Combustion-synthesized porous CuO-CeO_2-SiO_2 composites as novel solid catalysts for the alkenylation of $C(sp^3)$-H bonds adjacent to a heteroatom via cross-dehydrogenative coupling

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SUPPORTING INFORMATION

Table S1. H_2 consumption of the composite samples in the H_2-TPR analysis.

Sample	H_2 consumption (mmol g^{-1})	Cu:H_2 molar ratio
CuSi	1.077	1.09
$Cu_1Ce_{0.15}Si$	1.065	1.06
$Cu_1Ce_{0.45}Si$	1.020	1.03
$Cu_1Ce_{0.7}Si$	0.957	1.06
$Cu_1Ce_{0.91}Si$	0.898	1.09

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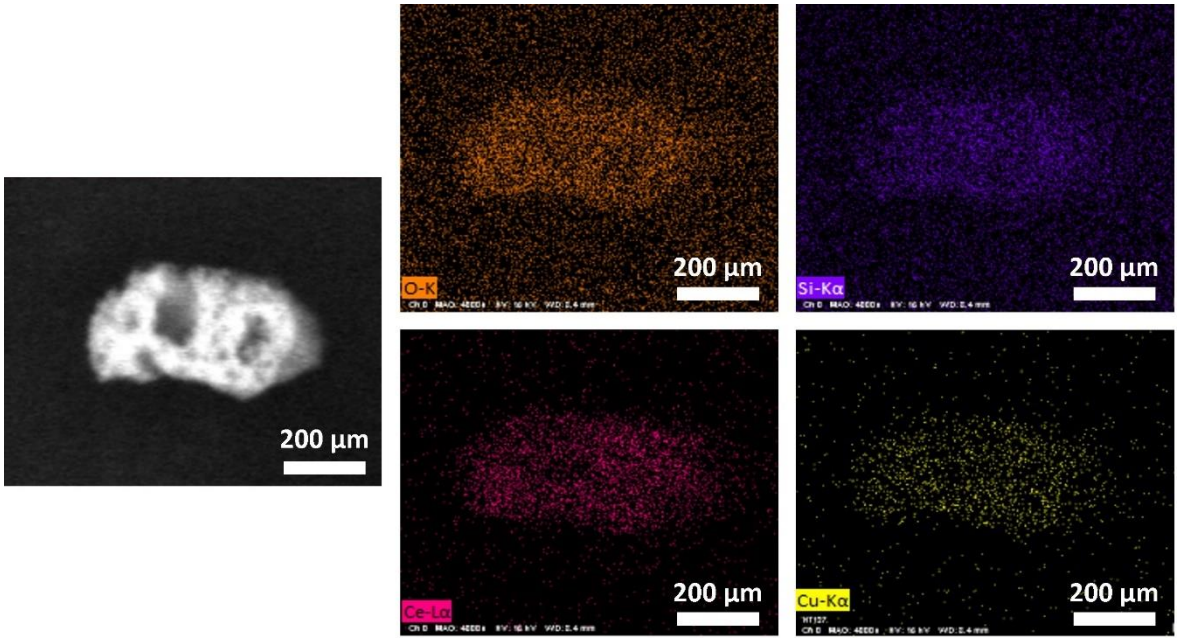

Figure S1. SEM/EDX elemental mapping images of O, Si, Ce and Cu for $Cu_1Ce_{0.7}Si$.

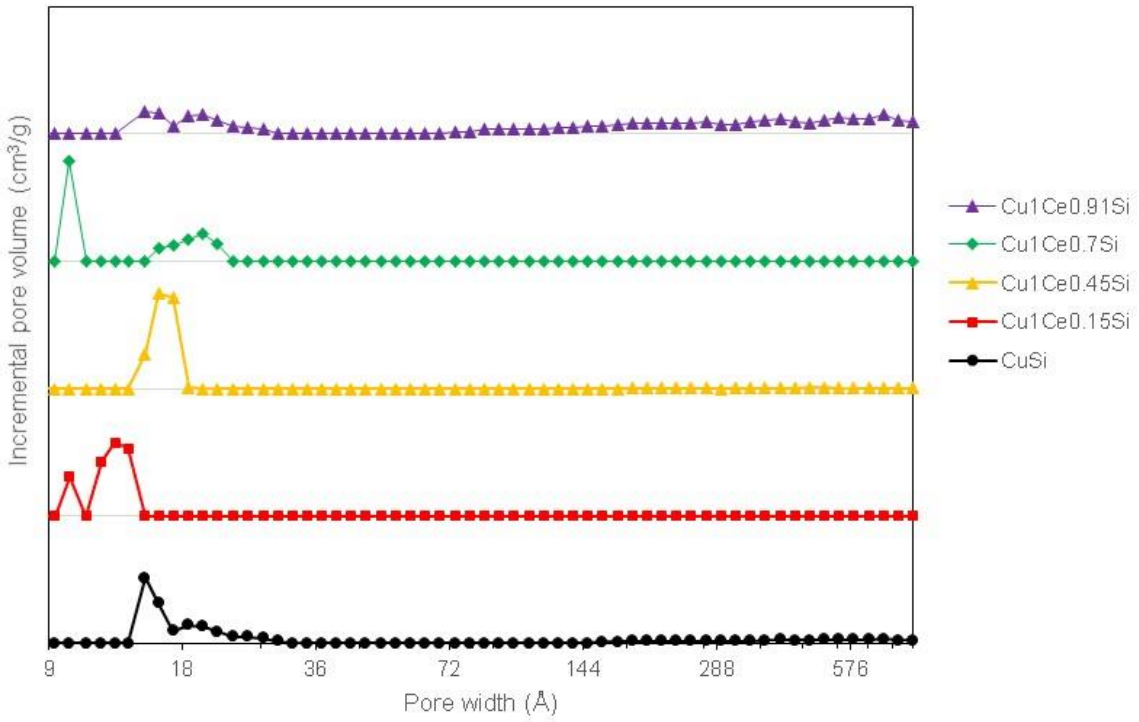

Figure S2. Pore size distribution results of the combustion-synthesized composites.

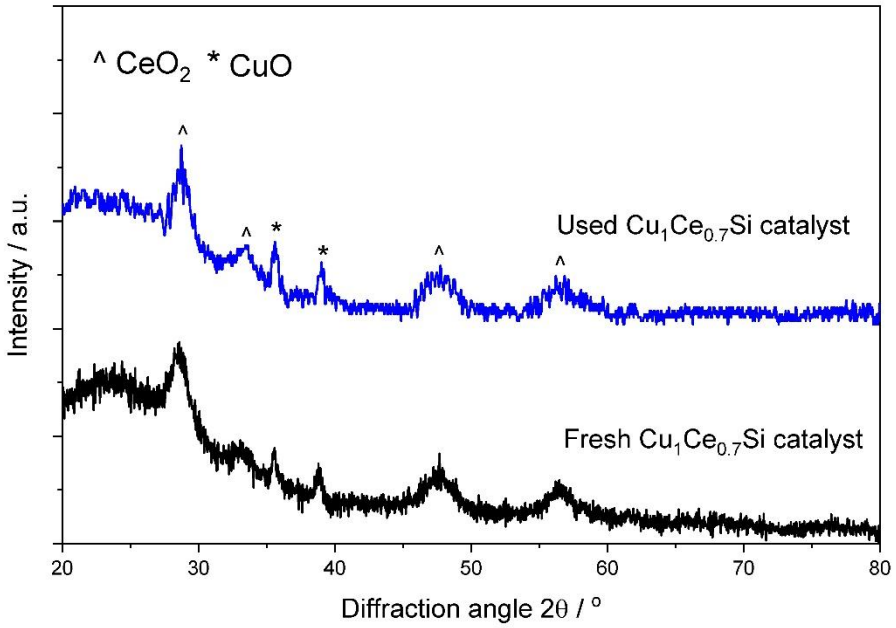

Figure S3. PXRD results of the fresh and used $Cu_1Ce_{0.7}Si$ catalysts.

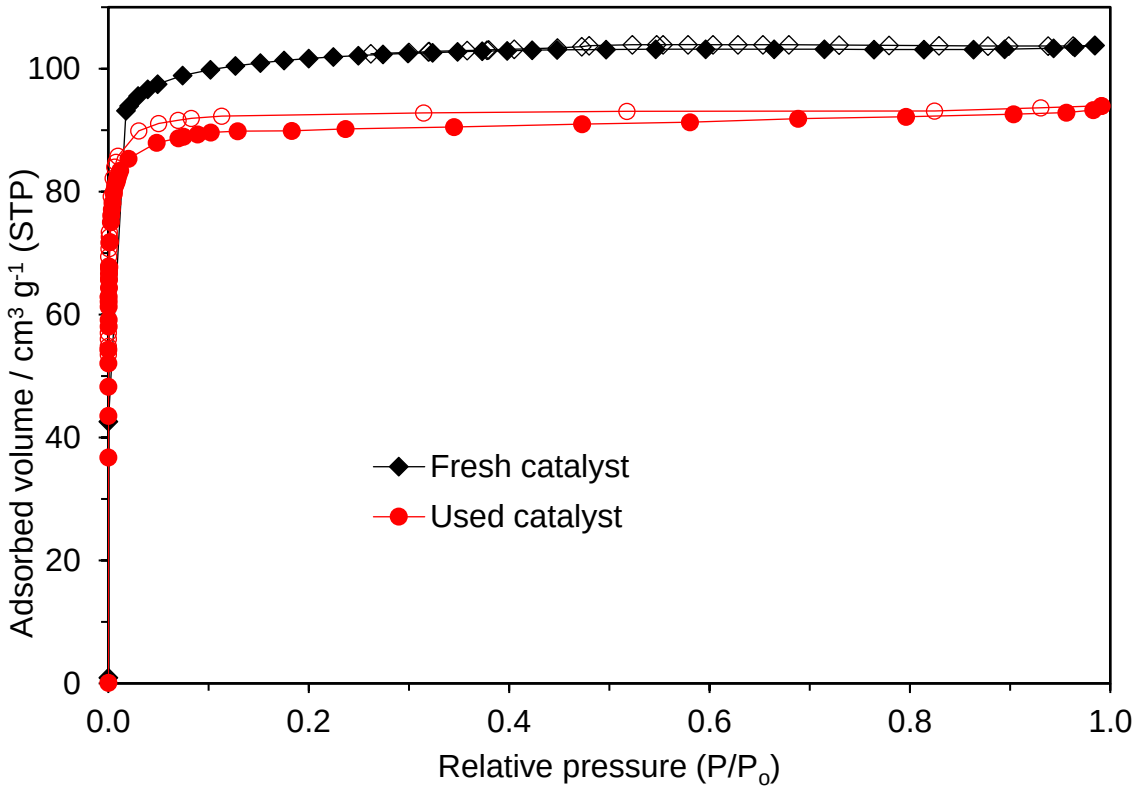

Figure S4. N_2-physisorption isotherms of the fresh and used $Cu_1Ce_{0.7}Si$ catalysts.

Synthesis conditions: 1,1-diphenylethylene (0.3 mmol, 54.0 mg), KI (20 mol%, 0.06 mmol), DTBP (4 equiv., 1.2 mmol) and $Cu_1Ce_{0.7}Si$ (4.8 mol%, 8.4 mg), tetrahydrofuran (1 mL) at 120 °C in 25 h, n-hexane:ethyl acetate = 20:1 for column chromatography, silica gel 60 F254, R_f = 0.32 for TLC, yielding a clear liquid product (56.3 mg, 75%).

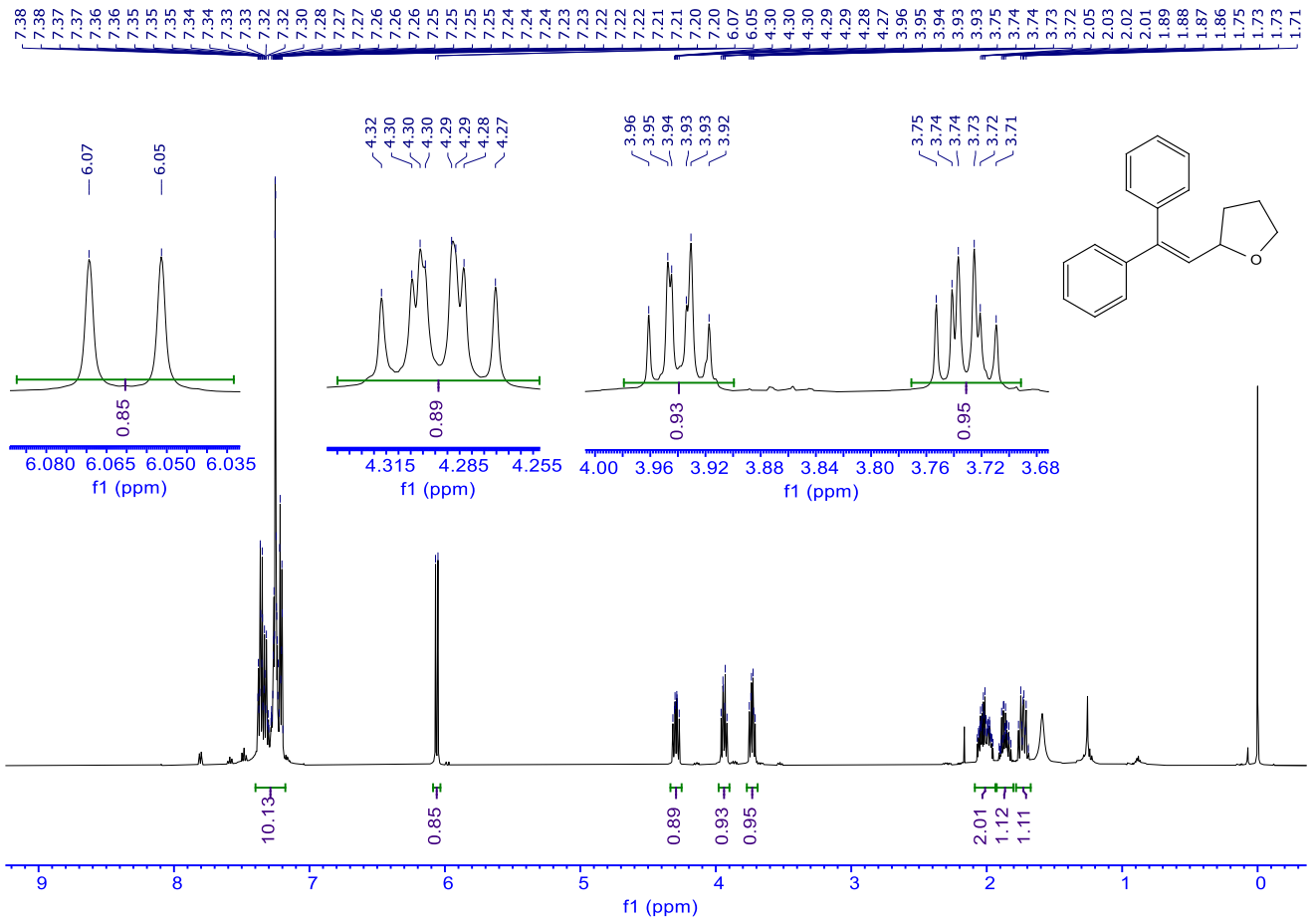

Figure S5. ^{1}H-NMR spectrum of 2-(2,2-diphenylvinyl)-tetrahydrofuran.

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 7.40 – 7.18 (m, 10H), 6.06 (d, 1H), 4.29 (ddd, 1H), 3.94 (dt, 1H), 3.73 (td, 1H), 2.09 – 1.94 (m, 2H), 1.93 – 1.80 (m, 1H), 1.78 – 1.68 (m, 1H).

