

SUPPORTING INFORMATION

Rhodium-Catalyzed Alkylation of Aromatic Ketones with Allylic Alcohols and α,β -Unsaturated KetonesWan-Di Li [†], Jia-Shuo Zhang [†], Lin-Yan Zhang, Zhong-Wen Liu, Juan Fan, and Xian-Ying Shi ^{*}

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Table of Contents

1. Procedure for the synthesis of 3l on 2 mmol scale	S2
2. Procedure for the synthesis of 4a on 1 mmol scale	S2
3. Mechanistic studies.....	S2
4. Copies of NMR spectra	S4

1. Procedure for the synthesis of 3I on 2 mmol scale

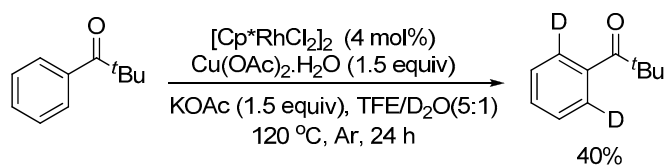
An oven-dried 50 mL Schlenk tube was charged with 2-(trimethylacetyl)thiophene (315 μ L, 2.0 mmol), 1-penten-3-ol (411 μ L, 4.0 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (Rh^* , 49 mg, 4 mol%, 0.08 mmol), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (599.0 mg, 1.5 equiv, 3.0 mmol), KOAc (294.4 mg, 1.5 equiv, 3.0 mmol), and TFE (6 mL). The mixture was stirred at 120 $^\circ\text{C}$ for 24 h under Ar conditions. After cooling to room temperature, the mixture was concentrated to give a crude product, purified by silica gel column chromatography using hexanes/EtOAc (10/1) to yield compound **3I** (0.424 g, 84%).

2. Procedure for the synthesis of 4a on 1 mmol scale

An oven-dried 50 mL Schlenk tube was charged with 2,2-dimethylpropiophenone (167 μ L, 1.0 mmol), 1-penten-3-one (148 μ L, 1.5 mmol), $[\text{RhCp}^*\text{Cl}_2]_2$ (18.5 mg, 3 mol%, 0.03 mmol), NaOAc (20.5 mg, 0.25 equiv, 0.25 mmol), and 1,1,1,3,3,3-hexafluoro-2-propanol (10 mL). The mixture was stirred at 120 $^\circ\text{C}$ for 16 h under Ar conditions. After cooling to room temperature, the mixture was concentrated to give a crude product, purified by silica gel column chromatography using hexanes/EtOAc (10/1) to yield compound **4a** (0.209 g, 85%).

3. Mechanistic studies

3.1. Ortho deuteration experiment



$[\text{Cp}^*\text{RhCl}_2]_2$ (Rh^* , 2.5 mg, 4 mol%, 0.004 mmol), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (29.9 mg, 0.15 mmol), KOAc (14.7 mg, 0.15 mmol), 2,2-dimethylpropiophenone (0.1 mmol), D_2O (0.05 mL), and TFE (0.25 mL) were successively added to a reaction vessel equipped with a stir bar. The vessel was sealed under Ar and heated at 120 $^\circ\text{C}$ (oil bath temperature) for 24 h. The resulting mixture was cooled to room temperature, before being filtered through a short column of silica gel. The solvent was removed under reduced pressure and the amount of *ortho*-deuterated benzaldehyde was determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard.

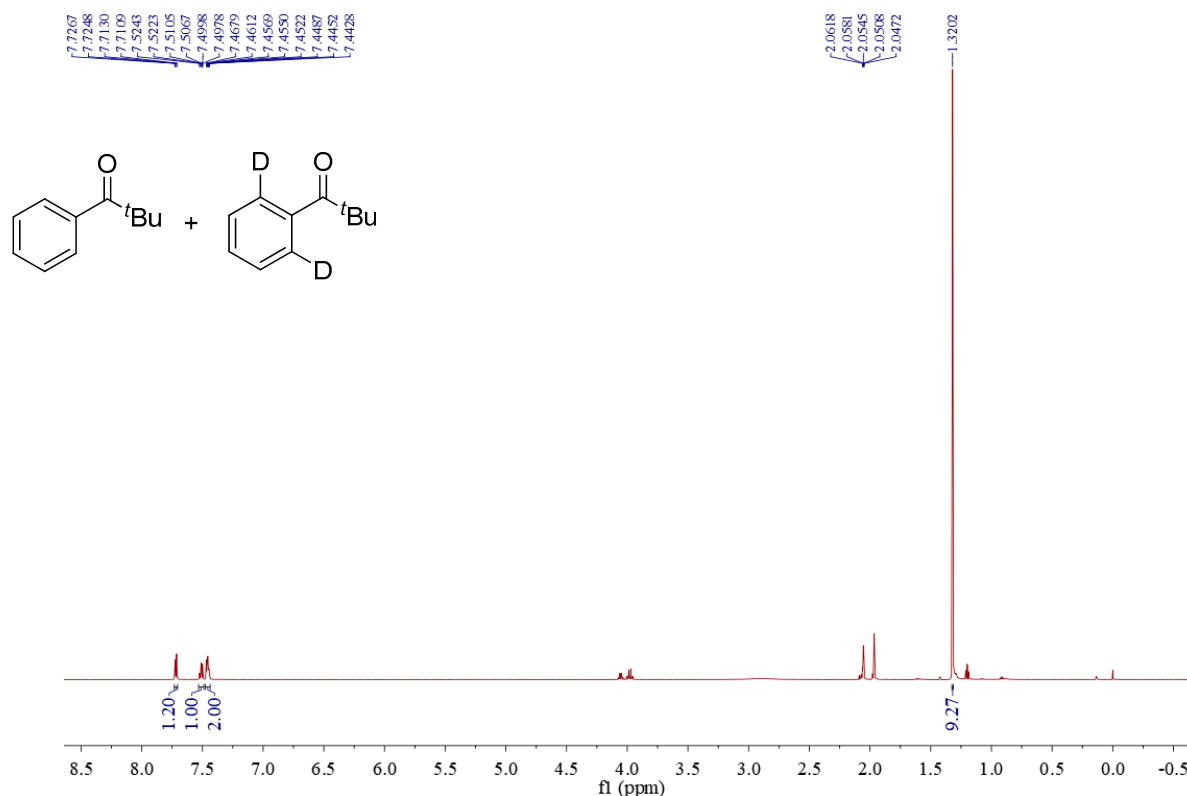
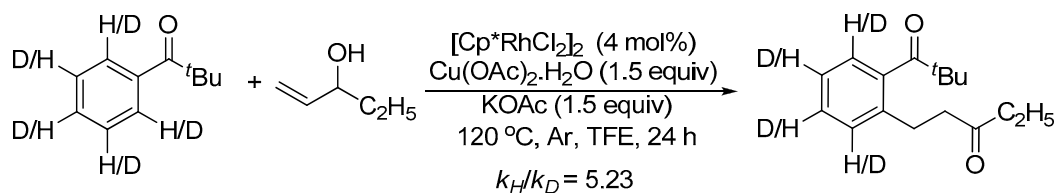
¹H NMR spectra of the crude reaction mixture of *ortho* deuteration experiment

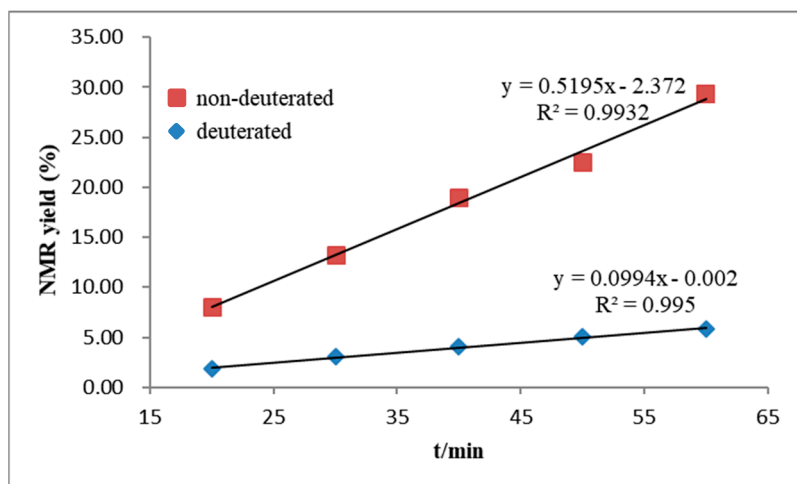
Figure S1. ¹H NMR spectra of crude reaction mixture of *ortho* deuteration experiment.

3.2 KIE experiment (parallel experiments)

$[\text{Cp}^*\text{RhCl}_2]_2$ (Rh^* , 2.5 mg, 4 mol%, 0.004 mmol), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (29.9 mg, 0.15 mmol), KOAc (14.7 mg, 0.15 mmol), 2,2-dimethylpropiophenone (0.1 mmol), 1-penten-3-ol (0.2 mmol), and TFE (0.6 mL) were successively added to a reaction vessel equipped with a stir bar. In another reaction vessel, 2,2-dimethylpropiophenone was replaced by D_5 -2,2-dimethylpropiophenone (0.1 mmol). The vessel was sealed under Ar conditions. The two reactions were stirred at 120°C (oil bath temperature) for 20 min, 30 min, 40 min, 50 min, and 60 min, respectively. Then, the two reaction mixtures were filtered through a short silica gel column. The solvent was then removed. The KIE was determined by ¹H NMR using 1,3,5-trimethoxybenzene as the internal standard. Thus, the KIE was found to be 5.23.

Table S1. The average yields of **3a** and *D*₅-**3a**.

Entry	Time (min)	Yield of 3a (%)	Yield of <i>D</i> ₅ - 3a (%)
1	20	8.04	1.88
2	30	13.20	3.04
3	40	18.94	4.04
4	50	22.49	5.08
5	60	29.37	5.83



4. Copies of NMR spectra

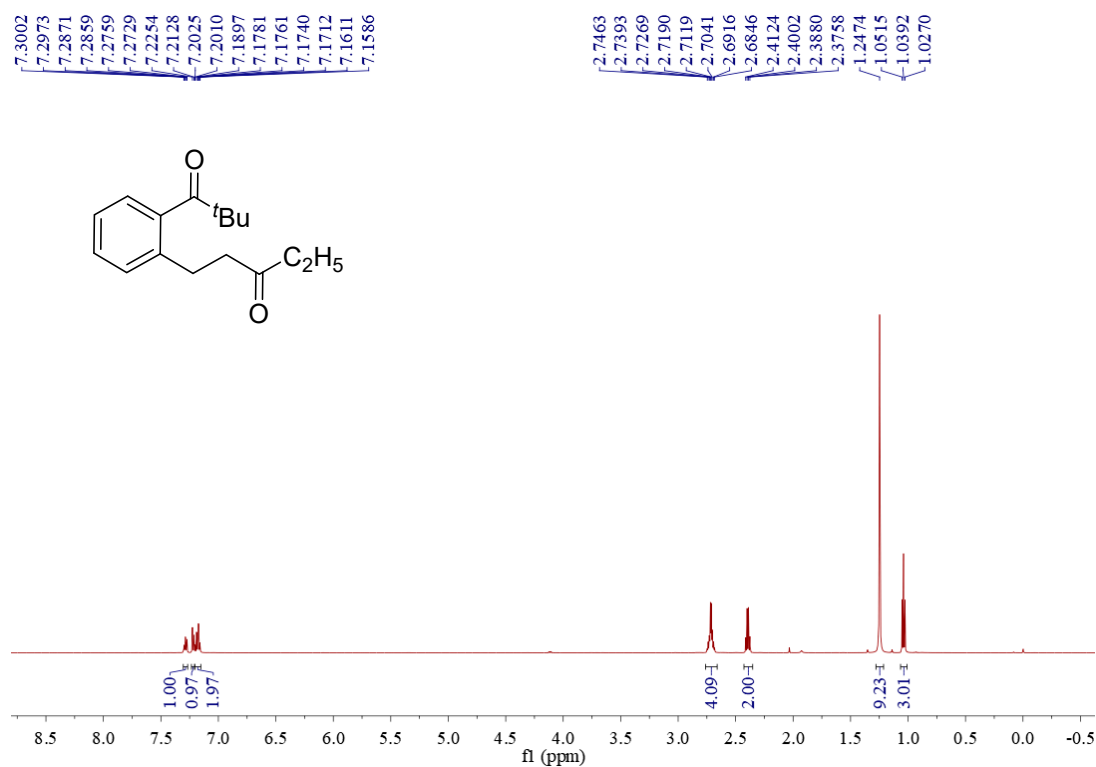


Figure S2. ¹H NMR spectra of compound 3a.

