Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Electronic Supporting Information

Evaluating hydrogen bonding control in the diastereoselective Diels-Alder cycloadditions of 9-(2-aminoethyl)-anthracene derivatives

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Experimental details of known compounds

Copies of 1H and 13C NMR spectra

Experimental details of known compounds

1-(9-Anthryl)ethanimine 7[1] A solution of methyl iodide (2.80 mL, 45 mmol) in dry diethyl ether (20 mL) was added drop-wise to a stirred suspension of magnesium turnings (1.45 g, 59.6 mmol) in dry ether (10 mL) at room temperature. The resulting Grignard reagent was heated at reflux for 45 min and cooled to room temperature. A warm solution of 9-cyanoanthracene **6** (3.00 g, 14.8 mmol) in dry toluene (100 mL) was added drop-wise over 25 min. The reaction mixture was heated at reflux under a nitrogen atmosphere for 72 h, cooled to 0 °C and saturated aqueous NH_4Cl (200 mL) was added slowly. The organic layer was separated, and the aqueous layer extracted with diethyl ether (2 x 10 mL). The combined organic layers were washed with brine (2 × 30 mL), dried over Na_2SO_4, filtered and the solvent evaporated. The crude imine was purified by column chromatography on silica gel, eluting with 30% EtOAc/CH_2Cl_2, giving the title compound **7** as brown crystals (1.81 g, 56%); mp 83–86 °C (lit.[2] 81–83 °C); δ_H (250 MHz; $CDCl_3$; Me_4Si) 8.38 (1 H, s, ArC*H*), 8.00–7.89 (4 H, m, ArC*H*), 7.53–7.43 (4 H, m, ArC*H*), 2.61 (3 H, s, CH_3); δ_C (63 MHz; $CDCl_3$; Me_4Si) 180.5 (*C*=N), 137.3 (Ar*C*), 131.2 (2 × Ar*C*), 128.7 (2 × Ar*C*H), 127.2 (Ar*C*H), 126.6 (2 × Ar*C*), 126.4 (2 × Ar*C*H), 125.5 (2 × Ar*C*H), 124.9 (2 × Ar*C*H), 29.1 (*C*H_3). NMR data was in accordance with the literature.

***rac*-1-(9-Anthryl)ethylamine 3**[1] $Na(CN)BH_3$ (5.11 g, 81.1 mmol), was added slowly to a stirred solution of 1-(9-anthryl)ethanimine **7** (5.19 g, 23.7 mmol) in glacial acetic acid (100 mL) and the reaction mixture was stirred for 72 h at room temperature. The resulting mixture was poured slowly into a beaker containing water (200 mL) and neutralized to pH 7 with solid Na_2CO_3. The mixture was extracted with CH_2Cl_2 (3 × 60 mL), dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure to give the target amine. The crude material was purified by column chromatography on silica gel eluting with 10% MeOH/CH_2Cl_2 to afford the desired amine **3** as yellow crystals (1.92 g, 37%); mp 104–107 °C [lit.[3] 113–115 °C for (*S*) enantiomer]; δ_H (250 MHz; $CDCl_3$; Me_4Si) 8.54 (2 H, br s, ArC*H*), 8.20 (1 H, s, ArC*H*), 7.86–7.82 (2 H, m, ArC*H*), 7.38–7.26 (4 H, m, ArC*H*), 5.61 (1 H, q, *J* 6.9, CH_3C*H*), 2.93 (2 H, br s, NH_2), 1.70 (3 H, d, *J* 6.9, CH_3); δ_C (63 MHz; $CDCl_3$; Me_4Si) 136.9 (Ar*C*), 131.9 (2 × Ar*C*), 129.5 (2 × Ar*C*H), 129.1 (2 × Ar*C*), 127.6 (Ar*C*H), 125.7 (2 × Ar*C*H), 125.4 (2 × Ar*C*H), 124.7 (2 × Ar*C*H), 46.4 (CH), 23.7 (CH_3). NMR data was in accordance with the literature.

(±)-*N*-[1-(9-Anthryl)ethyl]acetamide 8[4]

rac-1-(9-Anthryl)ethylamine **3** (1.89 g, 8.60 mmol) was dissolved in acetic anhydride (55 mL) and stirred for 2 h at room temperature. The reaction mixture was diluted with water (40 mL), neutralized to pH 7 with solid Na_2CO_3 and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic extracts were dried over Na_2SO_4, filtered and evaporated. The crude material was purified by column chromatography on silica gel eluting with 30% EtOAc/CH_2Cl_2 to give the title compound **8** as yellow crystals (0.66 g, 29% yield); Mpt. 205–208 °C (lit.[4] 209–211 °C); δ_H (250 MHz; $CDCl_3$; Me_4Si) 8.44 (2 H, d, *J* 8.9, ArC*H*), 8.43 (1 H, s, ArC*H*), 8.05–8.02 (2 H, m, ArC*H*), 7.58–7.45 (4 H, m, ArC*H*), 6.62 (1 H, pent, *J* 6.9, C*H*NH), 6.51 (1 H, br d, N*H*), 1.97 (3 H, s, CH_3CO), 1.94 (3 H, d, *J* 6.9, CH_3CH); δ_C (62.5 MHz; $CDCl_3$; Me_4Si) 169.6 (*C*=O), 133.8 (Ar*C*), 131.7 (2 × Ar*C*), 129.7 (2 × ArCH), 128.8 (2 × Ar*C*), 128.0 (Ar*C*H), 126.2 (2 × Ar*C*H), 124.8 (2 × Ar*C*H), 123.9 (2 × Ar*C*H), 44.9 (*C*H), 23.4 (*C*H_3), 21.6 (*C*H_3CO). The literature reference is missing a methyl signal at δ 1.97. Otherwise, NMR data was in accordance with the literature.

