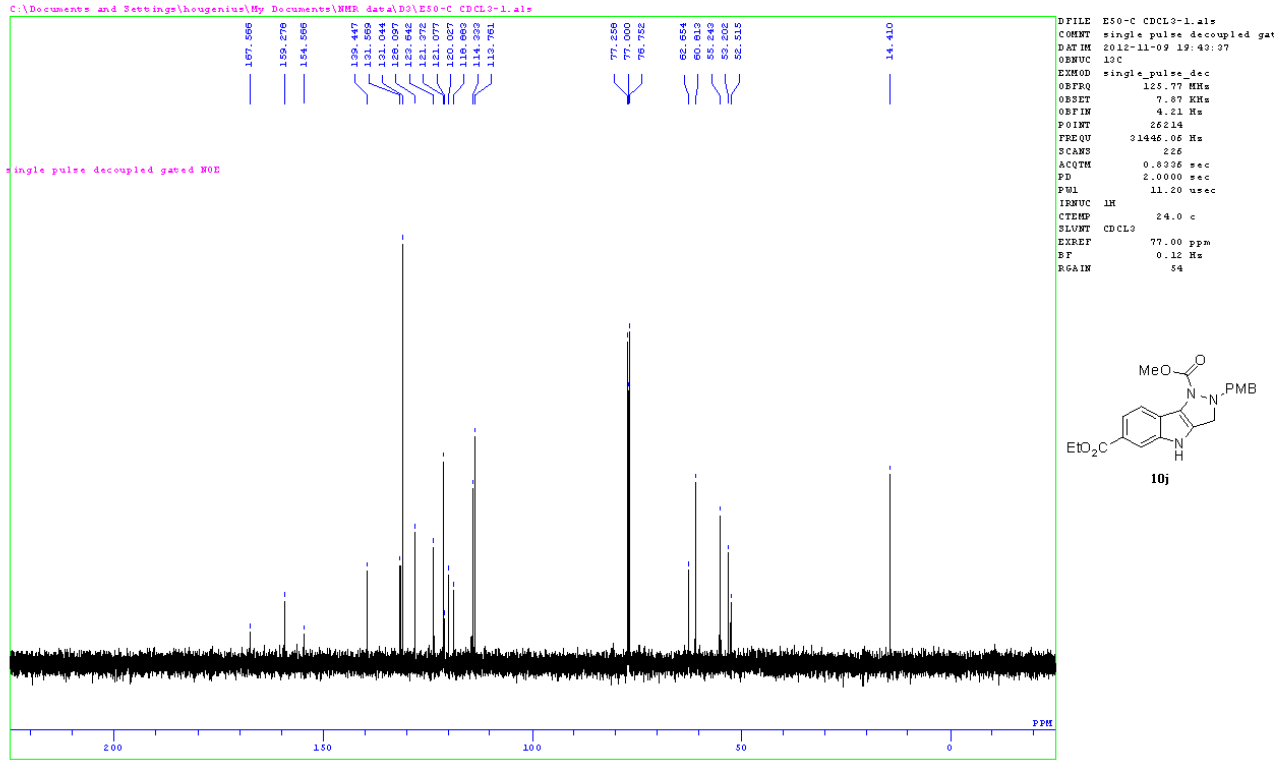


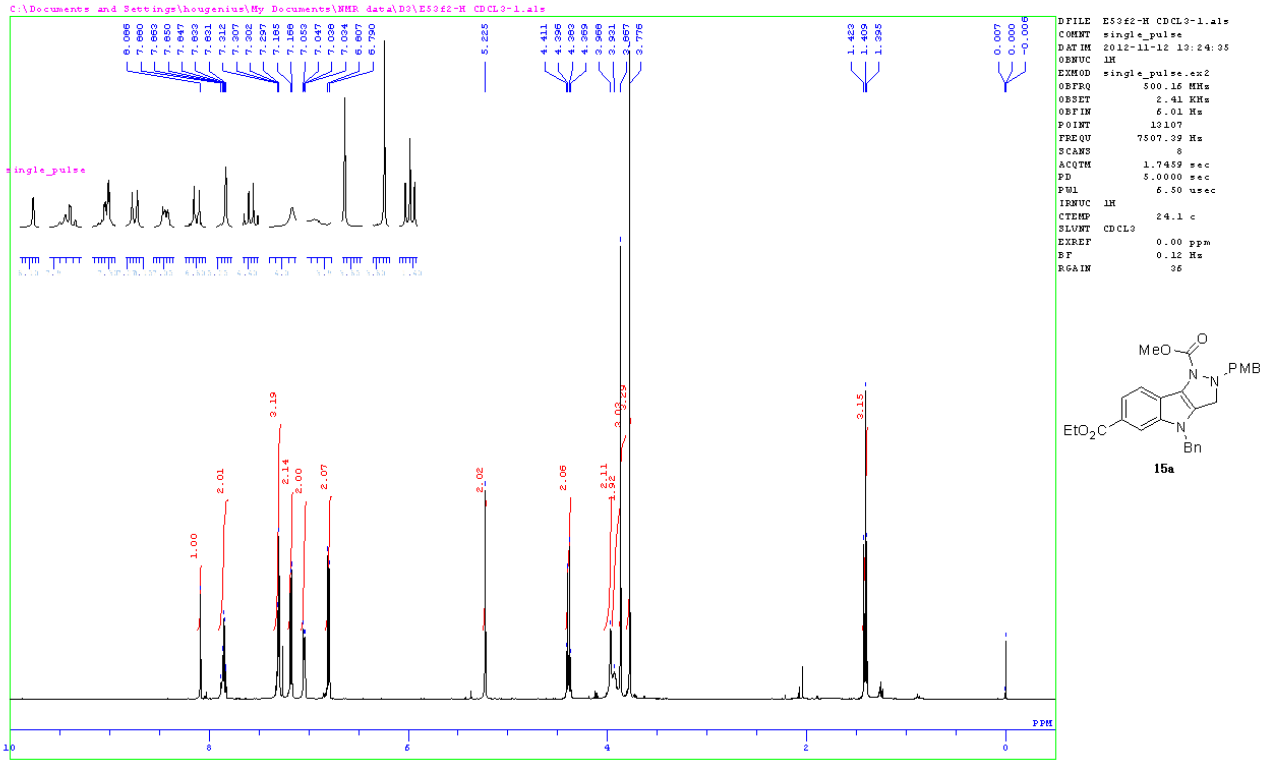
DFILE E43-C CDCL3-1.als
COMNT single pulse decoupled gat
DATIM 2012-11-02 11:06:51
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 122
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.73 usec
IRNUC 1H
CTEMP 24.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 54



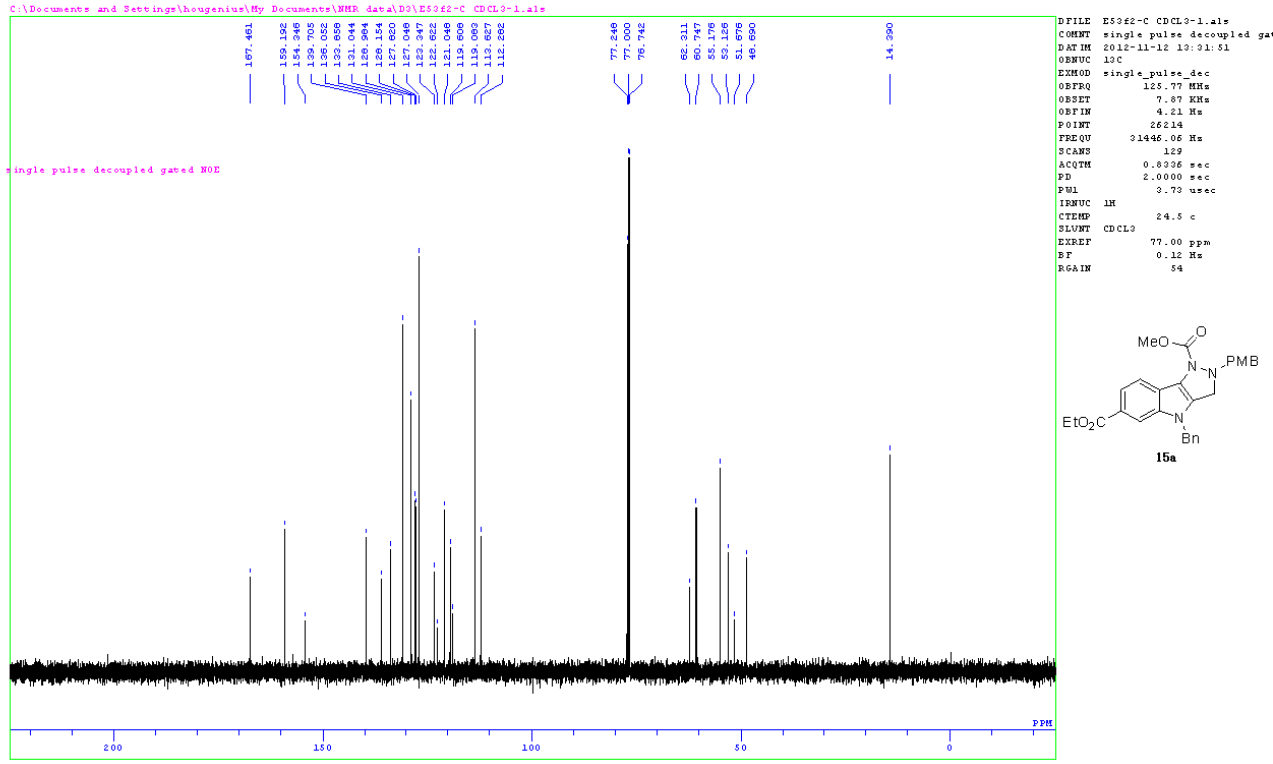
9k



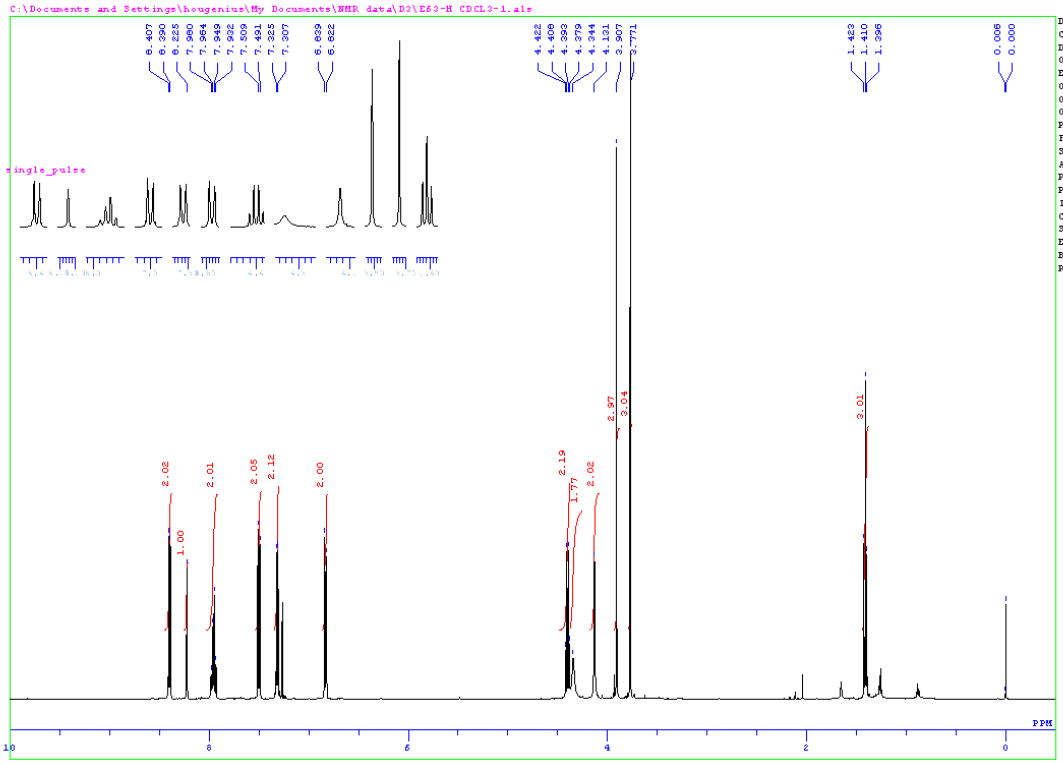


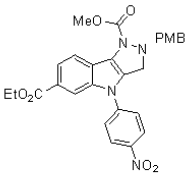


15a

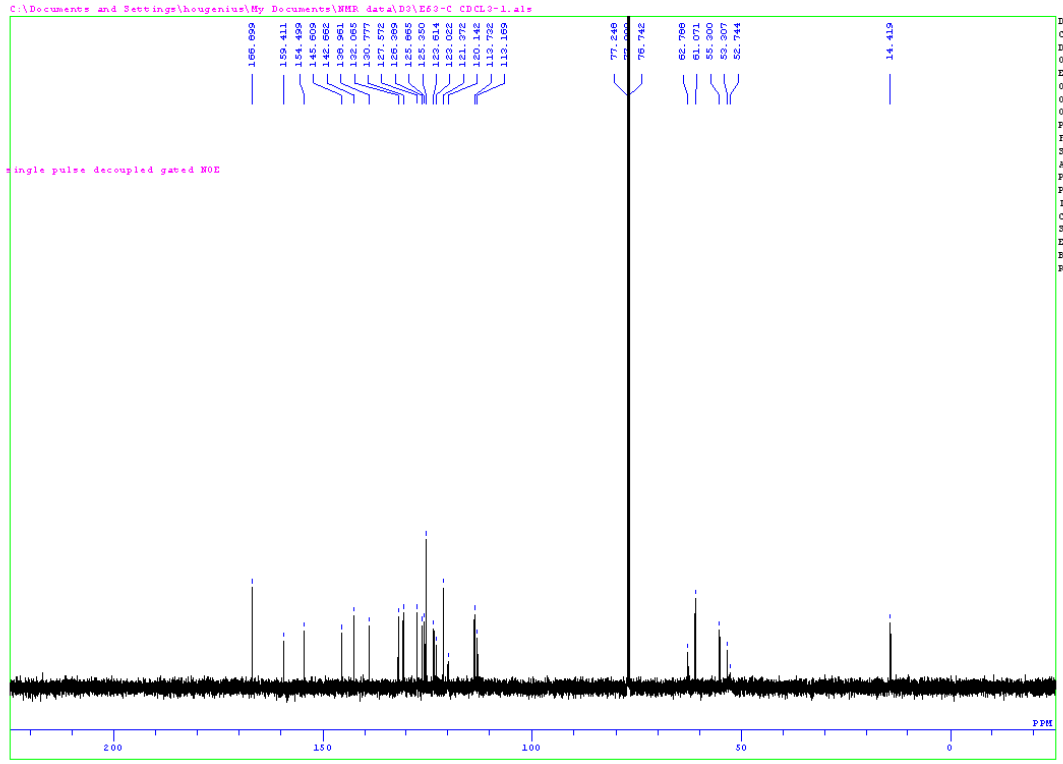


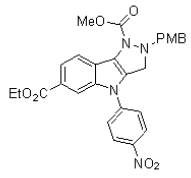
15a


C:\Documents and Settings\hougenius\My Documents\NMR data\D3\E63-H CDCL3-1.als
single_pulse
6.407 6.390 6.225 7.980 7.964 7.949 7.932 7.509 7.491 7.325 7.307 6.639 6.622
4.422 4.406 4.393 4.379 4.344 4.131 3.907 3.771
1.423 1.410 1.396
0.006 0.000
2.02 1.00 2.01 2.05 2.12 2.00 2.19 1.77 2.02 2.97 3.04 3.01
PPM
10 8 6 4 2 0
DFILE E63-H CDCL3-1.als
COMNT single_pulse
DATIM 2012-11-23 17:41:26
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 12107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 28.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 40

