Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

Environmentally Friendly Approach to α-Acyloxy carboxamides *via* a Chemoenzymatic Cascade

Daniel Paprocki,[a] Dominik Koszelewski,[a] Anna Żądło,[a] Peter Walde[b] and Ryszard Ostaszewski*[a]

[a] Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland. E-mail: ryszard.ostaszewski@icho.edu.pl

[b] Laboratory of Polymer Chemistry, Department of Materials, ETH Zurich, Vladimir-Prelog-Weg 5, 8093 Zurich, Switzerland

Synthesis of *N*-(4-methoxybenzyl)formamide:

Reaction conditions: 4-methoxybenzyl amine (30 mmol; 3.8 ml) and ethyl formate (12.5 ml) were heated under reflux overnight. After cooling the reaction mixture to room temperature, 5 ml hexane were added. The precipitate was filtered and washed with hexane. Yield 78 % (3.86 g).

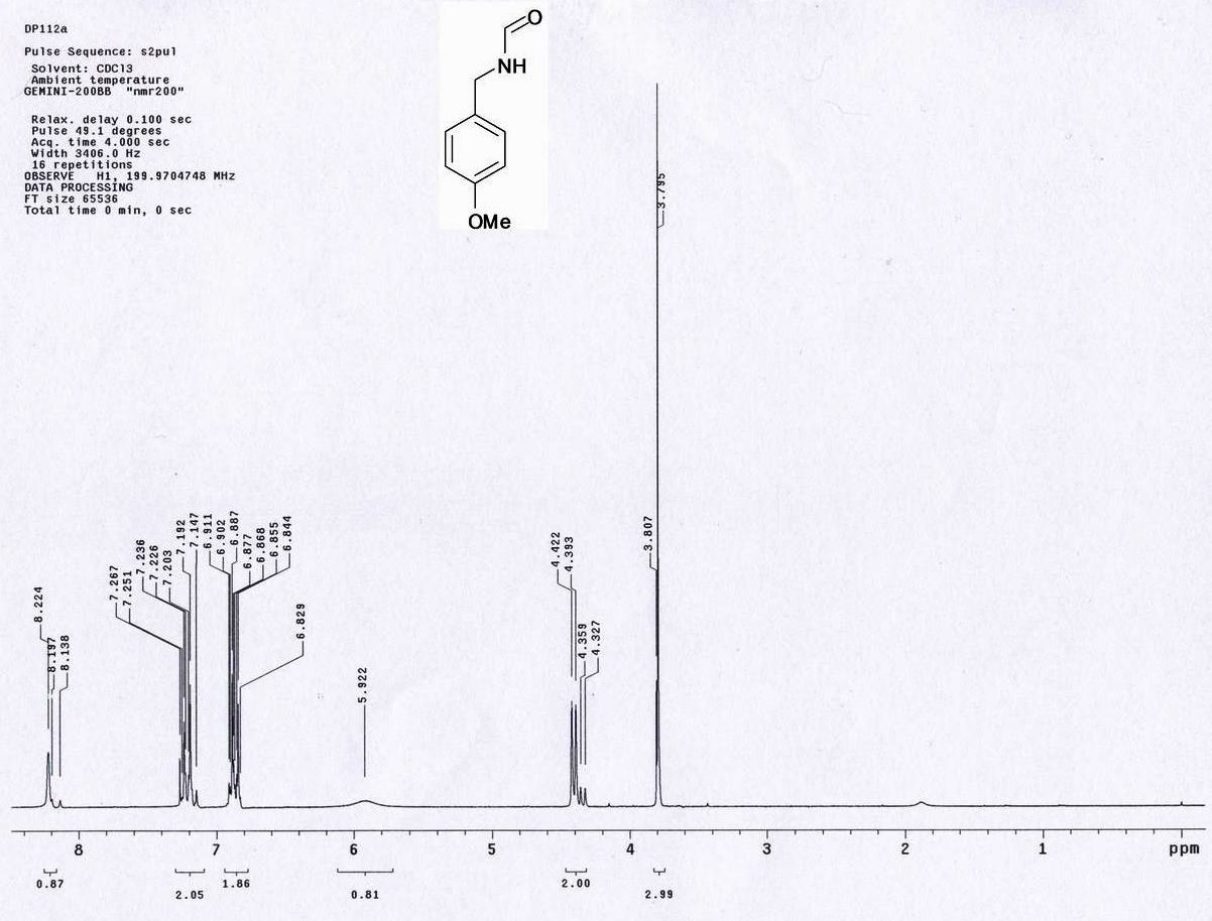


Figure S1. ^{1}H NMR spectrum of *N*-(4-methoxybenzyl)formamide (200 MHz, $CDCl_3$).

Synthesis of *p*-methoxybenzyl isocyanide (4a):

Reaction conditions: To a solution of *N*-(4-methoxybenzyl)formamide (16 mmol; 2.64 g) and triethylamine (48 mmol; 6.7 ml) in dry dichloromethane (20 ml) at -78°C phosphoryl oxychloride (20 mmol; 1.85 ml) was added dropwise. After 1 h of stirring at room temperature, the reaction mixture was quenched by adding a saturated solution of $NaHCO_3$ (20 mL), then extracted with dichloromethane (2×20 mL). The combined organic layers were dried with $MgSO_4$ and residuals of solvent were distilled under reduced pressure. The crude product was purified by column chromatography on silica gel using hexane/AcOEt as an eluent. Yield 80 % (1.88 g).

