

Supplementary information

Cobalt salt-catalyzed carbocyclization reactions of α -bromo-*N*-phenylacetamide derivatives

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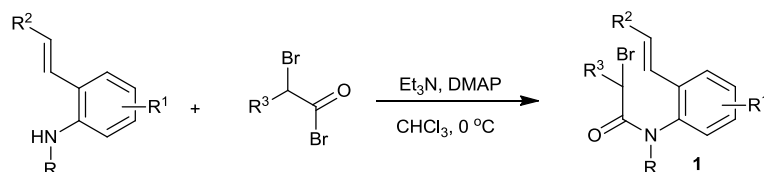
Contents

- 1) Experimental details and characterization data of the starting α -bromo-*N*-phenylacetamides.
- 2) Copies of ¹H and ¹³C NMR spectra for quinolin-2(1*H*)-ones.
- 3) Copies of ¹H and ¹³C NMR spectra for radical-trapping adducts.

1) Experimental details and characterization data of the starting α -bromo-*N*-phenylacetamides.

A. Synthesis of α -bromo-*N*-(2-(alkenylphenyl))acetamides 1:

The starting α -bromo-*N*-2-(alkenylphenyl)acetamides **1** were prepared by the reaction between 2-(alkenylphenyl)amines and α -bromoacetyl bromide.



Typical procedure for the preparation of α -bromo-*N*-(2-(alkenylphenyl))acetamides 1:

A solution of *N*-(2,4,6-trimethylbenzyl)-2-[(*E*)-(2-phenylethenyl)]phenylamine (1.04 g, 3.18 mmol), 2-bromoacetyl bromide (1.33 g, 6.59 mmol), triethylamine (691 mg, 6.84 mmol), and DMAP (44 mg, 0.36 mmol) in chloroform (20 mL) was stirred in an ice-water bath for 1 h. The reaction mixture was then diluted with 100 mL of ethyl acetate washed with water (3×50 mL), dried over Na_2SO_4 , and concentrated in vacuo. The residue was chromatographed over 20 g of silica gel (eluted with 1:20 ethyl acetate–hexanes) to give 1.30 g (91%) of **1a**.

2-Bromo-*N*-(2,4,6-trimethylbenzyl)-*N*-(2-[(*E*)-(2-phenylethenyl)]phenyl)acetamide 1a. Colorless crystals; mp $172\text{--}173\text{ }^\circ\text{C}$ (from ethyl acetate–hexanes); yield: 91%; (Found: C, 69.58; H, 5.87; N, 3.10. Calc. for $C_{26}H_{26}BrNO$: C, 69.64; H, 5.84; N, 3.12%); $\nu_{max}(KBr)/cm^{-1}$ 2955, 1670, 1375, 1195 and 1180; $\delta_H(400\text{ MHz}; CDCl_3; Me_4Si)$ 1.98 (s, 6H, $2 \times CH_3$), 2.13 (s, 3H, CH_3), 3.55 (d, $J = 11.0$ Hz, 1H, COCH), 3.63 (d, $J = 11.0$ Hz, 1H, COCH), 4.74 (d, $J = 14.1$ Hz, 1H, NCH), 5.34 (d, $J = 14.1$ Hz, 1H, NCH), 6.65 (s, 2H, $2 \times ArH$), 6.69 (dd, $J = 7.7, 1.2$ Hz, 1H, ArH), 6.90 (d, $J = 16.2$ Hz, 1H, CH), 7.02 (d, $J = 16.2$ Hz, 1H, CH), 7.11 (td, $J = 7.7, 1.2$ Hz, 1H, ArH), 7.27–7.41 (m, 4H, ArH), 7.41–7.47 (m, 2H, ArH) and 7.68 (dd, $J = 7.7, 1.0$ Hz, 1H, ArH); $\delta_C(100.6\text{ MHz}; CDCl_3; Me_4Si)$ 19.6 ($2 \times q$), 20.8 (q), 27.4 (t), 45.4 (t), 121.8 (d), 126.0 (d), 126.8 ($2 \times d$), 128.25 (d), 128.33 (d), 128.7 ($2 \times d$), 128.8 (s), 129.0 ($2 \times d$), 129.2 (d), 130.3 (d), 132.1 (d), 136.1 (s), 136.6 (s), 137.38 (s), 137.47 (s), 138.4 ($2 \times s$) and 166.3 (s).

***N*-Benzyl-2-bromo-*N*-(2-[(*E*)-(2-phenylethenyl)]phenyl)acetamide 1b.** Colorless needles; mp $97\text{--}98\text{ }^\circ\text{C}$ (from ethyl acetate–hexanes); yield: 95%; (Found: C, 67.82; H, 5.03; N, 3.43. Calc. for $C_{23}H_{20}BrNO$: C, 67.99; H, 4.96; N, 3.45%); $\nu_{max}(KBr)/cm^{-1}$ 2940, 1660, 1390, 1280 and 1205; $\delta_H(400\text{ MHz}; CDCl_3; Me_4Si)$ 3.59 (d, $J = 11.4$ Hz, 1H, COCH), 3.65 (d, $J = 11.4$ Hz, 1H, COCH), 4.63 (d, $J = 13.9$ Hz, 1H, NCH), 5.16 (d, $J = 13.9$ Hz, 1H, NCH), 6.80 (d, $J = 16.3$ Hz, 1H, CH), 6.96 (dd, $J = 7.7, 0.8$ Hz, 1H, ArH), 7.06 (d, $J = 16.3$ Hz, 1H, CH), 7.19–7.42 (m, 12H, ArH) and 7.74 (dd, $J = 7.7, 0.8$ Hz, 1H, ArH); $\delta_C(100.6\text{ MHz}; CDCl_3; Me_4Si)$ 27.5 (t), 53.4 (t), 122.2 (d), 126.3 (d), 126.7 ($2 \times d$), 127.7 (d), 128.2 (d), 128.3 ($2 \times d$), 128.46 (d), 128.55 ($2 \times d$), 129.1 (d), 129.38 ($2 \times d$), 129.41 (d), 132.0 (d), 135.3 (s), 136.0 (s), 136.3 (s), 138.4 (s) and 166.5 (s).

2-Bromo-*N*-ethyl-*N*-(2-[(*E*)-(2-phenylethenyl)]phenyl)acetamide 1c. Yellow oils; yield: 91%; $\nu_{max}(neat)/cm^{-1}$ 2975, 1660, 1400, 1310 and 1215; $\delta_H(400\text{ MHz}; CDCl_3; Me_4Si)$ 1.16 (t, $J = 7.2$ Hz, 3H, CH_3), 3.44 (dq, $J = 13.9, 7.2$ Hz, 1H, NCH), 3.58 (d, $J = 11.1$ Hz, 1H, COCH), 3.65 (d, $J = 11.1$ Hz, 1H, COCH), 4.11 (dq, $J = 13.9, 7.2$ Hz, 1H, NCH), 7.08 (d, $J = 16.3$ Hz, 1H, CH), 7.16 (d, $J = 16.3$ Hz, 1H, CH), 7.23 (dd, $J = 7.7, 1.2$ Hz, 1H, ArH), 7.27–7.33 (m, 1H, ArH), 7.33–7.40 (m, 3H, ArH), 7.44 (td, $J = 7.7, 1.2$ Hz, 1H, ArH), 7.47–7.52 (m, 2H, ArH) and 7.81 (dd, $J = 7.7, 1.2$ Hz, 1H, ArH); $\delta_C(100.6\text{ MHz}; CDCl_3; Me_4Si)$ 12.4 (q), 27.5 (t), 44.7 (t), 122.3 (d), 126.5 (d), 126.8 ($2 \times d$), 128.4 (d), 128.6 (d), 128.8 ($2 \times d$), 129.1 (d), 129.4 (d), 132.2 (d), 135.3 (s), 136.5 (s), 138.7 (s) and 166.4 (s); m/z (EI) 343.0565 (M^+ $C_{18}H_{18}BrNO$ requires 343.0572).

2-Bromo-*N*-(2-[(*E*)-(2-phenylethenyl)]phenyl)acetamide 1d. Colorless crystals; mp $155\text{--}156\text{ }^\circ\text{C}$ (from ethyl acetate–hexanes); yield: 99%; (Found: C, 60.46; H, 4.55; N, 4.40; Calc. for $C_{16}H_{14}BrNO$: C, 60.78; H, 4.46; N, 4.43%); $\nu_{max}(KBr)/cm^{-1}$ 3255, 3030, 1650, 1530, 1480 and 1315; $\delta_H(400\text{ MHz}; CDCl_3; Me_4Si)$ 4.08 (s, 2H, $COCH_2$), 7.03 (d, $J = 16.2$ Hz, 1H, CH), 7.18 (d, $J = 16.2$ Hz, 1H, CH), 7.22 (t, $J = 7.8$ Hz, 1H, ArH), 7.27–7.34 (m, 2H, ArH), 7.34–7.42 (m, 2H, ArH), 7.49–7.54 (m, 2H, ArH), 7.56 (d, $J = 7.8$ Hz, 1H, ArH), 7.87 (d, $J = 7.8$ Hz, 1H, ArH) and 8.32 (s, 1H, NH); $\delta_C(100.6\text{ MHz}; CDCl_3; Me_4Si)$ 29.8 (t), 122.6 (d), 123.4 (d), 126.1 (d), 126.7 ($2 \times d$), 127.1 (d), 128.3 (d), 128.4 (d), 128.8 ($2 \times d$), 130.4 (s), 133.3 (d), 133.8 (s), 136.8 (s) and 163.5 (s).

2-Bromo-*N*-(2,4,6-trimethylbenzyl)-*N*-(4-methyl-2-[(*E*)-(2-phenylethenyl)]phenyl)acetamide 1e. Colorless crystals; mp $221\text{--}222\text{ }^\circ\text{C}$ (from ethyl acetate–hexanes); yield: 99%; (Found: C, 69.76; H, 6.05; N, 2.97; Calc. for $C_{27}H_{28}BrNO$: C, 70.13; H, 6.10; N, 3.03%); $\nu_{max}(KBr)/cm^{-1}$ 2915, 1675, 1490, 1370 and 1185; $\delta_H(400\text{ MHz}; CDCl_3; Me_4Si)$ 1.99 (s, 6H, $2 \times CH_3$), 2.12 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 3.56 (d, $J = 11.1$ Hz, 1H, COCH), 3.62 (d, $J = 11.1$ Hz, 1H, COCH), 4.72 (d, $J = 14.1$ Hz, 1H, NCH), 5.31 (d, $J = 14.1$ Hz, 1H, NCH), 6.56 (d, $J = 8.0$ Hz, 1H, ArH), 6.65 (s, 2H, $2 \times ArH$), 6.85 (d, $J = 16.2$ Hz, 1H, CH), 6.90 (dd, $J = 8.0, 1.4$ Hz, 1H, ArH), 6.99 (d, $J = 16.2$ Hz, 1H, CH), 7.24–7.32 (m,

1H, ArH), 7.33–7.40 (m, 2H, ArH), 7.40–7.45 (m, 2H, ArH) and 7.47 (s, 1H, ArH); δ_c (100.6 MHz; CDCl₃; Me₄Si) 19.7 (2 × q), 20.8 (q), 21.3 (q), 27.5 (t), 45.4 (t), 122.0 (d), 126.4 (d), 126.8 (2 × d), 128.2 (d), 128.6 (2 × d), 128.91 (s), 128.97 (2 × d), 129.11 (d), 129.9 (d), 131.7 (d), 135.0 (s), 135.6 (s), 136.7 (s), 137.3 (s), 138.3 (2 × s), 139.1 (s) and 166.4 (s).

2-Bromo-N-(2,4,6-trimethylbenzyl)-N-{4,5-dimethyl-2-[(E)-(2-phenylethenyl)]phenyl}acetamide 1f. Colorless crystals; mp 221–222 °C (from ethyl acetate–hexanes); yield: 94%; (Found: C, 70.23; H, 6.36; N, 2.91; Calc. for C₂₈H₃₀BrNO: C, 70.58; H, 6.35; N, 2.94%); $\nu_{\max}$ (KBr)/cm⁻¹ 2950, 2920, 1670, 1370 and 1190; δ_h (400 MHz; CDCl₃; Me₄Si) 1.98 (s, 6H, 2 × CH₃), 2.08 (s, 3H, CH₃), 2.10 (s, 3H, CH₃), 2.27 (s, 3H, CH₃), 3.58 (d, *J* = 11.2 Hz, 1H, COCH), 3.63 (d, *J* = 11.2 Hz, 1H, COCH), 4.81 (d, *J* = 14.1 Hz, 1H, NCH), 5.21 (d, *J* = 14.1 Hz, 1H, NCH), 6.44 (s, 1H, ArH), 6.64 (s, 2H, 2 × ArH), 6.77 (d, *J* = 16.2 Hz, 1H, CH), 6.92 (d, *J* = 16.2 Hz, 1H, CH), 7.24–7.31 (m, 1H, ArH) and 7.32–7.42 (m, 5H, ArH); δ_c (100.6 MHz; CDCl₃; Me₄Si) 19.2 (q), 19.64 (q), 19.73 (2 × q), 20.8 (q), 27.7 (t), 45.5 (t), 122.0 (d), 126.67 (2 × d), 126.76 (d), 128.0 (d), 128.6 (2 × d), 128.9 (2 × d), 129.0 (s), 130.6 (d), 130.8 (d), 133.2 (s), 135.2 (s), 136.9 (s), 137.24 (s), 137.27 (s), 137.7(s), 138.4 (2 × s) and 166.4 (s).

2-Bromo-N-{4-fluoro-[(E)-(2-phenylethenyl)]phenyl}-N-(2,4,6-trimethylbenzyl)acetamide 1g. Colorless crystals; mp 190–191 °C (from ethyl acetate–hexanes); yield: 98%; (Found: C, 66.89; H, 5.45; N, 2.96; Calc. for C₂₆H₂₅BrFNO: C, 66.96; H, 5.40; N, 3.00%); $\nu_{\max}$ (KBr)/cm⁻¹ 2955, 1675, 1490, 1370 and 1180; δ_h (400 MHz; CDCl₃; Me₄Si) 2.00 (s, 6H, 2 × CH₃), 2.13 (s, 3H, CH₃), 3.53 (d, *J* = 10.9 Hz, 1H, COCH), 3.62 (d, *J* = 10.9 Hz, 1H, COCH), 4.66 (d, *J* = 14.3 Hz, 1H, NCH), 5.36 (d, *J* = 14.3 Hz, 1H, NCH), 6.64 (dd, *J* = 8.7, 5.7 Hz, 1H, ArH), 6.67 (s, 2H, 2 × ArH), 6.75–6.84 (m, 1H, ArH), 6.84 (d, *J* = 16.1 Hz, 1H, CH), 7.01 (d, *J* = 16.1 Hz, 1H, CH) and 7.29–7.48 (m, 6H, ArH); δ_c (100.6 MHz; CDCl₃; Me₄Si) 19.7 (2 × q), 20.8 (q), 27.0 (t), 45.4 (t), 112.2 (dd, *J*_{CF} = 23.1 Hz), 115.2 (dd, *J*_{CF} = 23.1 Hz), 120.9 (d), 127.0 (2 × d), 128.6 (s), 128.8 (3 × d), 129.1 (2 × d), 132.2 (dd, *J*_{CF} = 9.1 Hz), 133.4 (d+s), 136.1 (s), 137.6 (s), 138.29 (2 × s), 138.34 (s), 162.6 (sd, *J*_{CF} = 248.5 Hz) and 166.5 (s).

2-Bromo-N-{4-chloro-[(E)-(2-phenylethenyl)]phenyl}-N-(2,4,6-trimethylbenzyl)acetamide 1h. Colorless crystals; mp 224–225 °C (from ethyl acetate–hexanes); yield: 93%; (Found: C, 64.35; H, 5.23; N, 2.90; Calc. for C₂₆H₂₅BrClNO: C, 64.68; H, 5.22; N, 2.90%); $\nu_{\max}$ (KBr)/cm⁻¹ 2915, 1675, 1480, 1365 and 1195; δ_h (400 MHz; CDCl₃; Me₄Si) 2.00 (s, 6H, 2 × CH₃), 2.14 (s, 3H, CH₃), 3.51 (d, *J* = 10.9 Hz, 1H, COCH), 3.61 (d, *J* = 10.9 Hz, 1H, COCH), 4.67 (d, *J* = 14.2 Hz, 1H, NCH), 5.36 (d, *J* = 14.2 Hz, 1H, NCH), 6.60 (d, *J* = 8.4 Hz, 1H, ArH), 6.67 (s, 2H, 2 × ArH), 6.83 (d, *J* = 16.0 Hz, 1H, CH), 7.03 (d, *J* = 16.0 Hz, 1H, CH), 7.06 (dd, *J* = 8.4, 2.3 Hz, 1H, ArH), 7.30–7.36 (m, 1H, ArH), 7.36–7.42 (m, 2H, ArH), 7.42–7.47 (m, 2H, ArH) and 7.66 (s, *J* = 2.3 Hz, 1H, ArH); δ_c (100.6 MHz; CDCl₃; Me₄Si) 19.7 (2 × q), 20.8 (q), 26.9 (t), 45.3 (t), 120.6 (d), 125.8 (d), 127.0 (2 × d), 128.1 (d), 128.5 (s), 128.8 (3 × d), 129.2 (2 × d), 131.7 (d), 133.5 (d), 135.3 (s), 135.8 (s), 136.1 (s), 137.6 (s), 137.9 (s), 138.3 (2 × s) and 166.3 (s).

2-Bromo-N-{4-bromo-[(E)-(2-phenylethenyl)]phenyl}-N-(2,4,6-trimethylbenzyl)acetamide 1i. Colorless crystals; mp 224–225 °C (from ethyl acetate–hexanes); yield: 98%; (Found: C, 59.13; H, 4.82; N, 2.65; Calc. for C₂₆H₂₅Br₂NO: C, 59.22; H, 4.78; N, 2.66%); $\nu_{\max}$ (KBr)/cm⁻¹ 2955, 1675, 1475, 1365, 1190 and 1180; δ_h (400 MHz; CDCl₃; Me₄Si) 2.00 (s, 6H, 2 × CH₃), 2.14 (s, 3H, CH₃), 3.51 (d, *J* = 10.9 Hz, 1H, COCH), 3.61 (d, *J* = 10.9 Hz, 1H, COCH), 4.67 (d, *J* = 14.2 Hz, 1H, NCH), 5.35 (d, *J* = 14.2 Hz, 1H, NCH), 6.54 (d, *J* = 8.4 Hz, 1H, ArH), 6.67 (s, 2H, 2 × ArH), 6.82 (d, *J* = 16.2 Hz, 1H, CH), 7.02 (d, *J* = 16.2 Hz, 1H, CH), 7.21 (dd, *J* = 8.4, 2.2 Hz, 1H, ArH), 7.30–7.47 (m, 5H, ArH) and 7.81 (s, *J* = 2.2 Hz, 1H, ArH); δ_c (100.6 MHz; CDCl₃; Me₄Si) 19.7 (2 × q), 20.8 (q), 26.9 (t), 45.3 (t), 120.4 (d), 123.4 (s), 127.0 (2 × d), 128.5 (s), 128.78 (3 × d), 128.86 (d), 129.2 (2 × d), 131.1 (d), 131.9 (d), 133.5 (d), 136.1 (s), 136.3 (s), 137.6 (s), 138.19 (s), 138.25 (2 × s) and 166.2 (s).

2-Bromo-N-{4-methoxycarbonyl-[(E)-(2-phenylethenyl)]phenyl}-N-(2,4,6-trimethylbenzyl)acetamide 1j. Colorless crystals; mp 148–149 °C (from ethyl acetate–hexanes); yield: 99%; (Found: C, 66.33; H, 5.61; N, 2.76; Calc. for C₂₈H₂₈BrNO₃: C, 66.41; H, 5.57; N, 2.77%); $\nu_{\max}$ (KBr)/cm⁻¹ 2950, 1730, 1655, 1425, 1390 and 1300; δ_h (400 MHz; CDCl₃; Me₄Si) 1.98 (s, 6H, 2 × CH₃), 2.13 (s, 3H, CH₃), 3.49 (d, *J* = 10.9 Hz, 1H, COCH), 3.61 (d, *J* = 10.9 Hz, 1H, COCH), 3.95 (s, 3H, OCH₃), 4.70 (d, *J* = 14.2 Hz, 1H, NCH), 5.40 (d, *J* = 14.2 Hz, 1H, NCH), 6.65 (s, 2H, 2 × ArH), 6.75 (d, *J* = 8.2 Hz, 1H, ArH), 6.91 (d, *J* = 16.2 Hz, 1H, CH), 7.15 (d, *J* = 16.2 Hz, 1H, CH), 7.30–7.43 (m, 3H, ArH), 7.43–7.50 (m, 2H, ArH), 7.74 (dd, *J* = 8.2, 1.9 Hz, 1H, ArH) and 8.37 (d, *J* = 1.9 Hz, 1H, ArH); δ_c (100.6 MHz; CDCl₃; Me₄Si) 19.7 (2 × q), 20.8 (q), 26.9 (t), 45.3 (t), 52.5 (q), 120.8 (d), 127.0 (2 × d), 127.3 (d), 128.4 (s), 128.73 (d), 128.79 (3 × d), 129.2 (2 × d), 130.7 (d), 130.9 (s), 133.5 (d), 136.2 (s), 136.6 (s), 137.6 (s), 138.2 (2 × s), 141.1 (s), 165.9 (s) and 166.2 (s).

2-Bromo-N-(2,4,6-trimethylbenzyl)-N-{2-[(E)-[2-(4-methylphenyl)ethynyl]]phenyl}acetamide 1k. Colorless crystals; mp 171–172 °C (from ethyl acetate–hexanes); yield: 99% (98% conversion); (Found: C, 69.82; H, 6.07; N, 3.00; Calc. for C₂₇H₂₈BrNO: C, 70.13; H, 6.10; N, 3.03%); $\nu_{\max}$ (KBr)/cm⁻¹ 2915, 1660, 1425, 1395 and 1270; δ_h (400 MHz; CDCl₃; Me₄Si) 1.98 (s, 6H, 2 × CH₃), 2.14 (s, 3H, CH₃), 2.38 (s, 3H, CH₃), 3.55 (d, *J* = 11.1 Hz, 1H, COCH), 3.62 (d, *J* = 11.1 Hz, 1H, COCH), 4.68 (d, *J* = 14.1 Hz, 1H, NCH), 5.38 (d, *J* = 14.1 Hz, 1H, NCH), 6.65 (dd, *J* = 8.0, 1.1 Hz,

1H, ArH), 6.66 (s, 2H, 2 × ArH), 6.86 (d, J = 16.2 Hz, 1H, CH), 7.01 (d, J = 16.2 Hz, 1H, CH), 7.08 (td, J = 8.0, 1.1 Hz, 1H, ArH), 7.18 (d, J = 8.0 Hz, 2H, ArH), 7.33 (t, J = 8.0 Hz, 1H, ArH), 7.34 (d, J = 8.0 Hz, 2H, ArH) and 7.67 (d, J = 8.0 Hz, 1H, ArH); δ_C (100.6 MHz; CDCl₃; Me₄Si) 19.6 (2 × q), 20.8 (q), 21.3 (q), 27.5 (t), 45.3 (t), 120.8 (d), 125.9 (d), 126.8 (2 × d), 128.0 (d), 128.9 (s), 129.0 (2 × d), 129.2 (d), 129.4 (2 × d), 130.3 (d), 132.2 (d), 133.8 (s), 136.3 (s), 137.31 (s), 137.37 (s), 138.41 (2 × s), 138.44 (s) and 166.3 (s).

2-Bromo-*N*-{2-[(*E*)-[2-(4-methoxyphenyl)ethynyl]]phenyl}-*N*-(2,4,6-trimethylbenzyl)acetamide 1l. Colorless crystals; mp 213–214 °C (from ethyl acetate–hexanes); yield: 99%; (Found: C, 67.65; H, 5.88; N, 2.94; Calc. for C₂₇H₂₈BrNO₂: C, 67.78; H, 5.90; N, 2.93%); $\nu_{\max}$ (KBr)/cm^{−1} 2925, 1670, 1610, 1515, 1375 and 1250; δ_H (400 MHz; CDCl₃; Me₄Si) 1.98 (s, 6H, 2 × CH₃), 2.14 (s, 3H, CH₃), 3.55 (d, J = 11.1 Hz, 1H, COCH), 3.62 (d, J = 11.1 Hz, 1H, COCH), 3.85 (s, 3H, OCH₃), 4.68 (d, J = 14.1 Hz, 1H, NCH), 5.38 (d, J = 14.1 Hz, 1H, NCH), 6.64 (dd, J = 7.7, 0.9 Hz, 1H, ArH), 6.66 (s, 2H, 2 × ArH), 6.77 (d, J = 16.2 Hz, 1H, CH), 6.91 (d, J = 8.7 Hz, 2H, 2 × ArH), 6.98 (d, J = 16.2 Hz, 1H, CH), 7.06 (td, J = 7.7, 0.9 Hz, 1H, ArH), 7.32 (t, J = 7.7 Hz, 1H, ArH), 7.38 (d, J = 8.7 Hz, 2H, 2 × ArH) and 7.65 (d, J = 7.7 Hz, 1H, ArH); δ_C (100.6 MHz; CDCl₃; Me₄Si) 19.6 (2 × q), 20.8 (q), 27.5 (t), 45.3 (t), 55.4 (q), 114.1 (2 × d), 119.5 (d), 125.7 (d), 127.8 (d), 128.2 (2 × d), 128.9 (s), 129.0 (2 × d), 129.2 (d), 129.4 (s), 130.3 (d), 131.7 (d), 136.4 (s), 137.1 (s), 137.3 (s), 138.4 (2 × s), 159.9 (s) and 166.3 (s).

2-Bromo-*N*-{2-[(*E*)-[2-(4-chlorophenyl)ethynyl]]phenyl}-*N*-(2,4,6-trimethylbenzyl)acetamide 1m. Colorless crystals; mp 175–176 °C (from ethyl acetate–hexanes); yield: 87%; (Found: C, 64.32; H, 5.18; N, 2.88; Calc. for C₂₆H₂₅BrClNO: C, 64.68; H, 5.22; N, 2.90%); $\nu_{\max}$ (KBr)/cm^{−1} 2950, 1670, 1490, 1375 and 1180; δ_H (400 MHz; CDCl₃; Me₄Si) 1.97 (s, 6H, 2 × CH₃), 2.11 (s, 3H, CH₃), 3.55 (d, J = 11.0 Hz, 1H, COCH), 3.62 (d, J = 11.0 Hz, 1H, COCH), 4.82 (d, J = 14.1 Hz, 1H, NCH), 5.24 (d, J = 14.1 Hz, 1H, NCH), 6.64 (s, 2H, 2 × ArH), 6.74 (dd, J = 7.7, 1.0 Hz, 1H, ArH), 6.82 (d, J = 16.2 Hz, 1H, CH), 6.92 (d, J = 16.2 Hz, 1H, CH), 7.14 (td, J = 7.7, 1.0 Hz, 1H, ArH), 7.33 (s, 4H, ArH), 7.35 (t, J = 7.7 Hz, 1H, ArH) and 7.65 (d, J = 7.7 Hz, 1H, ArH); δ_C (100.6 MHz; CDCl₃; Me₄Si) 19.5 (2 × q), 20.7 (q), 27.2 (t), 45.4 (t), 122.4 (d), 125.9 (d), 127.9 (2 × d), 128.5 (d), 128.6 (s), 128.7 (2 × d), 128.9 (2 × d), 129.2 (d), 130.2 (d), 130.4 (d), 133.8 (s), 135.0 (s), 135.8 (s), 137.3 (s), 137.5 (s), 138.2 (2 × s) and 166.2 (s).

2-Bromo-*N*-{2-[(*E*)-[2-(4-cyanophenyl)ethynyl]]phenyl}-*N*-(2,4,6-trimethylbenzyl)acetamide 1n. White solids; mp 190–191 °C (from ethyl acetate–hexanes); yield: 99%; $\nu_{\max}$ (neat)/cm^{−1} 2955, 2230, 1665, 1375, 1195 and 1180; δ_H (400 MHz; CDCl₃; Me₄Si) 1.96 (s, 6H, 2 × CH₃), 2.07 (s, 3H, CH₃), 3.56 (d, J = 11.0 Hz, 1H, COCH), 3.62 (d, J = 11.0 Hz, 1H, COCH), 4.98 (d, J = 14.1 Hz, 1H, NCH), 5.09 (d, J = 14.1 Hz, 1H, NCH), 6.59 (s, 2H, 2 × ArH), 6.85 (dd, J = 7.7, 1.2 Hz, 1H, ArH), 6.89 (d, J = 16.5 Hz, 1H, CH), 6.93 (d, J = 16.5 Hz, 1H, CH), 7.23 (td, J = 7.7, 1.2 Hz, 1H, ArH), 7.39 (td, J = 7.7, 1.1 Hz, 1H, ArH), 7.46 (d, J = 8.4 Hz, 2H, 2 × ArH), 7.64 (d, J = 8.4 Hz, 2H, 2 × ArH) and 7.67 (dd, J = 7.7, 1.1 Hz, 1H, ArH); δ_C (100.6 MHz; CDCl₃; Me₄Si) 19.6 (2 × q), 20.7 (q), 27.1 (t), 45.7 (t), 111.1 (s), 118.7 (s), 125.7 (d), 126.2 (d), 127.1 (2 × d), 128.5 (s), 129.0 (2 × d), 129.34 (d), 129.39 (2 × d), 130.3 (d), 132.3 (2 × d), 135.3 (s), 137.4 (s), 138.1 (s), 138.2 (2 × s), 141.0 (s) and 166.2 (s); m/z (EI) 472.1146 (M^+ C₂₇H₂₅BrN₂O requires 472.1151).