References

1. S. Levinger, R. Nair, and A. Hassner, *Beilstein J. Org. Chem.*, 2008, **4**, 32.

2. M. Martynoff, *Compt. rend.*, 1956, **242**, 787–790.

3. M. Hernandez-Rodriguez, T. Castillo-Hernandez, and K. E. Trejo-Huizar, *Synthesis (Stuttg).*, 2011, 2817–2821.

4. M. Roje and V. Sunjić, *Chirality*, 2002, **14**, 625–31.

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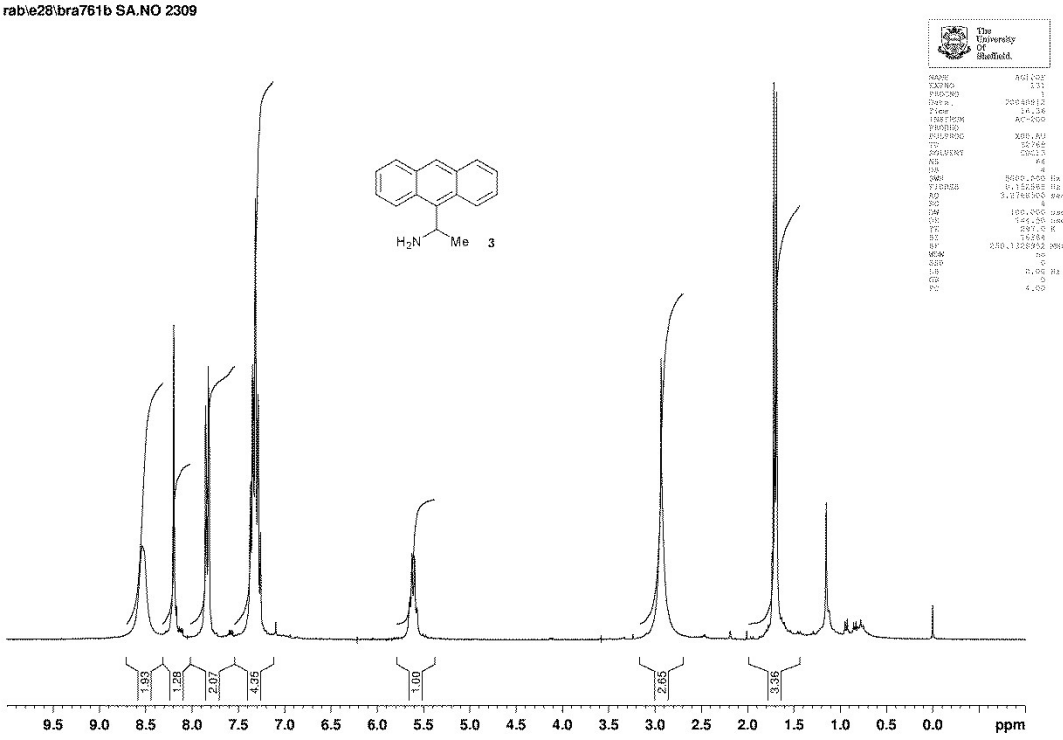

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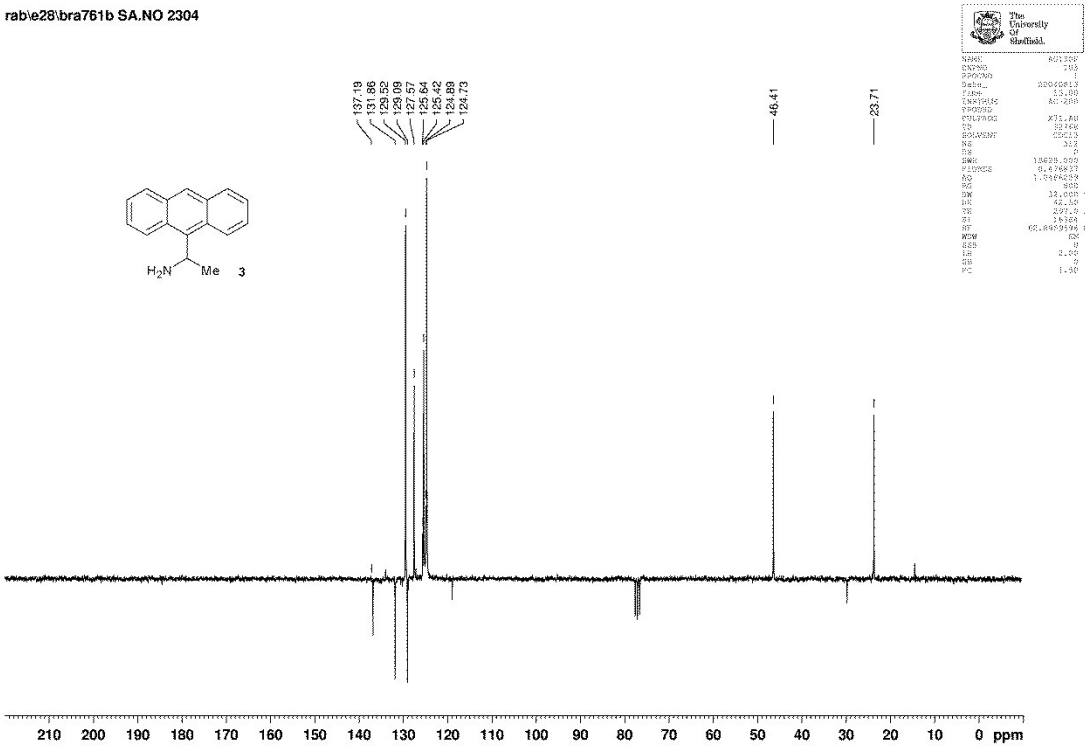

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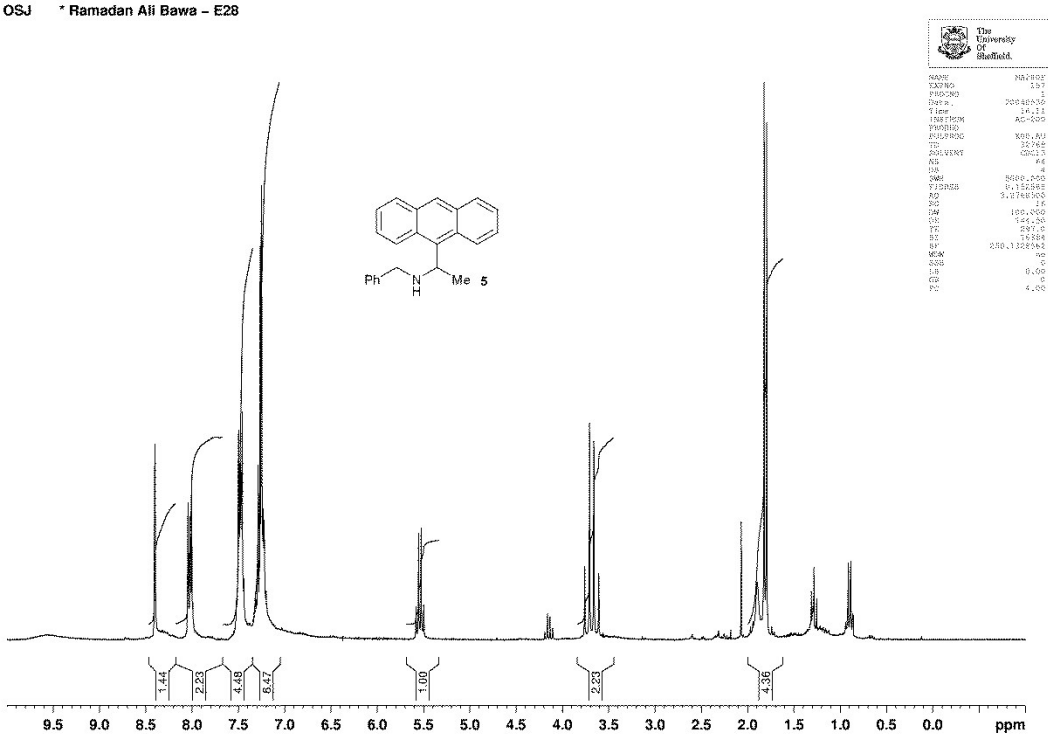