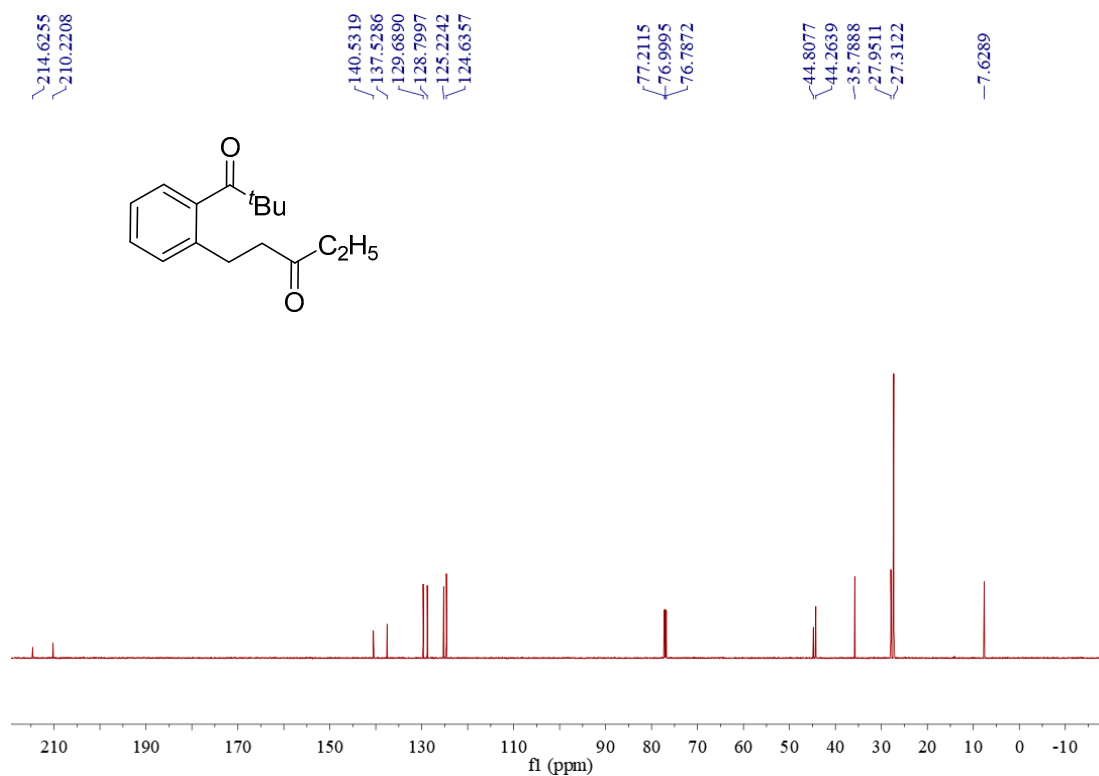
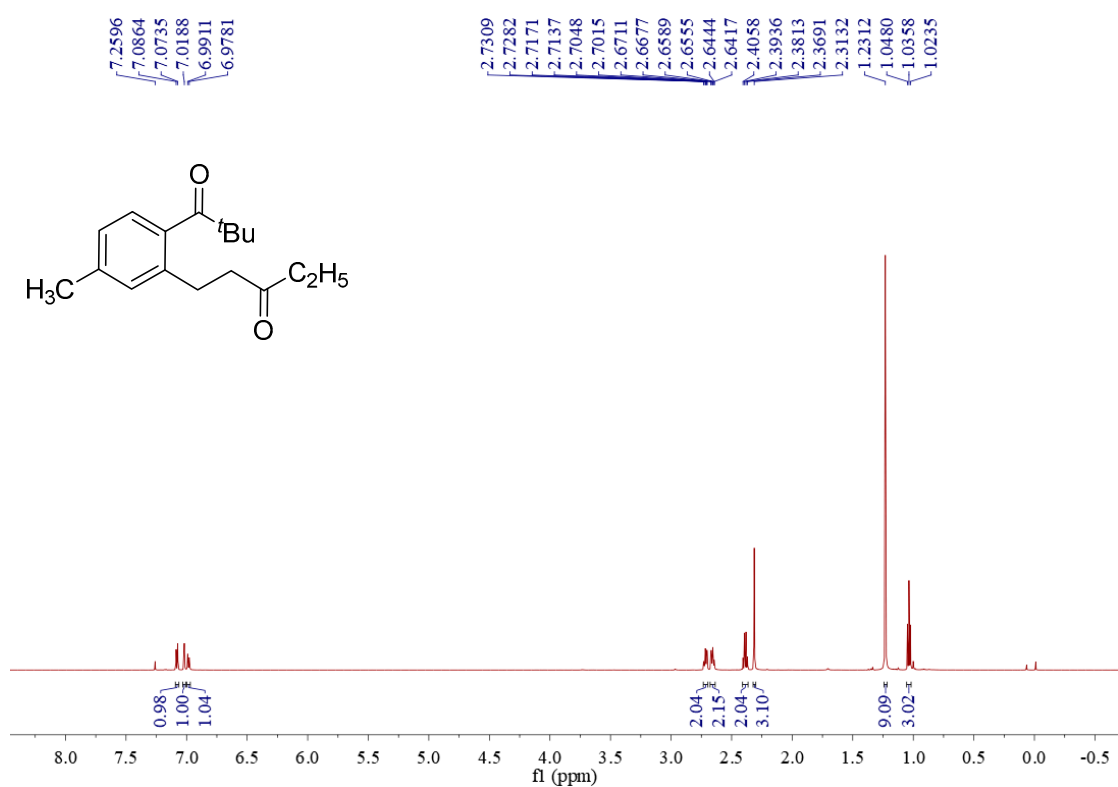
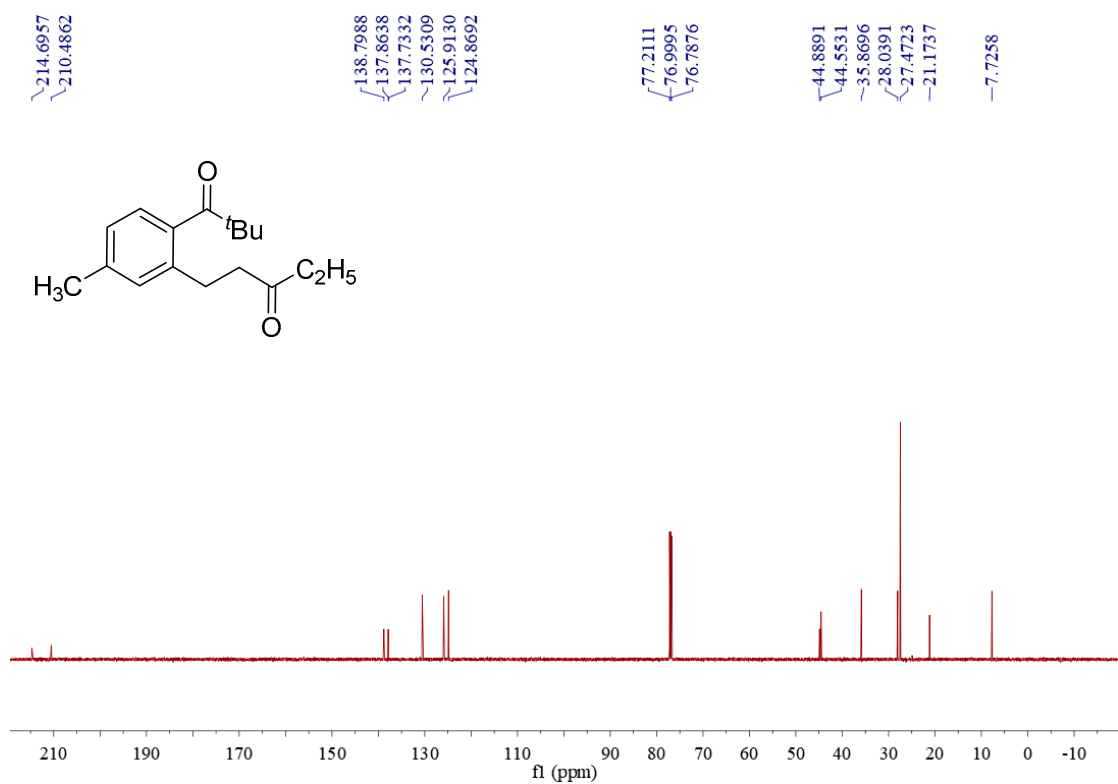
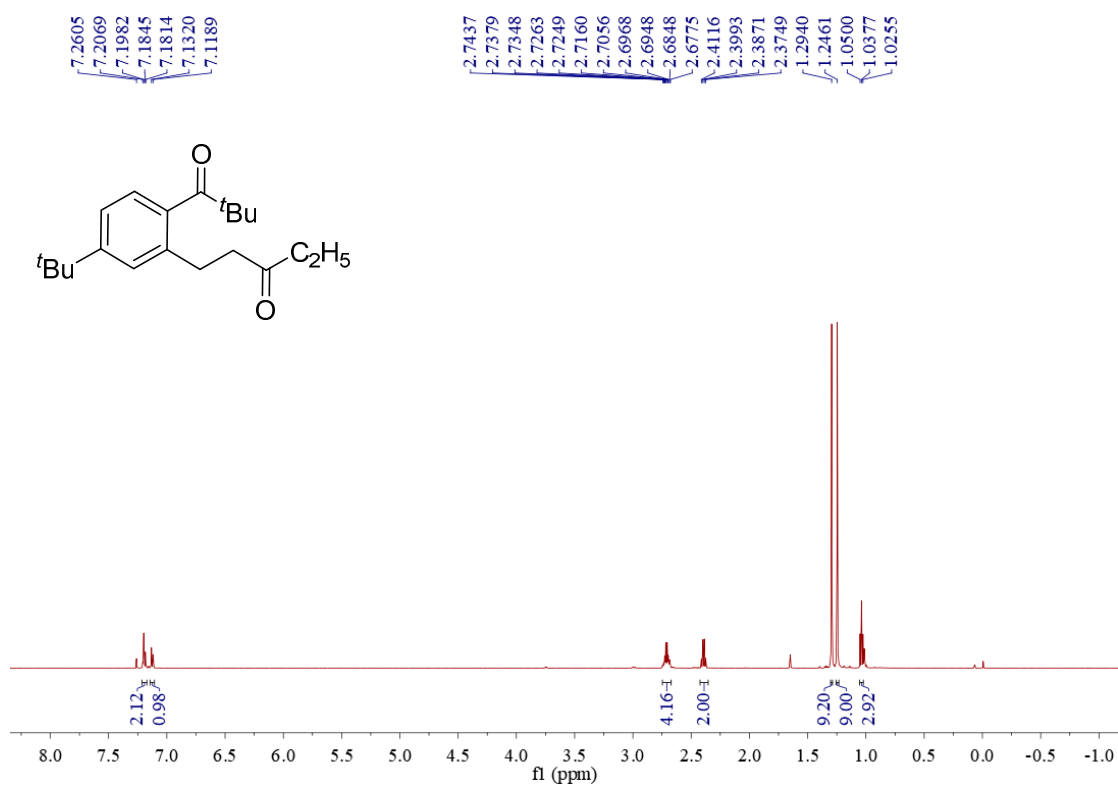
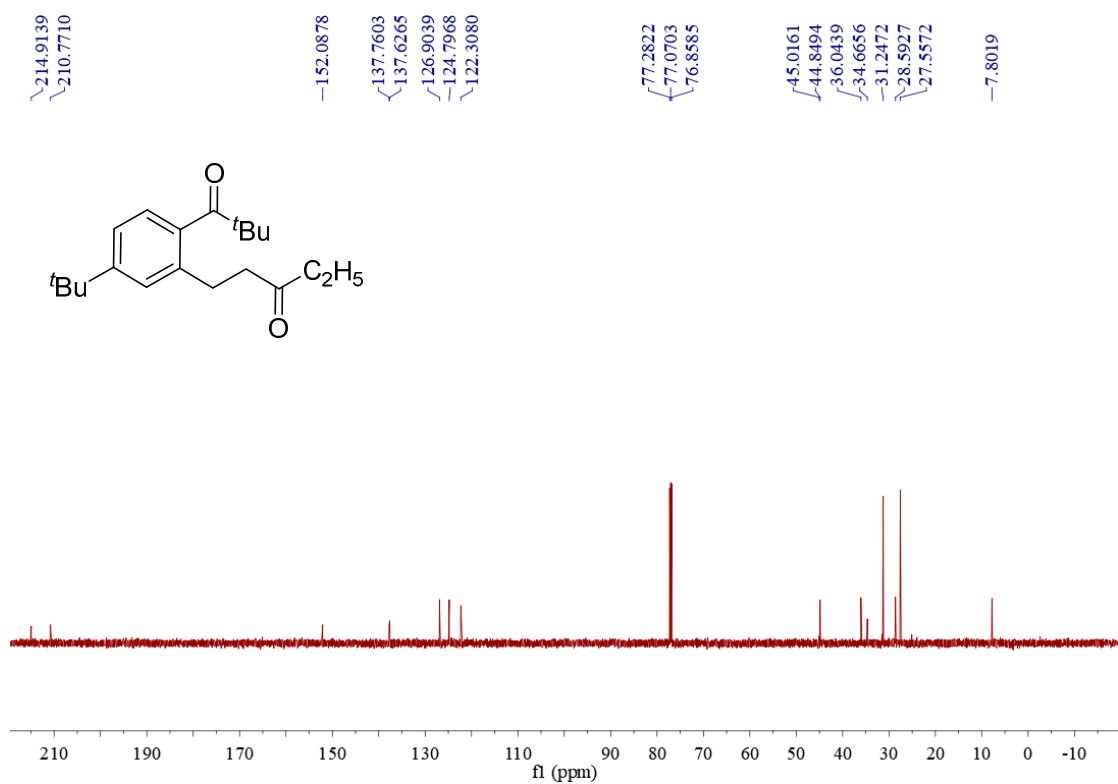
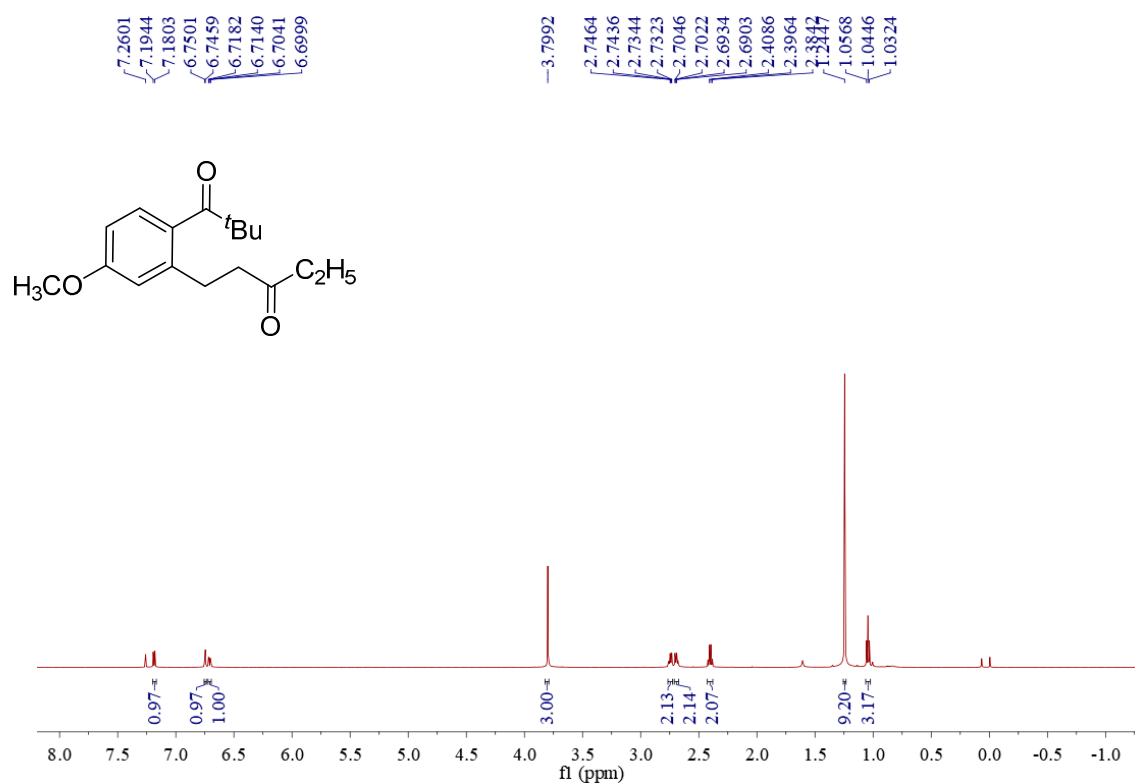
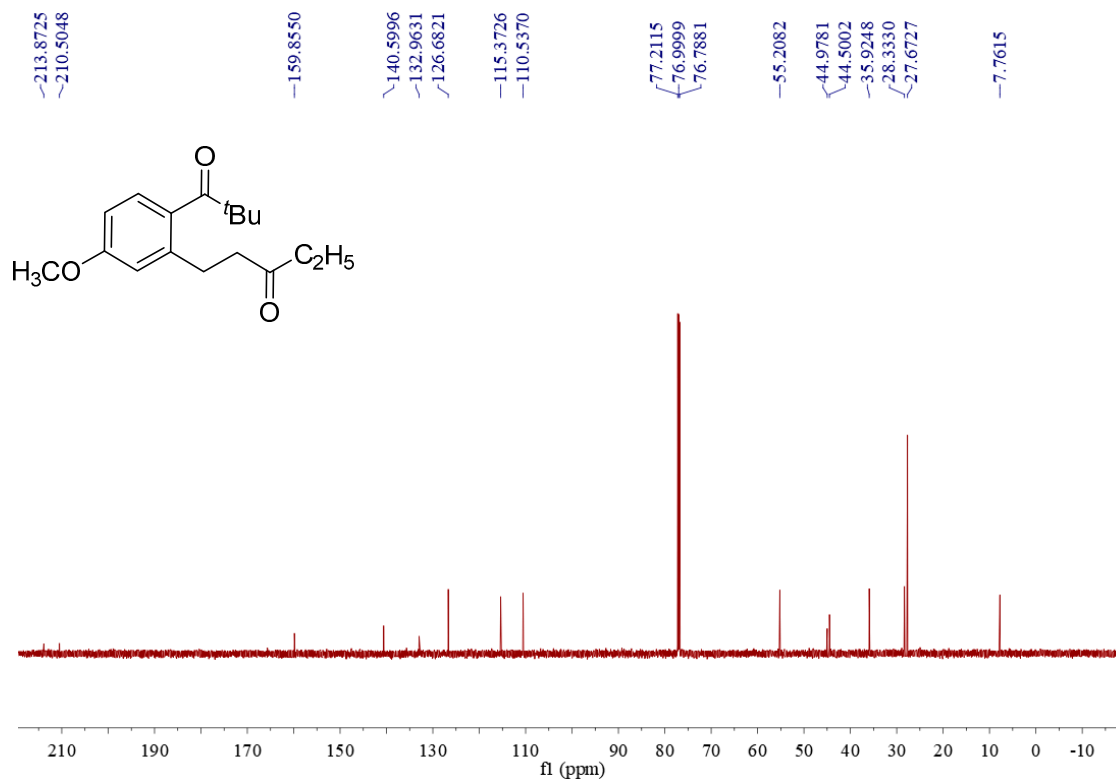
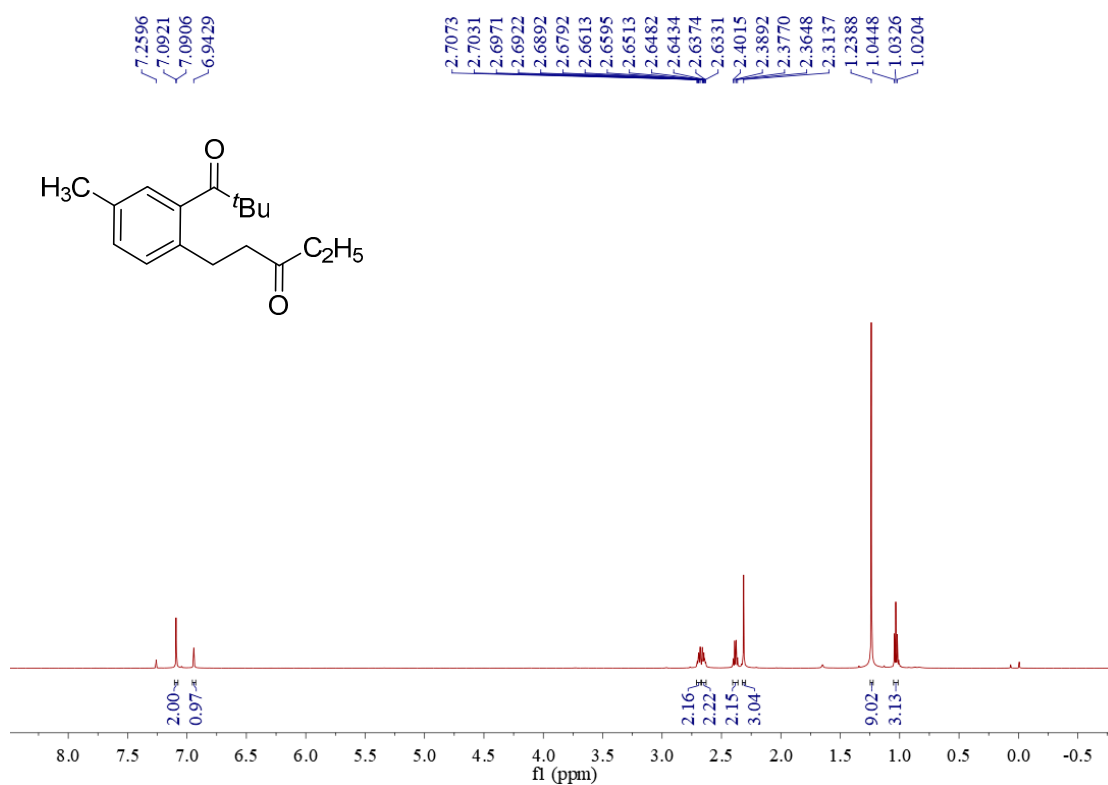
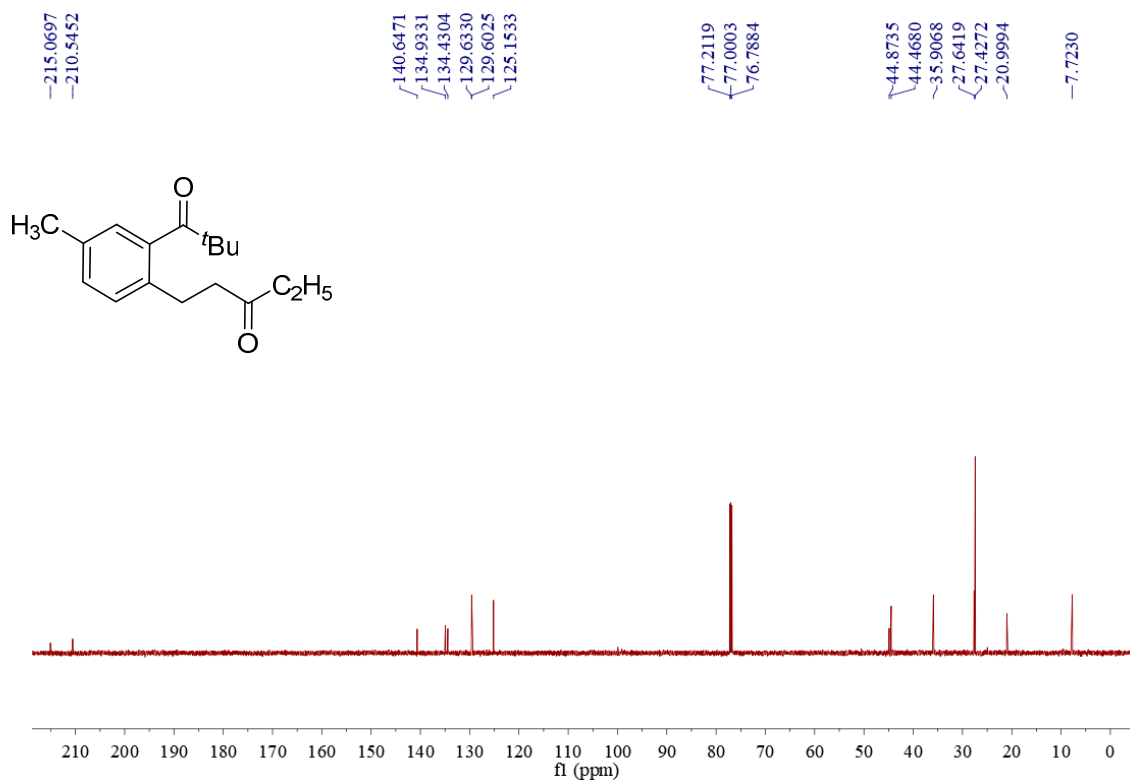


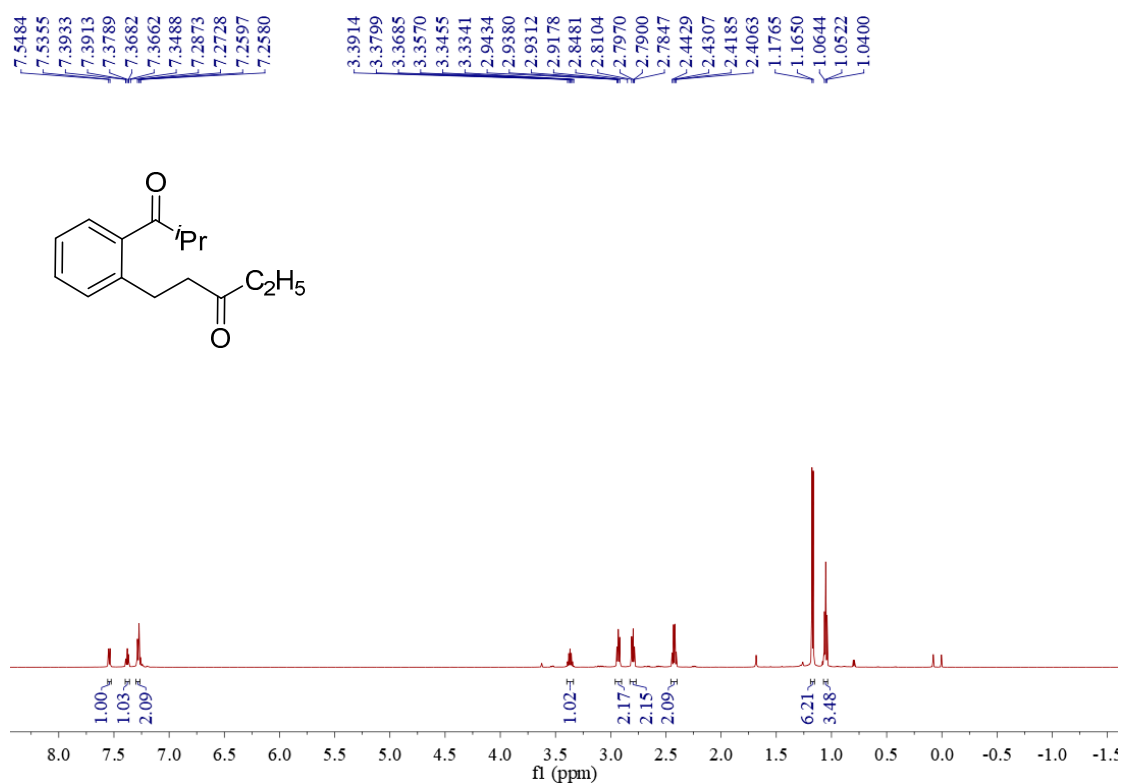
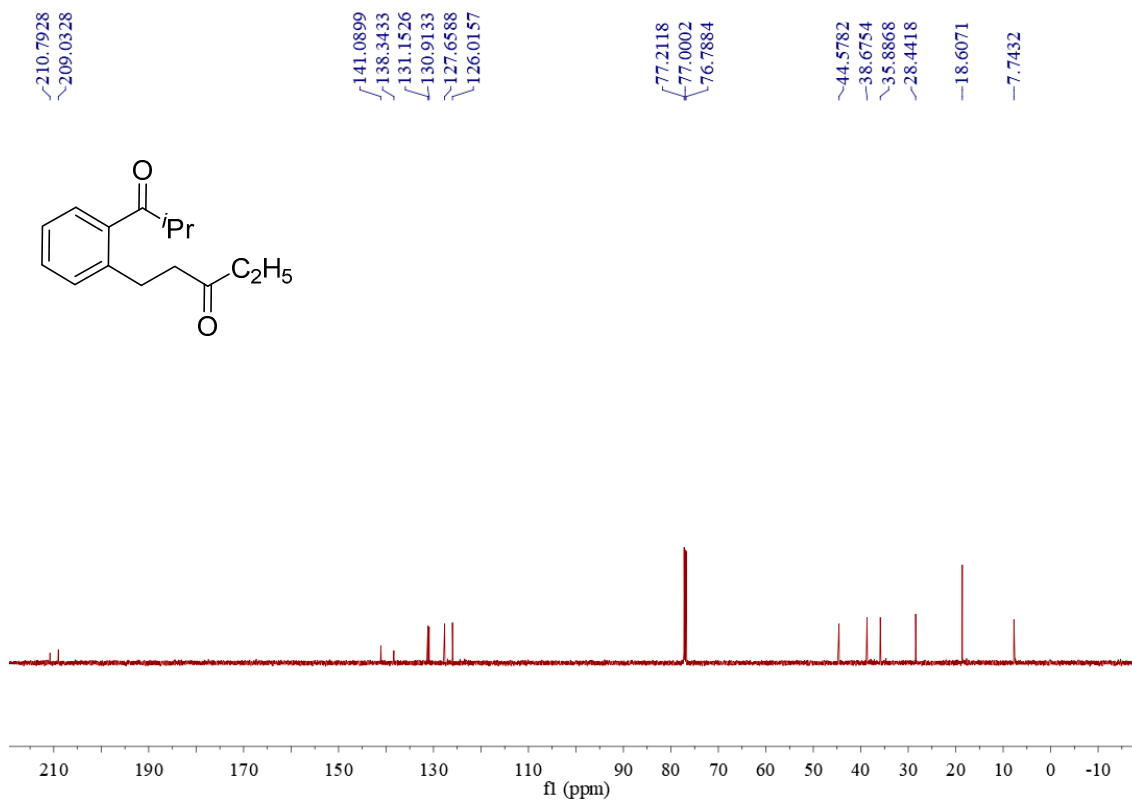
Figure S3. ¹³C NMR spectra of compound 3a.

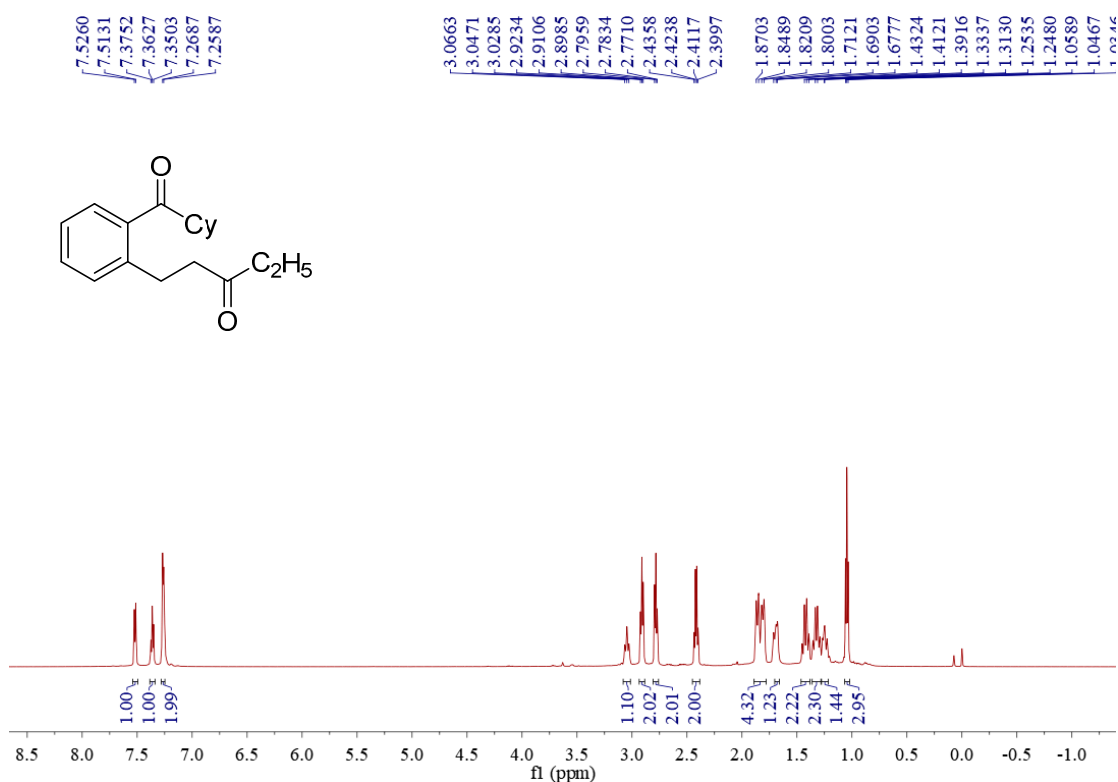
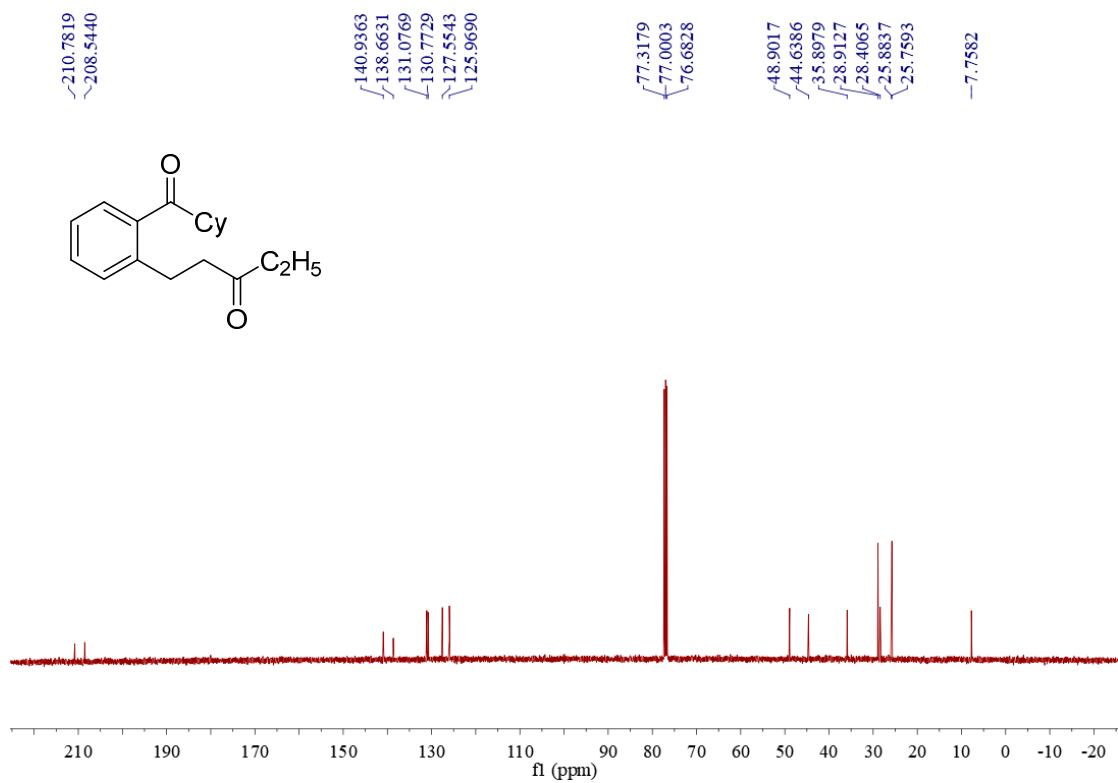
Figure S4. ¹H NMR spectra of compound **3b**.Figure S5. ¹³C NMR spectra of compound **3b**.