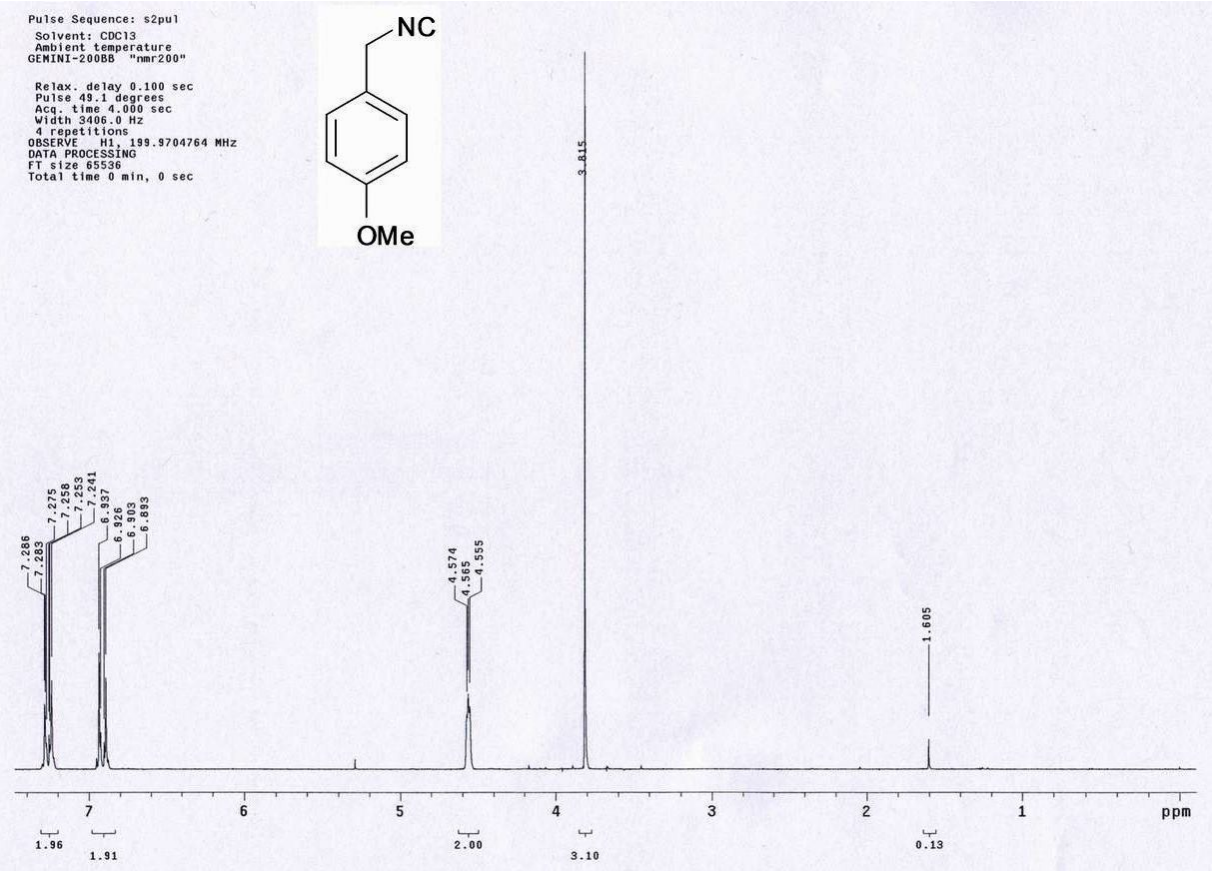


Figure S2. ^{1}H NMR spectrum of compound **4a** (200 MHz, $CDCl_3$).