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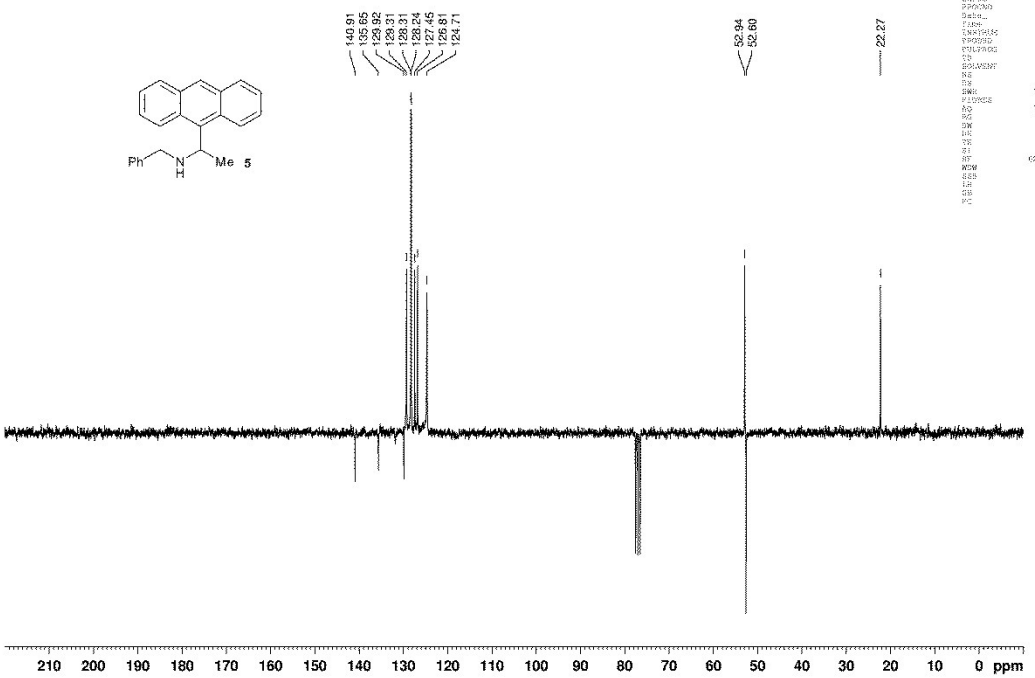

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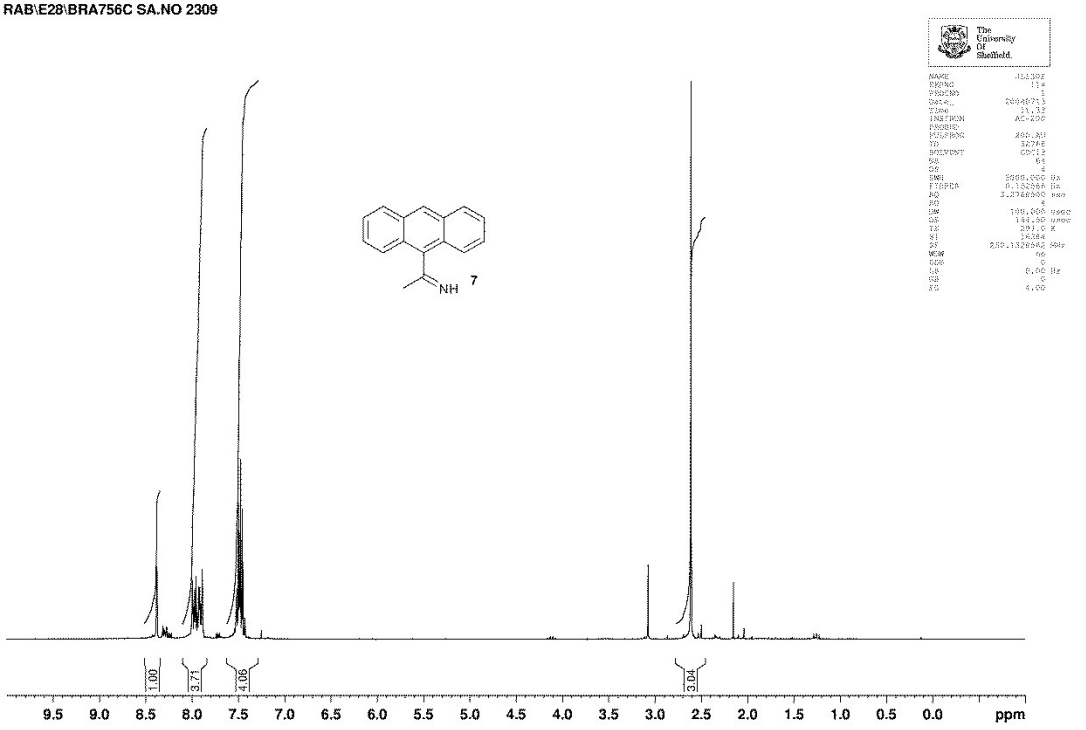

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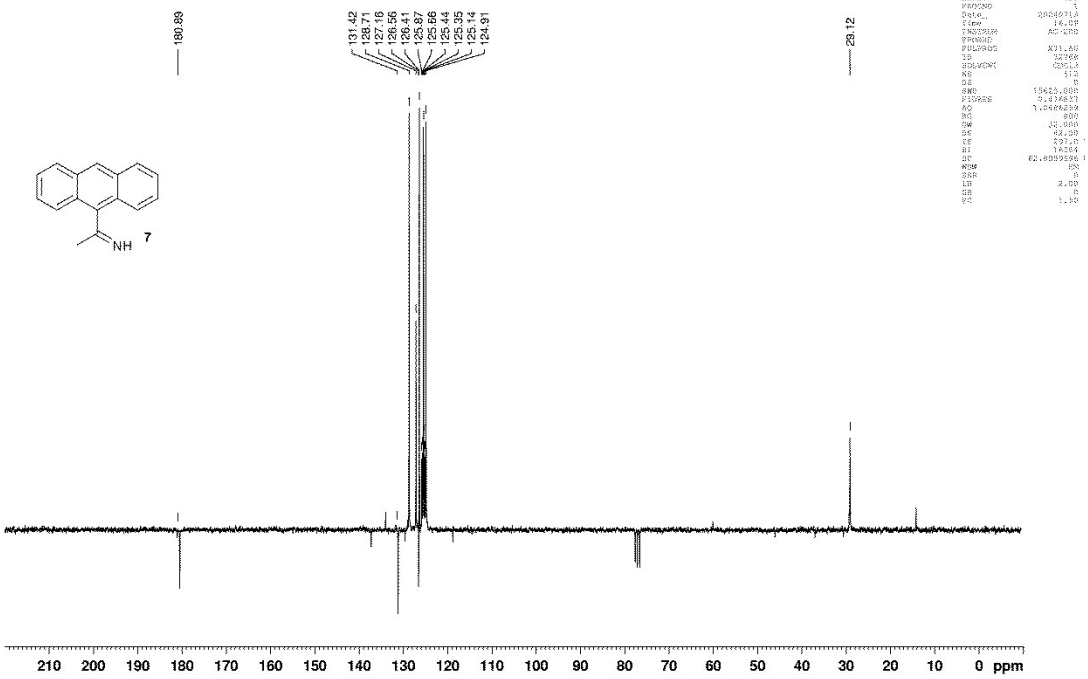