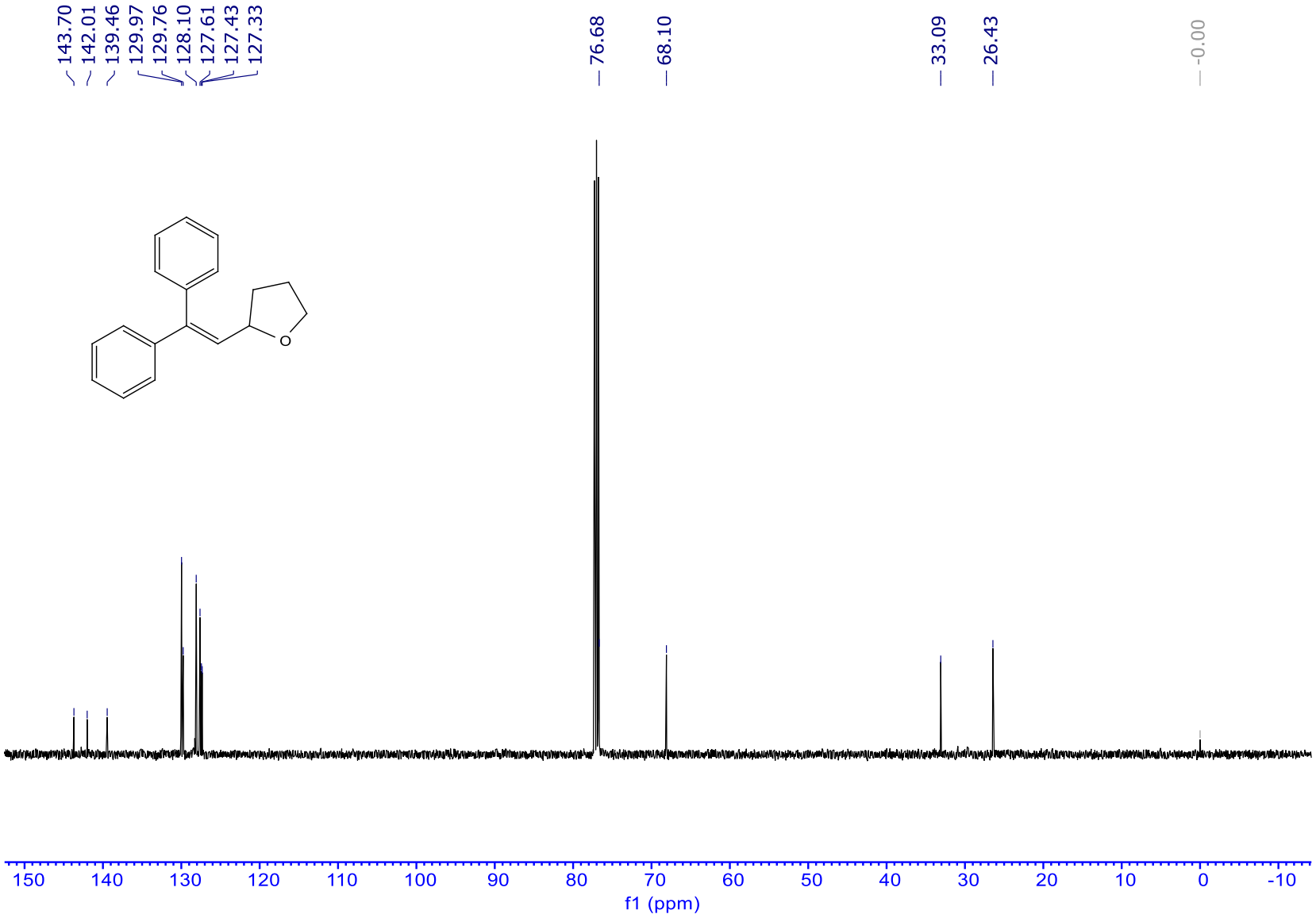

Figure S6. ^{13}C-NMR spectrum of 2-(2,2-diphenylvinyl)-tetrahydrofuran.

^{13}C-NMR (126 MHz, $CDCl_3$) δ (ppm) 143.70, 142.01, 139.46, 129.97, 129.76, 128.10, 127.61, 127.43, 127.33, 76.68, 68.10, 33.09, 26.43.

Synthesis conditions: 1,1-diphenylethylene (0.3 mmol, 54.0 mg), KI (20 mol%, 0.06 mmol), DTBP (4 equiv., 1.2 mmol) and $Cu_1Ce_{0.7}Si$ (4.8 mol%, 8.4 mg), 1,4-dioxane (1 mL) at 120 °C in 25 h, n-hexane:ethyl acetate = 15:1 for column chromatography, silica gel 60 F254, R_f = 0.38 for TLC, yielding a pale yellow solid product (55.9 mg, 70%).

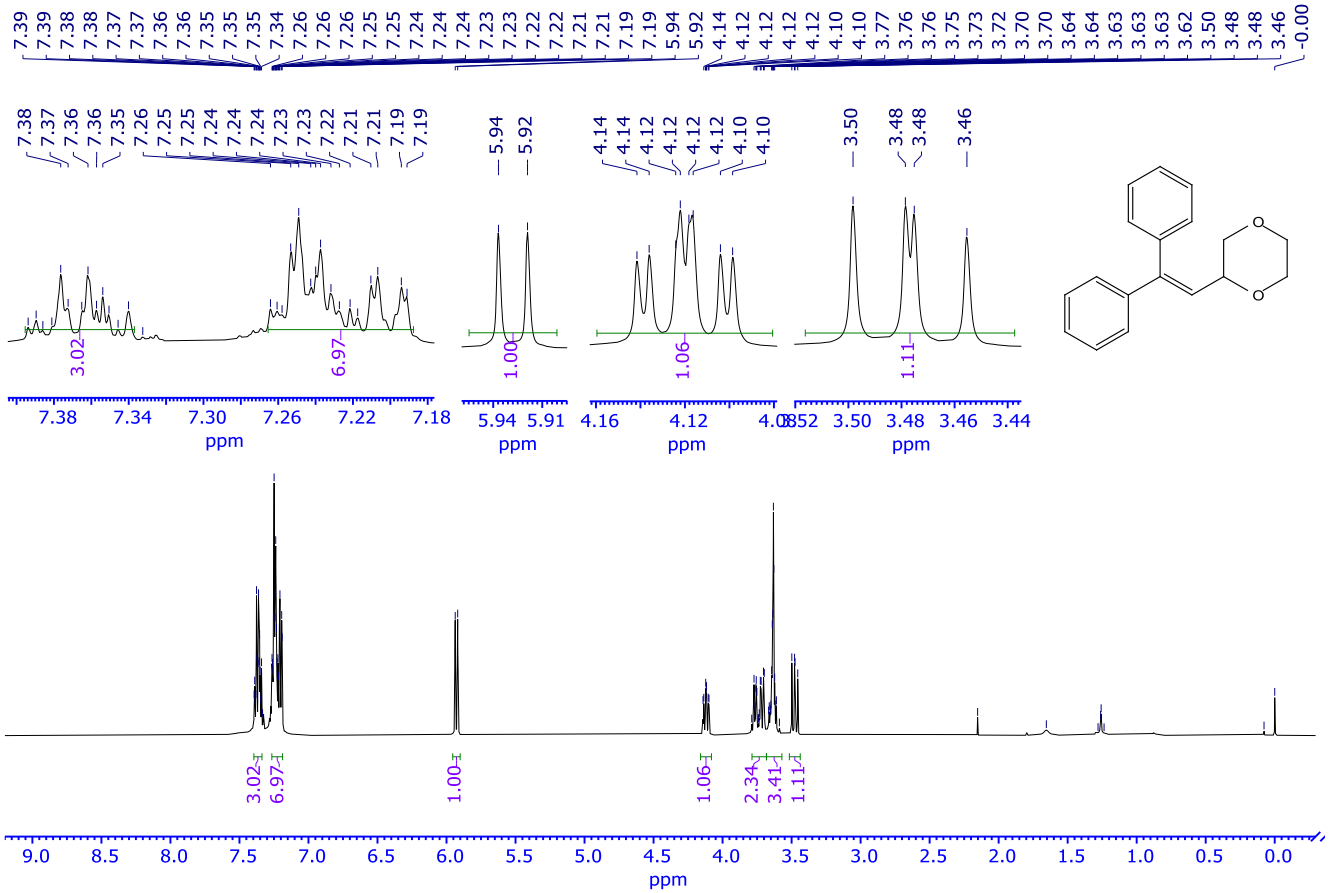

Figure S7. ^{1}H-NMR spectrum of 2-(2,2-diphenylvinyl)-1,4-dioxane.

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 7.43 (s, 1H), 7.44 – 7.31 (m, 3H), 7.31 – 7.22 (m, 4H), 7.22 (dd, 1H), 7.22 – 7.17 (m, 2H), 5.93 (d, 1H), 4.12 (ddd, 1H), 3.80 (s, 1H), 3.79 – 3.68 (m, 2H), 3.70 – 3.57 (m, 3H), 3.48 (dd, 1H).

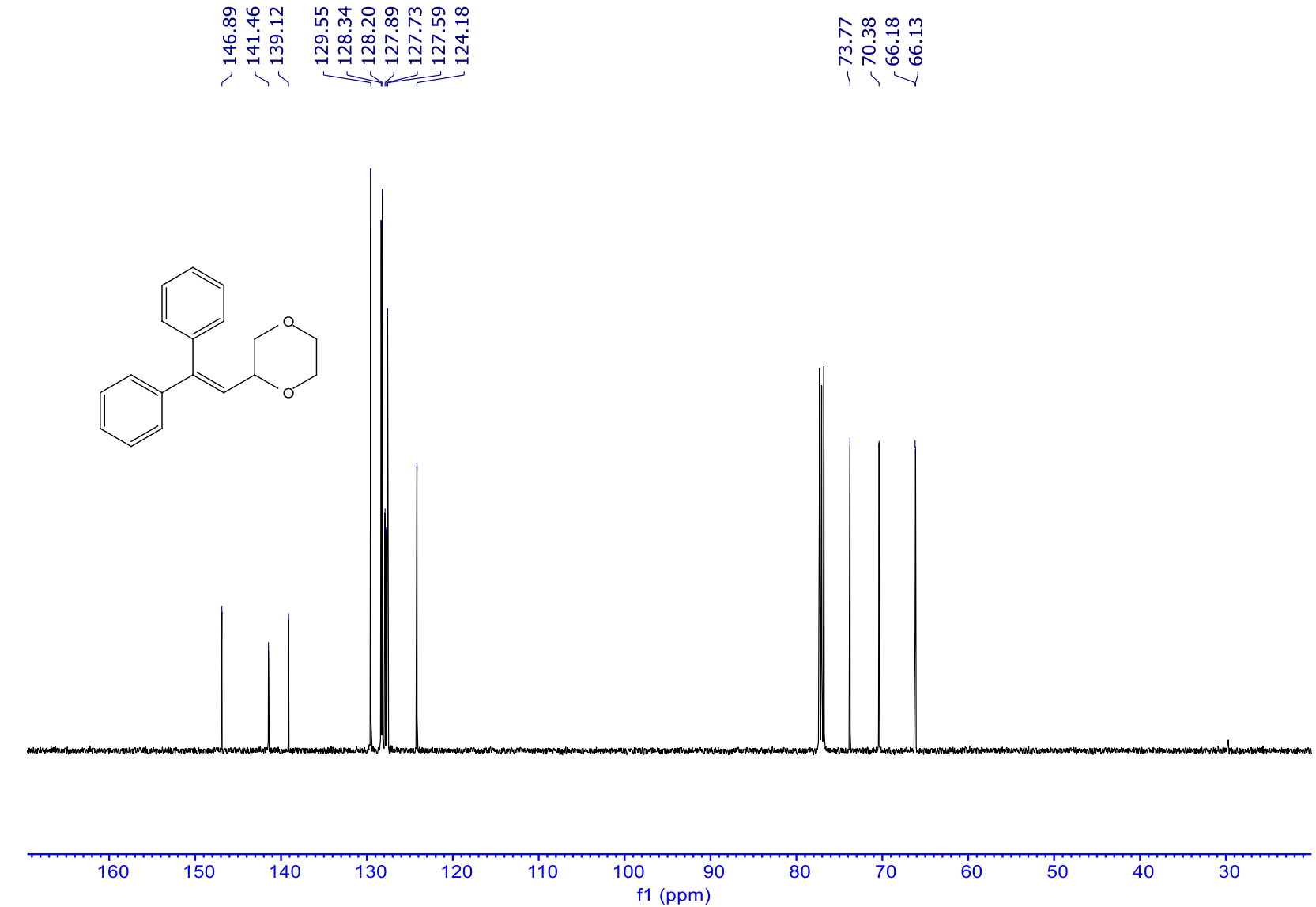

Figure S8. ^{13}C-NMR spectrum of 2-(2,2-diphenylvinyl)-1,4-dioxane.

^{13}C-NMR (126 MHz, $CDCl_3$) δ (ppm) 146.89, 141.46, 139.12, 129.55, 128.34, 128.20, 127.89, 127.73, 127.59, 124.18, 73.77, 70.38, 66.18, 66.13.

Synthesis conditions: 1,1-diphenylethylene (0.3 mmol, 54.0 mg), KI (20 mol%, 0.06 mmol), DTBP (4 equiv., 1.2 mmol) and $Cu_1Ce_{0.7}Si$ (4.8 mol%, 8.4 mg), *N*-methyl-2-pyrrolidin (1 mL) at 120 °C in 25 h, n-hexane:ethyl acetate = 7:1 for column chromatography, silica gel 60 F254, R_f = 0.39 for TLC, yielding a pale yellow solid product (54.2 mg, 65%).

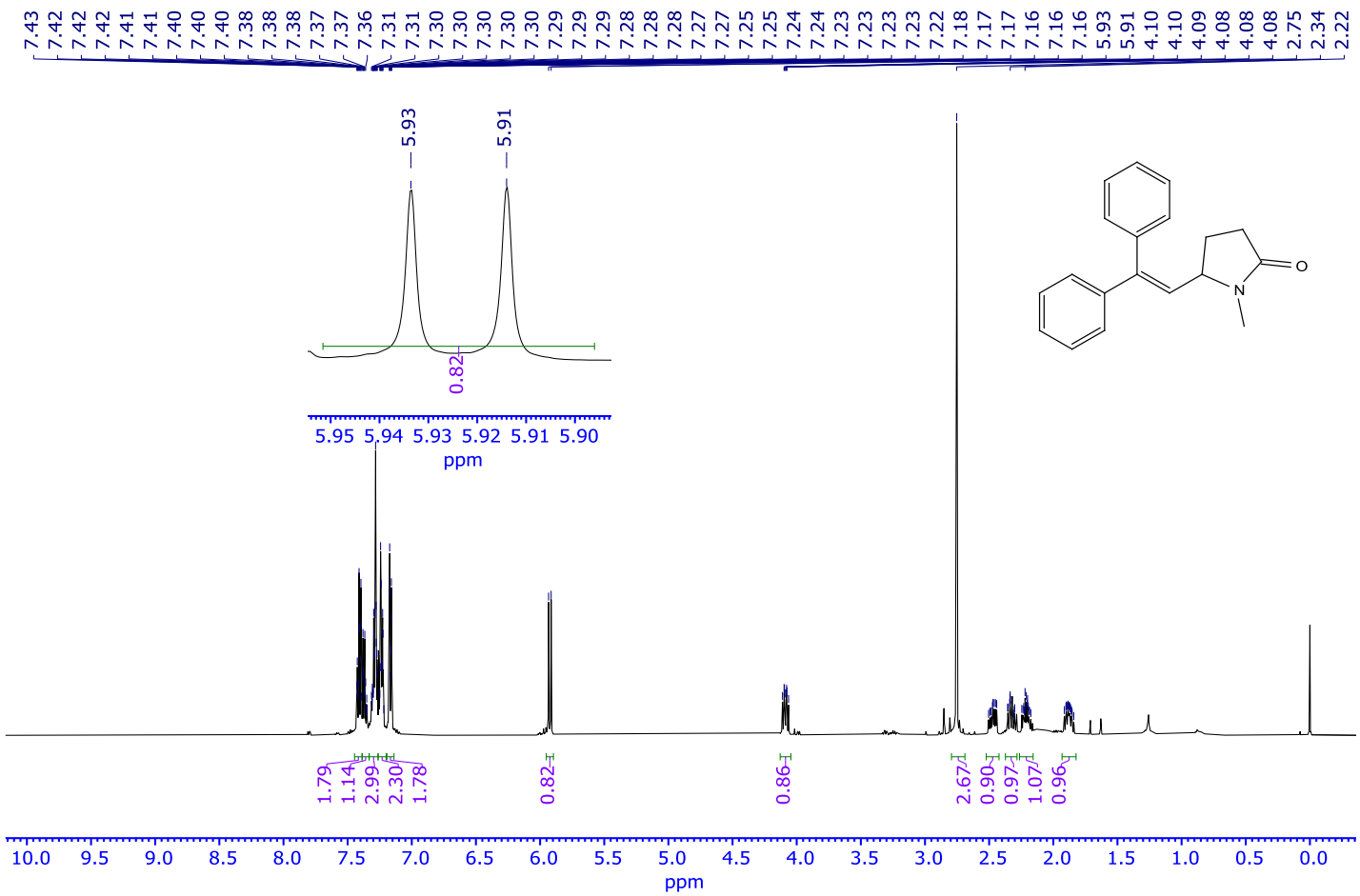

Figure S9. ^{1}H-NMR spectrum of 5-(2,2-diphenylvinyl)-1-methylpyrrolidin-2-one.