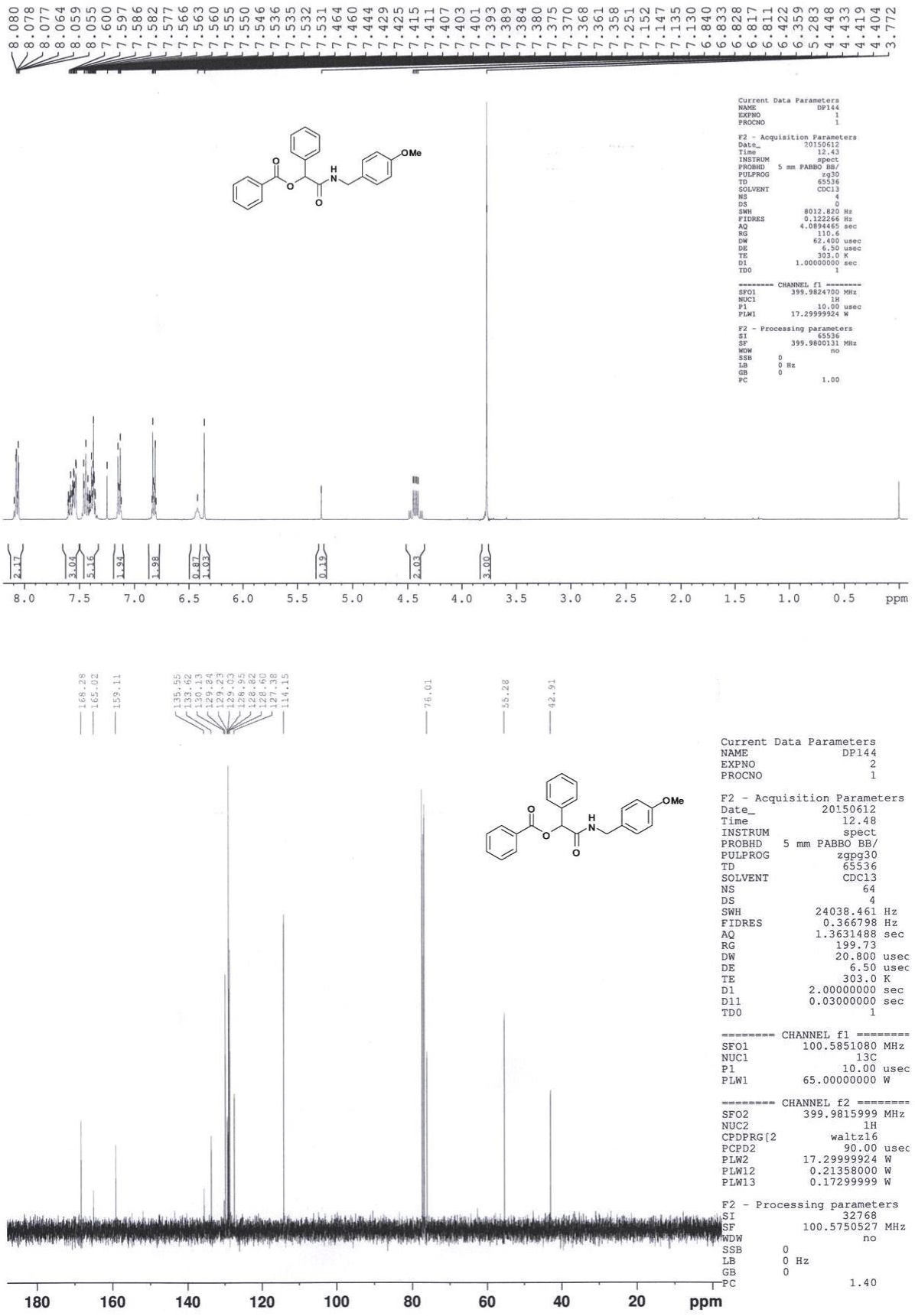


Figure S3. ^{1}H NMR (above) and ^{13}C NMR (below) spectra of compound **5a** (400 MHz, $CDCl_3$).

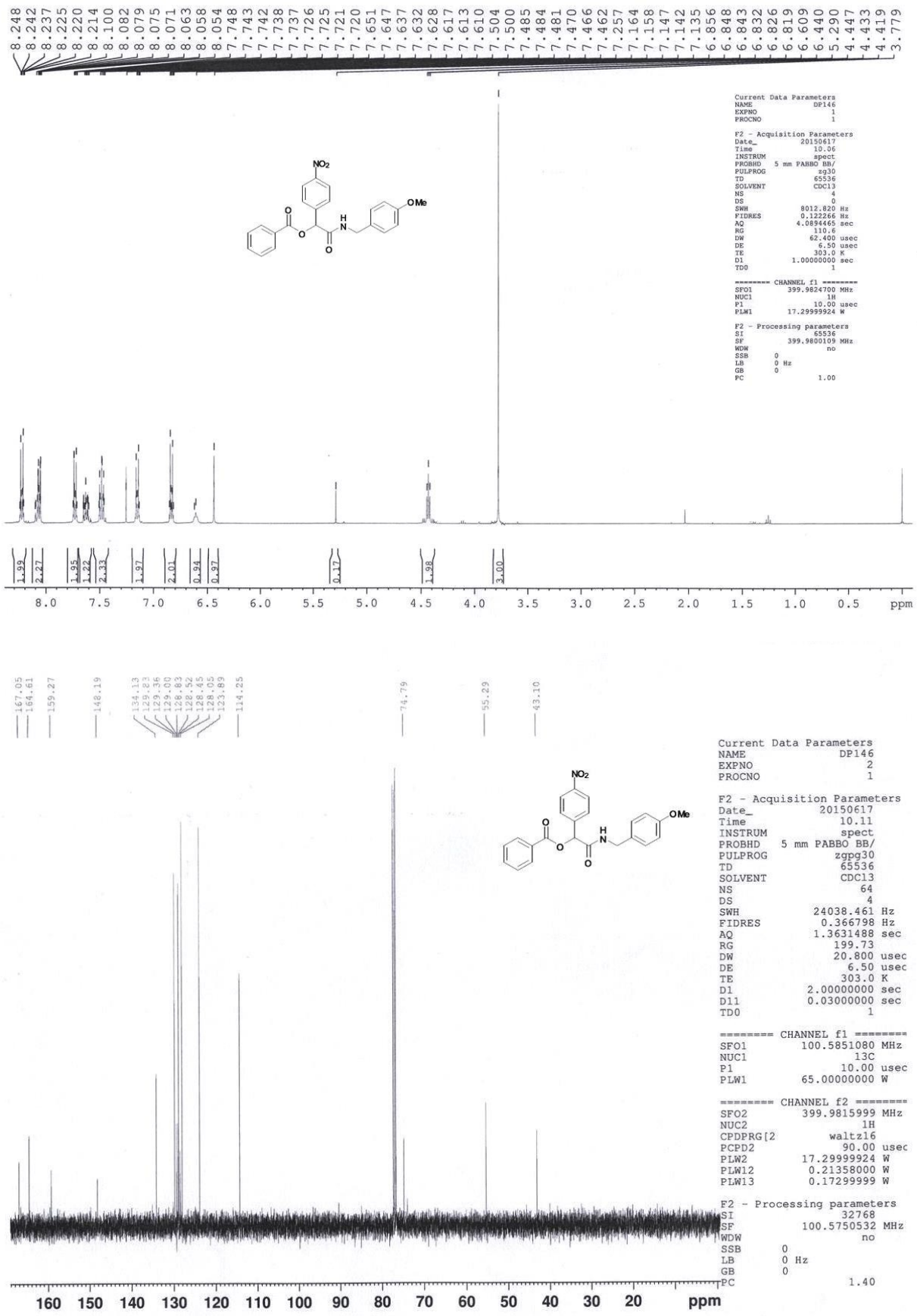


Figure S4. ^{1}H NMR (above) and ^{13}C NMR (below) spectra of compound **5b** (400 MHz, $CDCl_3$).