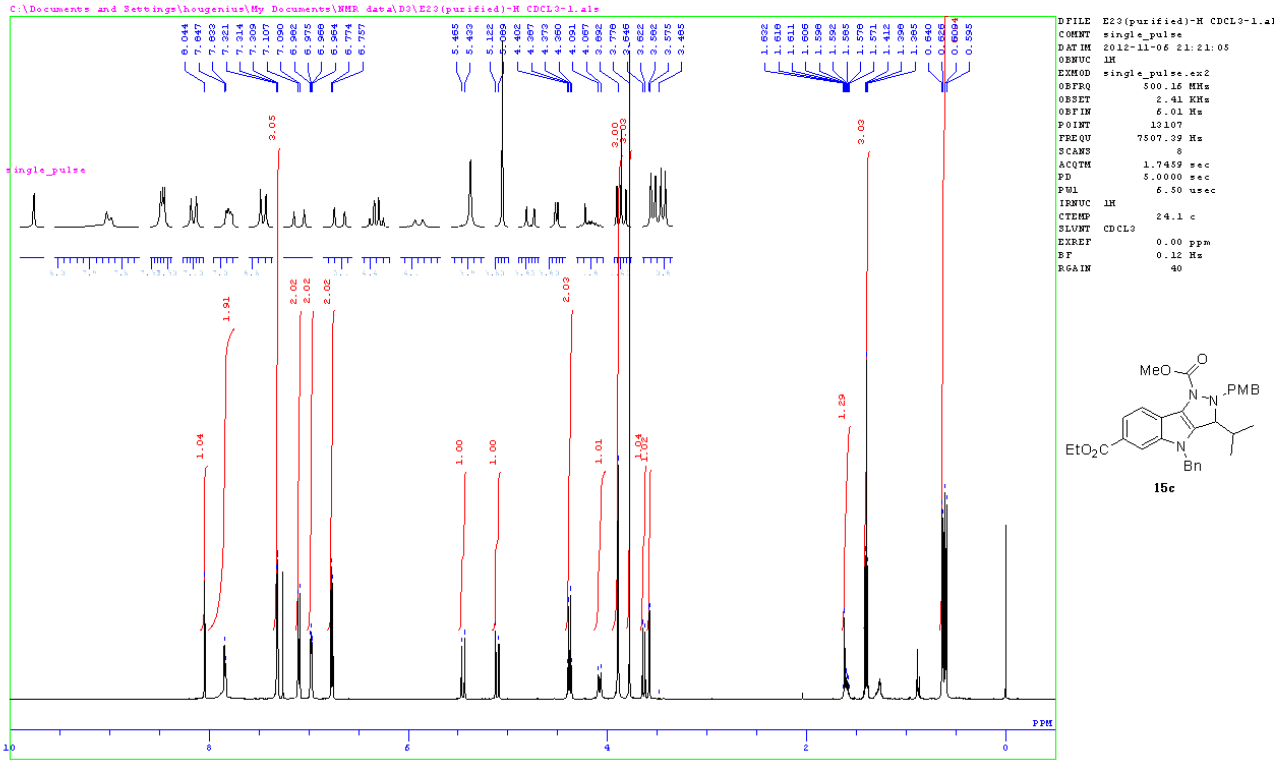

MeO
O
N
N
PMB
EtO2C
N
NO2

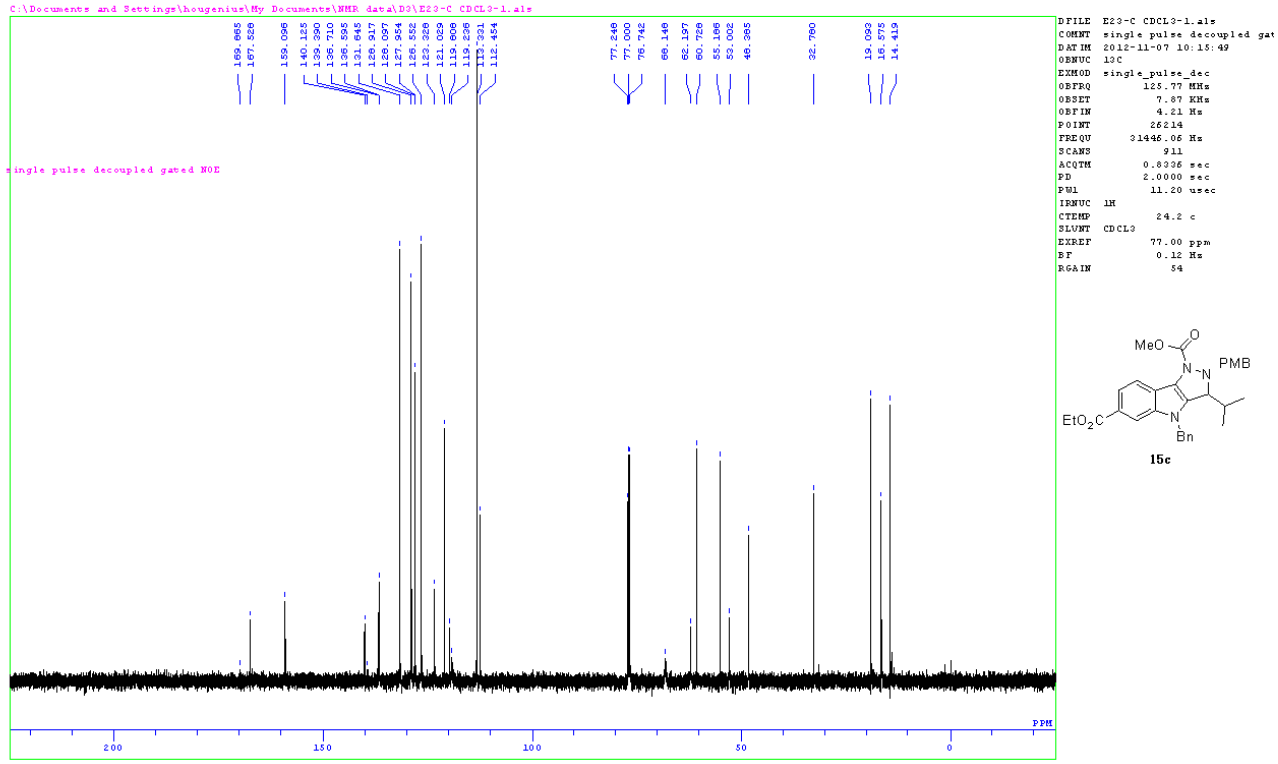
15b

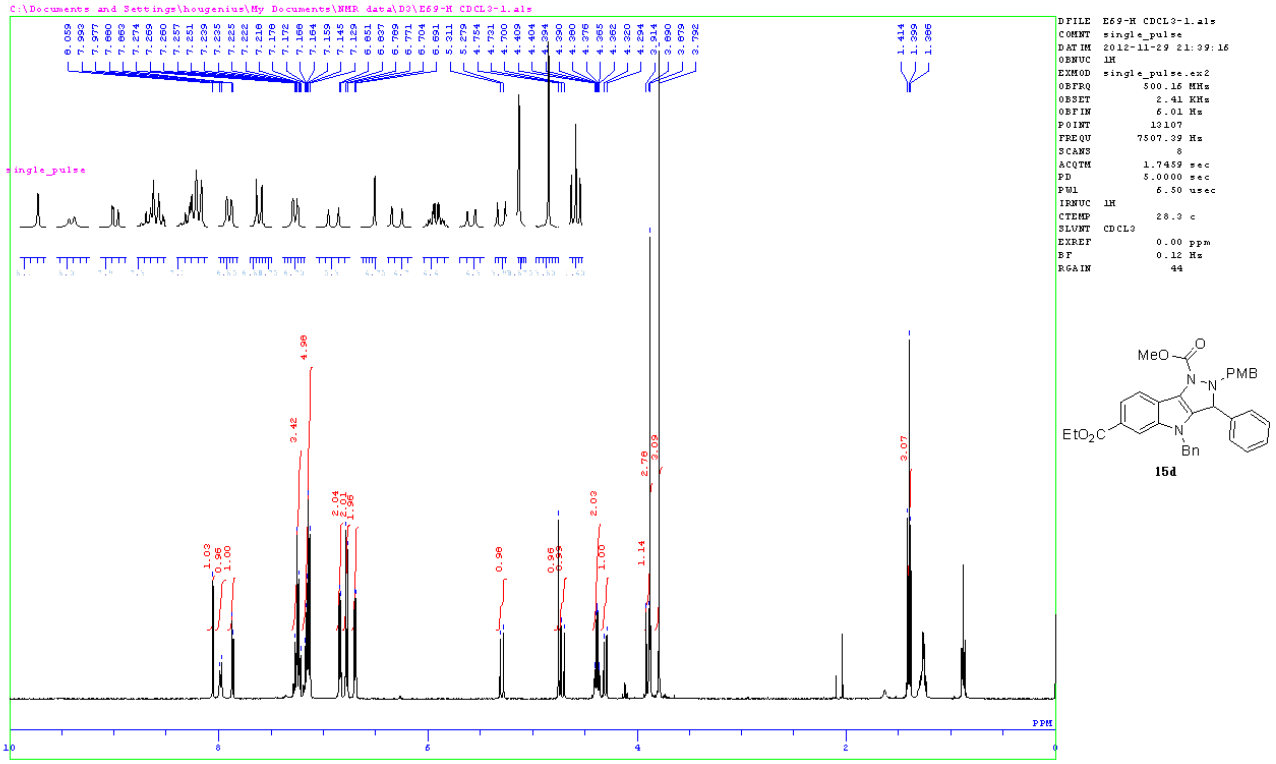

C:\Documents and Settings\hougenius\My Documents\NMR data\D3\E63-C CDCL3-1.als
single pulse decoupled gated NOE
166.699 159.411 154.499 145.609 142.662 136.961 132.065 130.777 127.572 126.369 125.665 125.350 123.614 123.022 121.972 120.142 113.782 113.169
77.248 77.000 76.742
62.788 61.071 55.300 53.307 52.744
14.419
PPM
200 150 100 50 0
DFILE E63-C CDCL3-1.als
COMNT single pulse decoupled gat
DATIM 2012-11-23 18:03:36
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 445
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.73 usec
IRNUC 1H
CTEMP 28.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 54

