

Supporting Information

Palladium-catalyzed esterification of aryl fluorosulfates with aryl formates

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Optimization of reaction conditions

Table S1. Optimization of reaction conditions by using different ligands^a

Entry	Ligand	Yield (%) ^b	Entry	Ligand	Yield (%) ^b
1	L1	0	11	L11	trace
2	L2	0	12	L12	8
3	L3	0	13	L13	82 (84) ^c
4	L4	0	14	L14	trace
5	L5	0	15	L15	trace
6	L6	trace	16	L16	trace
7	L7	75	17	L17	0
8	L8	76	18	L18	0
9	L9	78	19	L19	trace
10	L10	13	20	L20	0

^a The reactions were performed at 80 °C for 12 h under nitrogen atmosphere by using **1a** (0.5 mmol), **2a** (1.0 mmol), Pd(OAc)₂ (5 mol%), ligand (5 mol%), and Et₃N (1.0 mmol) in anhydrous DMF (2 mL). ^b Yields were determined by NMR analysis of crude reaction mixture after work-up by using 1,4-dimethoxybenzene as an internal standard.

^c Isolated yield.

Table S2. Optimization of reaction conditions by using different bases^a

$\text{1a (1 equiv.)} + \text{2a (2 equiv.)} \xrightarrow[\text{DMF, N}_2, 80\text{ }^\circ\text{C, 12 h}]{\text{Pd(OAc)}_2\text{ (5 mol\%)} \\ \text{XantPhos (5 mol\%)} \\ \text{base (2 equiv.)}}$

Entry	Base	Yield (%) ^b	Entry	Base	Yield (%) ^b
1	Et₃N	82 (84)^c	6	^t BuONa	15
2	DIPEA	79	7	Cs ₂ CO ₃	trace
3	DMAP	77	8	K ₂ CO ₃	28
4	DBU	0	9	NaHCO ₃	54
5	Pyridine	0	10	NaOH	trace

^a The reactions were performed at 80 °C for 12 h under nitrogen atmosphere by using **1a** (0.5 mmol), **2a** (1.0 mmol), Pd(OAc)₂ (5 mol%), XantPhos (5 mol%), and base (1.0 mmol) in anhydrous DMF (2 mL). ^b Yields were determined by NMR analysis of crude reaction mixture after work-up by using 1,4-dimethoxybenzene as an internal standard. ^c Isolated yield.

Table S3. Optimization of reaction conditions by using different solvents^a

$\text{1a (1 equiv.)} + \text{2a (2 equiv.)} \xrightarrow[\text{solvent, N}_2, 80\text{ }^\circ\text{C, 12 h}]{\text{Pd(OAc)}_2\text{ (5 mol\%)} \\ \text{XantPhos (5 mol\%)} \\ \text{Et}_3\text{N (2 equiv.)}}$

Entry	Solvent	Yield (%) ^b	Entry	Solvent	Yield (%) ^b
1	DMF	82 (84)^c	6	MeCN	10
2	DMA	15	7	MeOH	0
3	NMP	18	8	1,4-dioxane	30
4	DMPU	13	9	THF	80
5	DMSO	49	10	toluene	27

^a The reactions were performed at 80 °C for 12 h under nitrogen atmosphere by using **1a** (0.5 mmol), **2a** (1.0 mmol), Pd(OAc)₂ (5 mol%), XantPhos (5 mol%), and Et₃N (1.0 mmol) in solvent (2 mL). ^b Yields were determined by NMR analysis of crude reaction mixture after work-up by using 1,4-dimethoxybenzene as an internal standard. ^c Isolated yield.

Figure S1. ^1H NMR spectrum of **2s** (400 MHz, CDCl_3)

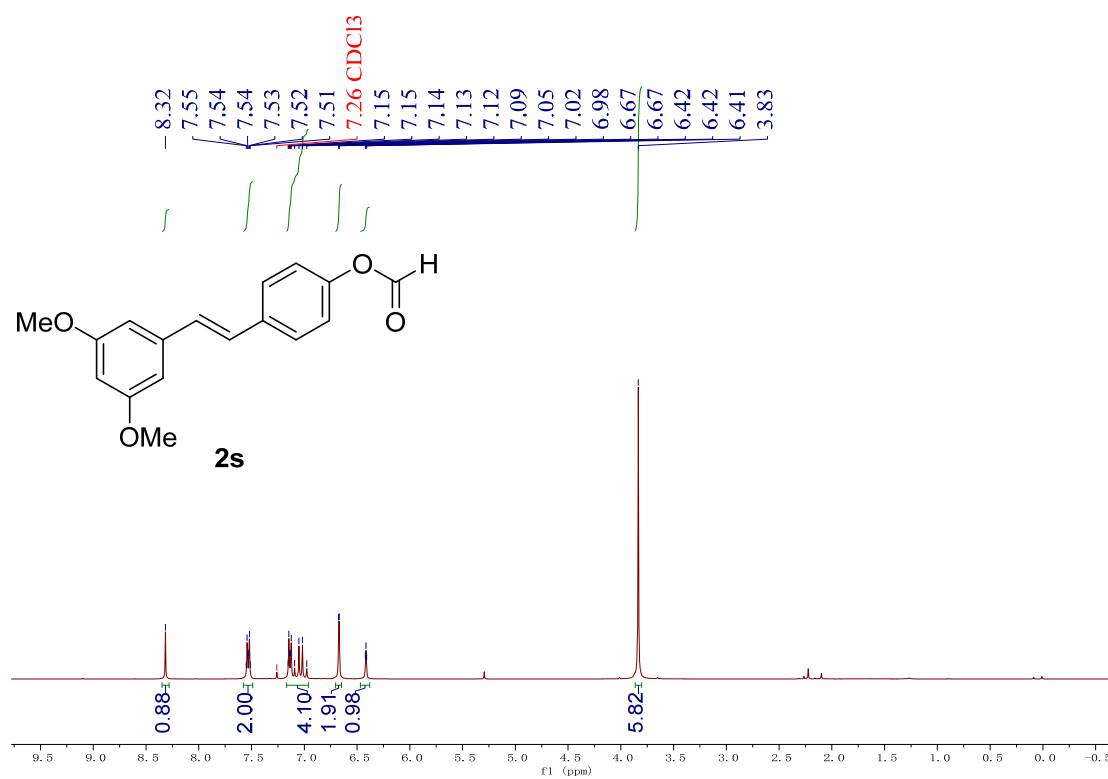


Figure S2. ^{13}C NMR spectrum of **2s** (100 MHz, CDCl_3)

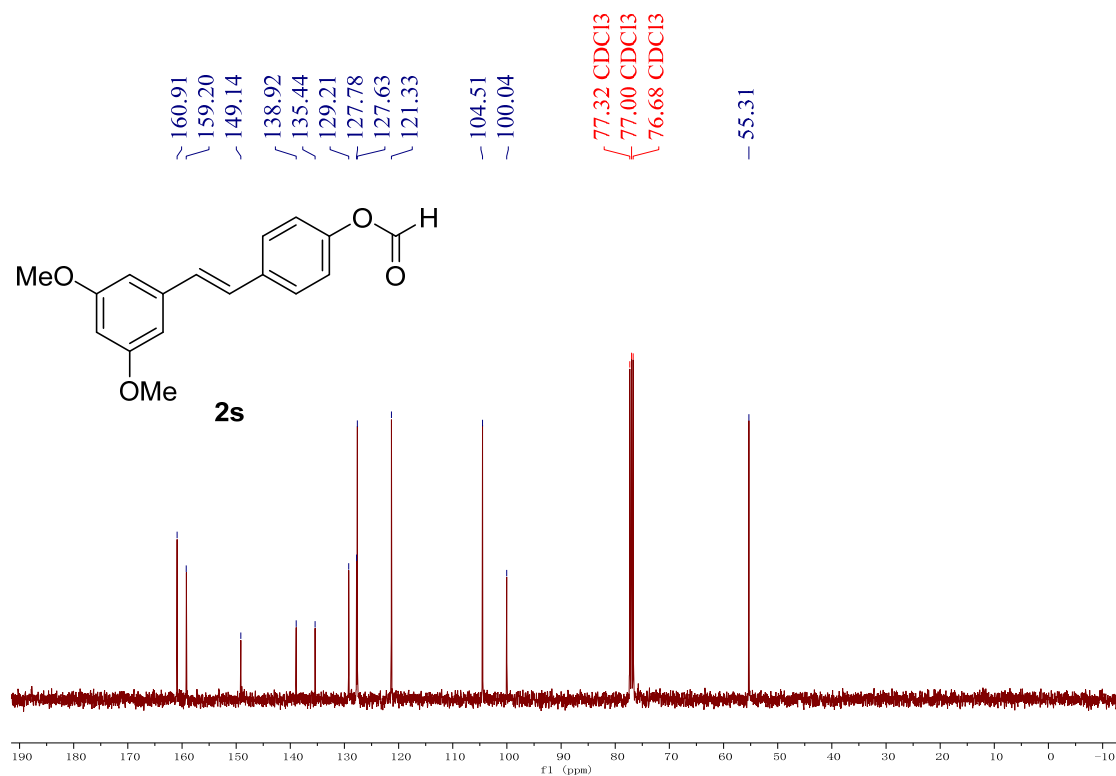


Figure S3. ^1H NMR spectrum of **3a** (400 MHz, CDCl_3)