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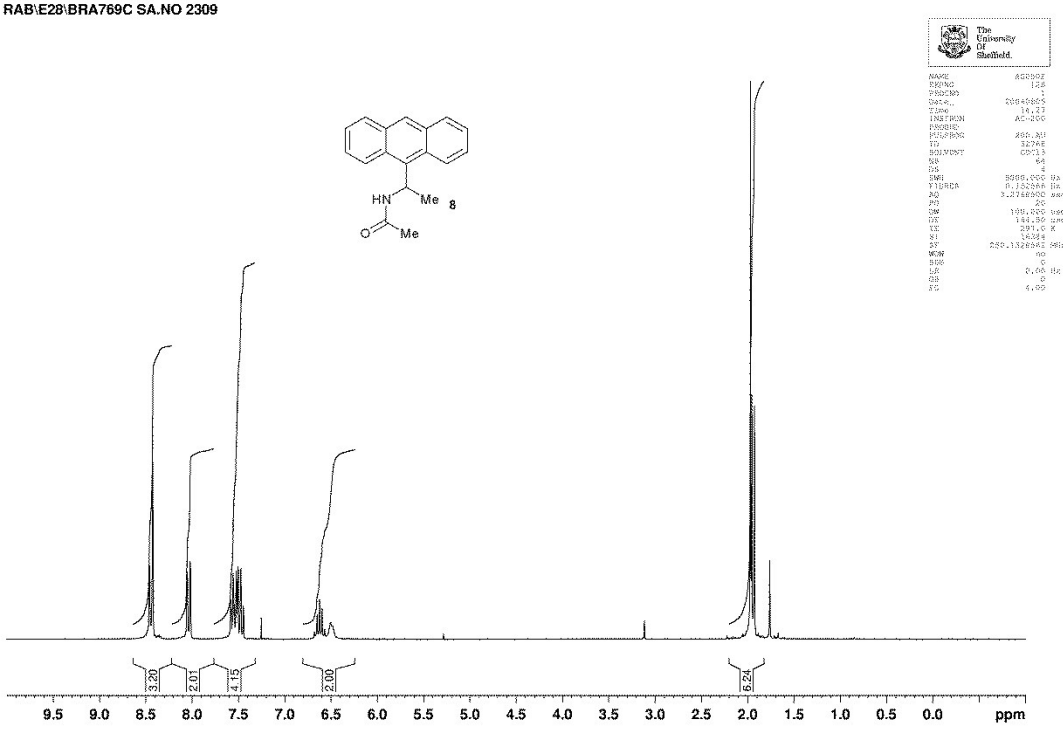

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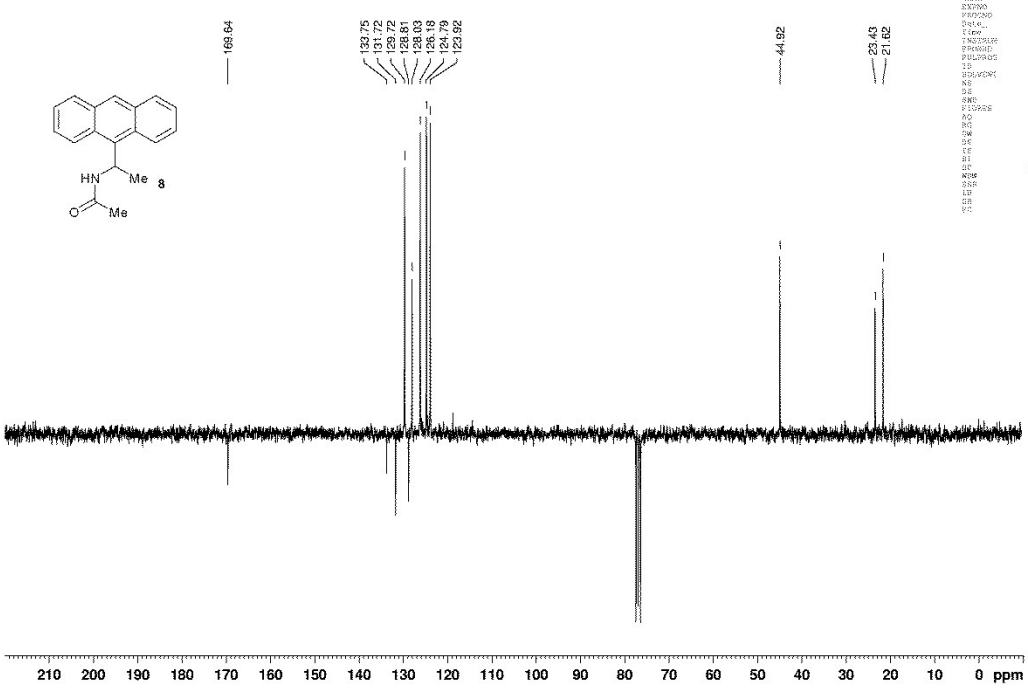