2-Bromo-*N*-(2,4,6-trimethylbenzyl)-*N*-{2-[(*E*)-(*n*-octen-1-yl)]phenyl}acetamide 1o. Colorless oils; yield: 90%; $\nu_{\max}$ (neat)/cm^{−1} 2925, 1665, 1390, 1265 and 1200; δ_H (400 MHz; CDCl₃; Me₄Si) 0.90 (t, J = 6.5 Hz, 3H, CH₃), 1.20–1.50 (m, 10H, CH₂), 1.97 (s, 6H, 2 × CH₃), 2.21 (s, 3H, CH₃), 3.50 (d, J = 11.2 Hz, 1H, COCH), 3.58 (d, J = 11.2 Hz, 1H, COCH), 4.41 (d, J = 14.1 Hz, 1H, NCH), 5.53 (d, J = 14.1 Hz, 1H, NCH), 6.23 (dt, J = 15.8, 6.2 Hz, 1H, CH), 6.30 (d, J = 15.8 Hz, 1H, CH), 6.47 (dd, J = 7.7, 1.3 Hz, 1H, ArH), 6.71 (s, 2H, 2 × ArH), 6.98 (td, J = 7.7, 1.3 Hz, 1H, ArH), 7.25 (td, J = 7.7, 1.1 Hz, 1H, ArH) and 7.50 (dd, J = 7.7, 1.1 Hz, 1H, ArH); δ_C (100.6 MHz; CDCl₃; Me₄Si) 14.1 (q), 19.6 (2 × q), 20.9 (q), 22.6 (t), 27.6 (t), 28.9 (t), 29.2 (t), 31.7 (t), 33.3 (t), 44.9 (t), 123.4 (d), 126.1 (d), 127.4 (d), 128.9 (2 × d), 129.0 (s + d), 130.1 (d), 135.9 (d), 136.4 (2 × s), 137.3 (s), 138.5 (2 × s) and 166.2 (s); m/z (EI) 455.1824 (M^+ C₂₆H₃₄BrNO requires 455.1824).

2-Bromo-*N*-(2,4,6-trimethylbenzyl)-*N*-{2-[(*E*)-[2-(pyridin-2-yl)ethynyl]]phenyl}acetamide 1p. Yellow crystals; mp 124–125 °C (from ethyl acetate–hexanes); yield: 94% (84% conversion); (Found: C, 66.73; H, 5.63; N, 6.23; Calc. for C₂₅H₂₅BrN₂O: C, 66.82; H, 5.61; N, 6.23%); $\nu_{\max}$ (KBr)/cm^{−1} 2920, 1670, 1460, 1375 and 1185; δ_H (400 MHz; CDCl₃; Me₄Si) 1.97 (s, 6H, 2 × CH₃), 2.10 (s, 3H, CH₃), 3.56 (d, J = 11.1 Hz, 1H, COCH), 3.65 (d, J = 11.1 Hz, 1H, COCH), 4.77 (d, J = 14.1 Hz, 1H, NCH), 5.33 (d, J = 14.1 Hz, 1H, NCH), 6.61 (s, 2H, 2 × ArH), 6.72 (d, J = 7.7 Hz, 1H, ArH), 7.07 (d, J = 16.1 Hz, 1H, CH), 7.15 (t, J = 7.7 Hz, 1H, ArH), 7.20 (dd, J = 6.7, 5.3 Hz, 1H, ArH), 7.32–7.43 (m, 3H, ArH), 7.64–7.76 (m, 2H, ArH) and 8.60 (d, J = 4.4 Hz, 1H, ArH); δ_C (100.6 MHz; CDCl₃; Me₄Si) 19.6 (2 × q), 20.8 (q), 27.4 (t), 45.5 (t), 121.7 (d), 122.5 (d), 126.2 (d), 126.5 (d), 128.7 (s), 128.92 (2 × d), 128.95 (d), 129.3 (d), 130.4 (d), 131.4 (d), 135.5 (s), 136.5 (d), 137.3 (s), 137.9 (s), 138.4 (2 × s), 149.4 (d), 154.9 (s) and 166.1 (s).

2-Bromo-*N*-(2,4,6-trimethylbenzyl)-*N*-{2-[(*E*)-[2-(phenylethenyl)]phenyl}propioamide 1q. Colorless crystals; mp 152–153 °C (from ethyl acetate–hexanes); yield: 99%; (Found: C, 69.98; H, 6.04; N, 2.99; Calc. for C₂₇H₂₈BrNO: C, 70.13; H, 6.10; N, 3.03%); $\nu_{\max}$ (KBr)/cm^{−1} 2920, 1655, 1450, 1390 and 1245; δ_H (400 MHz; CDCl₃; Me₄Si) (*E* form : *Z* form = 20 : 9) 1.70 (d, J = 6.7 Hz, 3H, CH₃_{*E*}), 1.75 (d, J = 6.6 Hz, 3H, CH₃_{*Z*}), 1.94 (s, 6H, 2 × CH₃_{*Z*}), 2.00 (s, 6H, 2 ×

CH₃ E), 2.02 (s, 3H, CH₃ Z), 2.18 (s, 3H, CH₃ E), 4.04 (q, *J* = 6.7 Hz, 1H, COCH E), 4.30 (q, *J* = 6.6 Hz, 1H, COCH Z), 4.47 (d, *J* = 14.2 Hz, 1H, NCH E), 5.02 (s, 2H, NCH₂ Z), 5.60 (d, *J* = 14.2 Hz, 1H, NCH E), 6.53 (s, 2H, 2 × ArH Z), 6.62 (dd, *J* = 7.8, 1.1 Hz, 1H, ArH E), 6.67 (dd, *J* = 7.8, 1.2 Hz, 1H, ArH Z), 6.70 (s, 2H, 2 × ArH E), 6.85 (d, *J* = 16.3 Hz, 1H, CH Z), 6.89 (d, *J* = 16.2 Hz, 1H, CH E), 7.00 (d, *J* = 16.3 Hz, 1H, CH Z), 7.06 (td, *J* = 7.8, 1.1 Hz, 1H, ArH E), 7.08 (d, *J* = 16.2 Hz, 1H, CH E), 7.14 (td, *J* = 7.8, 1.2 Hz, 1H, ArH Z), 7.24–7.48 (m, 12H, ArH), 7.676 (dd, *J* = 7.8, 1.2 Hz, 1H, ArH Z) and 7.685 (dd, *J* = 7.8, 1.1 Hz, 1H, ArH E).

2-Bromo-*N*-(2,4,6-trimethylbenzyl)-*N*-(4-methyl-2-[(*E*)-(2-phenylethenyl)]phenyl)propioamide 1r. Colorless crystals; mp 156–157 °C (from ethyl acetate–hexanes); yield: 99%; (Found: C, 70.59; H, 6.40; N, 2.93; Calc. for C₂₈H₃₀BrNO: C, 70.58; H, 6.35; N, 2.94%); $\nu_{\max}$ (KBr)/cm⁻¹ 2920, 1660, 1395, 1245 and 1175; δ_{H} (400 MHz; CDCl₃; Me₄Si) (E form : Z form = 20 : 9) 1.69 (d, *J* = 6.6 Hz, 3H, CH₃ E), 1.74 (d, *J* = 6.7 Hz, 3H, CH₃ Z), 1.95 (s, 3H, CH₃ E), 2.01 (s, 6H, 2 × CH₃ E), 2.02 (s, 3H, 2 × CH₃ Z), 2.18 (s, 3H, CH₃ E), 2.36 (s, 9H, 3 × CH₃ Z), 4.06 (q, *J* = 6.6 Hz, 1H, COCH E), 4.32 (q, *J* = 6.6 Hz, 1H, COCH Z), 4.45 (d, *J* = 14.1 Hz, 1H, NCH E), 5.00 (s, 2H, NCH Z), 5.57 (d, *J* = 14.1 Hz, 1H, NCH E), 6.50 (d, *J* = 8.0 Hz, 1H, ArH E), 6.54 (s, 2H, 2 × ArH Z), 6.55 (d, *J* = 8.1 Hz, 1H, ArH Z), 6.70 (s, 2H, 2 × ArH E), 6.83 (d, *J* = 16.3 Hz, 1H, CH Z), 6.79–6.89 (m, 1H, ArH), 6.85 (d, *J* = 16.2 Hz, 1H, CH E), 6.91–6.96 (m, 1H, ArH), 6.96 (d, *J* = 16.3 Hz, 1H, CH Z), 7.06 (d, *J* = 16.2 Hz, 1H, CH E) and 7.22–7.50 (m, 12H, ArH).

2-Bromo-*N*-(4-fluoro-2-[(*E*)-(2-phenylethenyl)]phenyl)-*N*-(2,4,6-trimethylbenzyl)propioamide 1s. Colorless crystals; mp 132–133 °C (from ethyl acetate–hexanes); yield: 97%; (Found: C, 67.53; H, 5.69; N, 2.86; Calc. for C₂₇H₂₇BrFNO: C, 67.50; H, 5.66; N, 2.92%); $\nu_{\max}$ (KBr)/cm⁻¹ 2915, 1660, 1485, 1395, 1250 and 1180; δ_{H} (400 MHz; CDCl₃; Me₄Si) (E form : Z form = 5 : 2) 1.70 (d, *J* = 6.6 Hz, 3H, CH₃ E), 1.76 (d, *J* = 6.6 Hz, 3H, CH₃ Z), 1.96 (s, 6H, 2 × CH₃ Z), 2.02 (s, 6H, 2 × CH₃ E), 2.03 (s, 3H, CH₃ Z), 2.18 (s, 3H, CH₃ E), 4.01 (q, *J* = 6.6 Hz, 1H, COCH E), 4.28 (q, *J* = 6.6 Hz, 1H, COCH Z), 4.42 (d, *J* = 14.1 Hz, 1H, NCH E), 4.94 (d, *J* = 14.1 Hz, 1H, NCH Z), 5.05 (d, *J* = 14.1 Hz, 1H, NCH Z), 5.60 (d, *J* = 14.1 Hz, 1H, NCH E), 6.55–6.65 (m, 2H, ArH), 6.56 (s, 2H, 2 × ArH Z), 6.70–6.78 (m, 1H, ArH), 6.71 (s, 2H, 2 × ArH E), 6.79–6.89 (m, 1H, ArH), 6.79–6.89 (m, 1H, CH Z), 6.83 (d, *J* = 16.2 Hz, 1H, CH E), 6.95 (dd, *J* = 16.2, 1.4 Hz, 1H, CH Z), 7.08 (d, *J* = 16.2 Hz, 1H, CH E) and 7.26–7.48 (m, 12H, ArH).

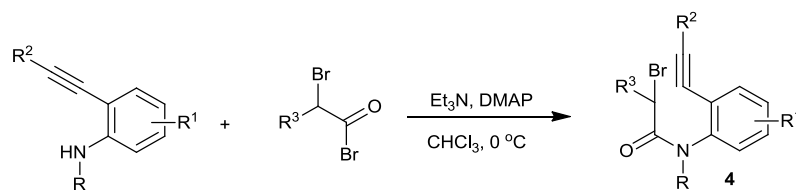
2-Bromo-*N*-(2,4,6-trimethylbenzyl)-2-phenyl-*N*-(2-[(*E*)-(2-phenylethenyl)]phenyl)acetamide 1t. Colorless crystals; mp 157–158 °C (from ethyl acetate–hexanes); yield: 99% (97% conversion); (Found: C, 73.24; H, 5.79; N, 2.69; Calc. for C₃₂H₃₀BrNO: C, 73.28; H, 5.77; N, 2.67%); $\nu_{\max}$ (KBr)/cm⁻¹ 2925, 1725, 1665, 1375 and 1170; δ_{H} (400 MHz; CDCl₃; Me₄Si) (E form : Z form = 10 : 7) 1.87 (s, 6H, 2 × CH₃ Z), 1.95 (s, 6H, 2 × CH₃ E), 2.04 (s, 3H, CH₃ Z), 2.09 (s, 3H, CH₃ E), 4.63 (d, *J* = 14.1 Hz, 1H, NCH E), 4.87 (d, *J* = 14.2 Hz, 1H, NCH Z), 5.16 (d, *J* = 14.2 Hz, 1H, NCH Z), 5.20 (s, 1H, COCH E), 5.27 (s, 1H, COCH Z), 5.37 (d, *J* = 14.1 Hz, 1H, NCH E), 6.29 (dd, *J* = 7.8, 1.2 Hz, 1H, ArH Z), 6.40 (d, *J* = 16.2 Hz, 1H, CH E), 6.53 (s, 2H, 2 × ArH Z), 6.60 (s, 2H, 2 × ArH E), 6.77 (dd, *J* = 7.8, 1.2 Hz, 1H, ArH Z), 6.83 (d, *J* = 16.2 Hz, 1H, CH E), 6.94–7.09 (m, 5H, ArH), 7.10–7.20 (m, 5H, ArH), 7.20–7.29 (m, 6H, ArH), 7.29–7.43 (m, 10H, ArH), 7.45–7.50 (m, 2H, ArH), 7.64 (d, *J* = 7.3 Hz, 1H, ArH E) and 7.72 (d, *J* = 7.3 Hz, 1H, ArH Z).

2-Bromo-*N*-(2,4,6-trimethylbenzyl)-*N*-(4-methyl-2-[(*E*)-(2-phenylethenyl)]phenyl)-2-phenylacetamide 1u. Colorless solids; mp 60–61 °C (from ethyl acetate–hexanes); yield: 99%; $\nu_{\max}$ (neat)/cm⁻¹ 2920, 1740, 1665, 1380 and 1180; δ_{H} (400 MHz; CDCl₃; Me₄Si) (E form : Z form = 4 : 3) 1.87 (s, 6H, 2 × CH₃ Z), 1.95 (s, 6H, 2 × CH₃ E), 2.05 (s, 3H, CH₃ Z), 2.10 (s, 3H, CH₃ E), 2.40 (s, 3H, CH₃ Z), 2.41 (s, 3H, CH₃ E), 4.61 (d, *J* = 14.1 Hz, 1H, NCH E), 4.85 (d, *J* = 14.0 Hz, 1H, NCH Z), 5.13 (d, *J* = 14.0 Hz, 1H, NCH Z), 5.21 (s, 1H, COCH E), 5.29 (s, 1H, COCH Z), 5.34 (d, *J* = 14.1 Hz, 1H, NCH E), 6.20 (d, *J* = 7.8 Hz, 1H, CH Z), 6.37 (d, *J* = 16.1 Hz, 1H, CH E), 6.54 (s, 2H, 2 × ArH Z), 6.60 (s, 2H, 2 × ArH E), 6.65 (d, *J* = 7.8 Hz, 1H, CH Z), 6.82 (d, *J* = 16.1 Hz, 1H, CH E), 6.80–6.85 (m, 1H, ArH), 6.93–7.01 (m, 2H, ArH), 7.01–7.09 (m, 2H, ArH), 7.11–7.19 (m, 4H, ArH), 7.19–7.33 (m, 5H, ArH) and 7.33–7.55 (m, 12H, ArH); *m/z* (EI) 537.1663 (M⁺ C₃₃H₃₂BrNO requires 537.1667).

2-Bromo-*N*-(4-fluoro-2-[(*E*)-(2-phenylethenyl)]phenyl)-*N*-(2,4,6-trimethylbenzyl)-2-phenylacetamide 1v. Colorless crystals; mp 162–163 °C (from ethyl acetate–hexanes); yield: 99%; (Found: C, 70.82; H, 5.38; N, 2.60; Calc. for C₃₂H₂₉BrFNO: C, 70.85; H, 5.39; N, 2.58%); $\nu_{\max}$ (KBr)/cm⁻¹ 2925, 1665, 1485, 1370 and 1170; δ_{H} (400 MHz; CDCl₃; Me₄Si) (E form : Z form = 10 : 7) 1.88 (s, 6H, 2 × CH₃ Z), 1.97 (s, 6H, 2 × CH₃ E), 2.05 (s, 3H, CH₃ Z), 2.11 (s, 3H, CH₃ E), 4.57 (d, *J* = 14.1 Hz, 1H, NCH E), 4.80 (d, *J* = 14.2 Hz, 1H, NCH Z), 5.16 (s, 1H, COCH E), 5.19 (d, *J* = 14.2 Hz, 1H, NCH Z), 5.25 (s, 1H, COCH Z), 5.38 (d, *J* = 14.1 Hz, 1H, NCH E), 6.21 (dd, *J* = 8.7, 5.4 Hz, 1H, ArH Z), 6.35 (dd, *J* = 16.1, 1.4 Hz, 1H, ArH E), 6.55 (s, 2H, 2 × ArH Z), 6.63 (s, 2H, 2 × ArH E), 6.64–6.75 (m, 2H, ArH), 6.79–6.88 (m, 2H, ArH), 6.97–7.02 (m, 2H, ArH), 7.03–7.11 (m, 2H, ArH), 7.12–7.20 (m, 4H, ArH), 7.22–7.30 (m, 4H, ArH), 7.30–7.36 (m, 4H, ArH), 7.36–7.44 (m, 6H, ArH) and 7.46–7.52 (m, 2H, ArH).

B. Synthesis of α -bromo- *N*-2-(alkynylphenyl)acetamides 4:

The starting α -bromo- *N*-2-(alkynylphenyl)acetamides **4** were prepared by the reaction between 2-(alkynylphenyl)amines and α -bromoacetyl bromide.



Typical procedure for the preparation of α -bromo-*N*-2-(alkynylphenyl)acetamides 4: A solution of *N*-(2,4,6-trimethylbenzyl)-2-(phenylethynyl)phenylamine (1.01 g, 3.10 mmol), 2-bromoacetyl bromide (1.27 g, 6.29 mmol), triethylamine (646 mg, 6.39 mmol), and DMAP (39 mg, 0.32 mmol) in chloroform (20 mL) was stirred in an ice-water bath for 1 h. After workup as described as above, the residue was chromatographed over 20 g of silica gel (eluted with 1:20 ethyl acetate–hexanes) to give **4a** (1.26 g, 91%).

2-Bromo-*N*-(2,4,6-trimethylbenzyl)-*N*-[2-(phenylethynyl)phenyl]acetamide 4a. Colorless crystals; mp 143–144 °C (from ethyl acetate–hexanes); yield: 91%; (Found: C, 69.95; H, 5.40; N, 3.12; Calc. for $C_{26}H_{24}BrNO$: C, 69.96; H, 5.42; N, 3.14%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2915, 2210, 1665, 1390 and 1270; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 2.02 (s, 6H, $2 \times \text{CH}_3$), 2.22 (s, 3H, CH_3), 3.62 (d, $J = 11.1 \text{ Hz}$, 1H, COCH), 3.74 (d, $J = 11.1 \text{ Hz}$, 1H, COCH), 4.42 (d, $J = 14.2 \text{ Hz}$, 1H, NCH), 5.74 (d, $J = 14.2 \text{ Hz}$, 1H, NCH), 6.49 (d, $J = 7.7 \text{ Hz}$, 1H, ArH), 6.72 (s, 2H, $2 \times \text{ArH}$), 7.08 (td, $J = 7.7, 1.4 \text{ Hz}$, 1H, ArH), 7.30 (td, $J = 7.7, 1.0 \text{ Hz}$, 1H, ArH), 7.35–7.41 (m, 3H, ArH) and 7.54–7.60 (m, 3H, ArH); $\delta_{\text{C}}(100.6 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 19.4 ($2 \times \text{q}$), 20.9 (q), 27.5 (t), 44.5 (t), 84.4 (s), 95.4 (s), 122.2 (s), 123.4 (s), 125.8 ($2 \times \text{d}$), 128.69 (d), 128.73 (d), 128.9 ($2 \times \text{d}$), 129.0 (d), 129.3 (s), 130.3 (s), 131.8 ($2 \times \text{d}$), 132.4 (d), 137.3 (s), 138.5 ($2 \times \text{s}$), 141.0 (s) and 166.5 (s).

***N*-Benzyl-2-bromo-*N*-[2-(phenylethynyl)phenyl]acetamide 4b.** Yellow oils; yield: 94%; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3030, 2220, 1665 and 1495; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 3.70 (d, $J = 11.4 \text{ Hz}$, 1H, COCH), 3.81 (d, $J = 11.4 \text{ Hz}$, 1H, COCH), 4.50 (d, $J = 14.3 \text{ Hz}$, 1H, NCH), 5.45 (d, $J = 14.3 \text{ Hz}$, 1H, NCH), 6.99 (d, $J = 7.8 \text{ Hz}$, 1H, ArH), 7.23 (s, 5H, ArH), 7.27 (td, $J = 7.8, 1.5 \text{ Hz}$, 1H, ArH), 7.32–7.39 (m, 4H, ArH), 7.45–7.51 (m, 2H, ArH) and 7.59 (dd, $J = 7.8, 1.5 \text{ Hz}$, 1H, ArH); $\delta_{\text{C}}(100.6 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 27.8 (t), 52.9 (t), 84.8 (s), 95.6 (s), 122.2 (s), 123.0 (s), 127.6 (d), 128.4 ($2 \times \text{d}$), 128.5 ($2 \times \text{d}$), 128.7 (d), 129.0 (d), 129.2 ($3 \times \text{d}$), 129.4 (d), 131.8 ($2 \times \text{d}$), 133.0 (d), 136.5 (s), 142.3 (s) and 166.7 (s); m/z (EI) 403.0570 (M^+ $\text{C}_{23}\text{H}_{18}\text{BrNO}$ requires 403.0572).

2-Bromo-*N*-ethyl-*N*-[2-(phenylethynyl)phenyl]acetamide 4c. Colorless oils; yield: 96%; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 2975, 1650, 1440, 1305 and 1205; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 1.18 (t, $J = 7.0 \text{ Hz}$, 3H, CH_3), 3.67 (d, $J = 11.3 \text{ Hz}$, 1H, COCH), 3.76 (d, $J = 11.3 \text{ Hz}$, 1H, COCH), 3.81 (dq, $J = 13.8, 7.0 \text{ Hz}$, 1H, NCH), 3.91 (dq, $J = 13.8, 7.0 \text{ Hz}$, 1H, NCH), 7.31–7.39 (m, 4H, ArH), 7.40 (td, $J = 7.3, 1.9 \text{ Hz}$, 2H, ArH), 7.46–7.52 (m, 2H, ArH) and 7.64 (dd, $J = 7.3, 1.9 \text{ Hz}$, 1H, ArH); $\delta_{\text{C}}(100.6 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ $\delta = 12.7$ (q), 27.8 (t), 44.9 (t), 85.1 (s), 95.5 (s), 122.2 (s), 123.4 (s), 128.51 ($2 \times \text{d}$), 128.59 (d), 129.0 (d), 129.1 (d), 129.6 (d), 131.7 ($2 \times \text{d}$), 133.0 (d), 142.6 (s) and 166.3 (s); m/z (EI) 341.0408 (M^+ $\text{C}_{18}\text{H}_{16}\text{BrNO}$ requires 341.0415).

2-Bromo-*N*-[2-(phenylethynyl)phenyl]acetamide 4d. Colorless needles; mp 131–132 °C (from ethyl acetate–hexanes); yield: 96%; (Found: C, 61.10; H, 3.88; N, 4.44; Calc. for $\text{C}_{16}\text{H}_{12}\text{BrNO}$: C, 61.17; H, 3.85; N, 4.46%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3280, 1665, 1535, 1315 and 1185; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 4.10 (s, 2H, COCH₂), 7.13 (td, $J = 7.8, 1.0 \text{ Hz}$, 1H, ArH), 7.35–7.41 (m, 4H, ArH), 7.53 (dd, $J = 7.8, 1.4 \text{ Hz}$, 1H, ArH), 7.56–7.62 (m, 2H, ArH), 8.41 (d, $J = 7.8 \text{ Hz}$, 1H, ArH) and 9.24 (brs, 1H, NH); $\delta_{\text{C}}(100.6 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 29.8 (t), 83.9 (s), 97.0 (s), 112.8 (s), 118.9 (d), 122.3 (s), 124.3 (d), 128.5 ($2 \times \text{d}$), 128.9 (d), 129.6 (d), 131.6 ($2 \times \text{d}$), 131.8 (d), 138.1 (s) and 163.2 (s).

2-Bromo-*N*-[4-fluoro-2-(phenylethynyl)phenyl]-*N*-(2,4,6-trimethylbenzyl)acetamide 4e. Colorless crystals; mp 124–125 °C (from ethyl acetate–hexanes); yield: 85%; (Found: C, 67.15; H, 5.00; N, 3.00; Calc. for $\text{C}_{26}\text{H}_{23}\text{BrFNO}$: C, 67.25; H, 4.99; N, 3.02%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2960, 2210, 1655, 1390 and 1195; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 2.04 (s, 6H, $2 \times \text{CH}_3$), 2.23 (s, 3H, CH_3), 3.60 (d, $J = 10.9 \text{ Hz}$, 1H, COCH), 3.73 (d, $J = 10.9 \text{ Hz}$, 1H, COCH), 4.38 (d, $J = 14.2 \text{ Hz}$, 1H, NCH), 5.73 (d, $J = 14.2 \text{ Hz}$, 1H, NCH), 6.44 (dd, $J = 8.6, 5.3 \text{ Hz}$, 1H, ArH), 6.74 (s, 2H, $2 \times \text{ArH}$), 6.76 (td, $J = 8.6, 2.6 \text{ Hz}$, 1H, ArH), 7.26 (dd, $J = 8.6, 2.6 \text{ Hz}$, 1H, ArH), 7.35–7.42 (m, 3H, ArH) and 7.53–7.59 (m, 2H, ArH); $\delta_{\text{C}}(100.6 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 19.4 ($2 \times \text{q}$), 20.9 (q), 27.2 (t), 44.5 (t), 83.4 (s), 96.5 (s), 115.9 (dd, $J_{\text{CF}} = 22.1 \text{ Hz}$), 118.8 (dd, $J_{\text{CF}} = 24.1 \text{ Hz}$), 121.7 (s), 125.2 (sd, $J_{\text{CF}} = 11.1 \text{ Hz}$), 128.6 ($2 \times \text{d}$), 129.0 ($2 \times \text{d}$), 129.4 (d), 132.0 ($2 \times \text{d}$), 132.1 (d), 137.1 ($2 \times \text{s}$), 137.4 (s), 138.4 ($2 \times \text{s}$), 161.8 (sd, $J_{\text{CF}} = 250.5 \text{ Hz}$) and 166.7 (s).

2-Bromo-*N*-[4-chloro-2-(phenylethynyl)phenyl]-*N*-(2,4,6-trimethylbenzyl)acetamide 4f. Colorless crystals; mp 137–138 °C (from ethyl acetate–hexanes); yield: 91%; (Found: C, 64.93; H, 4.93; N, 2.92; Calc. for $\text{C}_{26}\text{H}_{23}\text{BrClNO}$: C, 64.95; H, 4.82; N, 2.91%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2915, 2220, 1665, 1480 and 1270; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 2.04 (s, 6H, $2 \times \text{CH}_3$), 2.23 (s, 3H, CH_3), 3.59 (d, $J = 10.9 \text{ Hz}$, 1H, COCH), 3.72 (d, $J = 10.9 \text{ Hz}$, 1H, COCH), 4.38 (d, $J = 14.2 \text{ Hz}$, 1H, NCH), 5.73 (d, $J = 14.2 \text{ Hz}$, 1H, NCH), 6.40 (d, $J = 8.5 \text{ Hz}$, 1H, ArH), 6.75 (s, 2H, $2 \times \text{ArH}$), 7.04 (dd, $J = 8.5, 2.4 \text{ Hz}$, 1H, ArH), 7.34–7.42 (m, 3H, ArH) and 7.52–7.59 (m, 3H, ArH); $\delta_{\text{C}}(100.6 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 19.5 ($2 \times \text{q}$), 20.9 (q), 27.1

(t), 44.4 (t), 83.2 (s), 96.7 (s), 121.6 (s), 125.1 (s), 128.6 (2 × d), 128.8 (d), 128.9 (s), 129.0 (2 × d), 129.4 (d), 131.5 (d), 131.9 (3 × d), 134.6 (s), 137.5 (s), 138.4 (2 × s), 139.4 (s) and 166.5 (s).

2-Bromo-N-[4-bromo-2-(phenylethynyl)phenyl]-N-(2,4,6-trimethylbenzyl)acetamide 4g. Colorless crystals; mp 143–144 °C (from ethyl acetate–hexanes); yield: 88%; (Found: C, 59.46; H, 4.43; N, 2.64; Calc. for C₂₆H₂₃Br₂NO: C, 59.45; H, 4.41; N, 2.67%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2950, 2220, 1665, 1480 and 1390; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 2.04 (s, 6H, 2 × CH₃), 2.23 (s, 3H, CH₃), 3.59 (d, $J = 10.9 \text{ Hz}$, 1H, COCH), 3.72 (d, $J = 10.9 \text{ Hz}$, 1H, COCH), 4.38 (d, $J = 14.2 \text{ Hz}$, 1H, NCH), 5.72 (d, $J = 14.2 \text{ Hz}$, 1H, NCH), 6.33 (d, $J = 8.5 \text{ Hz}$, 1H, ArH), 6.75 (s, 2H, 2 × ArH), 7.19 (dd, $J = 8.5, 2.2 \text{ Hz}$, 1H, ArH), 7.35–7.42 (m, 3H, ArH), 7.52–7.59 (m, 2H, ArH) and 7.32 (d, $J = 2.2 \text{ Hz}$, 1H, ArH); $\delta_{\text{C}}(100.6 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 19.5 (2 × q), 20.9 (q), 27.2 (t), 44.4 (t), 83.1 (s), 96.8 (s), 121.6 (s), 122.4 (s), 125.4 (s), 128.6 (2 × d), 128.9 (s), 129.1 (2 × d), 129.5 (d), 131.7 (d), 131.8 (d), 132.0 (2 × d), 134.9 (d), 137.5 (s), 138.4 (2 × s), 139.9 (s) and 166.4 (s).