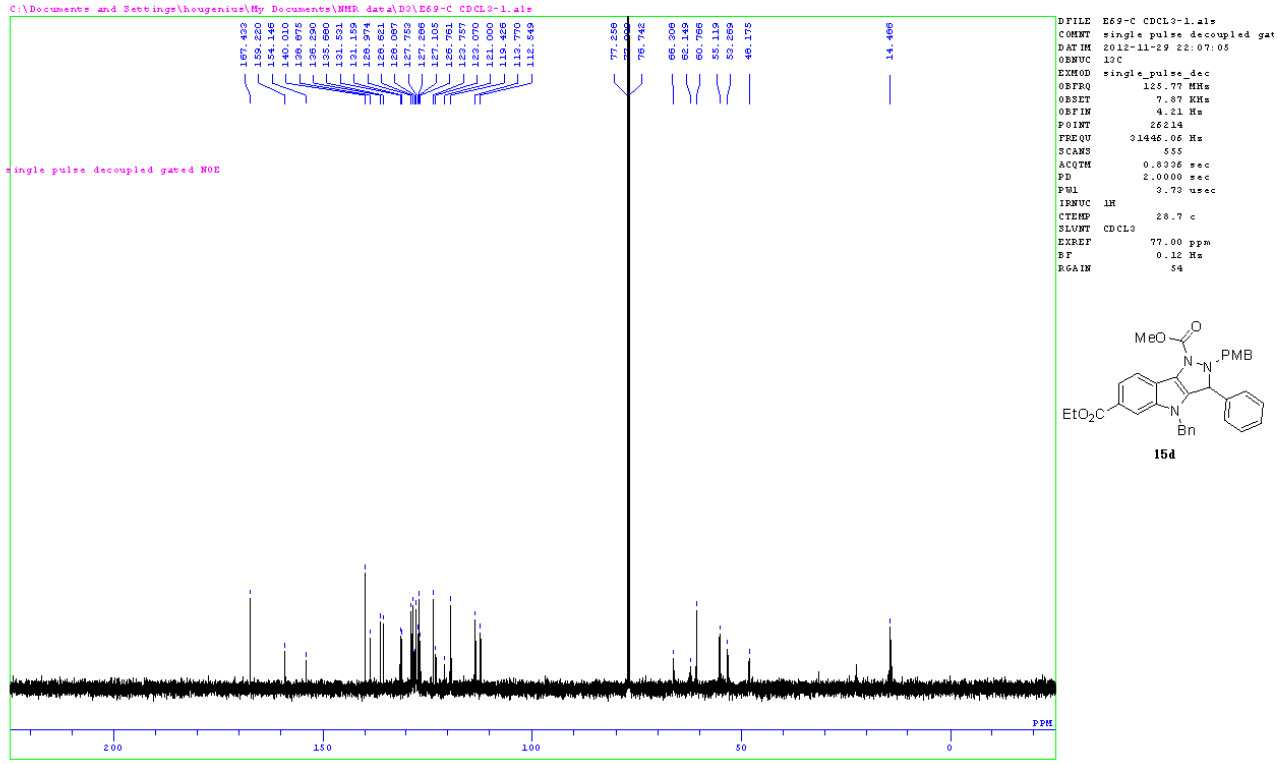

MeO
O
N
N
PMB
EtO2C
N
NO2

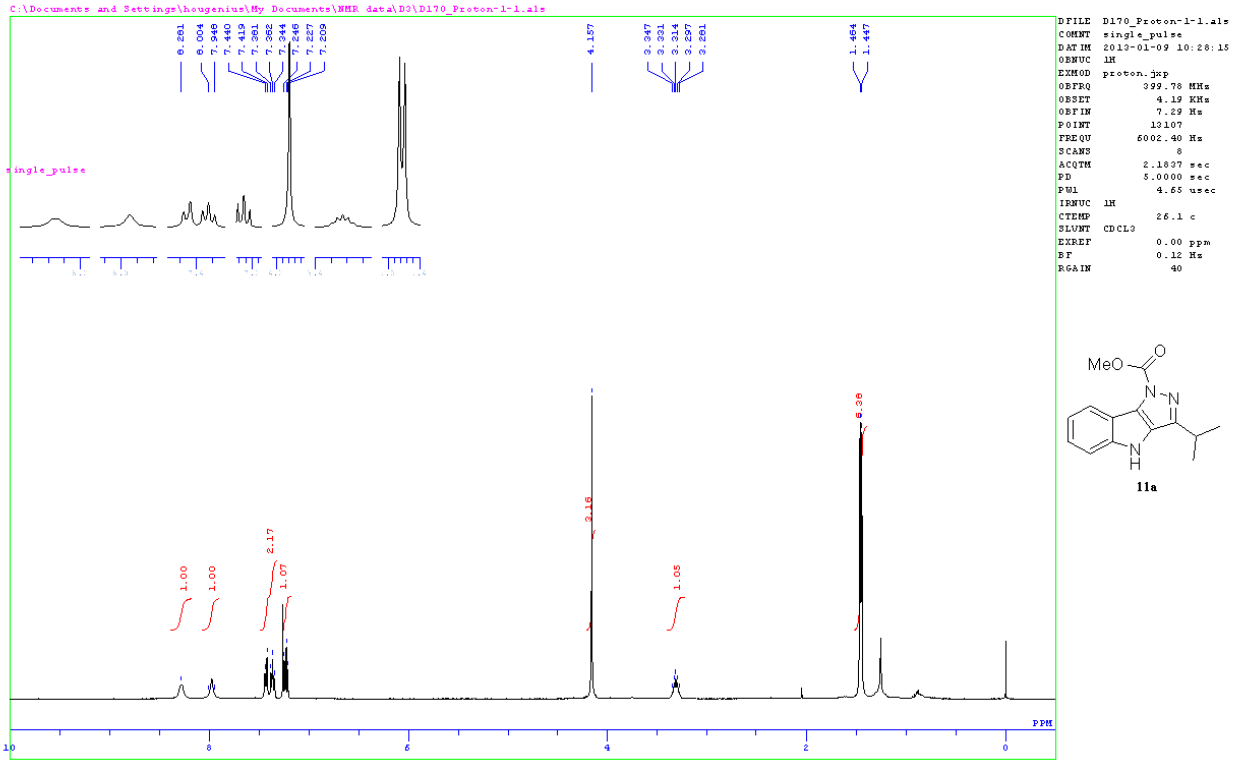
15b

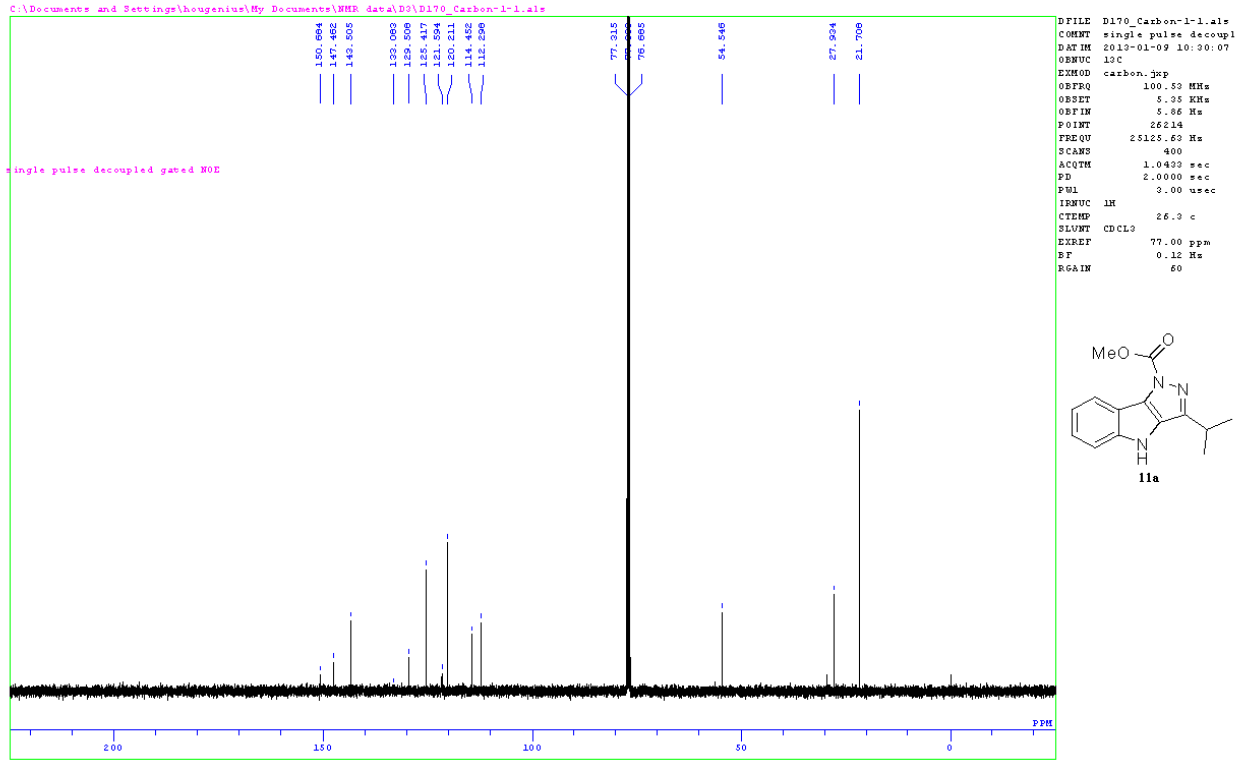


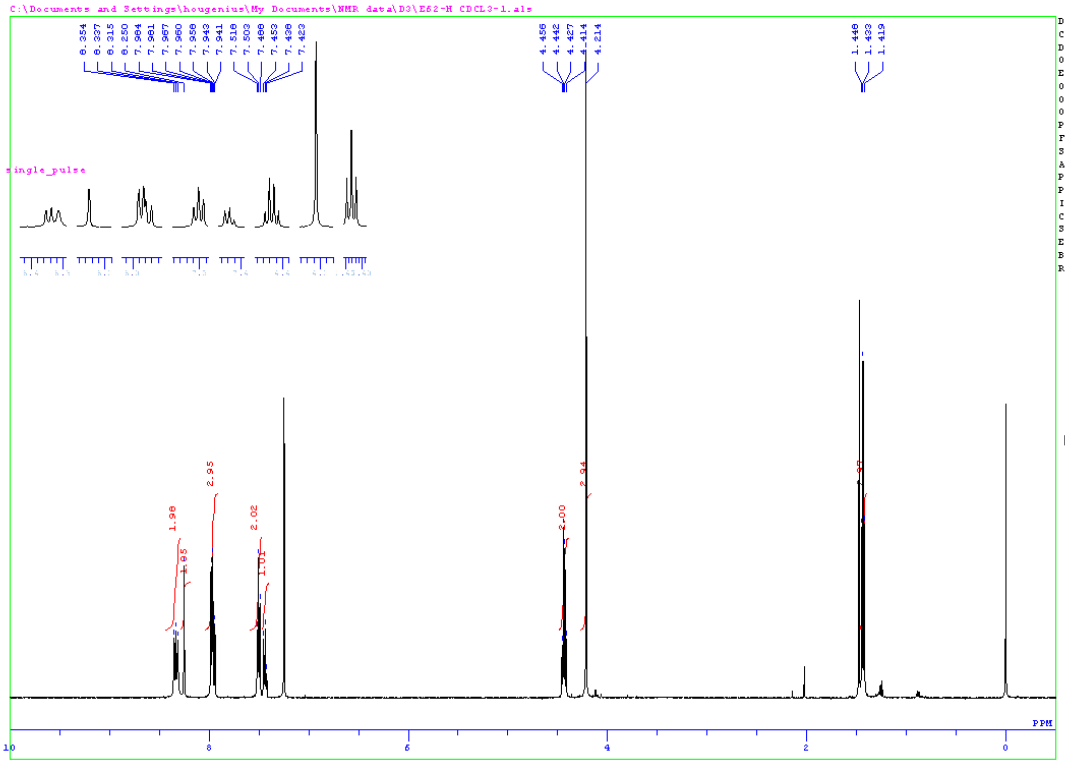




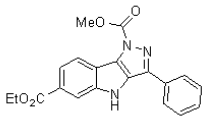



C:\Documents and Settings\hougenius\My Documents\NMR data\D3\D170_Proton-1-1.als
single_pulse
8.281
8.004
7.946
7.440
7.419
7.381
7.362
7.344
7.246
7.227
7.209
4.157
3.947
3.931
3.914
3.897
3.881
1.464
1.447
1.00
1.00
2.17
1.07
3.16
1.05
6.39
PPM
10
8
6
4
2
0
DFILE D170_Proton-1-1.als
COMNT single_pulse
DATIM 2013-01-09 10:28:15
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 4.55 usec
IRNUC 1H
CTEMP 26.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 40
MeO
O
N
N
N
H
11a

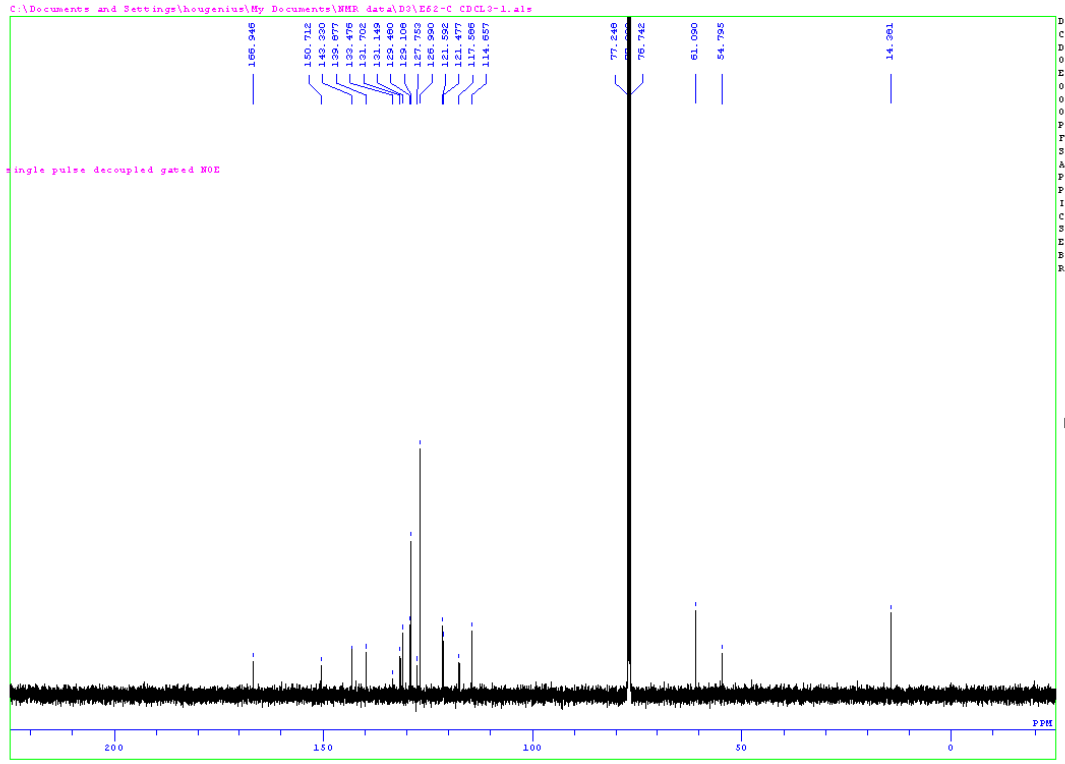

C:\Documents and Settings\hougenius\My Documents\NMR data\D3\D170_Carbon-1-1.als
single pulse decoupled gated NOE
150.694
147.462
140.505
133.063
129.508
125.417
121.594
120.211
114.452
112.296
77.215
77.000
76.665
54.546
27.924
21.708
PPM
200
150
100
50
0
DFILE D170_Carbon-1-1.als
COMNT single pulse decoupled gat
DATIM 2013-01-09 10:30:07
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 400
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.00 usec
IRNUC 1H
CTEMP 26.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60
MeO
O
N
N
N
H
11a



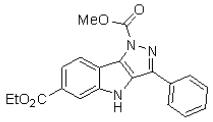

```
DFILE  E62-H CDCL3-1.als
COMNT  single_pulse
DATIM  2012-11-20 22:59:54
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         13107
FREQU       7507.39 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1           6.50 usec
IRNUC  1H
CTEMP         60.0 c
SLVNT  CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           52
```



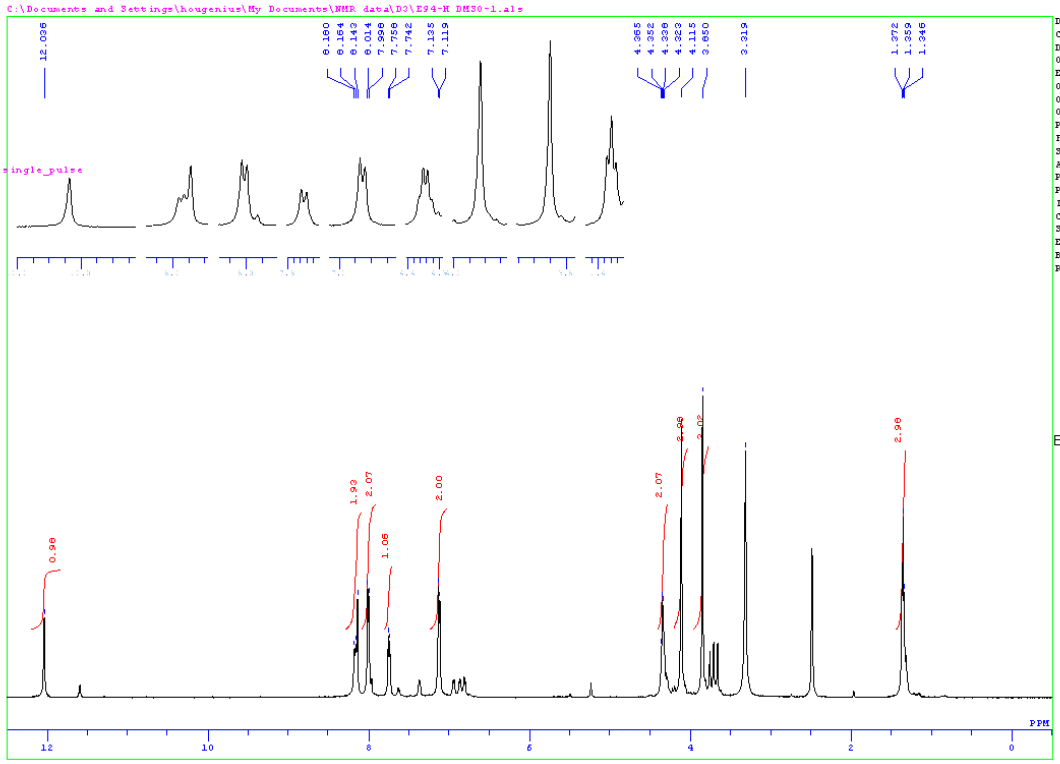
11b



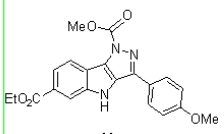

```
DFILE  E62-C CDCL3-1.als
COMNT  single pulse decoupled gat
DATIM  2012-11-21 09:17:18
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS         13040
ACQTM         0.8336 sec
PD            2.0000 sec
PW1           3.73 usec
IRNUC  1H
CTEMP         60.0 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF            0.12 Hz
RGAIN           56
```



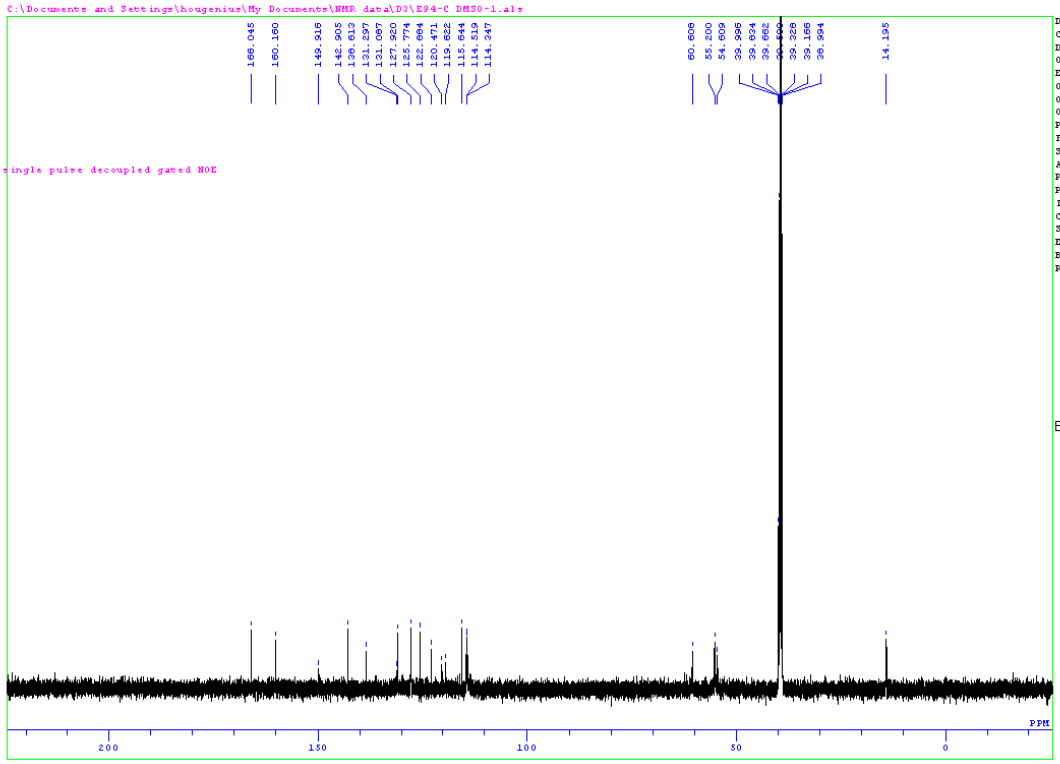
11b



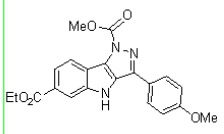

```
DFILE   E94-H DMSO-1.als
COMNT   single_pulse
DATIM   2012-12-21 11:02:50
OBNUC   1H
EXMOD   single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         12107
FREQU       7507.39 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1           6.50 usec
IRNUC   1H
CTEMP         27.1 c
SLVNT   DMSO
EXREF         2.49 ppm
BF            0.12 Hz
RGAIN           48
```



