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Article

Enantioselective Total Synthesis of Multifidene and a Sex Pheromone of Brown Algae

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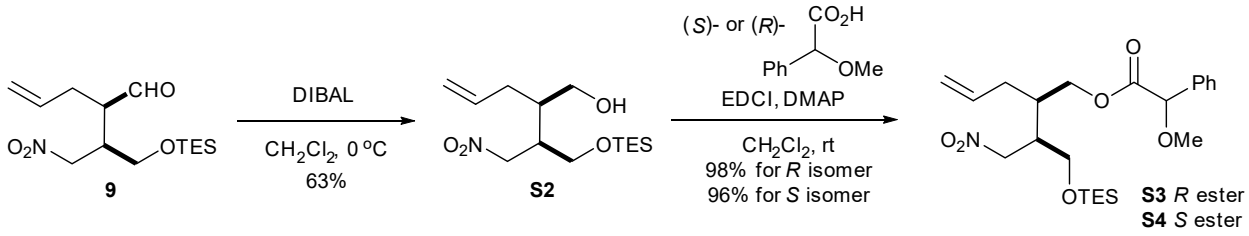


Determination of Enantiopurity of 9.

Alcohol S2.

To a solution of **9** (187 mg, 0.621 mmol) in CH_2Cl_2 (2.0 mL) was added DIBAL (1.00 M in toluene, 0.931 mL, 0.931 mmol) at 0 °C under Ar atmosphere. The mixture was stirred for 20 min, quenched with saturated Na,K-tartrate, stirred for 30 min, extracted with AcOEt, washed with brine, dried over Na_2SO_4, filtered, and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (hexane:EtOAc = 95:5 then 90:10) to give the alcohol **S2** (120 mg, 0.396 mmol, 63%) as a colorless oil: $[\alpha]_D^{23}$ +15.8 (*c* 2.50, $CHCl_3$); IR (neat) 3420, 3077, 2956, 2911, 2877, 1640, 1758, 1431, 1416, 1378, 1240, 1094, 1005, 916, 792 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.62 (6H, q, *J* = 7.8 Hz), 0.96 (9H, t, *J* = 7.8 Hz), 1.86-1.92 (1H, m), 2.08-2.18 (2H, m), 2.62-2.67 (1H, m), 3.62-3.68 (2H, m), 3.78 (1H, dd, *J* = 10.7, 4.9 Hz), 4.46 (1H, dd, *J* = 13.2, 4.9 Hz), 4.60 (1H, dd, *J* = 12.9, 9.3 Hz), 5.09 (1H, d, *J* = 9.2 Hz), 5.10 (1H, d, *J* = 17.9 Hz), 5.72-5.80 (1H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 4.0, 6.6, 33.6, 41.31, 41.37, 61.9, 62.8, 74.5, 117.4, 135.9.

R-Ester S3

To a solution of **S2** (8.20 mg, 0.0270 mmol) in CH_2Cl_2 (0.30 mL) were added (*R*)-α-methoxyphenylacetic acid (5.40 mg, 0.0324 mmol), DMAP (catalytic) and EDCI (7.70 mg, 0.0405 mmol) at room temperature under Ar atmosphere. The mixture was stirred at room

temperature for 3 h and purified by silica gel column chromatography (hexane:EtOAc = 95:5) to give the *R*-ester **S3** (12.0 mg, 0.0266 mmol, 98%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.55 (6H, q, *J* = 7.8 Hz), 0.91 (9H, t, *J* = 7.8 Hz), 1.85-2.03 (3H, m), 2.40-2.44 (1H, m), 3.54 (3H, s), 3.53-3.62 (2H, m), 4.09 (1H, dd, *J* = 11.7, 3.9 Hz), 4.19 (1H, dd, *J* = 11.7, 5.4 Hz), 4.24 (1H, d, *J* = 4.9 Hz), 4.40 (1H, dd, *J* = 13.7, 8.3 Hz), 4.74 (1H, s), 4.84 (1H, d, *J* = 17.0 Hz), 4.98 (1H, d, *J* = 10.2 Hz), 5.53-5.63 (1H, m), 7.34-7.43 (5H, m).

_S_-Ester S4

To a solution of **S2** (8.20 mg, 0.0270 mmol) in CH_2Cl_2 (0.30 mL) were added (*S*)-*α*-methoxyphenylacetic acid (5.40 mg, 0.0324 mmol), DMAP (catalytic) and EDCI (7.70 mg, 0.0405 mmol) at room temperature under Ar atmosphere. The mixture was stirred at room temperature for 3 h and purified by silica gel column chromatography (hexane:EtOAc = 95:5) to give the *S*-ester **S4** (11.7 mg, 0.0259 mmol, 96%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.48 (6H, q, *J* = 7.8 Hz), 0.84 (9H, t, *J* = 7.8 Hz), 1.86-2.06 (3H, m), 2.31-2.36 (1H, m), 3.39 (3H, s), 3.51 (2H, dd, *J* = 5.1, 1.5 Hz), 4.03-4.20 (4H, m), 4.68 (1H, s), 4.90 (1H, d, *J* = 17.0 Hz), 4.96 (1H, d, *J* = 10.2 Hz), 5.53-5.63 (1H, m), 7.28-7.36 (5H, m).