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 7.45 – 7.39 (m, 2H), 7.39 – 7.33 (m, 1H), 7.33 – 7.26 (m, 3H), 7.26 – 7.20 (m, 2H), 7.19 – 7.14 (m, 2H), 5.92 (d, 1H), 4.09 (ddd, 1H), 2.75 (s, 3H), 2.47 (m, 1H), 2.37 – 2.28 (m, 1H), 2.21 (m, 1H), 1.88 (m, 1H).

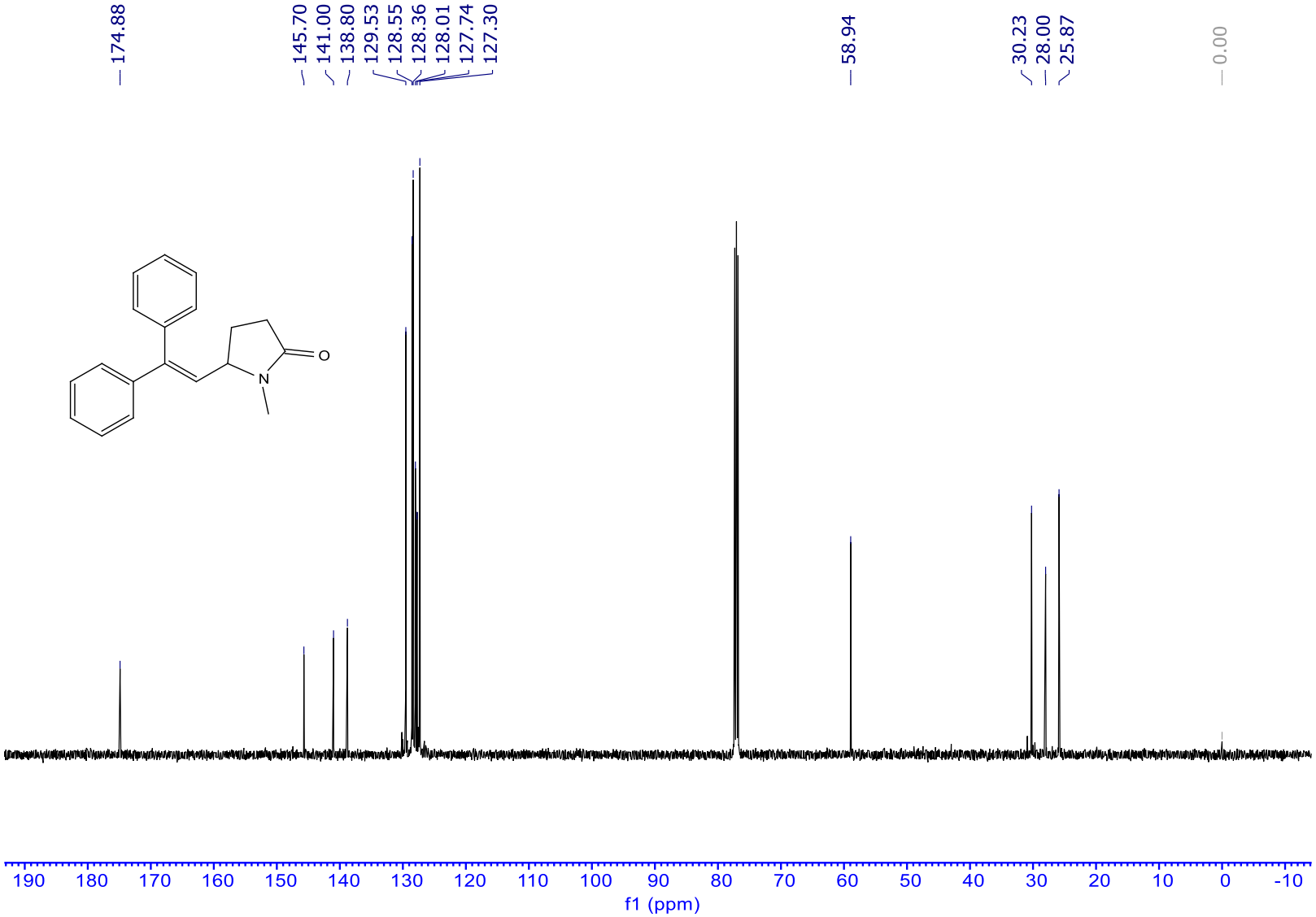

Figure S10. ^{13}C-NMR spectrum of 5-(2,2-diphenylvinyl)-1-methylpyrrolidin-2-one.

^{13}C-NMR (126 MHz, $CDCl_3$) δ (ppm) 174.88, 145.70, 141.00, 138.80, 129.53, 128.55, 128.36, 128.01, 127.74, 127.30, 58.94, 30.23, 28.00, 25.87.

Synthesis conditions: 1,1-diphenylethylene (0.3 mmol, 54.0 mg), KI (20 mol%, 0.06 mmol), DTBP (4 equiv.,1.2 mmol) and $Cu_1Ce_{0.7}Si$ (4.8 mol%, 8.4 mg), dimethylacetamide (1 mL) at 120 °C in 25 h, n-hexane:ethyl acetate = 1:1 for column chromatography, silica gel 60 F254, R_f = 0.30 for TLC, yielding a pale yellow solid product (25.25 mg, 30%).

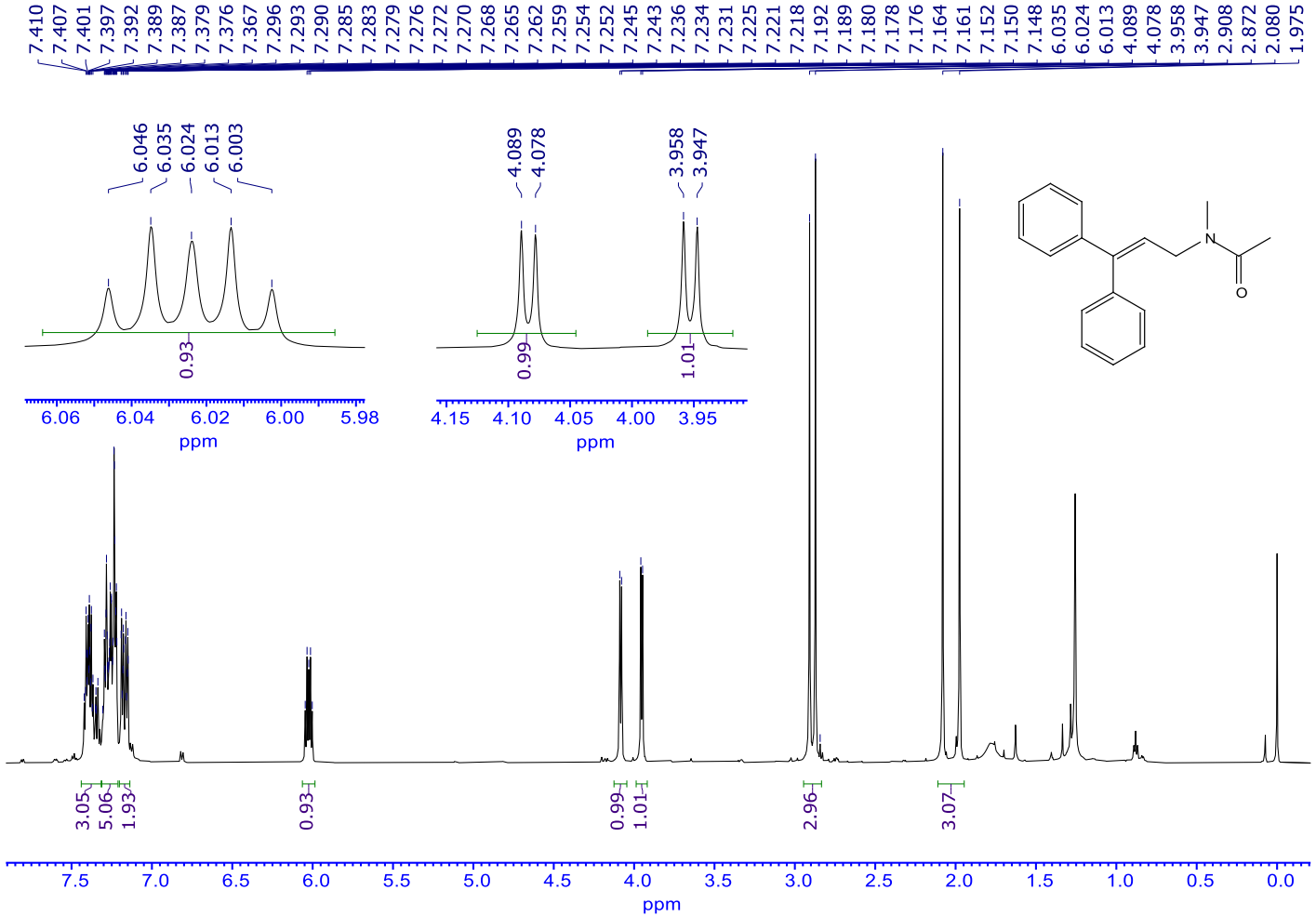

Figure S11. ^{1}H-NMR spectrum of *N*-(3,3-diphenylallyl)-*N*-methylacetamide.

^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 7.44 – 7.32 (m, 3H), 7.31 – 7.21 (m, 5H), 7.20 – 7.14 (m, 2H), 6.02 (dt, 1H), 4.08 (d, 1H), 3.95 (d, 1H), 2.95 – 2.83 (m, 3H), 2.11 – 1.95 (m, 3H).

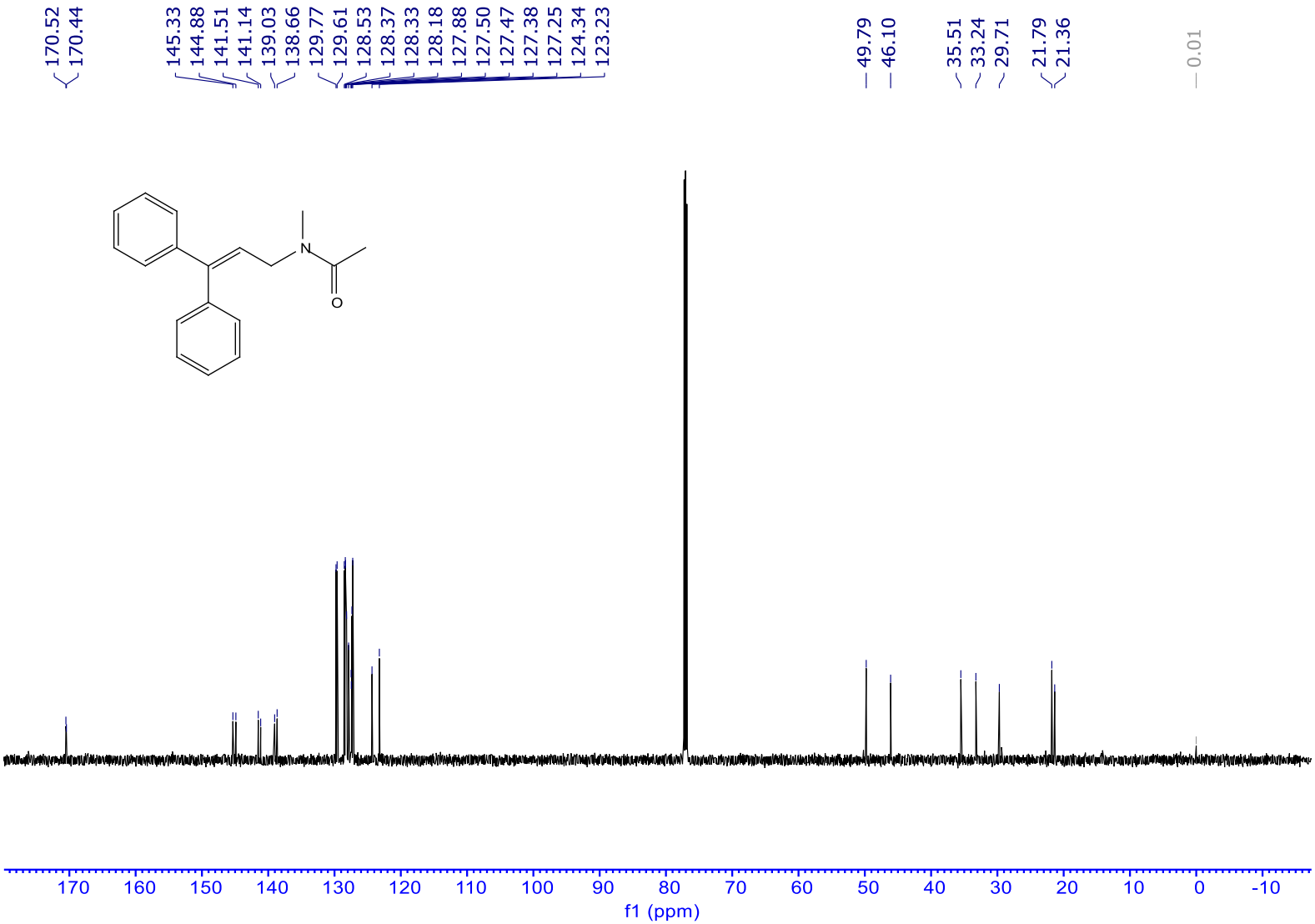

Figure S12. ^{13}C-NMR spectrum of *N*-(3,3-diphenylallyl)-*N*-methylacetamide.

^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 170.52, 170.44, 145.33, 144.88, 141.51, 141.14, 139.03, 138.66, 129.77, 129.61, 128.53, 128.37, 128.33, 128.18, 127.88, 127.50, 127.47, 127.38, 127.25, 124.34, 123.23, 49.79, 46.10, 35.51, 33.24, 29.71, 21.79, 21.36.

Synthesis conditions: coumarin (0.3 mmol, 43.8 mg), KI (20 mol%, 0.06 mmol), DTBP (4 equiv., 1.2 mmol) and $Cu_1Ce_{0.7}Si$ (4.8 mol%, 8.4 mg), tetrahydrofuran (1 mL) at 120 °C in 25 h, n-hexane:ethyl acetate = 5:1 for column chromatography, silica gel 60 F254, R_f = 0.34 for TLC, yielding a white solid product (18.3 mg, 28%).