2-Bromo-N-[4-methoxycarbonyl-2-(phenylethynyl)phenyl]-N-(2,4,6-trimethylbenzyl)acetamide 4h. Colorless crystals; mp 101–102 °C (from ethyl acetate–hexanes); yield: 94%; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2950, 2220, 1720, 1670 and 1265; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 2.03 (s, 6H, 2 × CH₃), 2.22 (s, 3H, CH₃), 3.57 (d, $J = 11.0 \text{ Hz}$, 1H, COCH), 3.73 (d, $J = 11.0 \text{ Hz}$, 1H, COCH), 3.93 (s, 3H, OCH₃), 4.43 (d, $J = 14.3 \text{ Hz}$, 1H, NCH), 5.76 (d, $J = 14.3 \text{ Hz}$, 1H, NCH), 6.56 (d, $J = 8.3 \text{ Hz}$, 1H, ArH), 6.73 (s, 2H, 2 × ArH), 7.36–7.42 (m, 3H, ArH), 7.54–7.61 (m, 2H, ArH), 7.72 (dd, $J = 8.3, 2.0 \text{ Hz}$, 1H, ArH) and 8.24 (d, $J = 2.0 \text{ Hz}$, 1H, ArH); $\delta_{\text{C}}(100.6 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 19.5 (2 × q), 20.9 (q), 27.1 (t), 44.5 (t), 52.5 (q), 83.6 (s), 96.4 (s), 121.8 (s), 124.0 (s), 128.6 (2 × d), 128.8 (s), 129.1 (2 × d), 129.4 (d), 129.5 (d), 130.53 (s), 130.59 (d), 131.9 (2 × d), 133.5 (d), 137.5 (s), 138.4 (2 × s), 144.7 (s), 165.5 (s) and 166.2 (s); m/z (EI) 503.1093 (M^+ C₂₈H₂₆BrNO₃ requires 503.1096).

2-Bromo-N-(2,4,6-trimethylbenzyl)-N-[4-methyl-2-(phenylethynyl)phenyl]acetamide 4i Colorless crystals; mp 129–130 °C (from ethyl acetate–hexanes); yield: 80%; (Found: C, 70.45; H, 5.74; N, 3.01; Calc. for C₂₇H₂₆BrNO: C, 70.44; H, 5.69; N, 3.04%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2950, 1665, 1500, 1390 and 1125; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 2.03 (s, 6H, 2 × CH₃), 2.22 (s, 3H, CH₃), 2.33 (s, 3H, CH₃), 3.62 (d, $J = 11.0 \text{ Hz}$, 1H, COCH), 3.73 (d, $J = 11.0 \text{ Hz}$, 1H, COCH), 4.41 (d, $J = 14.2 \text{ Hz}$, 1H, NCH), 5.71 (d, $J = 14.2 \text{ Hz}$, 1H, NCH), 6.37 (d, $J = 8.2 \text{ Hz}$, 1H, ArH), 6.73 (s, 2H, 2 × ArH), 6.88 (dd, $J = 8.2, 1.1 \text{ Hz}$, 1H, ArH), 7.34–7.42 (m, 4H, ArH) and 7.52–7.59 (m, 2H, ArH); $\delta_{\text{C}}(100.6 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 19.5 (2 × q), 20.92 (q), 20.98 (q), 27.6 (t), 44.5 (t), 84.6 (s), 95.0 (s), 122.3 (s), 123.0 (s), 128.5 (2 × d), 128.87 (2 × d), 128.93 (d), 129.4 (s), 129.6 (d), 129.9 (d), 131.8 (2 × d), 132.8 (d), 137.2 (s), 138.47 (s), 138.51 (2 × s), 138.8 (s) and 166.7 (s).

2-Bromo-N-(2,4,6-trimethylbenzyl)-N-[4,5-dimethyl-2-(phenylethynyl)phenyl]acetamide 4j. Colorless crystals; mp 136–137 °C (from ethyl acetate–hexanes); yield: 95%; (Found: C, 70.81; H, 5.99; N, 2.95; Calc. for C₂₈H₂₈BrNO: C, 70.88; H, 5.95; N, 2.95%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2920, 1660, 1485, 1385 and 1120; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 2.00 (s, 3H, CH₃), 2.02 (s, 6H, 2 × CH₃), 2.217 (s, 3H, CH₃), 2.223 (s, 3H, CH₃), 3.65 (d, $J = 11.1 \text{ Hz}$, 1H, COCH), 3.75 (d, $J = 11.1 \text{ Hz}$, 1H, COCH), 4.43 (d, $J = 14.1 \text{ Hz}$, 1H, NCH), 5.67 (d, $J = 14.1 \text{ Hz}$, 1H, NCH), 6.19 (s, 2H, ArH), 6.72 (s, 2H, 2 × ArH), 7.31 (s, 1H, ArH), 7.33–7.39 (m, 3H, ArH) and 7.50–7.56 (m, 2H, ArH); $\delta_{\text{C}}(100.6 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 19.3 (q), 19.4 (q), 19.5 (2 × q), 20.9 (q), 27.8 (t), 44.5 (t), 84.7 (s), 94.2 (s), 120.2 (s), 122.6 (s), 128.4 (2 × d), 128.69 (d), 128.74 (2 × d), 129.5 (s), 131.0 (d), 131.7 (2 × d), 133.1 (d), 137.1 (s), 137.3 (s), 138.0 (s), 138.5 (2 × s), 138.6 (s) and 166.6 (s).

2-Bromo-N-(2,4,6-trimethylbenzyl)-N-{2-[(4-methylphenyl)ethynyl]phenyl}acetamide 4k. Colorless crystals; mp 169–170 °C (from ethyl acetate–hexanes); yield: 91%; (Found: C, 70.45; H, 5.74; N, 3.03; Calc. for C₂₇H₂₆BrNO: C, 70.44; H, 5.69; N, 3.04%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2910, 2215, 1675, 1480 and 1375; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 2.02 (s, 6H, 2 × CH₃), 2.16 (s, 3H, CH₃), 2.38 (s, 3H, CH₃), 3.62 (d, $J = 11.0 \text{ Hz}$, 1H, COCH), 3.74 (d, $J = 11.0 \text{ Hz}$, 1H, COCH), 4.42 (d, $J = 14.2 \text{ Hz}$, 1H, NCH), 5.73 (d, $J = 14.2 \text{ Hz}$, 1H, NCH), 6.47 (d, $J = 7.8 \text{ Hz}$, 1H, ArH), 6.72 (s, 2H, 2 × ArH), 7.06 (td, $J = 7.8, 1.3 \text{ Hz}$, 1H, ArH), 7.18 (d, $J = 7.9 \text{ Hz}$, 2H, ArH), 7.29 (td, $J = 7.8, 1.0 \text{ Hz}$, 1H, ArH), 7.46 (d, $J = 7.9 \text{ Hz}$, 2H, ArH) and 7.55 (dd, $J = 7.8, 1.3 \text{ Hz}$, 1H, ArH); $\delta_{\text{C}}(100.6 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 19.4 (2 × q), 20.9 (q), 21.6 (q), 27.6 (t), 44.5 (t), 83.8 (s), 95.7 (s), 119.1 (s), 123.6 (s), 128.5 (d), 128.6 (d), 128.9 (2 × d), 129.3 (s + 2 × d), 130.3 (s), 131.7 (2 × d), 132.3 (d), 137.2 (s), 138.5 (2 × s), 139.4 (s), 140.9 (s) and 166.5 (s).

2-Bromo-N-{2-[(4-methoxyphenyl)ethynyl]phenyl}-N-(2,4,6-trimethylbenzyl)acetamide 4l. Colorless crystals; mp 146–147 °C (from ethyl acetate–hexanes); yield: 87%; (Found: C, 68.06; H, 5.55; N, 2.91; Calc. for C₂₇H₂₆BrNO₂: C, 68.07; H, 5.50; N, 2.94%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2950, 2210, 1675, 1510 and 1375; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 2.02 (s, 6H, 2 × CH₃), 2.12 (s, 3H, CH₃), 3.62 (d, $J = 11.1 \text{ Hz}$, 1H, COCH), 3.74 (d, $J = 11.1 \text{ Hz}$, 1H, COCH), 3.84 (s, 3H, OCH₃), 4.40 (d, $J = 14.2 \text{ Hz}$, 1H, NCH), 5.73 (d, $J = 14.2 \text{ Hz}$, 1H, NCH), 6.46 (d, $J = 7.7 \text{ Hz}$, 1H, ArH), 6.72 (s, 2H, 2 × ArH), 6.90 (d, $J = 8.6 \text{ Hz}$, 2H, ArH), 7.04 (t, $J = 7.7 \text{ Hz}$, 1H, ArH), 7.28 (t, $J = 7.7 \text{ Hz}$, 1H, ArH), 7.51 (d, $J = 8.6 \text{ Hz}$, 2H, ArH) and 7.53 (d, $J = 7.7 \text{ Hz}$, 1H, ArH); $\delta_{\text{C}}(100.6 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 19.4 (2 × q), 20.9 (q), 27.6 (t), 44.4 (t), 55.3 (q), 83.3 (s), 95.7 (s), 114.2 (2 × d), 114.3 (s), 123.8 (s), 128.3 (d), 128.6 (d), 128.9 (2 × d), 129.3 (s), 130.2 (d), 132.0 (d),

133.4 (2 × d), 137.2 (s), 138.5 (2 × s), 140.7 (s), 160.2 (s) and 166.6 (s).

2-Bromo-N-{2-[(4-chlorophenyl)ethynyl]phenyl}-N-(2,4,6-trimethylbenzyl)acetamide 4m Colorless crystals; mp 161–162 °C (from ethyl acetate–hexanes); yield: 94%; (Found: C, 64.91; H, 4.86; N, 2.90; Calc. for C₂₆H₂₃BrClNO: C, 64.95; H, 4.82; N, 2.91%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2950, 1675, 1490, 1370 and 1185; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 2.01 (s, 6H, 2 × CH₃), 2.22 (s, 3H, CH₃), 3.61 (d, $J = 11.1 \text{ Hz}$, 1H, COCH), 3.72 (d, $J = 11.1 \text{ Hz}$, 1H, COCH), 4.40 (d, $J = 14.2 \text{ Hz}$, 1H, NCH), 5.71 (d, $J = 14.2 \text{ Hz}$, 1H, NCH), 6.49 (d, $J = 7.7 \text{ Hz}$, 1H, ArH), 6.72 (s, 2H, 2 × ArH), 7.10 (td, $J = 7.7, 1.3 \text{ Hz}$, 1H, ArH), 7.31 (td, $J = 7.7, 1.0 \text{ Hz}$, 1H, ArH), 7.35 (d, $J = 8.5 \text{ Hz}$, 2H, ArH), 7.49 (d, $J = 8.5 \text{ Hz}$, 2H, ArH) and 7.56 (dd, $J = 7.7, 1.3 \text{ Hz}$, 1H, ArH); $\delta_{\text{C}}(100.6 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 19.4 (2 × q), 20.9 (q), 27.5 (t), 44.6 (t), 85.4 (s), 94.3 (s), 120.7 (s), 123.1 (s), 128.8 (d), 128.89 (2 × d), 128.91 (2 × d), 129.0 (d), 129.1 (s), 130.3 (d), 132.4 (d), 133.0 (2 × d), 135.2 (s), 137.2 (s), 138.5 (2 × s), 141.1 (s) and 166.6(s).

2-Bromo-N-{2-[(4-cyanophenyl)ethynyl]phenyl}-N-(2,4,6-trimethylbenzyl)acetamide 4n Colorless crystals; mp 175–176 °C (from ethyl acetate–hexanes); yield: 99%; (Found: C, 68.41; H, 4.95; N, 5.90; Calc. for C₂₇H₂₃BrN₂O: C, 68.79; H, 4.92; N, 5.94%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2950, 2230, 1675, 1375 and 1225; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 2.00 (s, 6H, 2 × CH₃), 2.22 (s, 3H, CH₃), 3.60 (d, $J = 11.1 \text{ Hz}$, 1H, COCH), 3.71 (d, $J = 11.1 \text{ Hz}$, 1H, COCH), 4.39 (d, $J = 14.2 \text{ Hz}$, 1H, NCH), 5.71 (d, $J = 14.2 \text{ Hz}$, 1H, NCH), 6.52 (d, $J = 7.8, 1.0 \text{ Hz}$, 1H, ArH), 6.73 (s, 2H, 2 × ArH), 7.15 (td, $J = 7.8, 1.4 \text{ Hz}$, 1H, ArH), 7.35 (td, $J = 7.8, 1.0 \text{ Hz}$, 1H, ArH), 7.59 (dd, $J = 7.8, 1.4 \text{ Hz}$, 1H, ArH) and 7.62–7.70 (m, 4H, ArH); $\delta_{\text{C}}(100.6 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 19.4 (2 × q), 20.9 (q), 27.3 (t), 44.7 (t), 88.5 (s), 93.4 (s), 112.3 (s), 118.3 (s), 122.5 (s), 127.0 (s), 128.9 (d), 128.95 (s), 128.97 (2 × d), 129.8 (d), 130.5 (d), 132.2 (2 × d), 132.3 (2 × d), 132.7 (d), 137.4 (s), 138.4 (2 × s), 141.4 (s) and 166.6(s).

2-Bromo-N-(2,4,6-trimethylbenzyl)-N-[2-(2-thienylethynyl)phenyl]acetamide 4o. Colorless crystals; mp 163–164 °C (from ethyl acetate–hexanes); yield: 89%; (Found: C, 63.73; H, 4.94; N, 3.07; Calc. for C₂₄H₂₂BrNOS: C, 63.72; H, 4.90; N, 3.10%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2950, 2210, 1660, 1420 and 1390; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 2.02 (s, 6H, 2 × CH₃), 2.22 (s, 3H, CH₃), 3.61 (d, $J = 11.1 \text{ Hz}$, 1H, COCH), 3.73 (d, $J = 11.1 \text{ Hz}$, 1H, COCH), 4.41 (d, $J = 14.2 \text{ Hz}$, 1H, NCH), 5.70 (d, $J = 14.2 \text{ Hz}$, 1H, NCH), 6.48 (d, $J = 7.7 \text{ Hz}$, 1H, ArH), 6.73 (s, 2H, 2 × ArH), 7.07 (td, $J = 7.7, 1.3 \text{ Hz}$, 1H, ArH), 7.23 (dd, $J = 5.0, 1.0 \text{ Hz}$, 1H, ArH), 7.29 (td, $J = 7.7, 1.0 \text{ Hz}$, 1H, ArH), 7.33 (dd, $J = 5.0, 3.1 \text{ Hz}$, 1H, ArH), 7.54 (dd, $J = 7.7, 1.3 \text{ Hz}$, 1H, ArH) and 7.62 (dd, $J = 3.1, 1.0 \text{ Hz}$, 1H, ArH); $\delta_{\text{C}}(100.6 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 19.4 (2 × q), 20.9 (q), 27.6 (t), 44.5 (t), 84.1 (s), 90.7 (s), 121.3 (s), 123.4 (s), 125.7 (d), 128.63 (d), 128.68 (d), 128.9 (2 × d), 129.2 (s), 129.8 (d), 130.0 (d), 130.3 (d), 132.1 (d), 137.3 (s), 138.5 (2 × s), 140.9 (s) and 166.6 (s).

2-Bromo-N-[2-(*n*-hexyn-1-yl)phenyl]-N-(2,4,6-trimethylbenzyl)acetamide 4p. Colorless crystals; mp 85–86 °C (from ethyl acetate–hexanes); yield: 95%; (Found: C, 67.66; H, 6.61; N, 3.21; Calc. for C₂₄H₂₈BrNO: C, 67.60; H, 6.62; N, 3.28%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2930, 1650, 1485, 1390 and 1265; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 0.96 (t, $J = 7.3 \text{ Hz}$, 3H, CH₃), 1.47 (sextet, $J = 7.3 \text{ Hz}$, 2H, CH₂), 1.55–1.65 (m, 2H, CH₂), 2.01 (s, 6H, 2 × CH₃), 2.21 (s, 3H, CH₃), 2.44 (t, $J = 7.1 \text{ Hz}$, 2H, CH₂), 3.55 (d, $J = 11.1 \text{ Hz}$, 1H, COCH), 3.68 (d, $J = 11.1 \text{ Hz}$, 1H, COCH), 4.37 (d, $J = 14.2 \text{ Hz}$, 1H, NCH), 5.05 (d, $J = 14.2 \text{ Hz}$, 1H, NCH), 6.42 (d, $J = 7.7 \text{ Hz}$, 1H, ArH), 6.72 (s, 2H, 2 × ArH), 7.00 (td, $J = 7.7, 1.3 \text{ Hz}$, 1H, ArH), 7.22 (td, $J = 7.7, 1.0 \text{ Hz}$, 1H, ArH) and 7.42 (dd, $J = 7.7, 1.3 \text{ Hz}$, 1H, ArH); $\delta_{\text{C}}(100.6 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 13.6 (q), 19.2 (t), 19.4 (2 × q), 20.9 (q), 22.1 (t), 27.8 (t), 30.6 (t), 44.3 (t), 75.8 (s), 97.0 (s), 124.1 (s), 128.0 (d), 128.5 (d), 128.8 (2 × d), 129.4 (s), 130.1 (d), 132.7 (d), 137.2 (s), 138.5 (2 × s), 140.8 (s) and 166.2 (s).

2-Bromo-N-[2-(ethyn-1-yl)phenyl]-N-(2,4,6-trimethylbenzyl)acetamide 4q. Colorless crystals; mp 104–105 °C (from ethyl acetate–hexanes); yield: 80%; (Found: C, 64.91; H, 5.46; N, 3.74; Calc. for C₂₀H₂₀BrNO: C, 64.87; H, 5.44; N, 3.78%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3285, 2955, 1660, 1390, 1205 cm^{-1} ; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 2.01 (s, 6H, 2 × CH₃), 2.22 (s, 3H, CH₃), 3.34 (s, 1H, CH), 3.53 (d, $J = 11.1 \text{ Hz}$, 1H, COCH), 3.70 (d, $J = 11.1 \text{ Hz}$, 1H, COCH), 4.38 (d, $J = 14.3 \text{ Hz}$, 1H, NCH), 5.70 (d, $J = 14.3 \text{ Hz}$, 1H, NCH), 6.46 (dd, $J = 7.8, 0.9 \text{ Hz}$, 1H, ArH), 6.72 (s, 2H, 2 × ArH), 7.10 (td, $J = 7.8, 1.4 \text{ Hz}$, 1H, ArH), 7.28 (td, $J = 7.8, 0.9 \text{ Hz}$, 1H, ArH) and 7.54 (dd, $J = 7.8, 1.4 \text{ Hz}$, 1H, ArH); $\delta_{\text{C}}(100.6 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 19.4 (2 × q), 20.9 (q), 27.4 (t), 44.4 (t), 78.8 (s), 83.2 (d), 122.2 (s), 128.7 (d), 128.9 (2 × d), 129.1 (s), 129.4 (d), 130.5 (d), 133.4 (d), 137.3 (s), 138.5 (2 × s), 141.4 (s) and 166.1 (s).

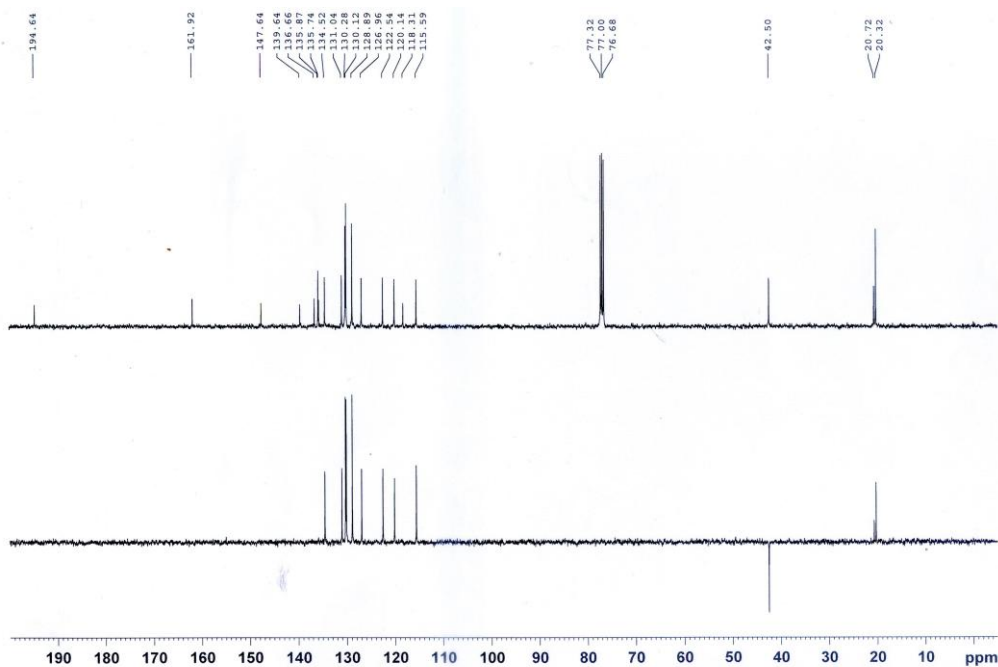
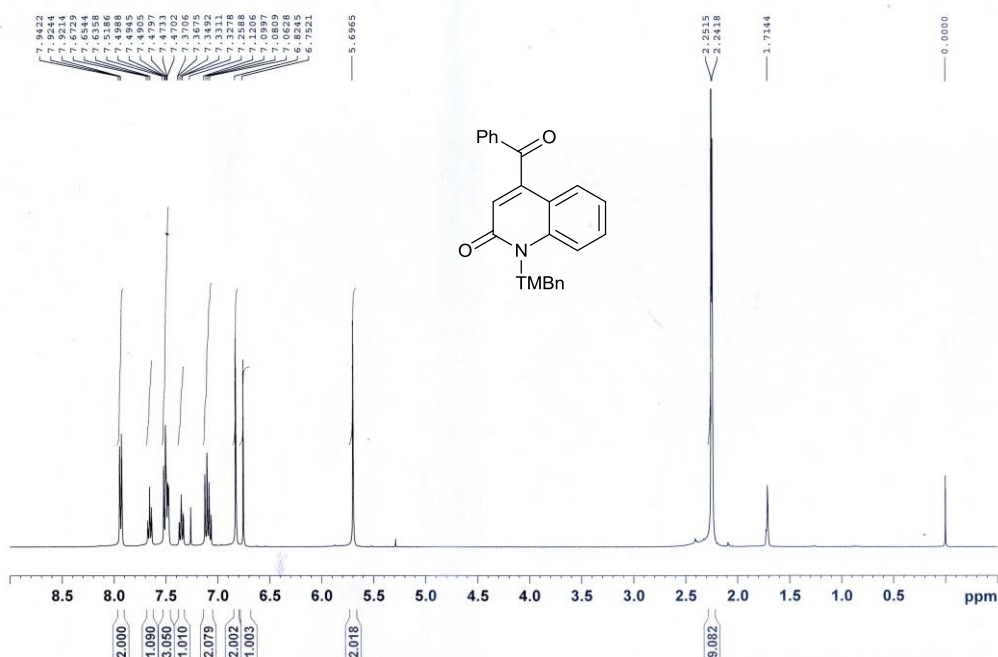
2-Bromo-N-(2,4,6-trimethylbenzyl)-N-[2-(phenylethynyl)phenyl]propioamide 4r. Colorless crystals; mp 150–151 °C (from ethyl acetate–hexanes); yield: 89%; (Found: C, 70.42; H, 5.69; N, 3.00; Calc. for C₂₇H₂₆BrNO: C, 70.44; H, 5.69; N, 3.04%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2920, 2215, 1665, 1395 and 1235; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ (Z form : E form = 1.2:1) 1.74 (d, $J = 6.8 \text{ Hz}$, 3H, CH₃_Z), 1.78 (d, $J = 6.6 \text{ Hz}$, 3H, CH₃_E), 2.00 (s, 6H, 2 × CH₃_Z), 2.03 (s, 6H, 2 × CH₃_E), 2.20 (s, 3H, CH₃_Z), 2.22 (s, 3H, CH₃_E), 4.15 (q, $J = 6.6 \text{ Hz}$, 1H, COCH_E), 4.30 (q, $J = 6.8 \text{ Hz}$, 1H, COCH_Z), 4.34 (d, $J = 14.2 \text{ Hz}$, 1H, NCH_E), 4.58 (d, $J = 14.3 \text{ Hz}$, 1H, NCH_Z), 5.66 (d, $J = 14.3 \text{ Hz}$, 1H, NCH_Z), 5.80 (d, $J = 14.2 \text{ Hz}$, 1H, NCH_E), 6.41 (d, $J = 7.7 \text{ Hz}$, 1H, ArH_Z), 6.50 (d, $J = 7.7 \text{ Hz}$, 1H, CH_E), 6.69 (s, 2H, 2 × ArH_Z), 6.73 (s, 2H, 2 × ArH_E), 7.08 (td, $J = 7.7, 1.3 \text{ Hz}$, 2H, ArH), 7.30 (td, $J = 7.7, 0.9 \text{ Hz}$, 2H, ArH), 7.34–7.42 (m, 6H, ArH) and 7.52–7.63 (m, 6H, ArH).

2-Bromo-N-(2,4,6-trimethylbenzyl)-2-phenyl-N-[2-(phenylethynyl)phenyl]acetamide 4s. Colorless oils; yield: 95%; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 2920, 2220, 1675, 1455 and 1385; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ (Z form : E form = 1.2:1) 1.85

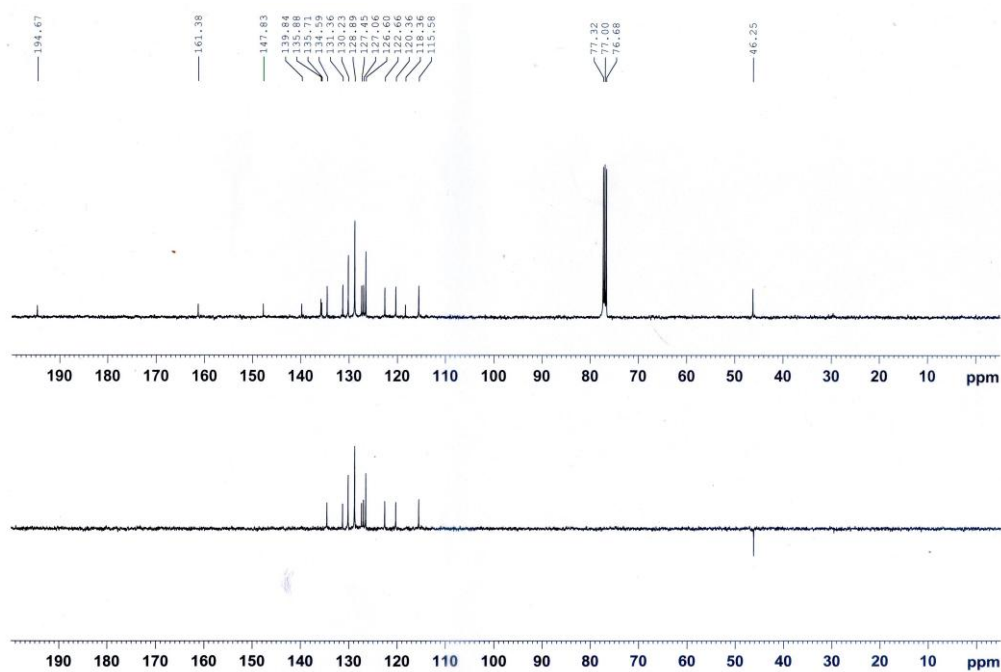
(s, 6H, 2 × CH₃_Z), 2.05 (s, 6H, 2 × CH₃_E), 2.15 (s, 3H, CH₃_Z), 2.22 (s, 3H, CH₃_E), 4.38 (d, *J* = 14.2 Hz, 1H, NCH_E), 4.50 (d, *J* = 14.2 Hz, 1H, NCH_Z), 5.13 (s, 1H, COCH_E), 5.41 (s, 1H, COCH_Z), 5.67 (d, *J* = 14.2 Hz, 1H, NCH_Z), 5.75 (d, *J* = 14.2 Hz, 1H, NCH_E), 5.89 (d, *J* = 7.8 Hz, 1H, ArH_Z), 6.61 (s, 2H, 2 × ArH_Z), 6.62 (d, *J* = 10.9 Hz, 1H, ArH_E), 6.73 (s, 2H, 2 × ArH_E), 6.90 (t, *J* = 7.8 Hz, 1H, ArH_Z), 7.05–7.11 (m, 3H, ArH), 7.11–7.32 (m, 12H, ArH), 7.33–7.38 (m, 2H, ArH), 7.38–7.43 (m, 3H, ArH), 7.51–7.56 (m, 3H, ArH), 7.56–7.64 (m, 3H, ArH) and 7.65–7.71 (m, 2H, ArH); *m/z* (FAB) 521.1354 (*M*⁺ C₃₂H₂₈BrNO requires 521.1354).

2) Copies of ¹H and ¹³C NMR spectra for quinolin-2(1*H*)-ones.