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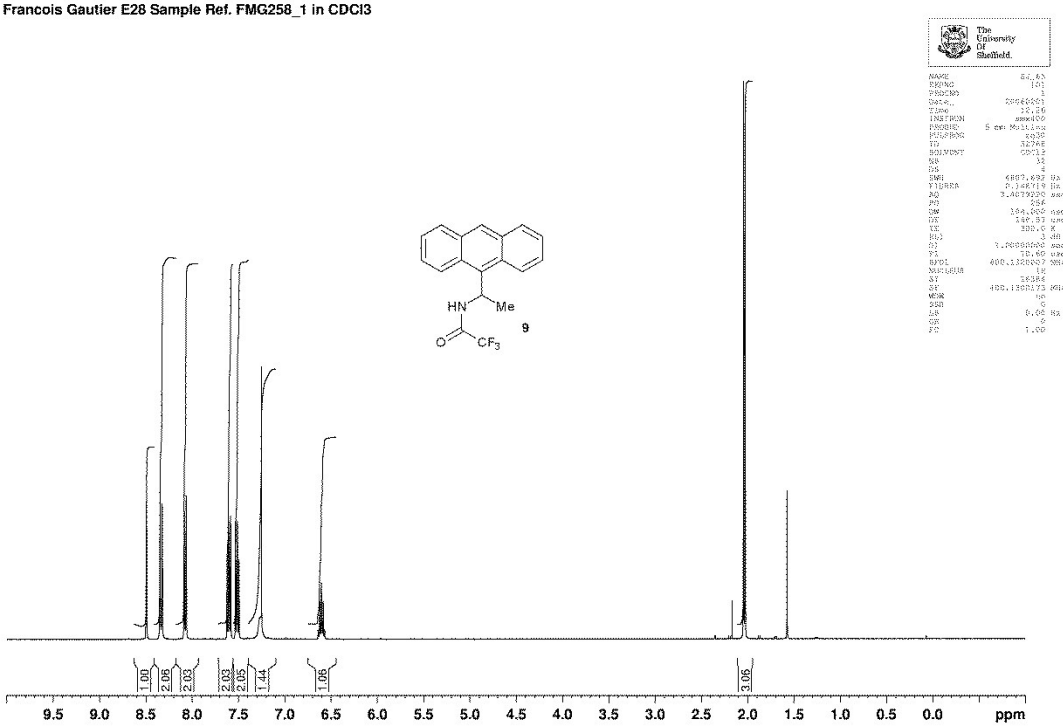

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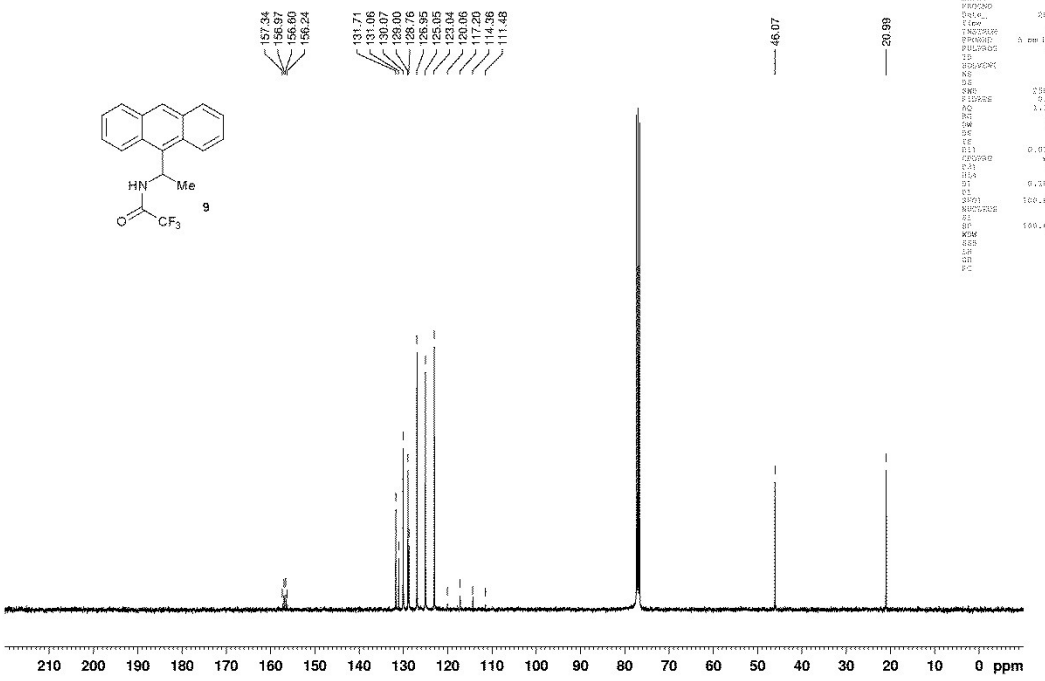

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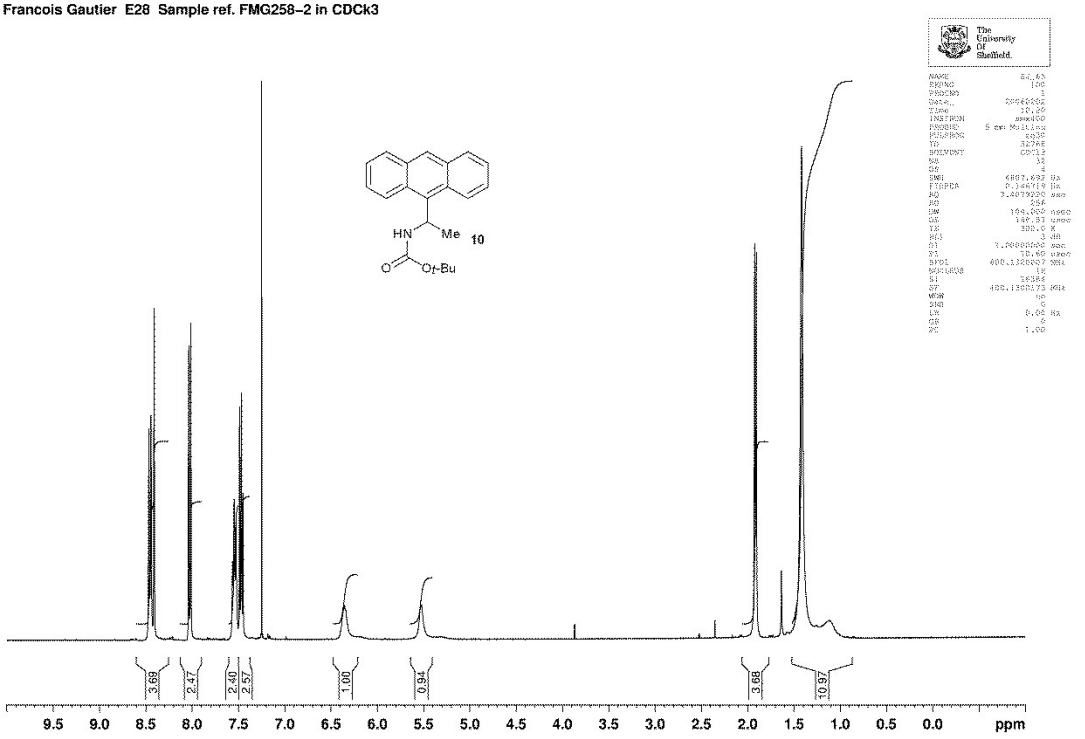