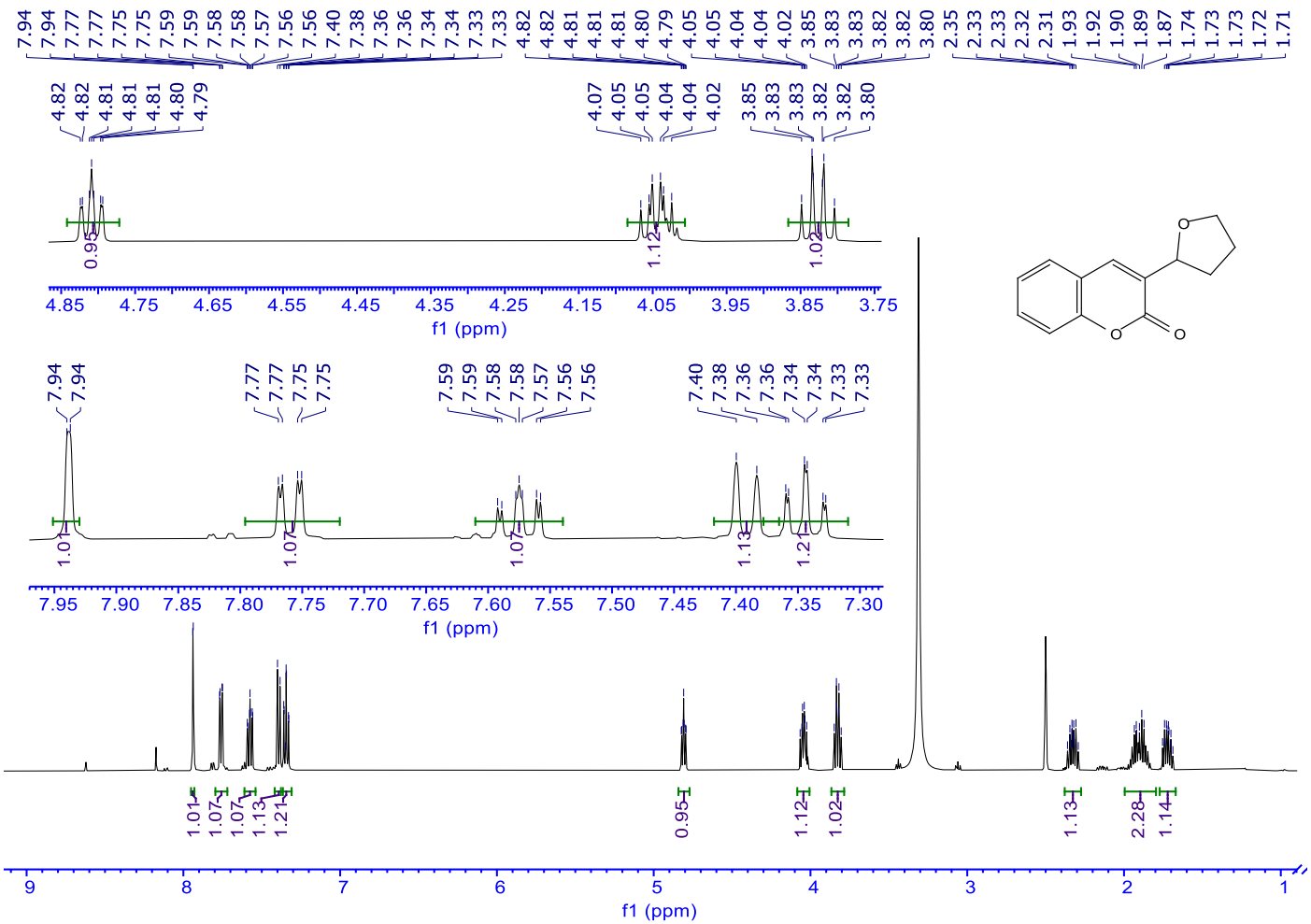

Figure S13. ^{1}H-NMR spectrum of 3-(tetrahydrofuran-2-yl)-2H-chromen-2-one.

^{1}H-NMR (500 MHz, DMSO-d_6) δ (ppm) 7.94 (d, 1H), 7.76 (dd, 1H), 7.57 (ddd, 1H), 7.39 (d, 1H), 7.34 (td, 1H), 4.81 (ddd, 1H), 4.05 (td, 1H), 3.83 (dt, 1H), 2.38 – 2.27 (m, 1H), 2.00 – 1.80 (m, 2H), 1.72 (m, 1H).

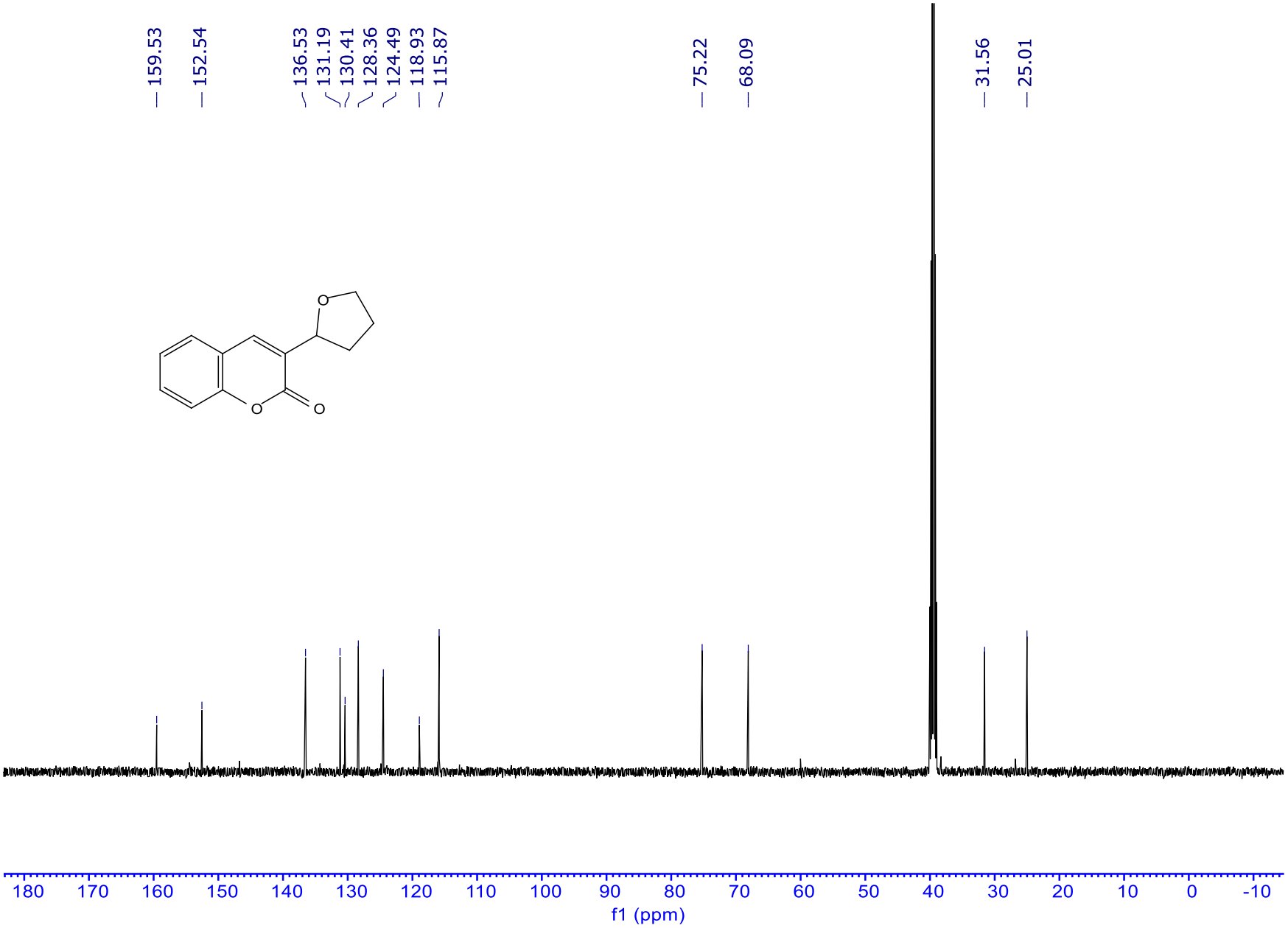

Figure S14. ^{13}C-NMR spectrum of 3-(tetrahydrofuran-2-yl)-2H-chromen-2-one.

^{13}C-NMR (126 MHz, DMSO-d_6) δ (ppm) 159.53, 152.54, 136.53, 131.19, 130.41, 128.36, 124.49, 118.93, 115.87, 75.22, 68.09, 31.56, 25.01.

Synthesis conditions: coumarin (0.3 mmol, 43.8 mg), KI (20 mol%, 0.06 mmol), DTBP (4 equiv., 1.2 mmol) and $Cu_1Ce_{0.7}Si$ (4.8 mol%, 8.4 mg), dimethylacetamide (1 mL) at 120 °C in 25 h, n-hexane:ethyl acetate = 1:15 for column chromatography, silica gel 60 F254, R_f = 0.28 for TLC, yielding a pale yellow solid product (40.95 mg, 58%).

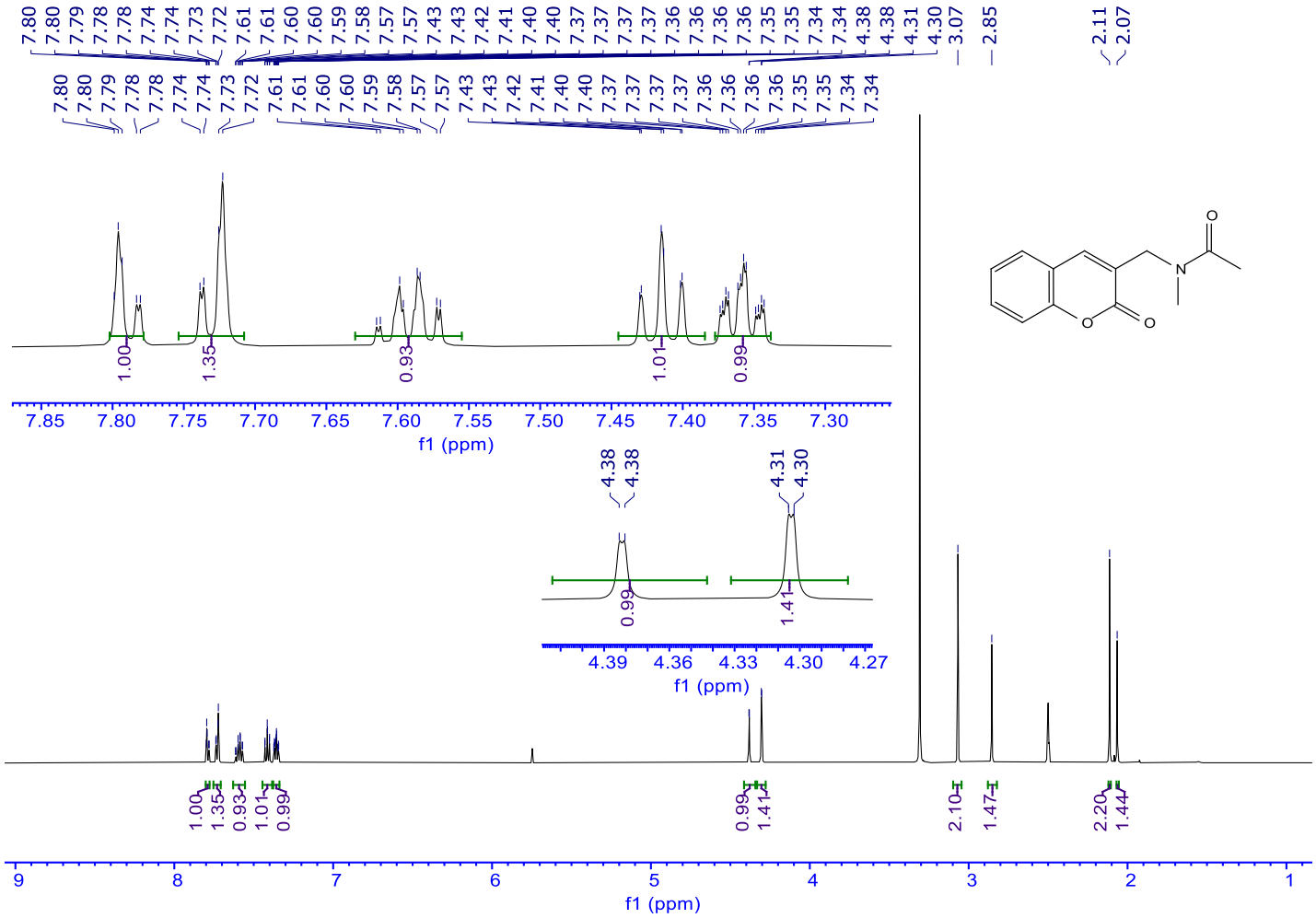

Figure S15. ^{1}H-NMR spectrum of *N*-methyl-*N*-((2-oxo-2H-chromen-3-yl)methyl)acetamide.

^{1}H-NMR (600 MHz, DMSO-d_6) δ (ppm) 7.80 – 7.78 (m, 1H), 7.74 – 7.71 (m, 1H), 7.63 – 7.55 (m, 1H), 7.45 – 7.38 (m, 1H), 7.38 – 7.34 (m, 1H), 4.38 (d, 1H), 4.30 (d, 1H), 3.07 (s, 2H), 2.85 (s, 1H), 2.11 (s, 2H), 2.07 (s, 1H).

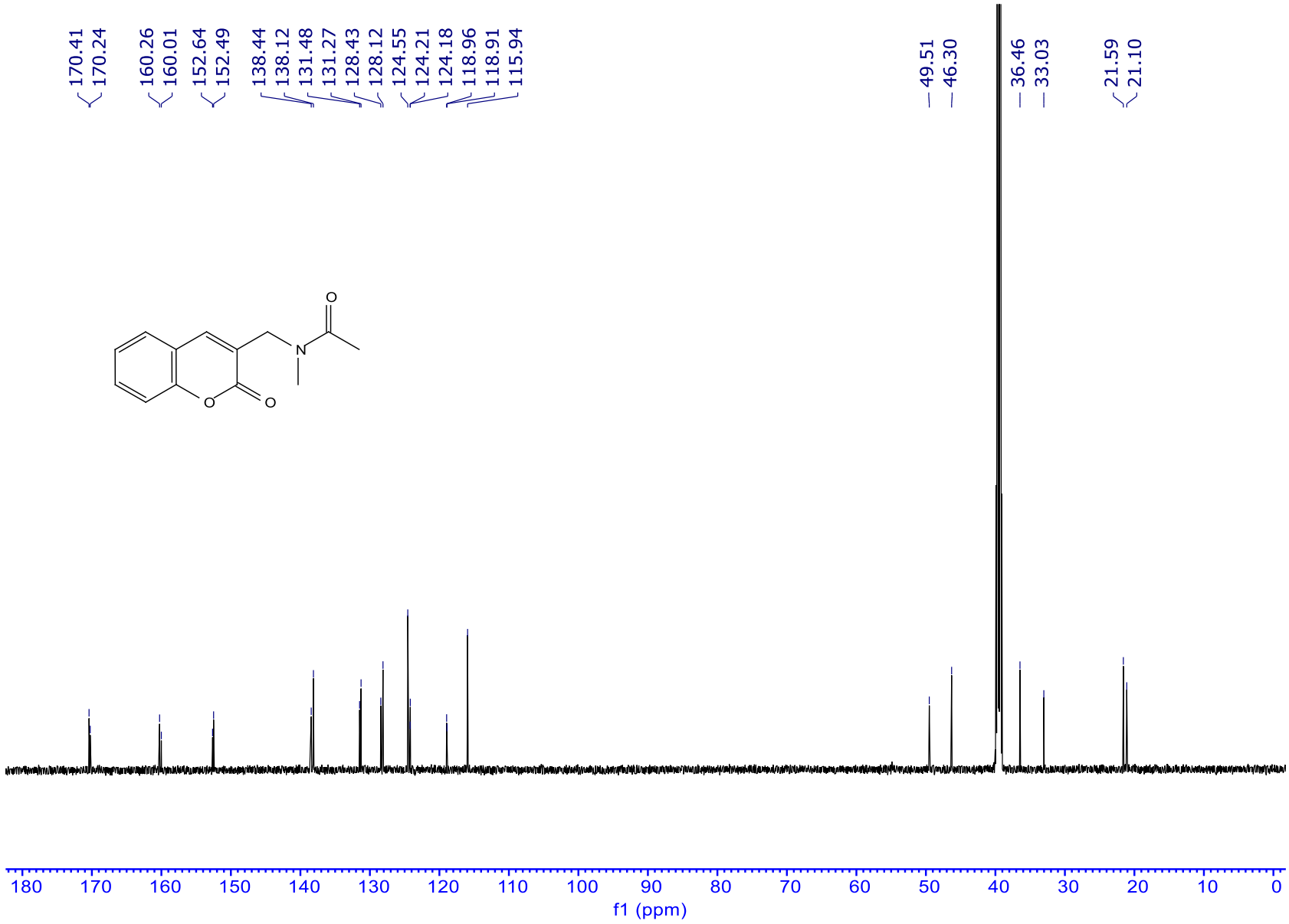

Figure S16. ^{13}C-NMR spectrum of *N*-methyl-*N*-((2-oxo-2H-chromen-3-yl)methyl)acetamide.