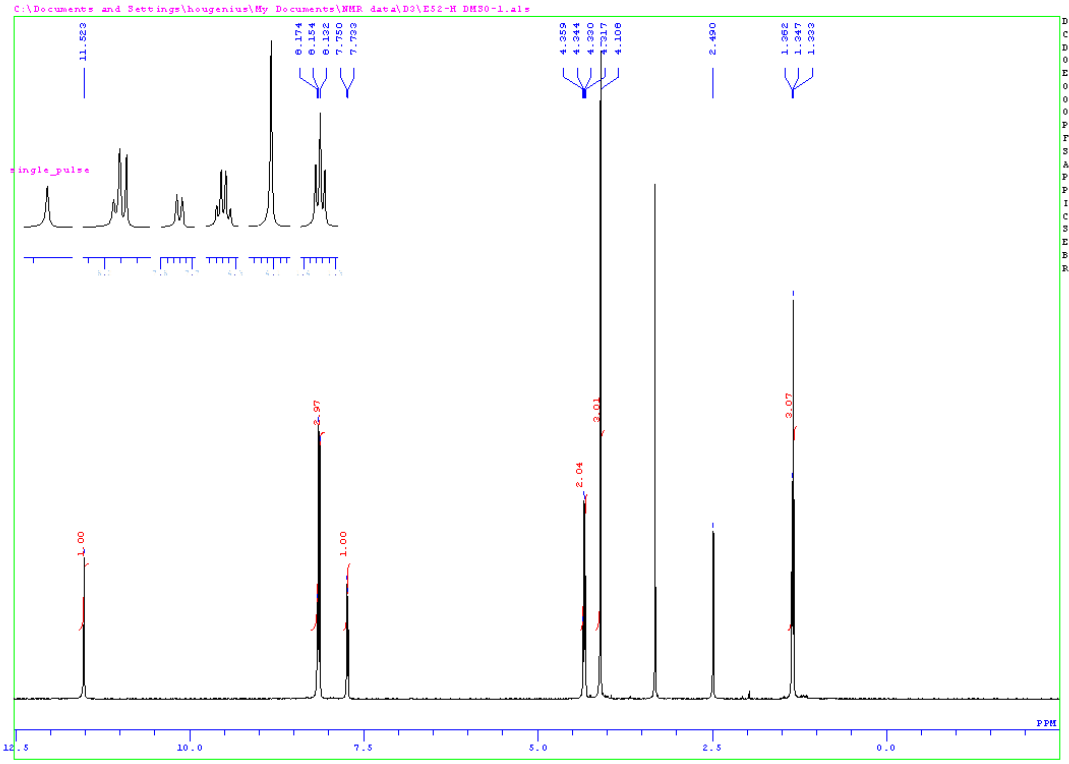
11c



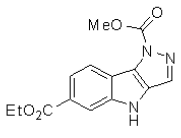

```
DFILE   E94-C DMSO-1.als
COMNT   single pulse decoupled gat
DATIM   2012-12-26 18:55:19
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS          1000
ACQTM         0.8336 sec
PD            2.0000 sec
PW1           3.73 usec
IRNUC   1H
CTEMP         27.6 c
SLVNT   DMSO
EXREF         39.50 ppm
BF            0.12 Hz
RGAIN           56
```



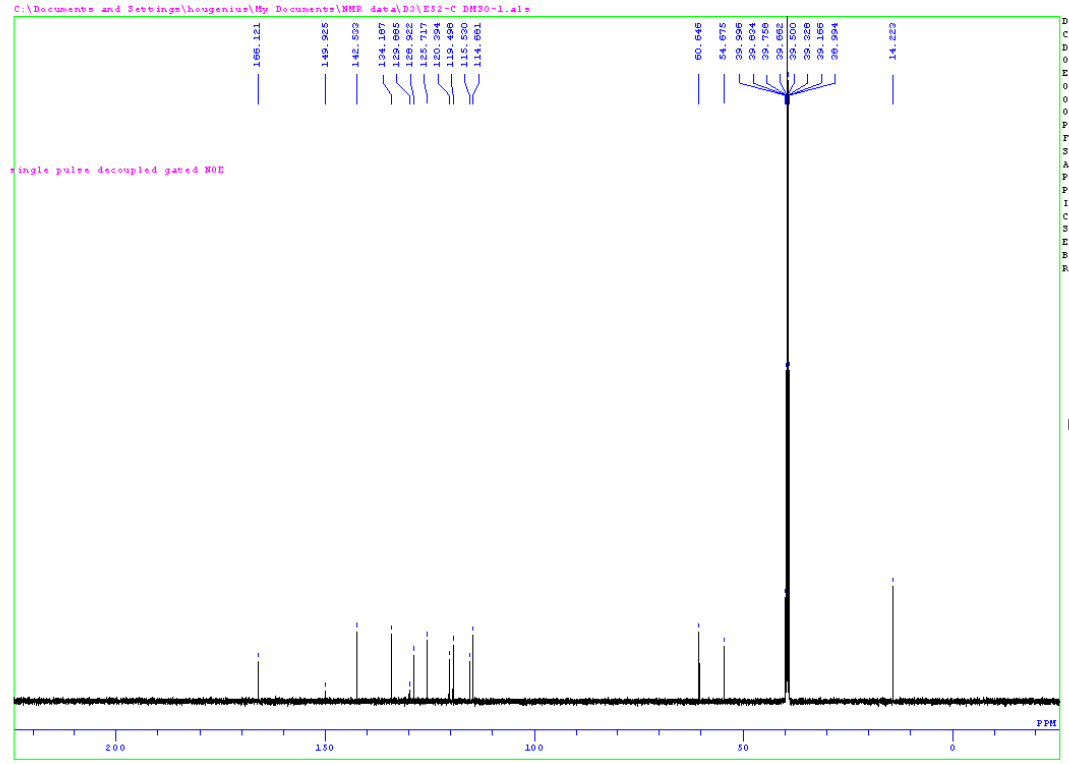
11c



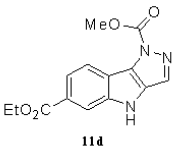

```
DFILE  E52-H DMSO-1.als
COMNT  single_pulse
DATIM  2012-11-12 15:23:02
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         12107
FREQU       7507.39 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1           6.50 usec
IRNUC  1H
CTEMP         24.5 c
SLVNT  DMSO
EXREF         2.49 ppm
BF            0.12 Hz
RGAIN           46
```



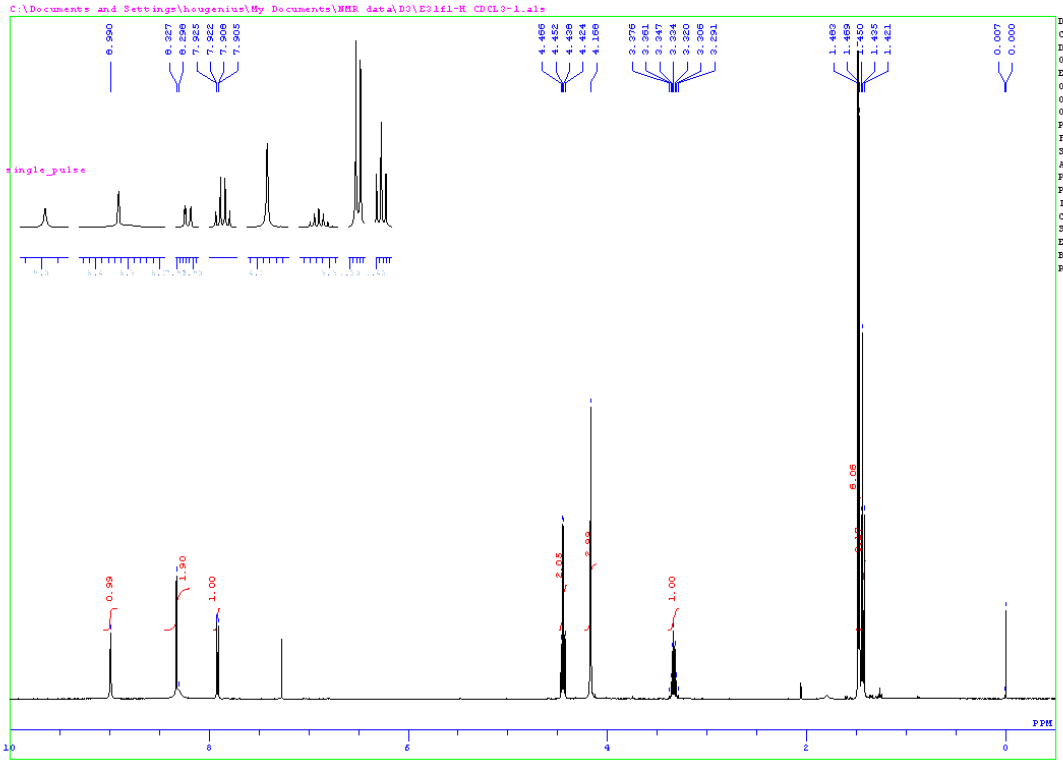
11d



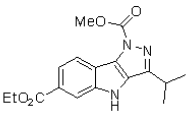

```
DFILE  E52-C DMSO-1.als
COMNT  single pulse decoupled gat
DATIM  2012-11-12 16:11:44
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS           958
ACQTM         0.8336 sec
PD            2.0000 sec
PW1           3.73 usec
IRNUC  1H
CTEMP         24.6 c
SLVNT  DMSO
EXREF         39.50 ppm
BF            0.12 Hz
RGAIN           54
```



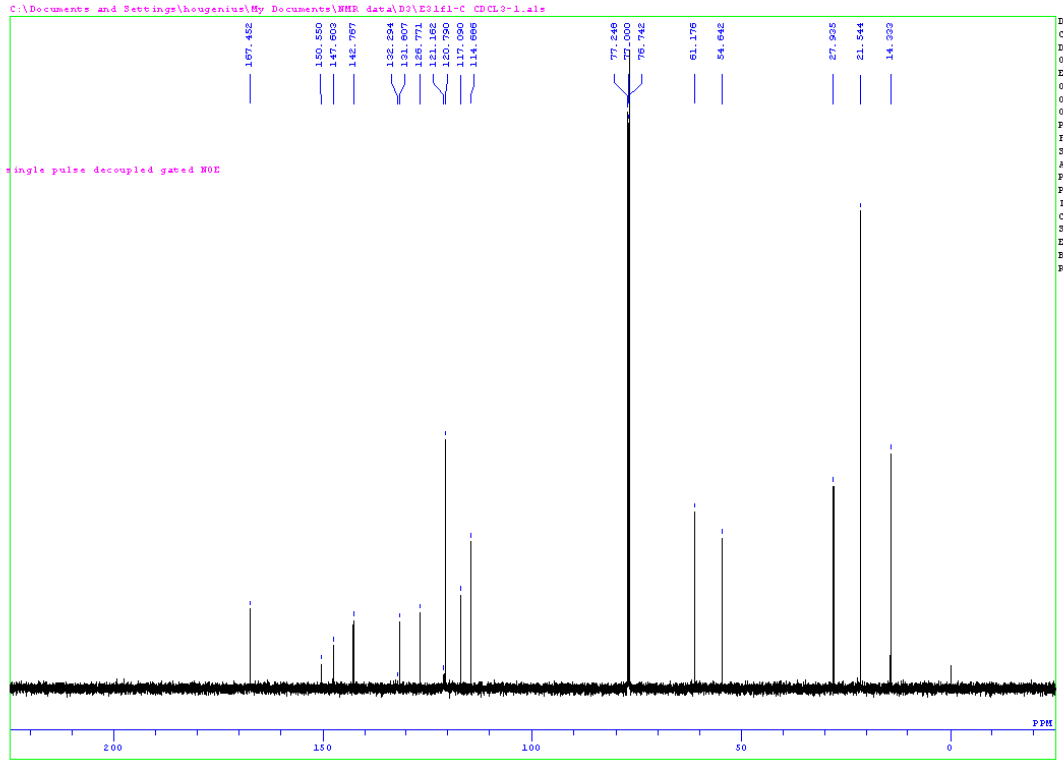
11d



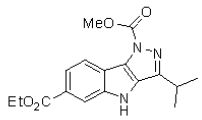
DFILE E31f1-H CDCL3-1.als
COMNT single_pulse
DATIM 2012-10-02 13:32:02
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 12107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 25.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 40



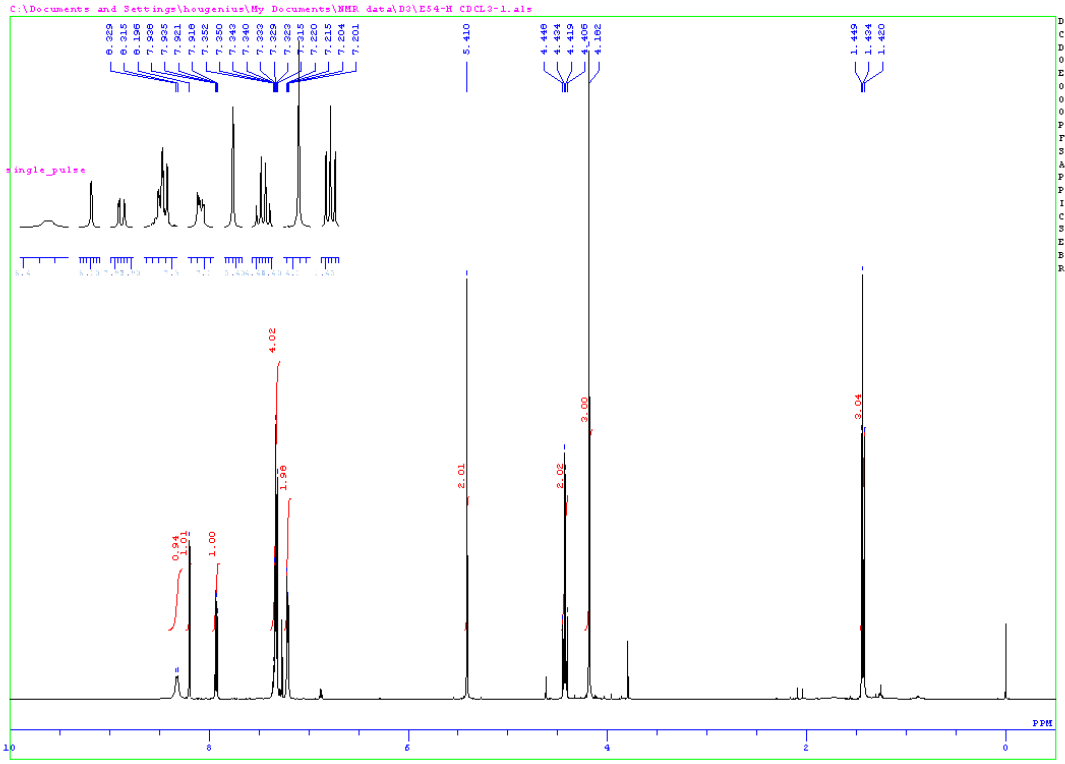
11e



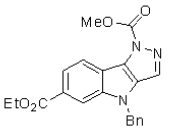
DFILE E31f1-C CDCL3-1.als
COMNT single pulse decoupled gat
DATIM 2012-10-02 14:02:54
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 605
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.73 usec
IRNUC 1H
CTEMP 25.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 52



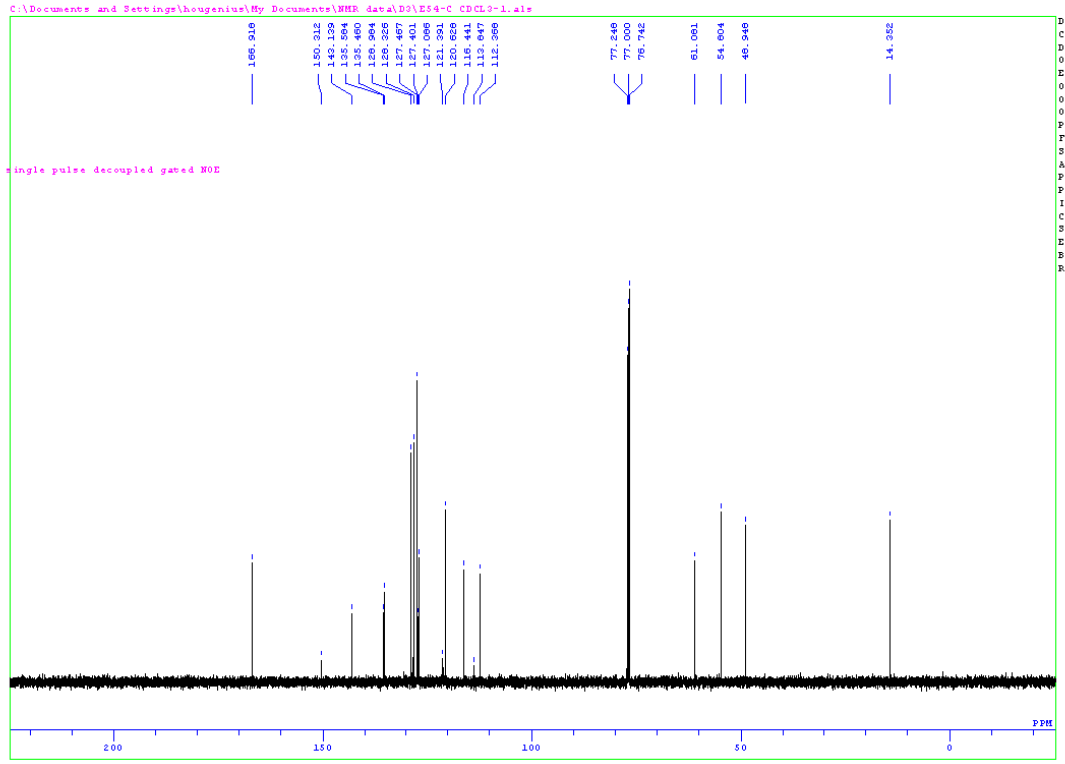
11e



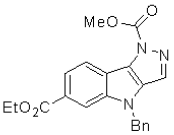

```
DFILE  E54-H CDCL3-1.als
COMNT  single_pulse
DATIM  2012-11-13 19:29:21
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         12107
FREQU       7507.39 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1           6.50 usec
IRNUC  1H
CTEMP         23.1 c
SLVNT  CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           38
```