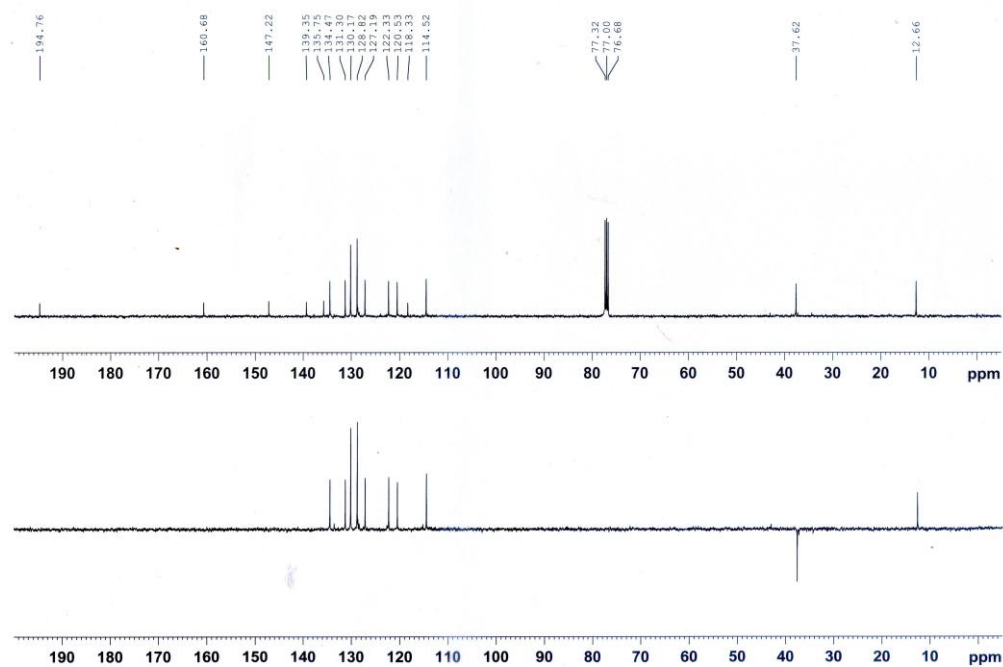
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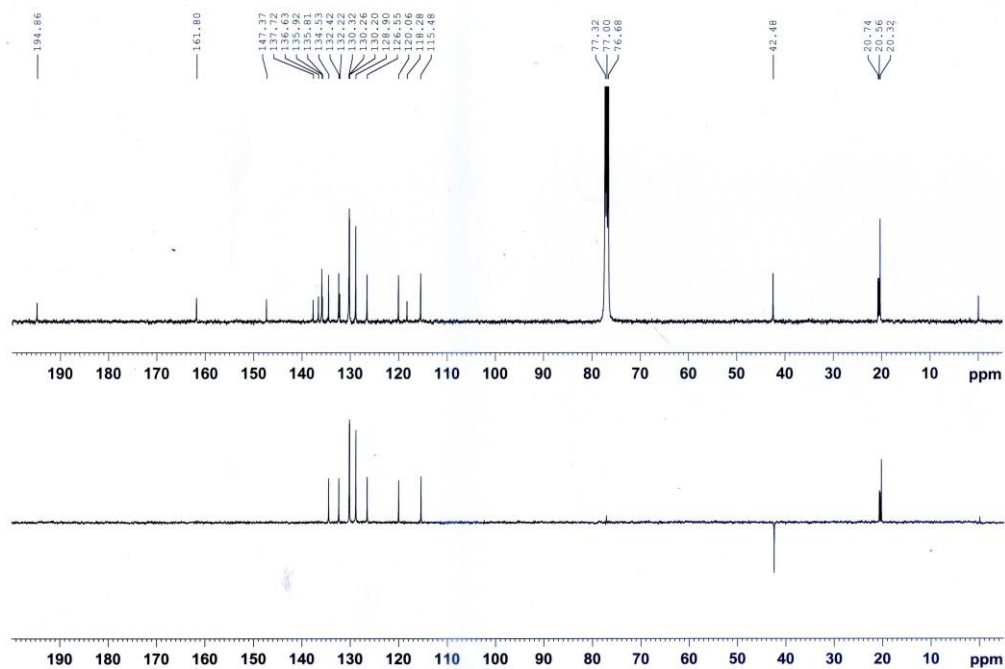
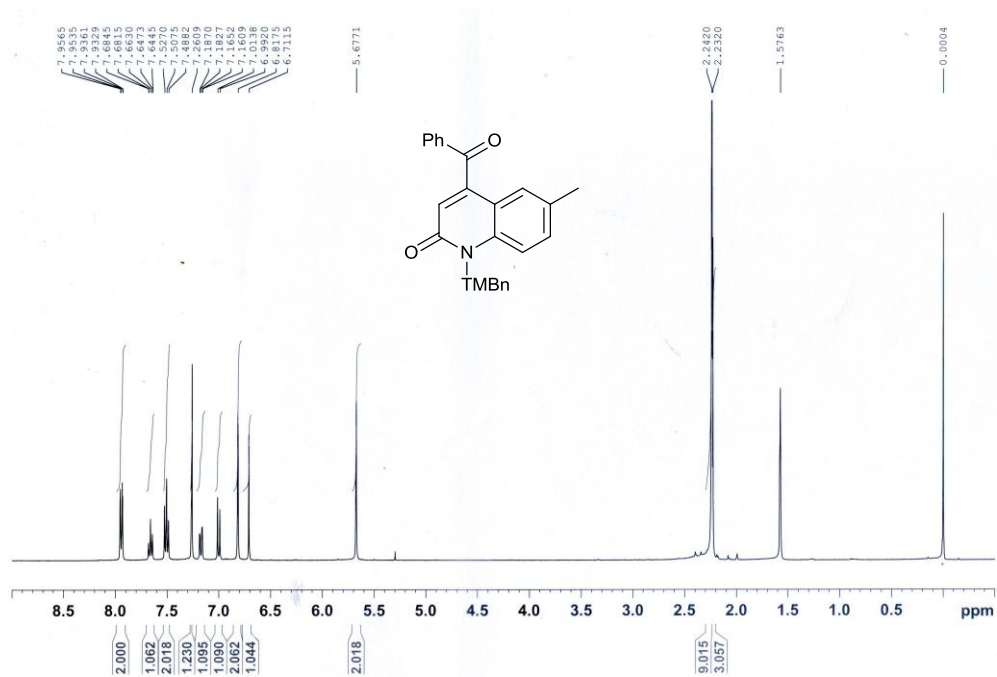
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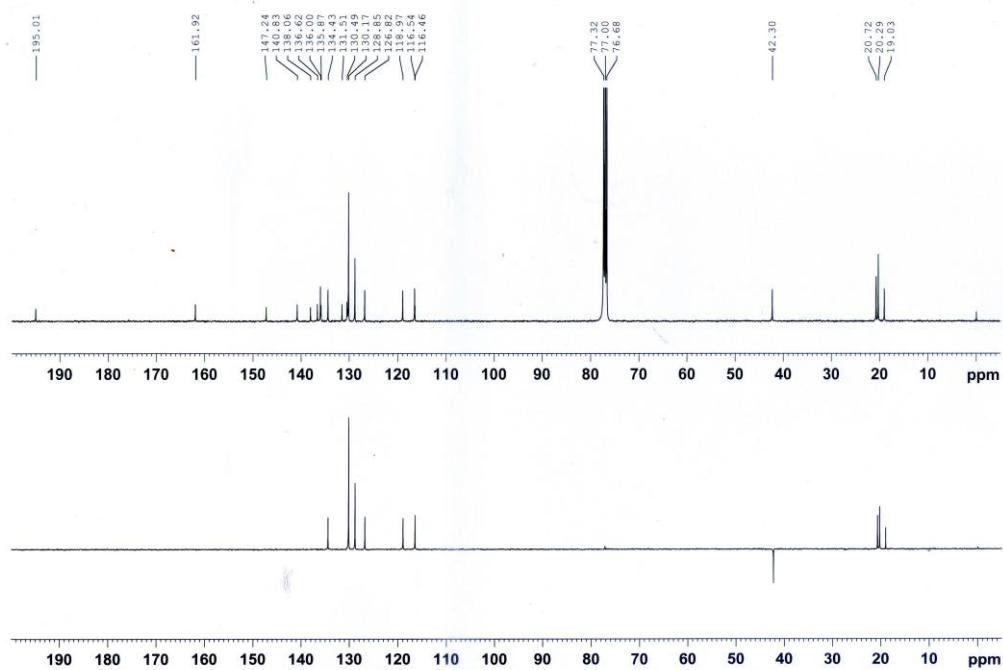
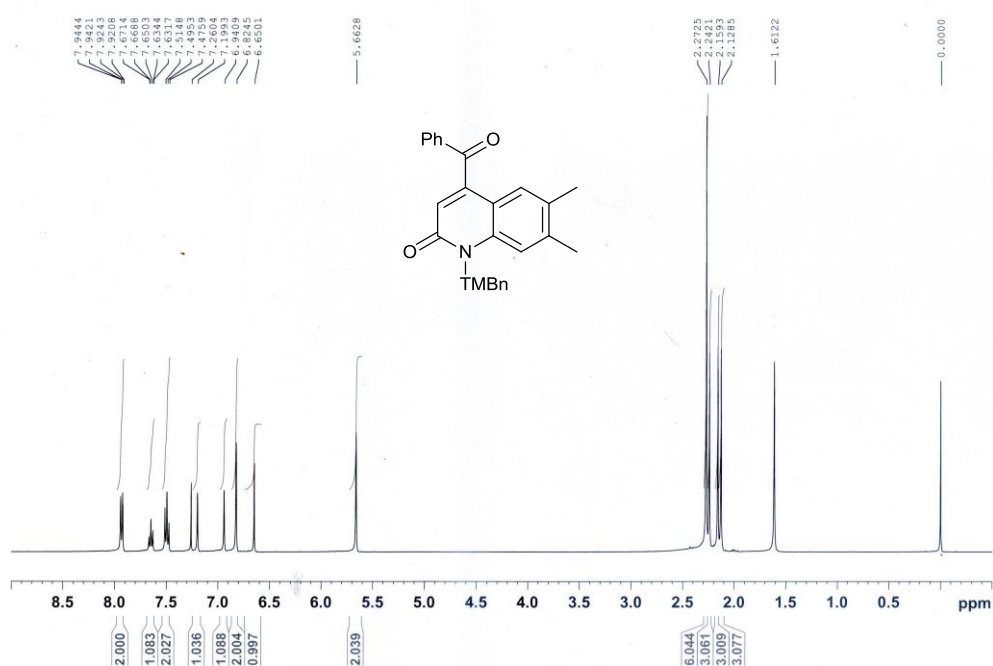
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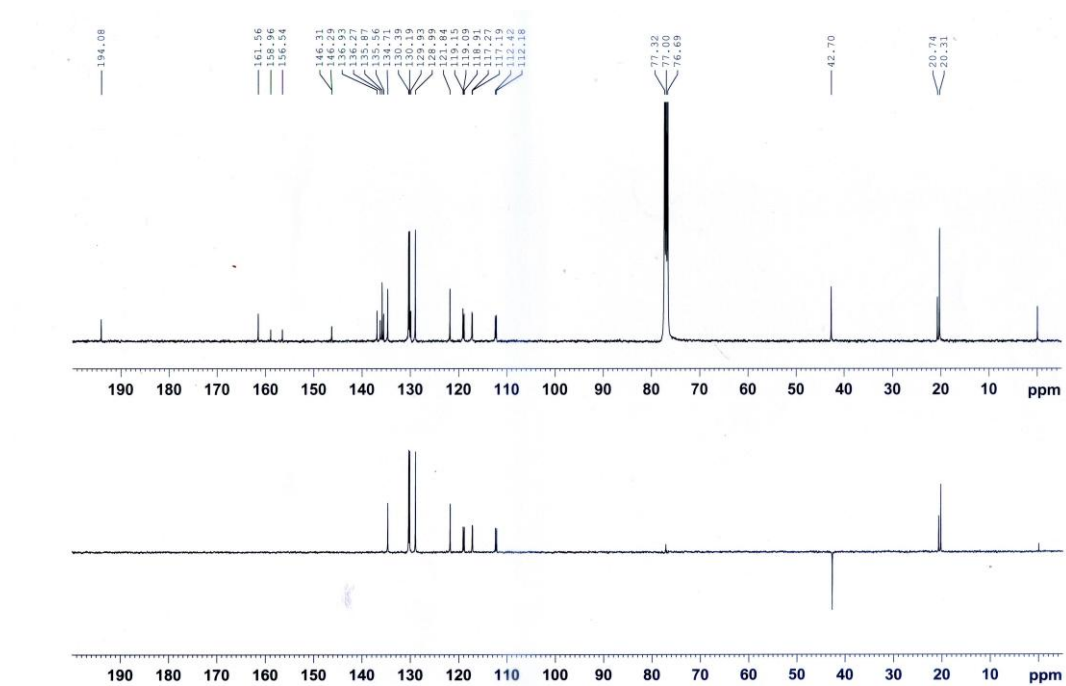
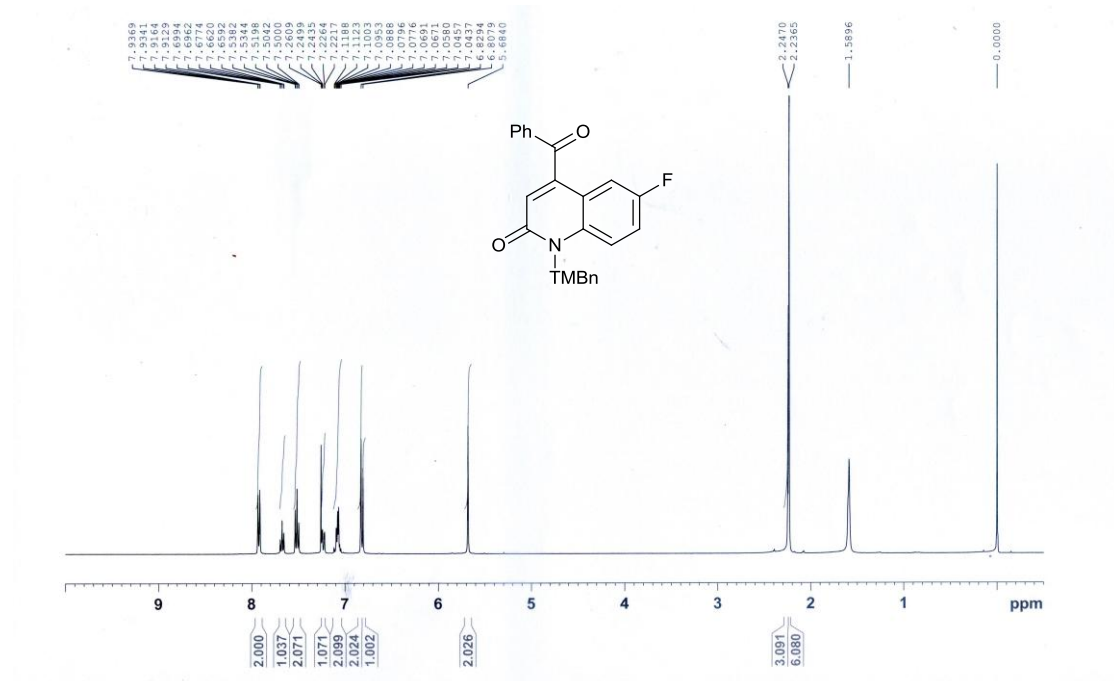
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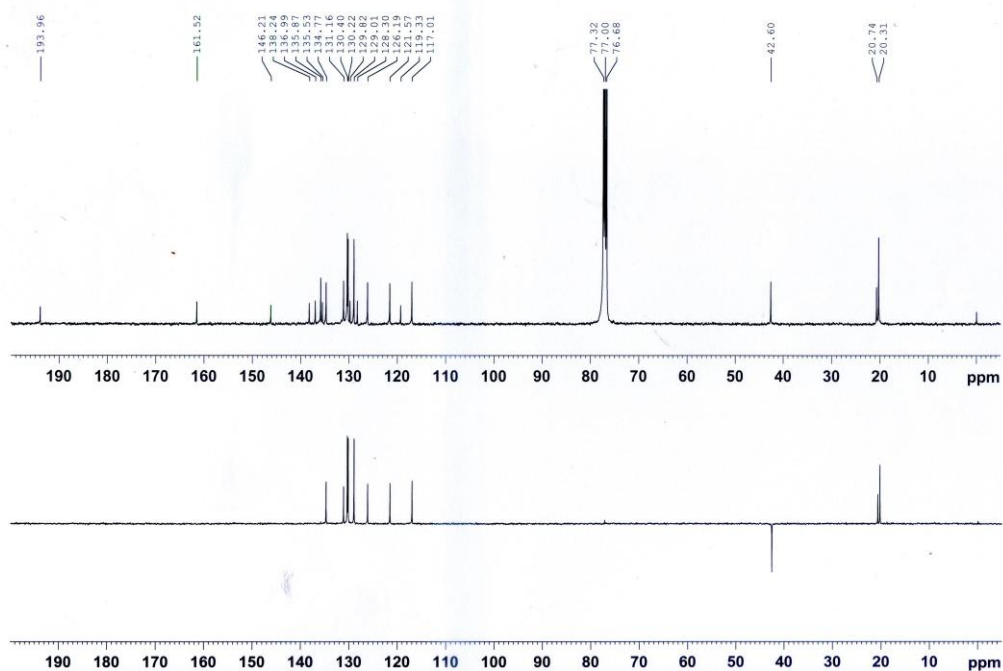
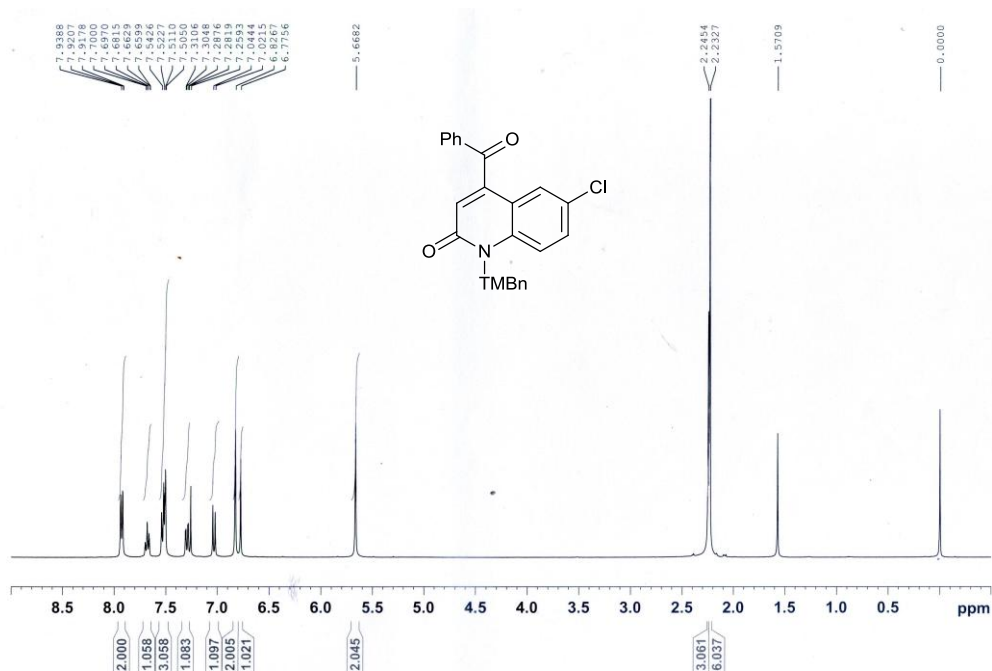
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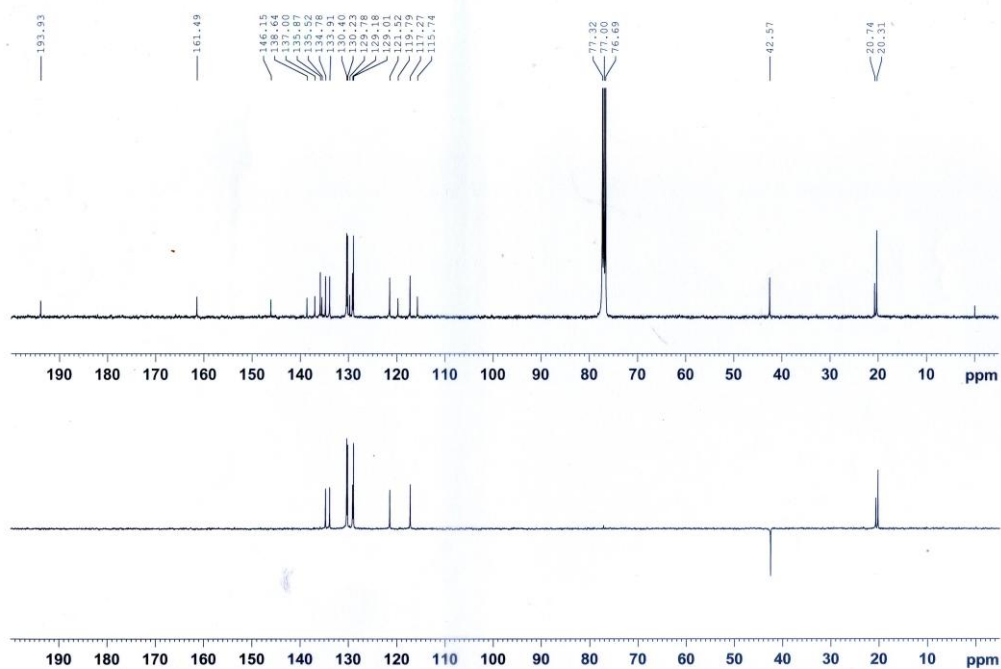
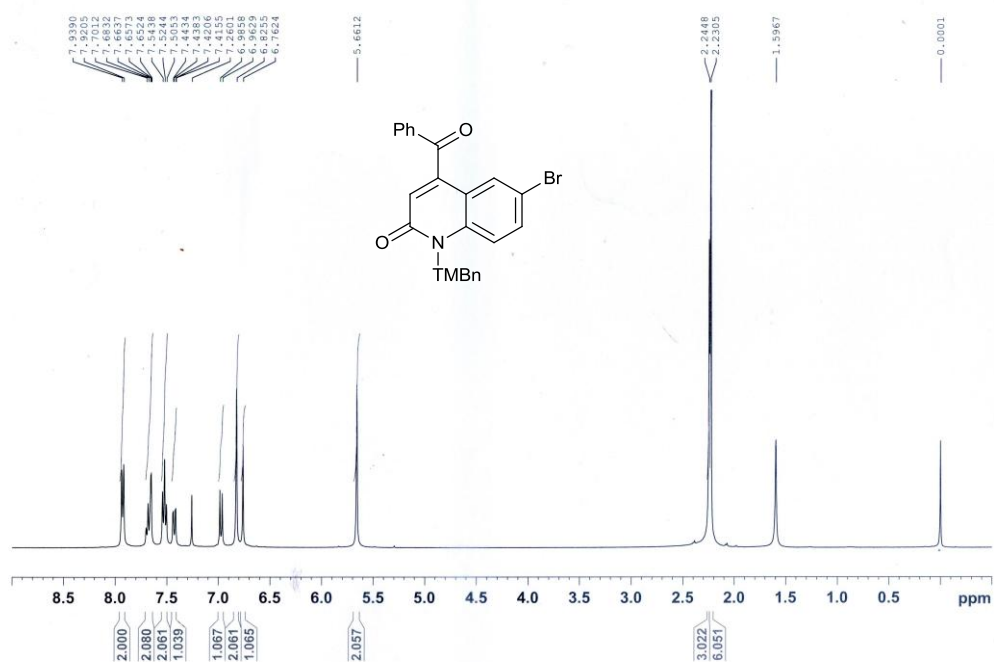
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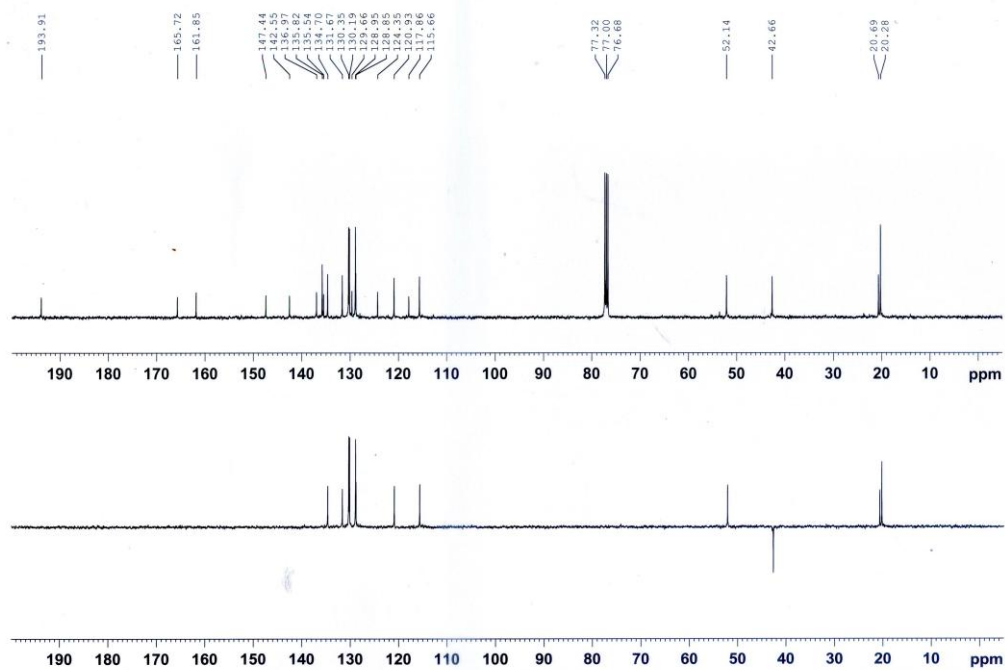
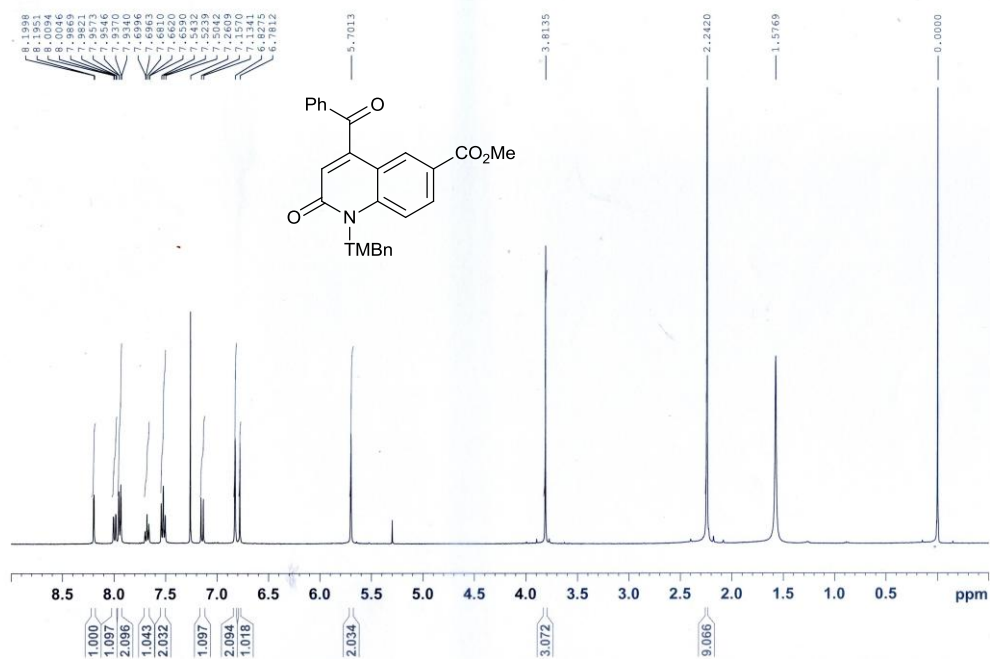
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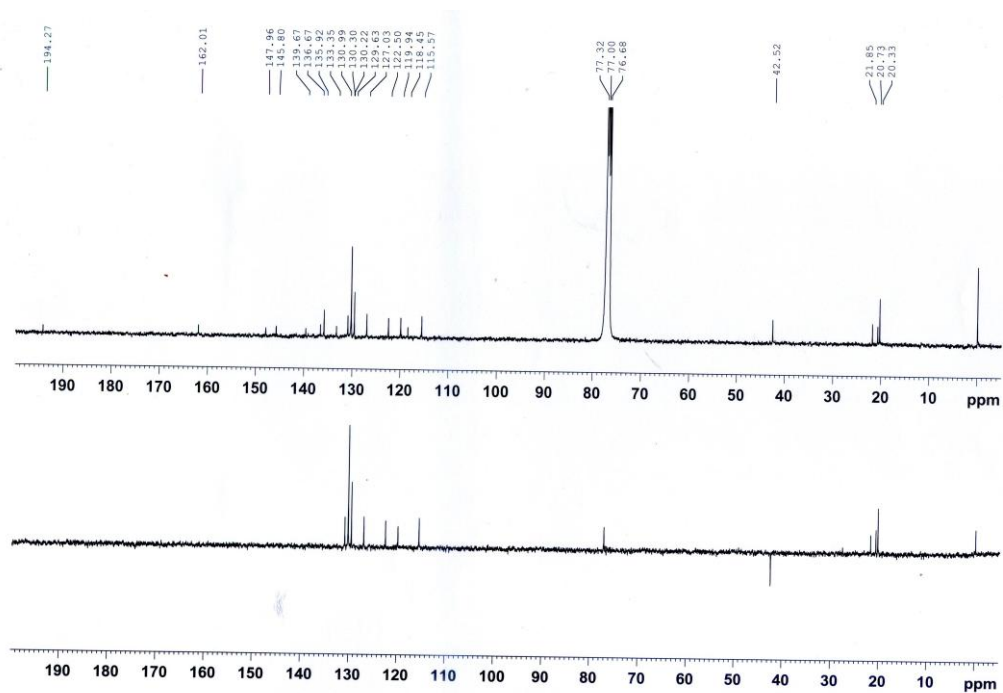
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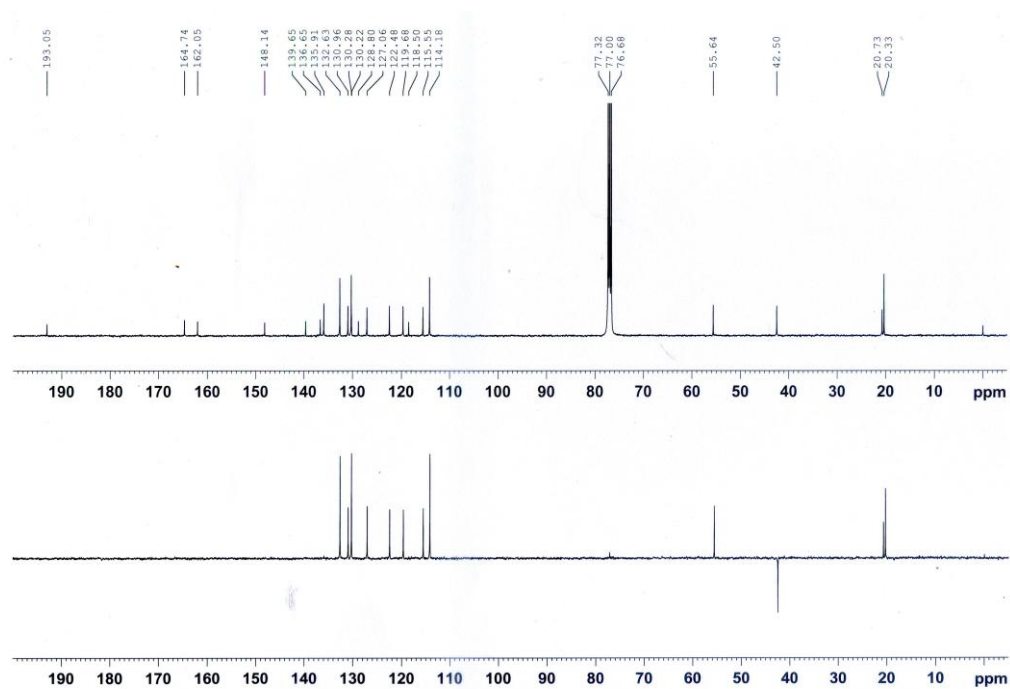
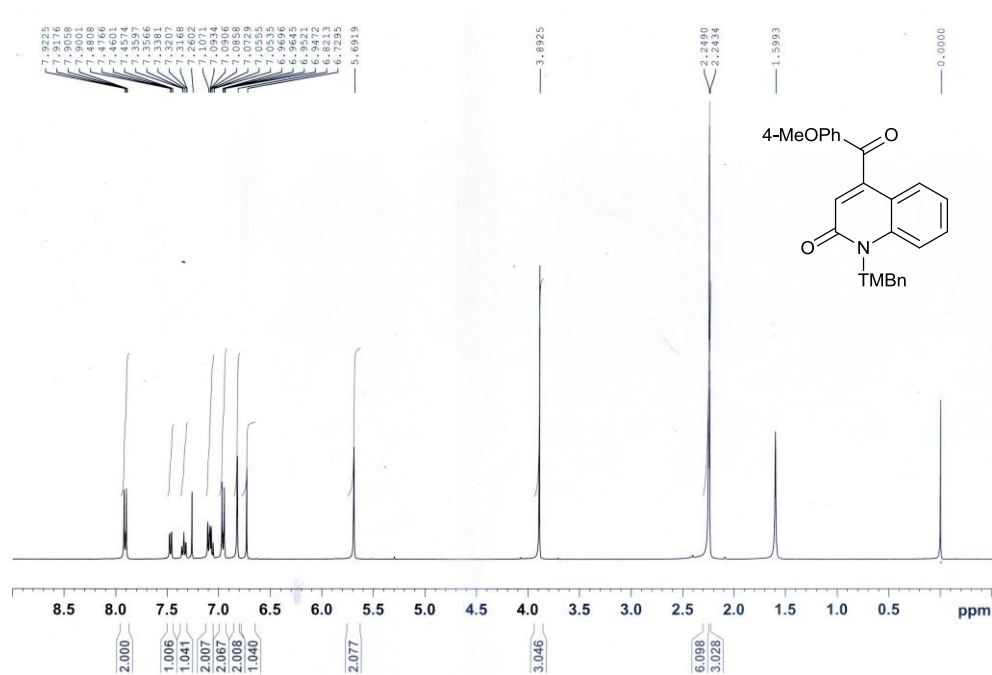