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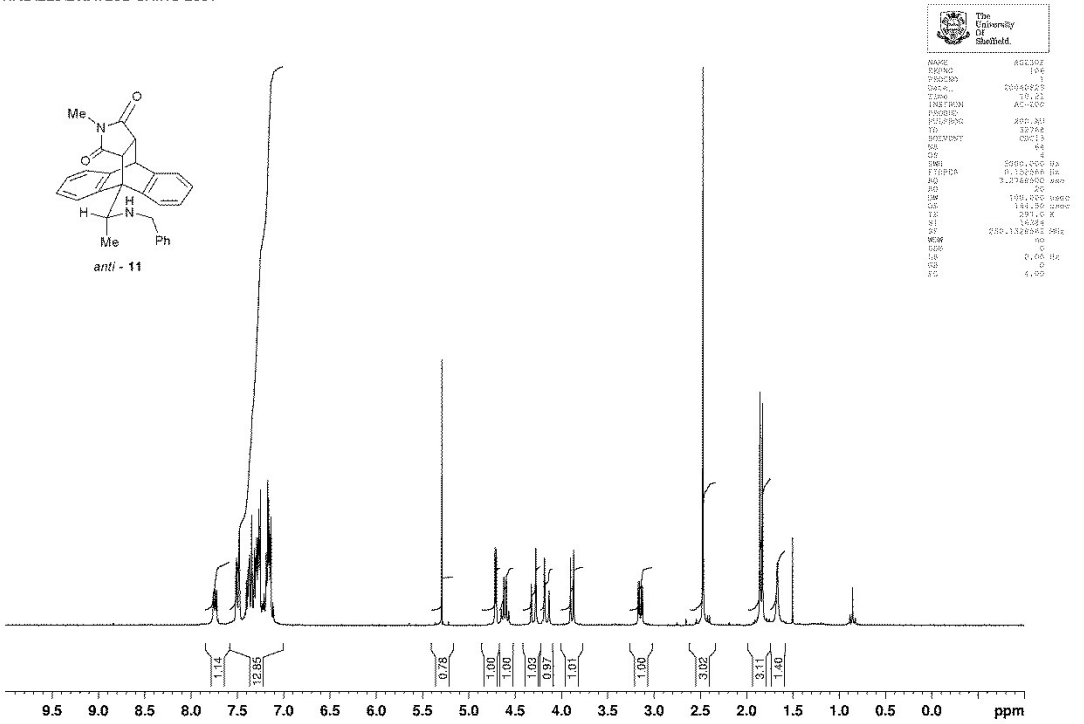

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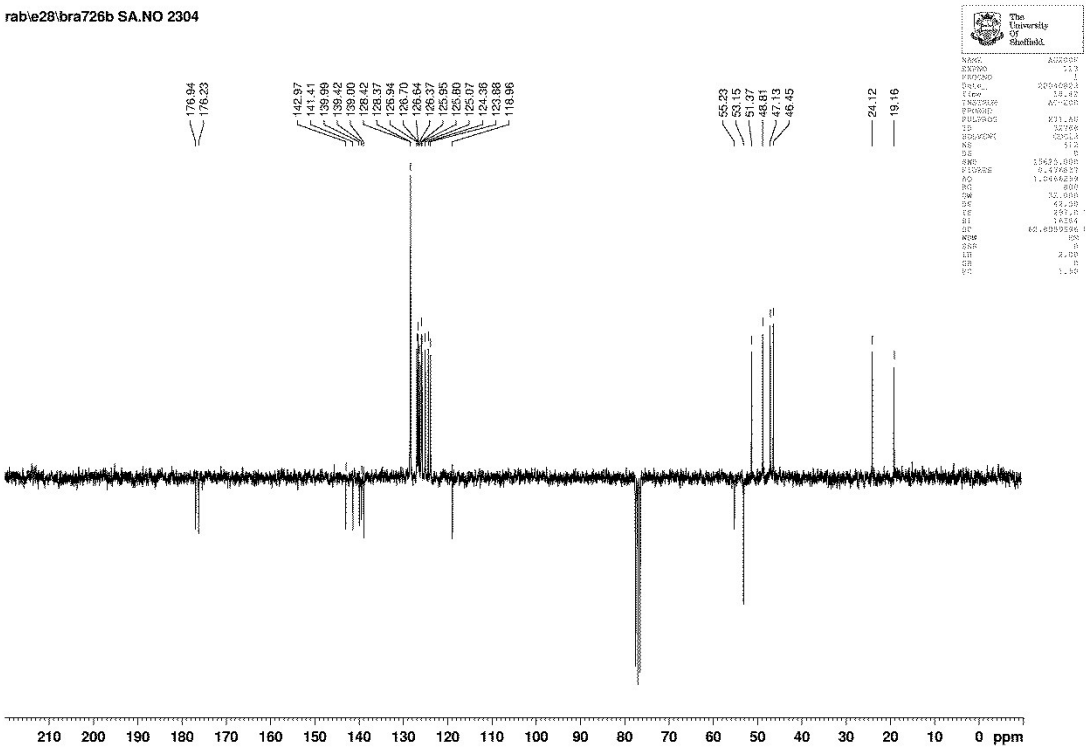

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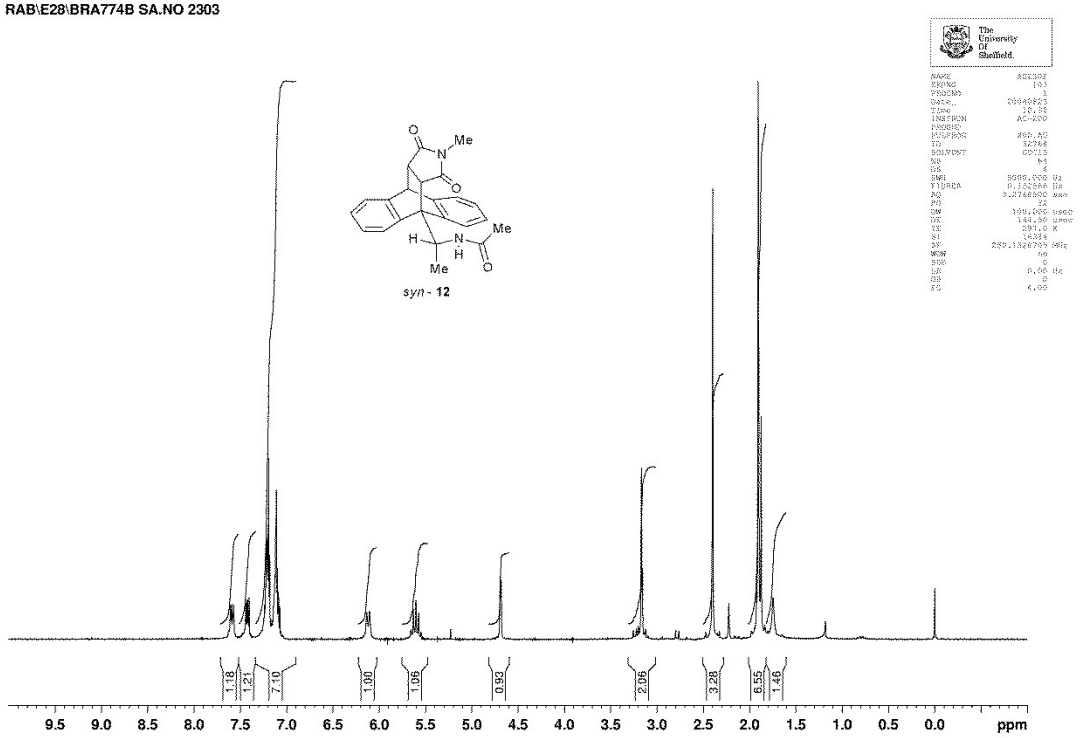