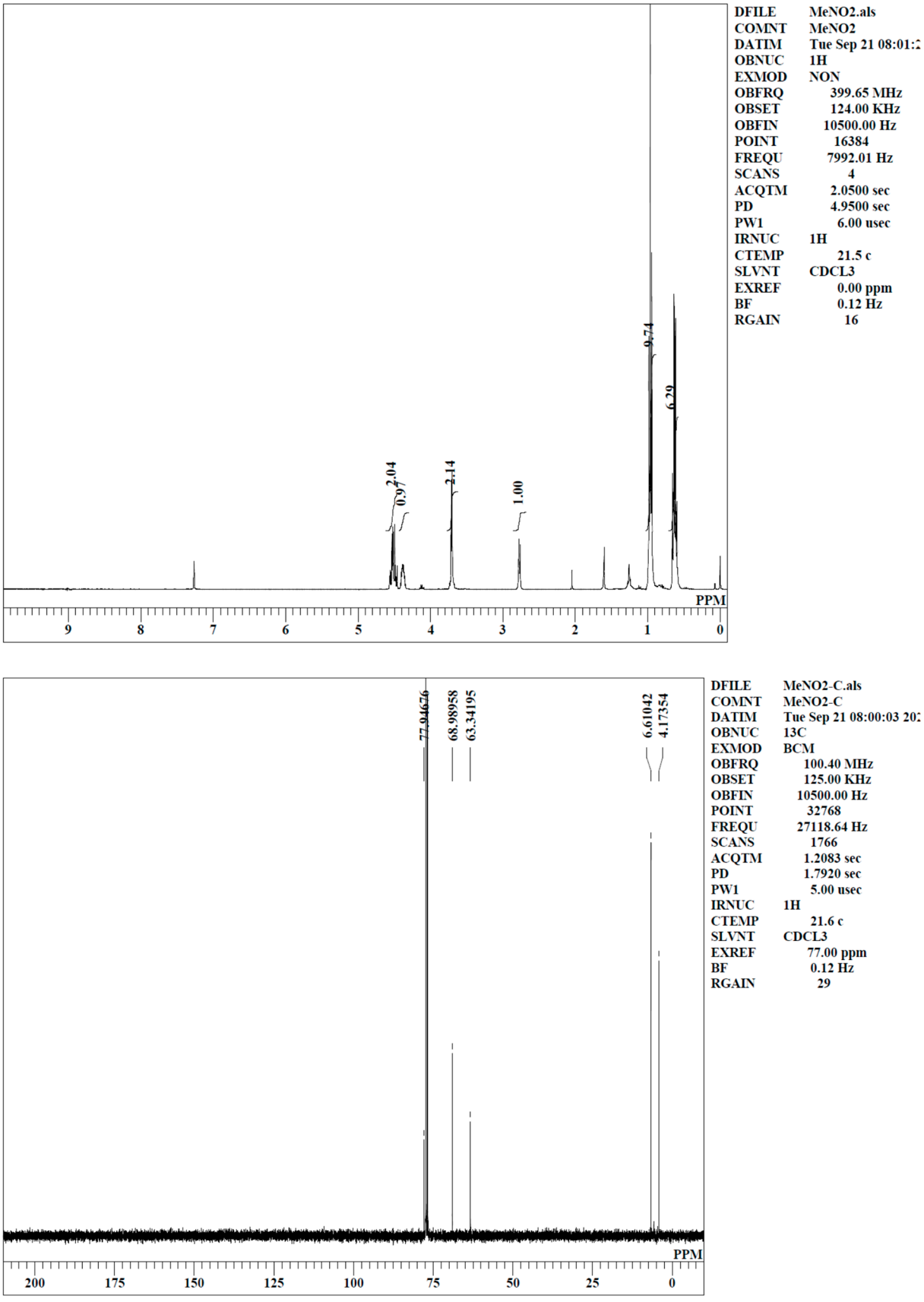
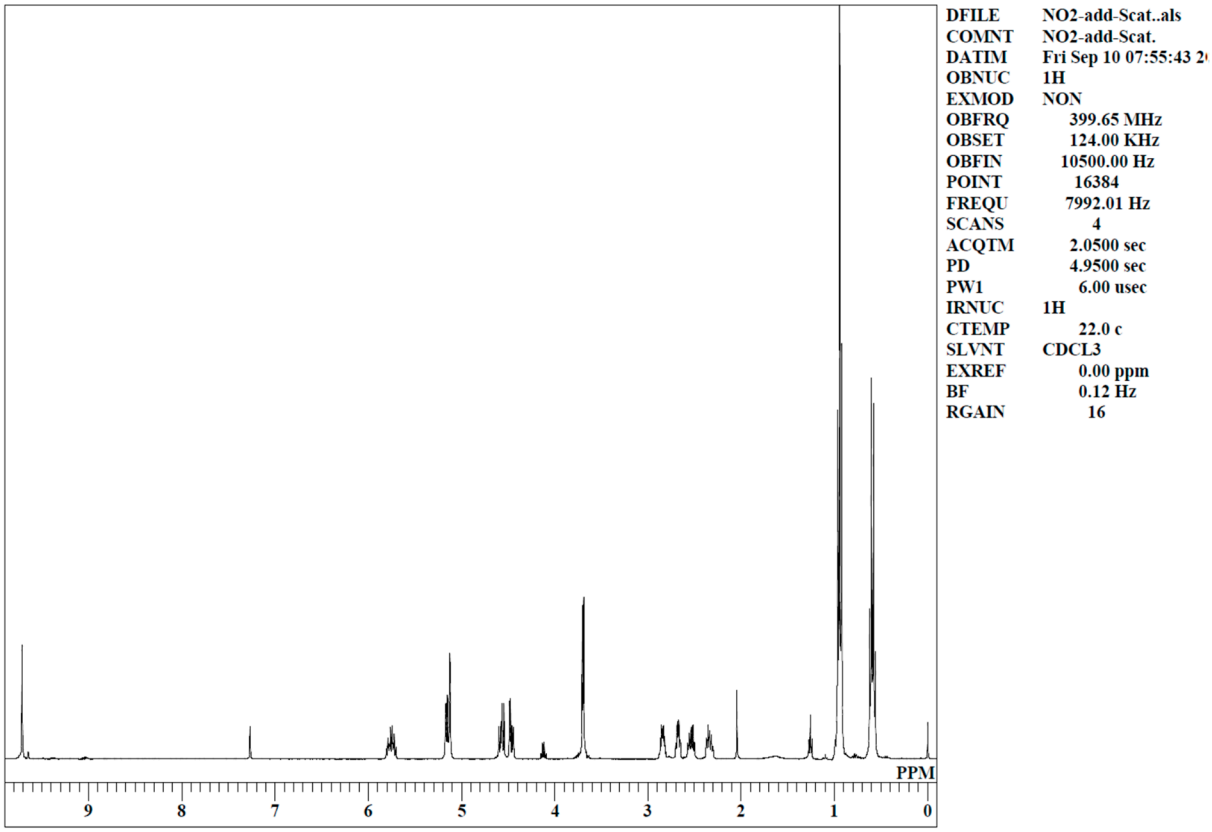