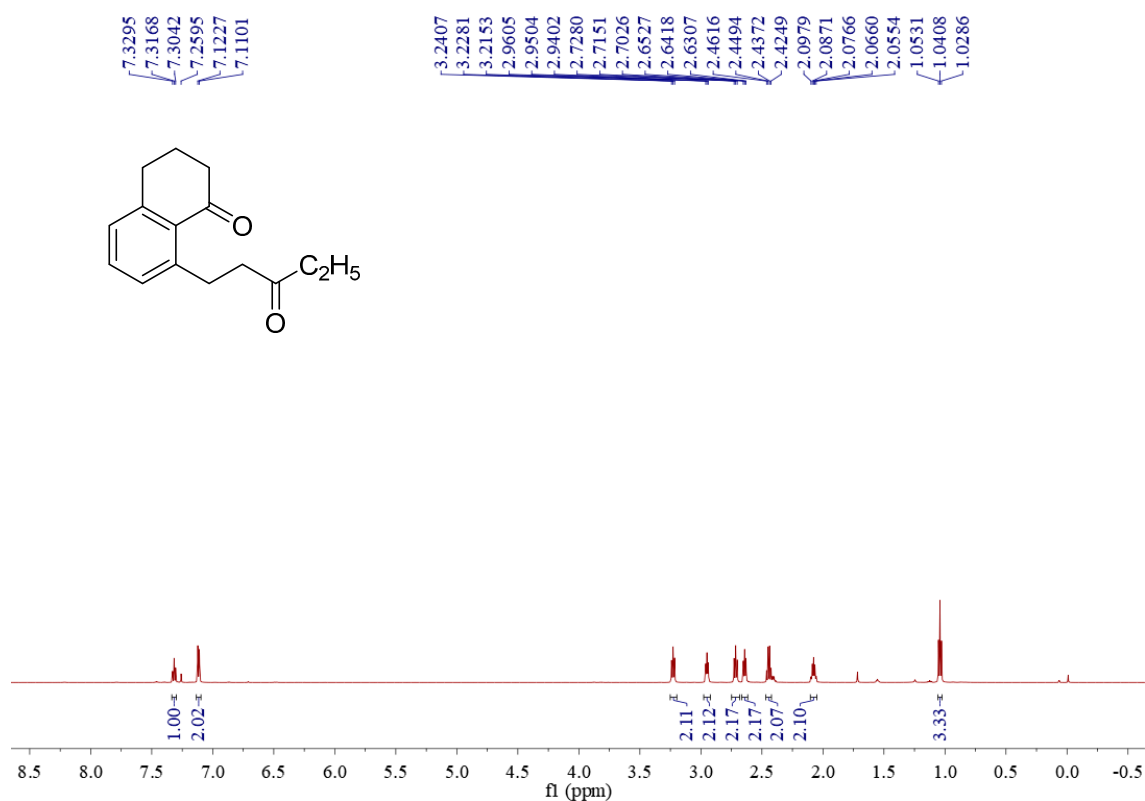
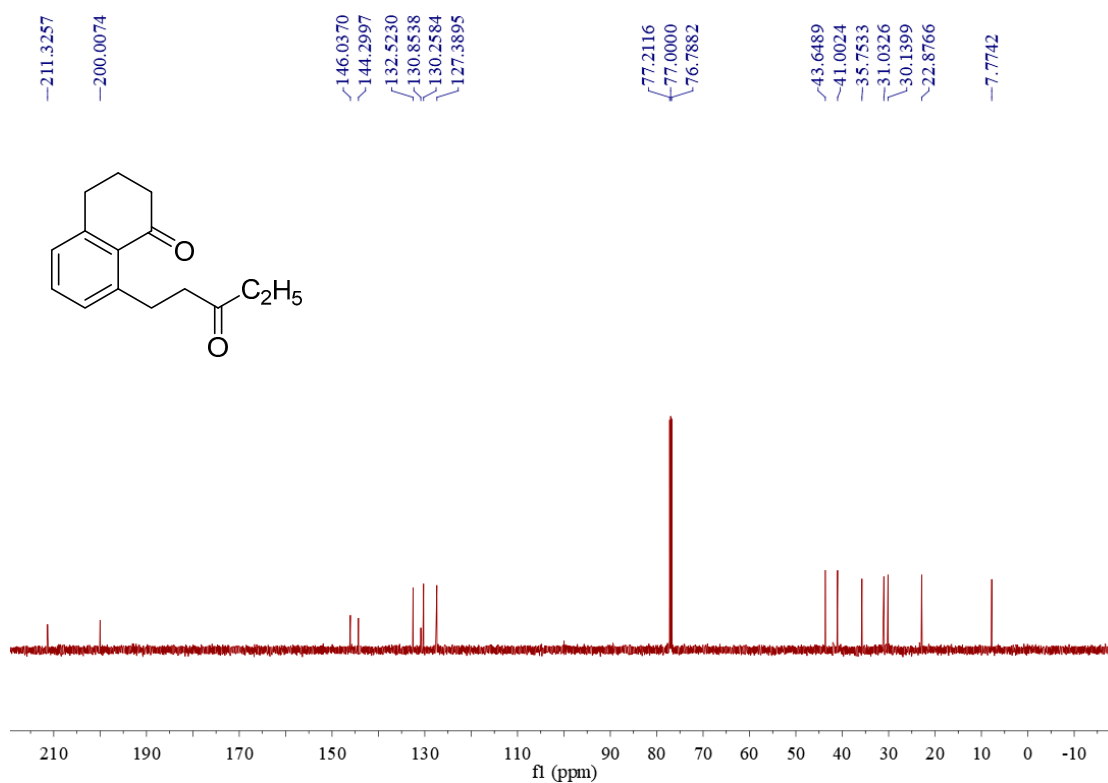
Figure S6. ¹H NMR spectra of compound 3c.Figure S7. ¹³C NMR spectra of compound 3c.

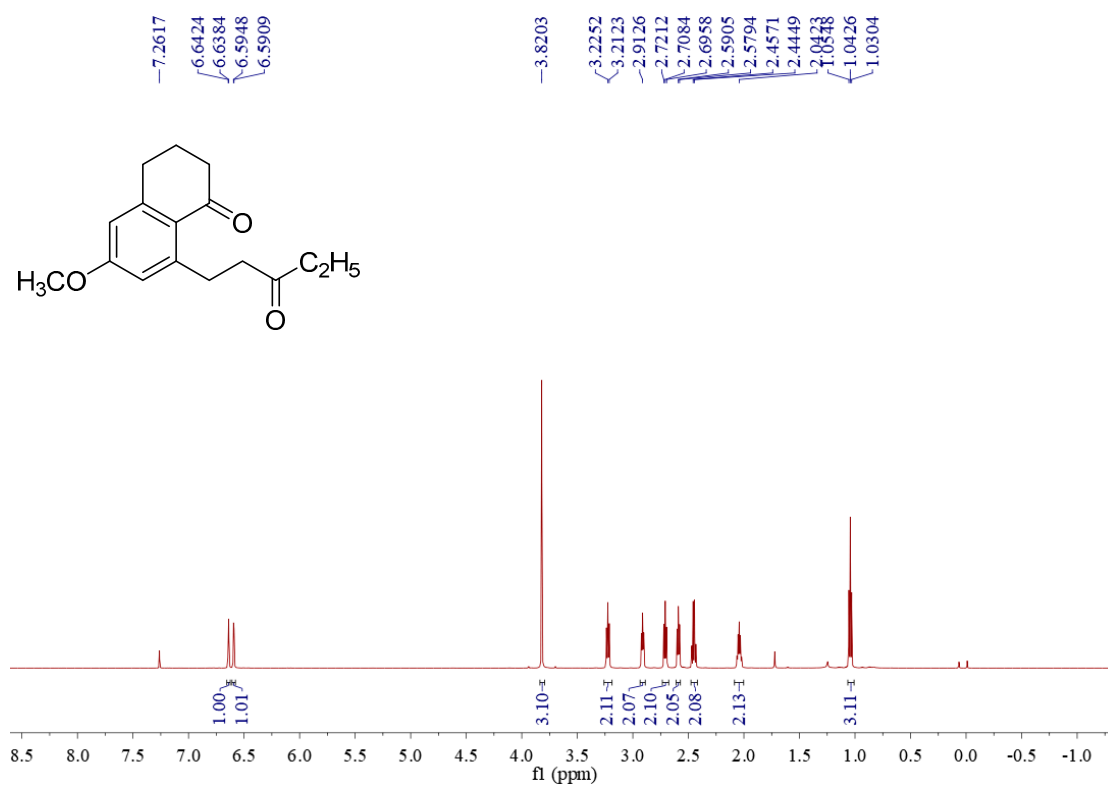
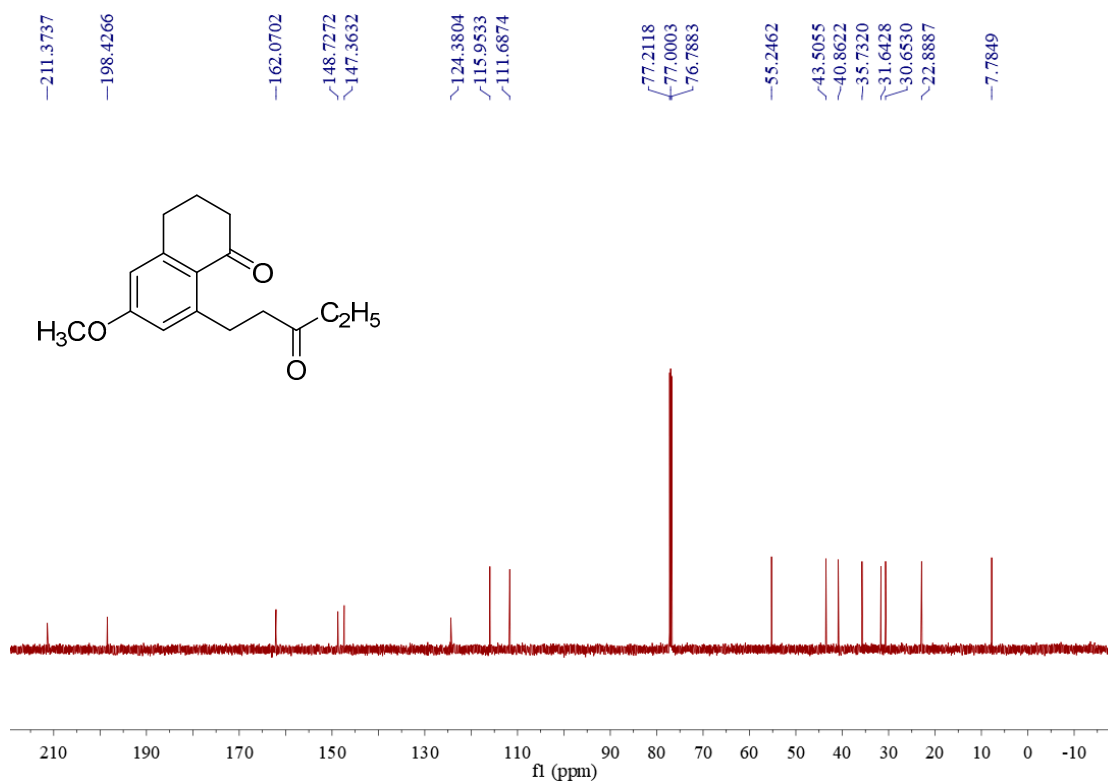
Figure S8. ¹H NMR spectra of compound 3d.Figure S9. ¹³C NMR spectra of compound 3d.

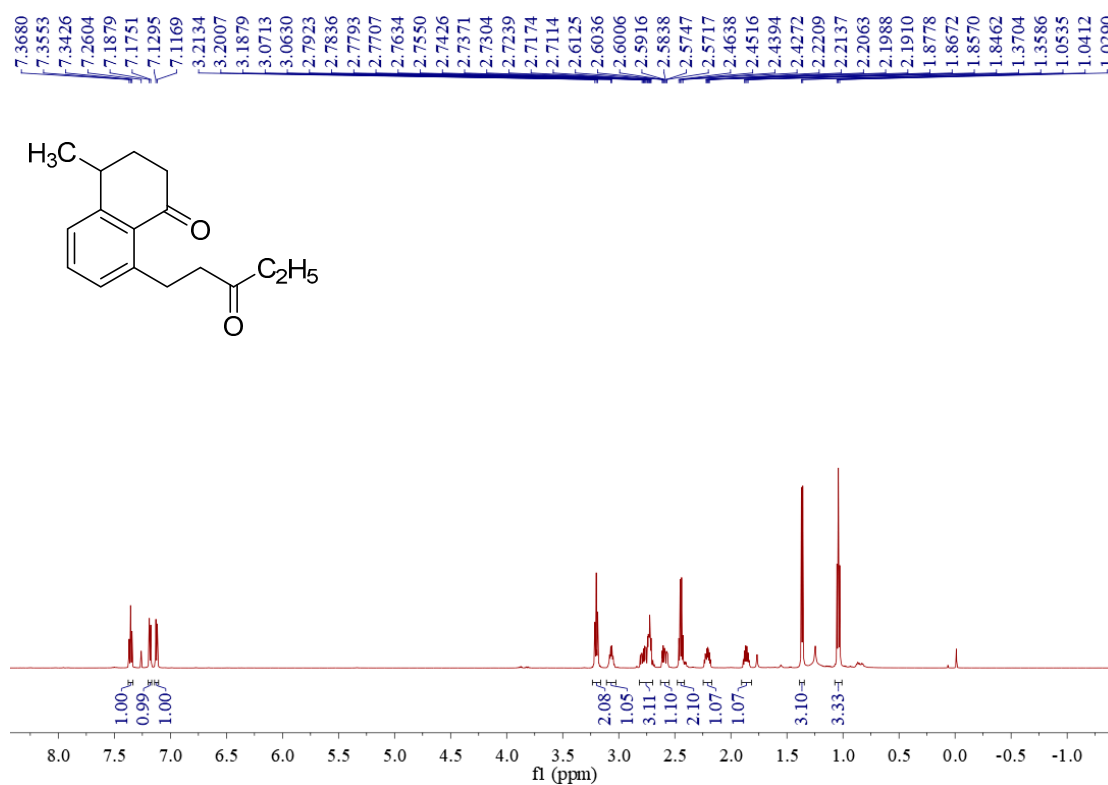
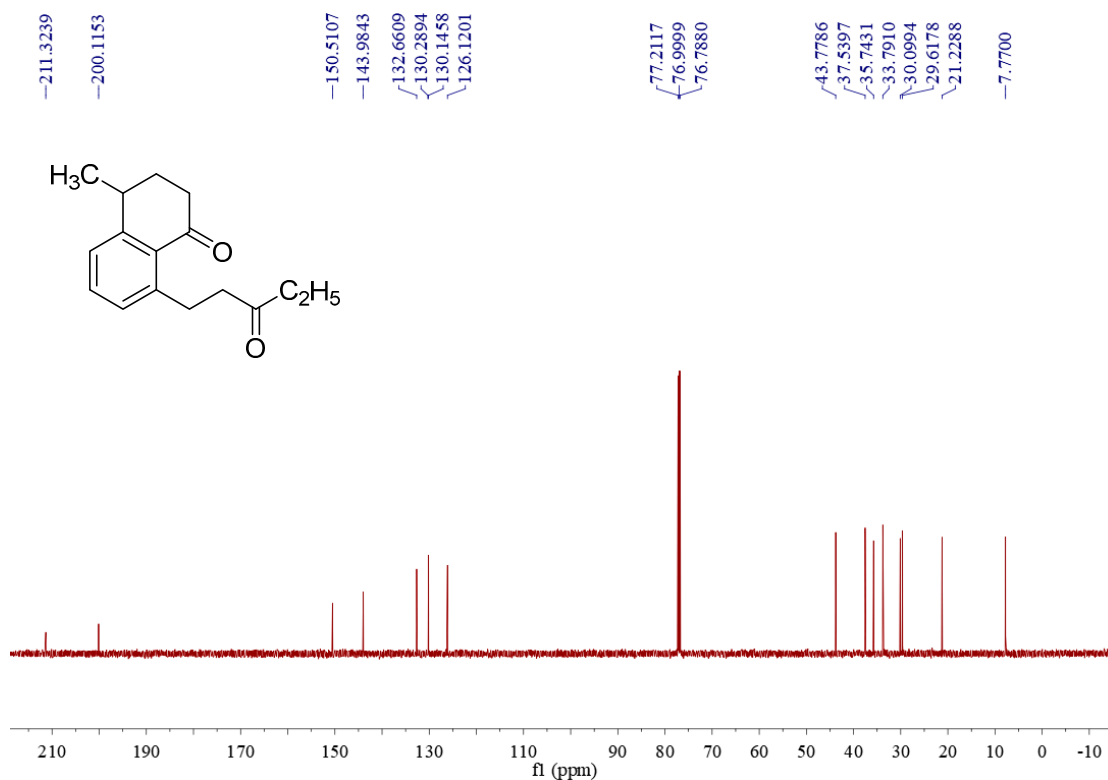
Figure S10. ¹H NMR spectra of compound 3e.Figure S11. ¹³C NMR spectra of compound 3e.

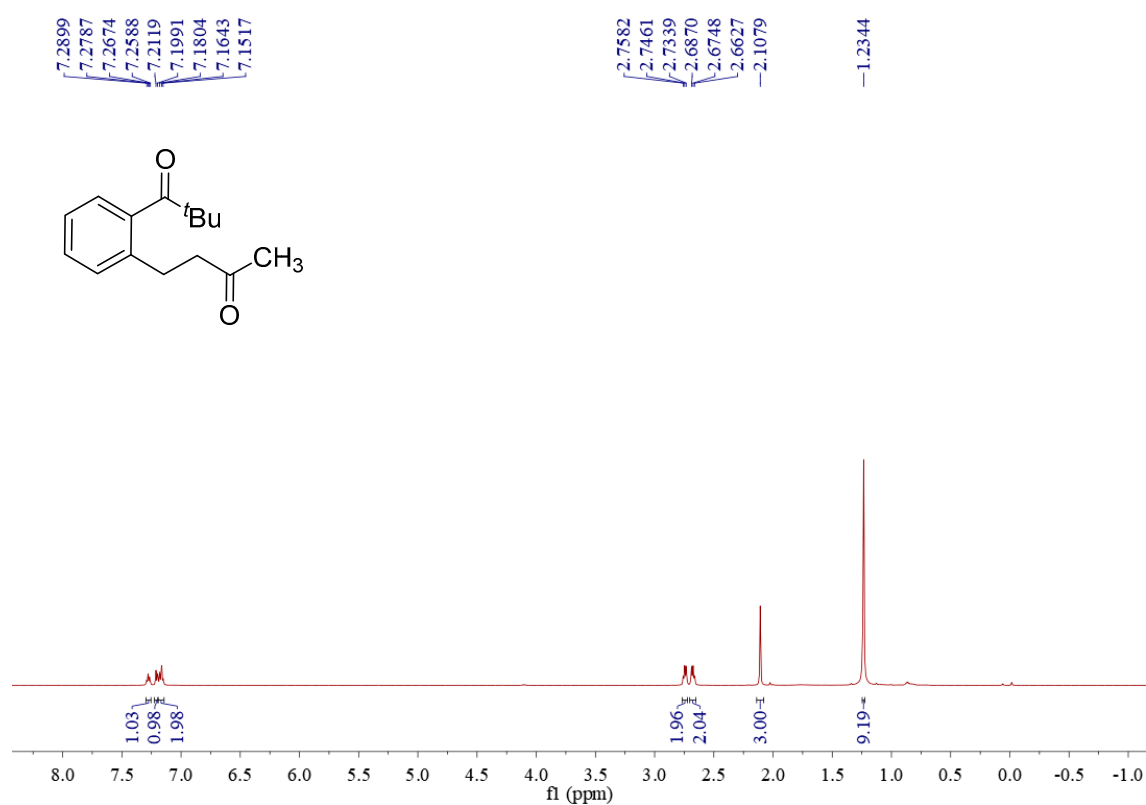
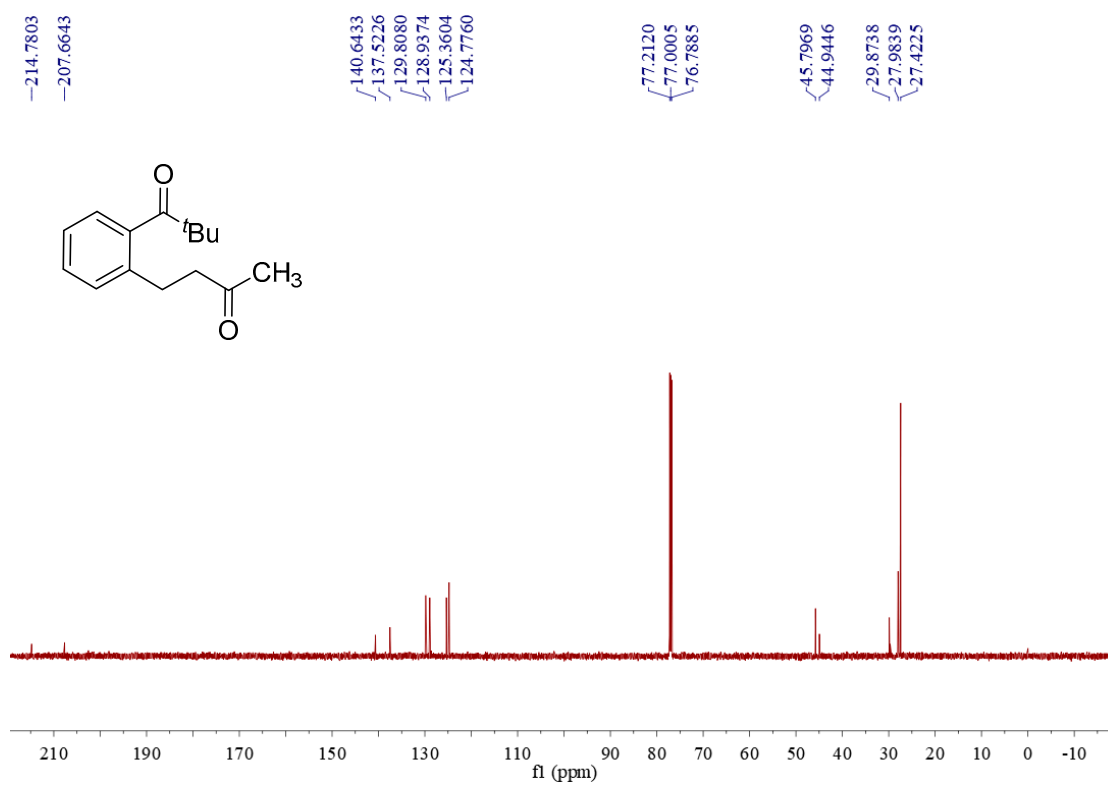
Figure S12. ¹H NMR spectra of compound 3f.Figure S13. ¹³C NMR spectra of compound 3f.