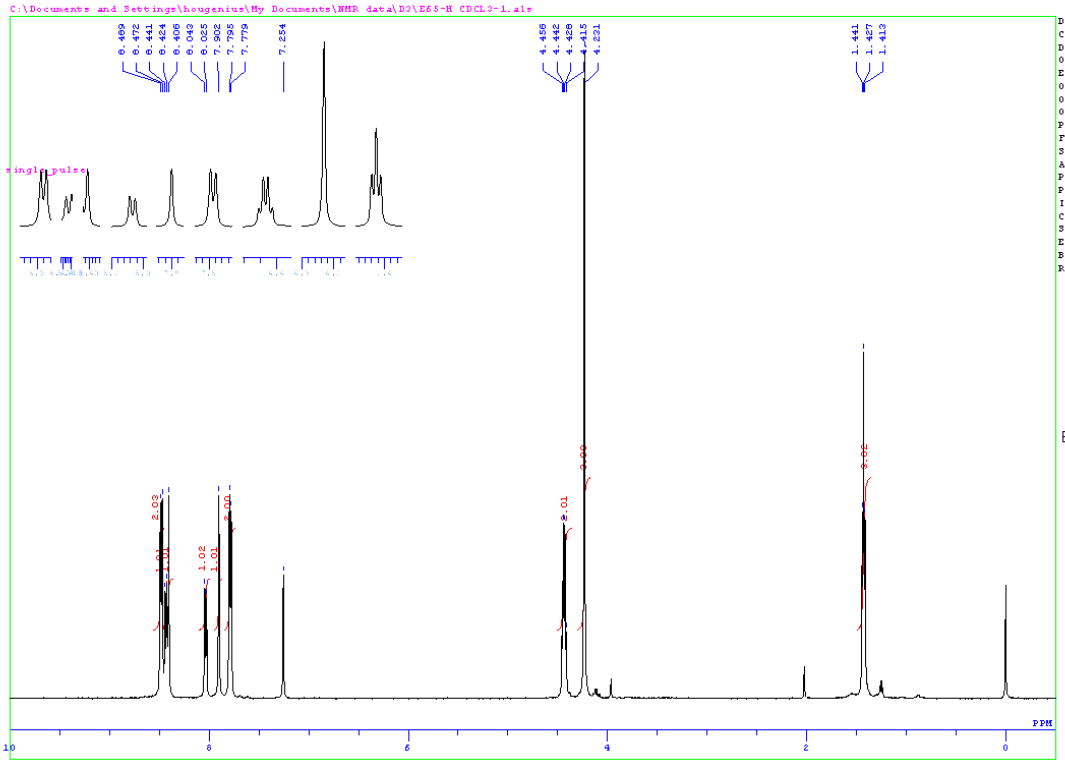
11f

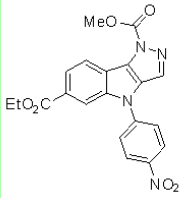



```
DFILE  E54-C CDCL3-1.als
COMNT  single pulse decoupled gat
DATIM  2012-11-13 19:40:40
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS           224
ACQTM         0.8336 sec
PD            2.0000 sec
PW1           3.73 usec
IRNUC  1H
CTEMP         23.4 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF            0.12 Hz
RGAIN           54
```

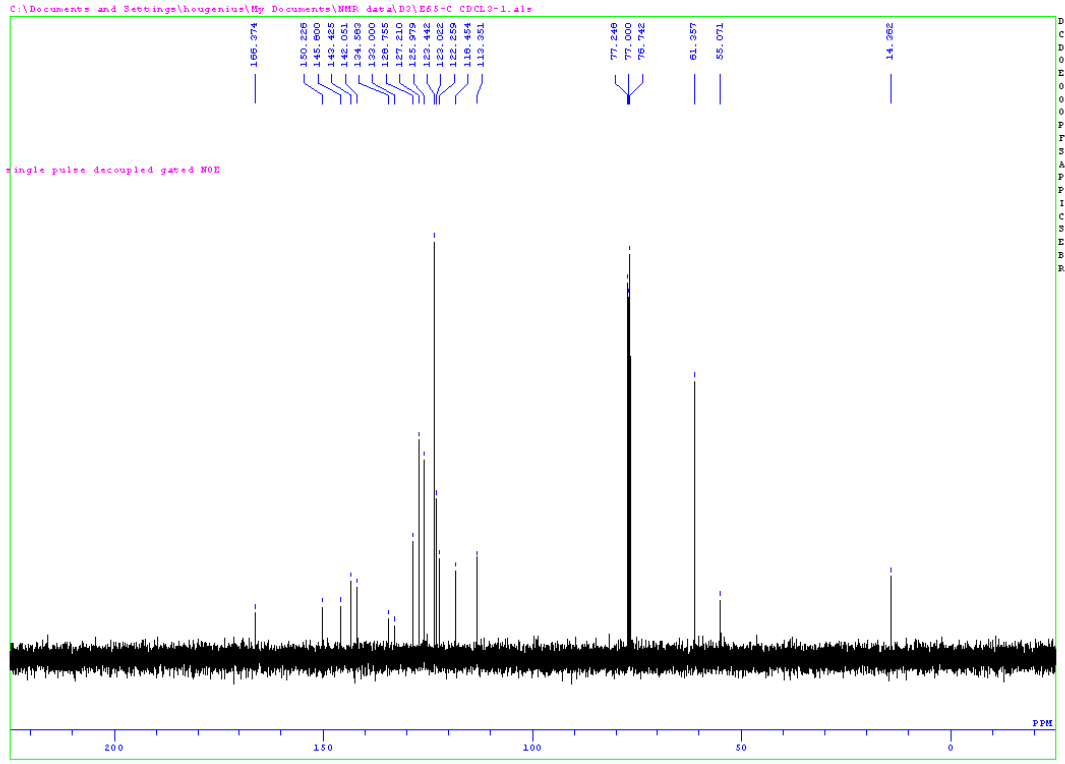


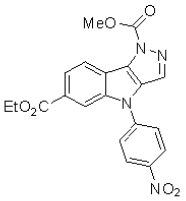
11f


C:\Documents and Settings\hougenius\My Documents\NMR data\D3\E65-H CDCL3-1.als
single pulse
DFILE E65-H CDCL3-1.als
COMNT single_pulse
DATIM 2012-11-24 16:29:31
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 12107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 60.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 50
PPM

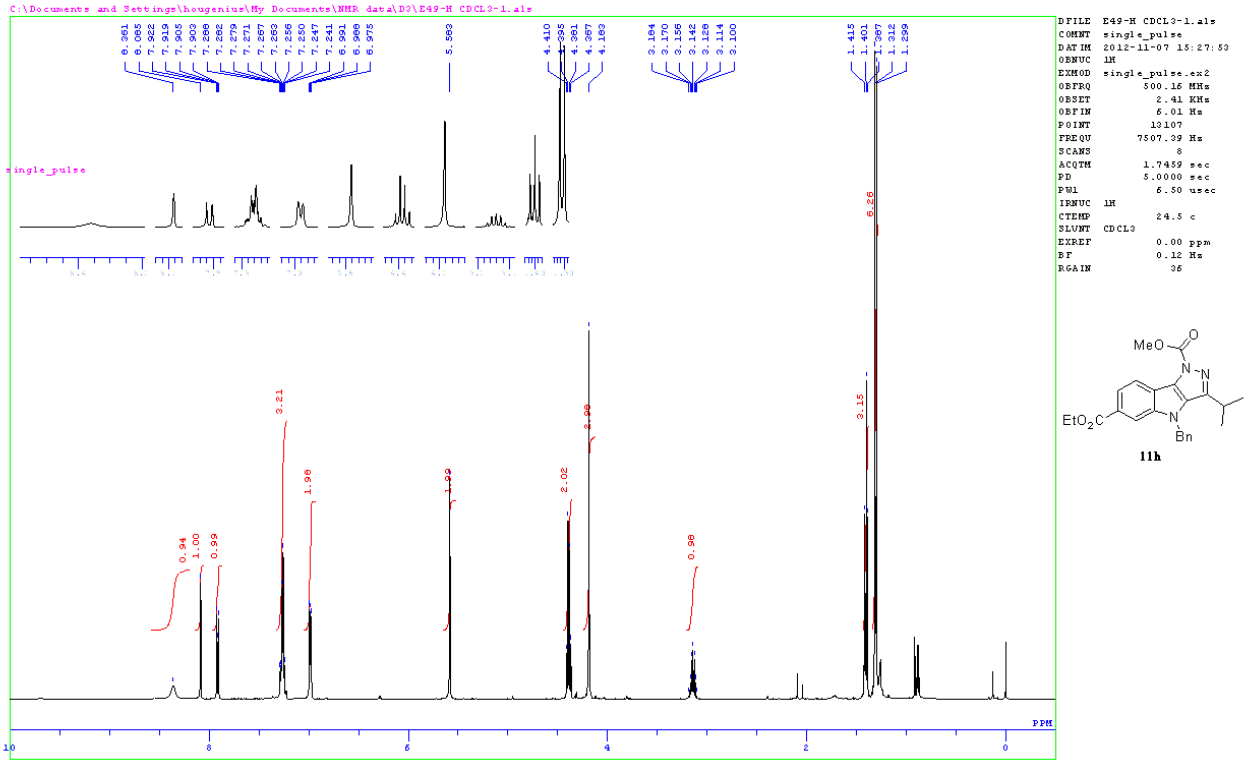


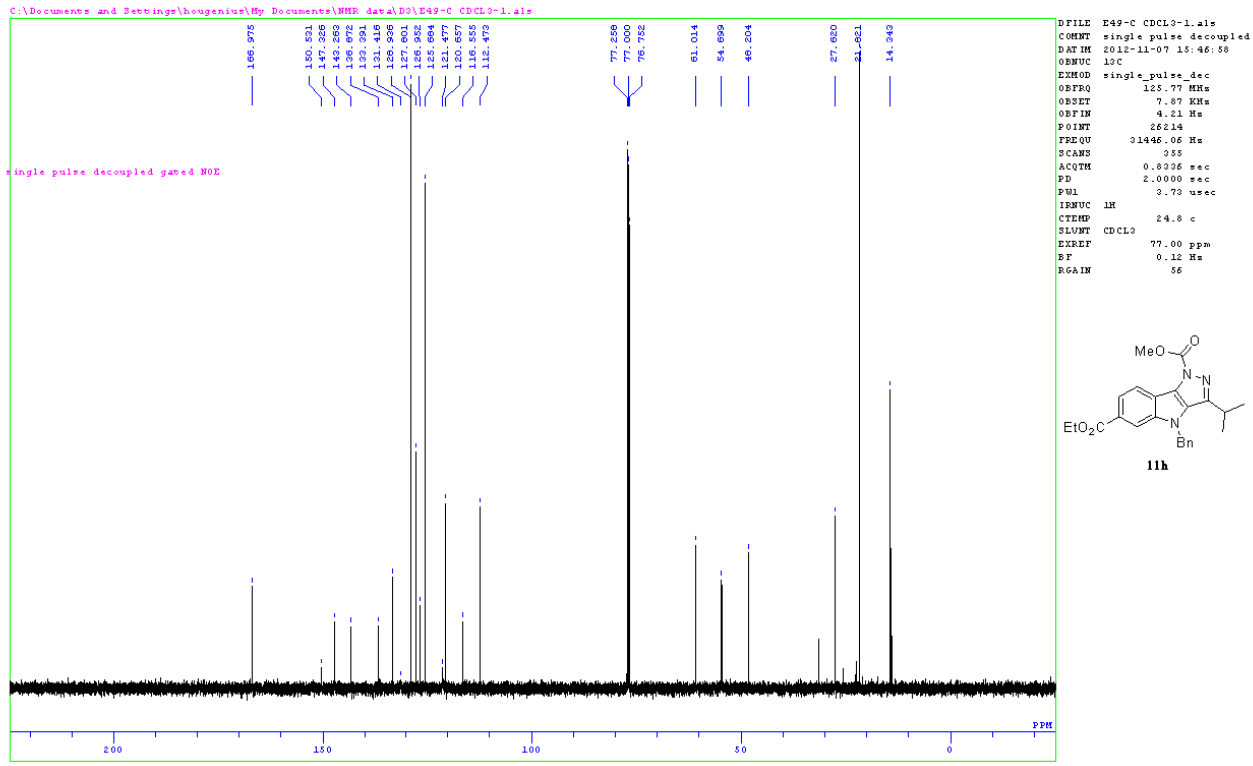
11g

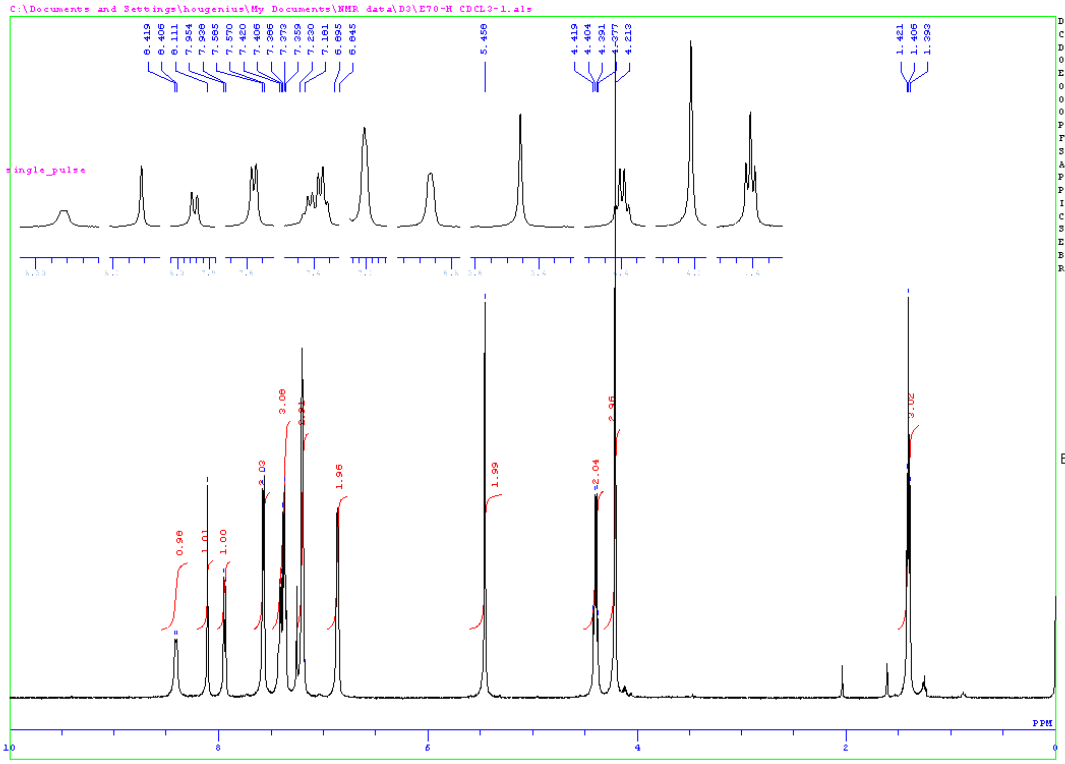

C:\Documents and Settings\hougenius\My Documents\NMR data\D3\E65-C CDCL3-1.als
single pulse decoupled gated NOE
DFILE E65-C CDCL3-1.als
COMNT single pulse decoupled gat
DATIM 2012-11-24 16:50:48
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 425
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 11.20 usec
IRNUC 1H
CTEMP 60.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 58
PPM