Figure S1. ^{1}H and ^{13}C NMR spectra of **S1.**



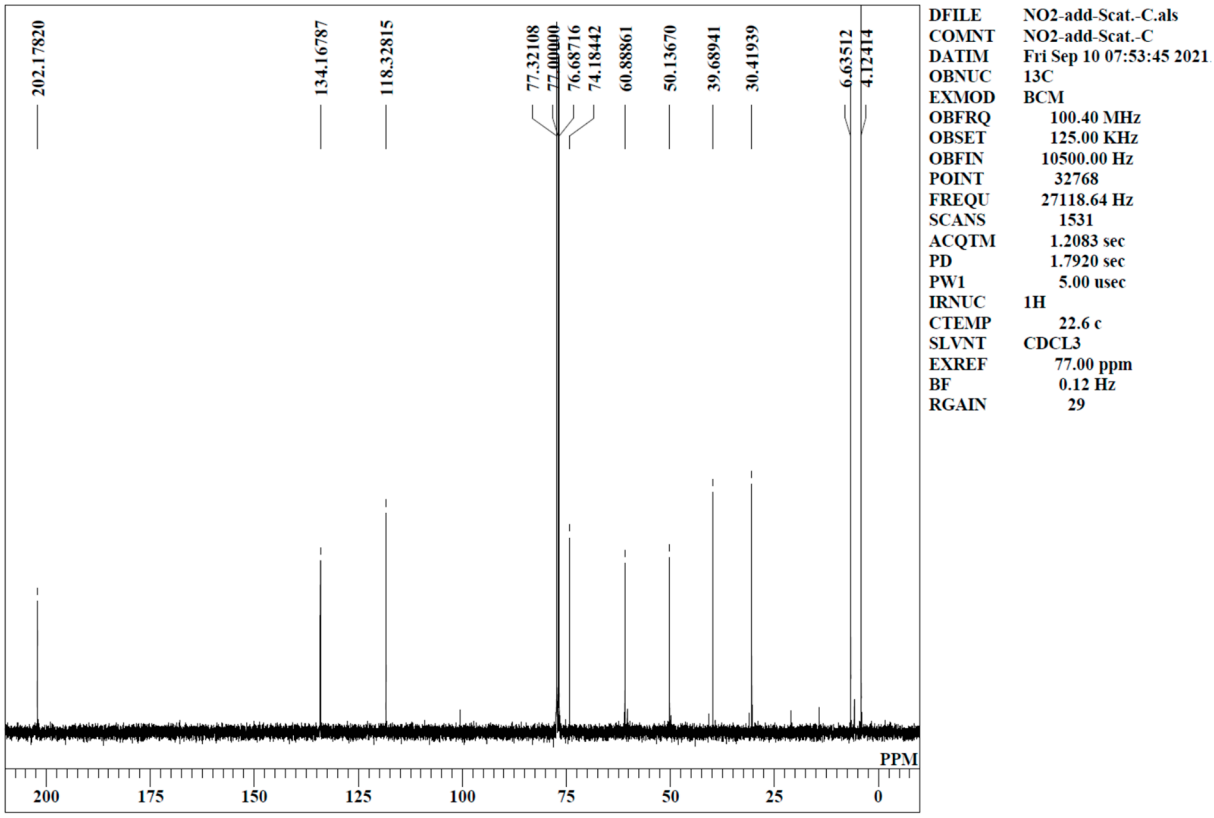


Figure S2. ^{1}H and ^{13}C NMR spectra of **9.**