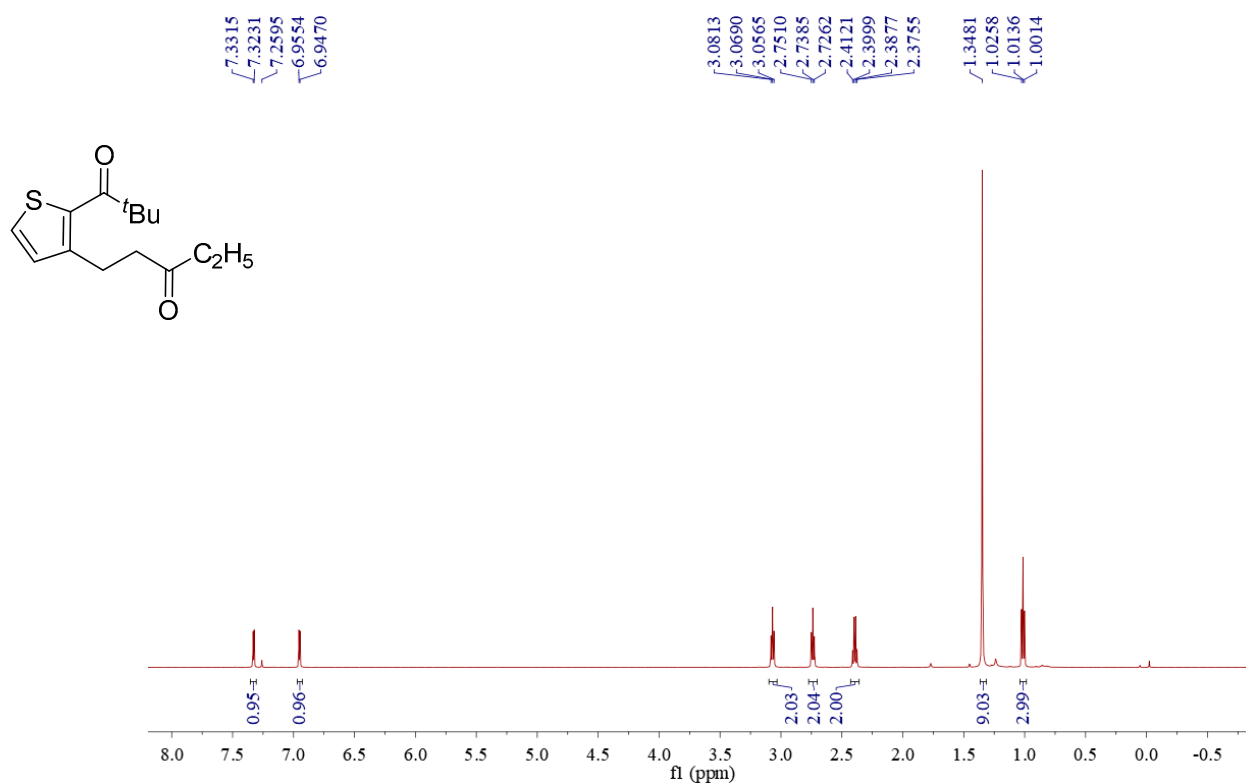
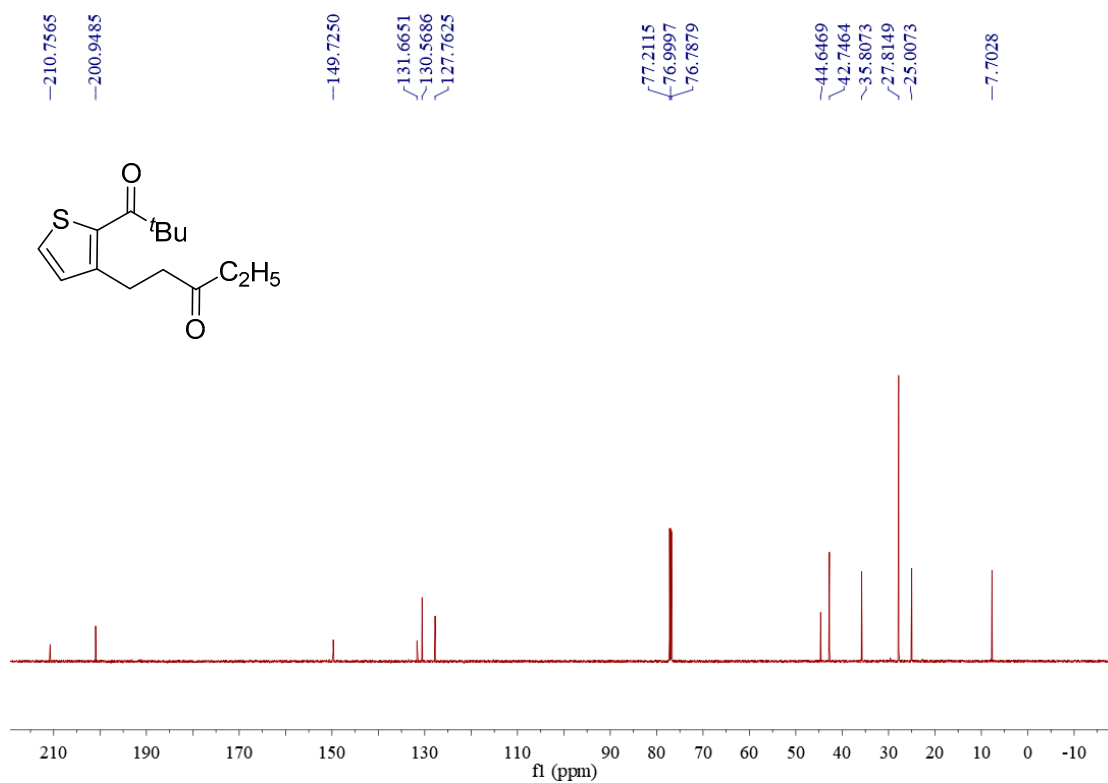
Figure S14. ¹H NMR spectra of compound 3g.Figure S15. ¹³C NMR spectra of compound 3g.

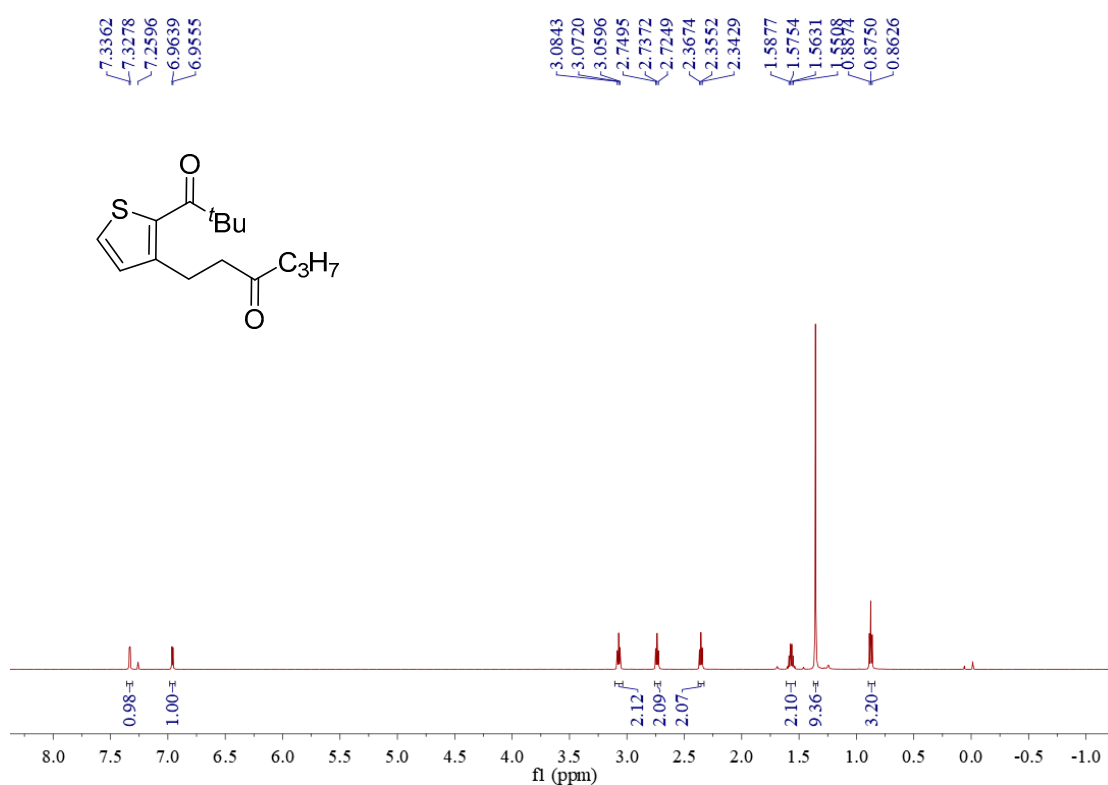
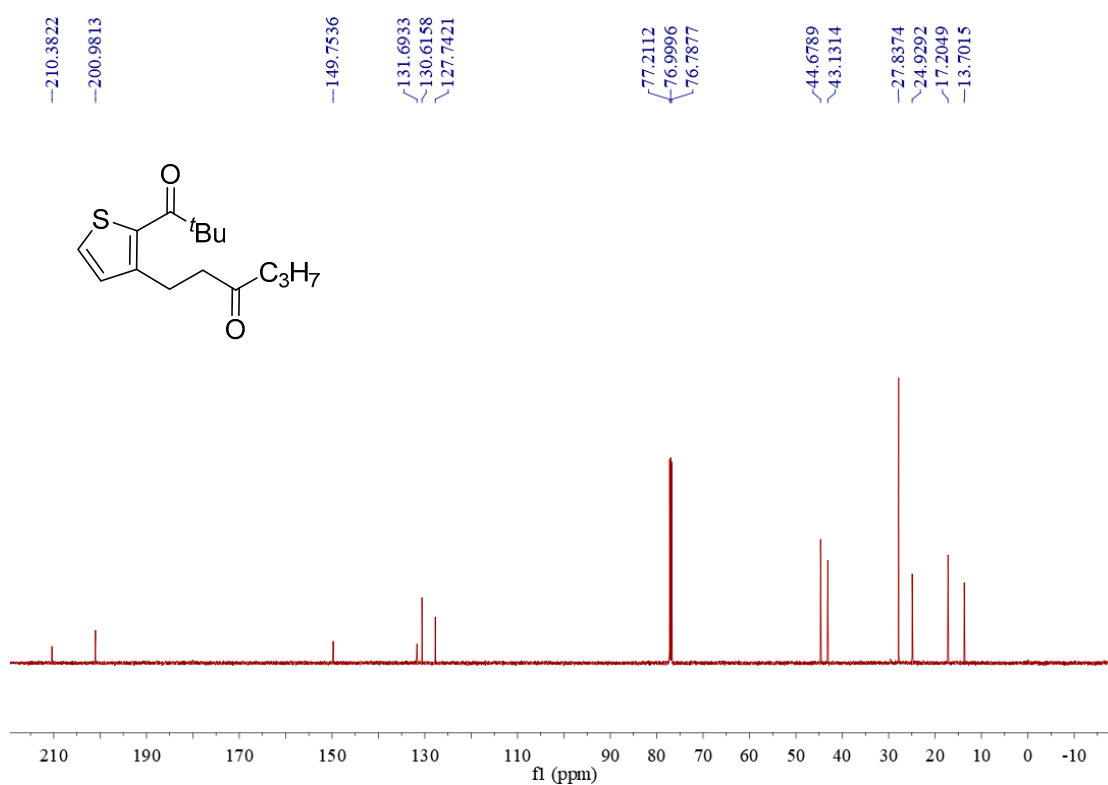
Figure S16. ¹H NMR spectra of compound 3h.Figure S17. ¹³C NMR spectra of compound 3h.

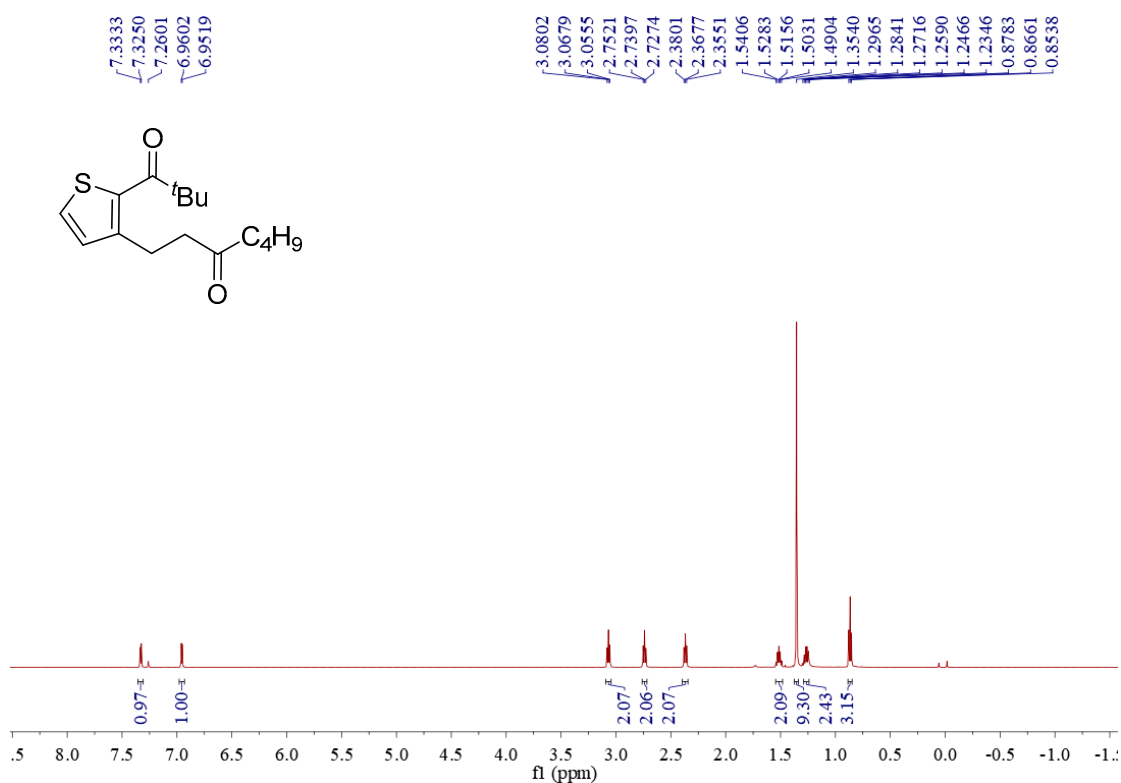
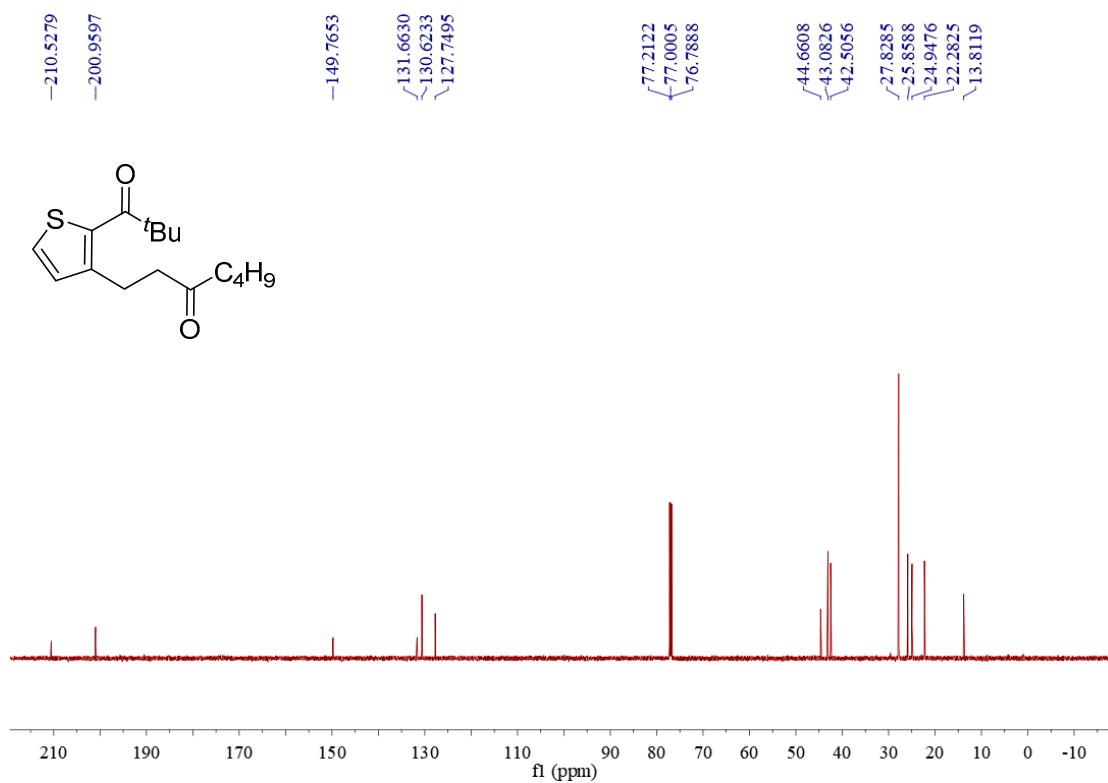
Figure S18. ^1H NMR spectra of compound **3i**.Figure S19. ^{13}C NMR spectra of compound **3i**.

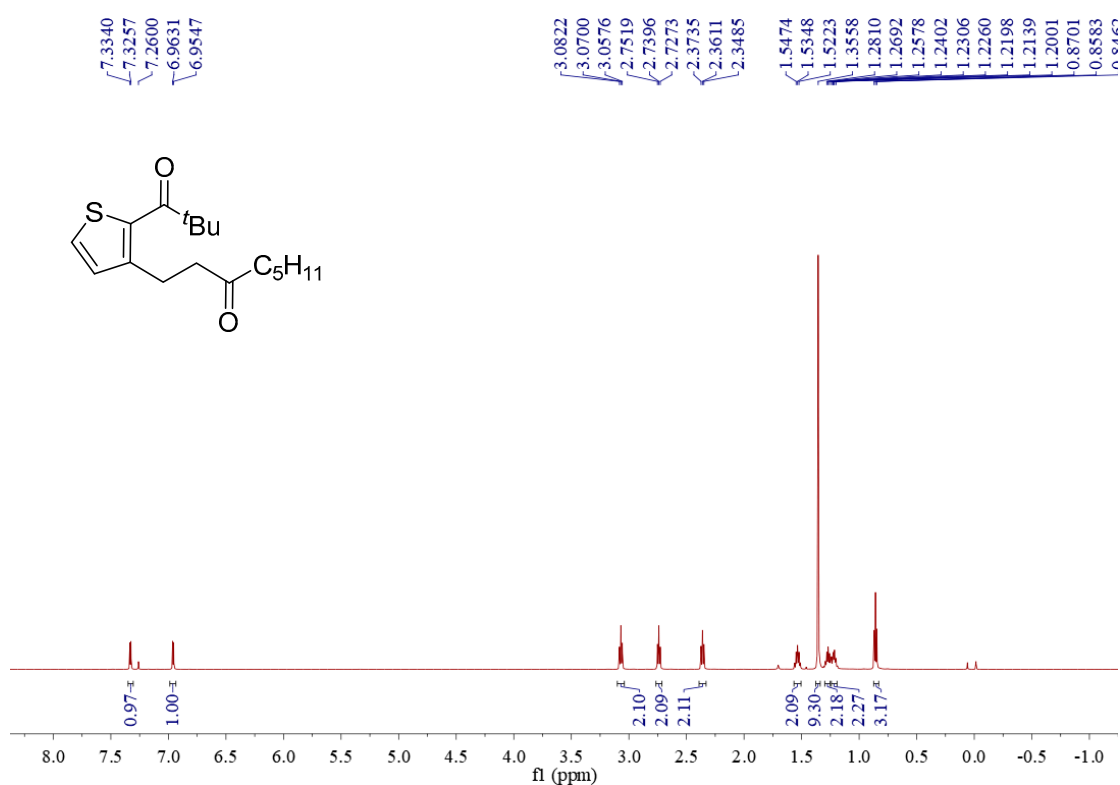
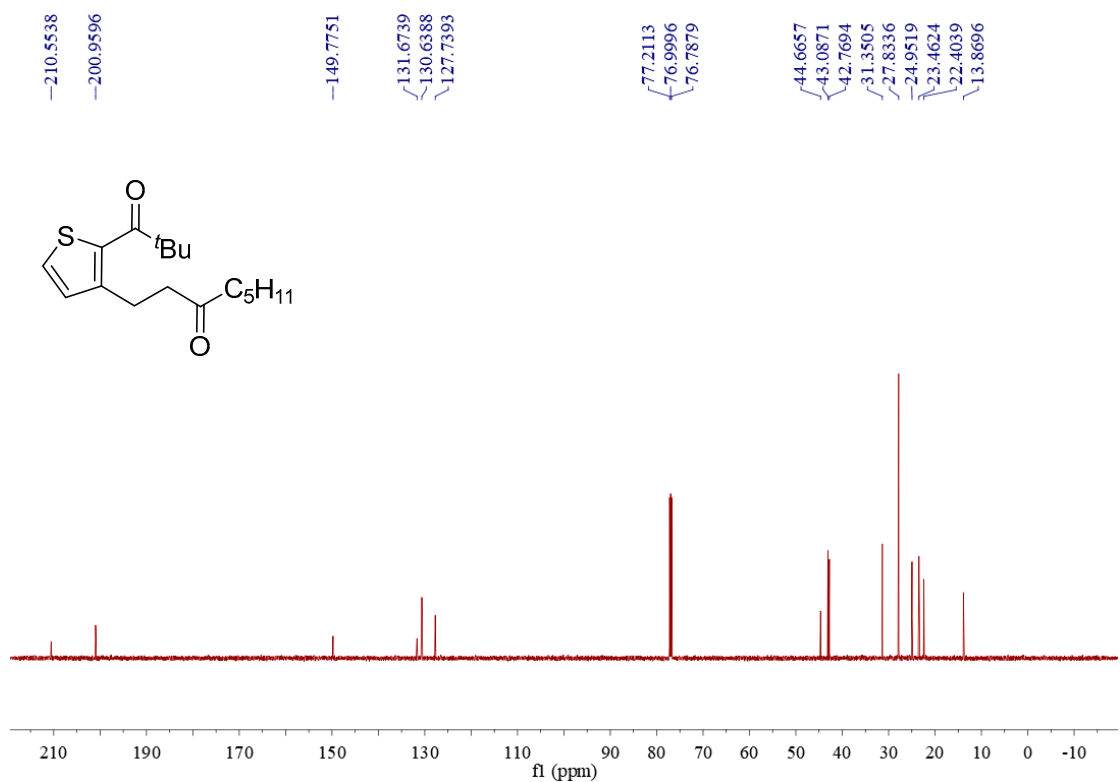
Figure S20. ¹H NMR spectra of compound 3j.Figure S21. ¹³C NMR spectra of compound 3j.