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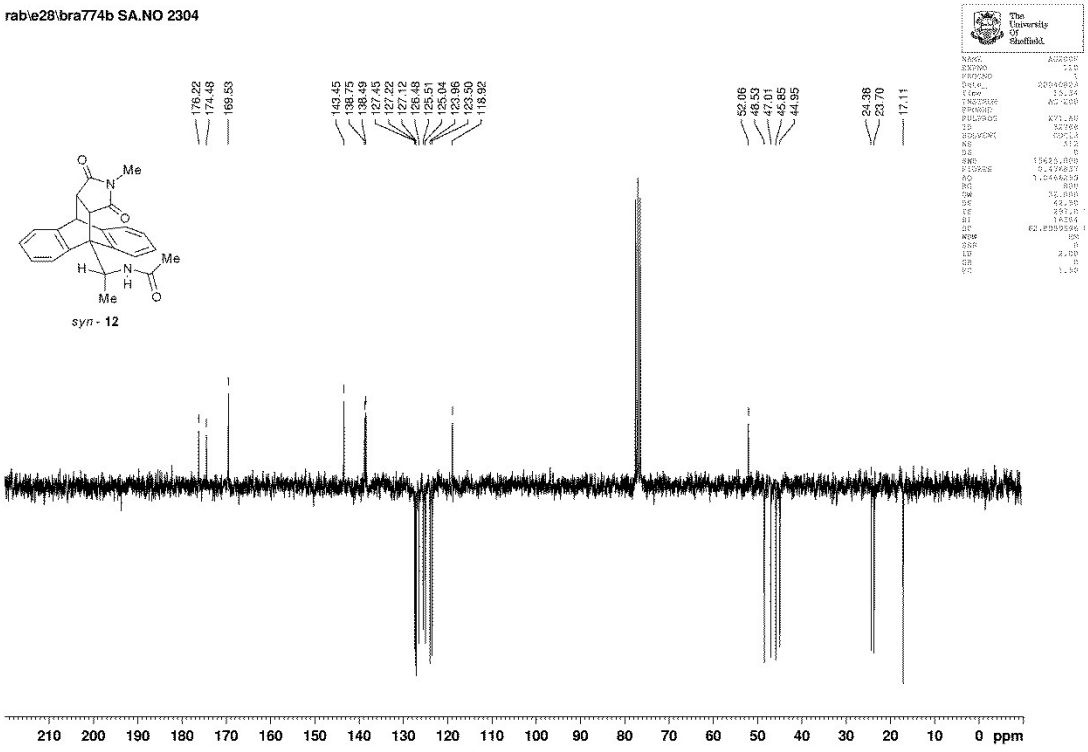

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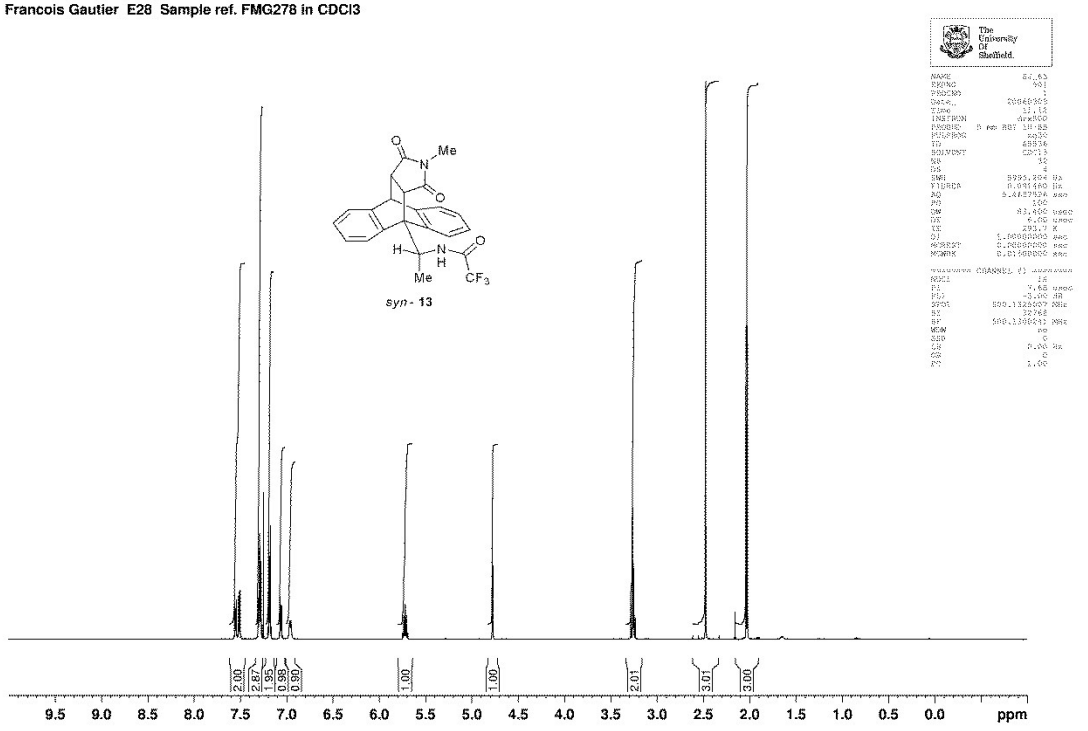