^{13}C-NMR (151 MHz, DMSO-d_6) δ (ppm) 170.41, 170.24, 160.26, 160.01, 152.64, 152.49, 138.44, 138.12, 131.48, 131.27, 128.43, 128.12, 124.55, 124.21, 124.18, 118.96, 118.91, 115.94, 49.51, 46.30, 36.46, 33.03, 21.59, 21.10.

Synthesis conditions: 7-methoxy-4-methylcoumarin (0.3 mmol, 57 mg), KI (20 mol%, 0.06 mmol), DTBP (4 equiv., 1.2 mmol) and $Cu_1Ce_{0.7}Si$ (4.8 mol%, 8.4 mg), tetrahydrofuran (1 mL) at 120 °C in 25 h, n-hexane:ethyl acetate = 2:1 for column chromatography, silica gel 60 F254, R_f = 0.35 for TLC, yielding a yellow solid product (44.45 mg, 57%).

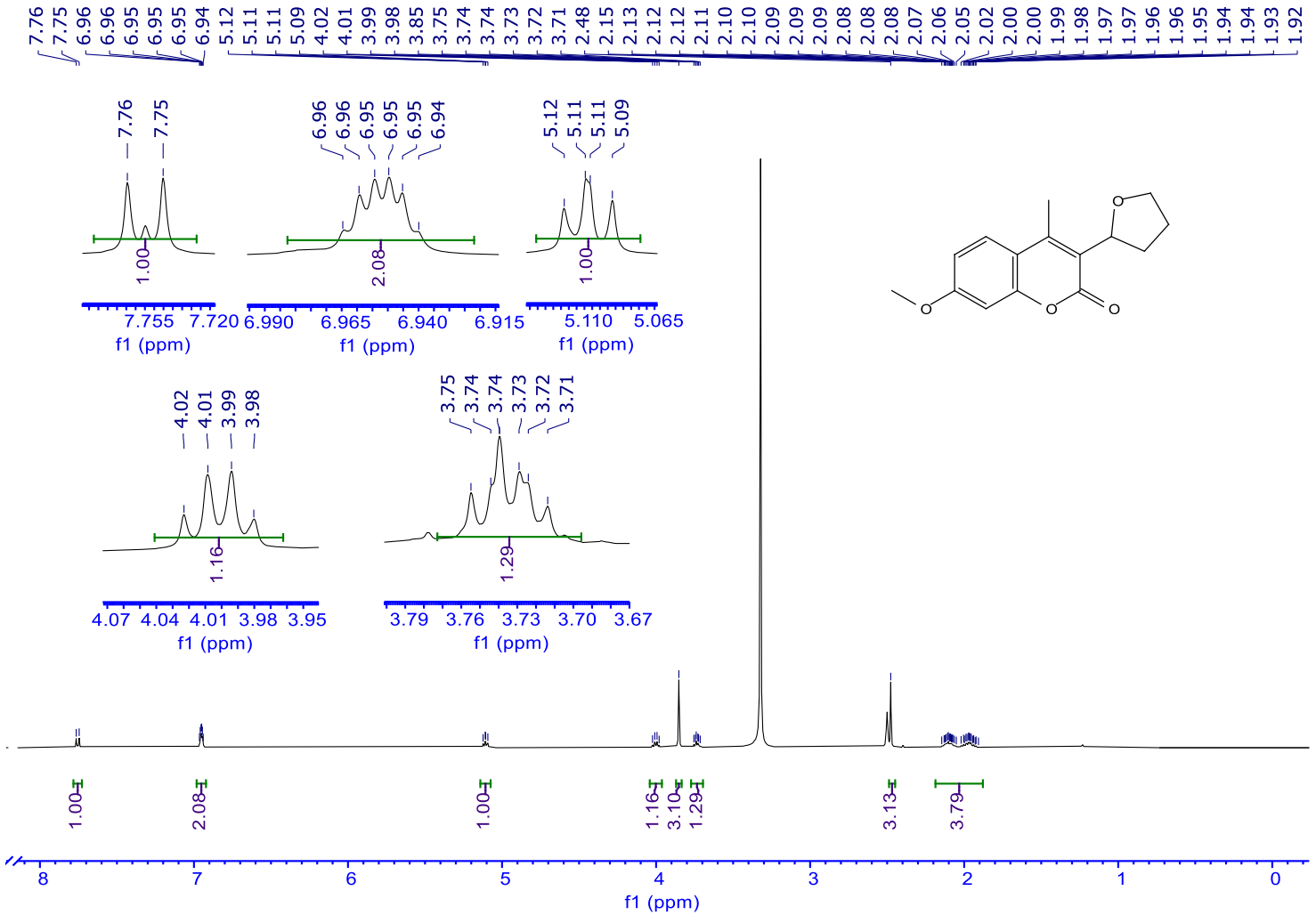

Figure S17.[1]H-NMR spectrum of 7-methoxy-4-methyl-3-(tetrahydrofuran-2-yl)-2H-chromen-2-one.

[1]H-NMR (500 MHz, DMSO-d_6) δ (ppm) 7.75 (m, 1H), 6.95 (m, 2H), 5.11 (dd, 1H), 4.00 (q, 1H), 3.85 (s, 3H), 3.73 (td, 1H), 2.48 (s, 3H), 2.19 – 1.88 (m, 4H).

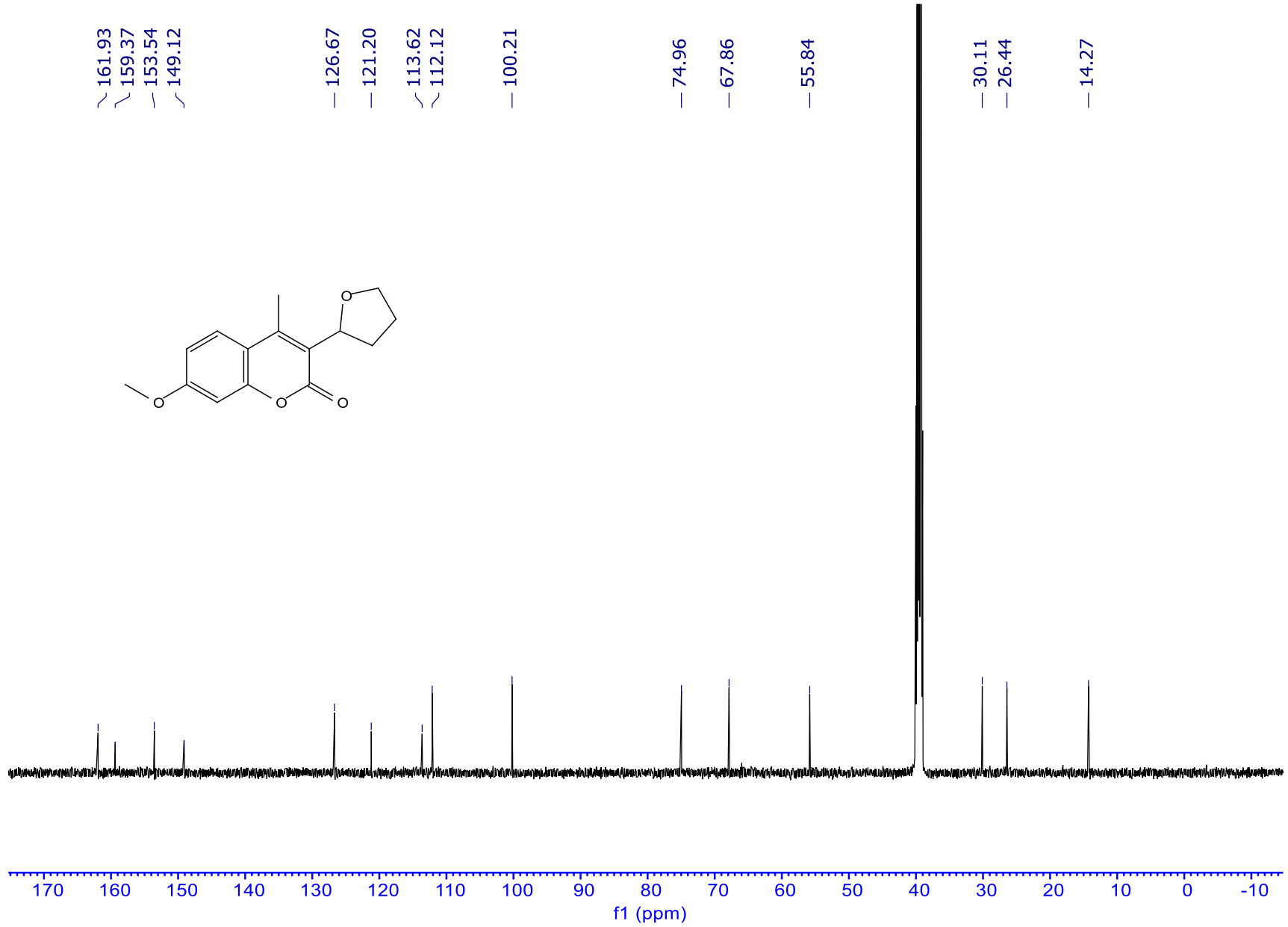

Figure S18. ^{13}C-NMR spectrum of 7-methoxy-4-methyl-3-(tetrahydrofuran-2-yl)-2H-chromen-2-one.

^{13}C-NMR (126 MHz, DMSO-d_6) δ (ppm) 161.93, 159.37, 153.54, 149.12, 126.67, 121.20, 113.62, 112.12, 100.21, 74.96, 67.86, 55.84, 30.11, 26.44, 14.27.

Synthesis conditions: 7-methoxy-4-methylcoumarin (0.3 mmol, 57 mg), KI (20 mol%, 0.06 mmol), DTBP (4 equiv., 1.2 mmol) and $Cu_1Ce_{0.7}Si$ (4.8 mol%, 8.4 mg), 1,4-dioxane (1 mL) at 120 °C in 25 h, n-hexane:ethyl acetate = 3:2 for column chromatography, silica gel 60 F254, R_f = 0.33 for TLC, yielding a white solid product (27.4 mg, 32%).

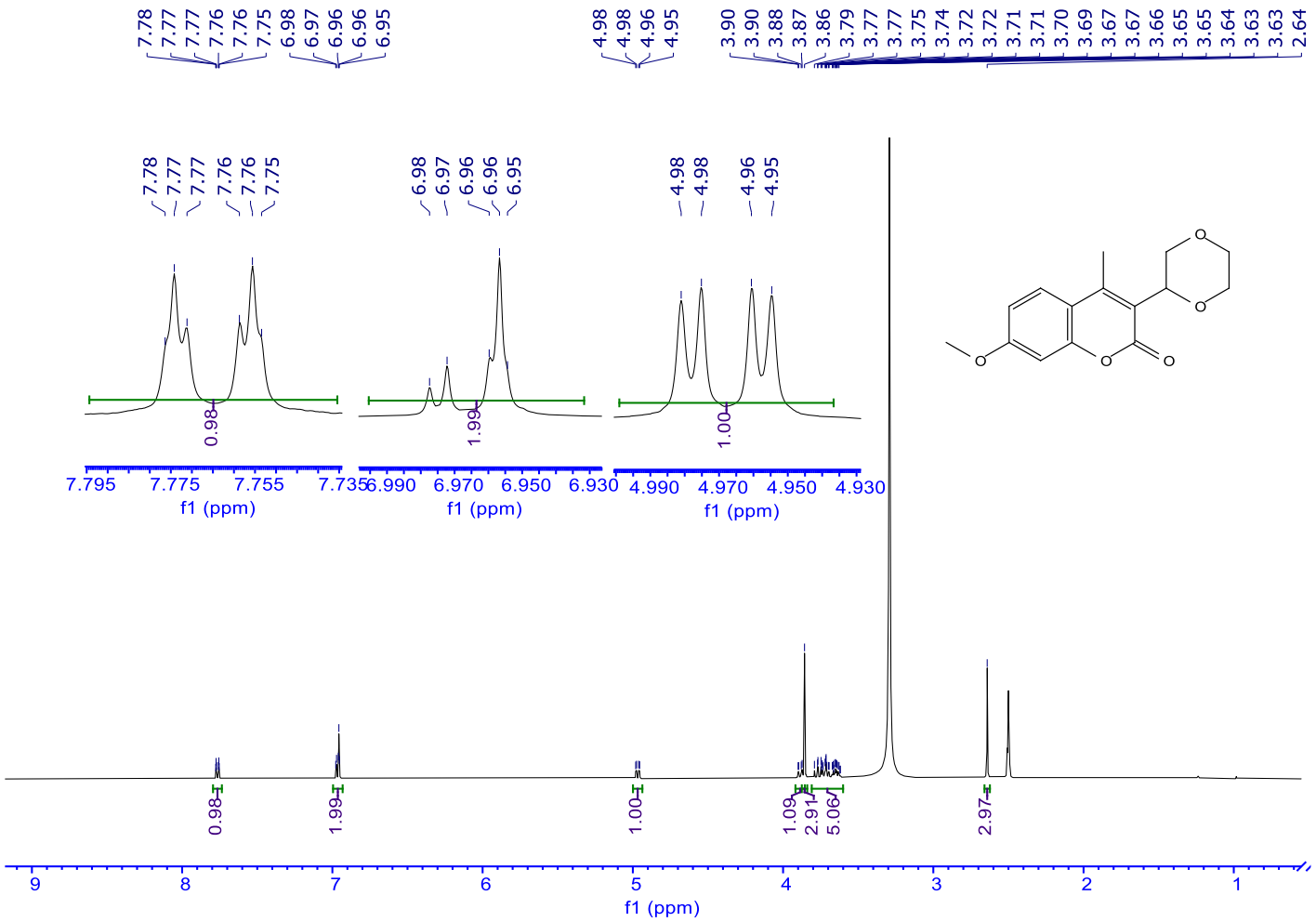

Figure S19. ^{1}H-NMR spectrum of 3-(1,4-dioxan-2-yl)-7-methoxy-4-methyl-2H-chromen-2-one.

^{1}H-NMR (500 MHz, DMSO-d_6) δ (ppm) 7.79 – 7.74 (m, 1H), 7.00 – 6.93 (m, 2H), 4.97 (dd, 1H), 3.89 (dd, 1H), 3.86 (s, 3H), 3.81 – 3.60 (m, 5H), 2.64 (s, 3H).