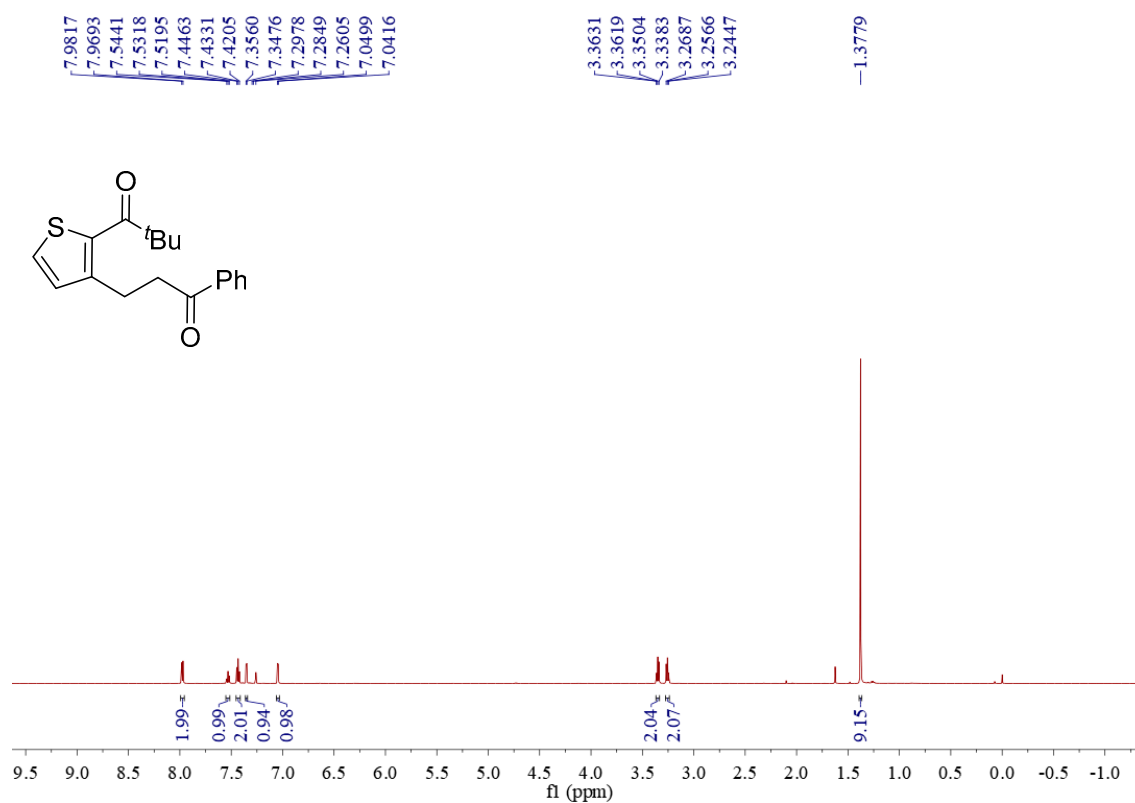
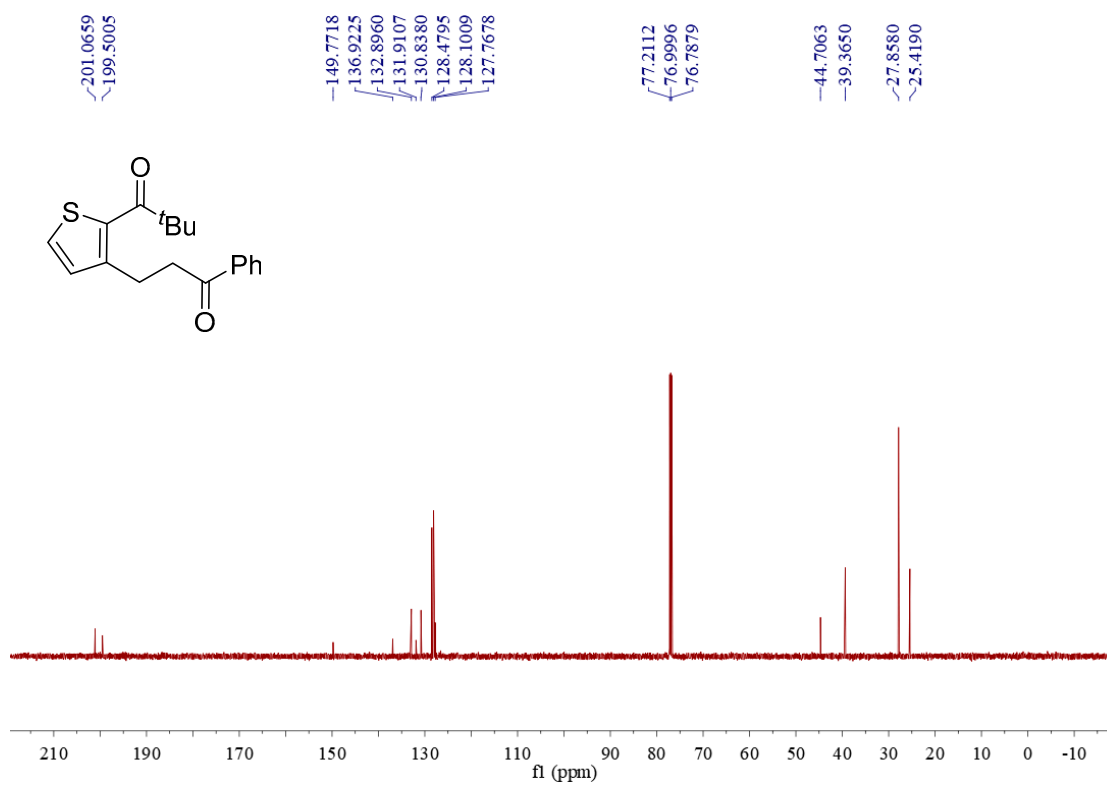
Figure S22. ¹H NMR spectra of compound 3k.Figure S23. ¹³C NMR spectra of compound 3k.

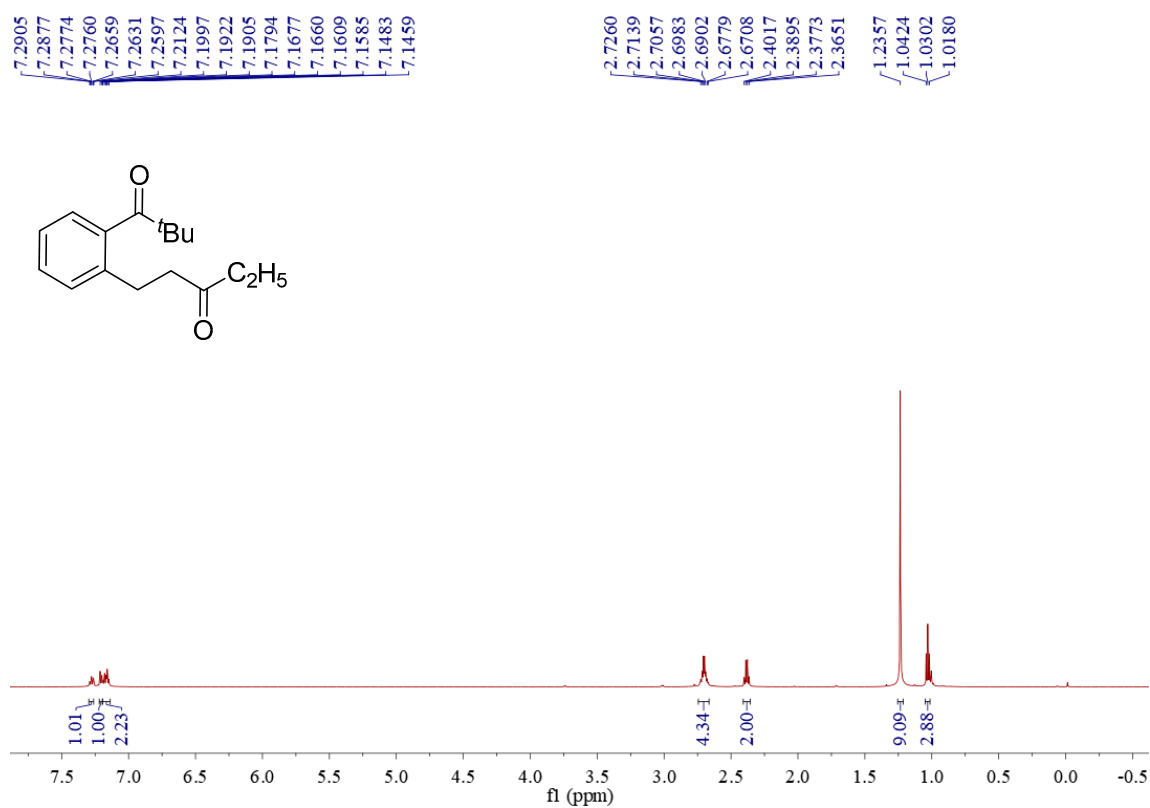
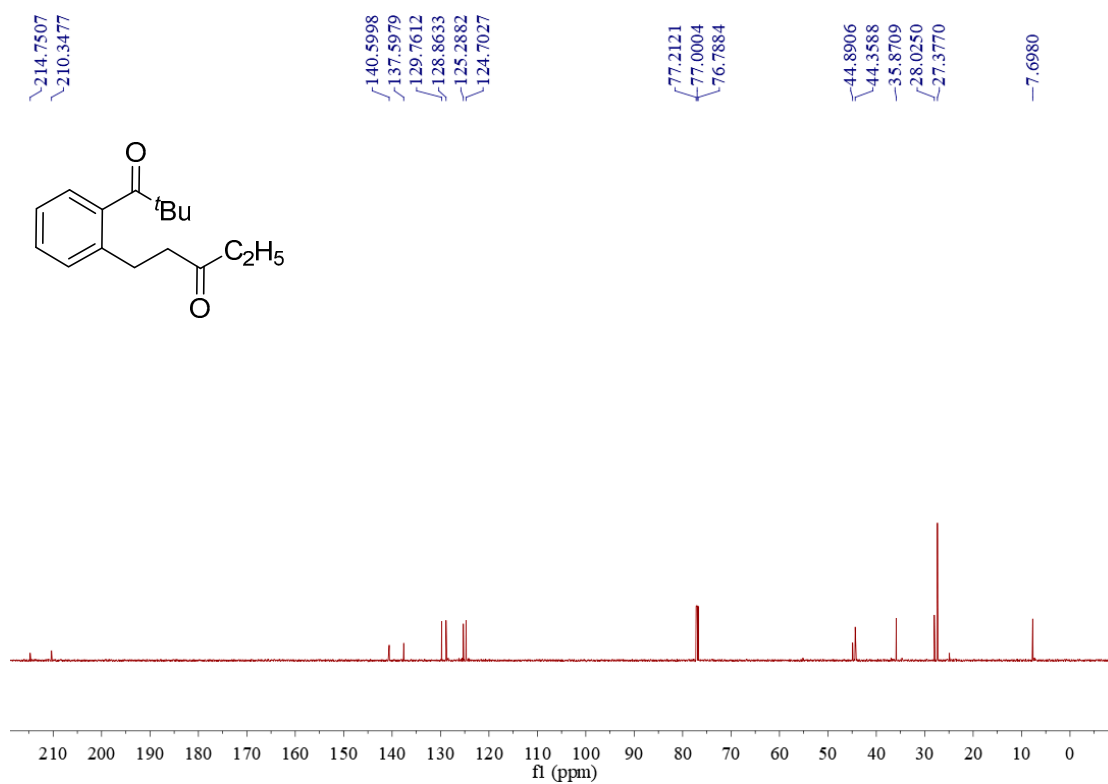
Figure S24. ¹H NMR spectra of compound 3l.Figure S25. ¹³C NMR spectra of compound 3l.

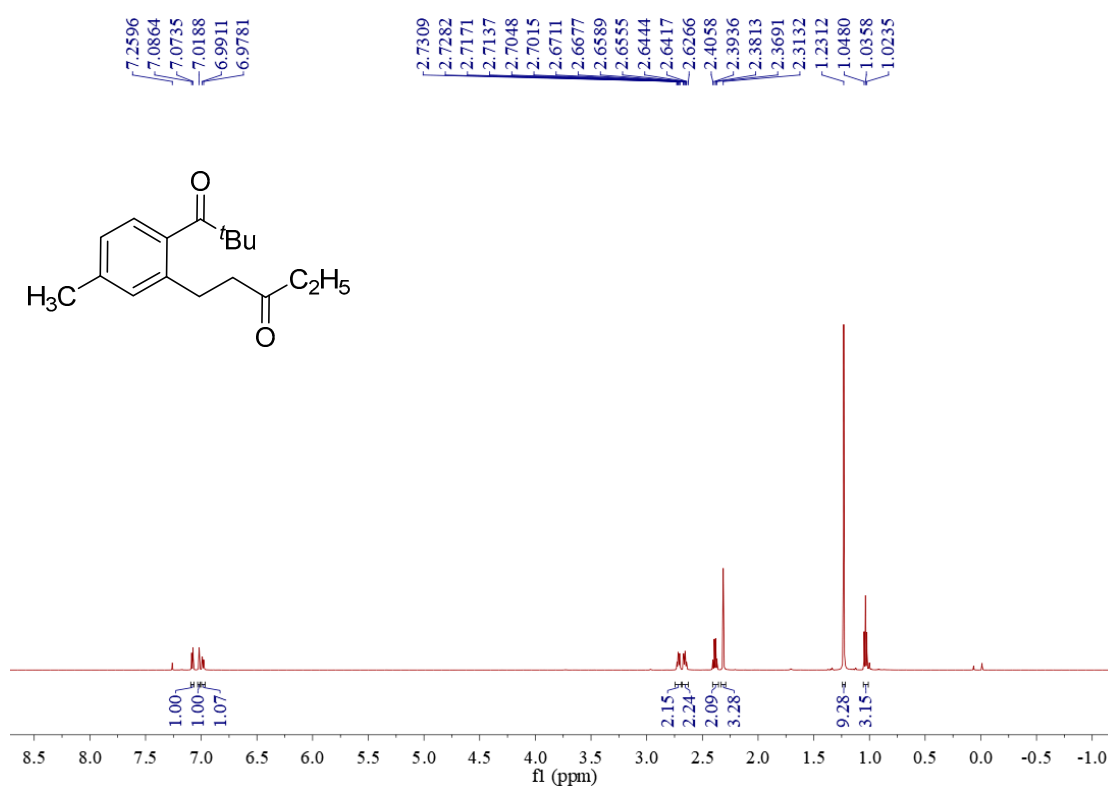
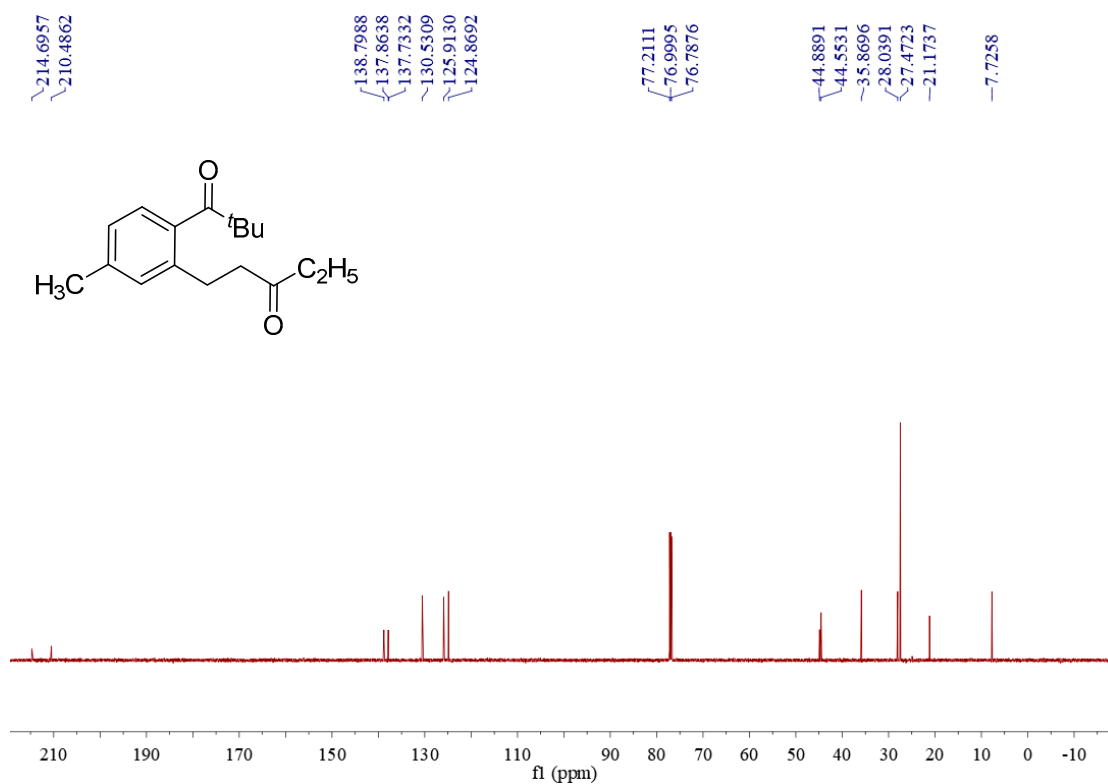
Figure S26. ^1H NMR spectra of compound **3m**.Figure S27. ^{13}C NMR spectra of compound **3m**.

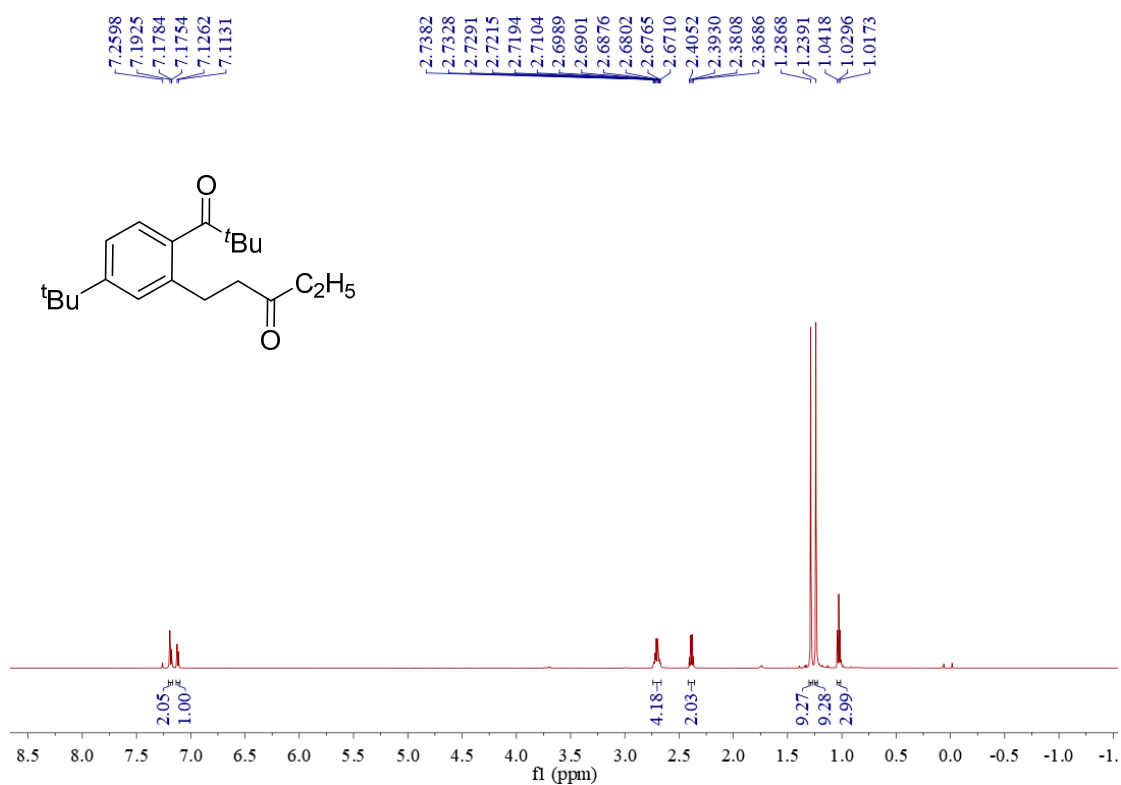
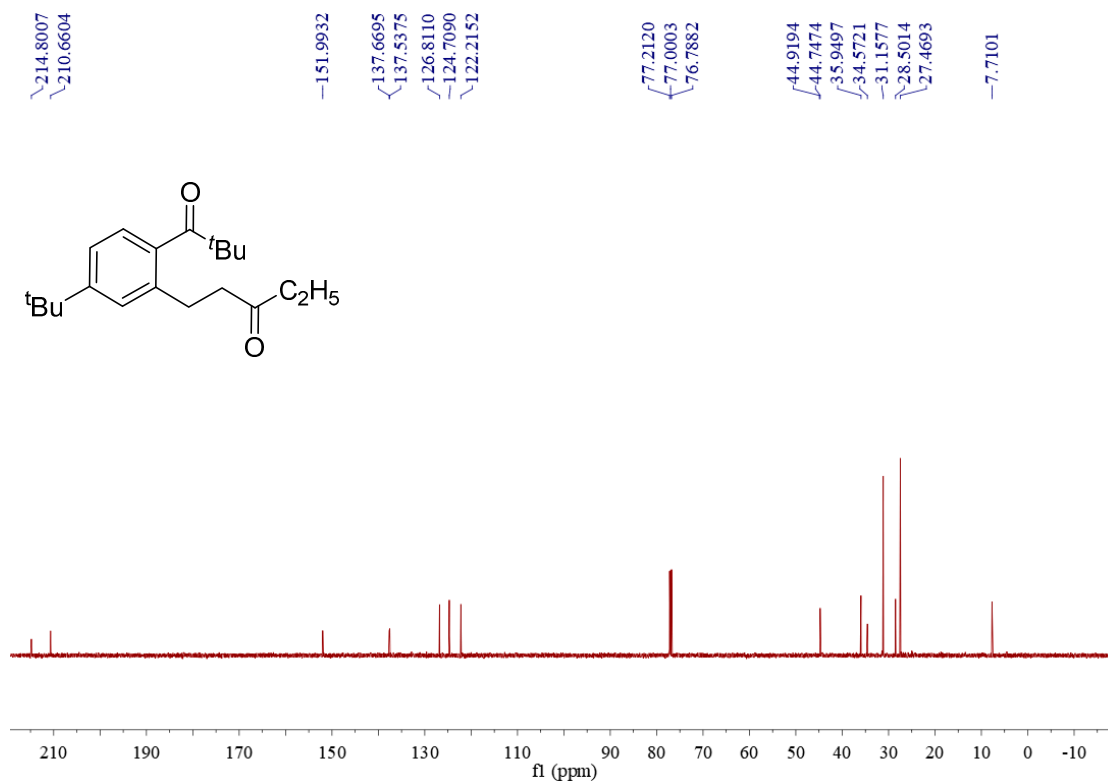
Figure S28. ¹H NMR spectra of compound 3n.Figure S29. ¹³C NMR spectra of compound 3n.

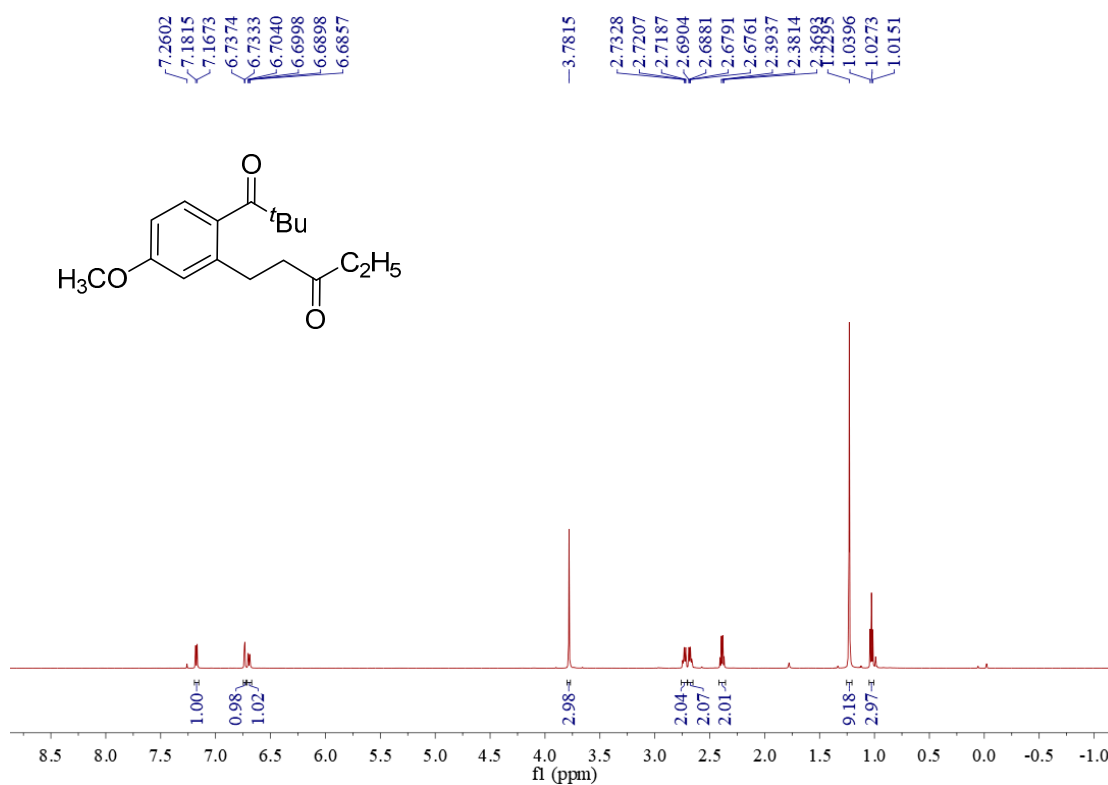
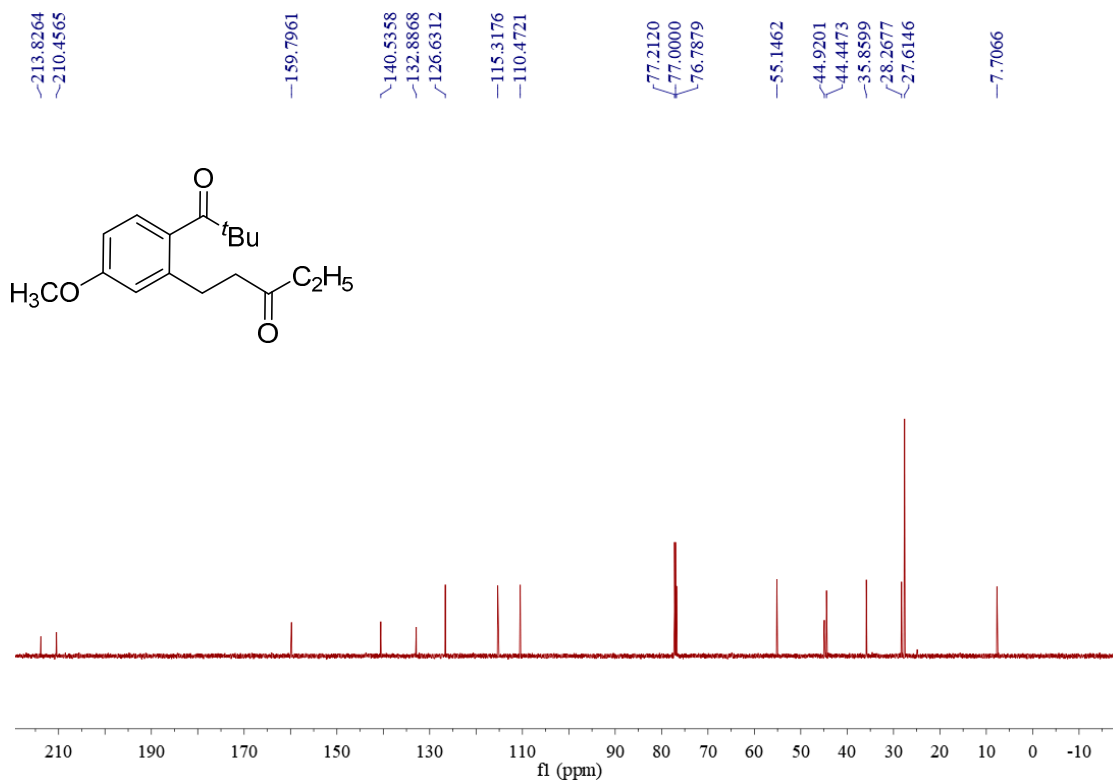
Figure S30. ¹H NMR spectra of compound **3o**.Figure S31. ¹³C NMR spectra of compound **3o**.