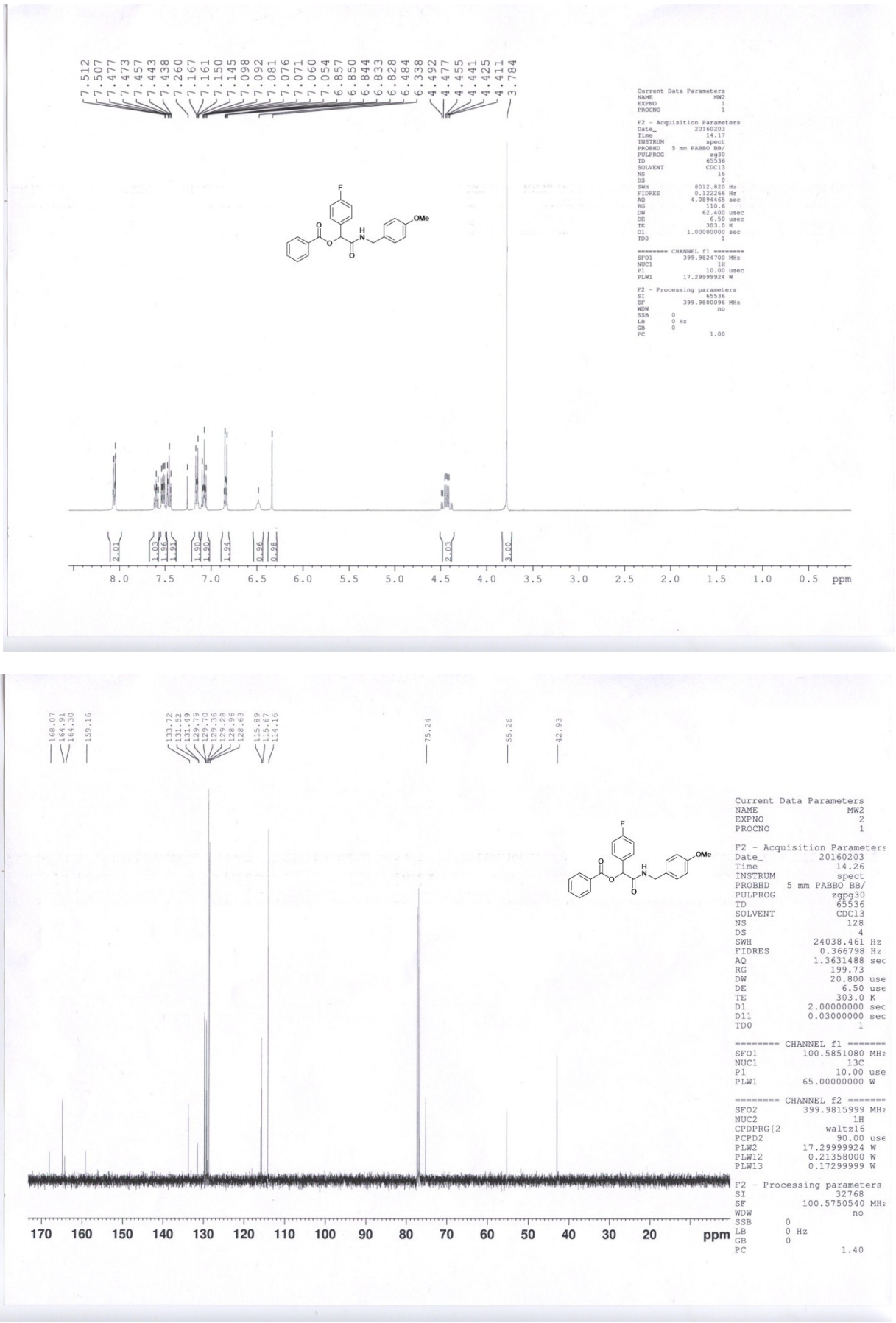


Figure S5. ^{1}H NMR (above) and ^{13}C NMR (below) spectra of compound **5c** (400 MHz, $CDCl_3$).