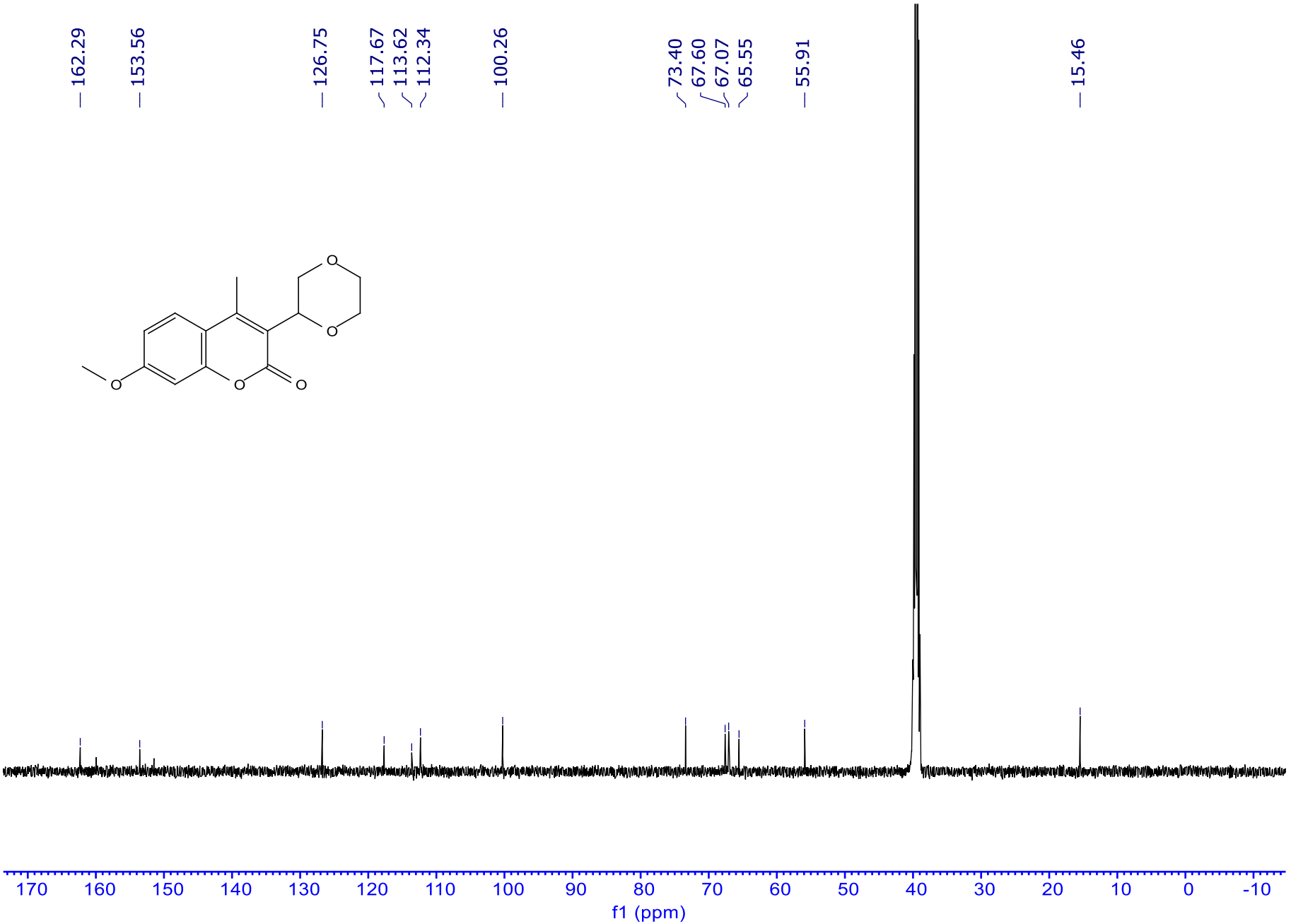

Figure S20. ^{13}C-NMR spectrum of 3-(1,4-dioxan-2-yl)-7-methoxy-4-methyl-2H-chromen-2-one.

^{13}C-NMR (126 MHz, DMSO-d_6) δ (ppm) 162.29, 153.56, 126.75, 117.67, 113.62, 112.34, 100.26, 73.40, 67.60, 67.07, 65.55, 55.91, 15.46.

Synthesis conditions: 7-methoxy-4-methylcoumarin (0.3 mmol, 57 mg), KI (20 mol%, 0.06 mmol), DTBP (4 equiv., 1.2 mmol) and $Cu_1Ce_{0.7}Si$ (4.8 mol%, 8.4 mg), dimethylacetamide (1 mL) at 120 °C in 25 h, dichloromethane:methanol = 100:3 for column chromatography, silica gel 60 F254, R_f = 0.38 for TLC, yielding a pale yellow solid product (34.7 mg, 41%).

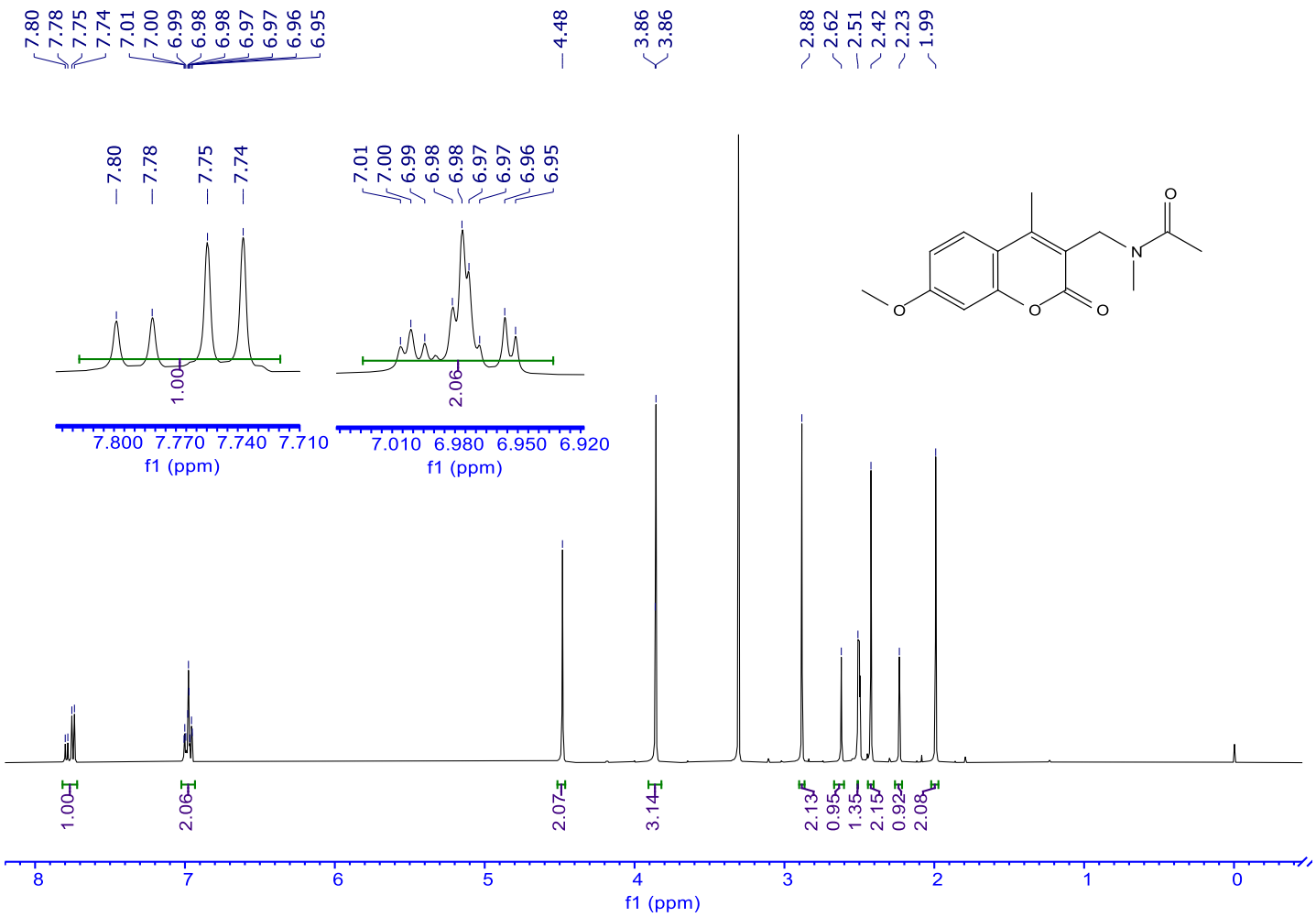

Figure S21. ^{1}H-NMR spectrum of *N*-((7-methoxy-4-methyl-2-oxo-2H-chromen-3-yl)methyl)-*N* methylacetamide.

^{1}H-NMR (500 MHz, DMSO-d_6) δ (ppm) 7.79 – 7.74 (m, 1H), 7.02 – 6.93 (m, 2H), 4.48 (s, 2H), 3.86 (d, 3H), 2.88 – 2.62 (s, 3H), 2.51 – 2.42 (s, 3H), 2.23 – 1.99 (s, 3H).

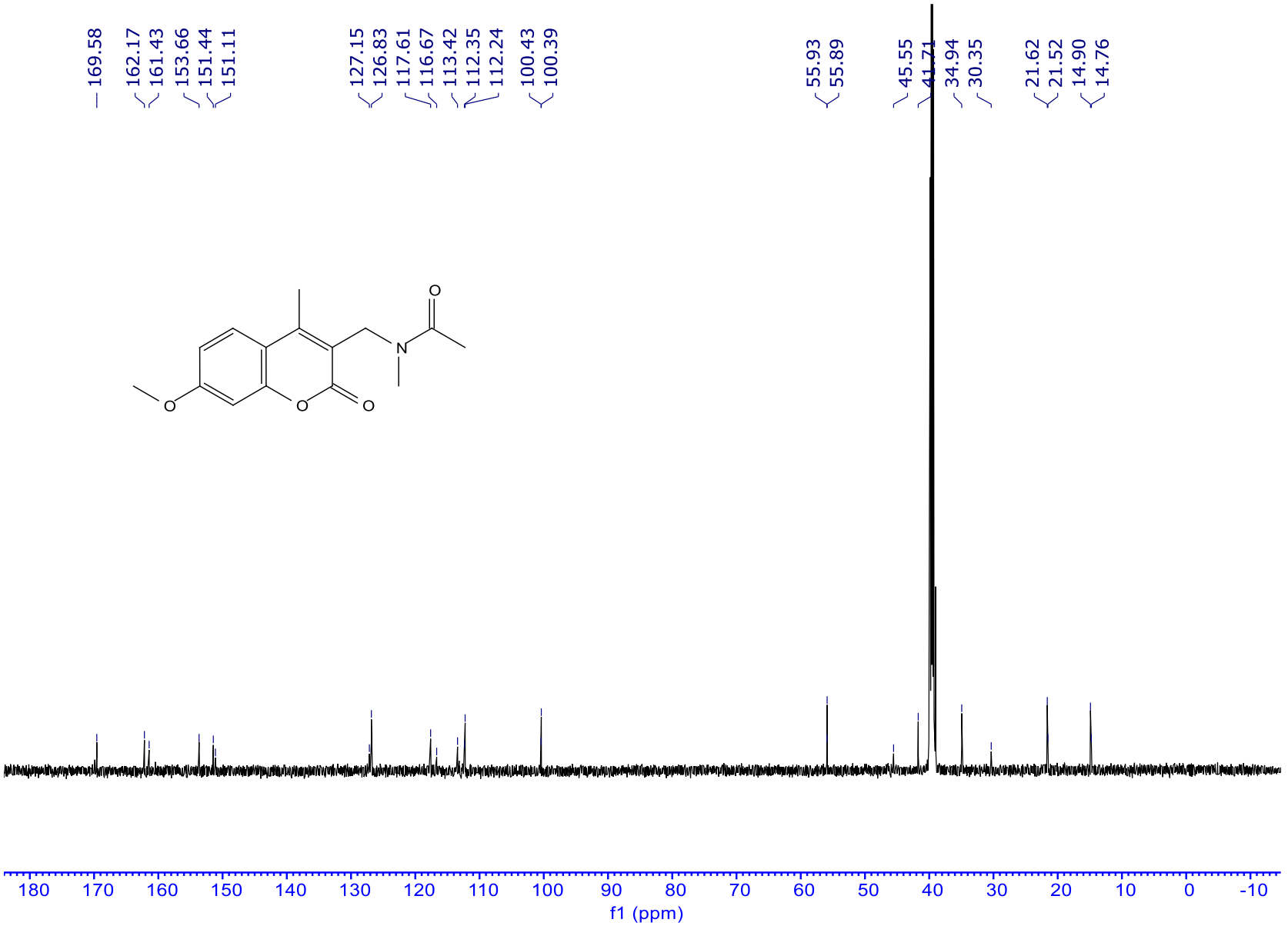

Figure S22. ^{13}C-NMR spectrum of *N*-((7-methoxy-4-methyl-2-oxo-2H-chromen-3-yl)methyl)-*N* methylacetamide

^{13}C-NMR (126 MHz, DMSO-d_6) δ (ppm) 169.58, 162.17, 161.43, 153.66, 151.44, 151.11, 127.15, 126.83, 117.61, 116.67, 113.42, 112.35, 112.24, 100.43, 100.39, 55.93, 55.89, 45.55, 41.71, 34.94, 30.35, 21.62, 21.52, 14.90, 14.76.

Synthesis conditions: 6-hydroxycoumarin (0.3 mmol, 48.6 mg), KI (20 mol%, 0.06 mmol), DTBP (4 equiv., 1.2 mmol) and $Cu_1Ce_{0.7}Si$ (4.8 mol%, 8.4 mg), tetrahydrofuran (1 mL) at 120 °C in 25 h, n-hexane:ethyl acetate = 1:1 for column chromatography, silica gel 60 F254, R_f = 0.42 for TLC, yielding a pale yellow solid product (27 mg, 38%).

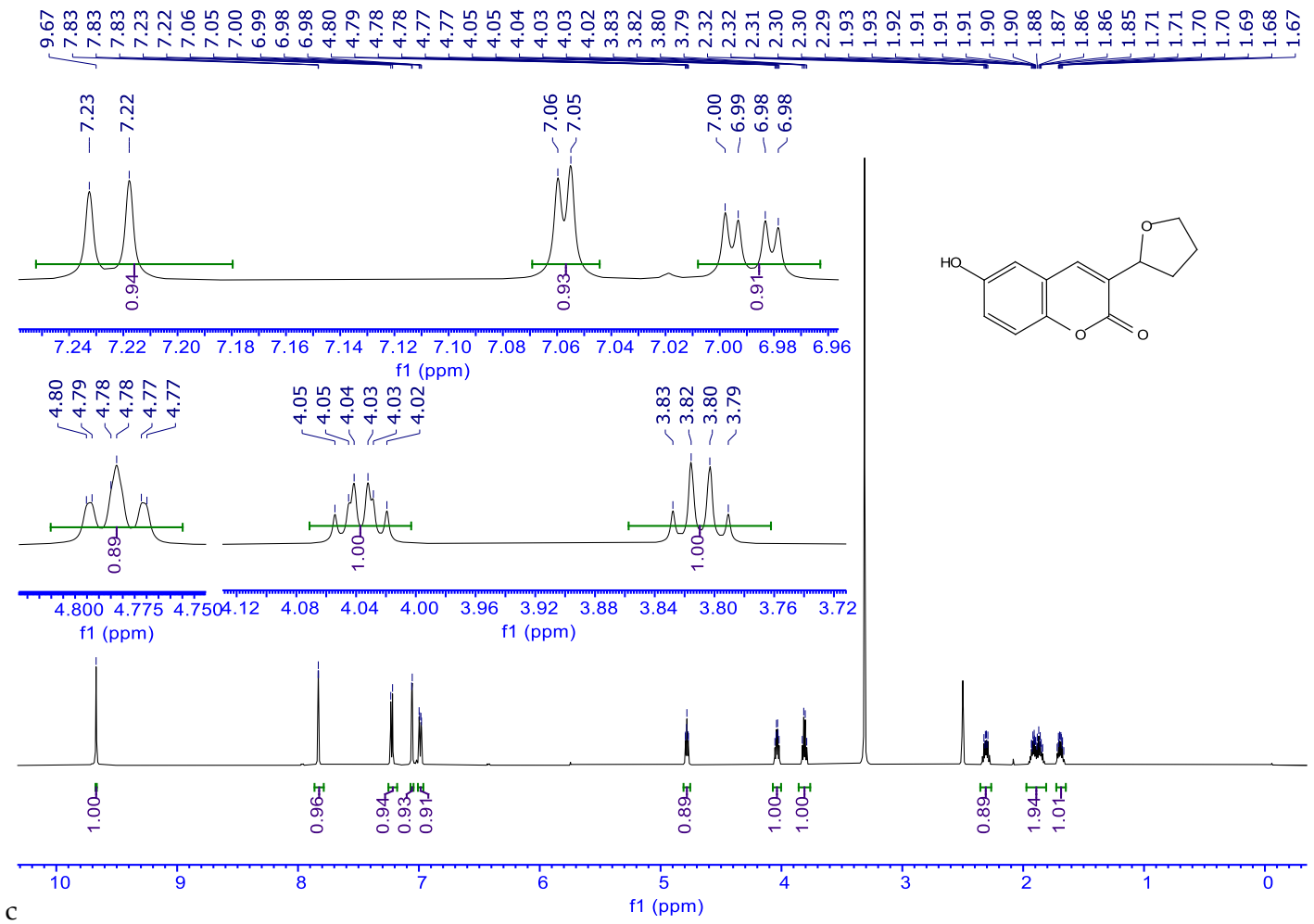

Figure S23. ^{1}H-NMR spectrum of 6-hydroxy-3-(tetrahydrofuran-2-yl)-2H-chromen-2-one.