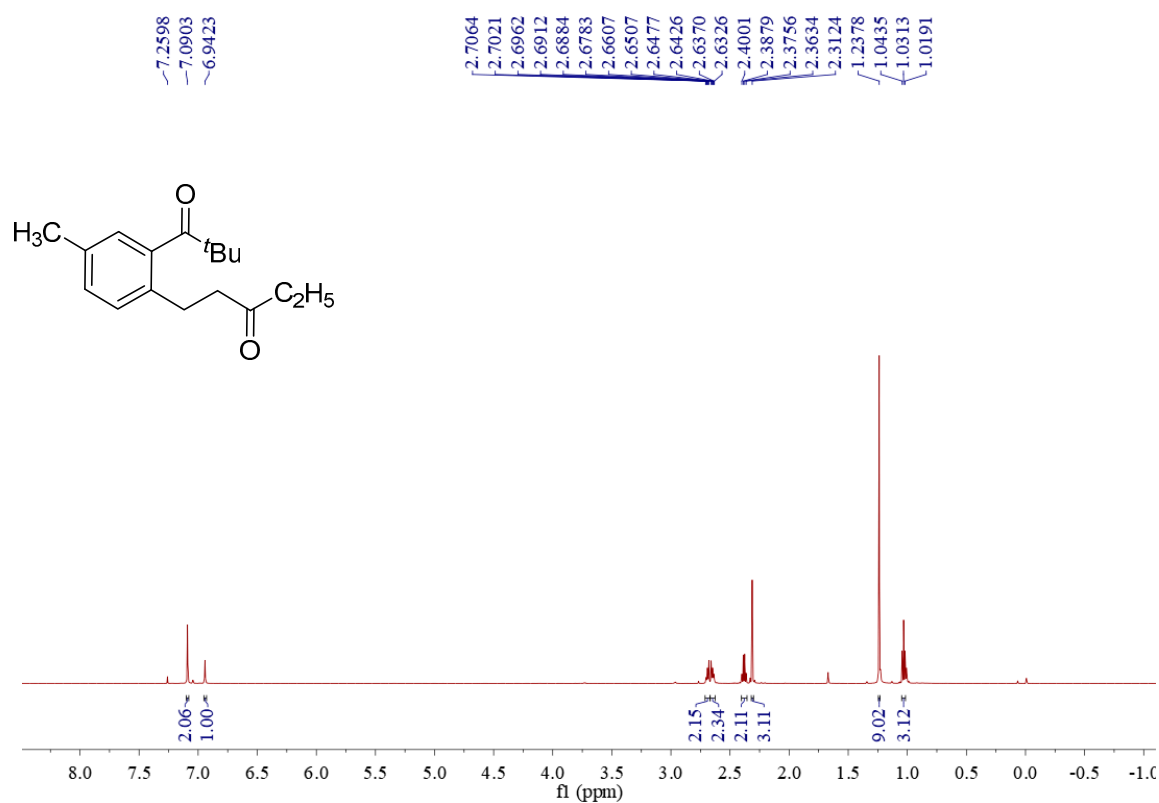
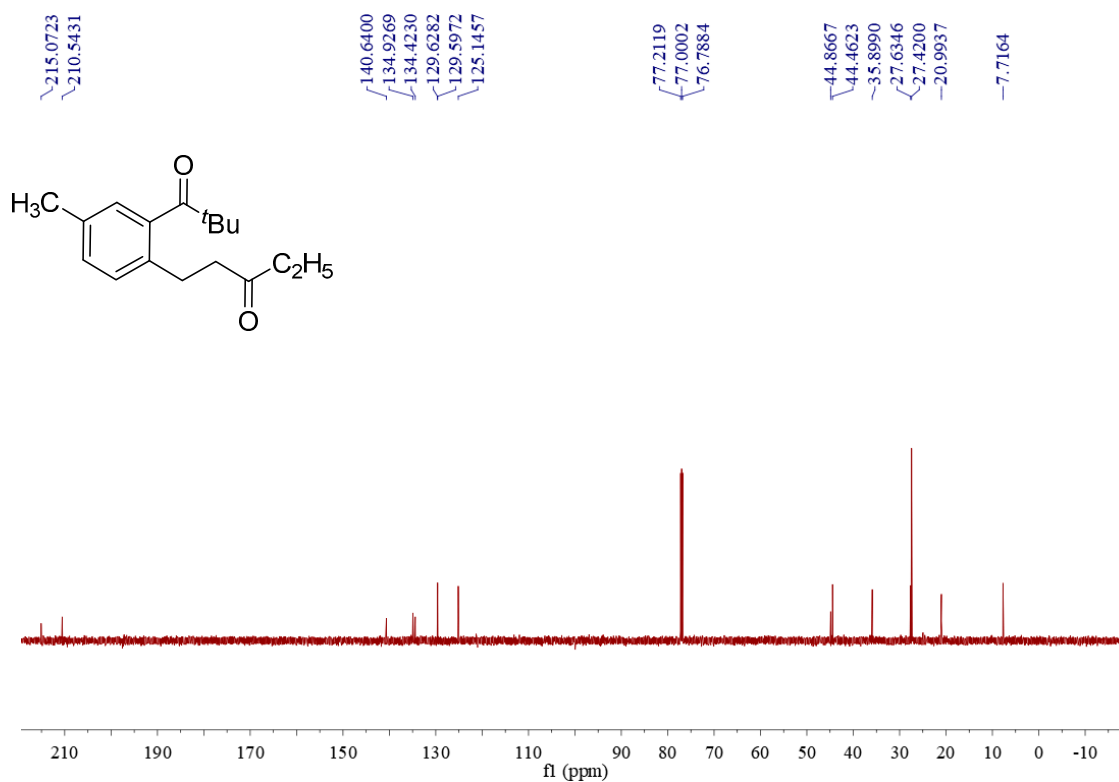
Figure S32. ¹H NMR spectra of compound 3p.Figure S33. ¹³C NMR spectra of compound 3p.

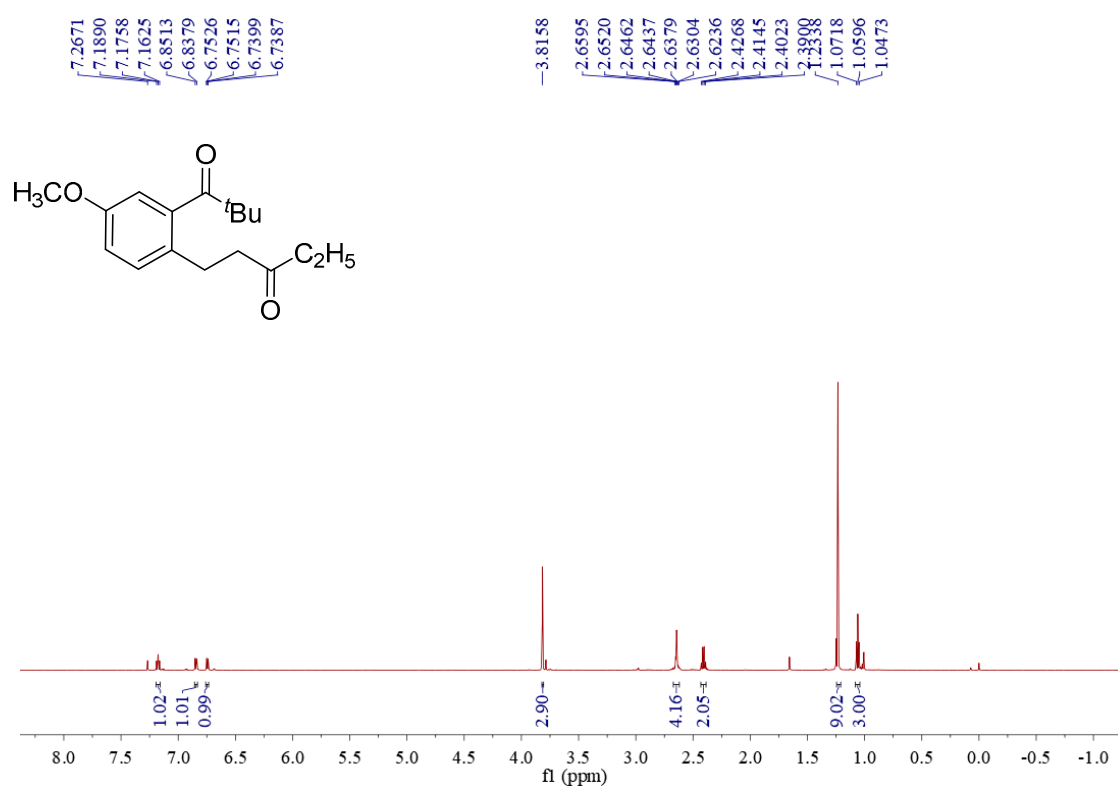
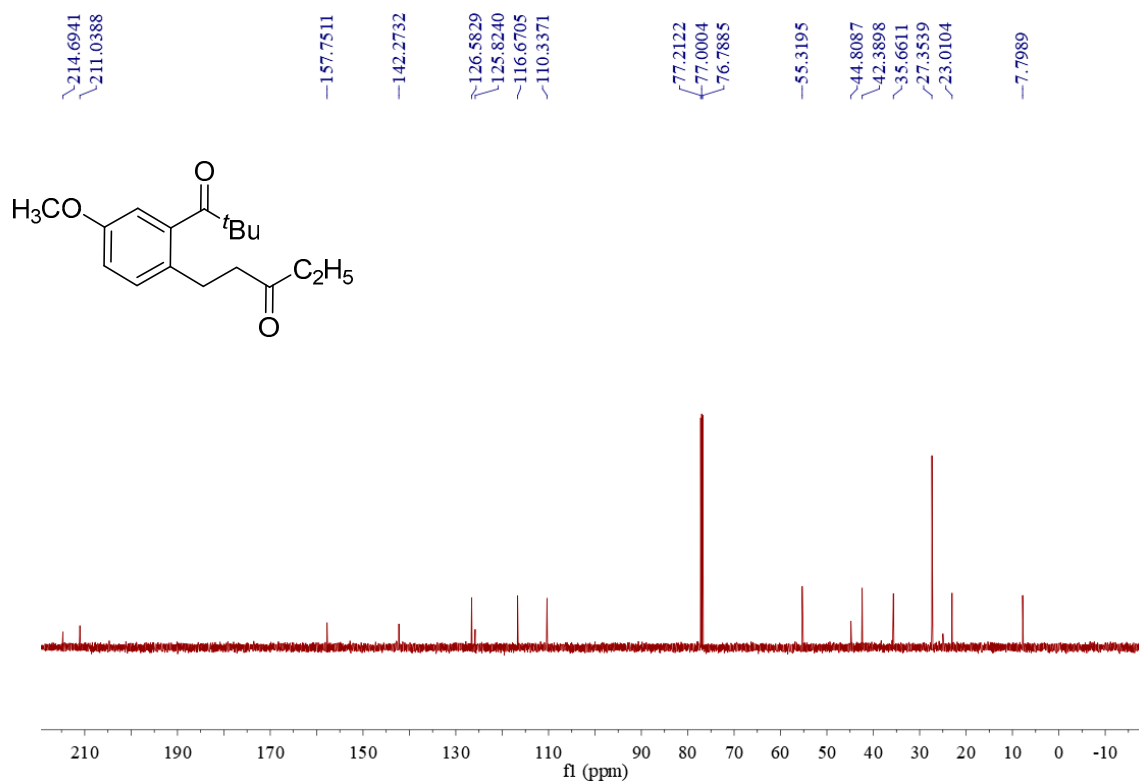
Figure S34. ¹H NMR spectra of compound 4a.Figure S35. ¹³C NMR spectra of compound 4a.

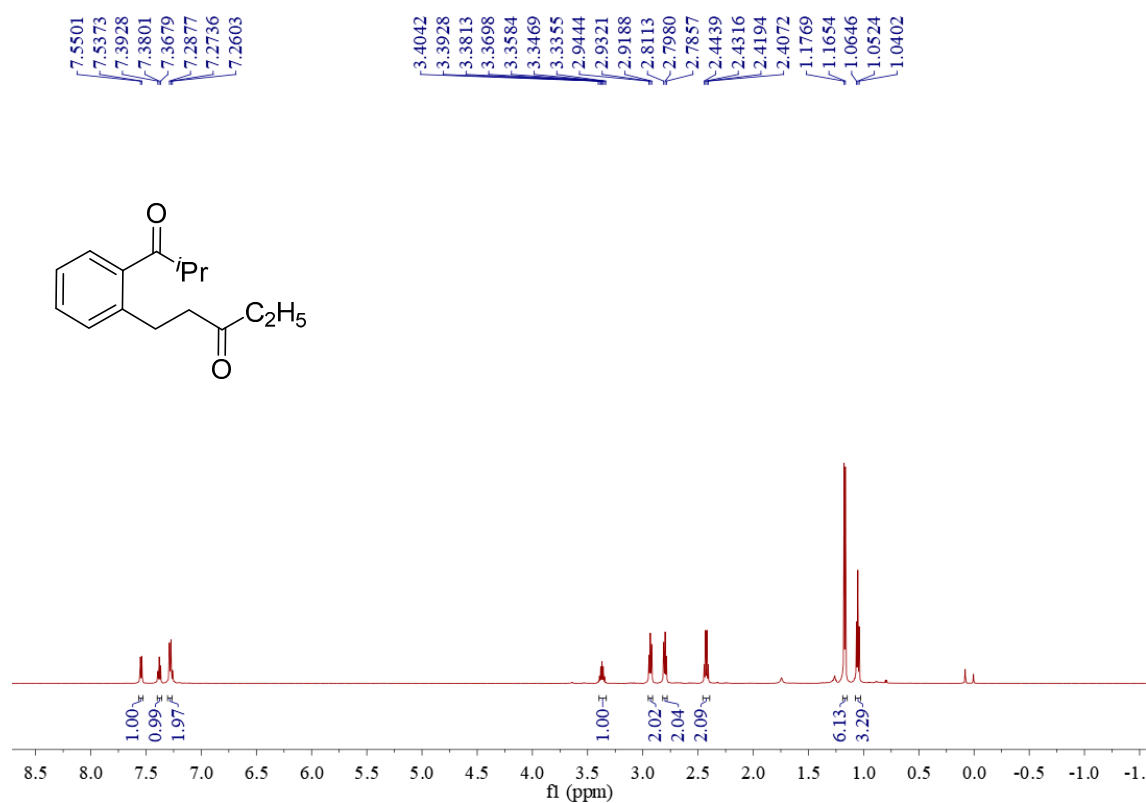
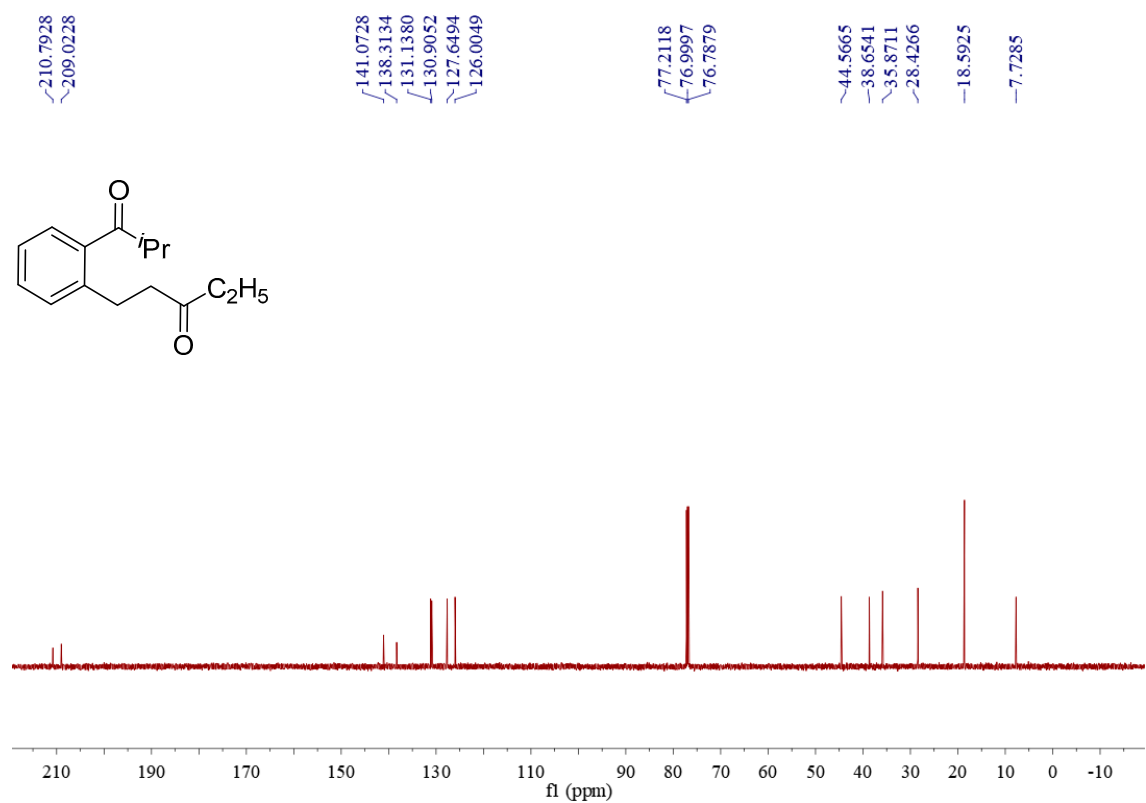
Figure S36. ¹H NMR spectra of compound **4b**.Figure S37. ¹³C NMR spectra of compound **4b**.

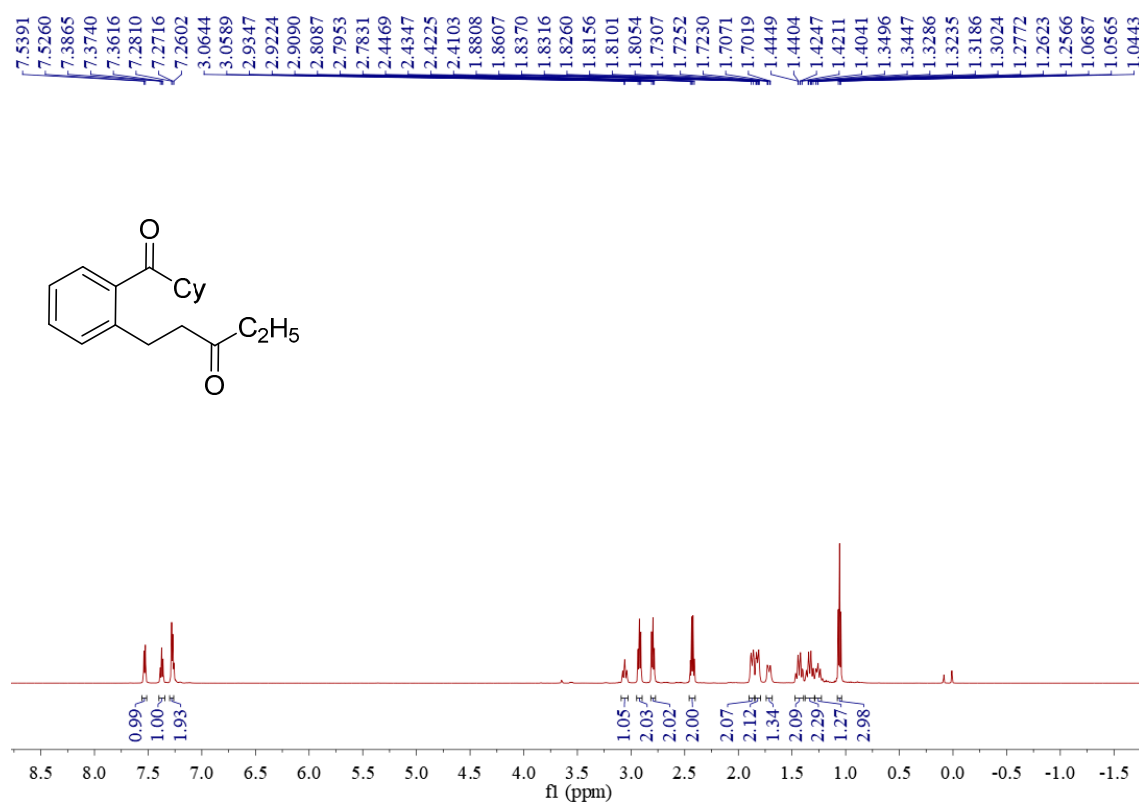
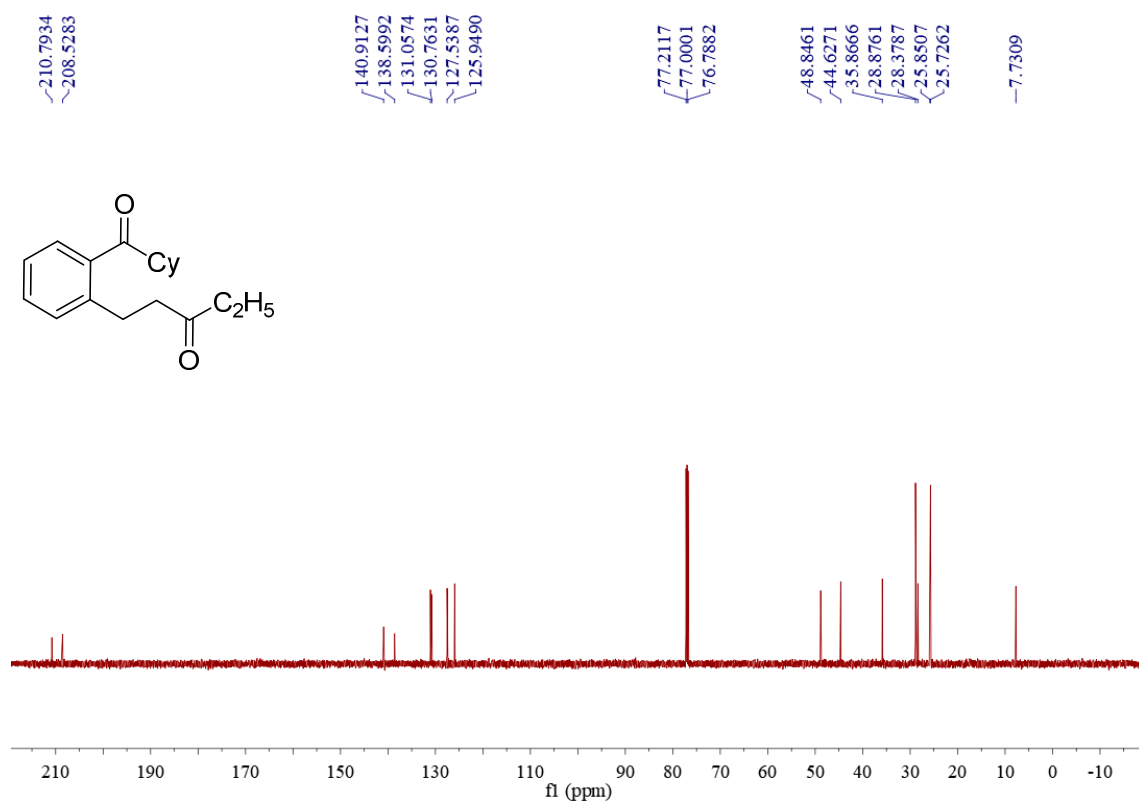
Figure S38. ¹H NMR spectra of compound 4c.Figure S39. ¹³C NMR spectra of compound 4c.