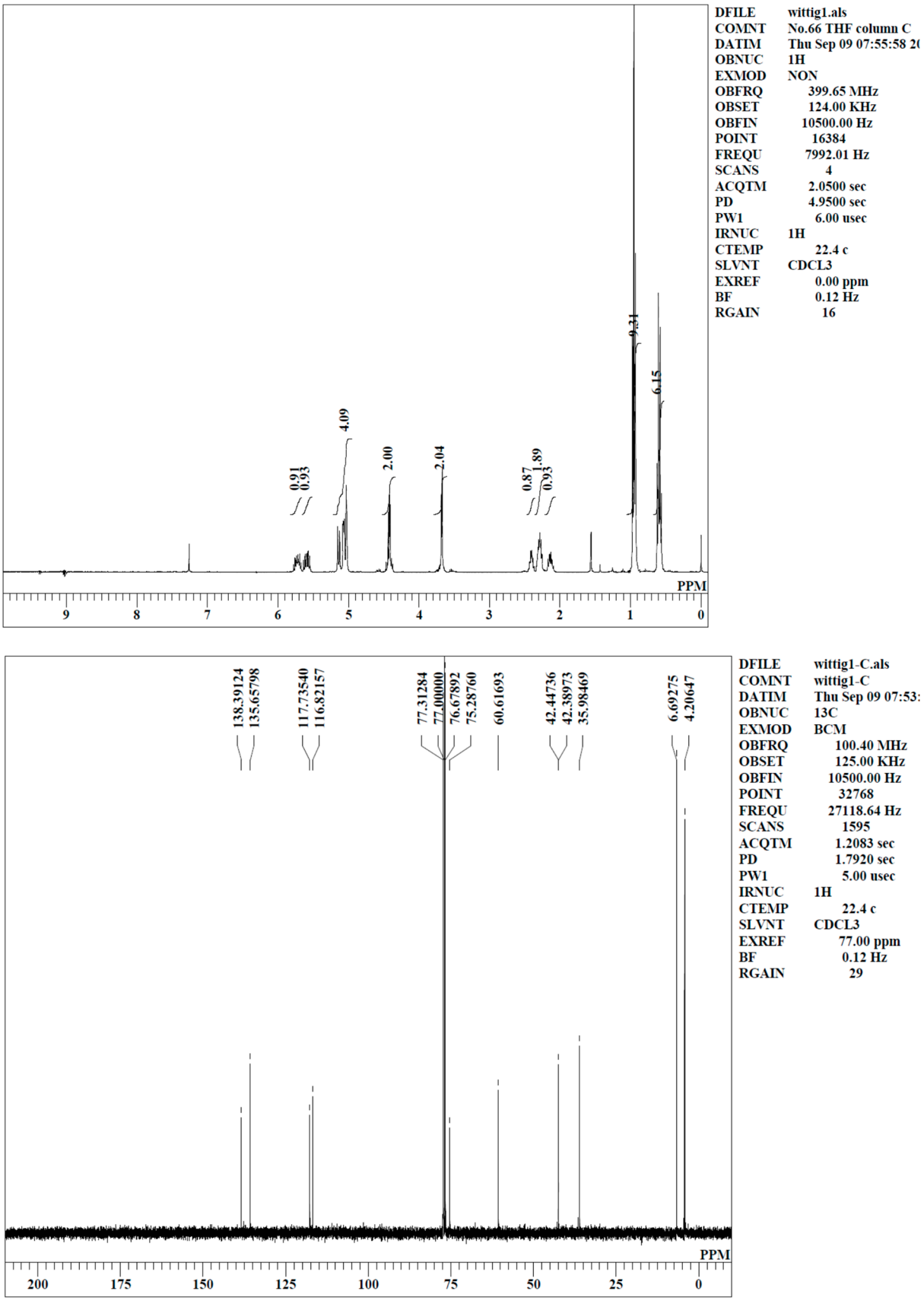


Figure S3. ^{1}H and ^{13}C NMR spectra of **10.**