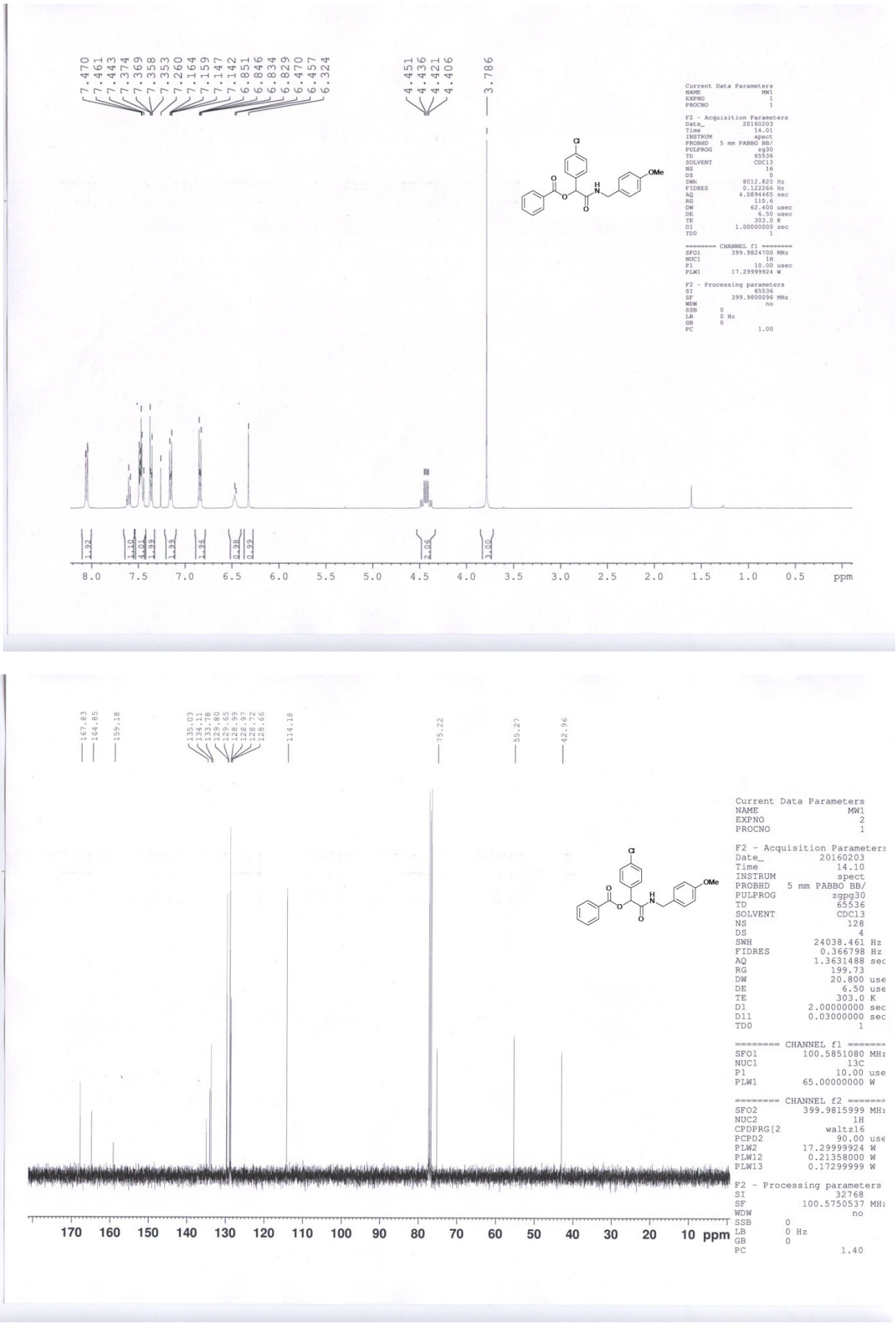
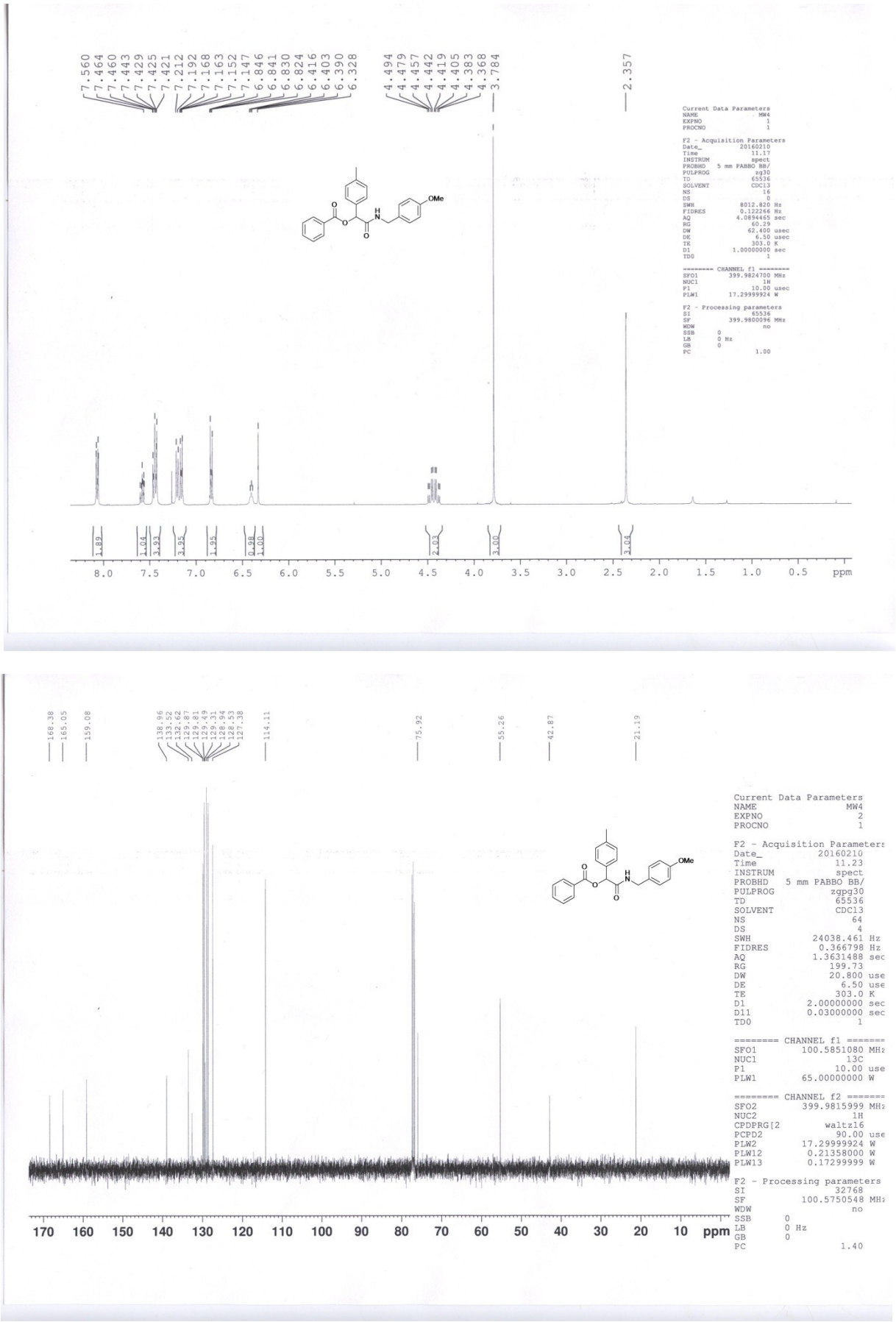


Figure S6. ^{1}H NMR (above) and ^{13}C NMR (below) spectra of compound **5d** (400 MHz, $CDCl_3$).