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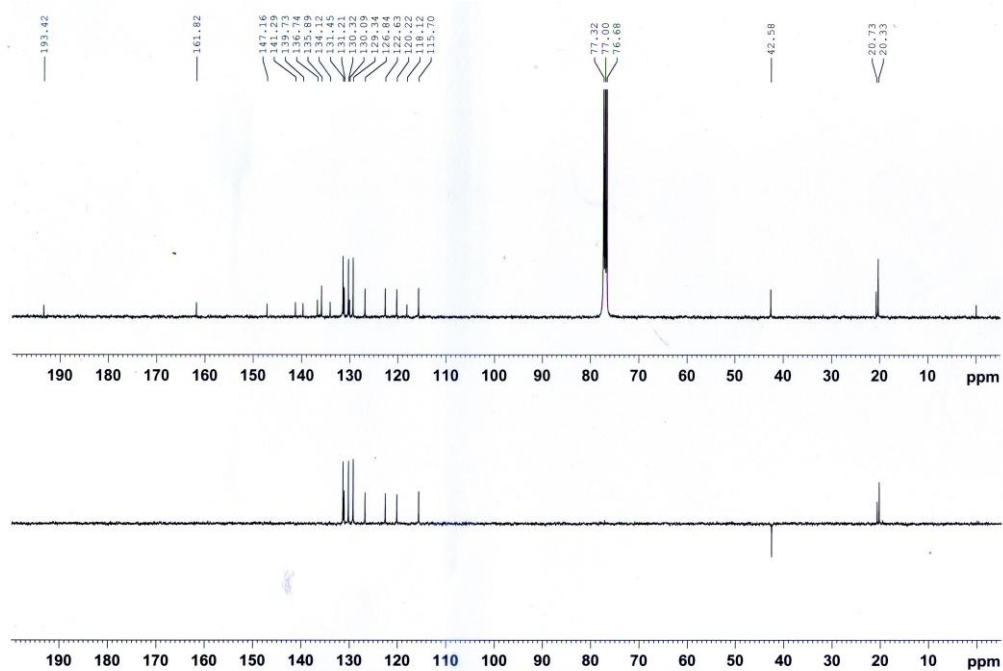
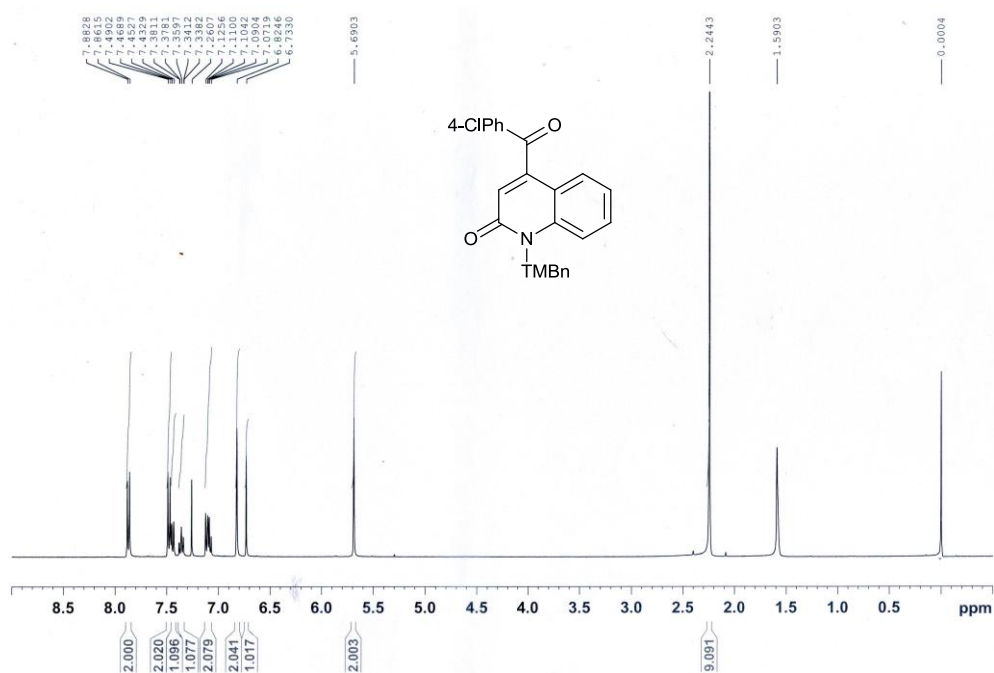


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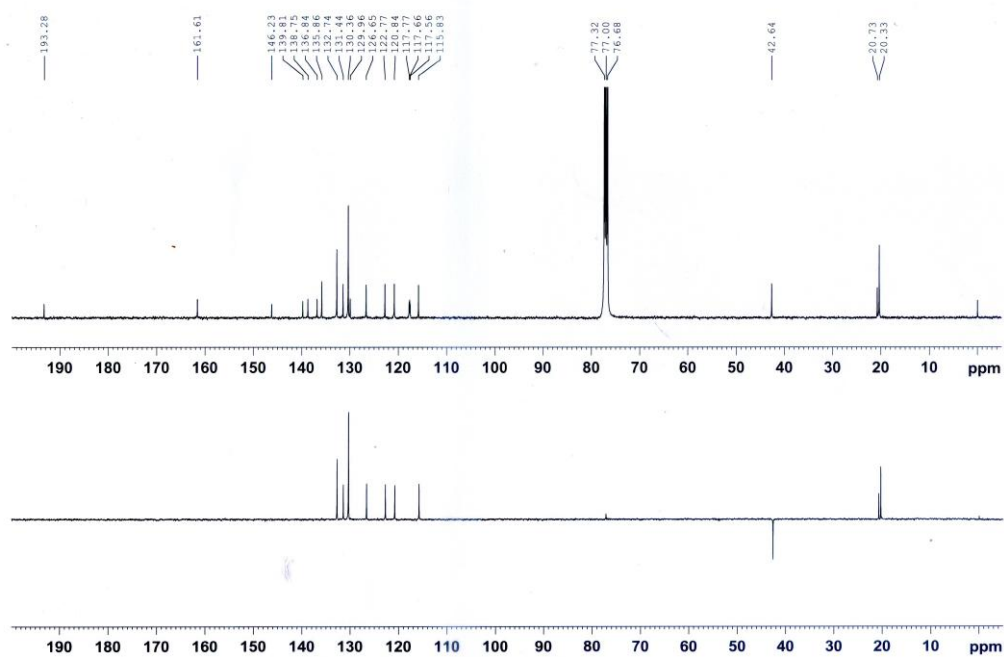
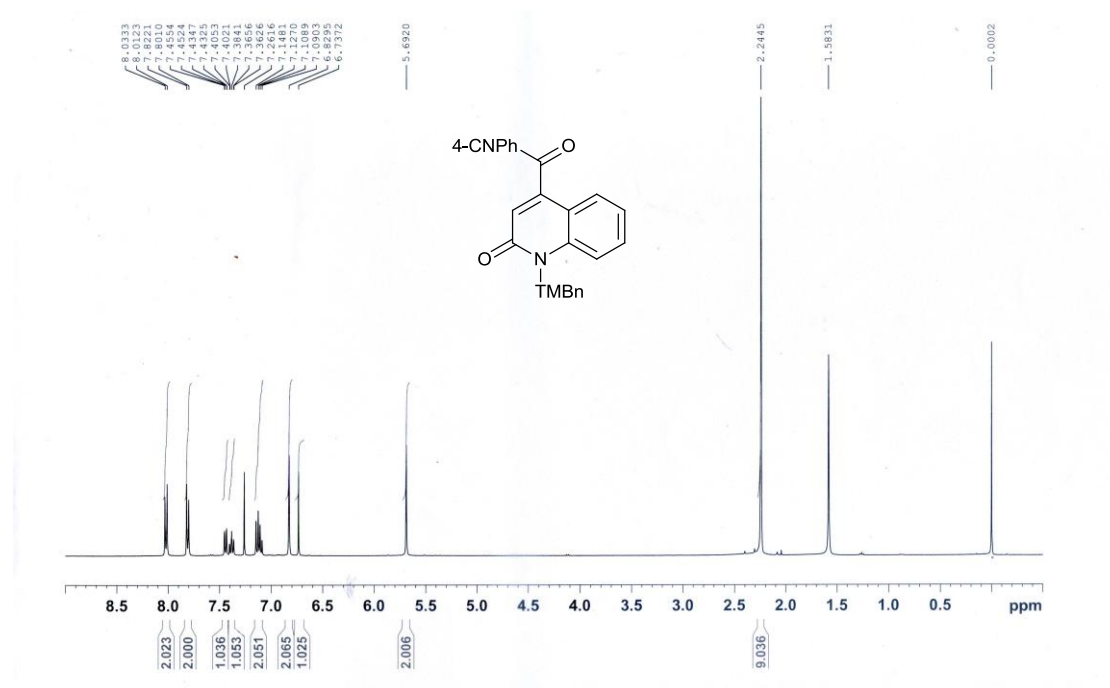