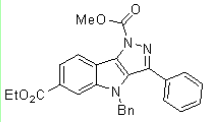
11g



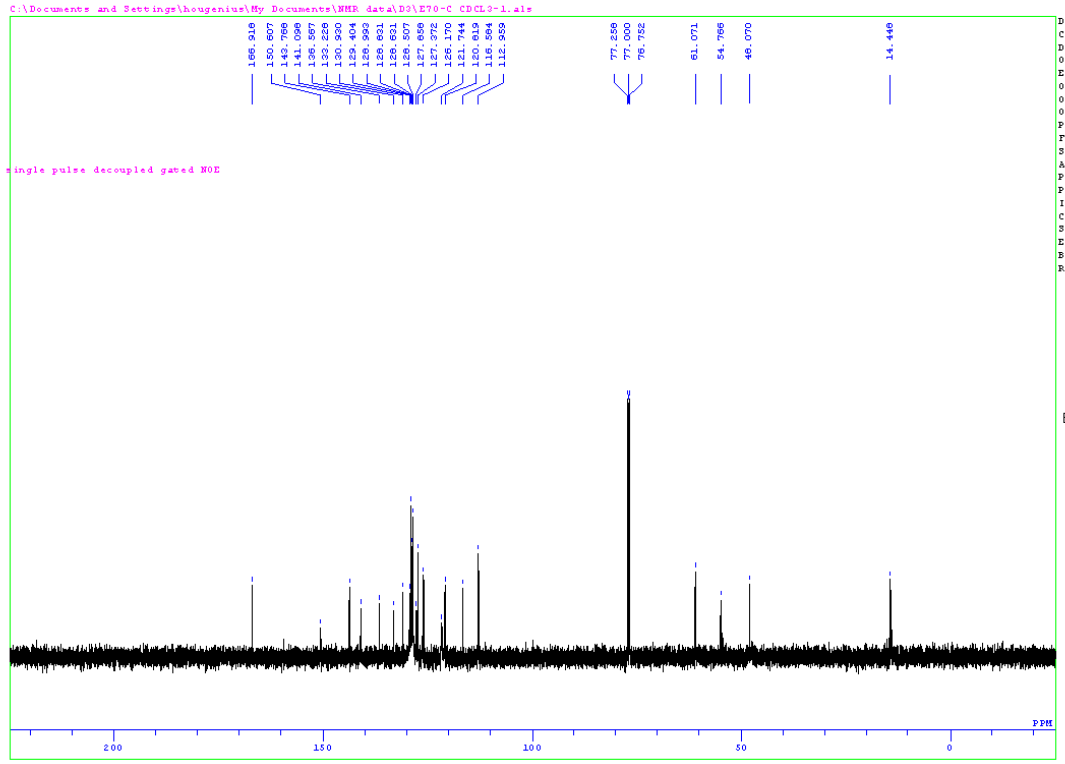




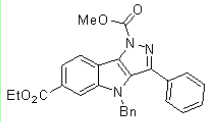

```
DFILE   E70-H CDCL3-1.als
COMNT   single_pulse
DATIM   2012-11-20 13:52:48
OBNUC   1H
EXMOD   single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         12107
FREQU       7507.39 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1           6.50 usec
IRNUC   1H
CTEMP        27.9 c
SLVNT   CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           48
```



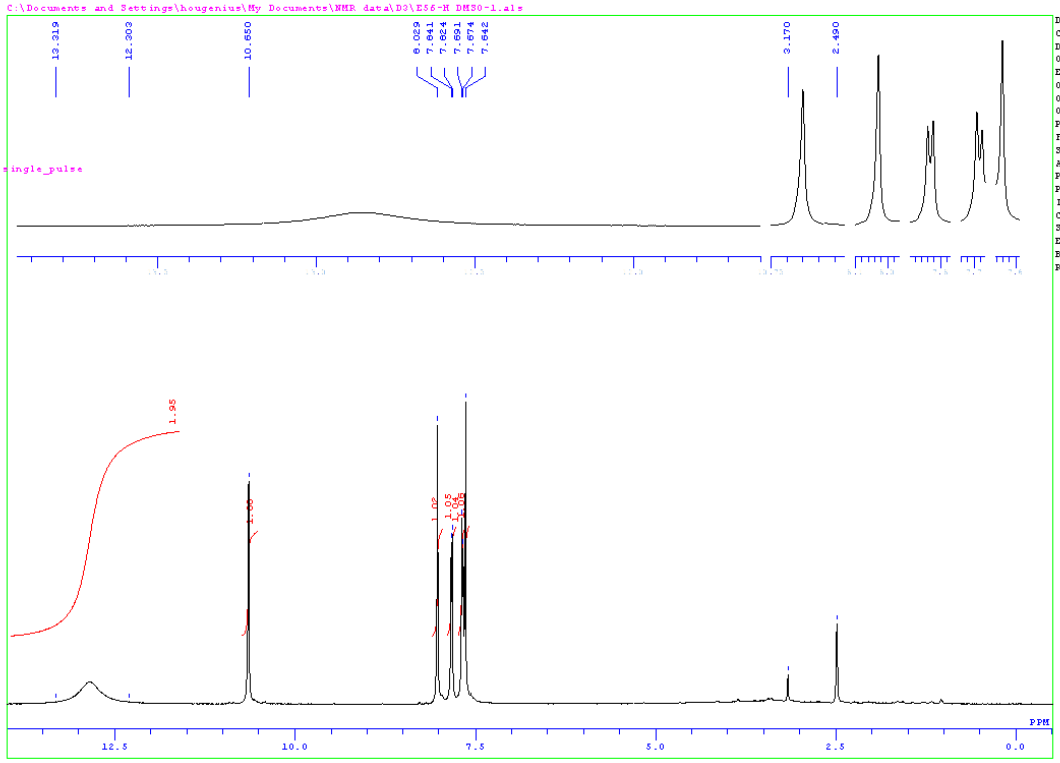
11i



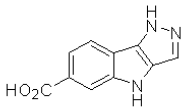

```
DFILE   E70-C CDCL3-1.als
COMNT   single pulse decoupled gat
DATIM   2012-11-20 14:13:01
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS          411
ACQTM         0.8336 sec
PD            2.0000 sec
PW1           11.20 usec
IRNUC   1H
CTEMP        28.0 c
SLVNT   CDCL3
EXREF         77.00 ppm
BF            0.12 Hz
RGAIN           54
```



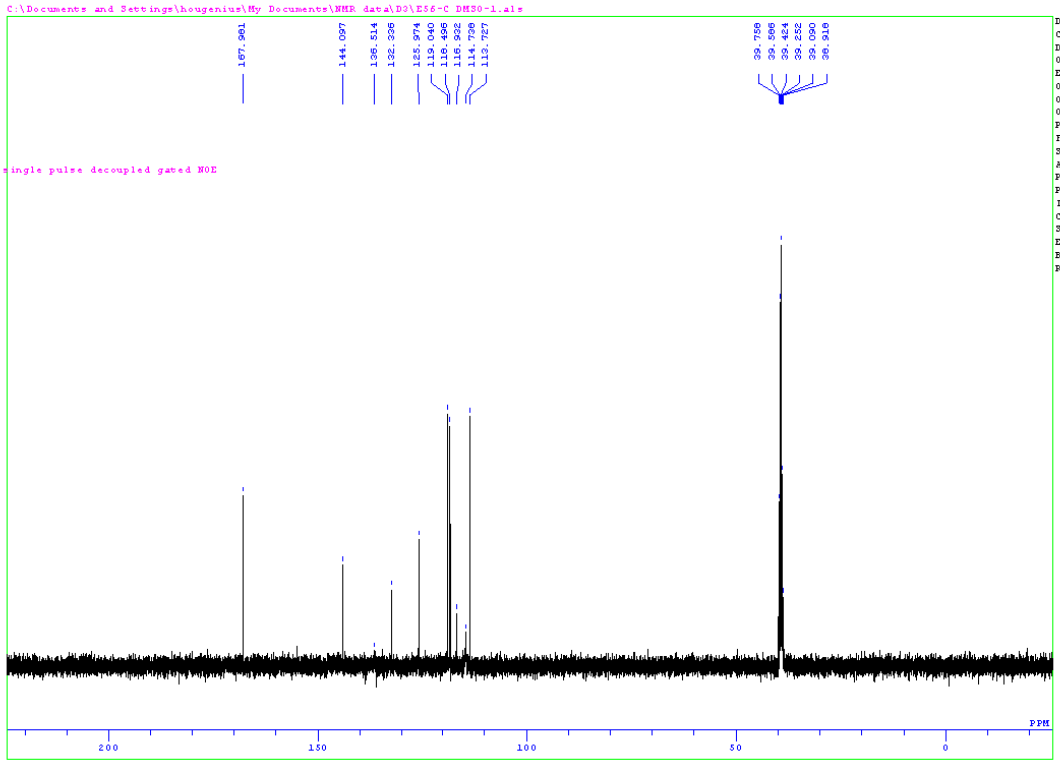
11i



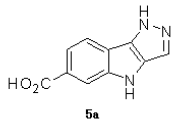

```
DFILE  E56-H DMSO-1.als
COMNT  single_pulse
DATIM  2012-11-27 17:44:34
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         13107
FREQU      10019.89 Hz
SCANS             8
ACQTM         1.3081 sec
PD            5.0000 sec
PW1           6.50 usec
IRNUC  1H
CTEMP         28.6 c
SLVNT  DMSO
EXREF         2.49 ppm
BF             0.12 Hz
RGAIN            42
```



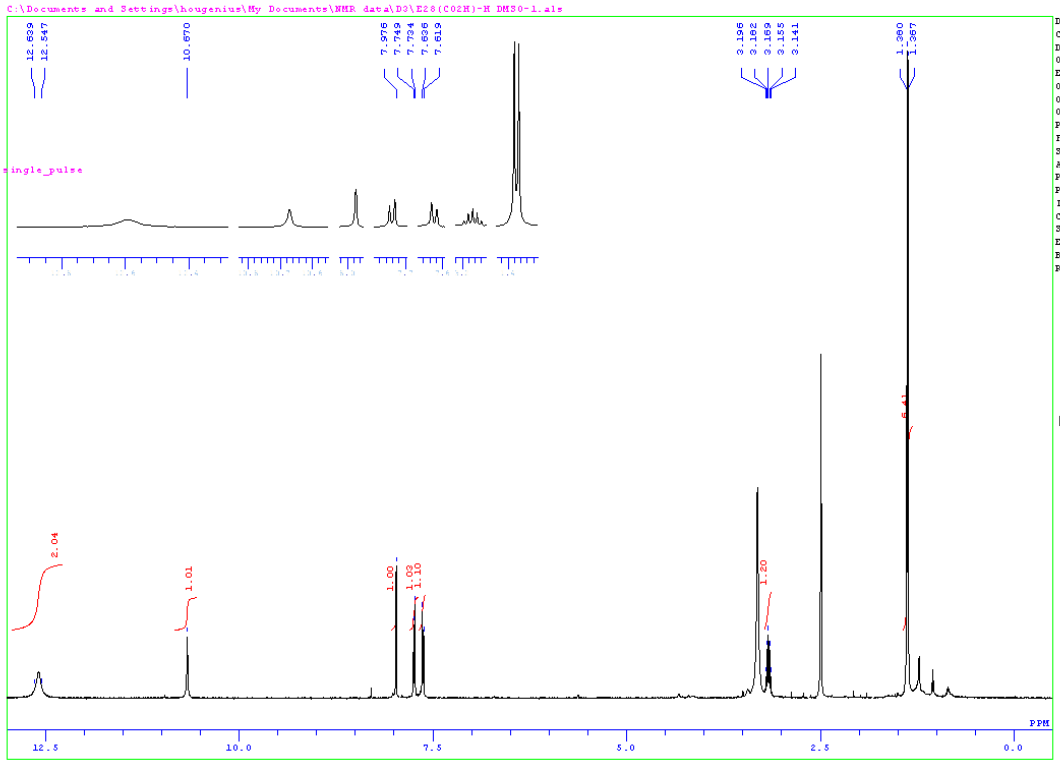
5a



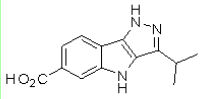

```
DFILE  E56-C DMSO-1.als
COMNT  single pulse decoupled gat
DATIM  2012-11-27 17:55:24
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS           182
ACQTM         0.8336 sec
PD            2.0000 sec
PW1           11.20 usec
IRNUC  1H
CTEMP         29.0 c
SLVNT  DMSO
EXREF         39.50 ppm
BF             0.12 Hz
RGAIN            56
```



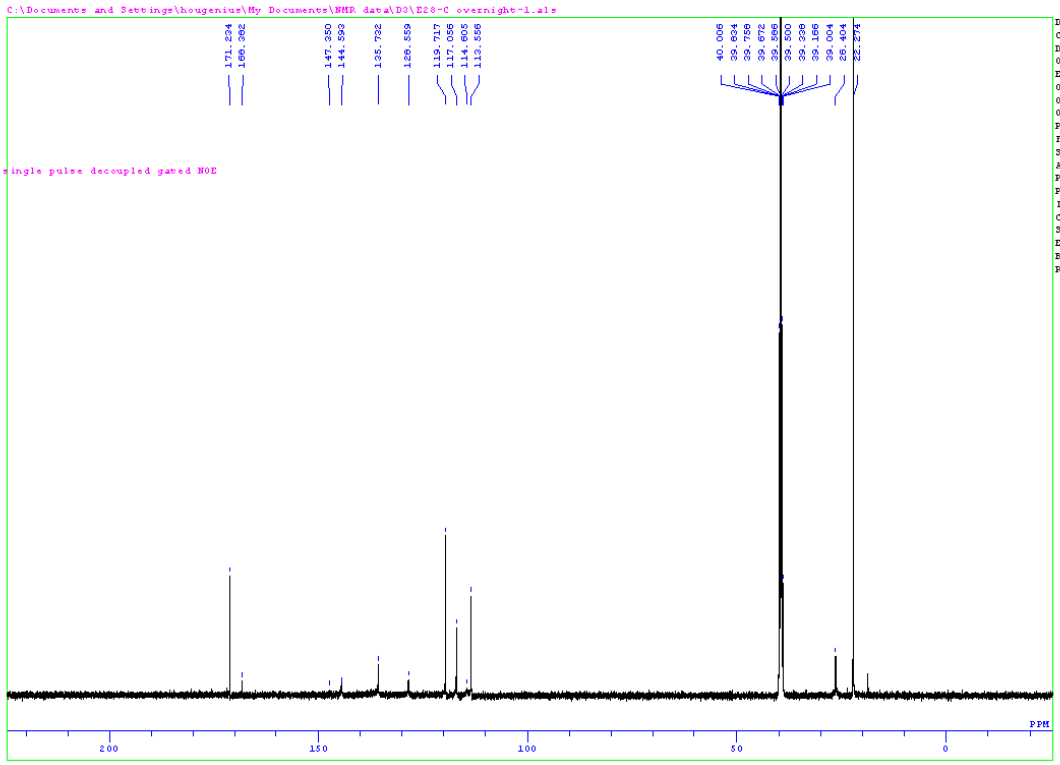
5a



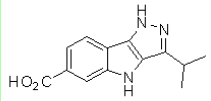

```
DFILE  E28(CO2H)-H DMSO-1.als
COMNT  single_pulse
DATIM  2012-11-19 17:02:35
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         13107
FREQU      10019.89 Hz
SCANS             8
ACQTM         1.3081 sec
PD            5.0000 sec
PW1             6.50 usec
IRNUC  1H
CTEMP         27.5 c
SLVNT  DMSO
EXREF         2.49 ppm
BF             0.12 Hz
RGAIN           56
```