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PROCNO 1

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Figure S7. ^{1}H NMR (above) and ^{13}C NMR (below) spectra of compound **5e** (400 MHz, $CDCl_3$).

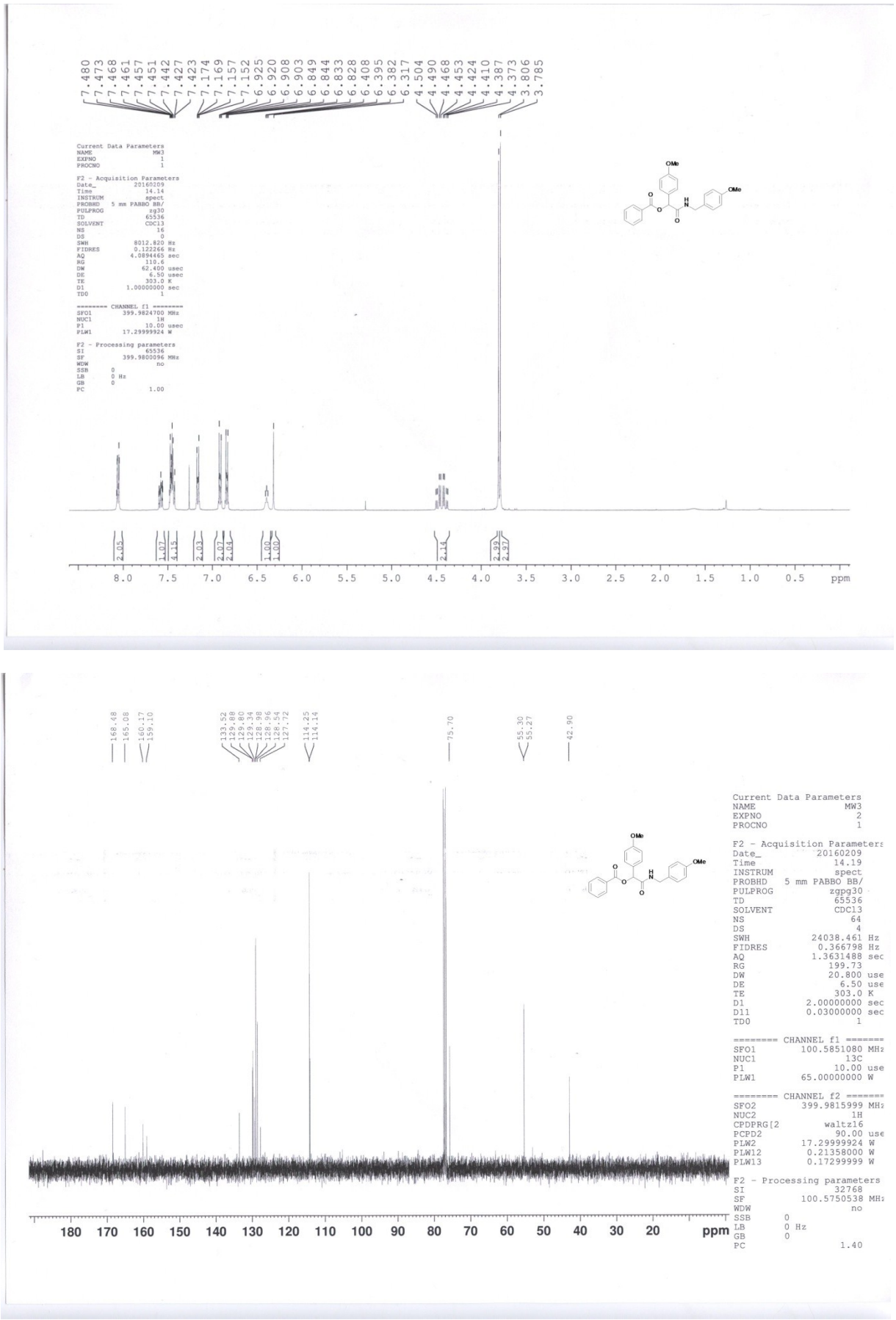

Figure S8. ^{1}H NMR (above) and ^{13}C NMR (below) spectra of compound **5f** (400 MHz, $CDCl_3$).