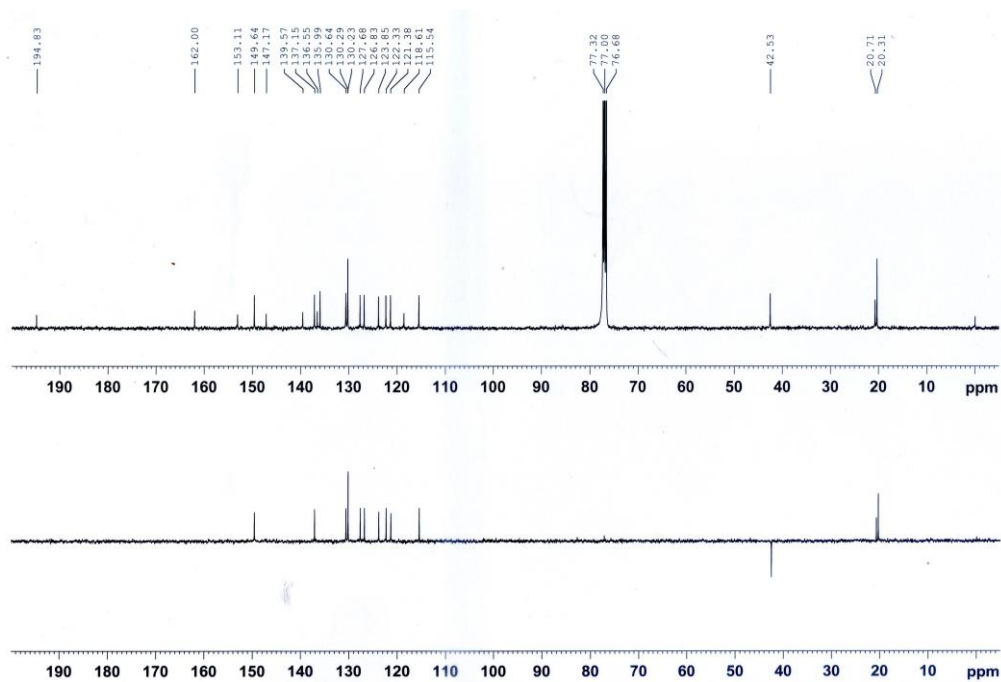
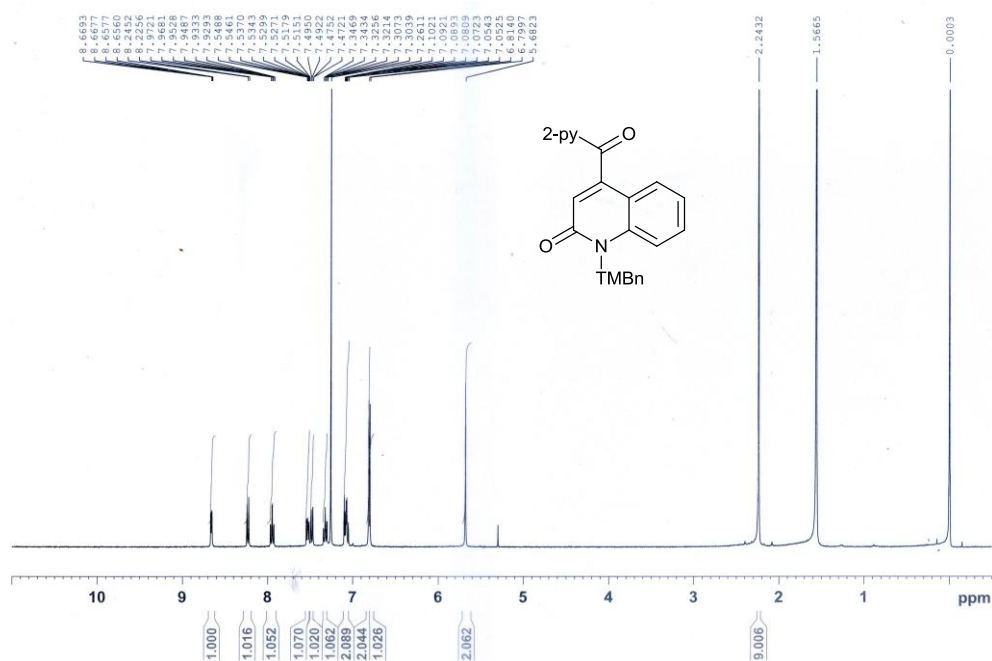
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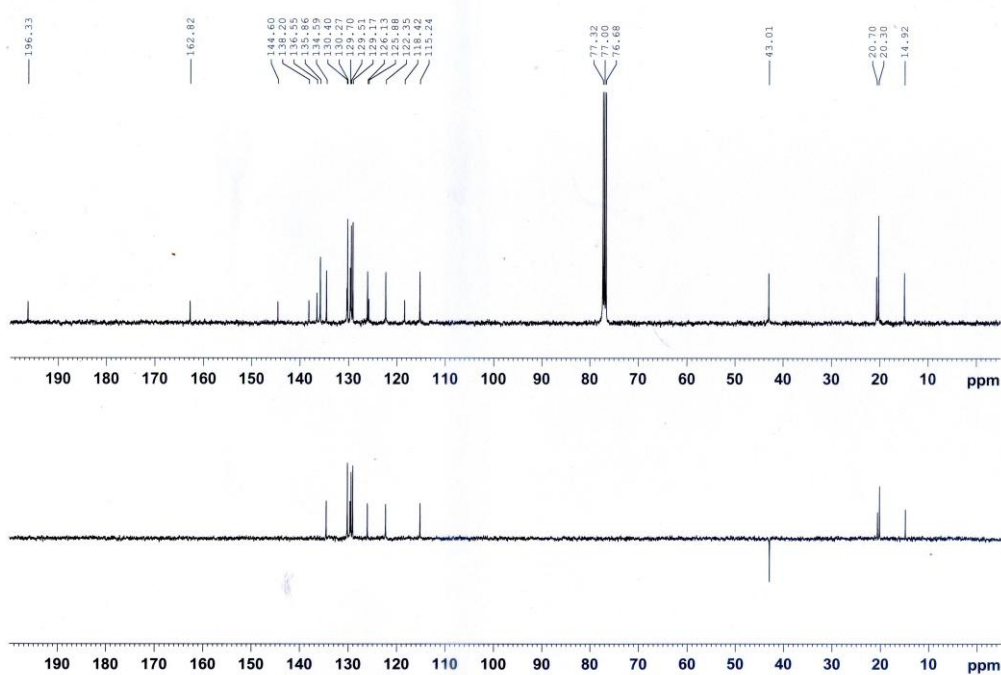
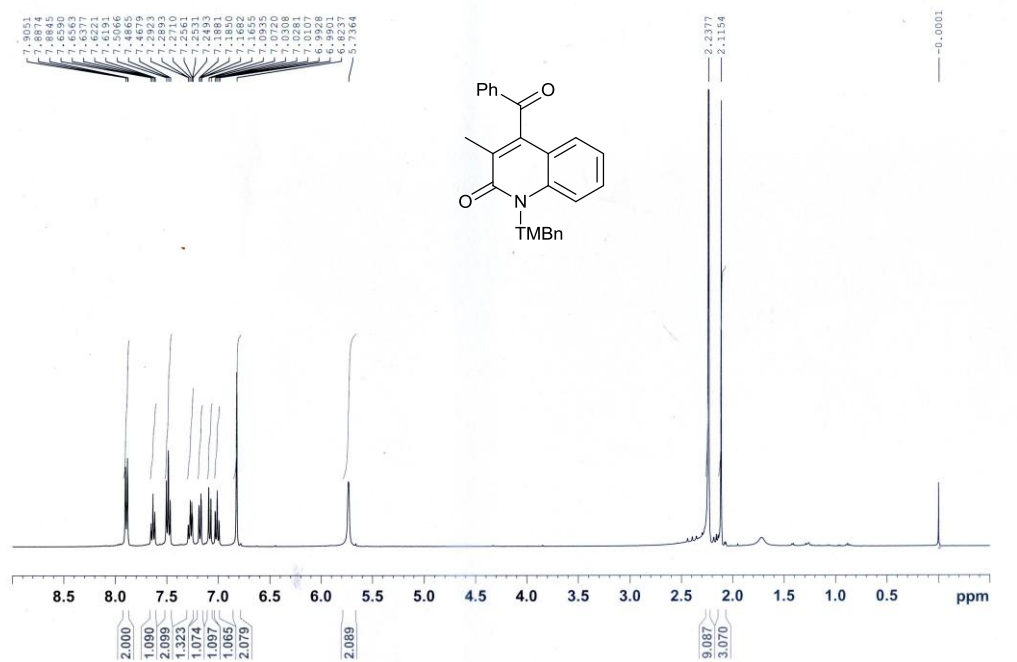
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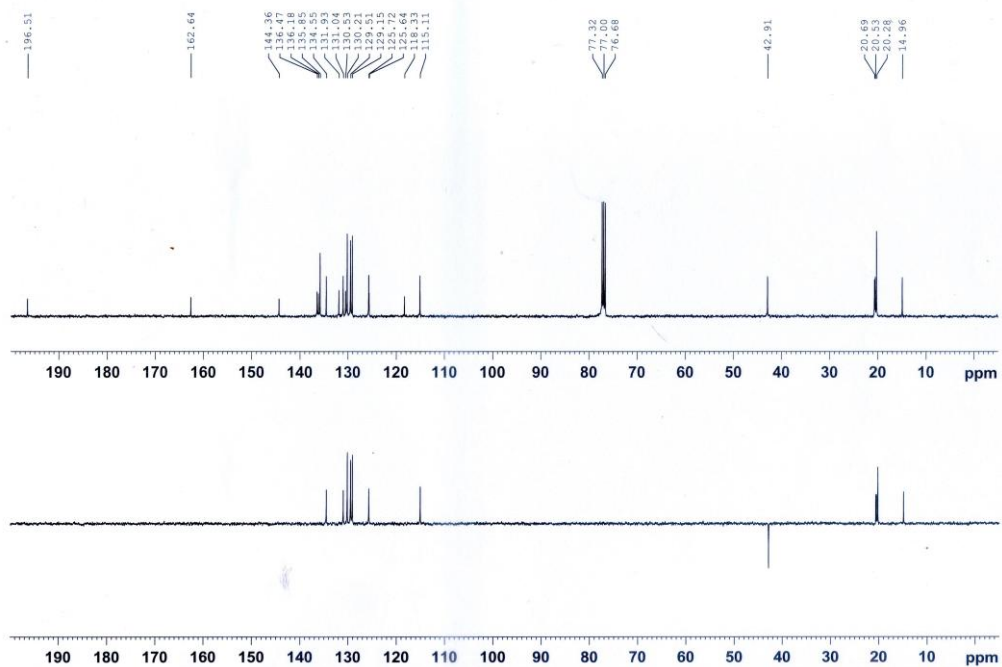
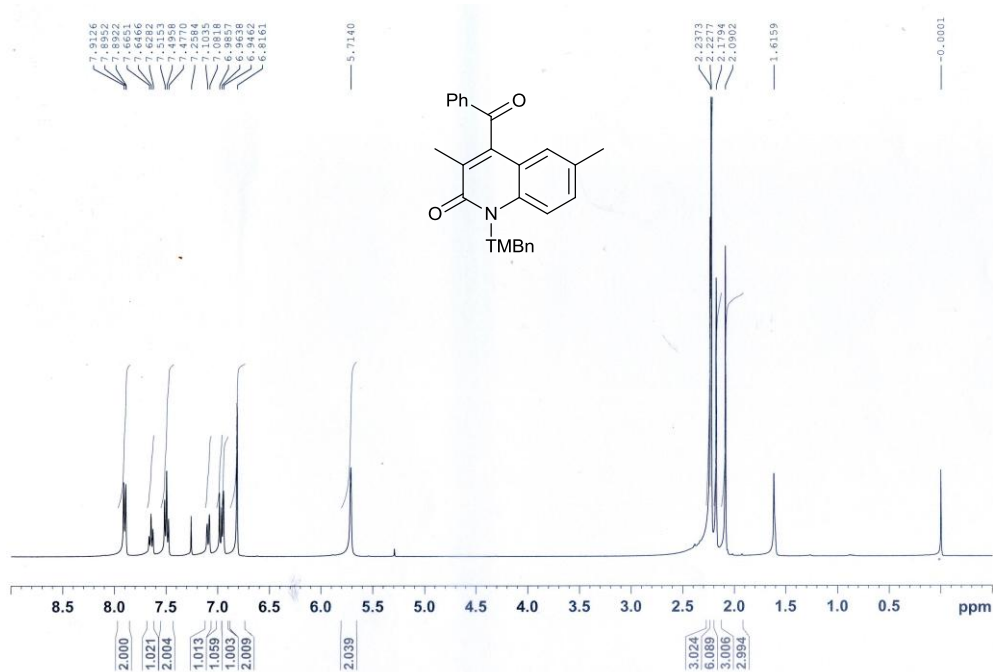
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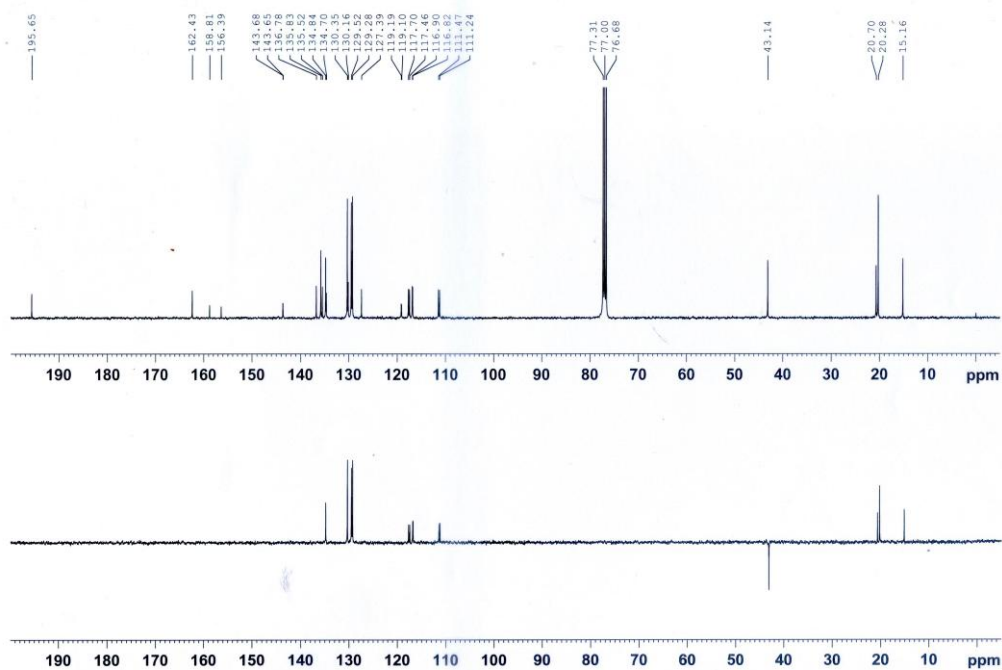
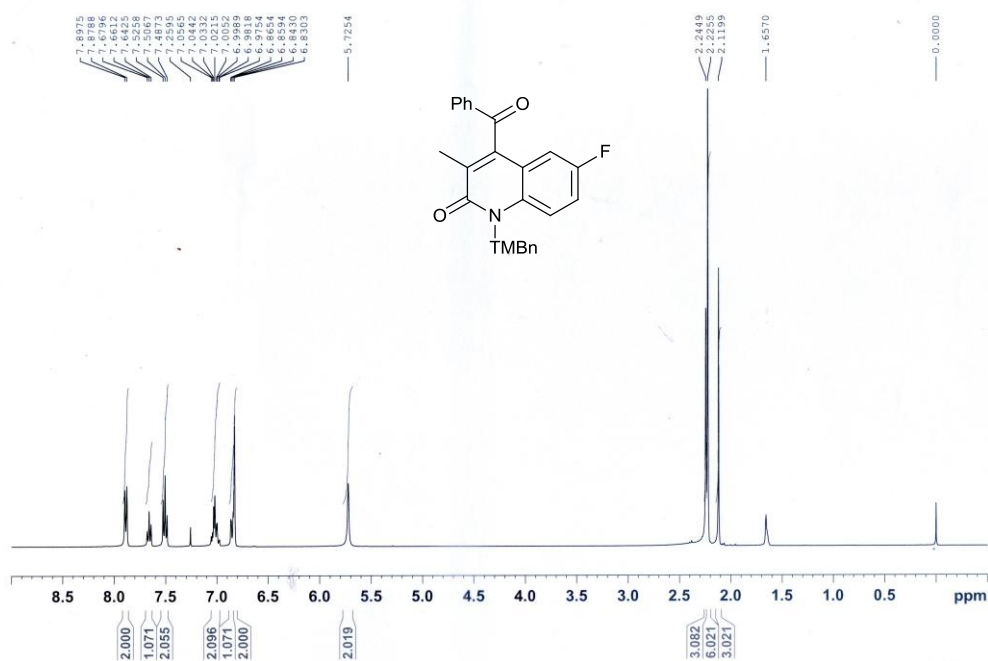
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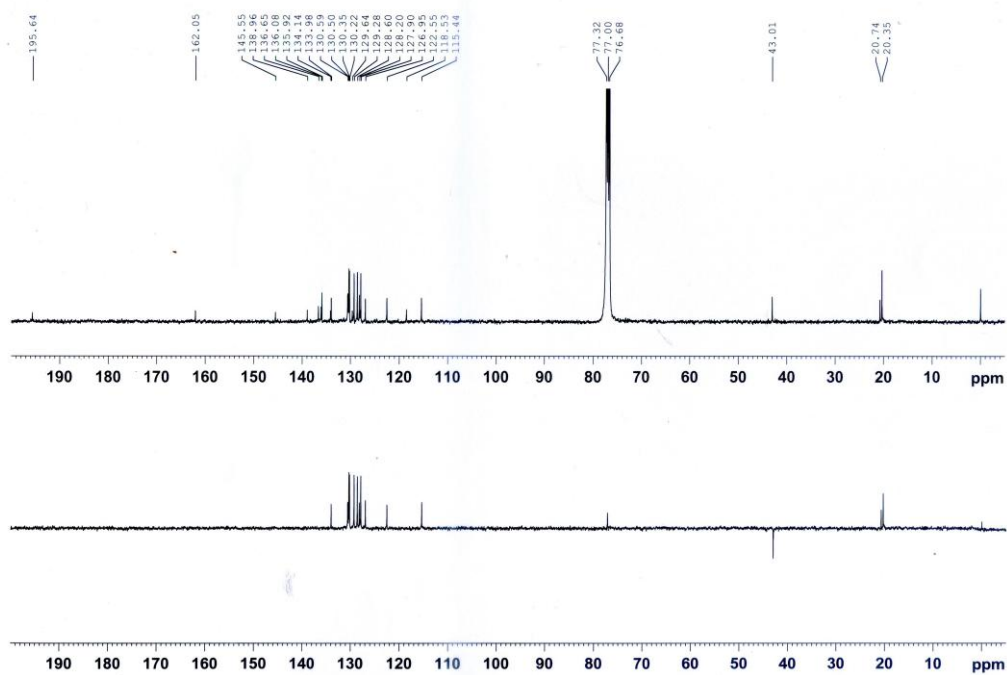
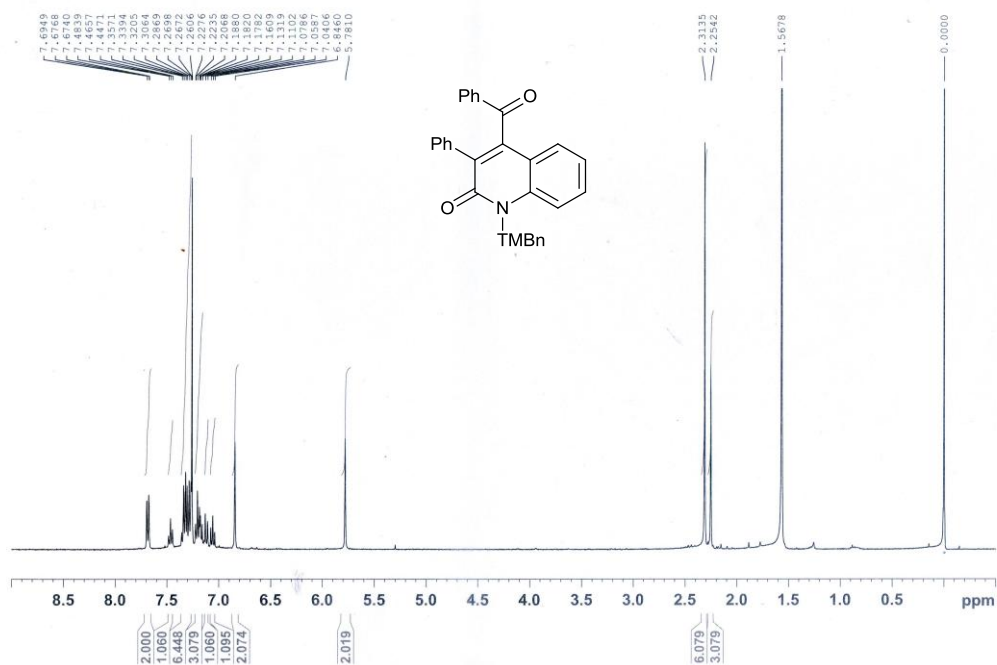
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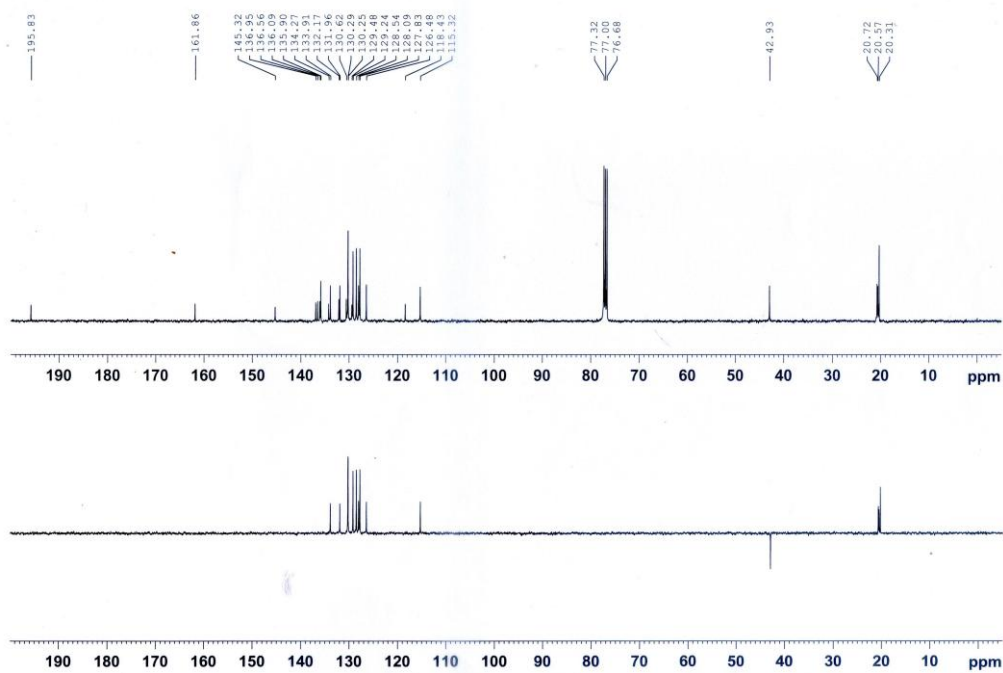
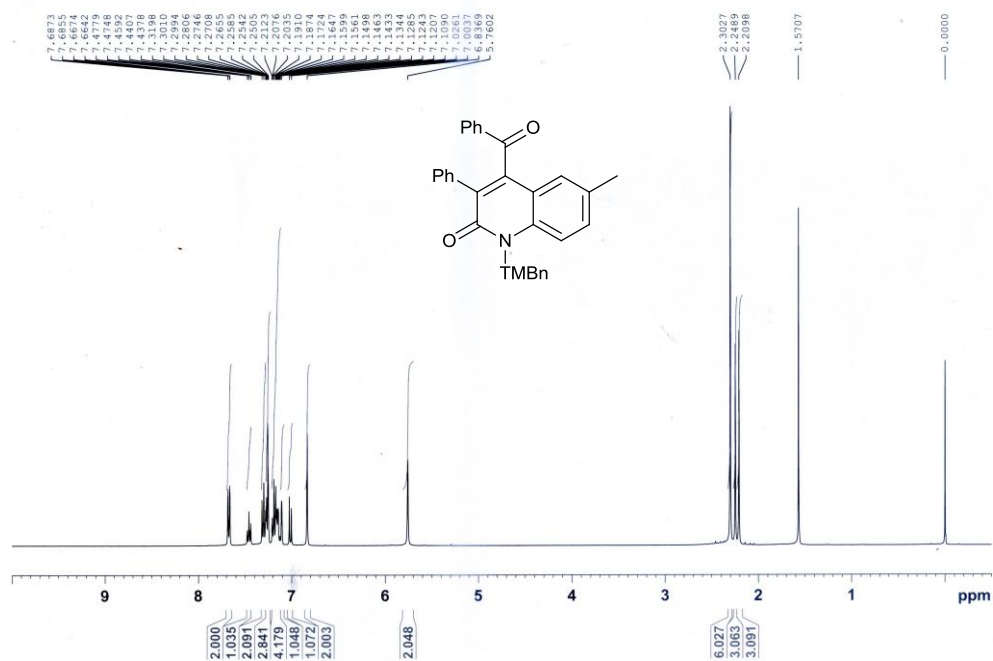
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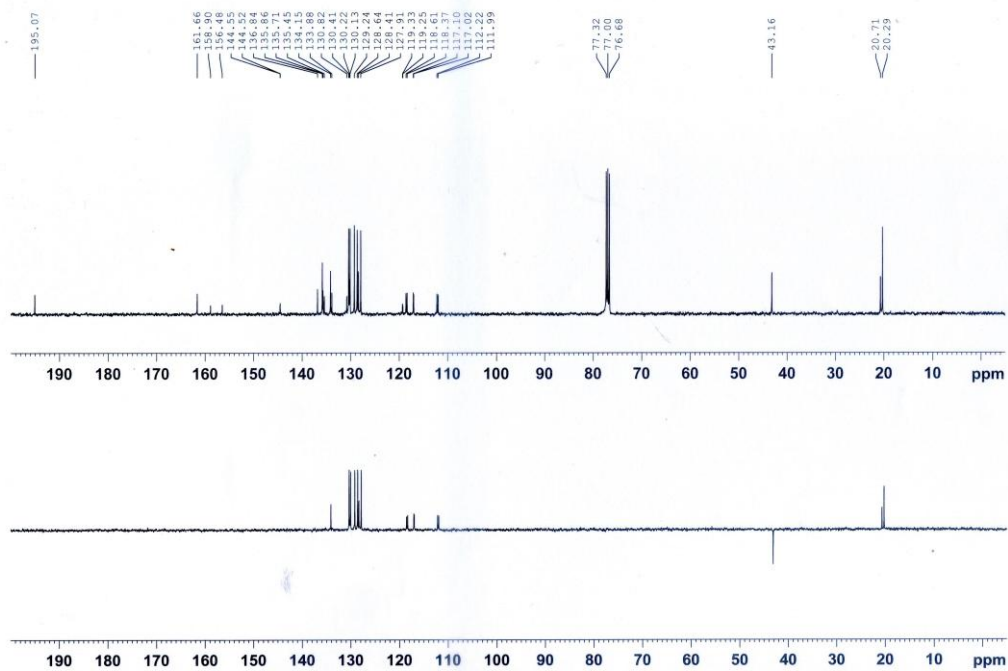
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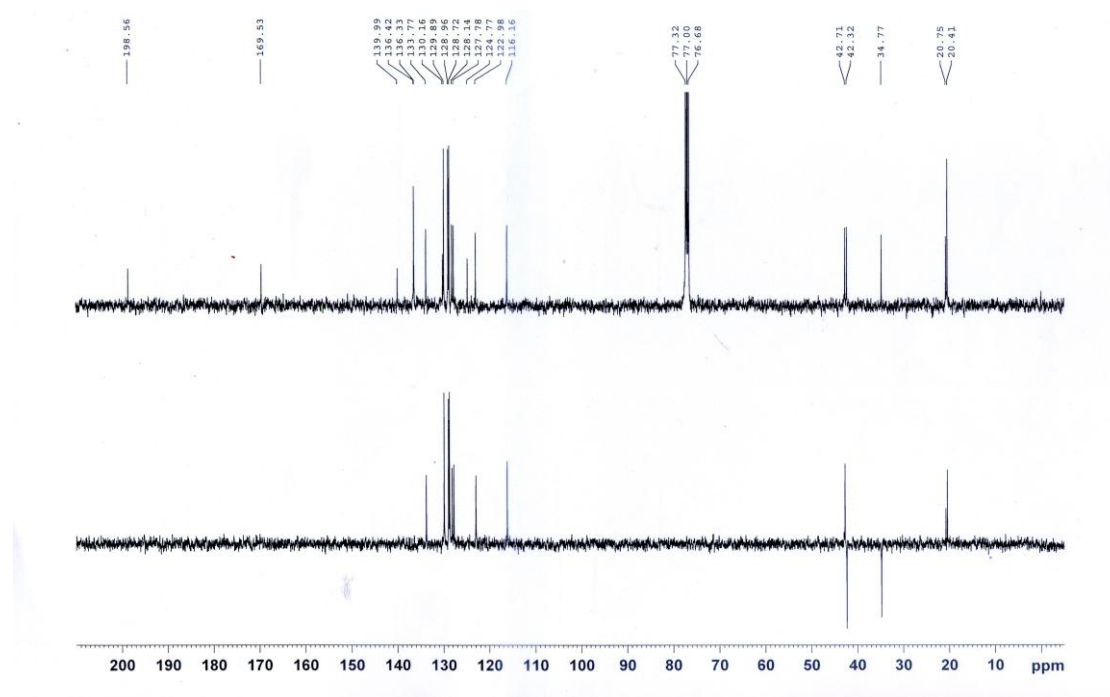
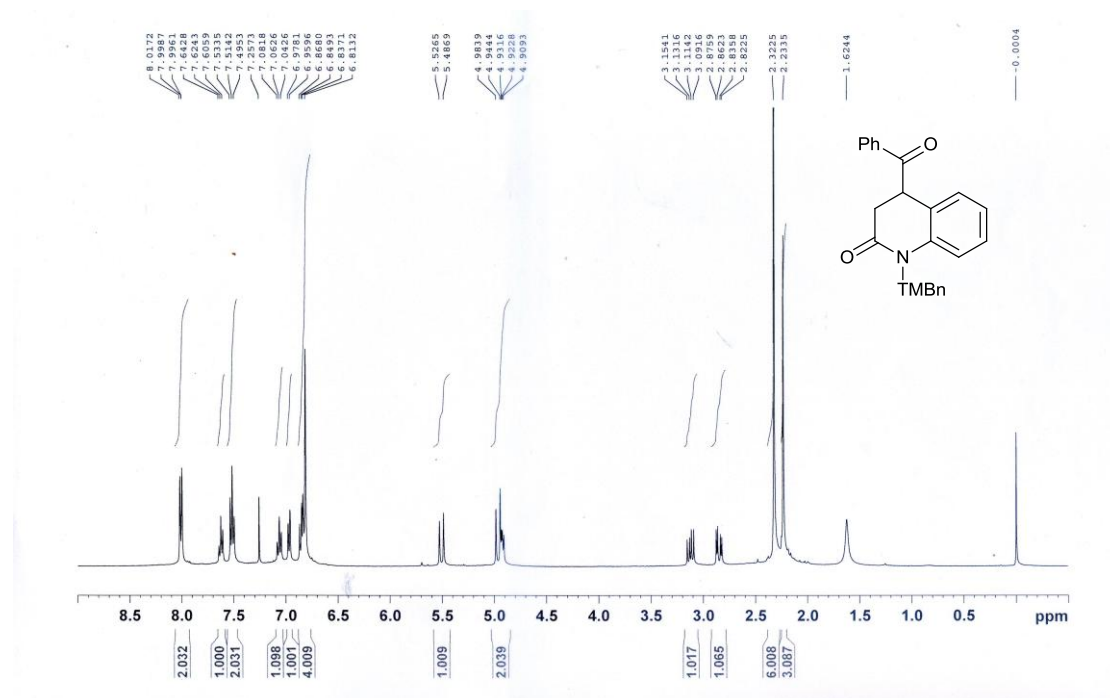
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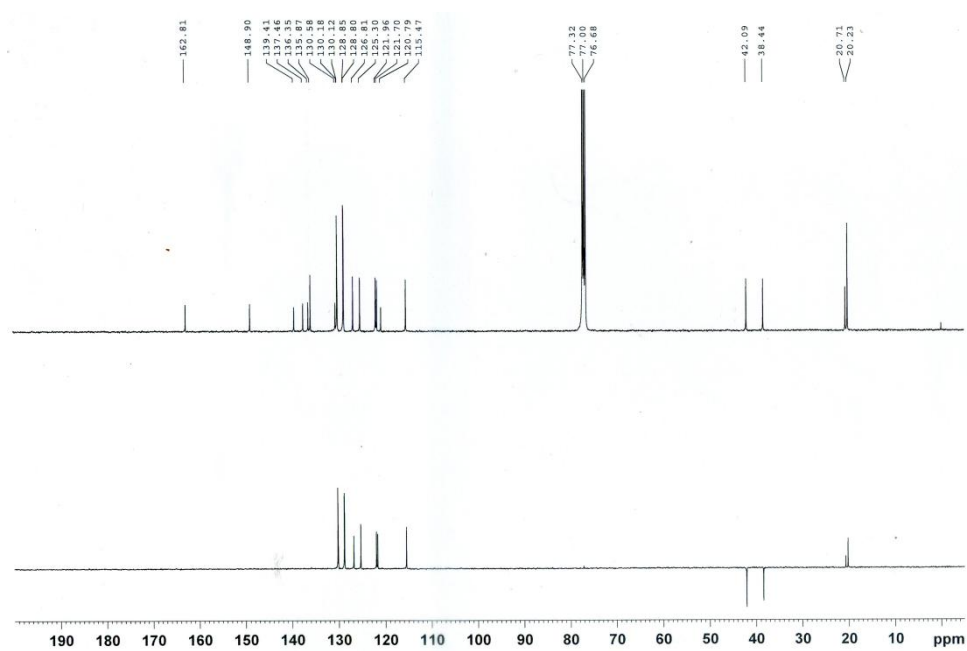
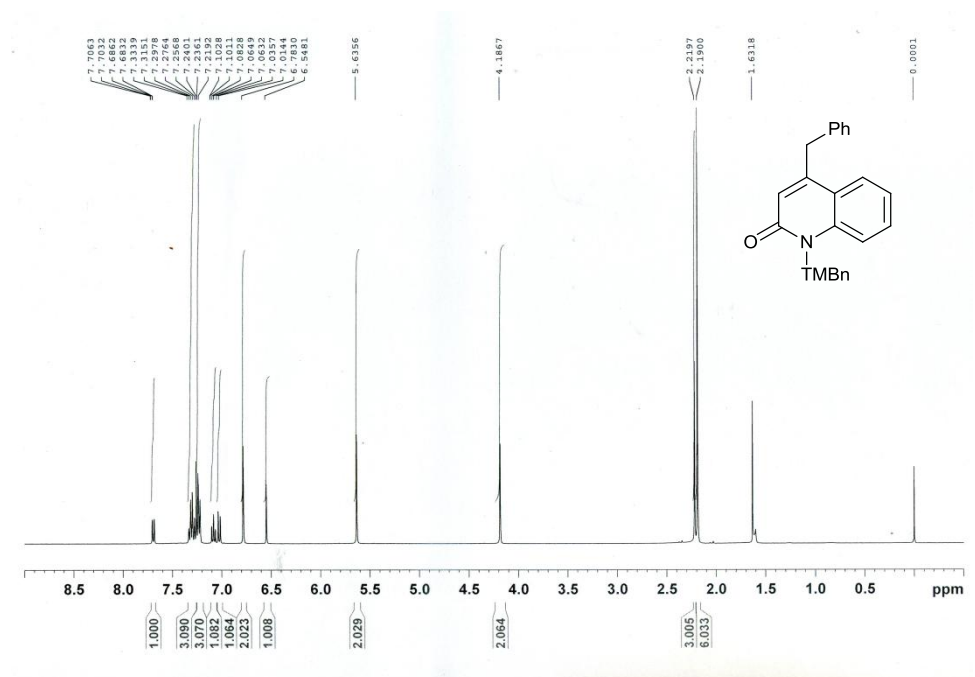
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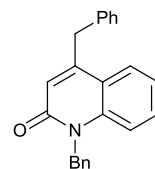
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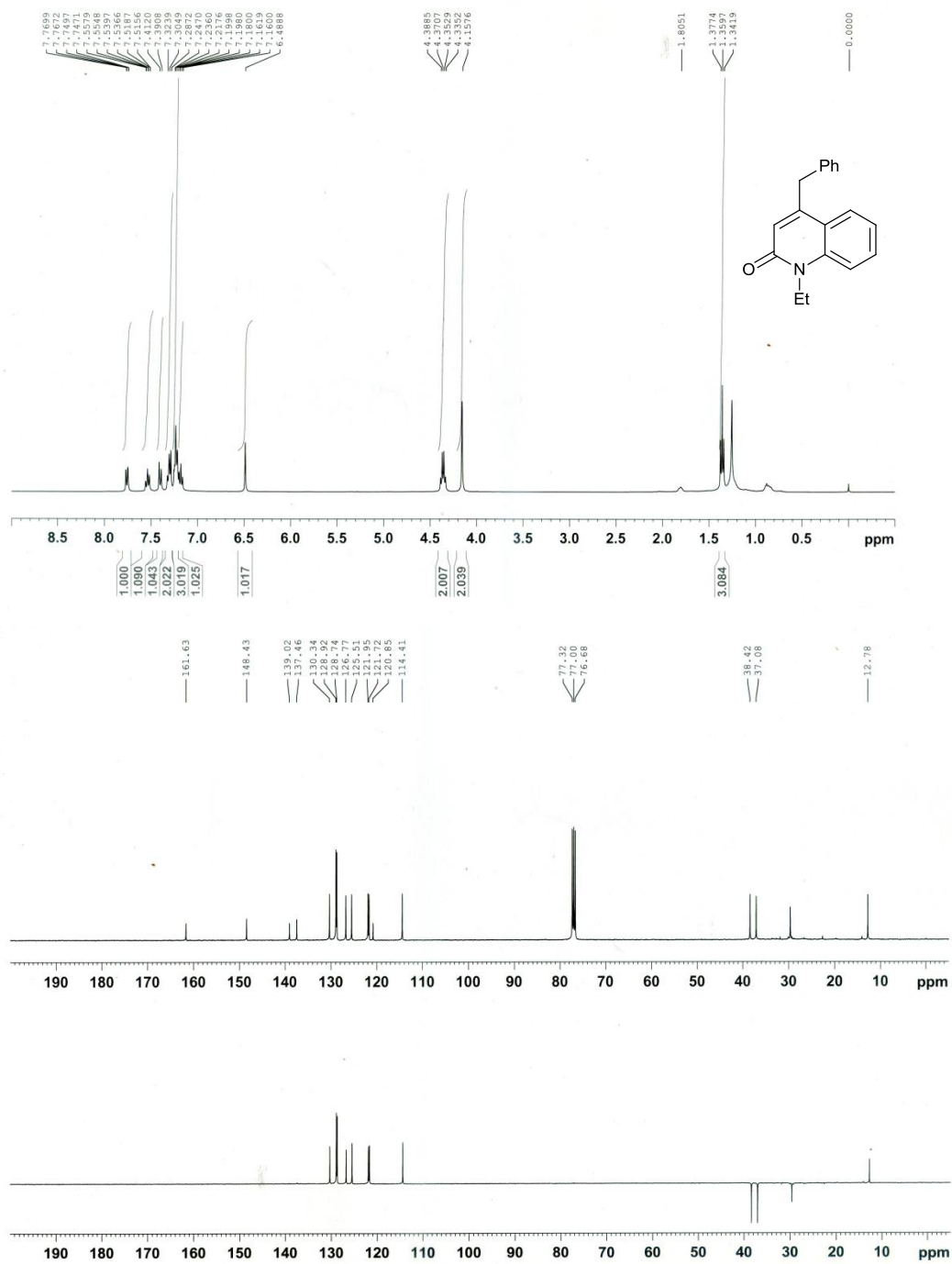
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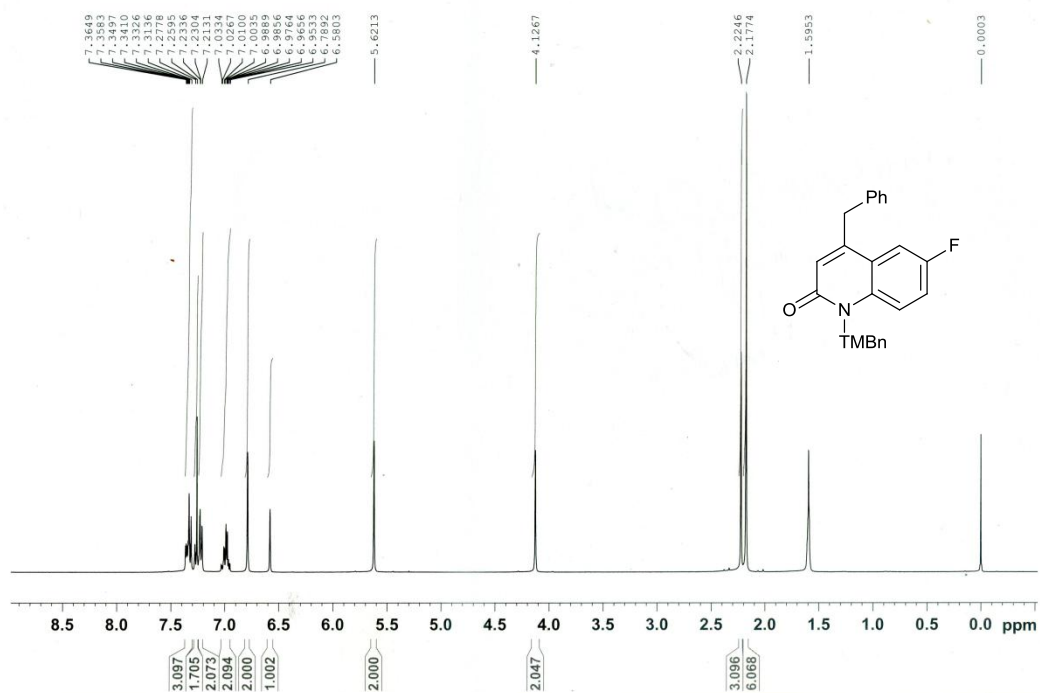
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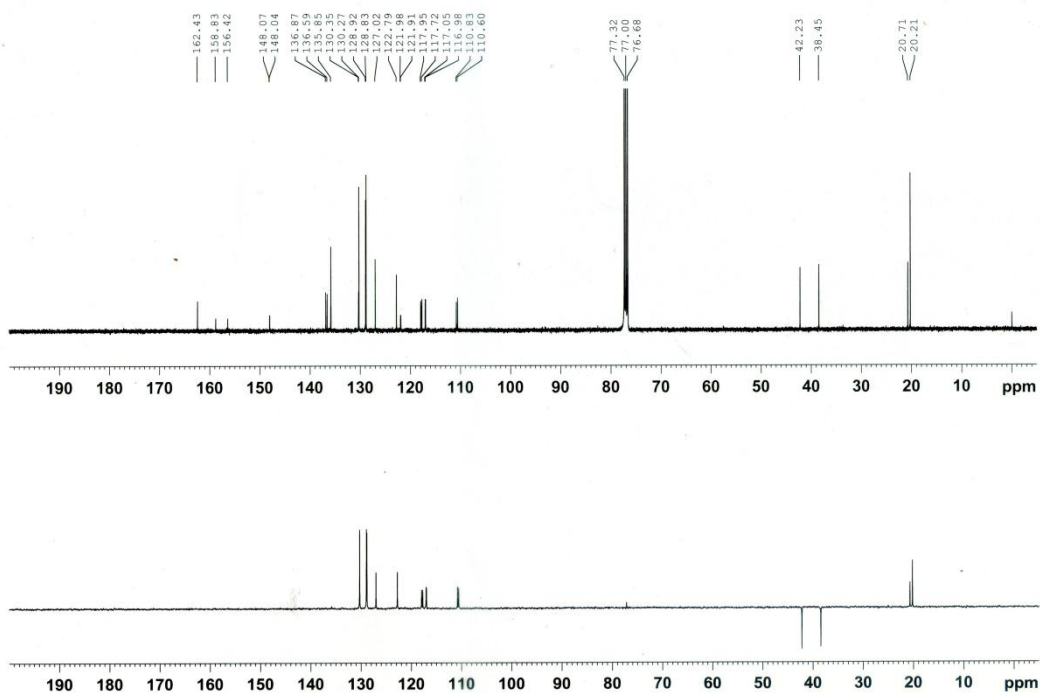
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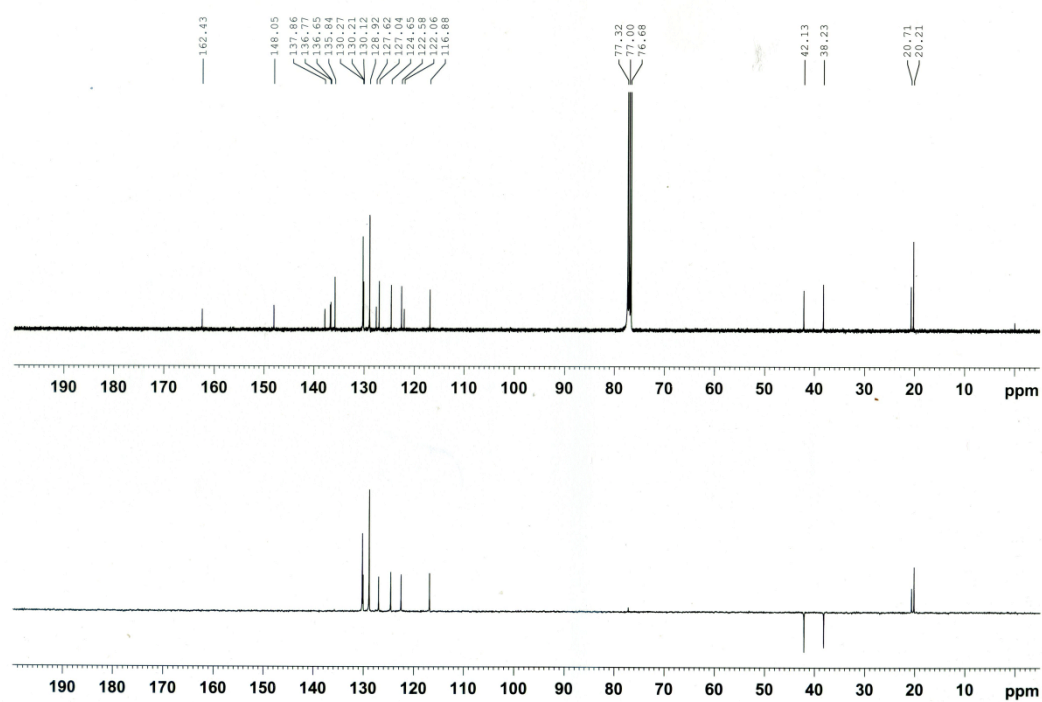
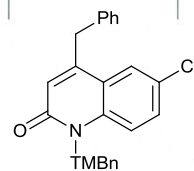
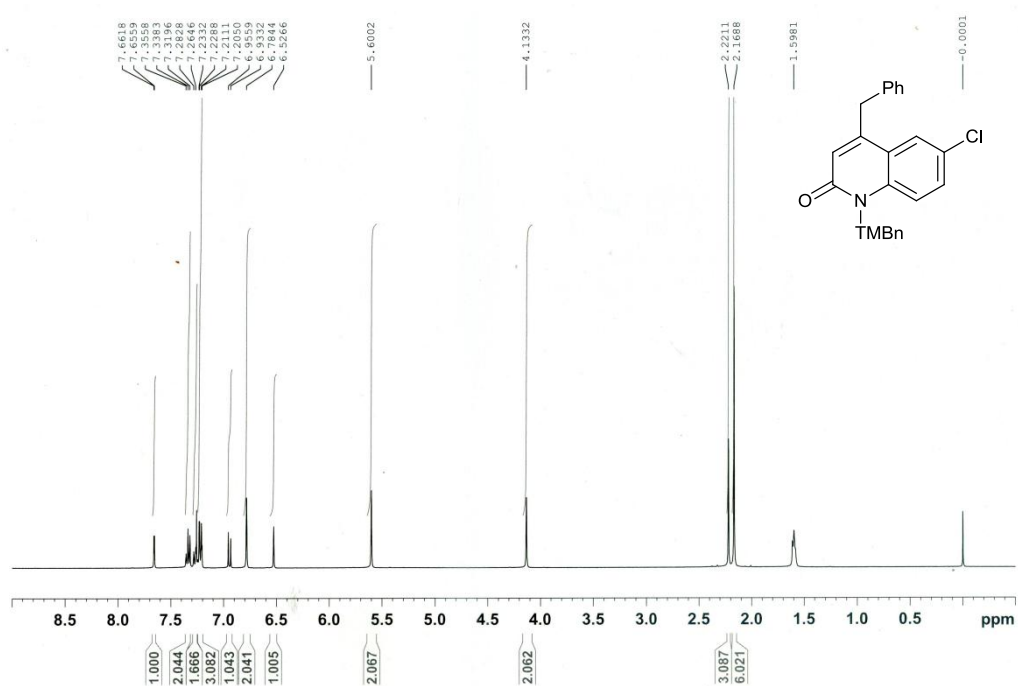
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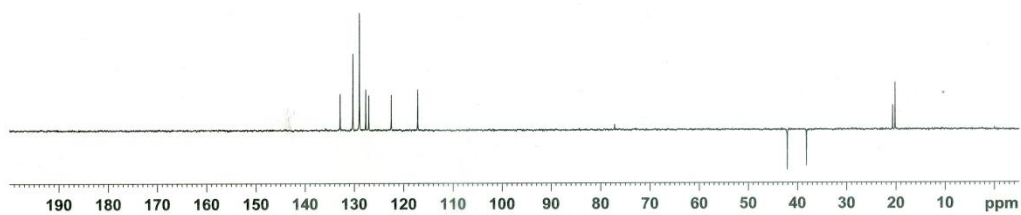
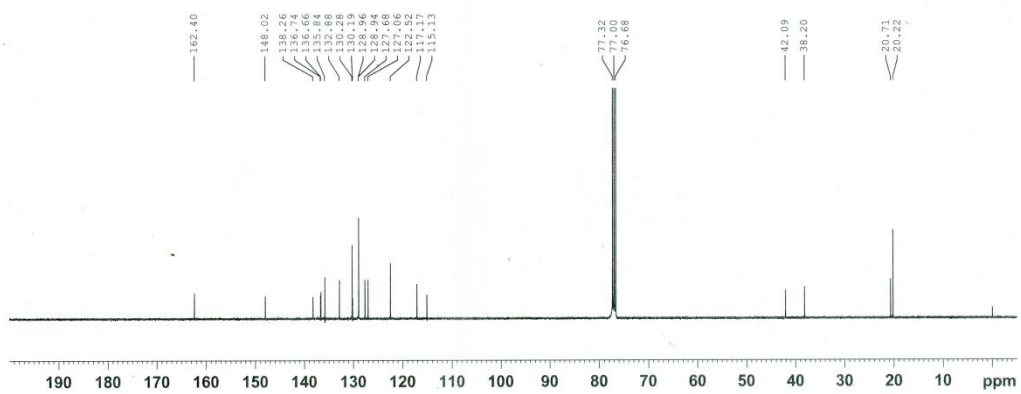
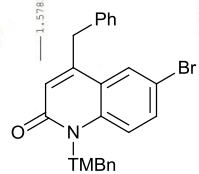
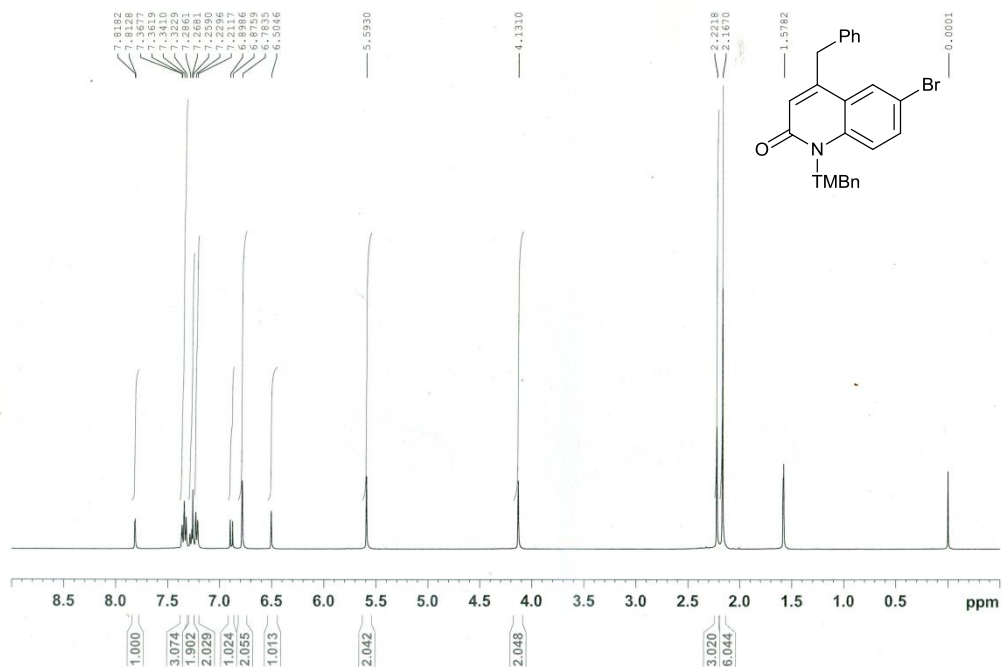
YYC14-110 CDCl₃ 2016/09/06 av400-2/YYC dept135 (23)