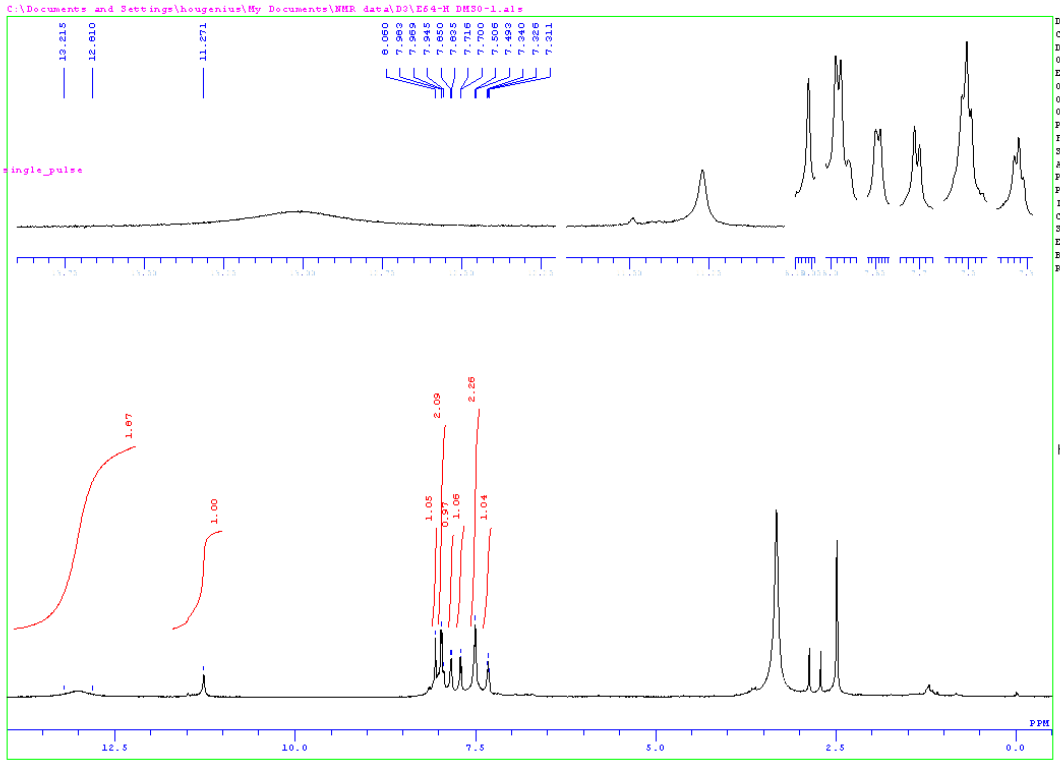
5b



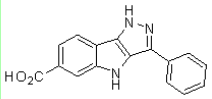

```
DFILE  E28-C overnight-1.als
COMNT  single pulse decoupled gat
DATIM  2012-10-05 09:18:50
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS         13462
ACQTM         0.8336 sec
PD            2.0000 sec
PW1            11.20 usec
IRNUC  1H
CTEMP         25.3 c
SLVNT  DMSO
EXREF         39.50 ppm
BF             0.12 Hz
RGAIN           54
```



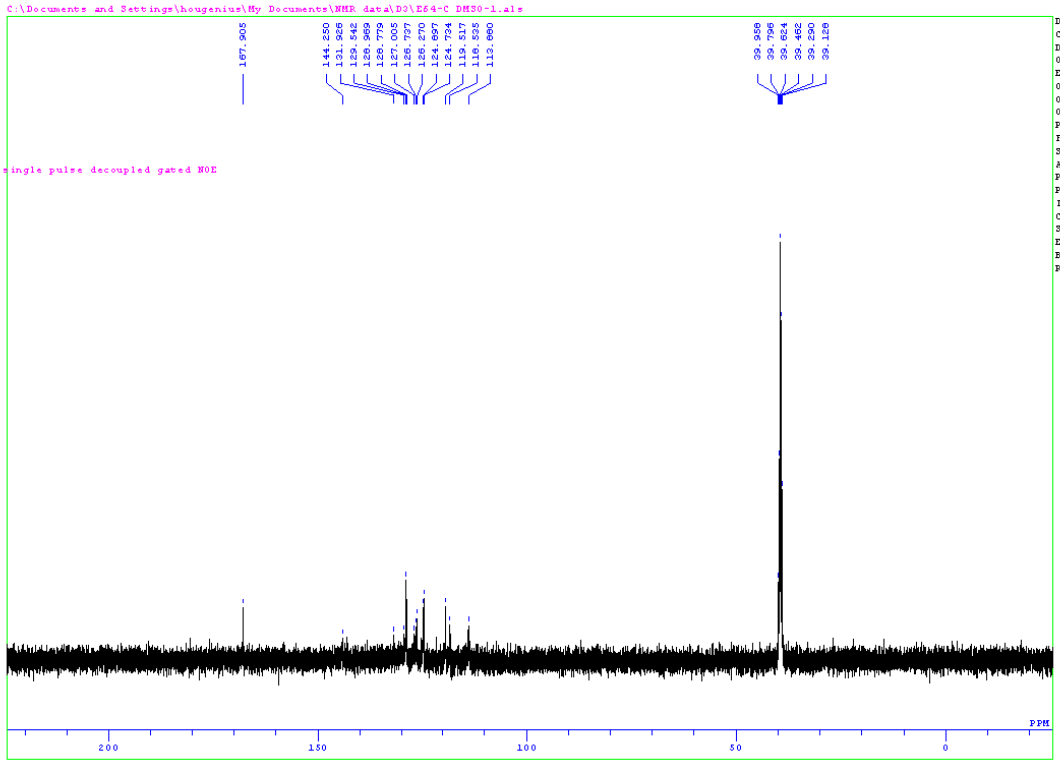
5b



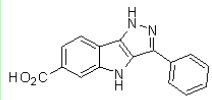

```
DFILE  E64-H DMSO-1.als
COMNT  single_pulse
DATIM  2012-11-20 19:23:10
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         13107
FREQU      10019.89 Hz
SCANS             8
ACQTM         1.3081 sec
PD            5.0000 sec
PW1           6.50 usec
IRNUC  1H
CTEMP         27.8 c
SLVNT  DMSO
EXREF         2.49 ppm
BF            0.12 Hz
RGAIN           44
```



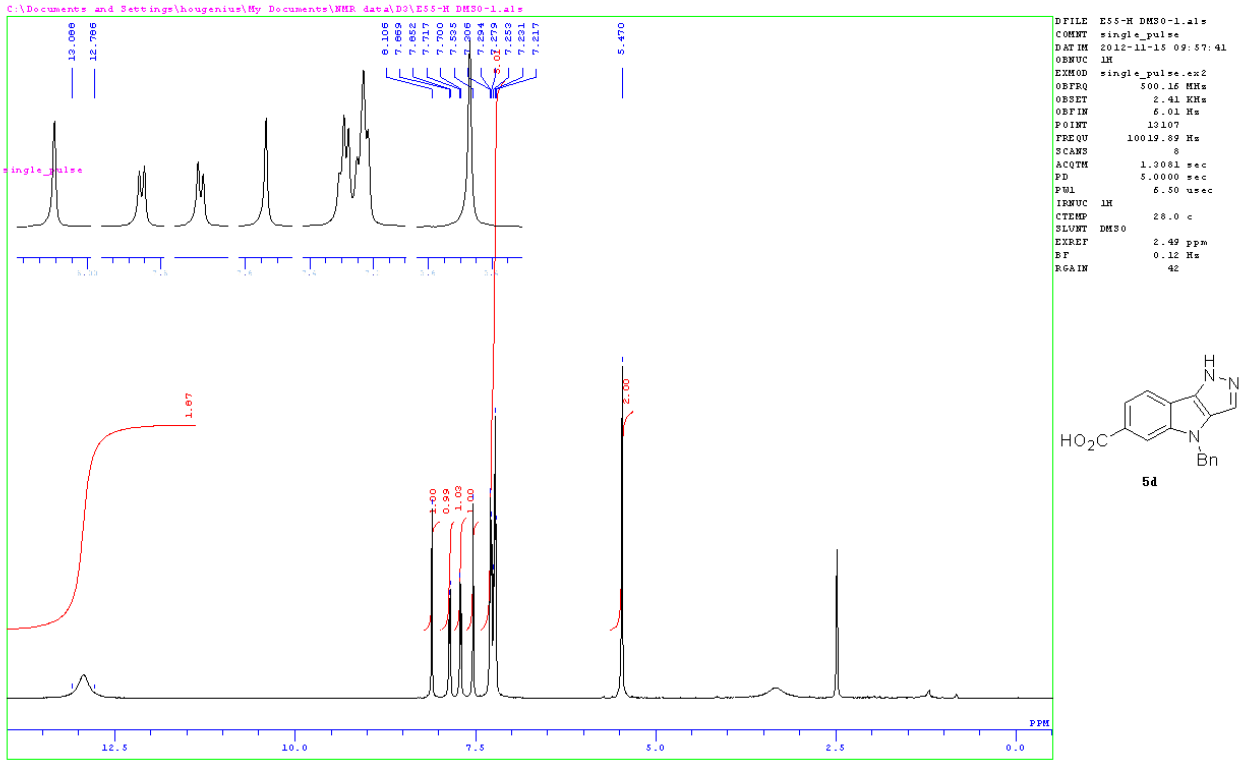
5c

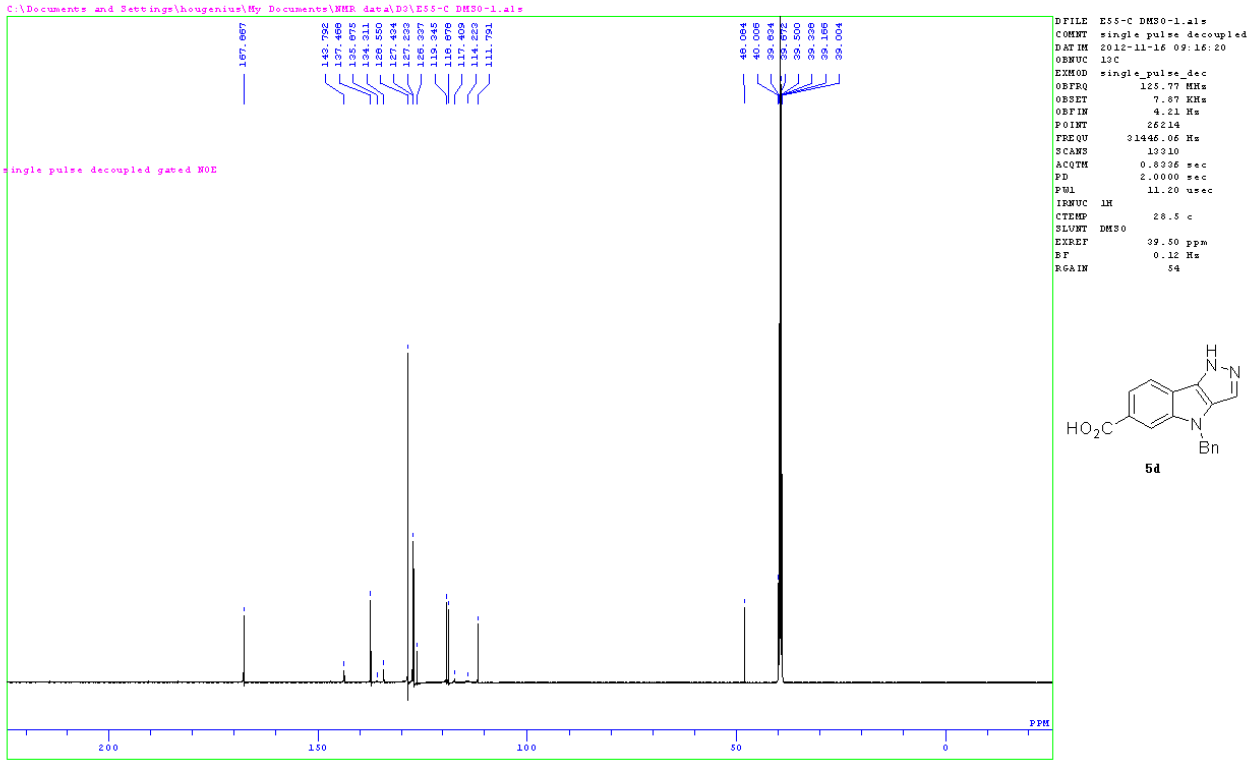


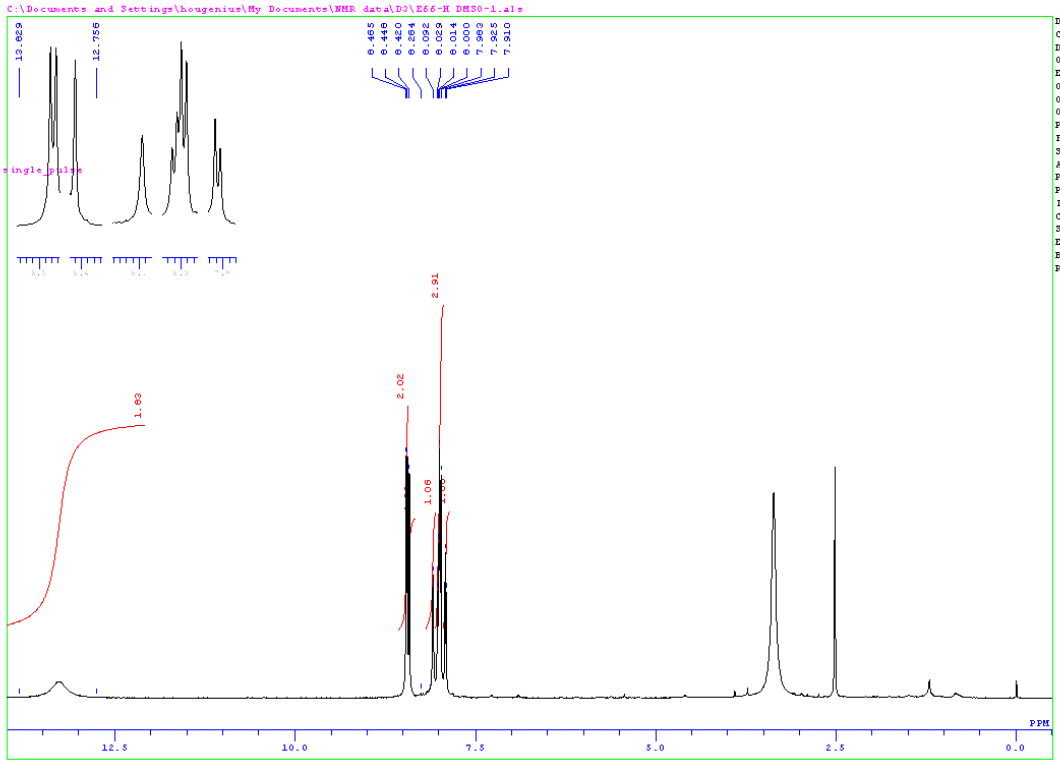

```
DFILE  E64-C DMSO-1.als
COMNT  single pulse decoupled gat
DATIM  2012-11-20 16:42:15
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS          1000
ACQTM         0.8336 sec
PD            2.0000 sec
PW1           11.20 usec
IRNUC  1H
CTEMP         28.2 c
SLVNT  DMSO
EXREF         39.50 ppm
BF            0.12 Hz
RGAIN           58
```