^{1}H-NMR (600 MHz, DMSO-d_6) δ (ppm) 9.67 (s, 1H), 7.86 – 7.79 (m, 1H), 7.23 (d, 1H), 7.06 (d, 1H), 6.99 (dd, 1H), 4.81 – 4.75 (m, 1H), 4.04 (td, 1H), 3.81 (q, 1H), 2.35 – 2.26 (m, 1H), 1.97 – 1.81 (m, 2H), 1.69 (m, 1H).

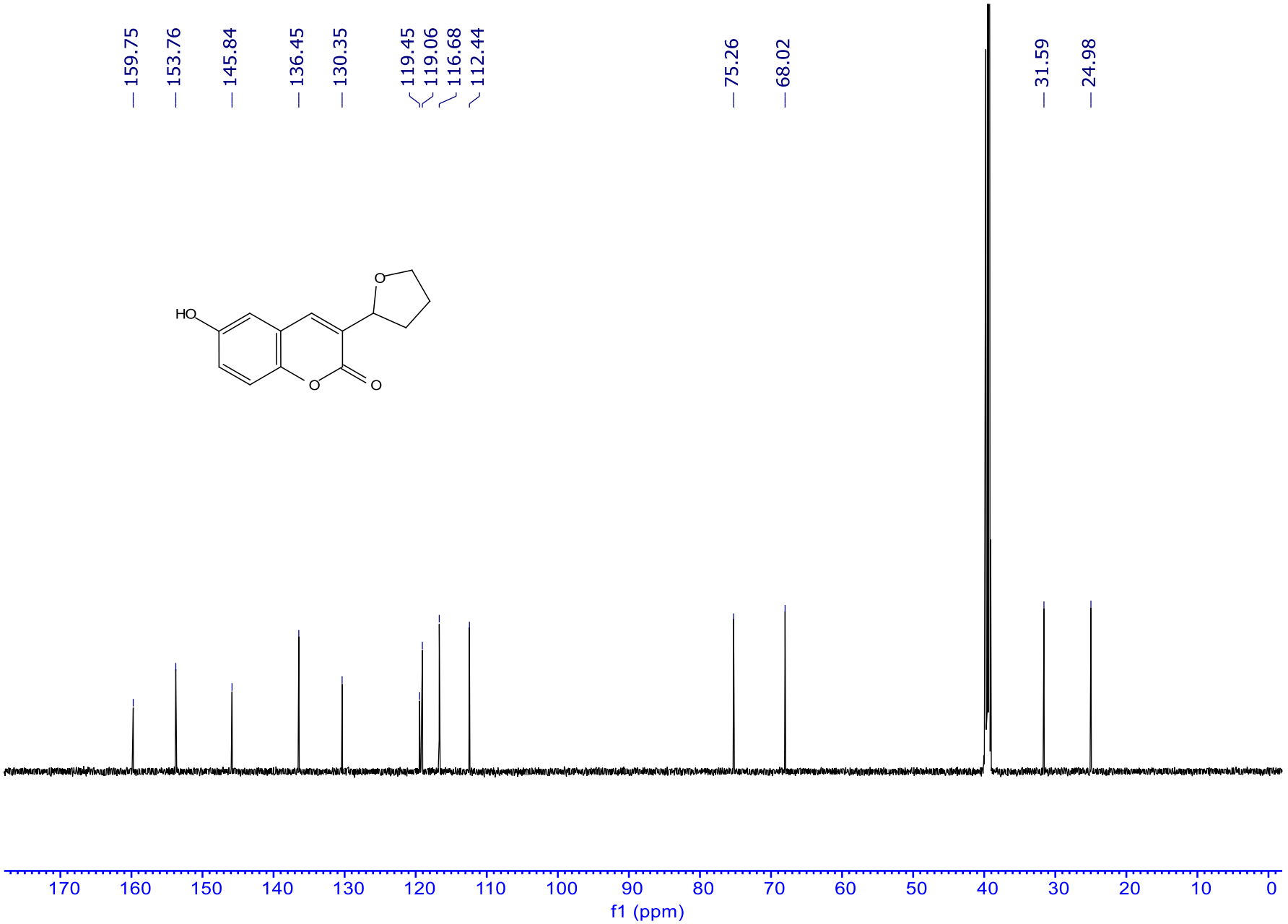

Figure S24. ^{13}C-NMR spectrum of 6-hydroxy-3-(tetrahydrofuran-2-yl)-2H-chromen-2-one.

^{13}C-NMR (151 MHz, DMSO-d_6) δ (ppm) 159.75, 153.76, 145.84, 136.45, 130.35, 119.45, 119.06, 116.68, 112.44, 75.26, 68.02, 31.59, 24.98.

Synthesis conditions: 6-hydroxycoumarin (0.3 mmol, 48.6 mg), KI (20 mol%, 0.06 mmol), DTBP (4 equiv., 1.2 mmol) and $Cu_1Ce_{0.7}Si$ (4.8 mol%, 8.4 mg), 1,4-dioxane (1 mL) at 120 °C in 25 h, dichloromethane:ethyl acetate = 10:1 for column chromatography, silica gel 60 F254, R_f = 0.28 for TLC, yielding a pale yellow solid product (27.6 mg, 37%).

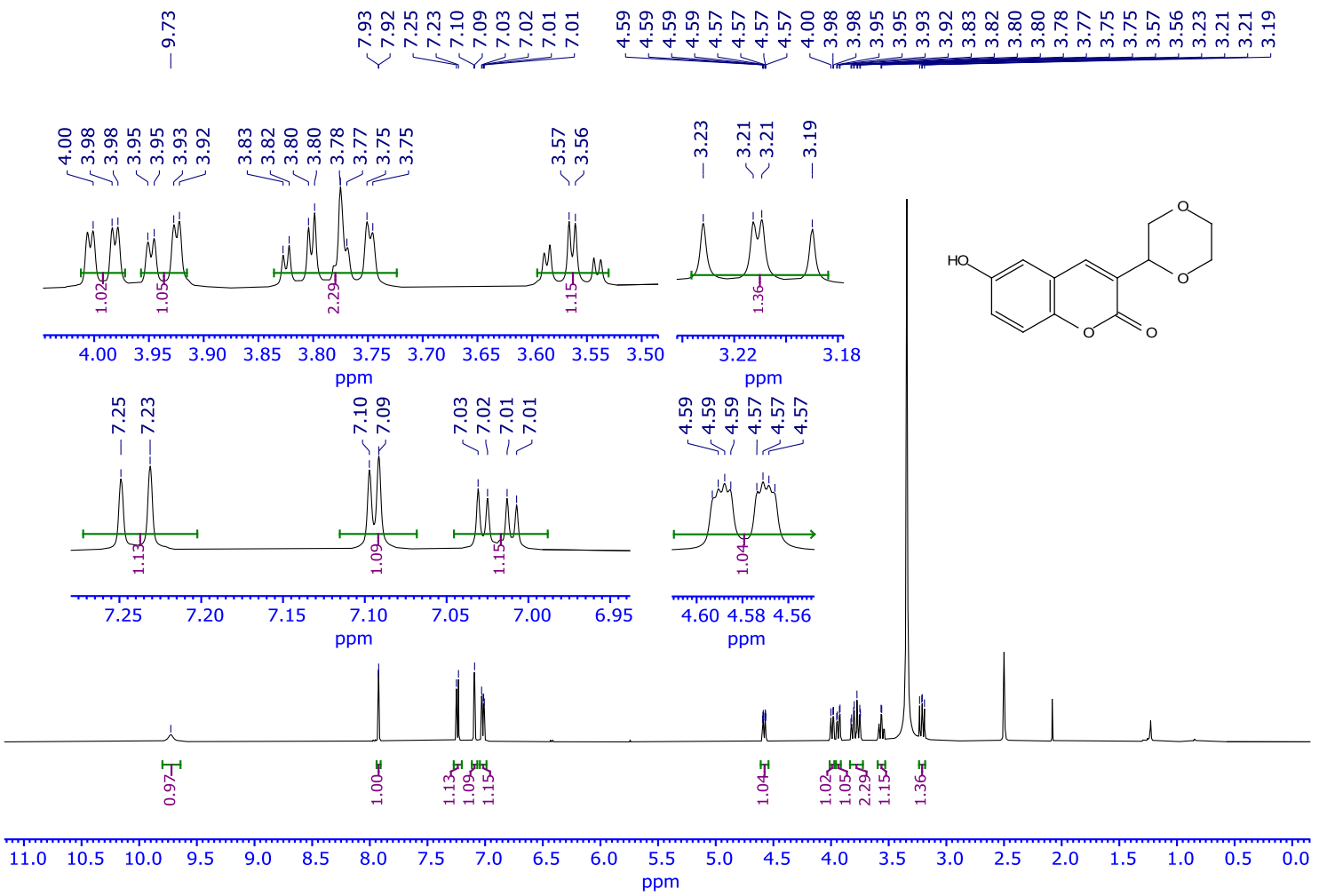

Figure S25. ^{1}H-NMR spectrum of 3-(1,4-dioxan-2-yl)-6-hydroxy-2H-chromen-2-one.

^{1}H-NMR (500 MHz, DMSO-d_6) δ (ppm) 9.73 (s, 1H), 7.92 (d, 1H), 7.24 (d, 1H), 7.09 (d, 1H), 7.02 (dd, 1H), 4.58 (ddd, 1H), 3.99 (dd, 1H), 3.94 (dd, 1H), 3.84 – 3.73 (m, 2H), 3.56 (td, 1H), 3.21 (dd, 1H).

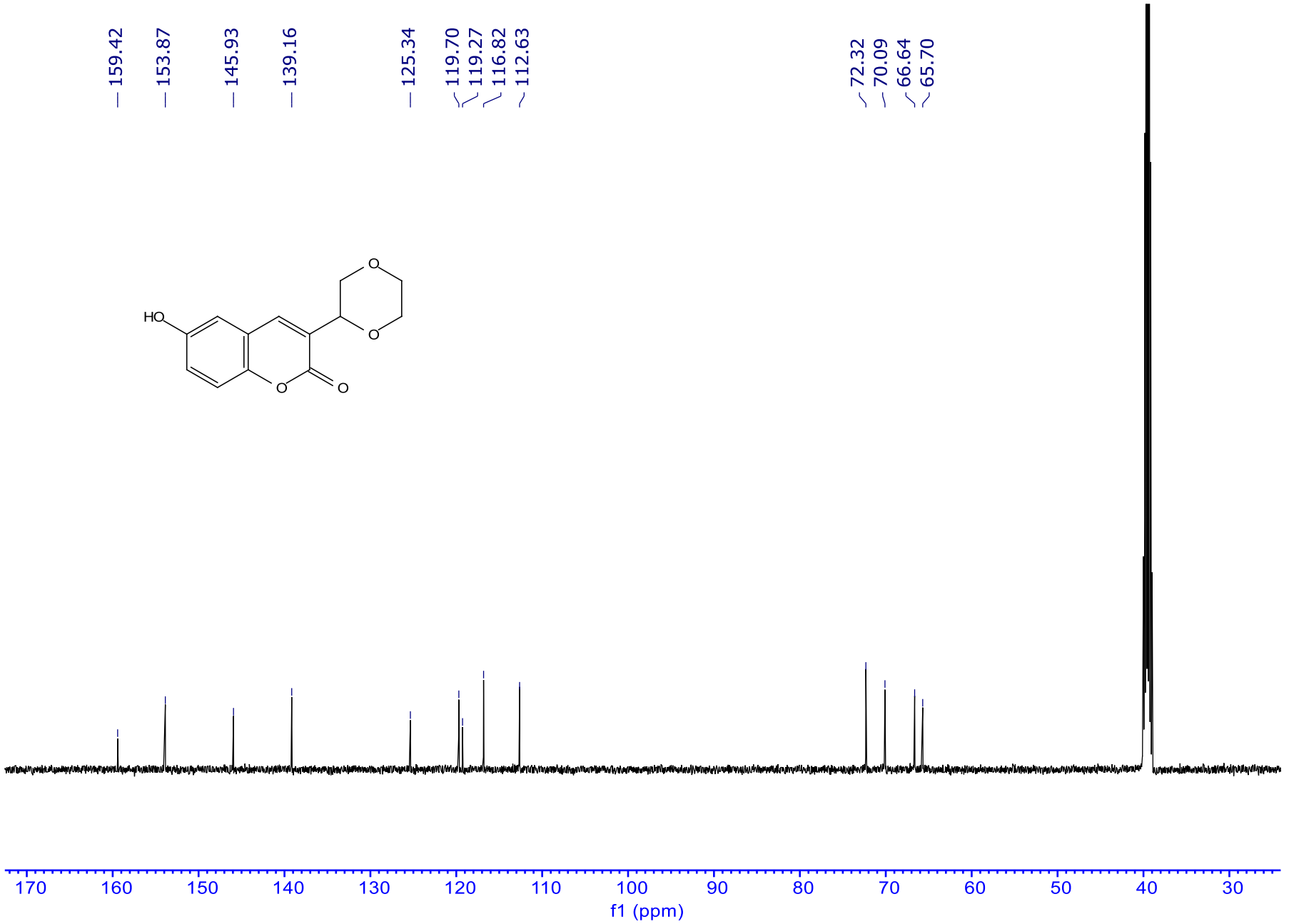

Figure S26. ^{13}C-NMR spectrum of 3-(1,4-dioxan-2-yl)-6-hydroxy-2H-chromen-2-one.

^{13}C-NMR (126 MHz, DMSO-d_6) δ (ppm) 159.42, 153.87, 145.93, 139.16, 125.34, 119.70, 119.27, 116.82, 112.63, 72.32, 70.09, 66.64, 65.70.

Synthesis conditions: 7-diethylamino-4-methylcoumarin (0.3 mmol, 69.4 mg), KI (20 mol%, 0.06 mmol), DTBP (4 equiv., 1.2 mmol) and $Cu_1Ce_{0.7}Si$ (4.8 mol%, 8.4 mg), dimethylacetamide (1 mL) at 120 °C in 25 h, n-hexane:ethyl acetate = 1:4 for column chromatography, silica gel 60 F254, R_f = 0.4 for TLC, yielding a yellow solid product (32.6 mg, 40%).