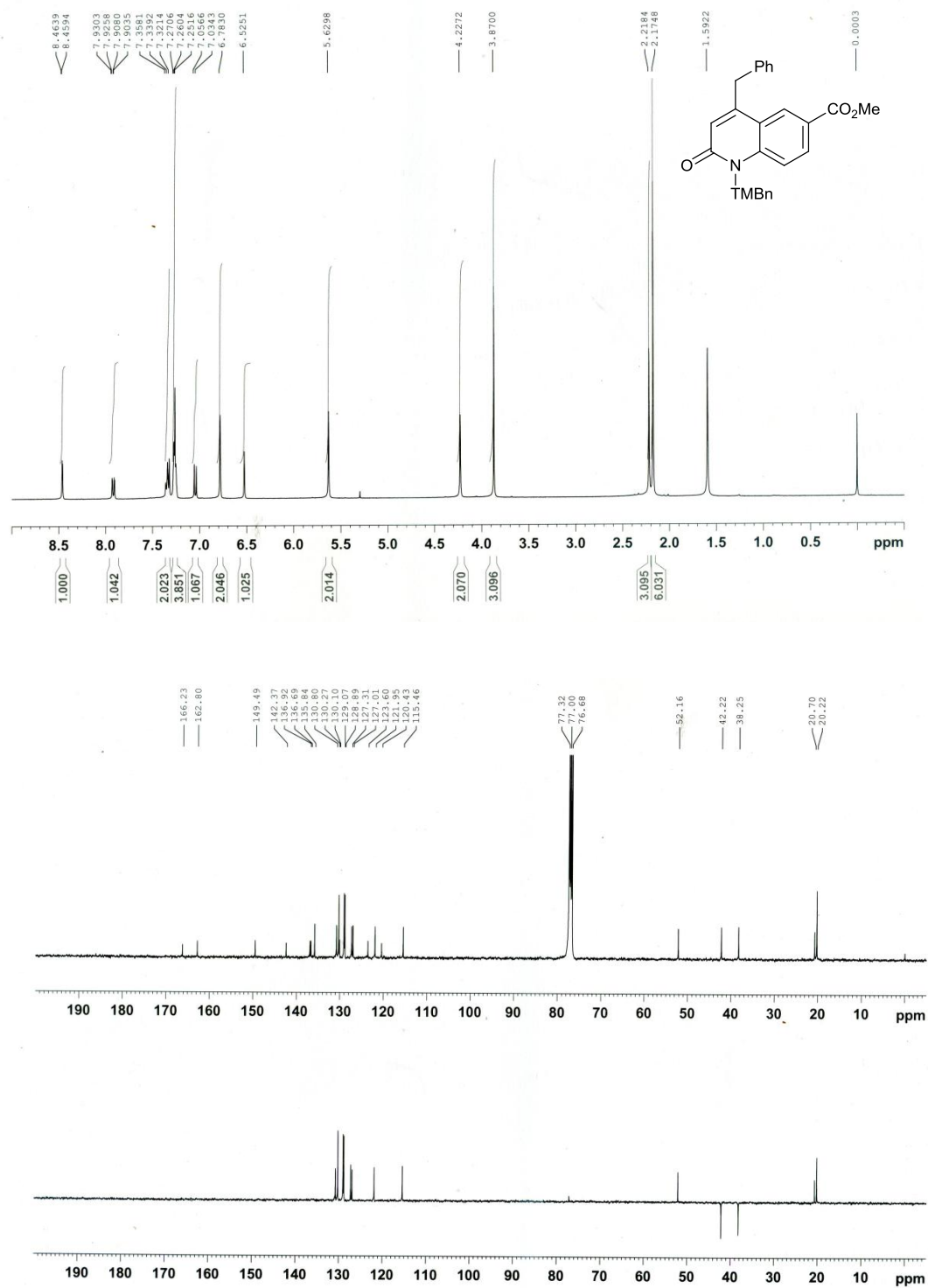
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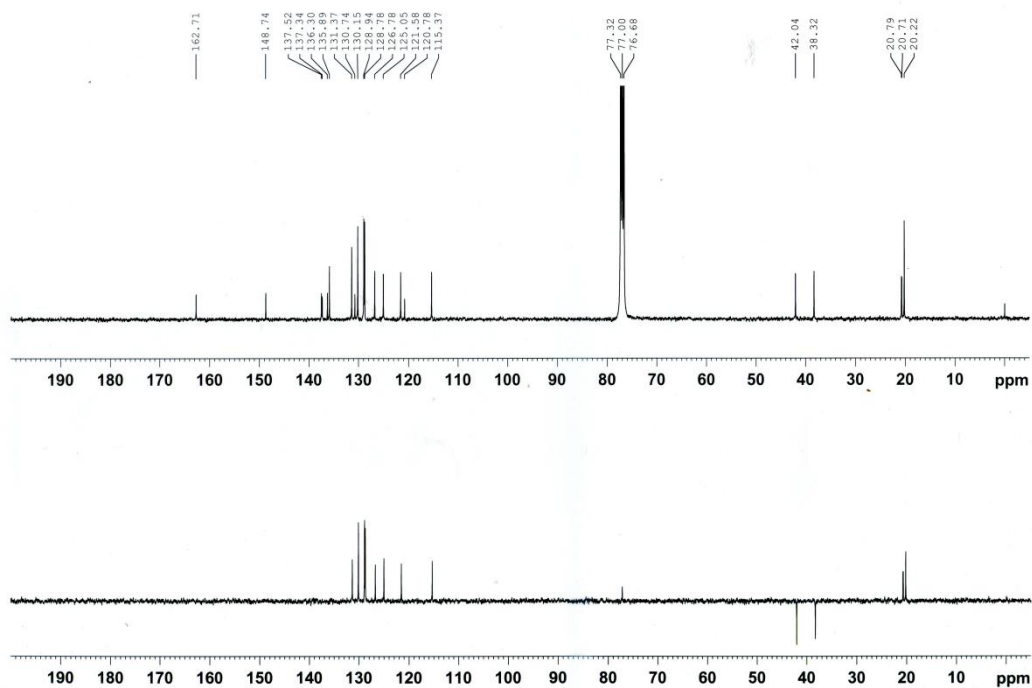
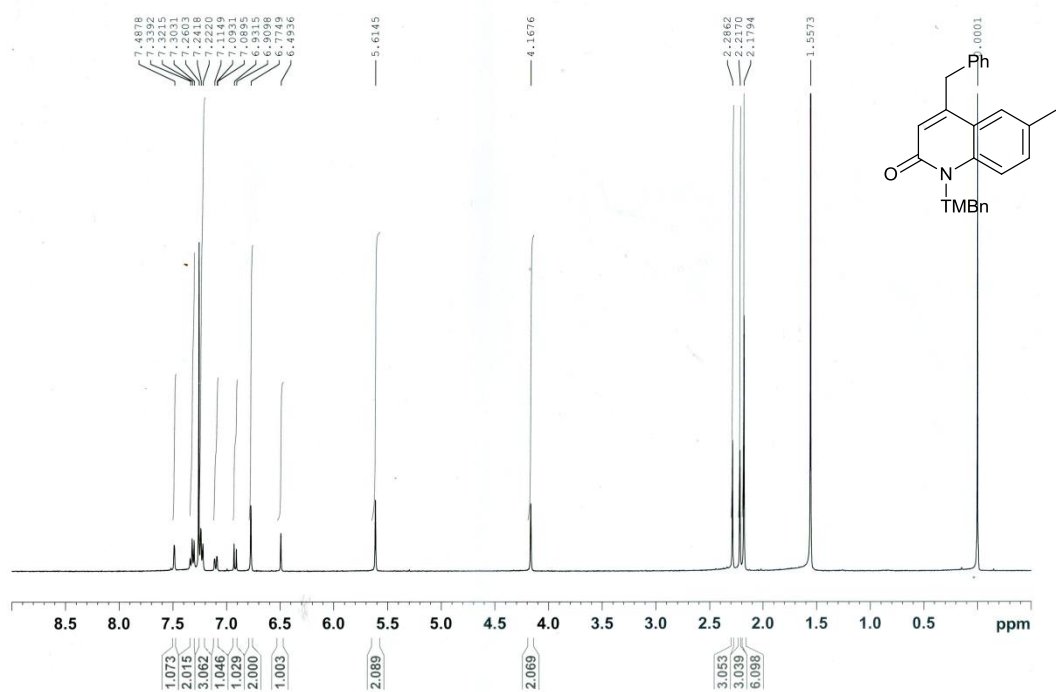
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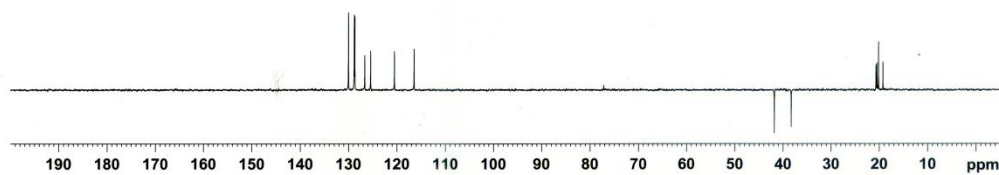
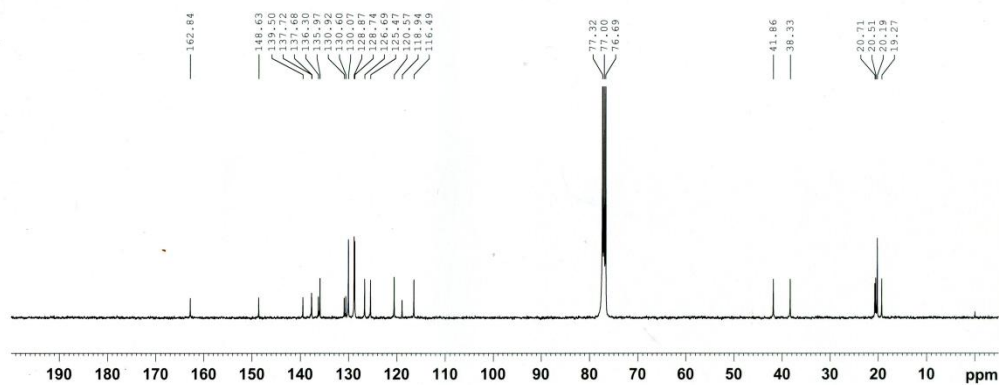
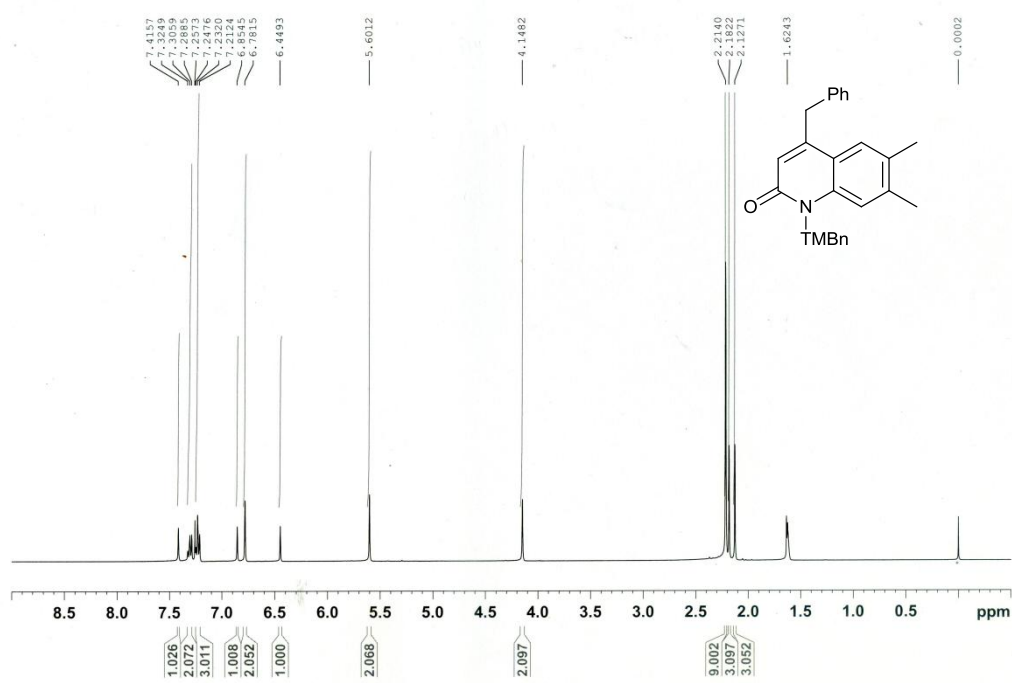
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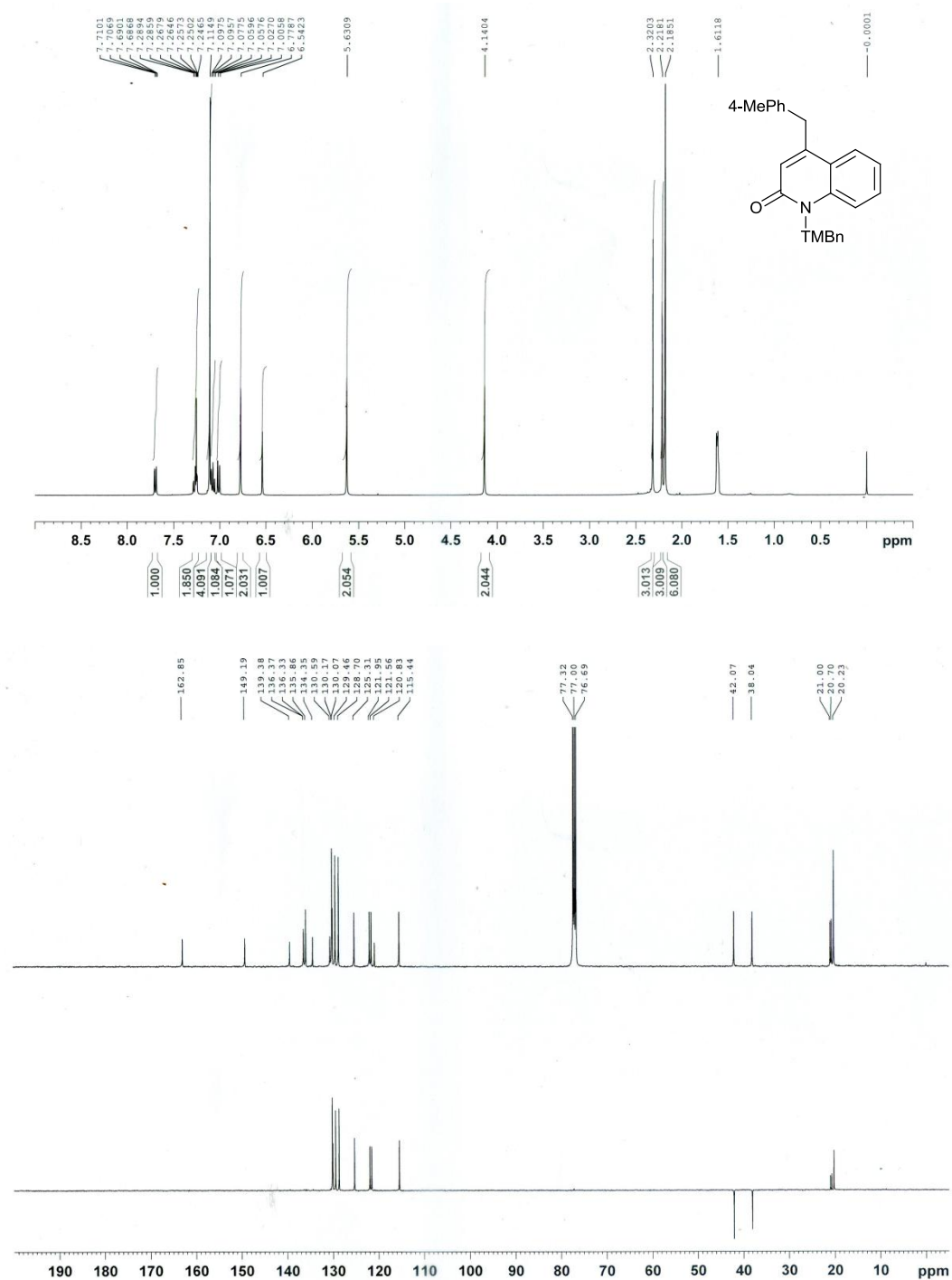
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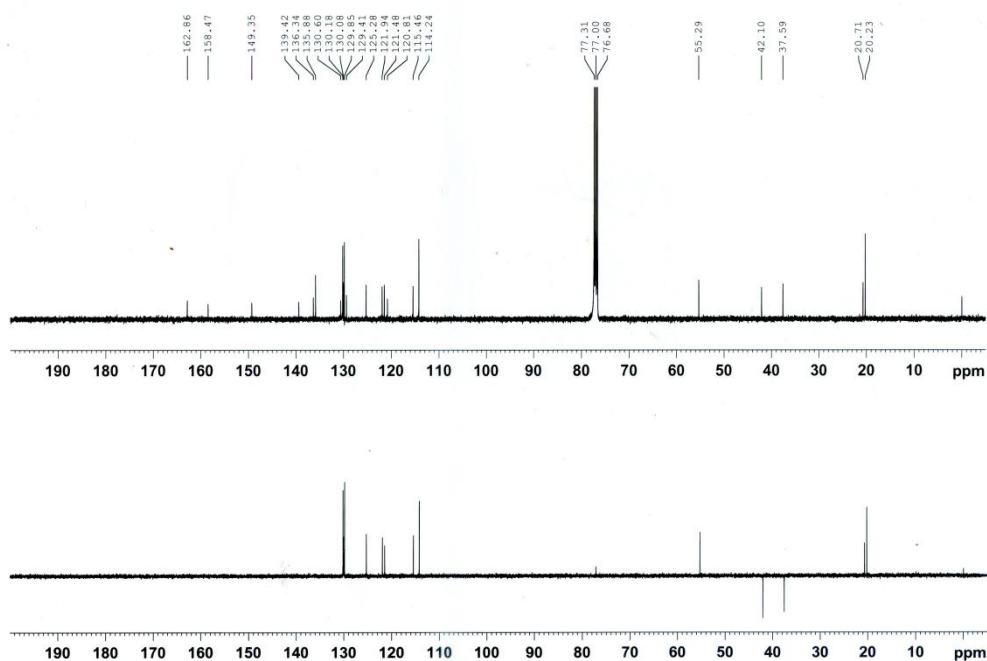
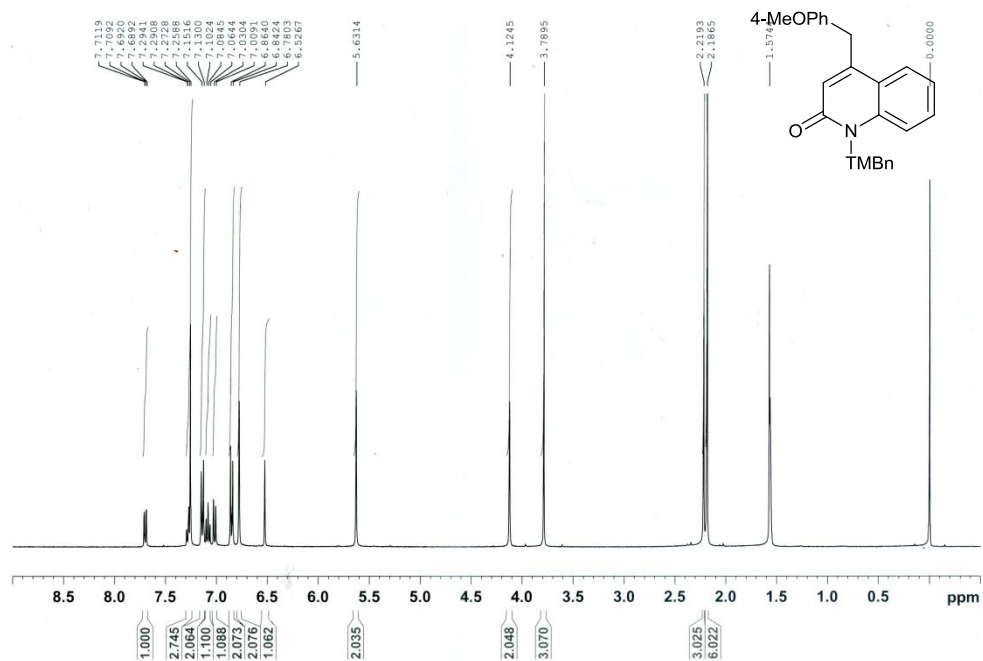


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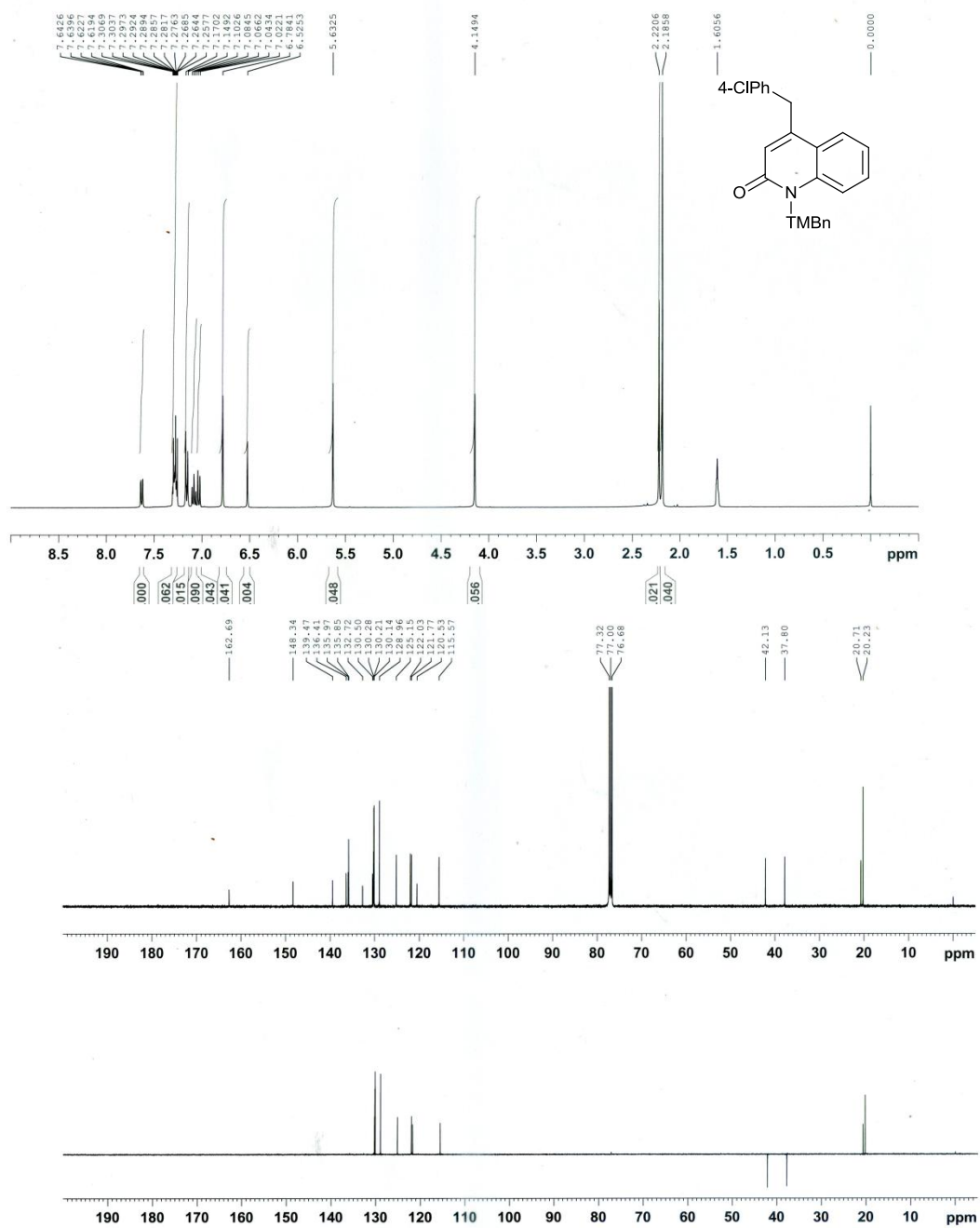