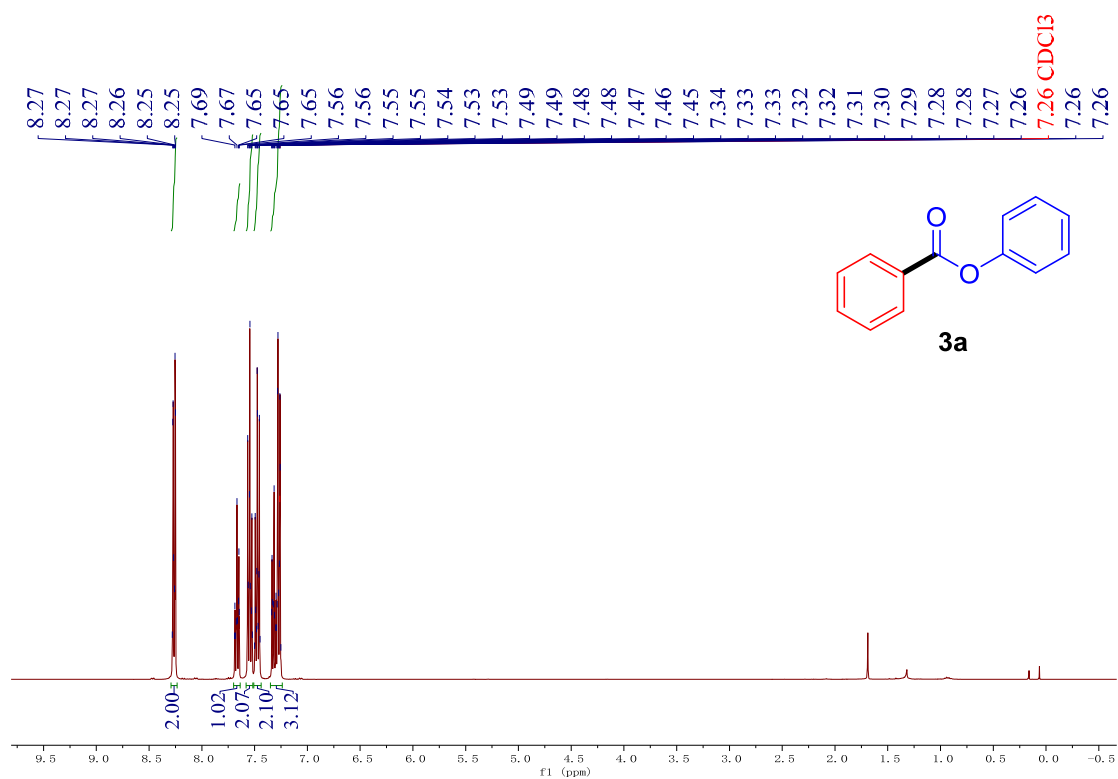


Figure S4. ^{13}C NMR spectrum of **3a** (100 MHz, CDCl_3)

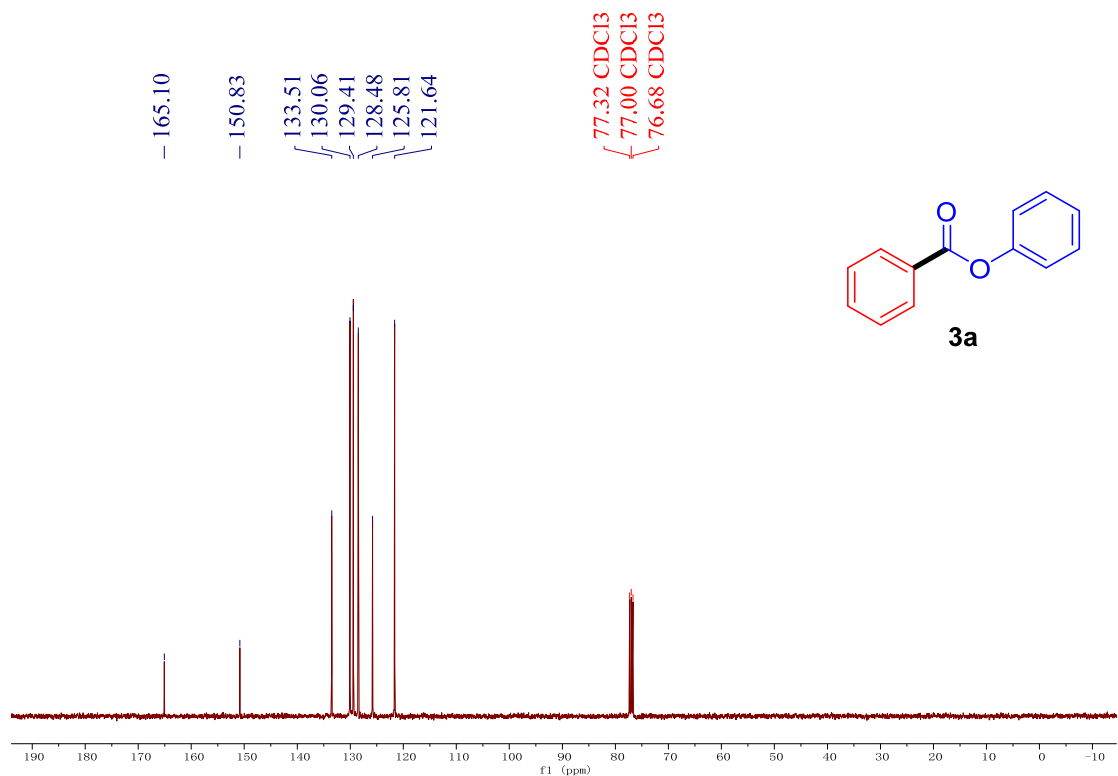


Figure S5. ^1H NMR spectrum of **3b** (400 MHz, CDCl_3)

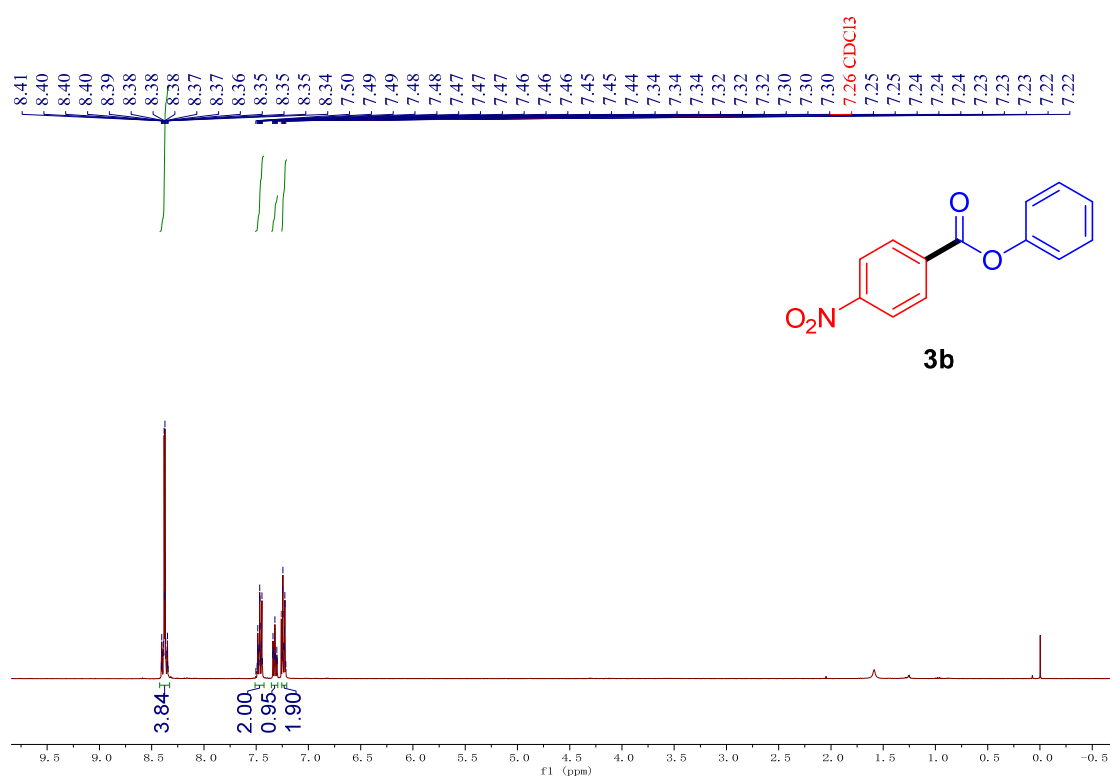


Figure S6. ^{13}C NMR spectrum of **3b** (100 MHz, CDCl_3)