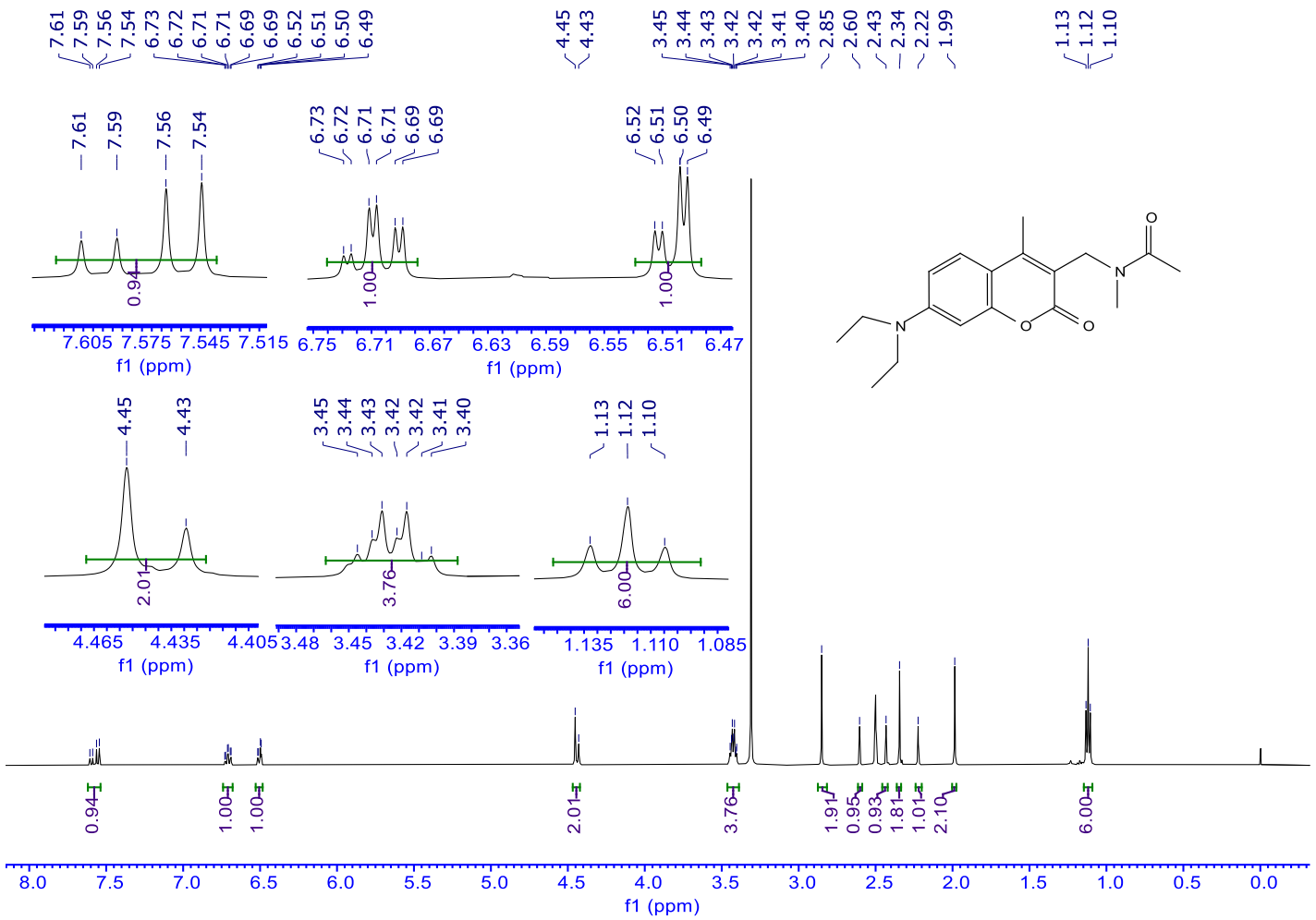

Figure S27. ^{1}H-NMR spectrum of *N*-((7-(diethylamino)-4-methyl-2-oxo-2H-chromen-3-yl)methyl)-*N* methylacetamide.

^{1}H-NMR (500 MHz, DMSO-d_6) δ (ppm) 7.61 – 7.55 (m, 1H), 6.73 – 6.69 (m, 1H), 6.50 (m, 1H), 4.45 – 4.42 (m, 2H), 3.46 – 3.39 (m, 4H), 2.85 – 2.60 (s, 3H), 2.43 – 2.34 (s, 3H), 2.22 – 1.99 (s, 3H), 1.12 (t, 6H).

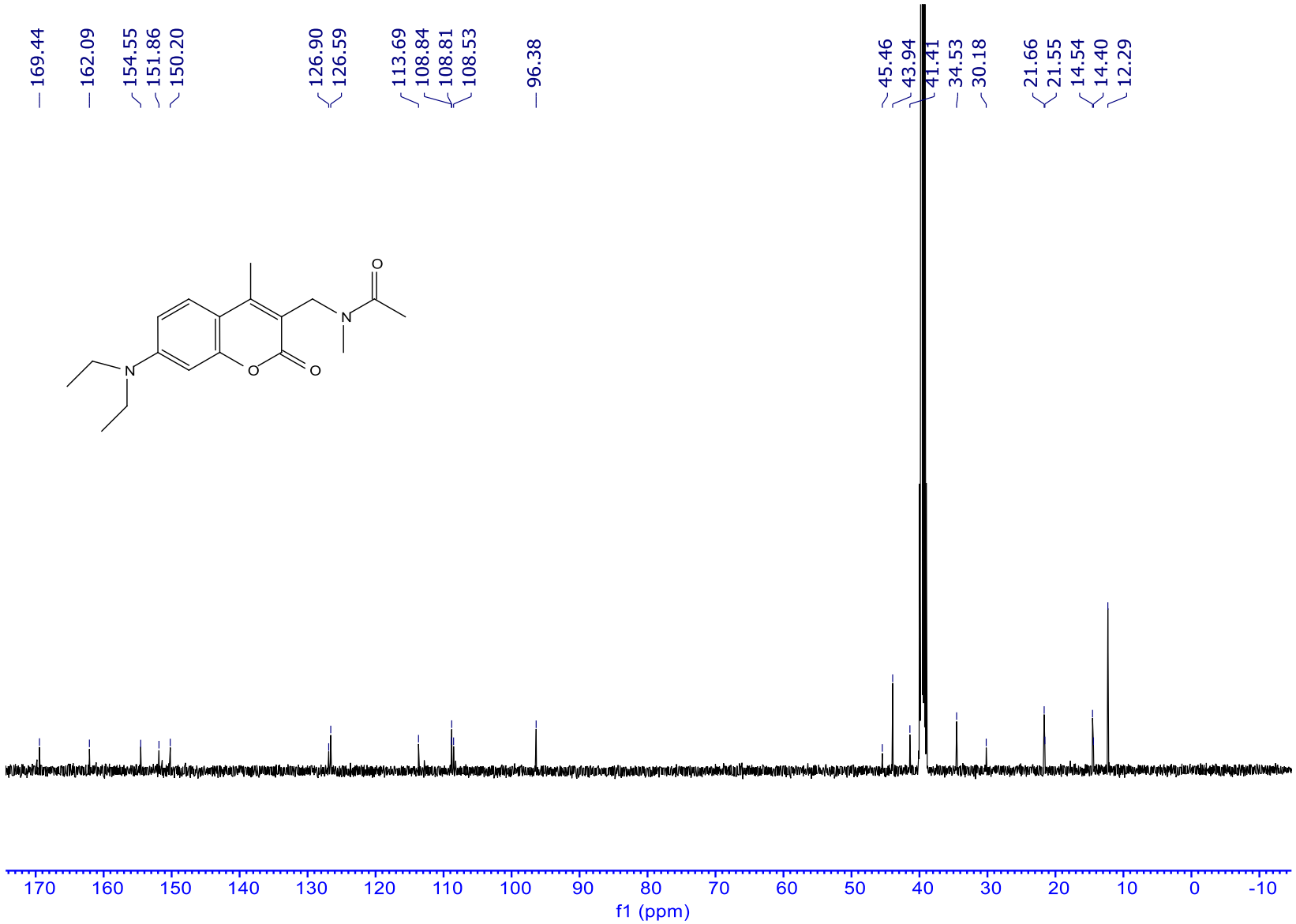

Figure S28. ^{13}C-NMR spectrum of *N*-((7-(diethylamino)-4-methyl-2-oxo-2H-chromen-3-yl)methyl)-*N* methylacetamide.

^{13}C-NMR (126 MHz, DMSO-d_6) δ (ppm) 169.44, 162.09, 154.55, 151.86, 150.20, 126.90, 126.59, 113.69, 108.84, 108.81, 108.53, 96.38, 45.46, 43.94, 41.41, 34.53, 30.18, 21.66, 21.55, 14.54, 14.40, 12.29.

Synthesis conditions: 6-methylcoumarin (0.3 mmol, 48.1 mg), KI (20 mol%, 0.06 mmol), DTBP (4 equiv., 1.2 mmol) and $Cu_1Ce_{0.7}Si$ (4.8 mol%, 8.4 mg), dimethylacetamide (1 mL) at 120 °C in 25 h, n-hexane:ethyl acetate = 1:4 for column chromatography, silica gel 60 F254, R_f = 0.30 for TLC, yielding a white solid product (43.8 mg, 30%).

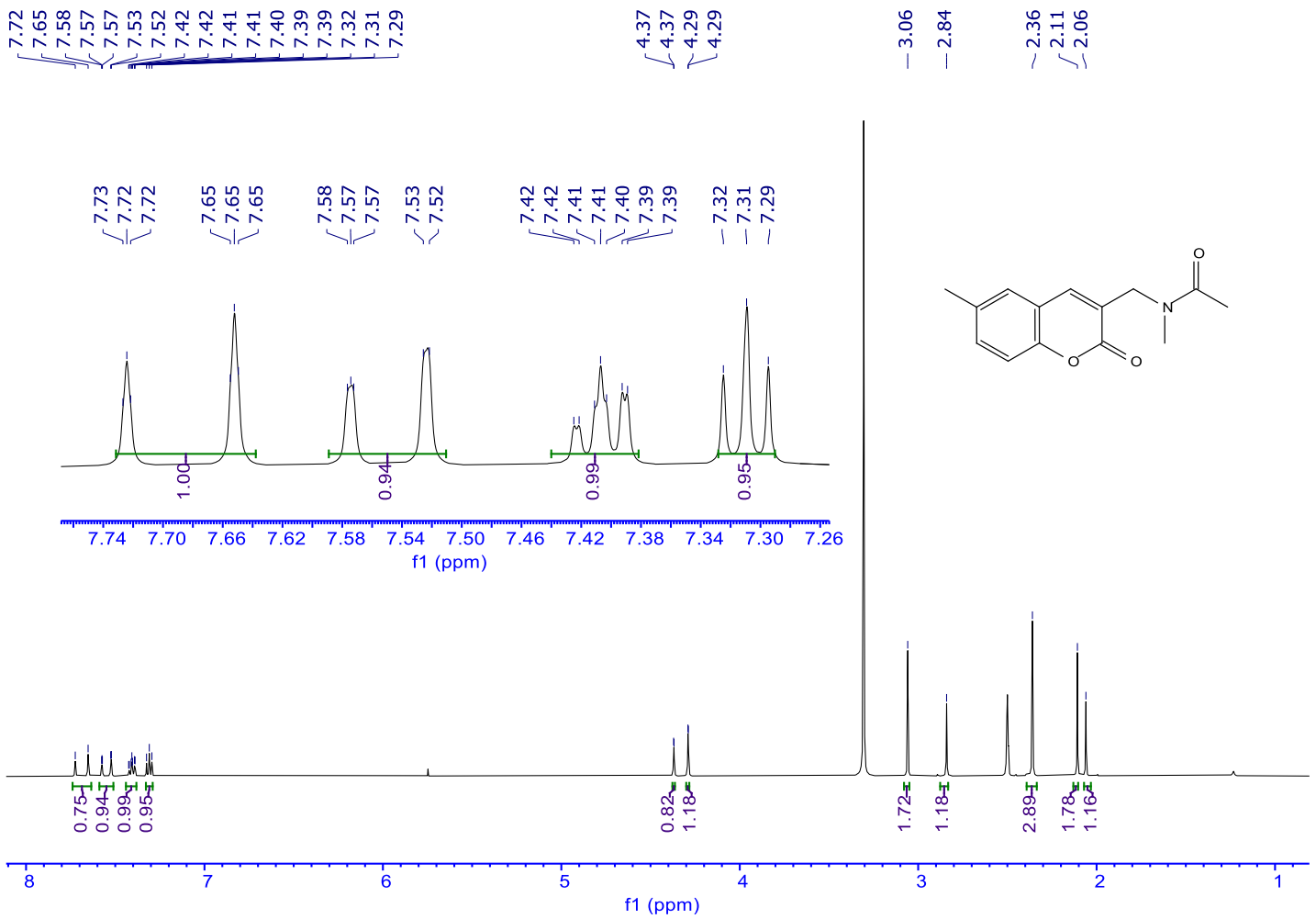

Figure S29. ^{1}H-NMR spectrum of *N*-methyl-*N*-((6-methyl-2-oxo-2H-chromen-3-yl)methyl)acetamide.

^{1}H-NMR (600 MHz, DMSO-d_6) δ (ppm) 7.73 – 7.64 (m, 1H), 7.59 – 7.51 (m, 1H), 7.42 – 7.39 (m, 1H), 7.32 – 7.29 (m, 1H), 4.37 – 4.29 (d, 2H), 3.06 – 2.84 (s, 3H), 2.36 (s, 3H), 2.11 – 2.06 (s, 3H).

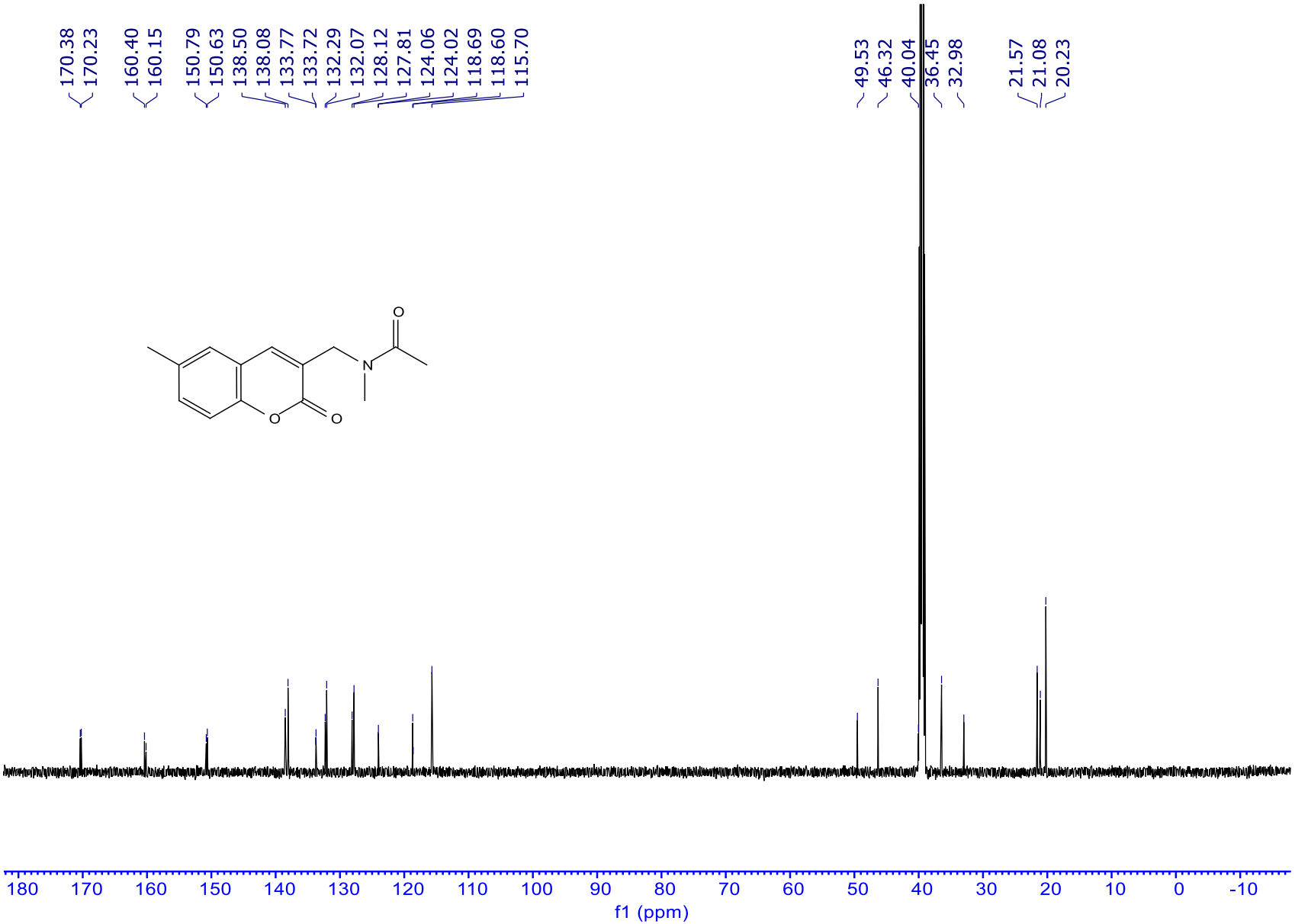

Figure S30. ^{13}C-NMR spectrum of *N*-methyl-*N*-((6-methyl-2-oxo-2H-chromen-3-yl)methyl)acetamide.

^{13}C-NMR (151 MHz, DMSO-d_6) δ (ppm) 170.38, 170.23, 160.40, 160.15, 150.79, 150.63, 138.50, 138.08, 133.76, 133.72, 132.29, 132.07, 128.11, 127.82, 124.06, 124.02, 118.68, 118.60, 115.69, 49.53, 46.32, 36.44, 32.98, 21.57, 21.08, 20.23.