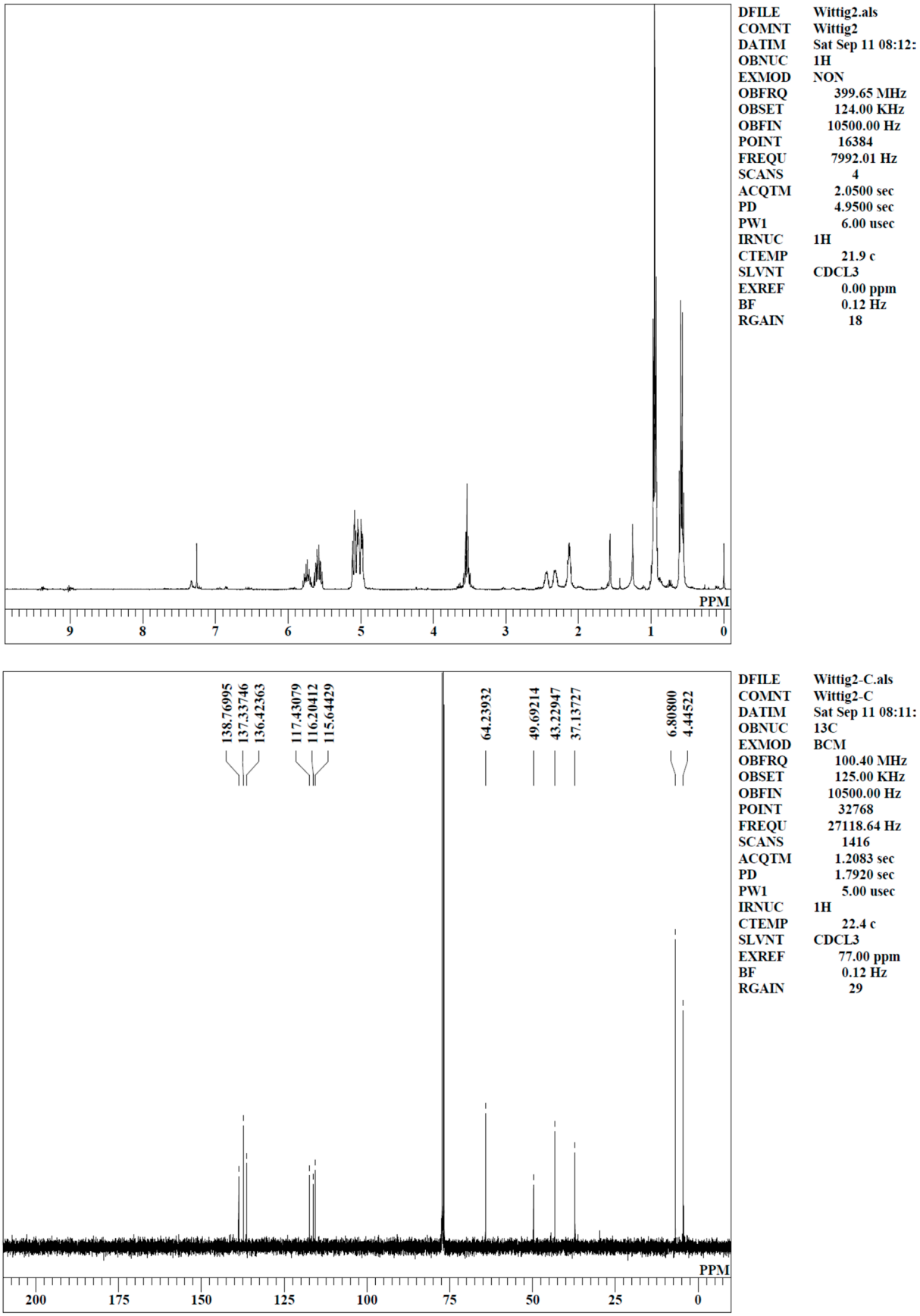


Figure S4. ^{1}H and ^{13}C NMR spectra of **14.**

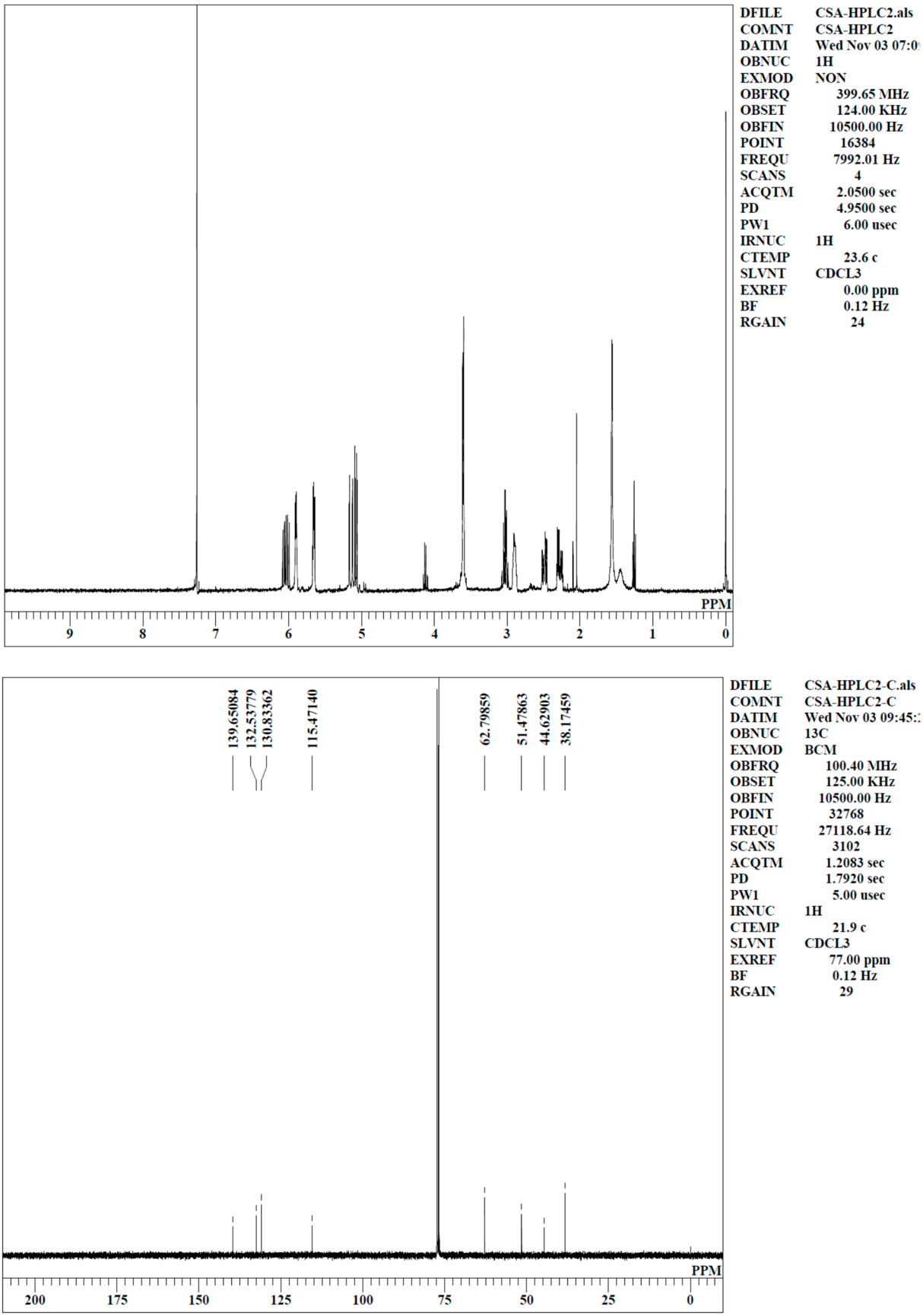