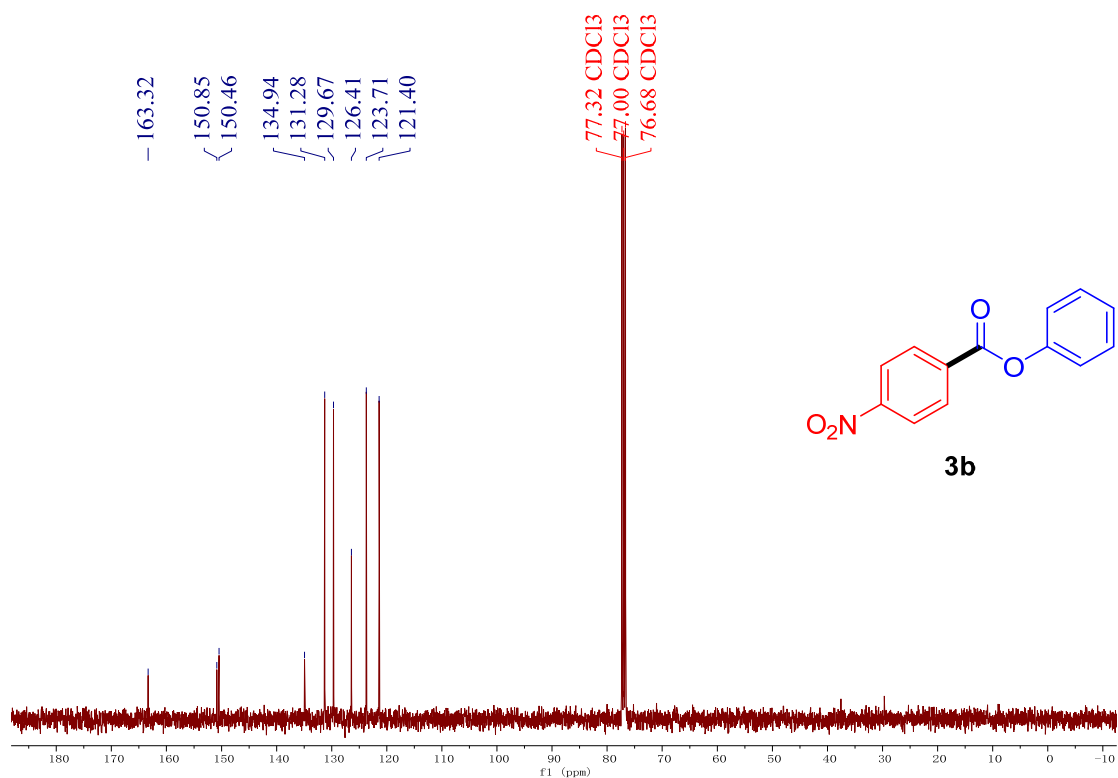


Figure S7. ^1H NMR spectrum of **3c** (400 MHz, CDCl_3)

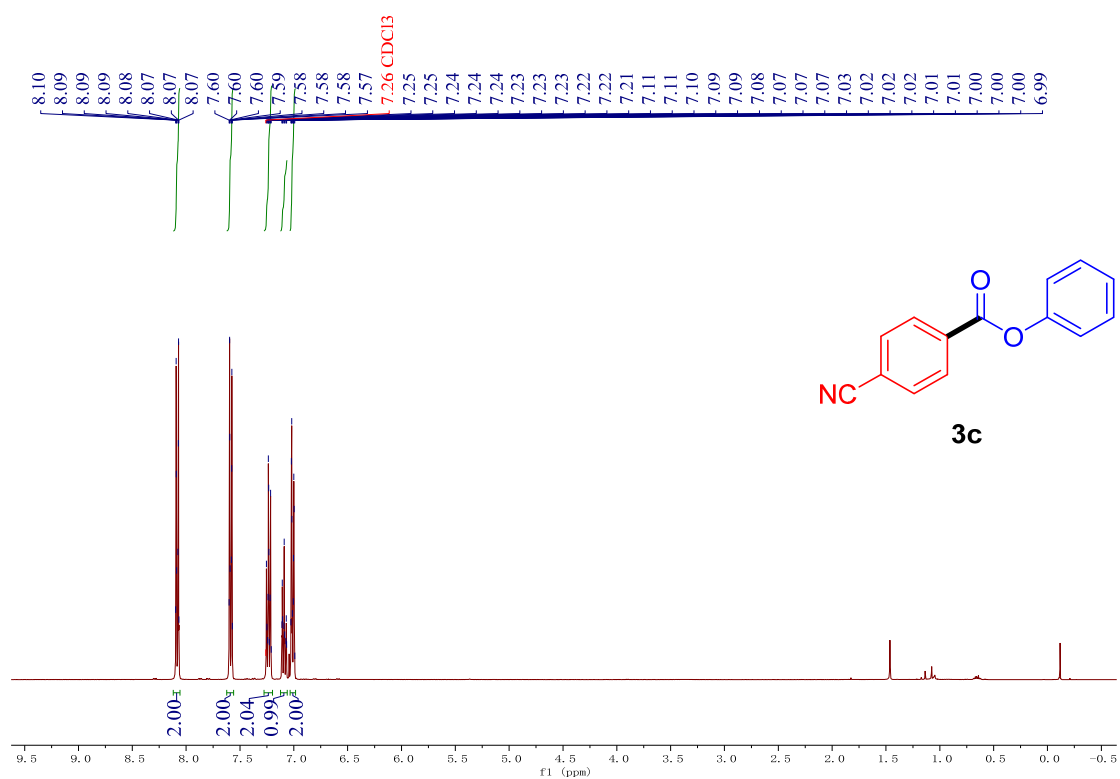


Figure S8. ^{13}C NMR spectrum of **3c** (100 MHz, CDCl_3)

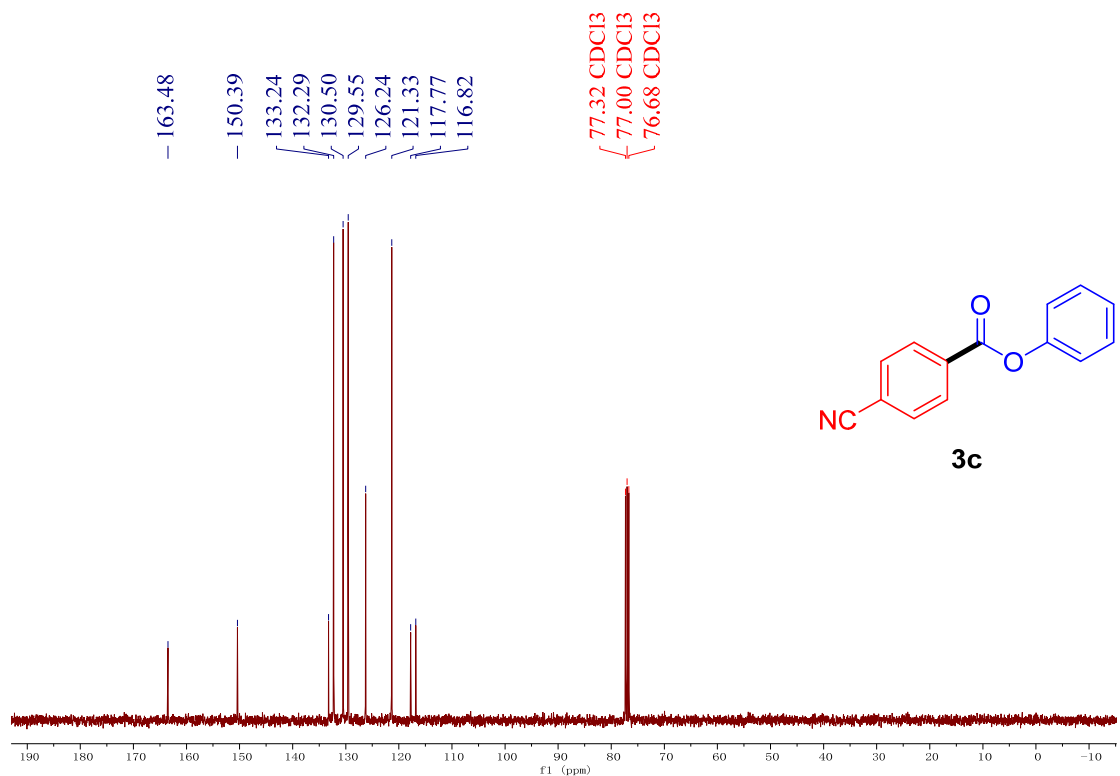


Figure S9. ^1H NMR spectrum of **3d** (400 MHz, CDCl_3)

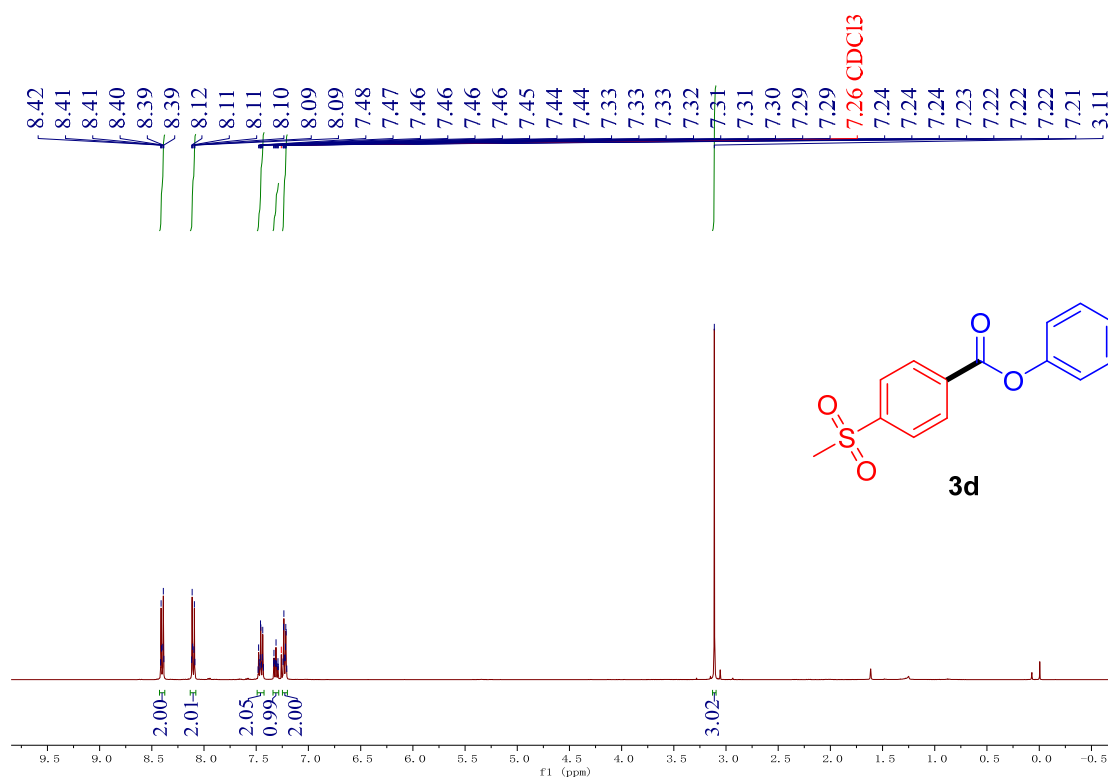


Figure S10. ^{13}C NMR spectrum of **3d** (100 MHz, CDCl_3)