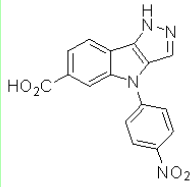
5c



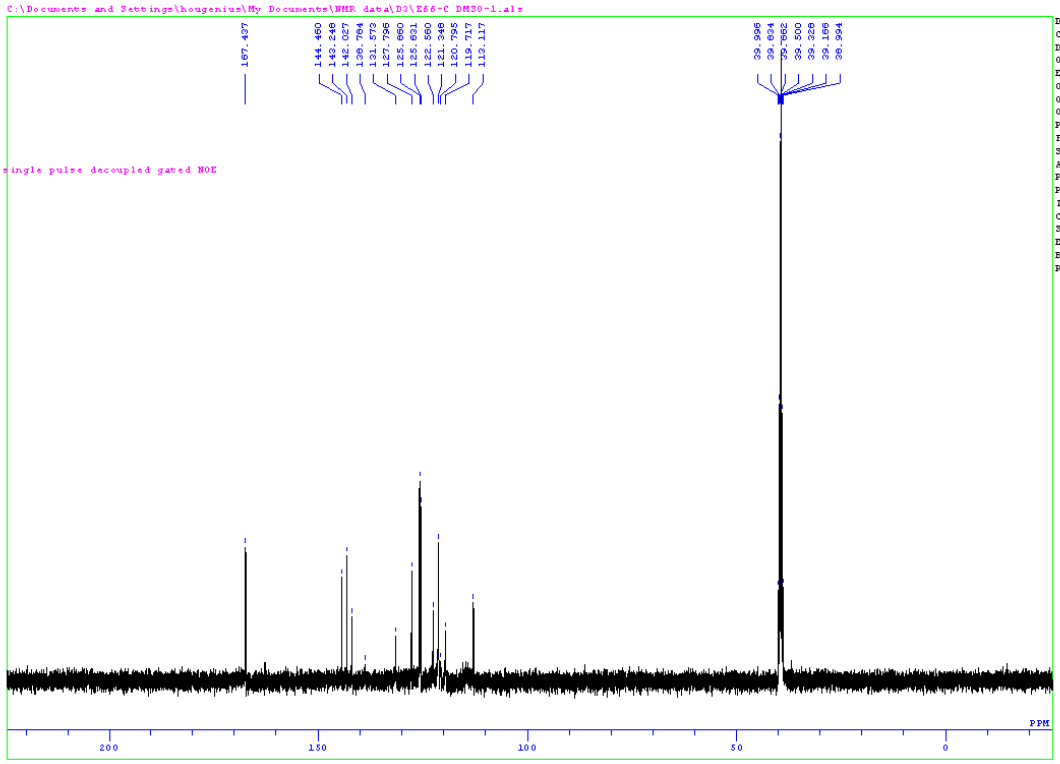




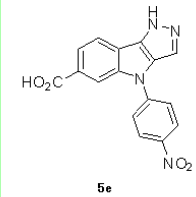

```
DFILE  E66-H DMSO-1.als
COMNT  single_pulse
DATIM  2012-11-27 14:04:21
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         13107
FREQU      10019.89 Hz
SCANS             8
ACQTM         1.3081 sec
PD            5.0000 sec
PW1           6.50 usec
IRNUC  1H
CTEMP         28.8 c
SLVNT  DMSO
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           44
```



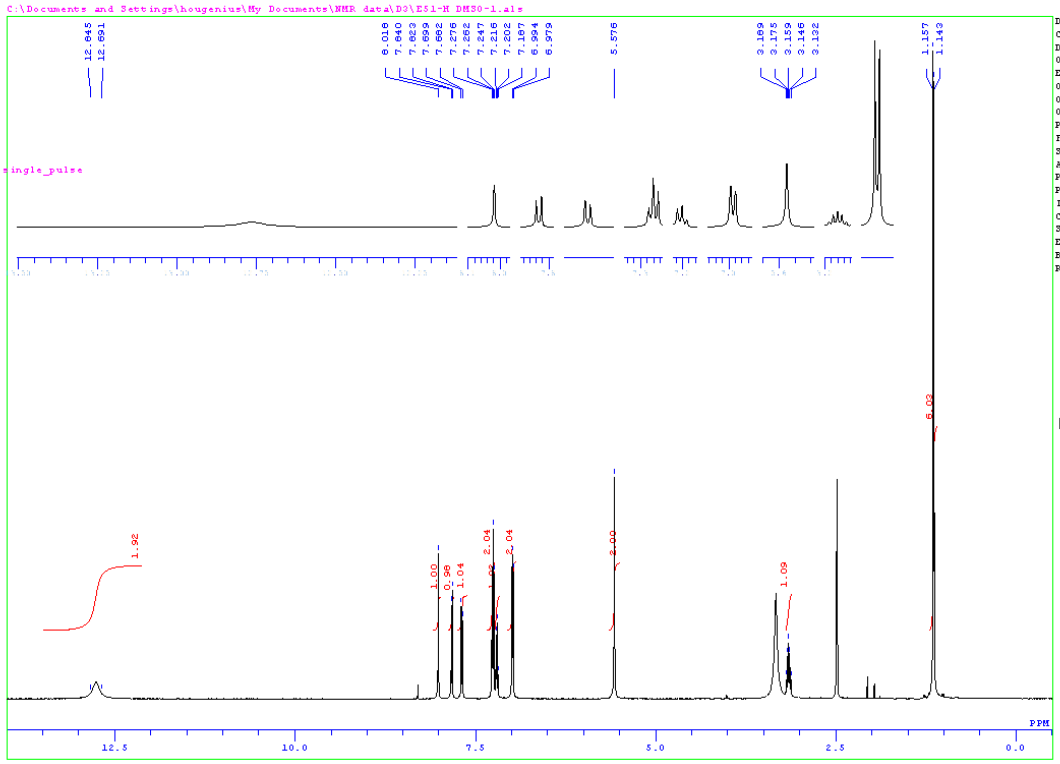
5e

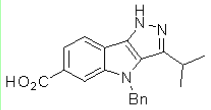



```
DFILE  E66-C DMSO-1.als
COMNT  single pulse decoupled gat
DATIM  2012-11-27 13:37:30
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.06 Hz
SCANS           427
ACQTM         0.8336 sec
PD            2.0000 sec
PW1           11.20 usec
IRNUC  1H
CTEMP         28.8 c
SLVNT  DMSO
EXREF         39.50 ppm
BF            0.12 Hz
RGAIN           58
```

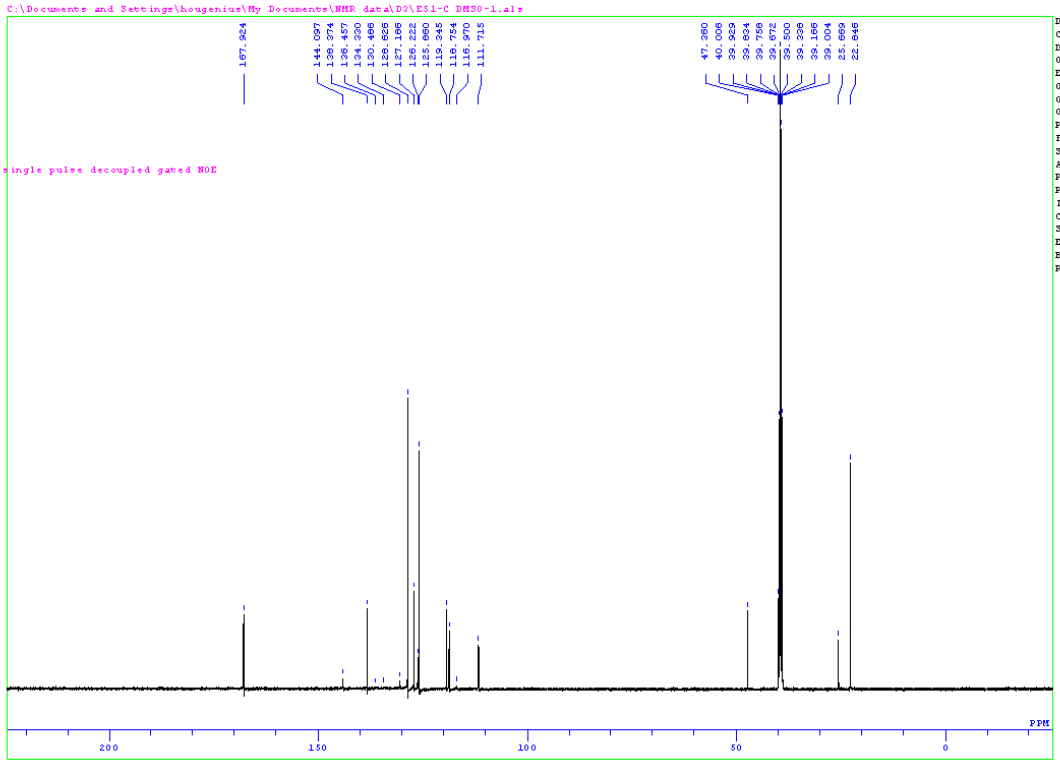


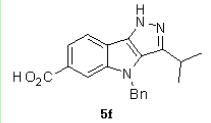
5e


C:\Documents and Settings\hougenius\My Documents\NMR data\D3\E51-H DMSO-1.als
12.845
12.691
8.016
7.840
7.823
7.699
7.692
7.276
7.262
7.247
7.216
7.202
7.167
6.994
6.979
5.576
3.169
3.175
3.159
3.146
3.132
1.157
1.143
single_pulse
1.92
1.00
0.98
1.04
2.04
2.04
3.00
1.09
6.02
PPM
12.5
10.0
7.5
5.0
2.5
0.0
DFILE E51-H DMSO-1.als
COMNT single_pulse
DATIM 2012-11-13 22:51:45
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 10019.89 Hz
SCANS 8
ACQTM 1.3081 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 23.1 c
SLVNT DMSO
EXREF 2.49 ppm
BF 0.12 Hz
RGAIN 44

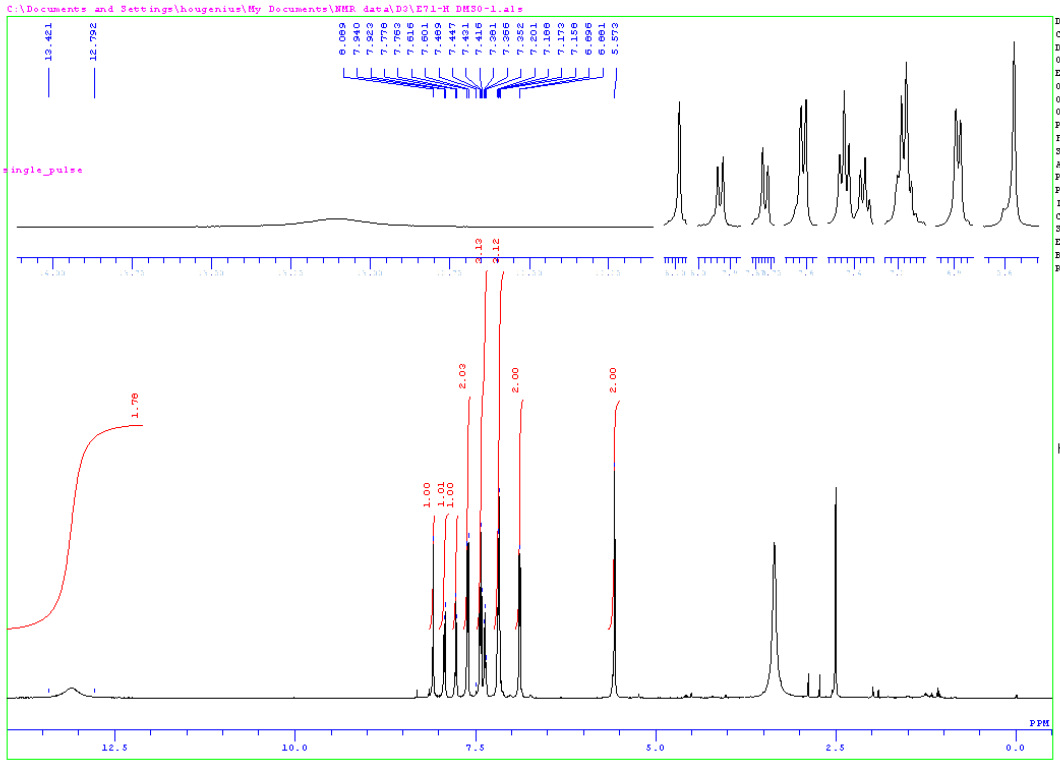

H
N
N
HO2C
N
Bn

5f

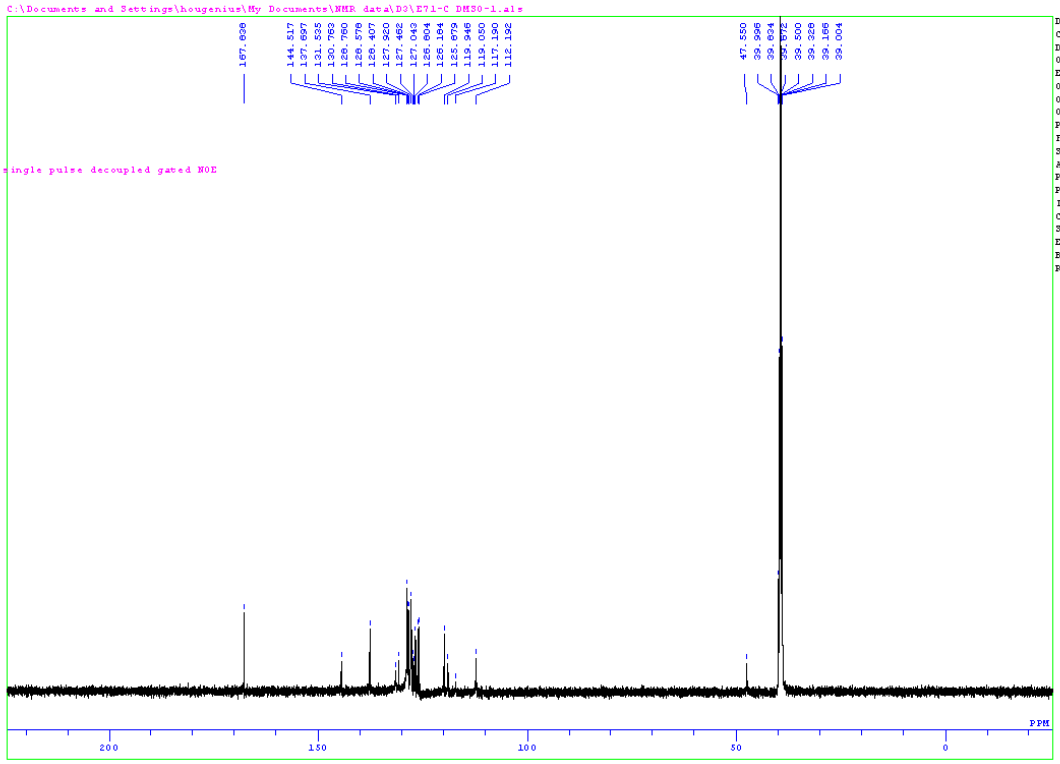

C:\Documents and Settings\hougenius\My Documents\NMR data\D3\E51-C DMSO-1.als
167.924
144.097
138.274
136.457
134.230
130.466
128.625
127.166
126.222
125.660
119.345
118.754
116.970
111.715
47.360
40.006
39.823
39.634
39.756
39.672
39.500
39.338
39.166
39.004
25.669
22.646
single pulse decoupled gated NOE
PPM
200
150
100
50
0
DFILE E51-C DMSO-1.als
COMNT single pulse decoupled gat
DATIM 2012-11-14 09:18:17
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 13215
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 11.20 usec
IRNUC 1H
CTEMP 23.3 c
SLVNT DMSO
EXREF 39.50 ppm
BF 0.12 Hz
RGAIN 54


H
N
N
HO2C
N
Bn

5f


C:\Documents and Settings\hougenius\My Documents\NMR data\D3\E71-H DMSO-1.als
single_pulse
12.421
12.792
8.099
7.940
7.923
7.778
7.763
7.616
7.601
7.469
7.447
7.431
7.416
7.361
7.266
7.252
7.201
7.166
7.173
7.150
6.696
6.681
5.573
1.78
2.03
2.13
2.12
2.00
2.00
1.00
1.01
1.00
PPM
12.5
10.0
7.5
5.0
2.5
0.0
DFILE E71-H DMSO-1.als
COMNT single_pulse
DATIM 2012-12-18 09:54:49
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 10019.89 Hz
SCANS 8
ACQTM 1.3081 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 26.4 c
SLVNT DMSO
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 42
HO2C
N
H
N
Bn

5g


C:\Documents and Settings\hougenius\My Documents\NMR data\D3\E71-C DMSO-1.als
single pulse decoupled gated NOE
167.606
144.517
137.697
131.585
130.782
129.760
128.579
128.407
127.320
127.462
127.043
126.604
126.184
125.879
119.946
119.050
117.190
112.192
47.550
39.996
39.834
39.672
39.500
39.328
39.166
39.004
PPM
200
150
100
50
0
DFILE E71-C DMSO-1.als
COMNT single pulse decoupled gat
DATIM 2012-12-03 10:44:03
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 1000
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 11.20 usec
IRNUC 1H
CTEMP 27.7 c
SLVNT DMSO
EXREF 39.50 ppm
BF 0.12 Hz
RGAIN 58
HO2C
N
H
N
Bn

5g