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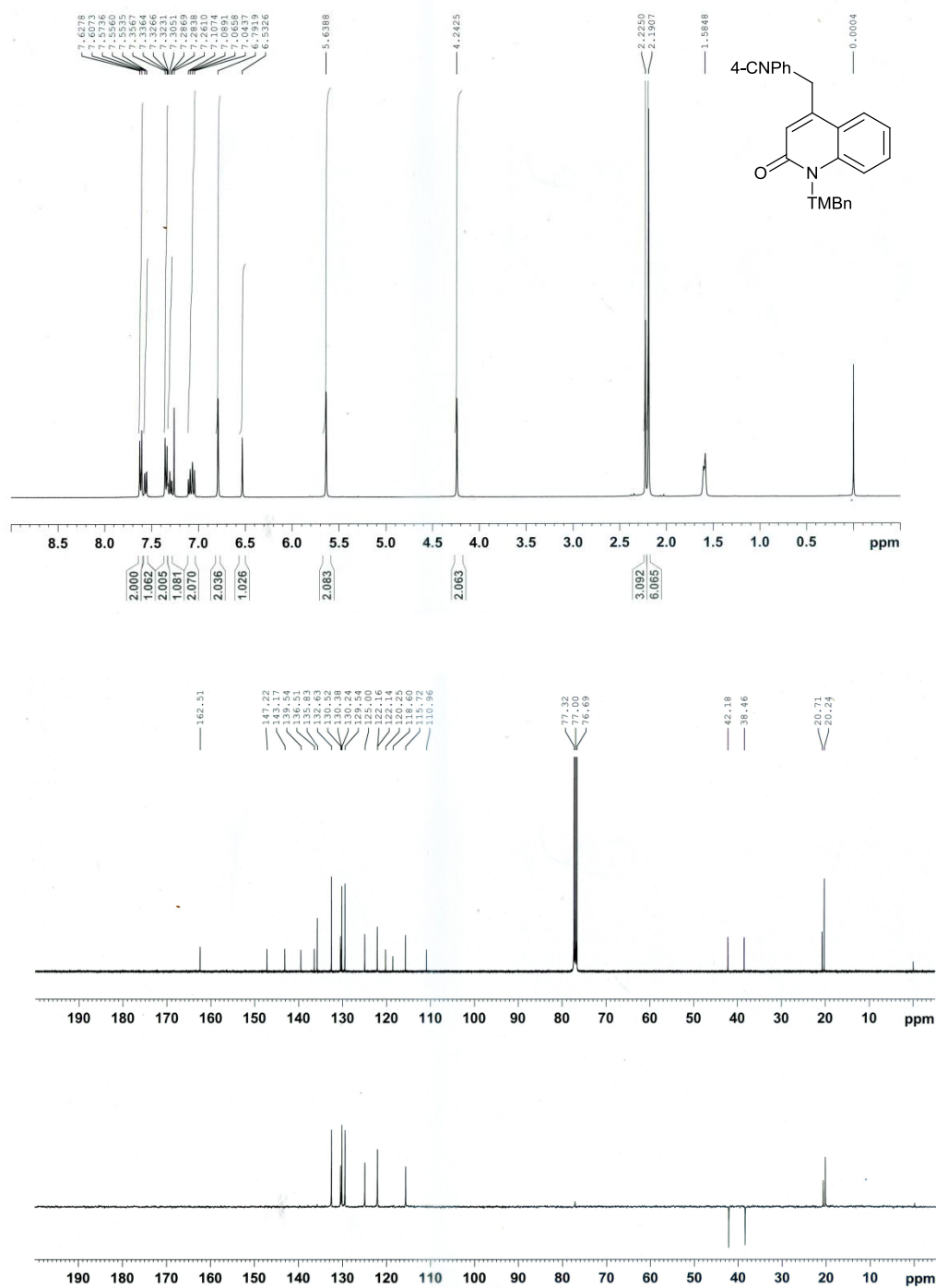




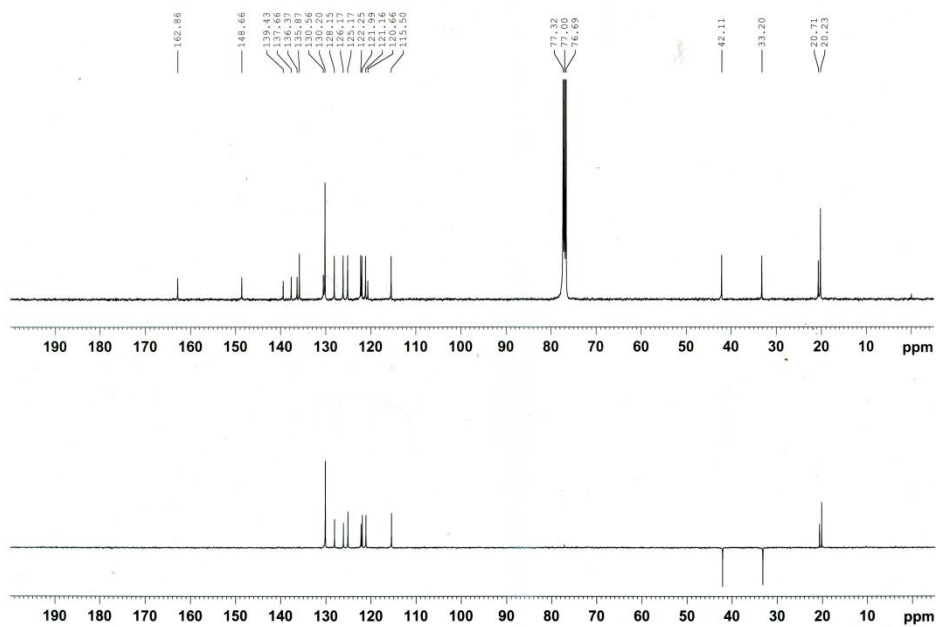
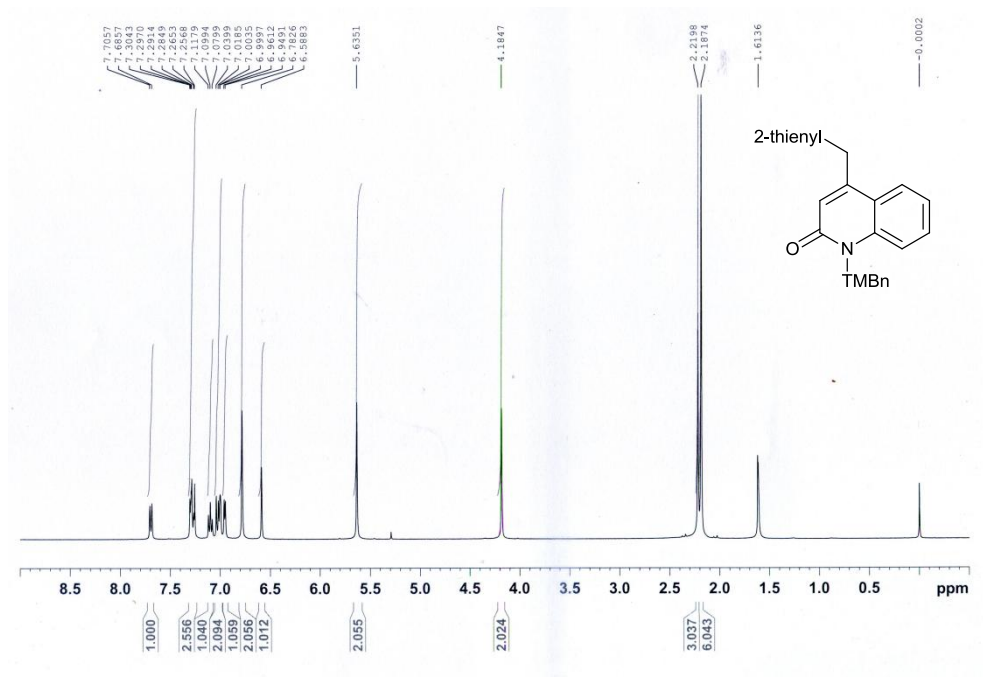
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5n

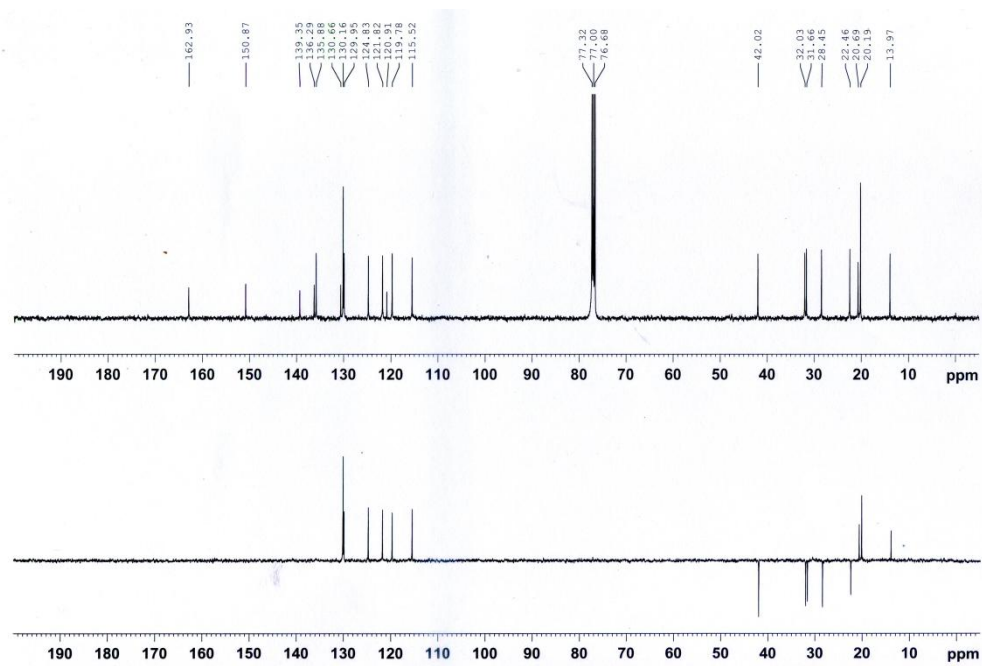
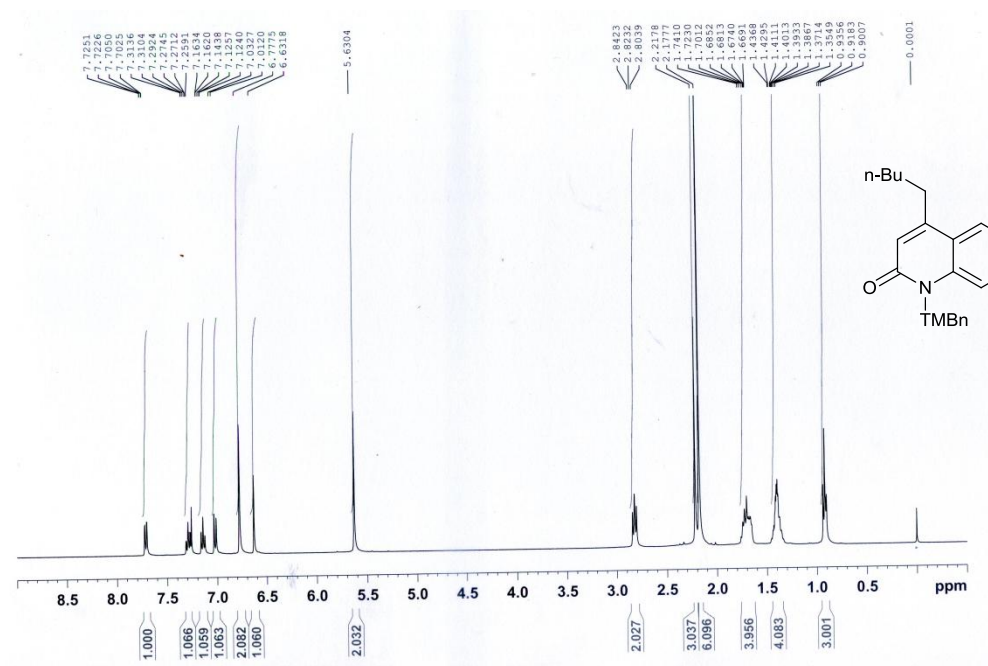


50

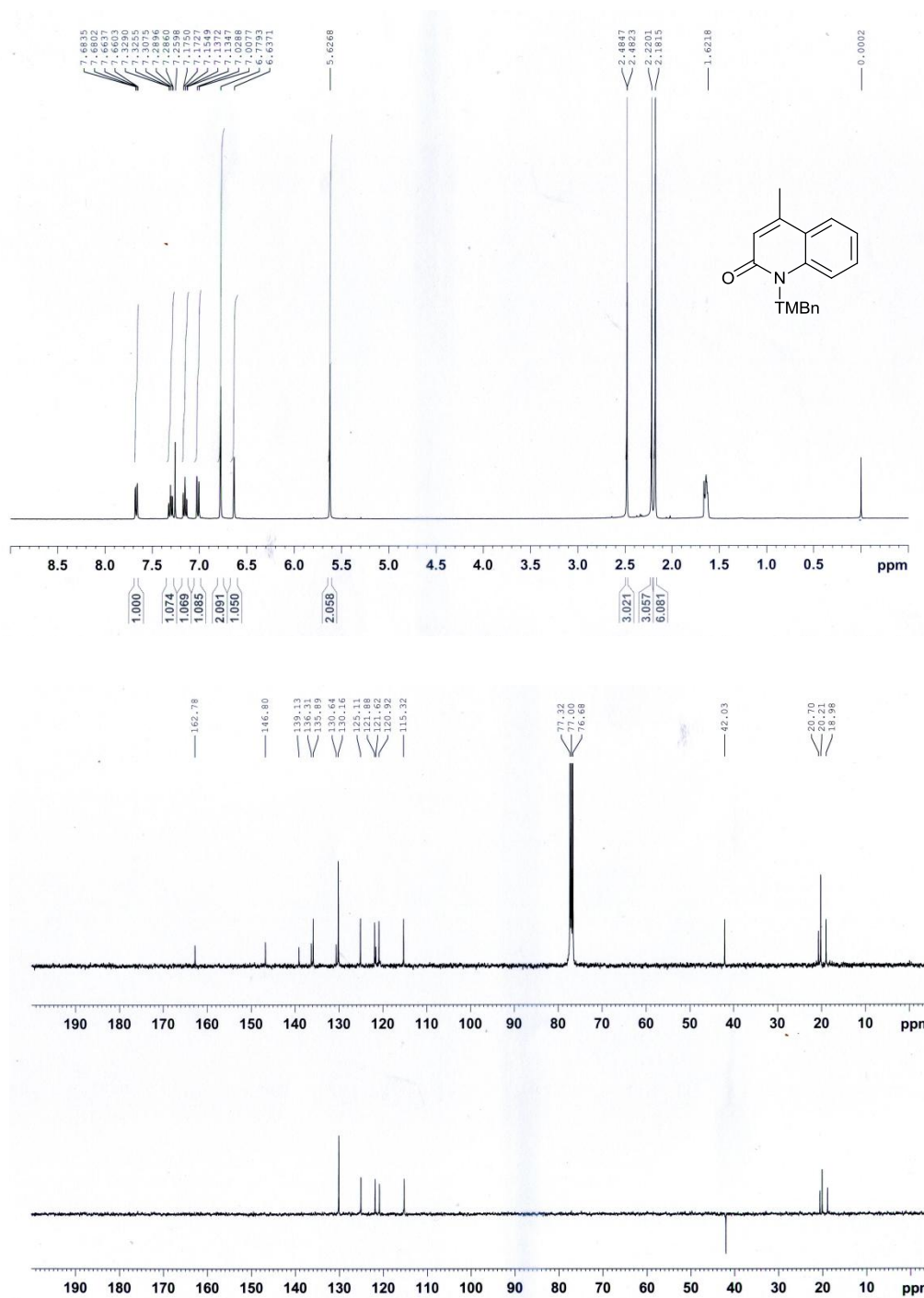


44

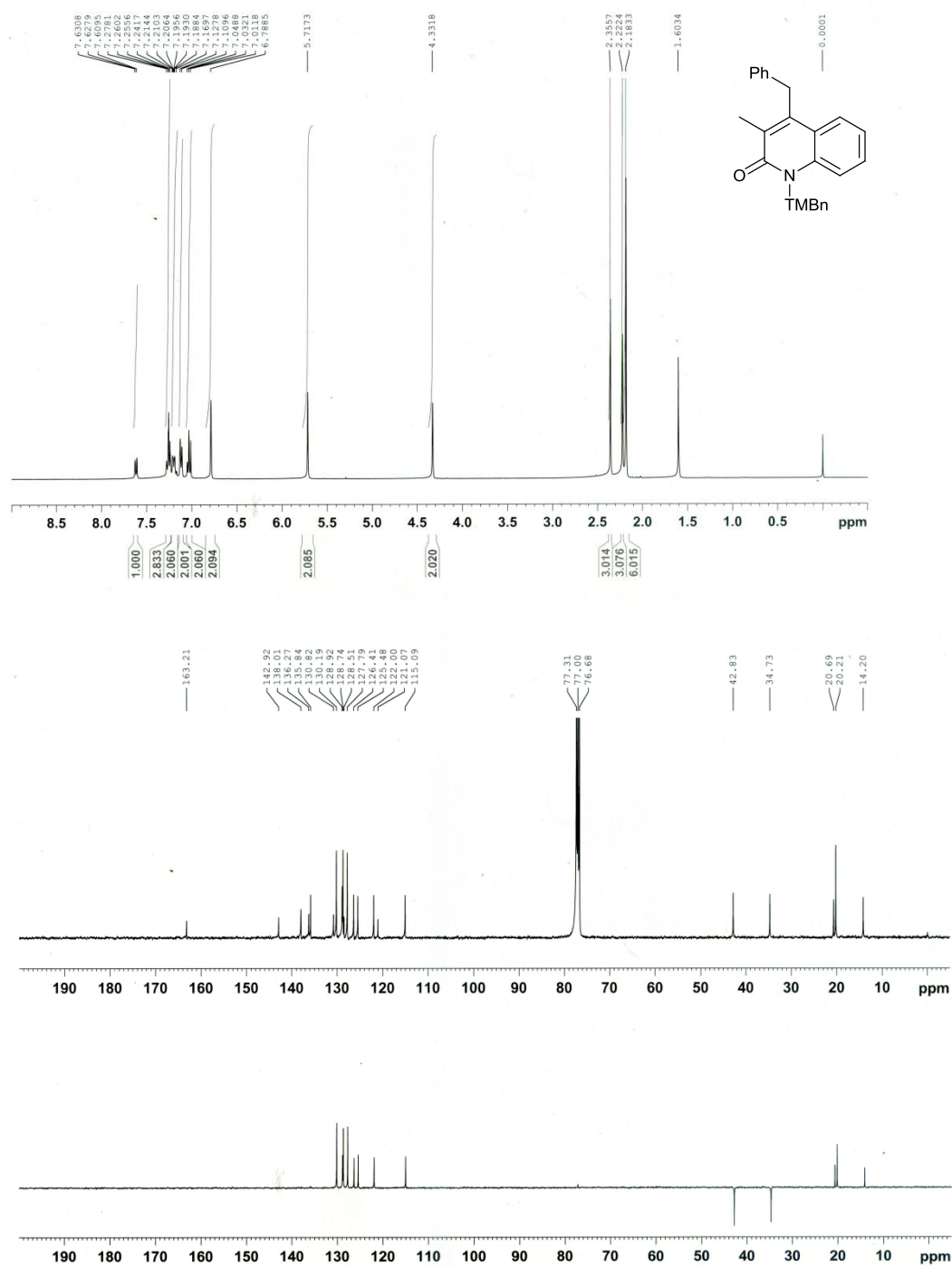
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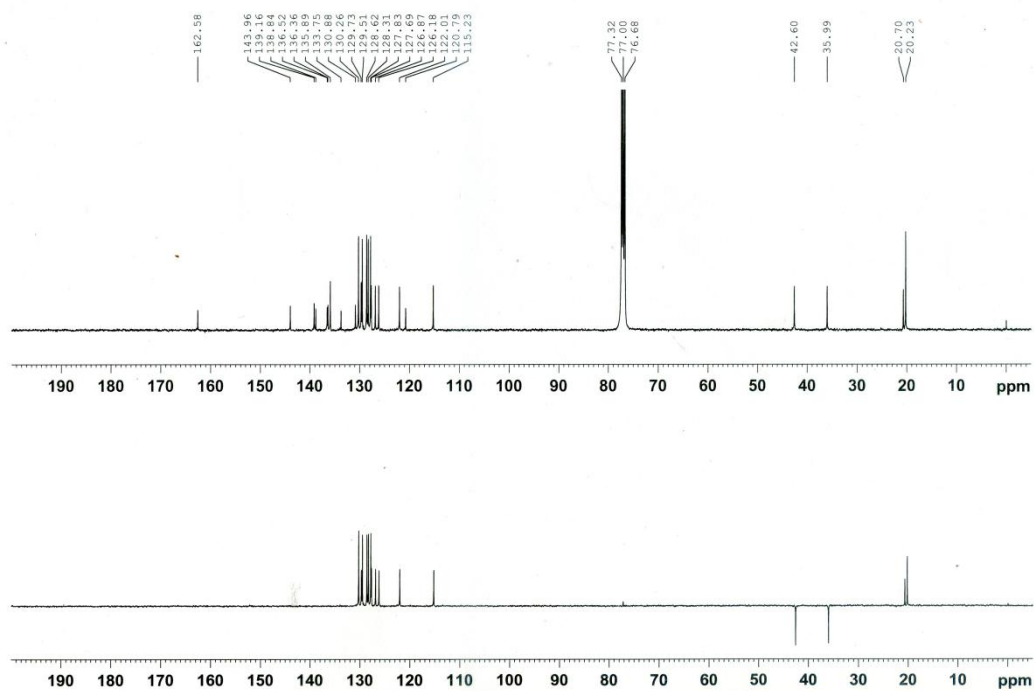
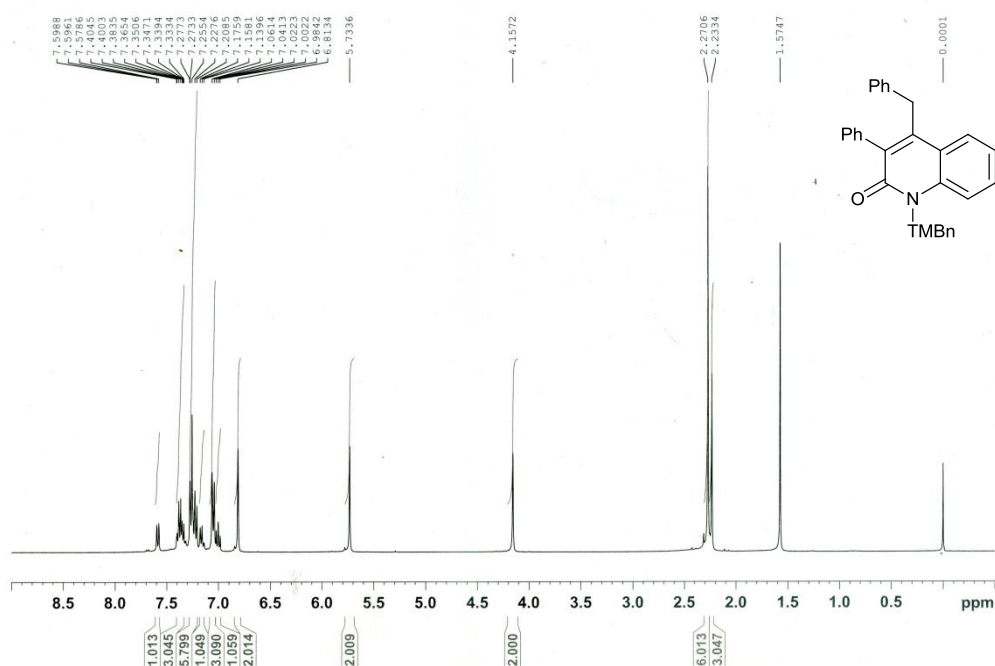
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5r

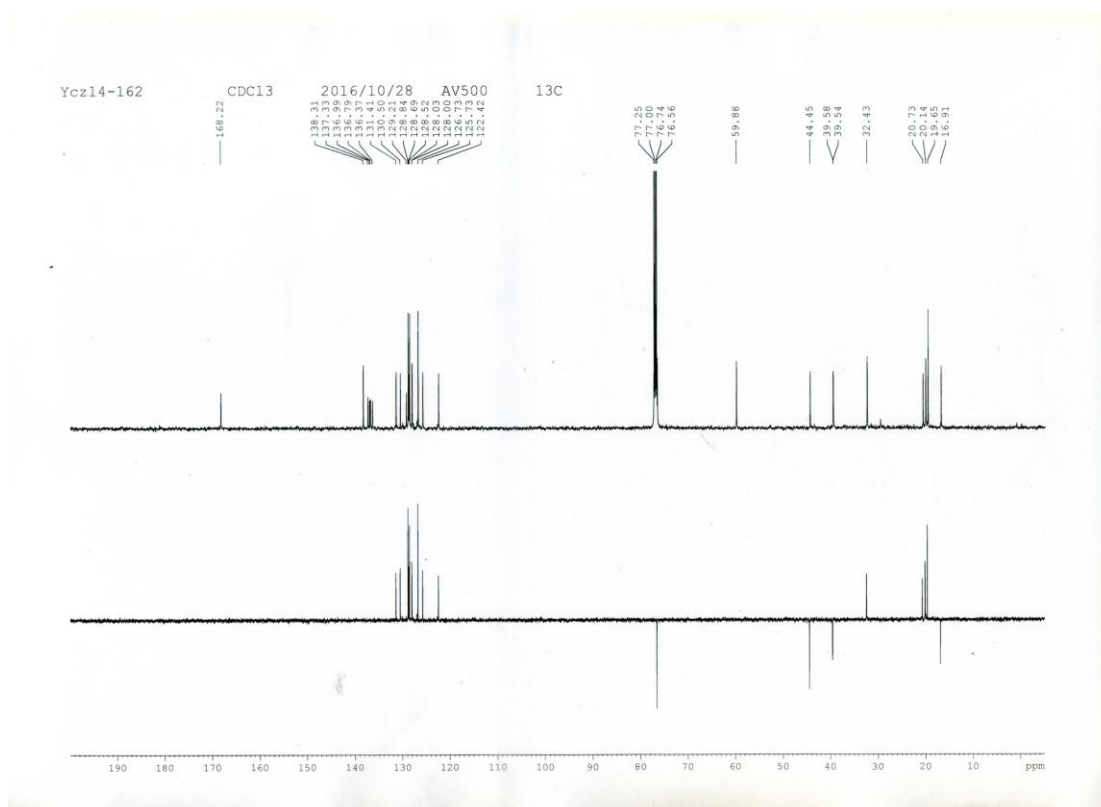
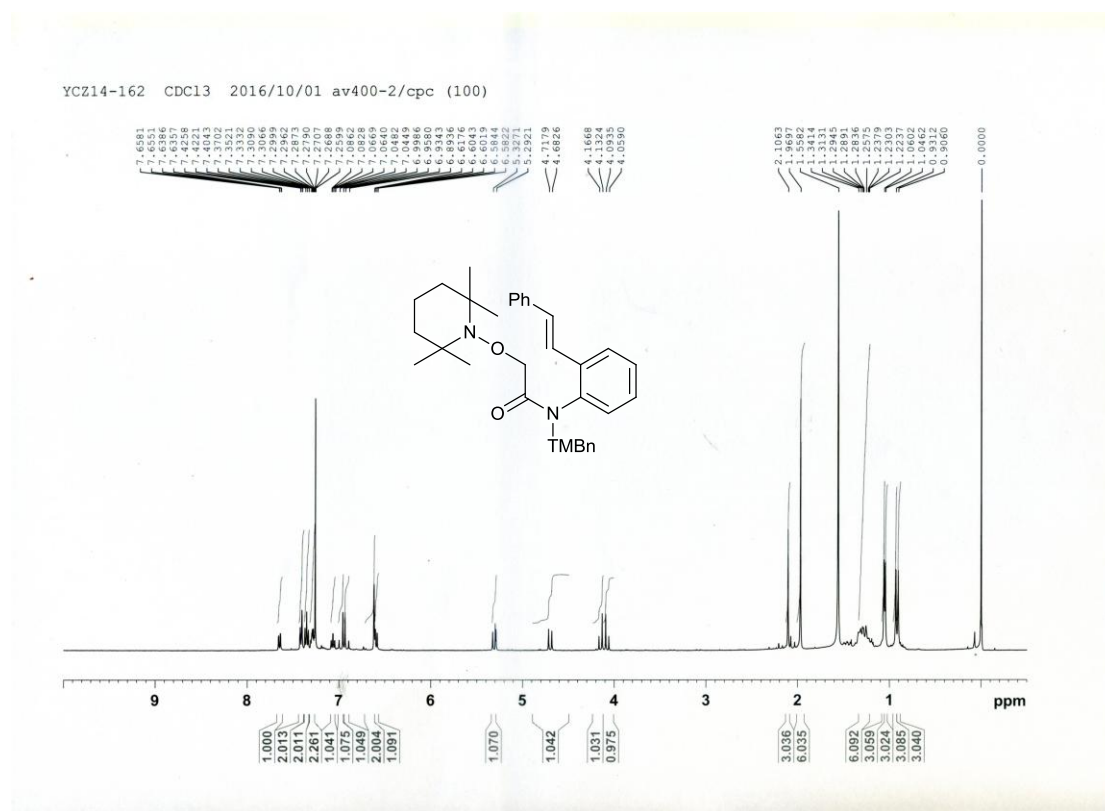


5s



3) Copies of ^1H and ^{13}C NMR spectra for radical-trapping adduct.

7a



8a