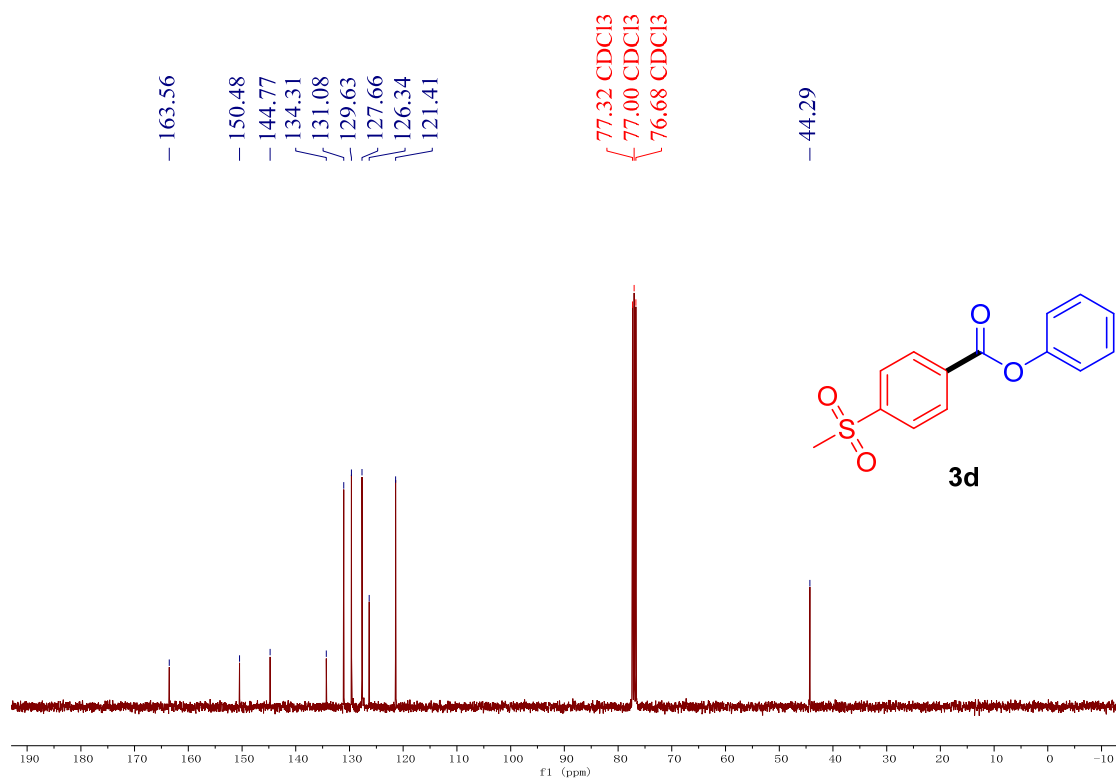


Figure S11. ^1H NMR spectrum of **3e** (400 MHz, CDCl_3)

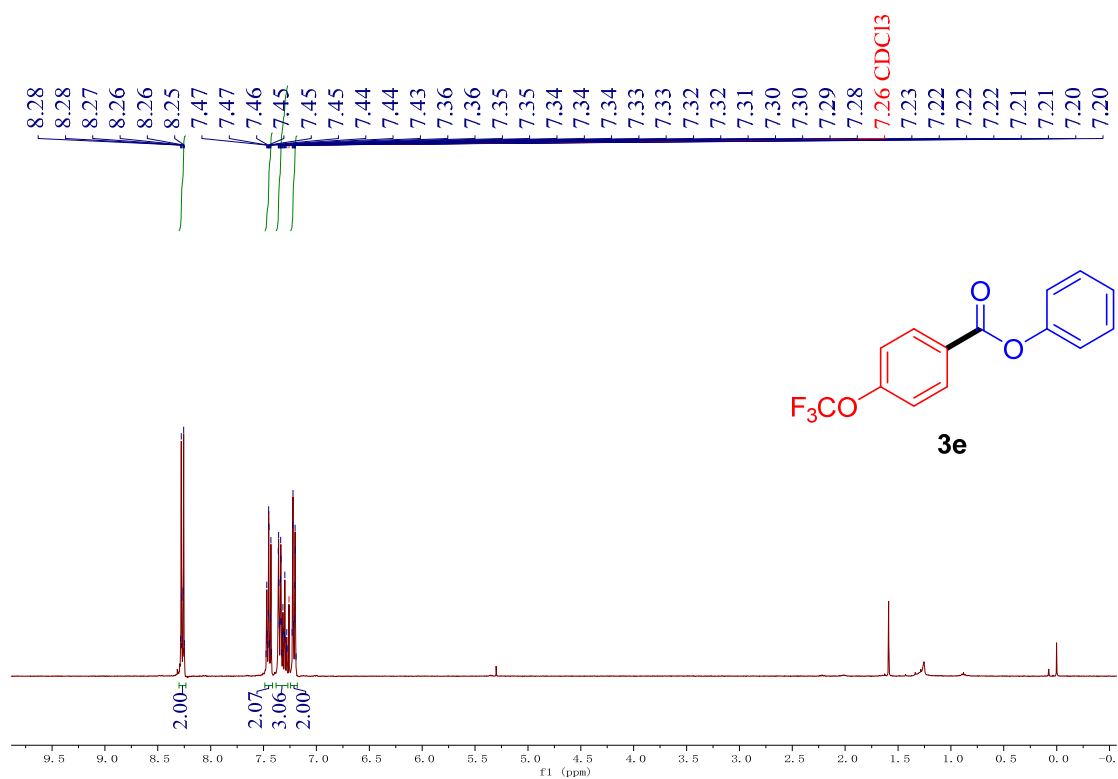


Figure S12. ^{13}C NMR spectrum of **3e** (100 MHz, CDCl_3)

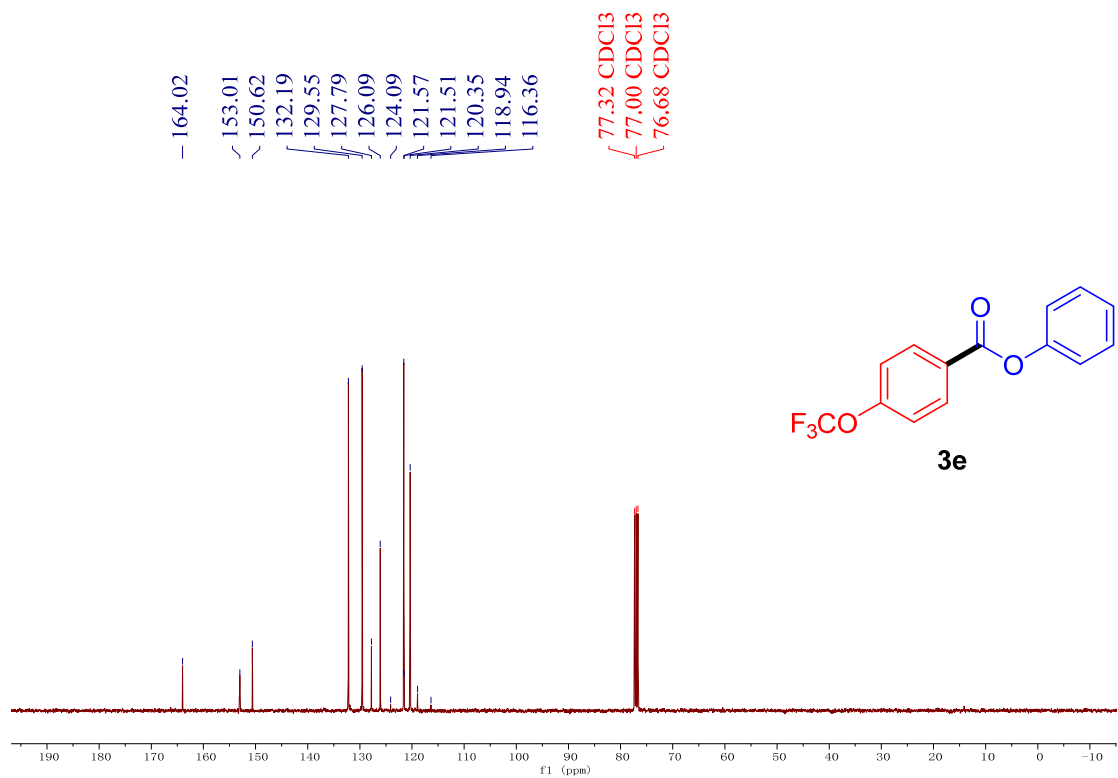


Figure S13. ^{19}F NMR spectrum of **3e** (376 MHz, CDCl_3)