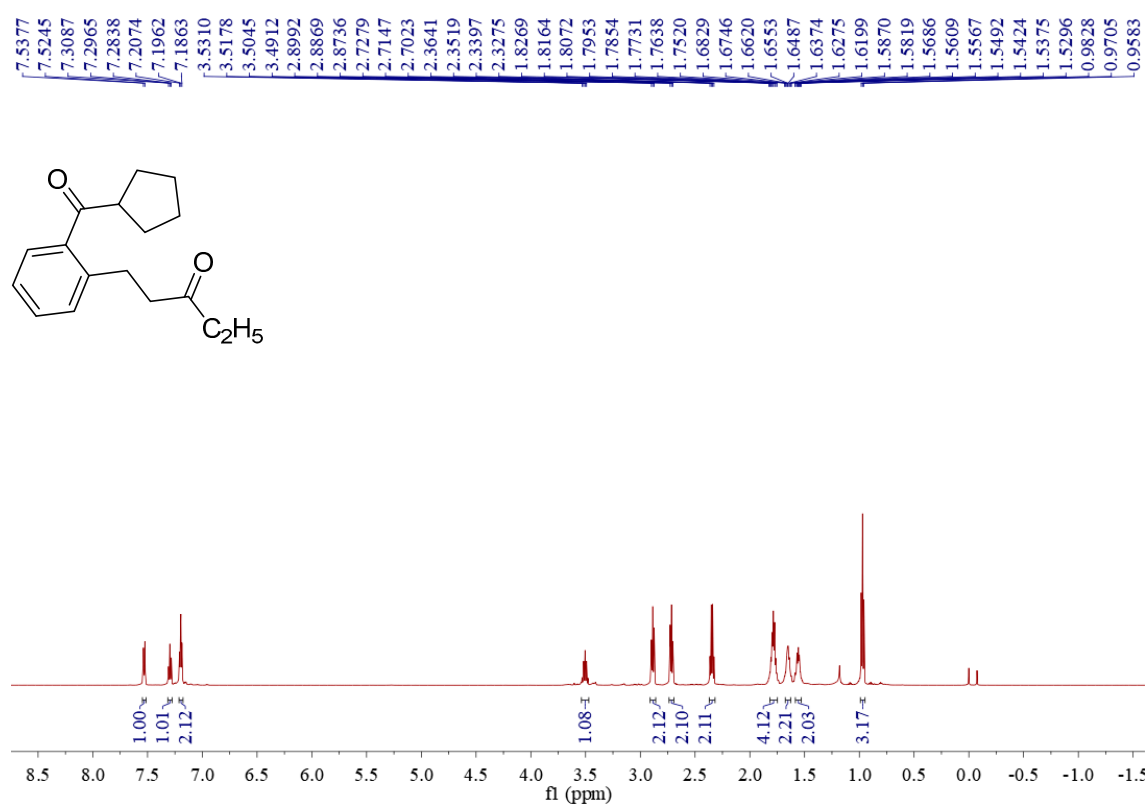
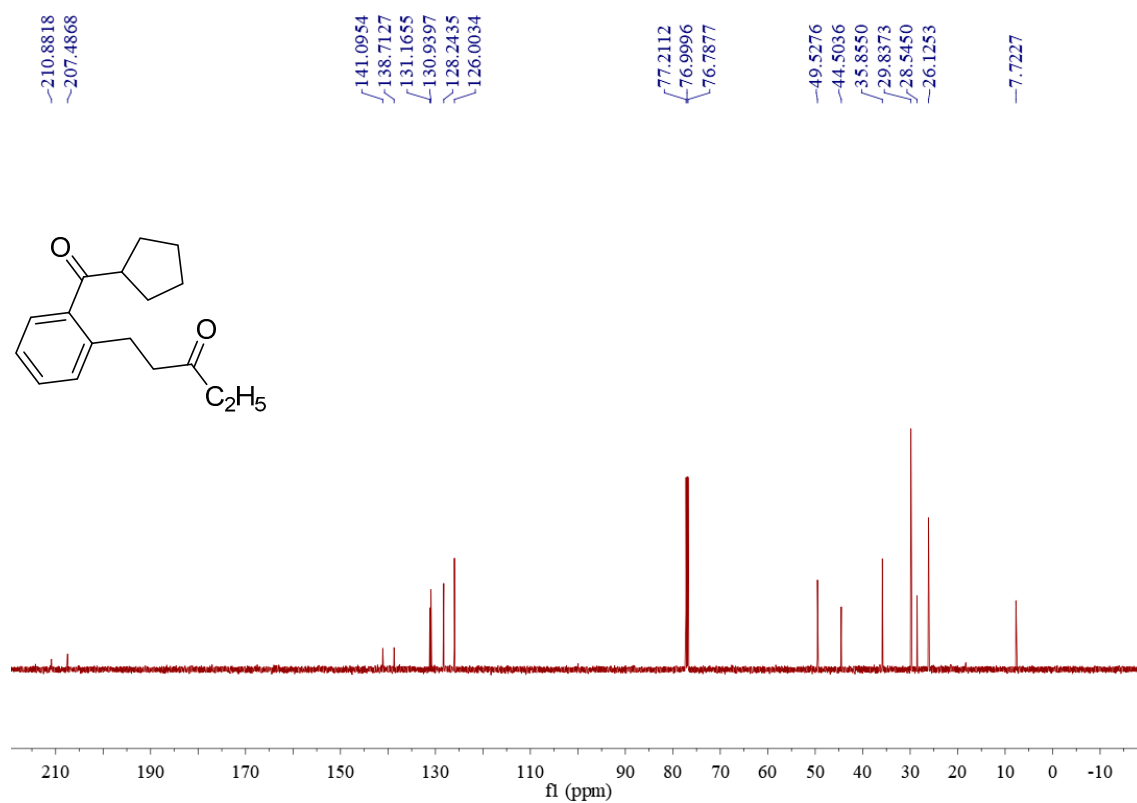
Figure S40. ¹H NMR spectra of compound 4d.Figure S41. ¹³C NMR spectra of compound 4d.

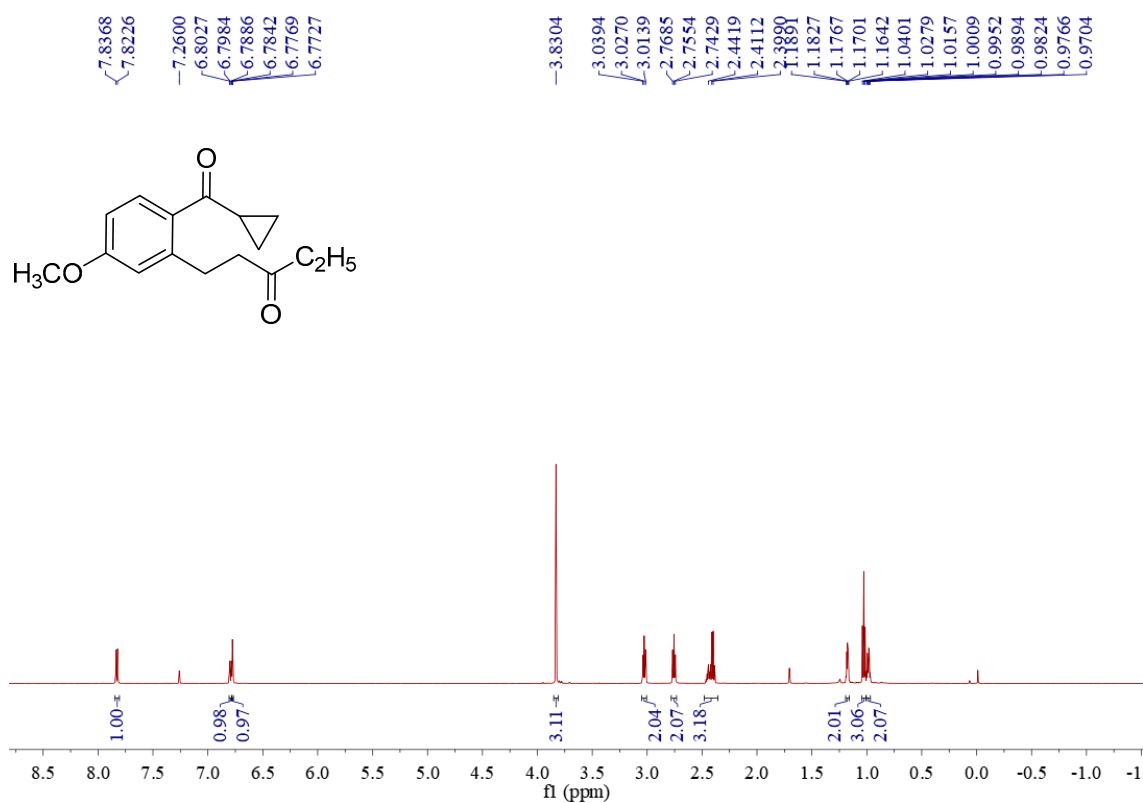
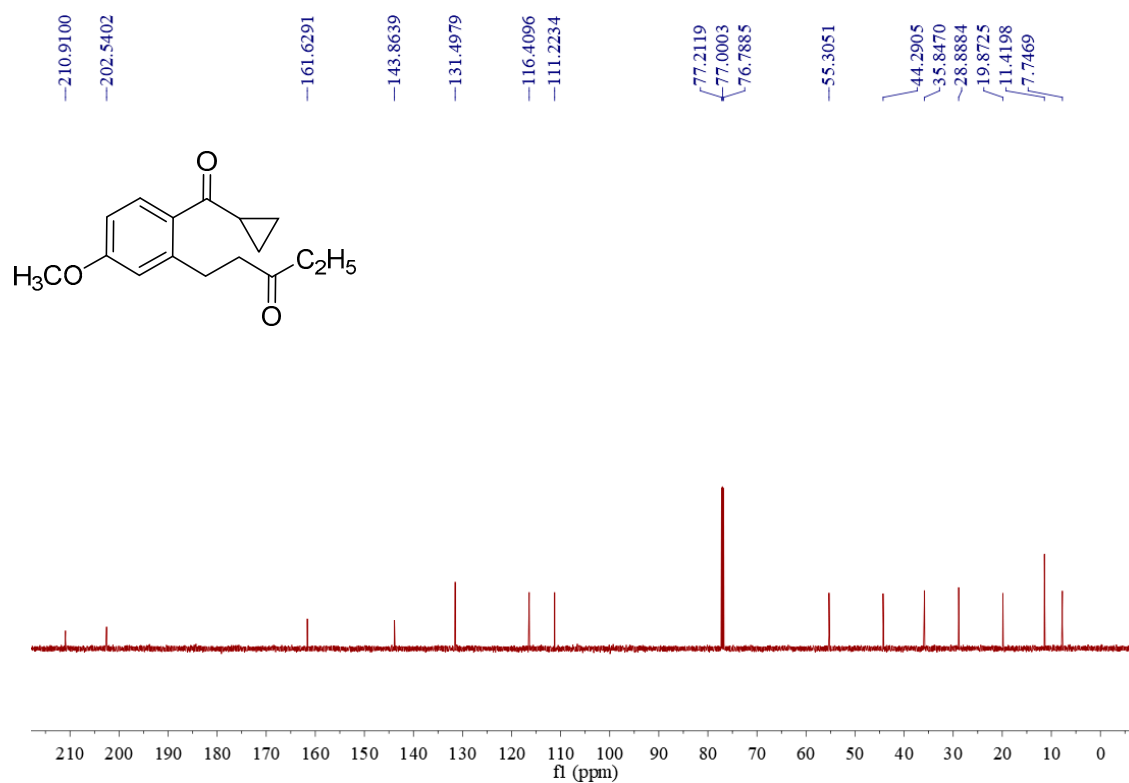
Figure S42. ¹H NMR spectra of compound 4e.Figure S43. ¹³C NMR spectra of compound 4e.

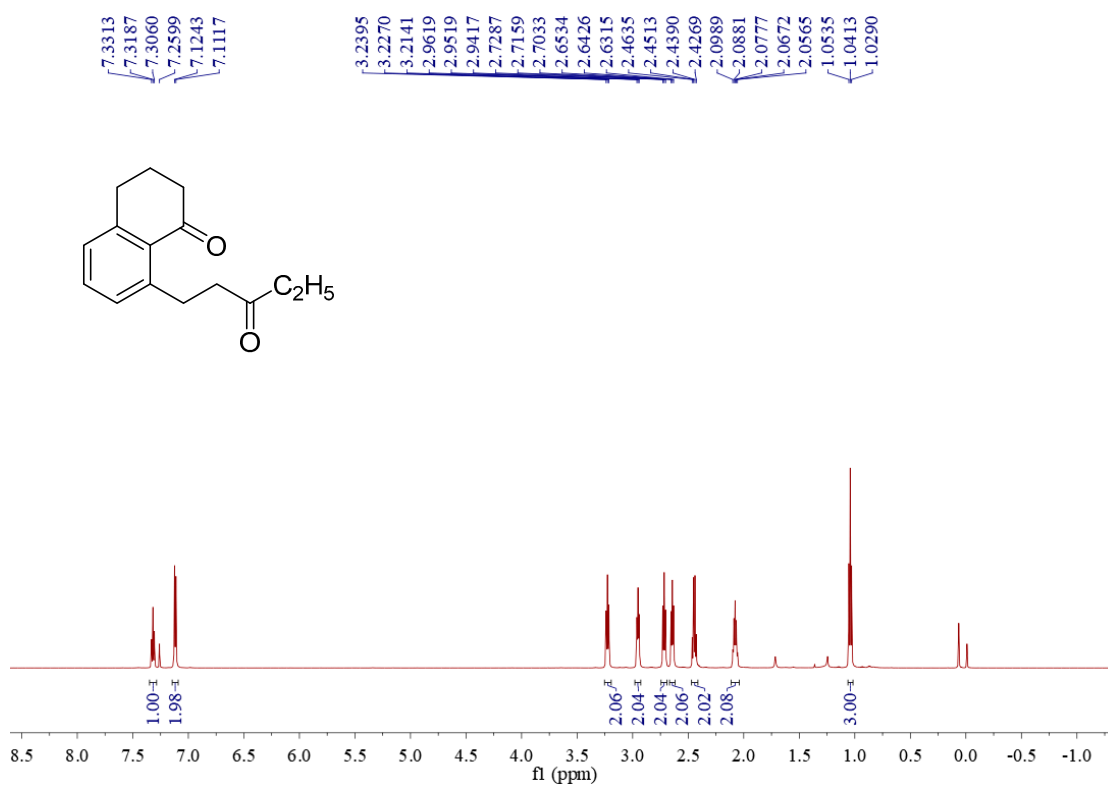
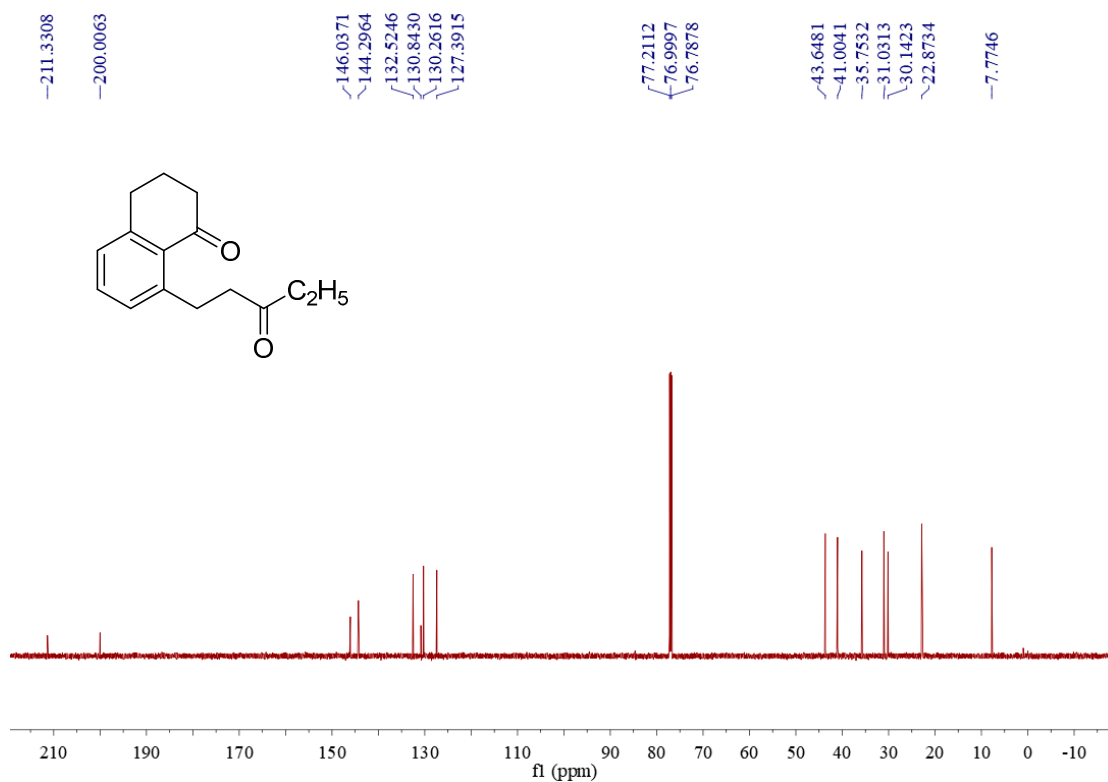
Figure S44. ¹H NMR spectra of compound 4f.Figure S45. ¹³C NMR spectra of compound 4f.

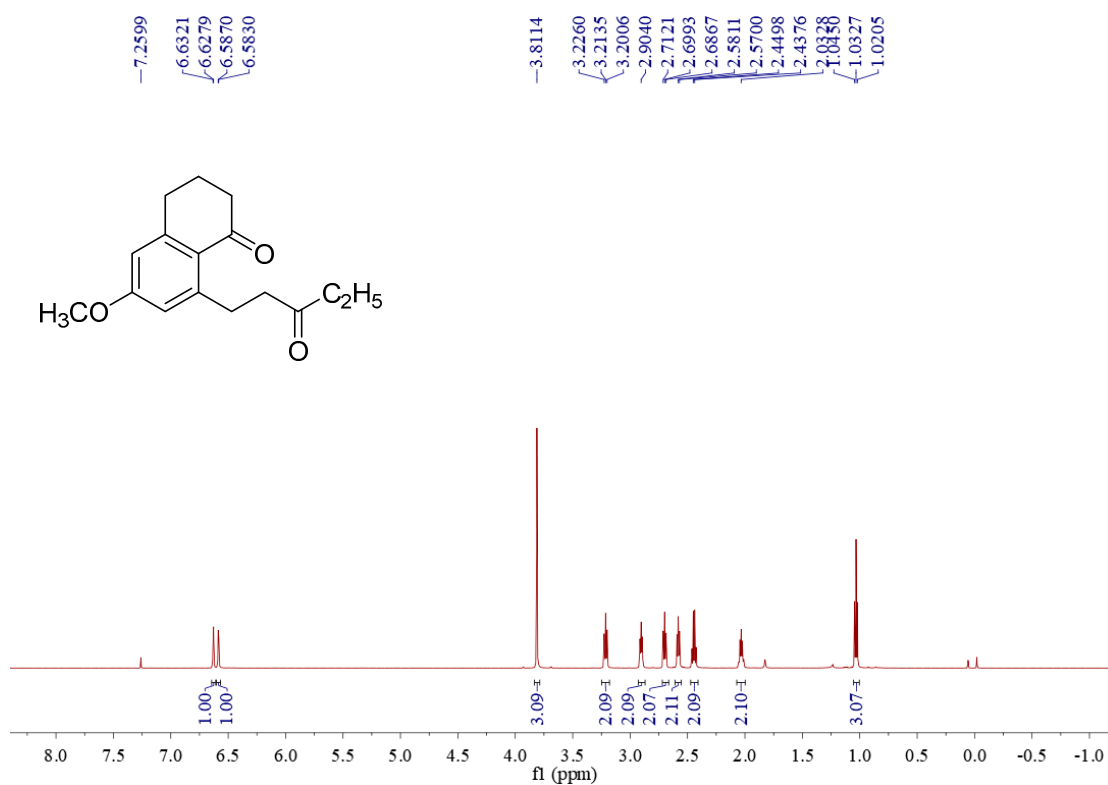
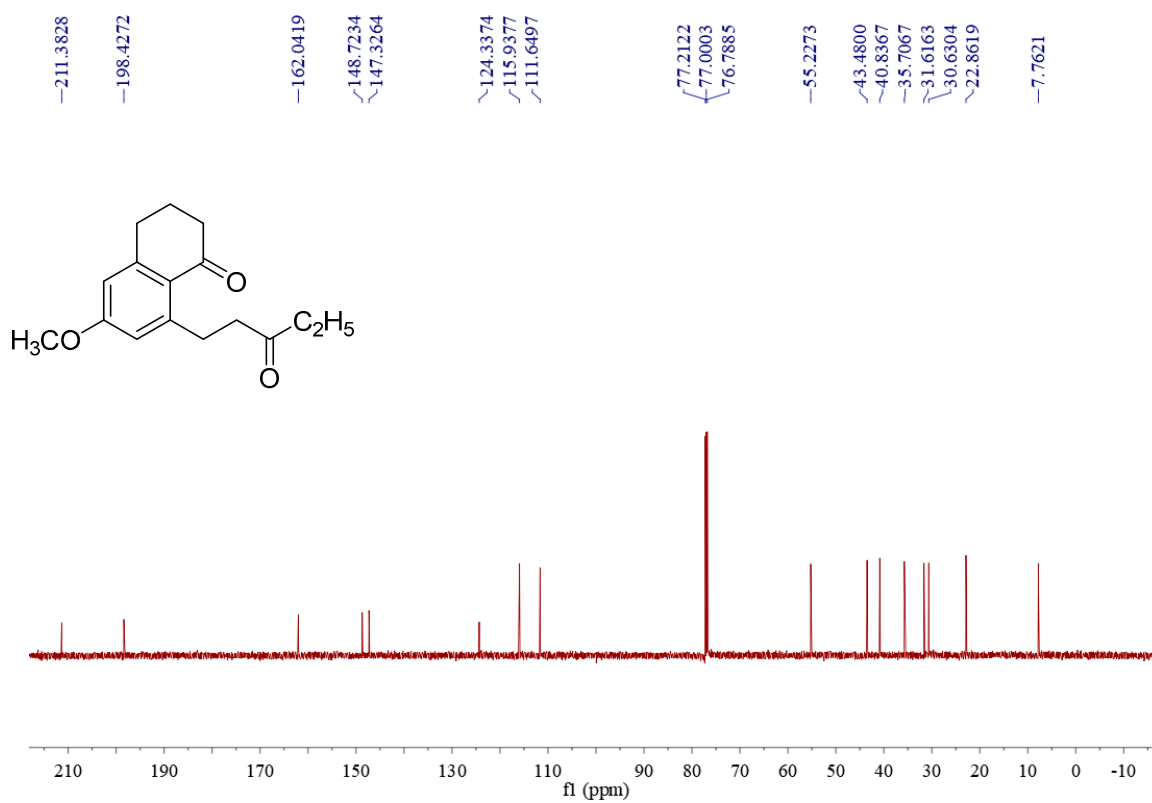
Figure S46. ¹H NMR spectra of compound **4g**.Figure S47. ¹³C NMR spectra of compound **4g**.