Figure S5. ^{1}H and ^{13}C NMR spectra of **15.**

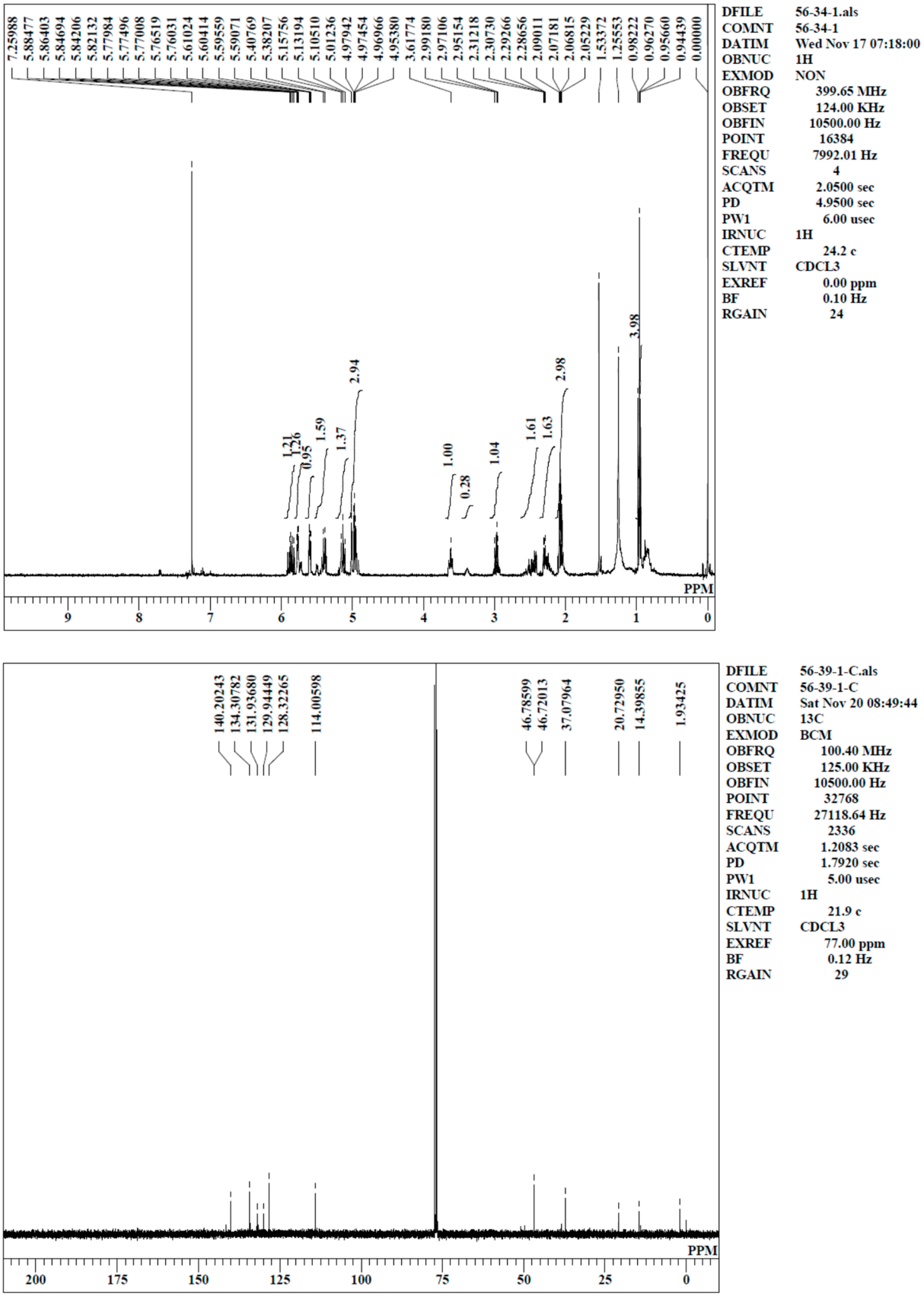


Figure S6. ^{1}H and ^{13}C NMR spectra of **1.**