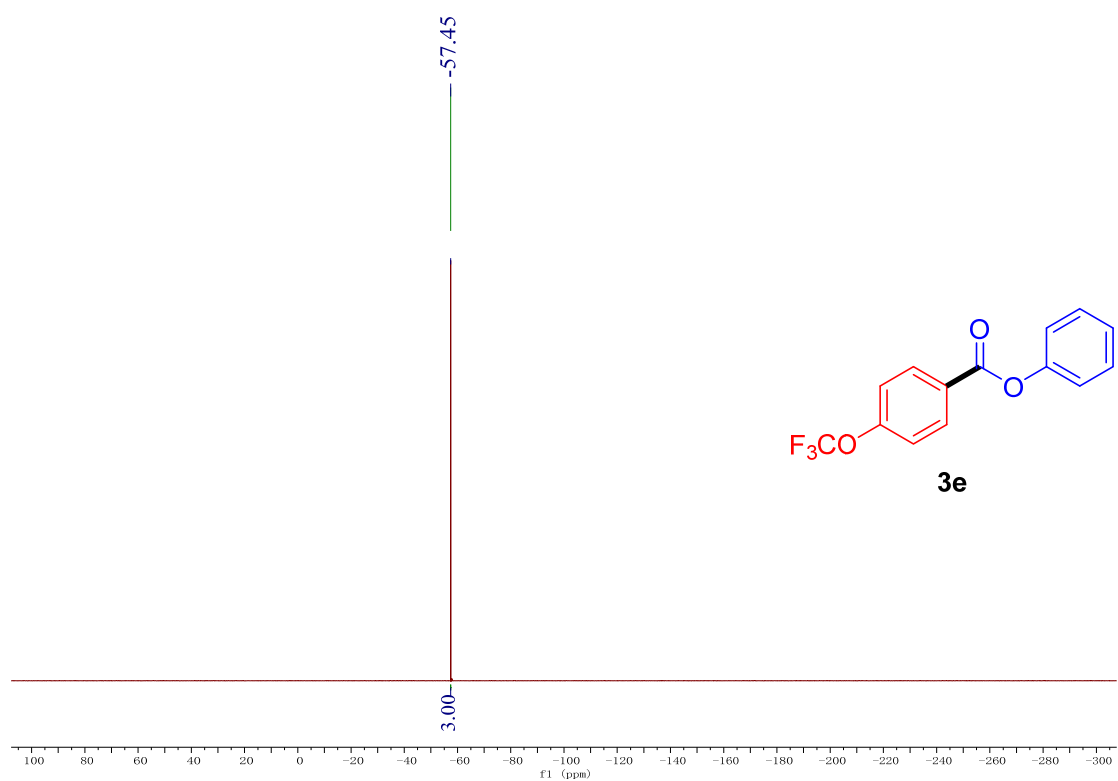


Figure S14. ^1H NMR spectrum of **3f** (400 MHz, CDCl_3)

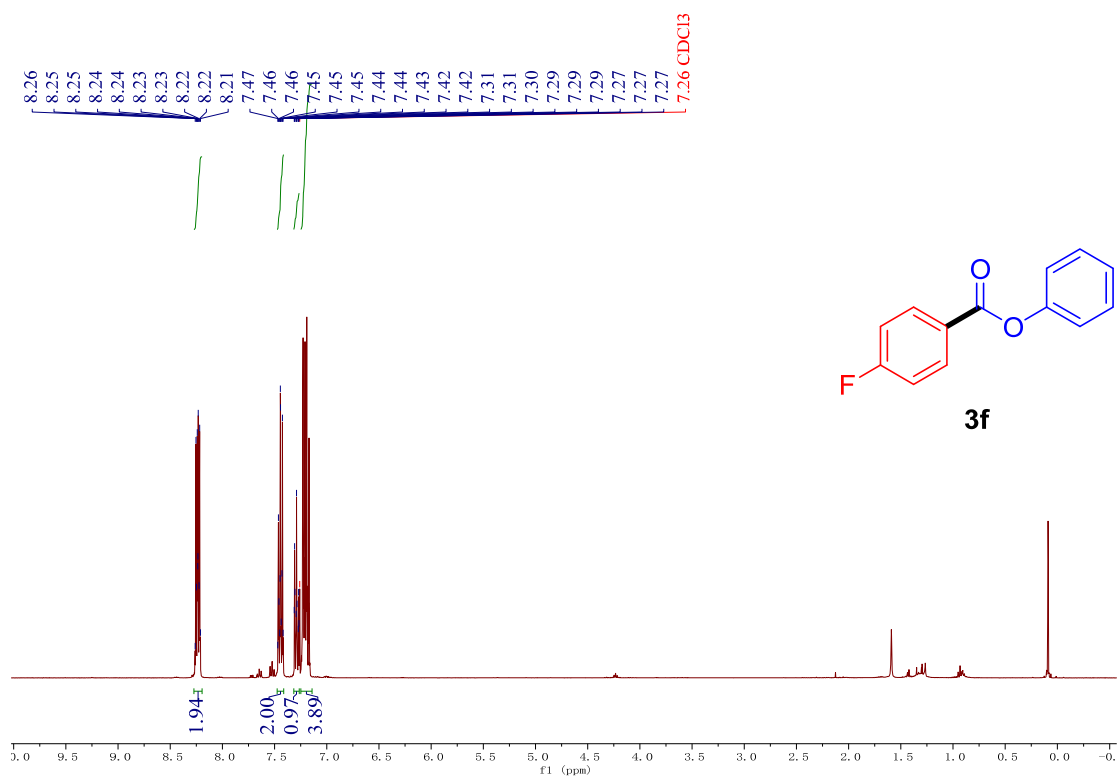


Figure S15. ^{13}C NMR spectrum of **3f** (100 MHz, CDCl_3)

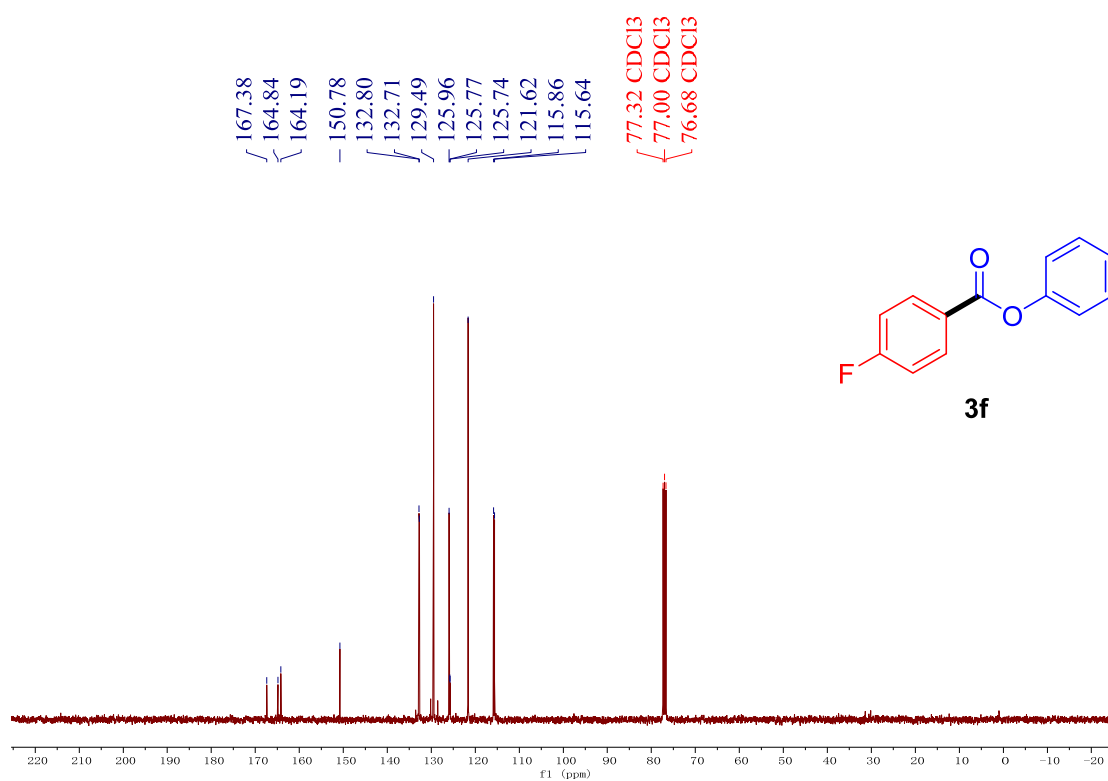


Figure S16. ^{19}F NMR spectrum of **3f** (376 MHz, CDCl_3)