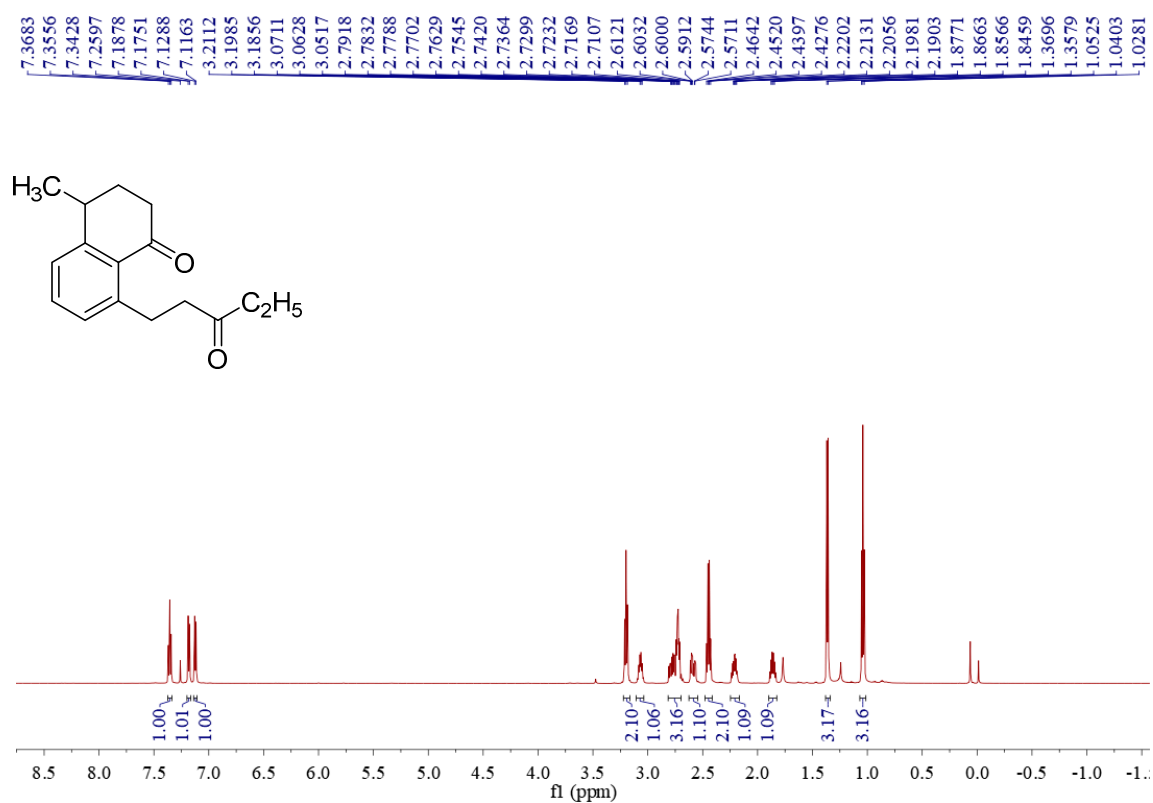
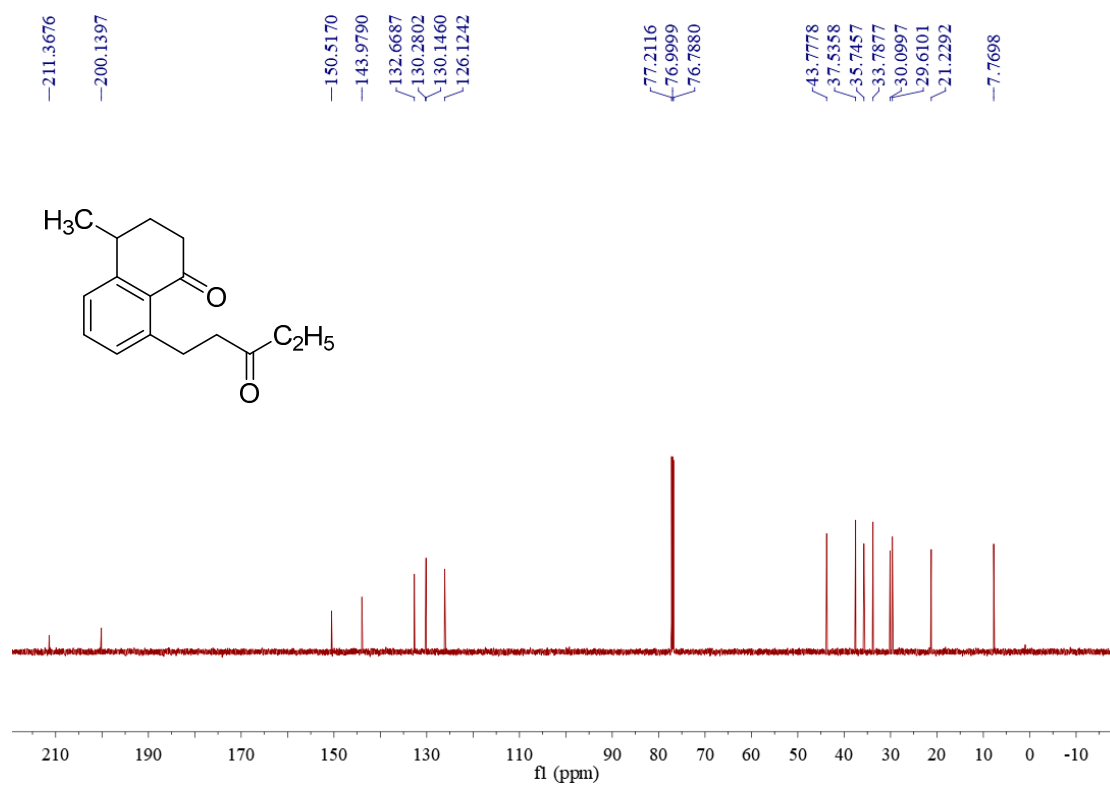
Figure S48. ¹H NMR spectra of compound 4h.Figure S49. ¹³C NMR spectra of compound 4h.

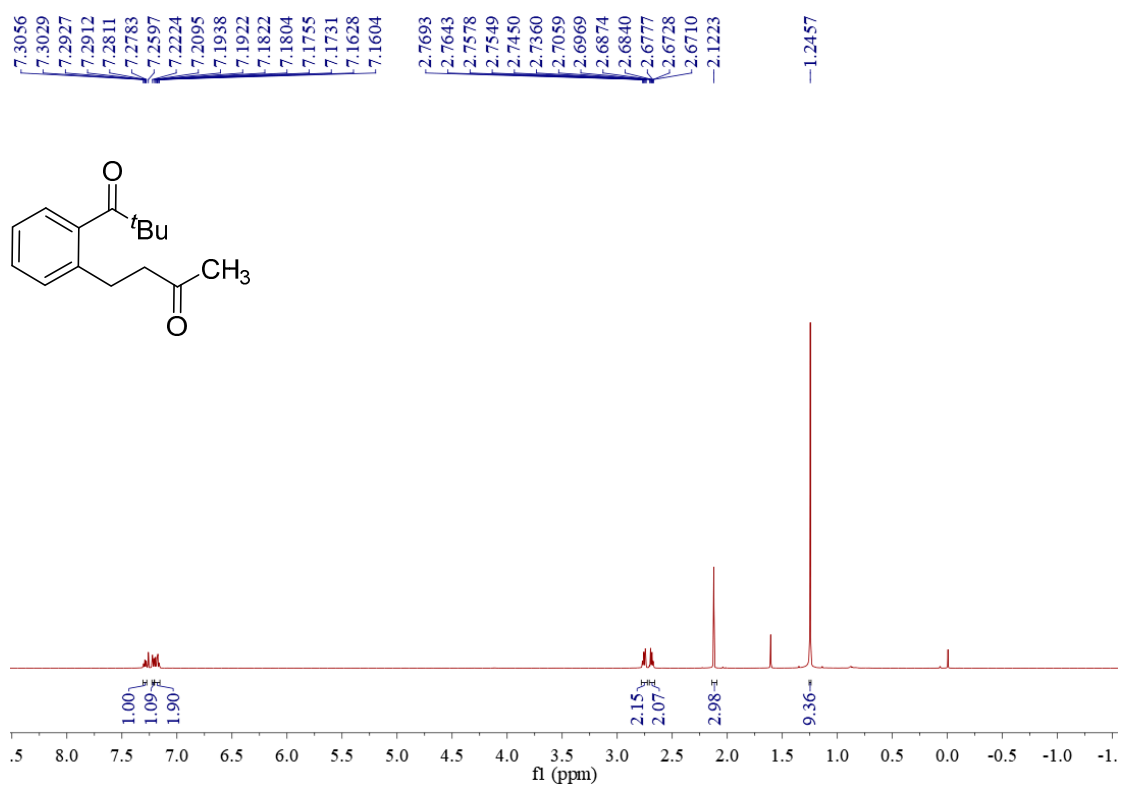
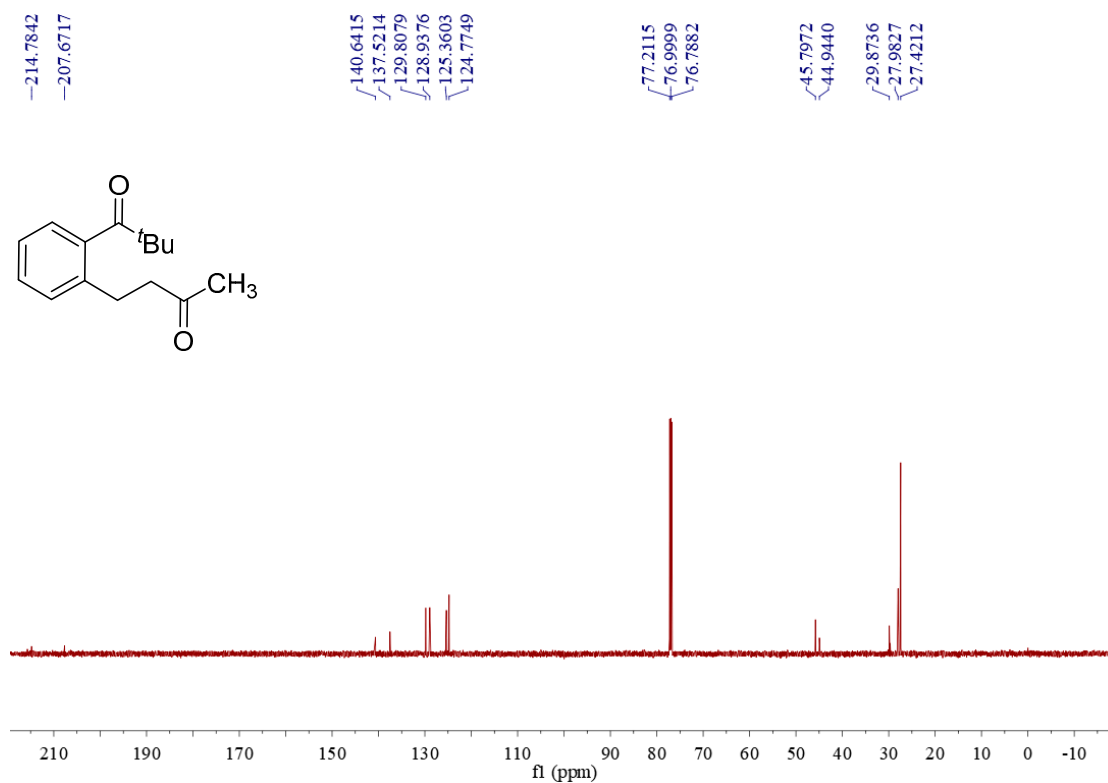
Figure S50. ¹H NMR spectra of compound **4i**.Figure S51. ¹³C NMR spectra of compound **4i**.

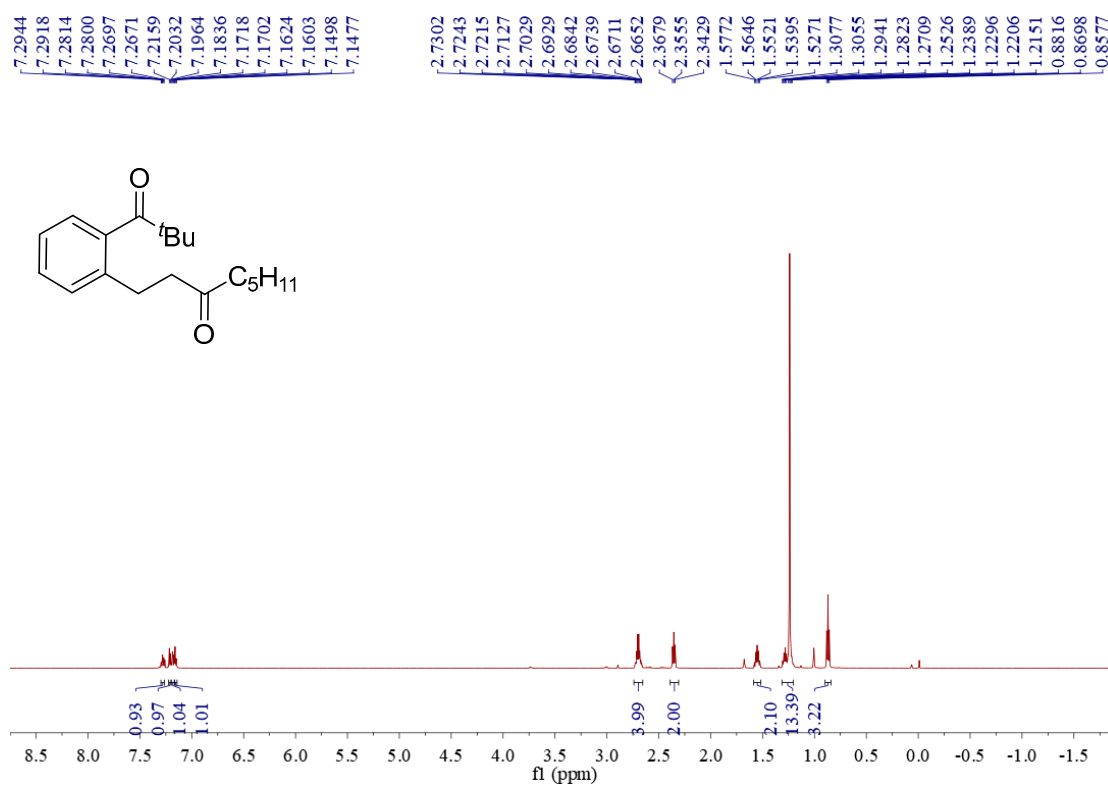
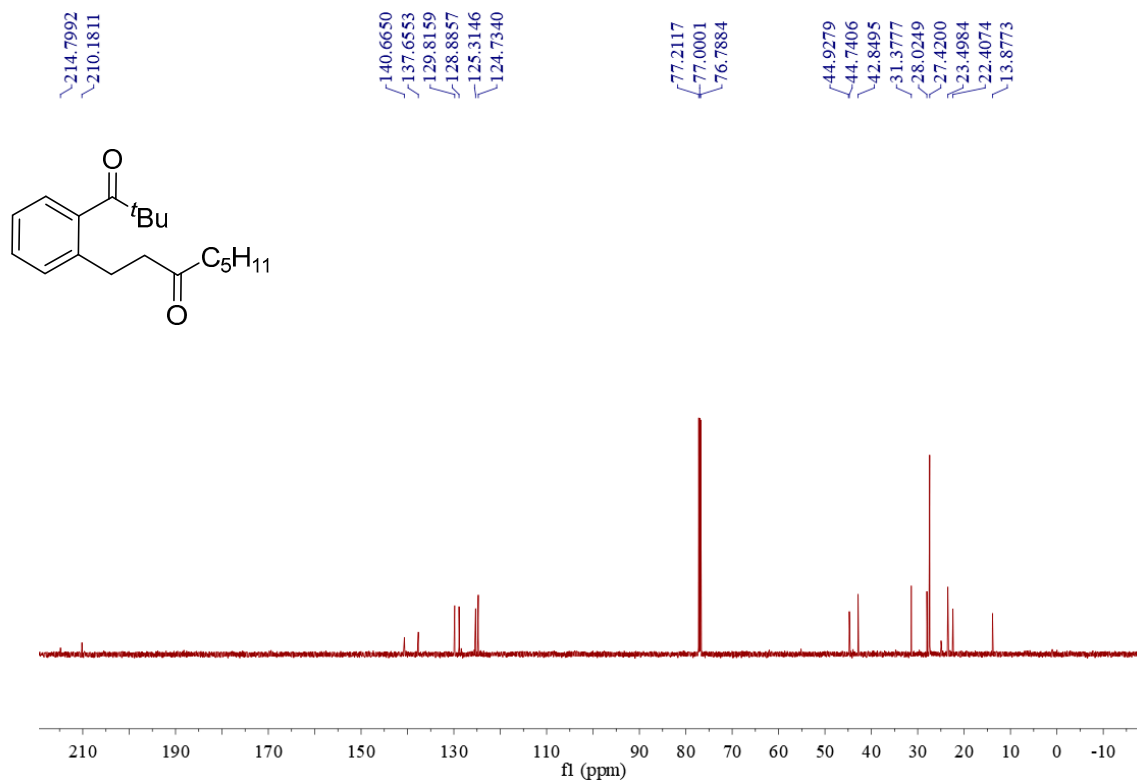
Figure S52. ¹H NMR spectra of compound **4j**.Figure S53. ¹³C NMR spectra of compound **4j**.

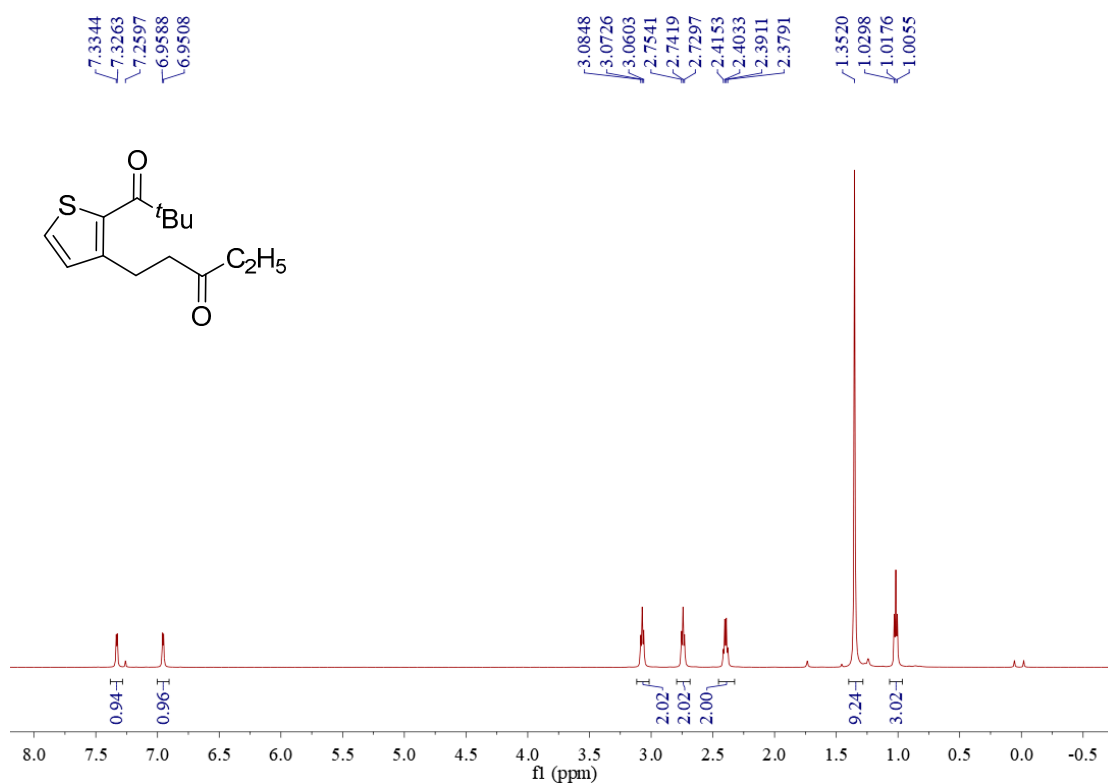
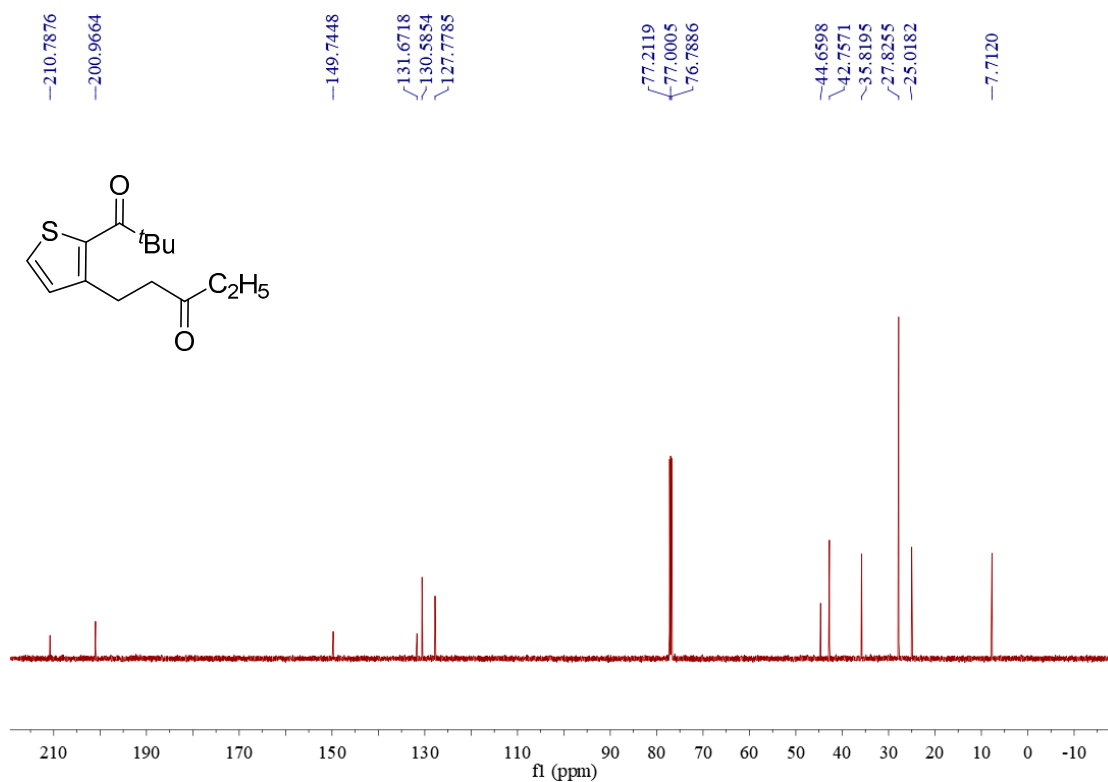
Figure S54. ¹H NMR spectra of compound 4k.Figure S55. ¹³C NMR spectra of compound 4k.

Figure S56. ¹H NMR spectra of compound 4l.Figure S57. ¹³C NMR spectra of compound 4l.

Figure S58. ¹H NMR spectra of compound 4m.Figure S59. ¹³C NMR spectra of compound 4m.

Figure S60. ¹H NMR spectra of compound 4n.Figure S61. ¹³C NMR spectra of compound 4n.

Figure S62. ¹H NMR spectra of compound **4o**.Figure S63. ¹³C NMR spectra of compound **4o**.

Figure S64. ¹H NMR spectra of compound 4p.Figure S65. ¹³C NMR spectra of compound 4p.