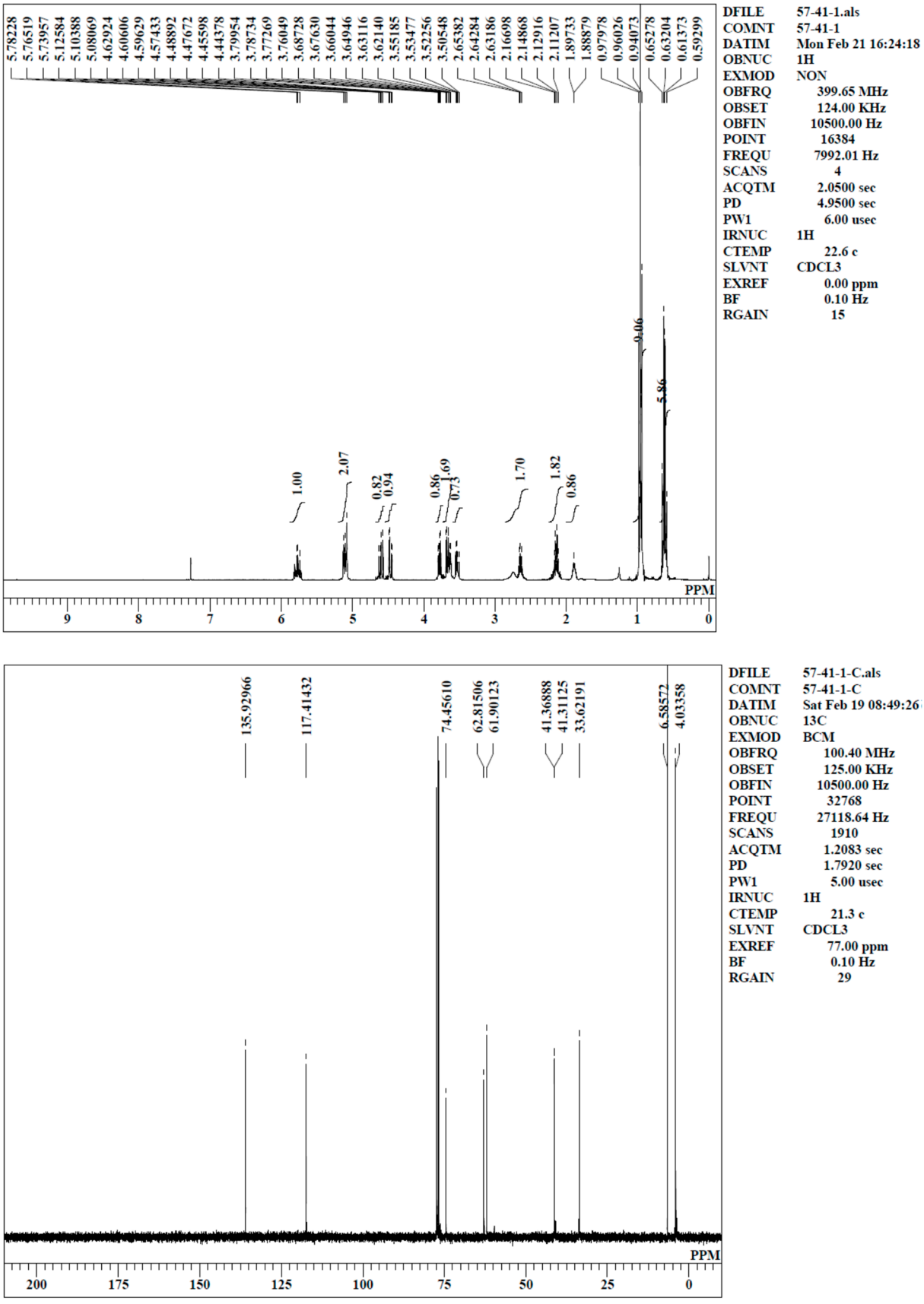


Figure S7. ^{1}H and ^{13}C NMR spectra of **S2.**

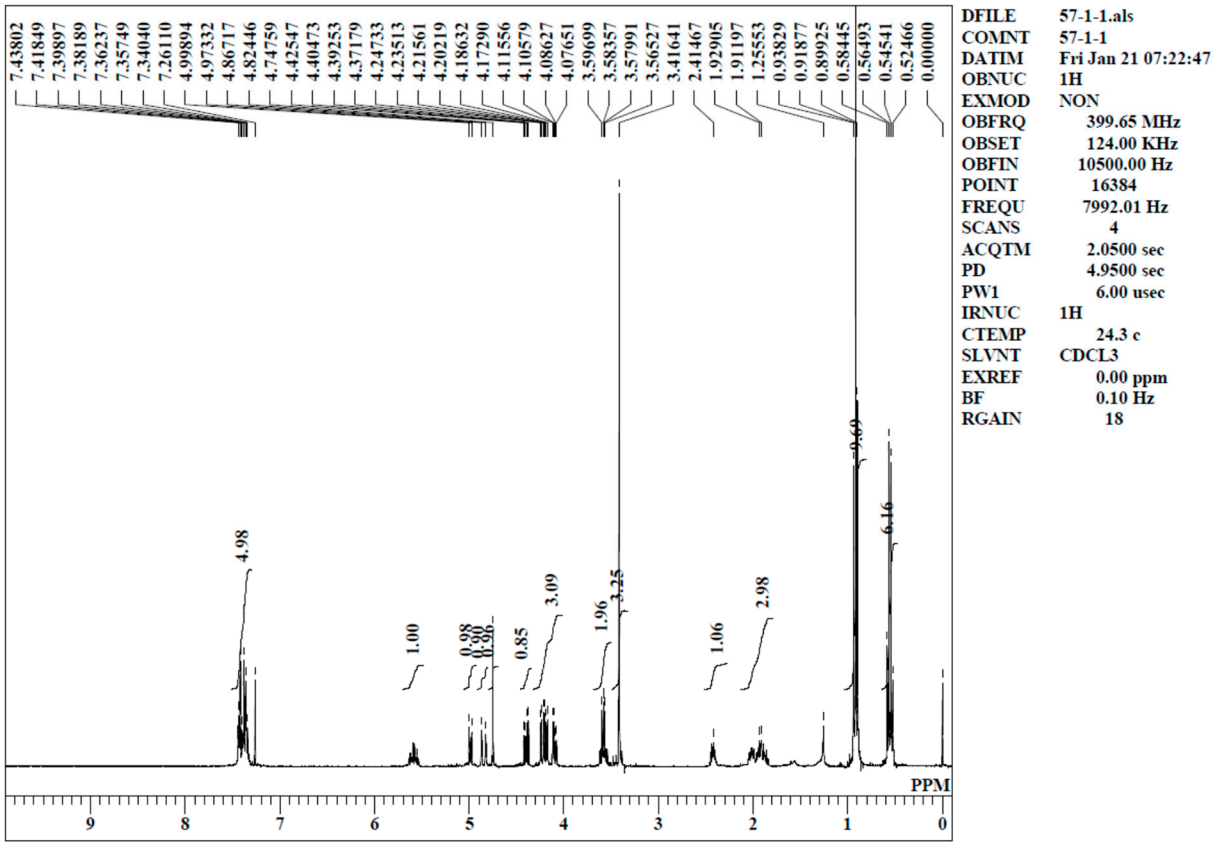