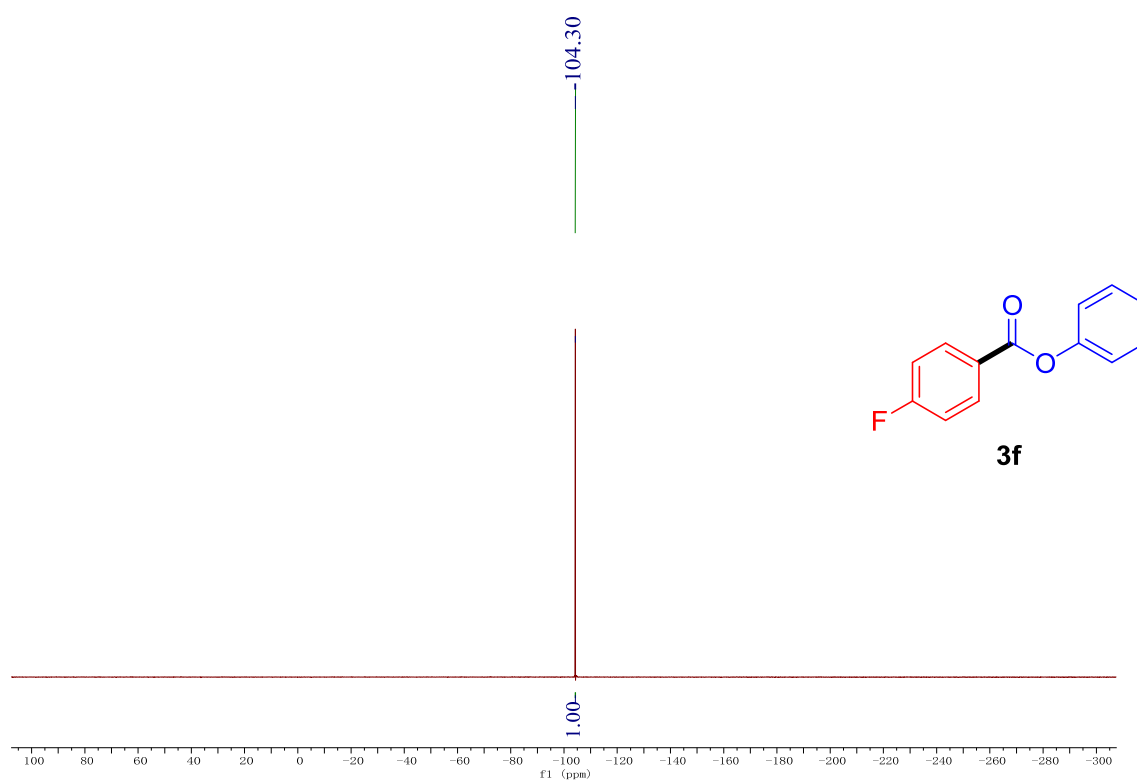


Figure S17. ^1H NMR spectrum of **3g** (400 MHz, CDCl_3)

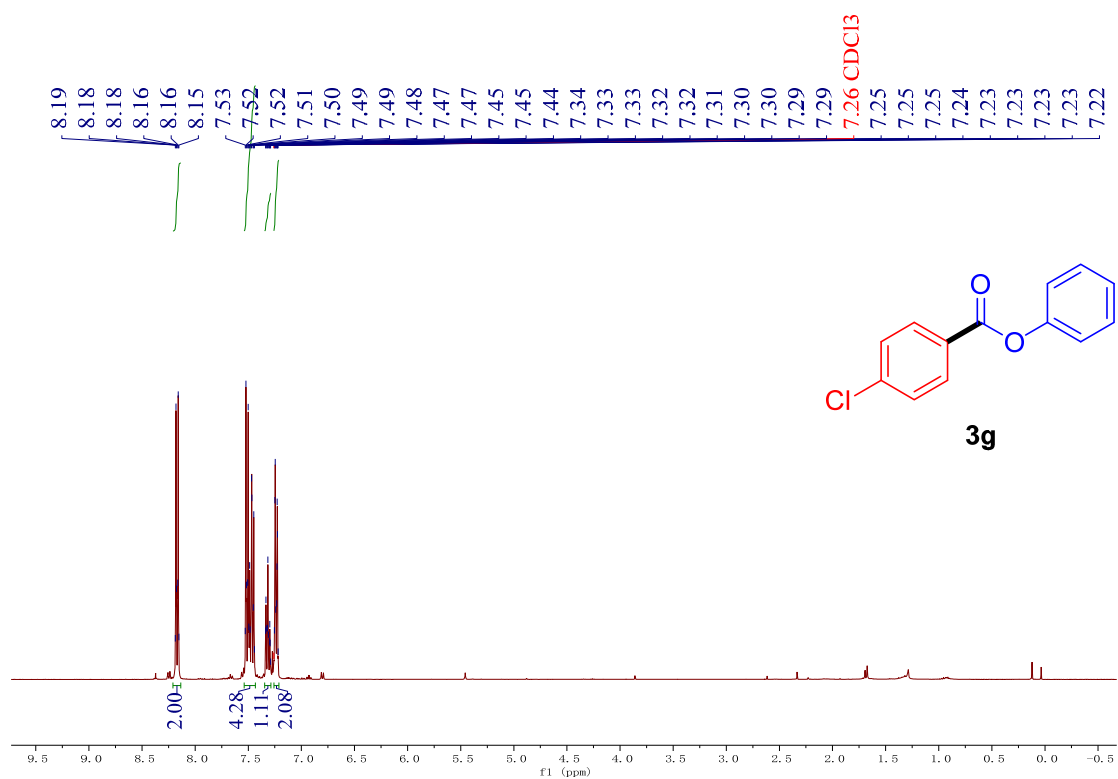


Figure S18. ^{13}C NMR spectrum of **3g** (100 MHz, CDCl_3)

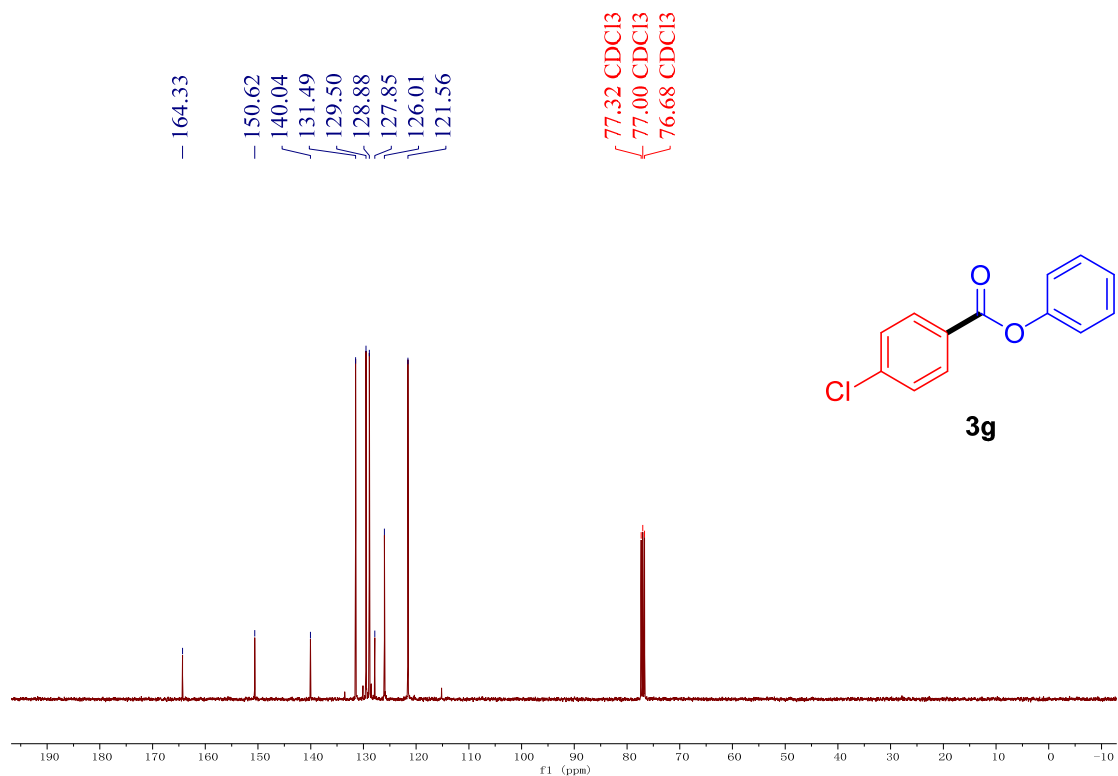


Figure S19. ^1H NMR spectrum of **3h** (400 MHz, CDCl_3)