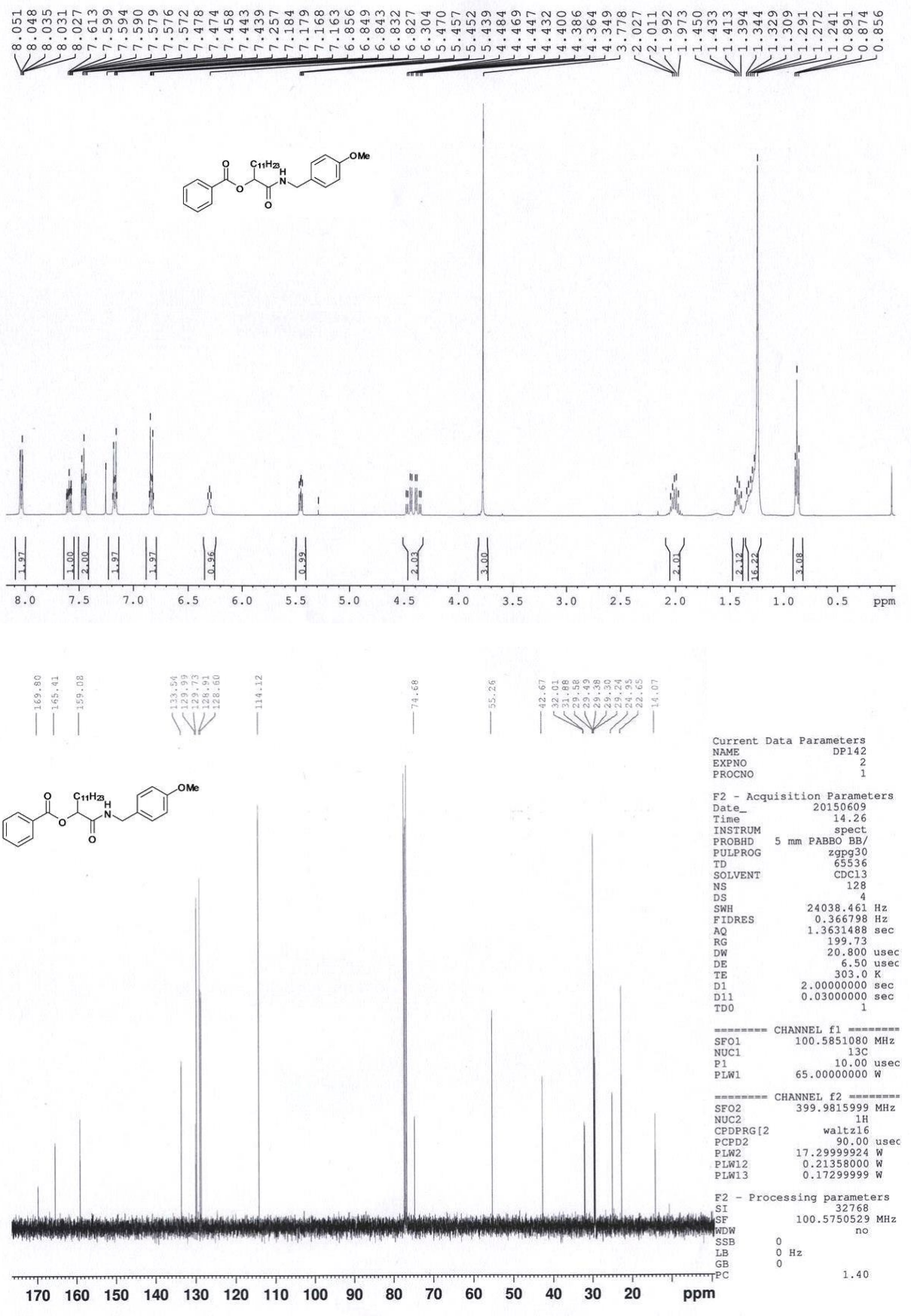

Figure S9. ^{1}H NMR (above) and ^{13}C NMR (below) spectra of compound **5g** (400 MHz, $CDCl_3$).