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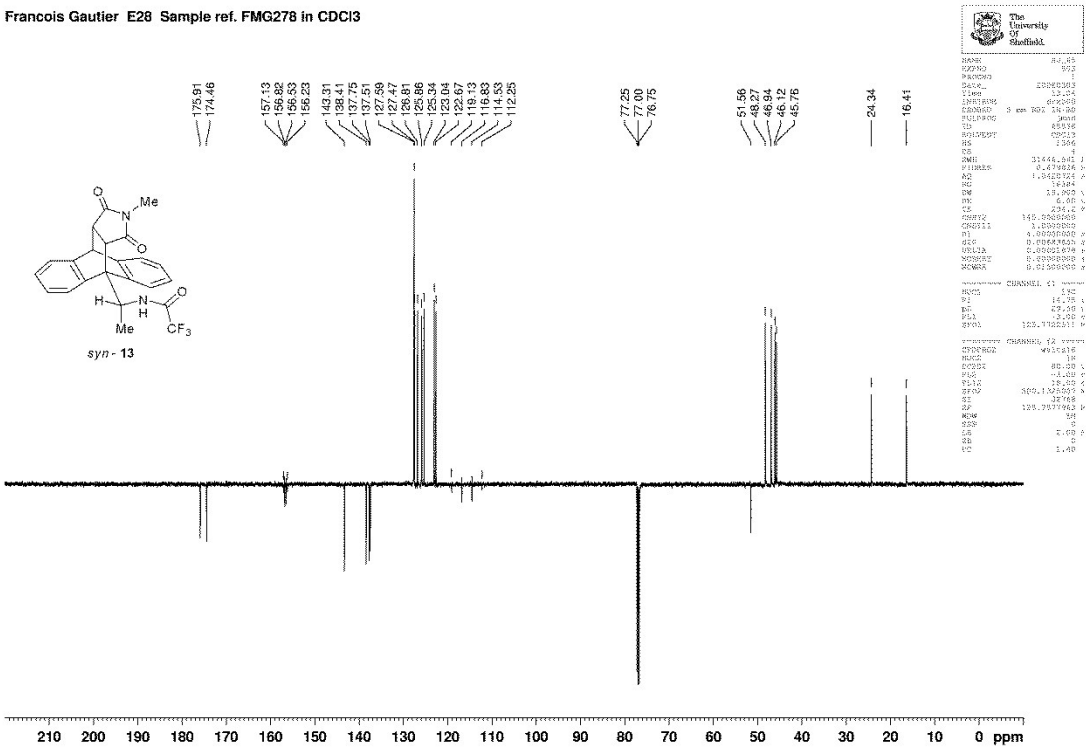

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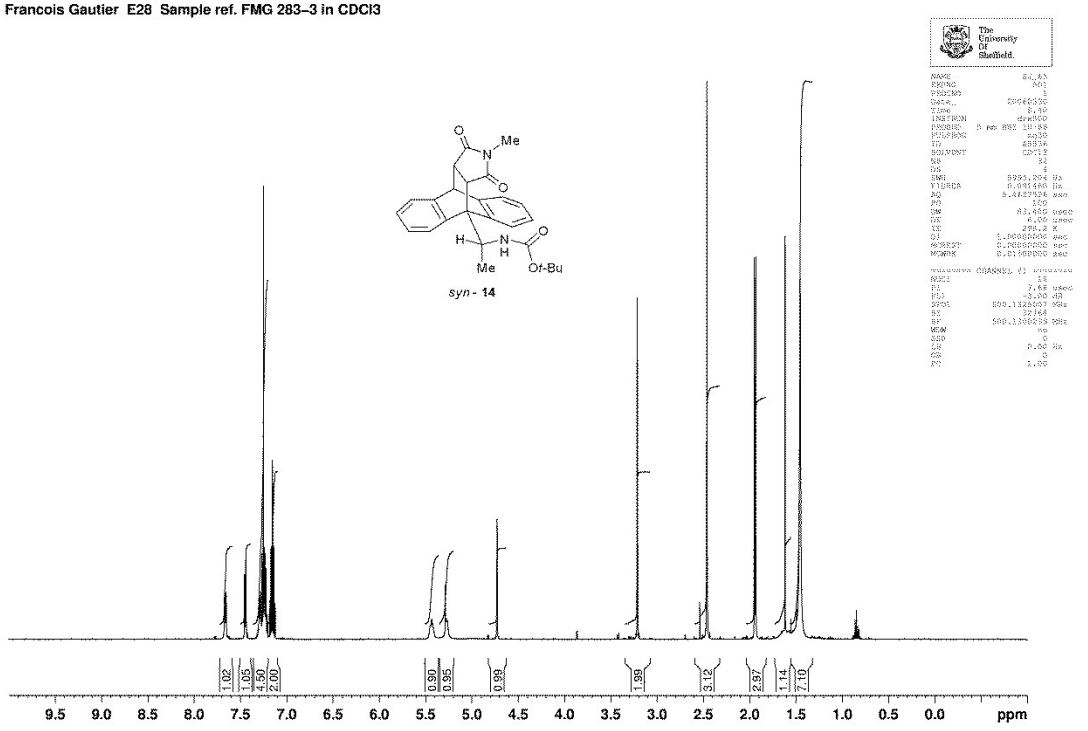

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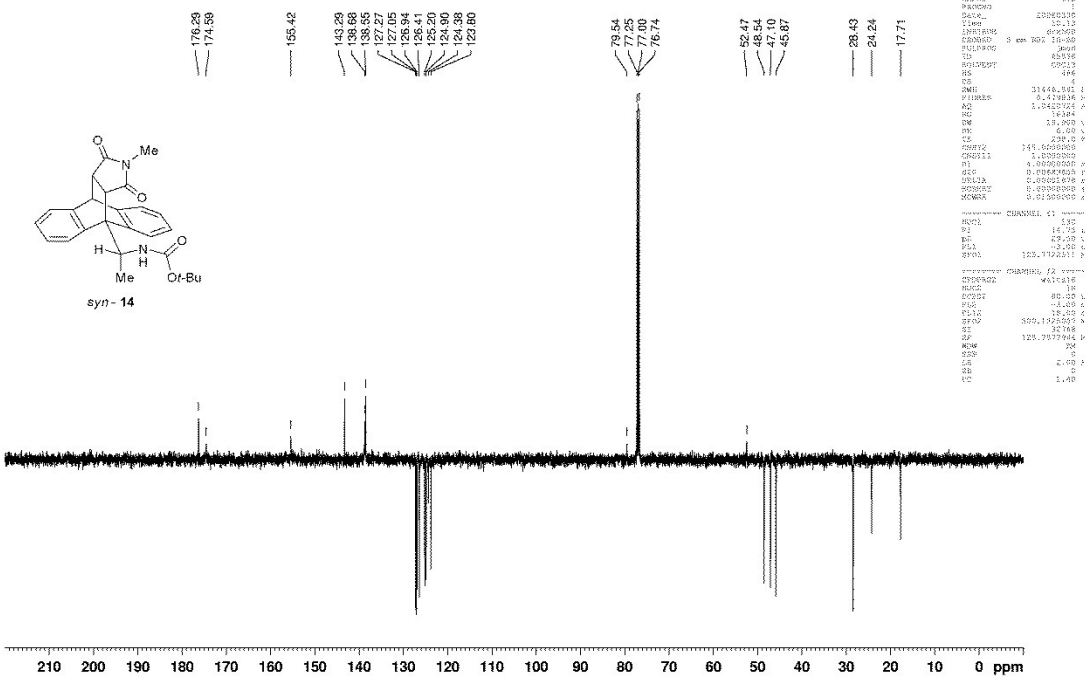

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