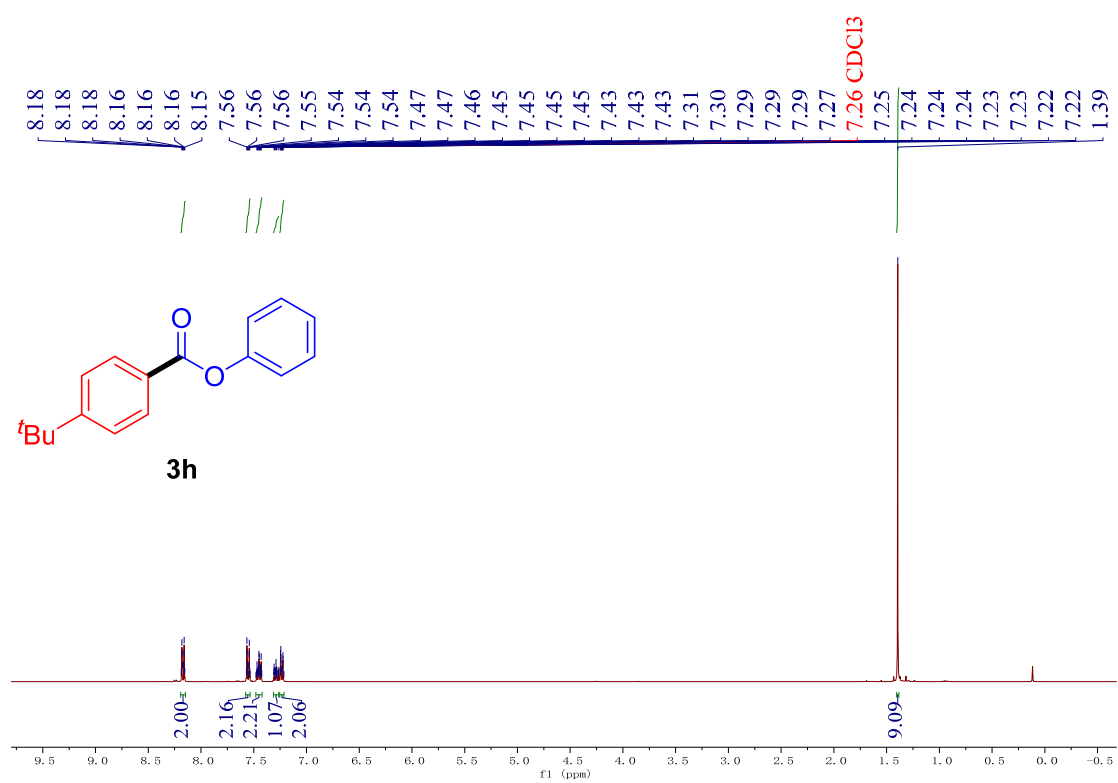


Figure S20. ^{13}C NMR spectrum of **3h** (100 MHz, CDCl_3)

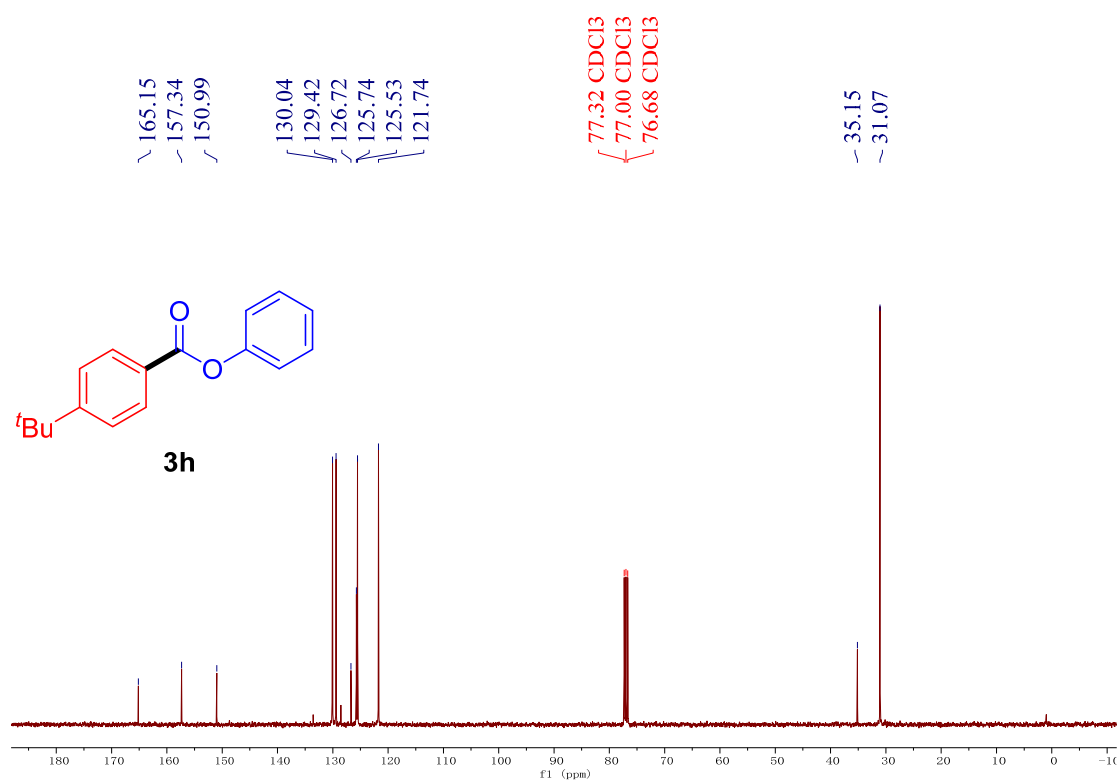


Figure S21. ^1H NMR spectrum of **3i** (400 MHz, CDCl_3)

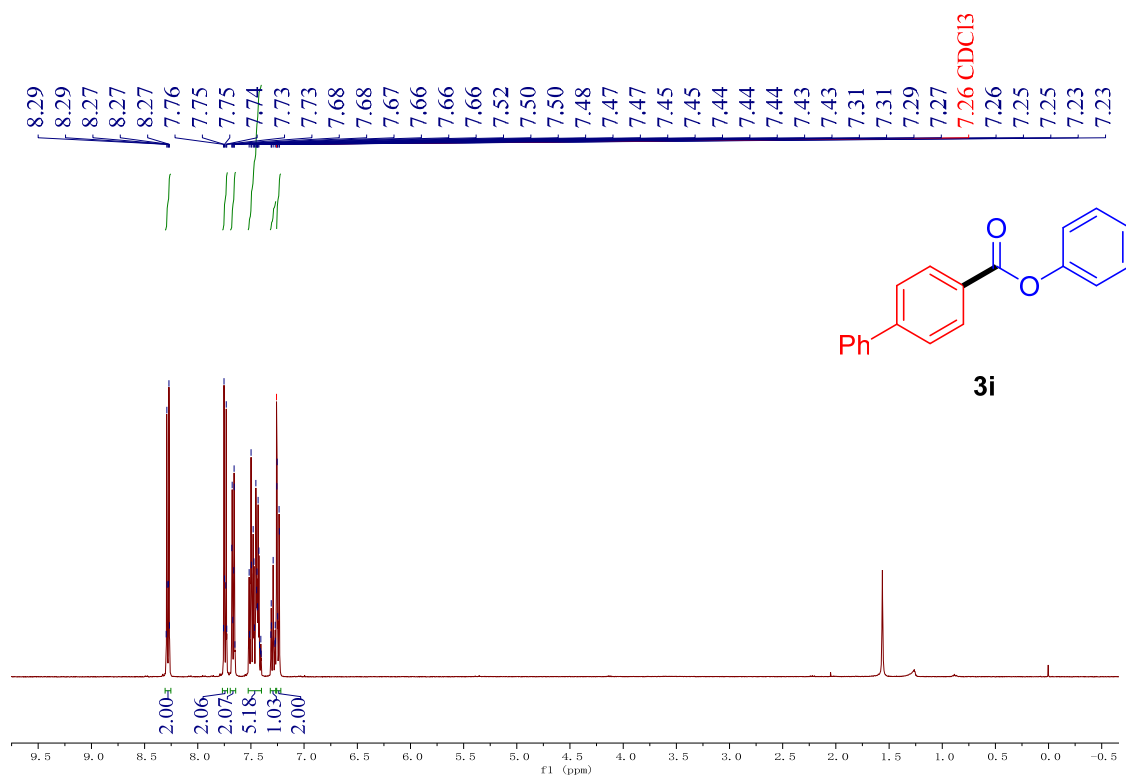


Figure S22. ^{13}C NMR spectrum of **3i** (100 MHz, CDCl_3)

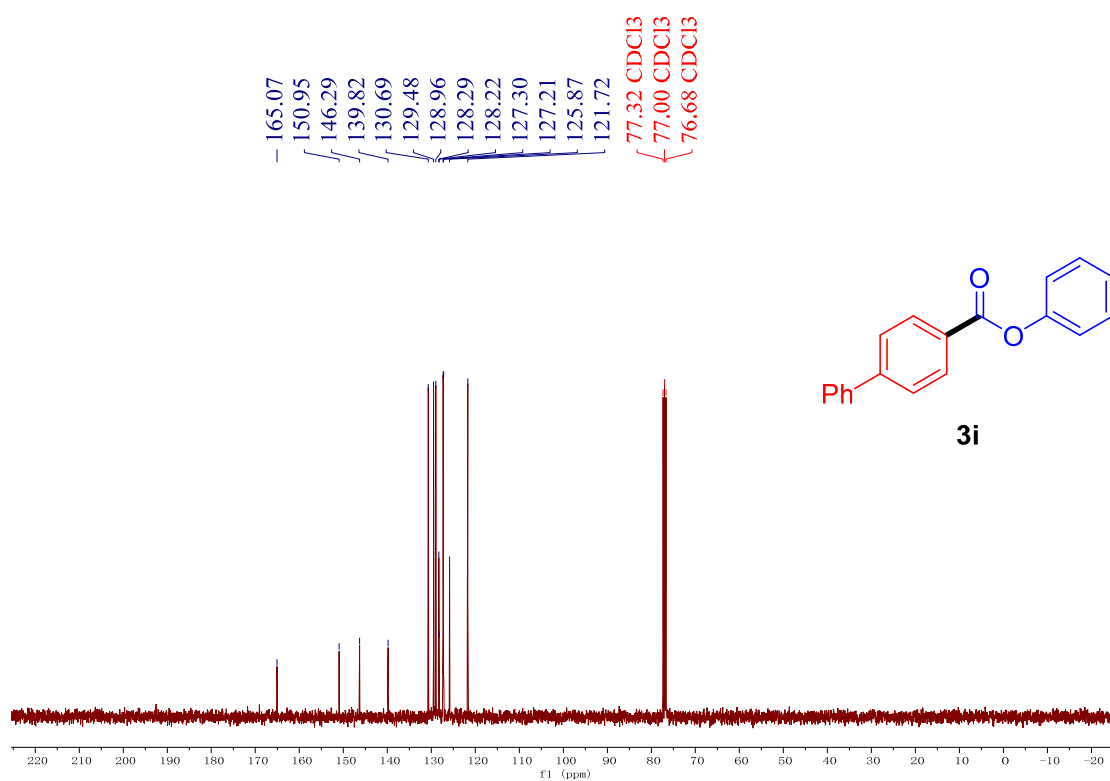


Figure S23. ^1H NMR spectrum of **3j** (400 MHz, CDCl_3)