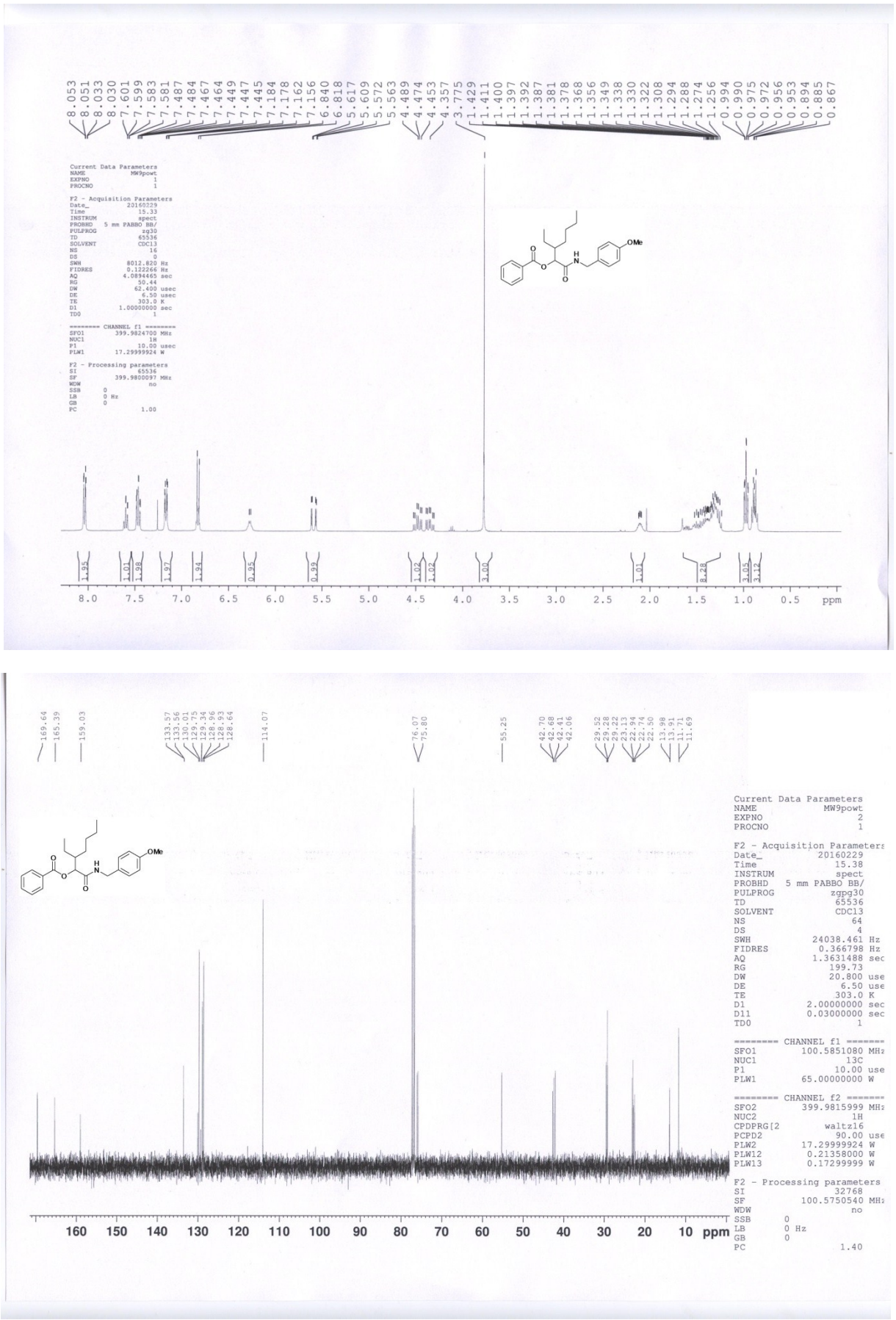

Figure S10. ^{1}H NMR (above) and ^{13}C NMR (below) spectra of compound **5h** (400 MHz, $CDCl_3$).

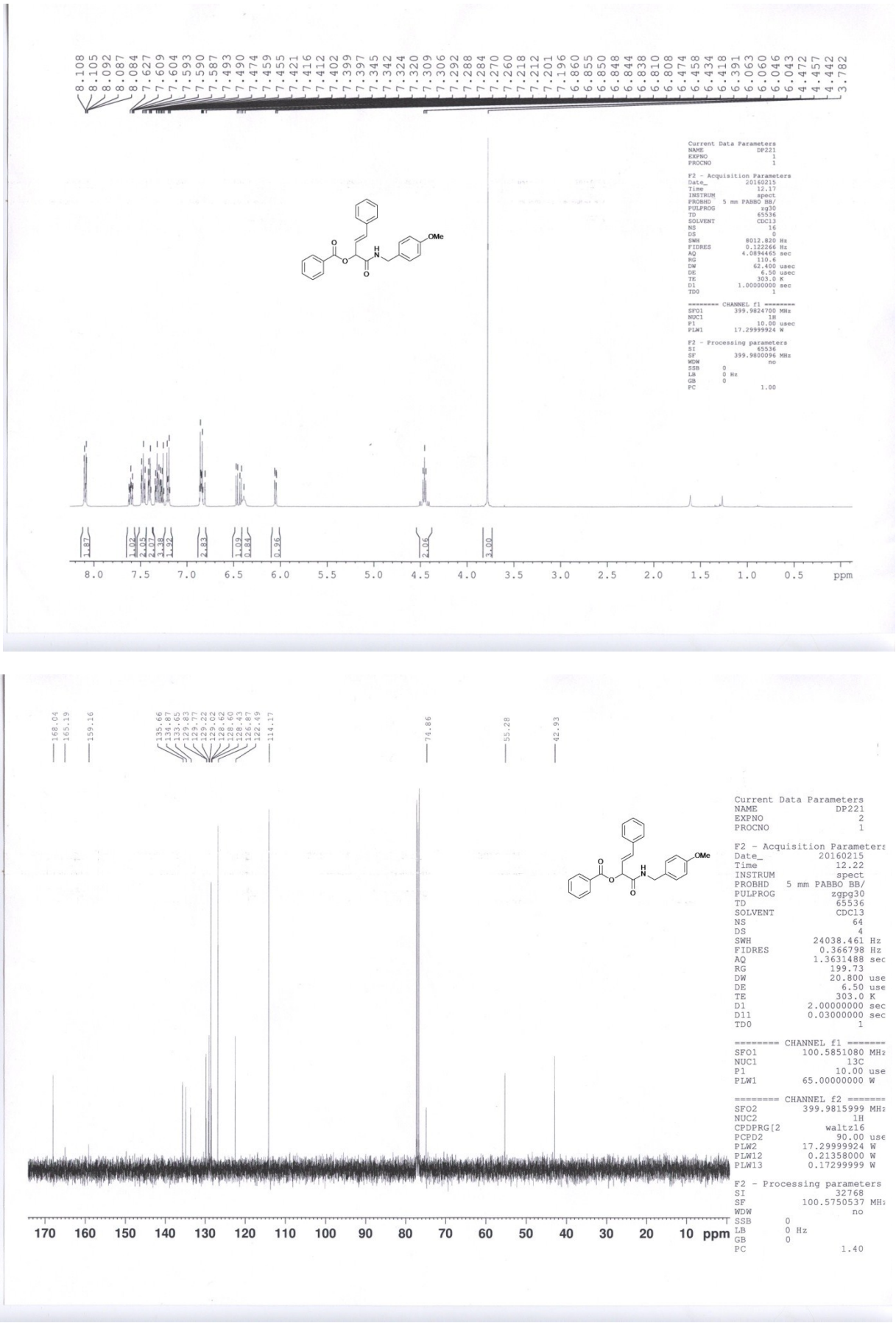

Figure S11. ^{1}H NMR (above) and ^{13}C NMR (below) spectra of compound **5i** (400 MHz, $CDCl_3$).