Figure S8. ^{1}H NMR spectrum of **S3.**

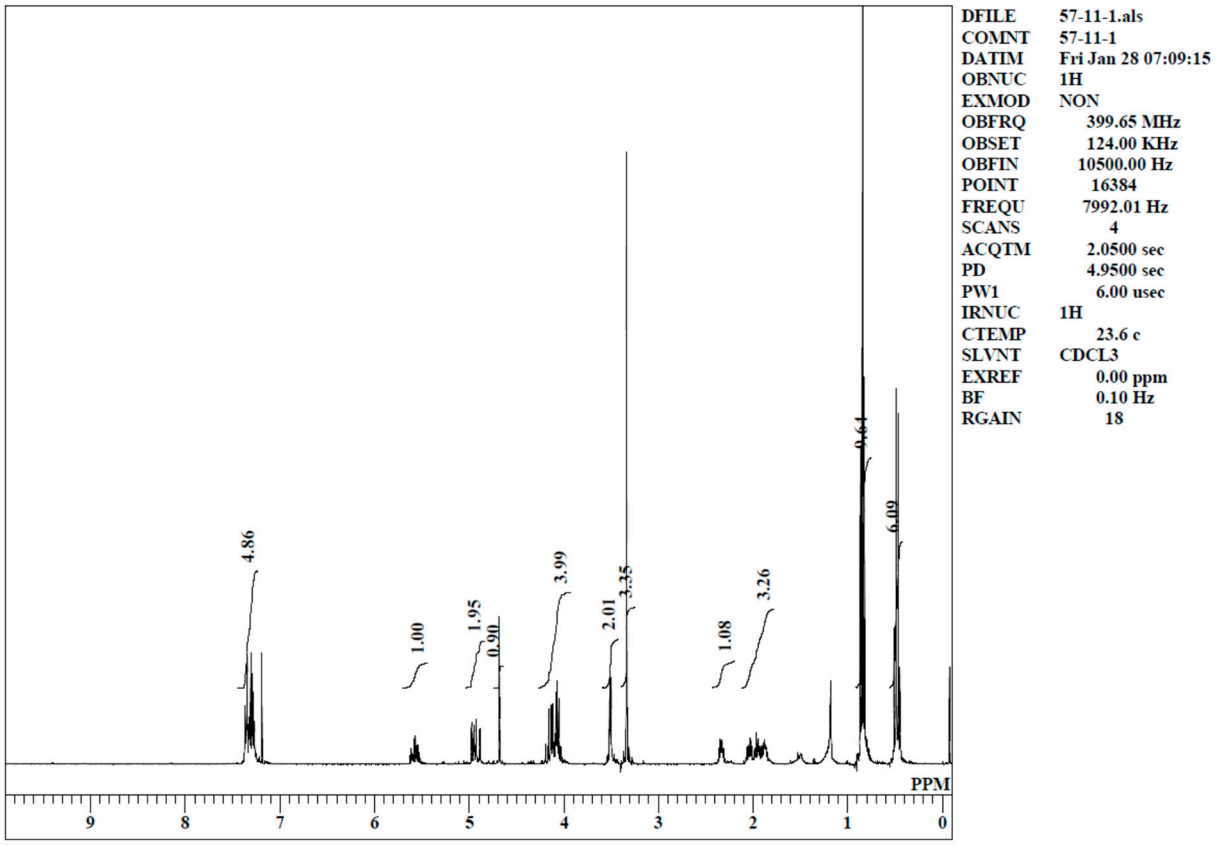


Figure S9. ^{1}H NMR spectrum of **S4.**