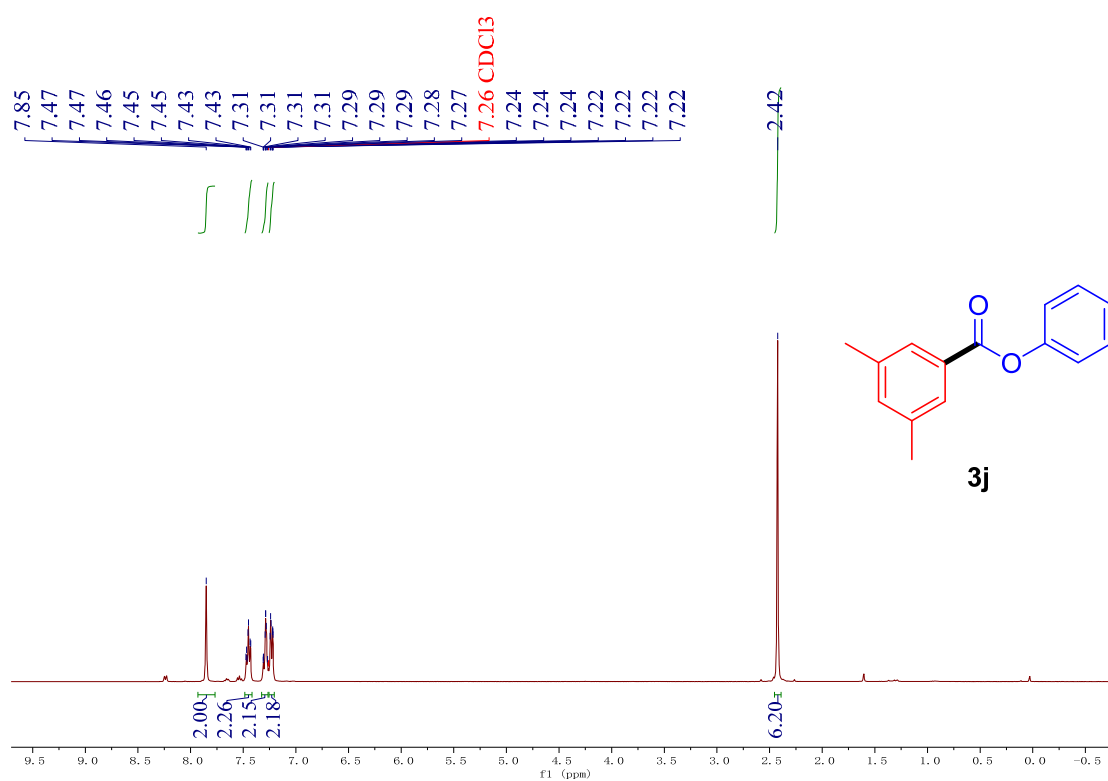


Figure S24. ^{13}C NMR spectrum of **3j** (100 MHz, CDCl_3)

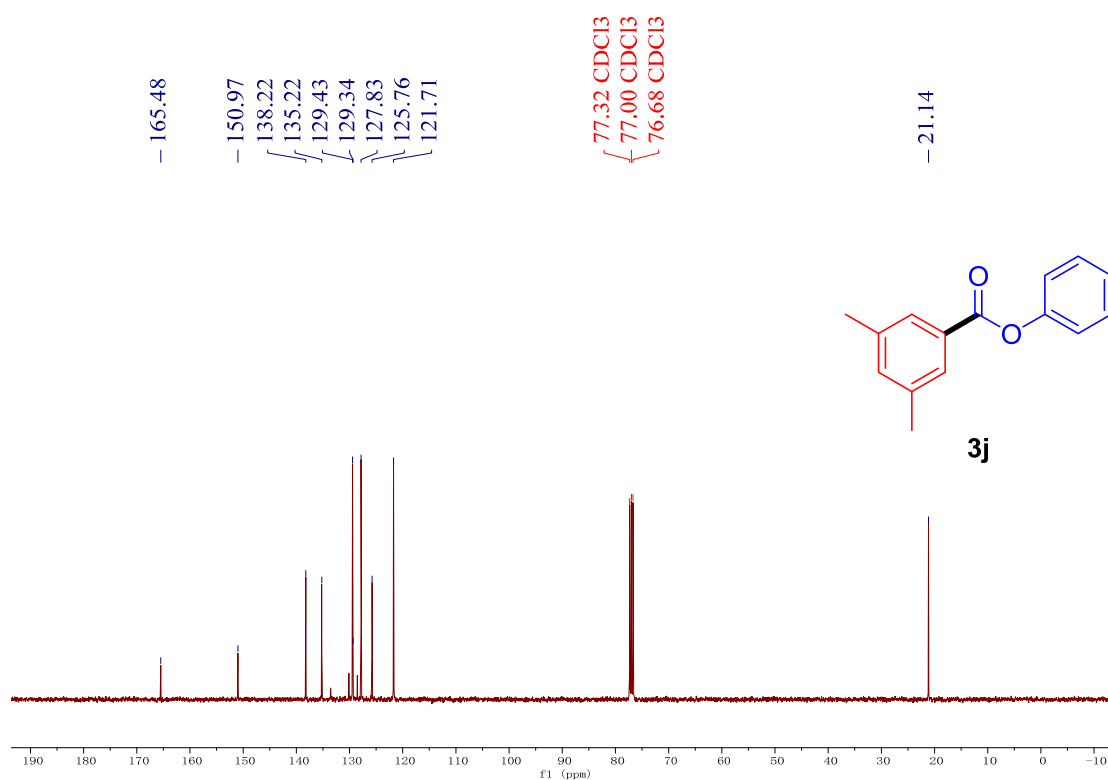


Figure S25. ^1H NMR spectrum of **3k** (400 MHz, CDCl_3)

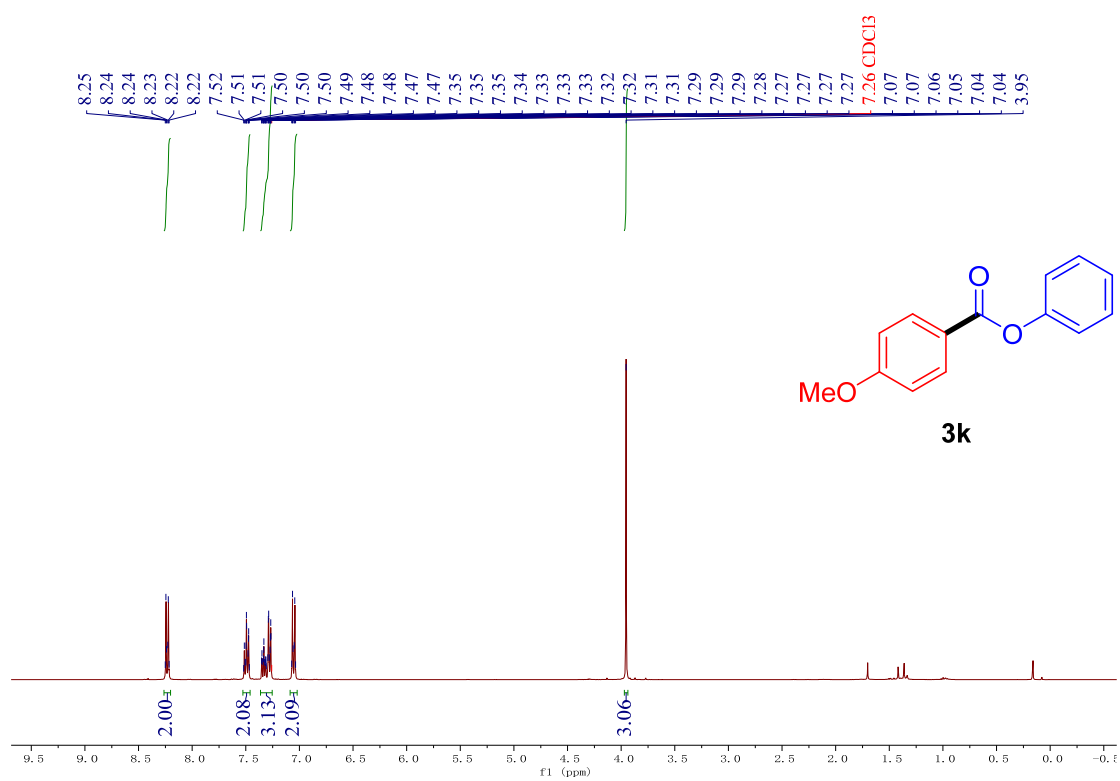


Figure S26. ^{13}C NMR spectrum of **3k** (100 MHz, CDCl_3)

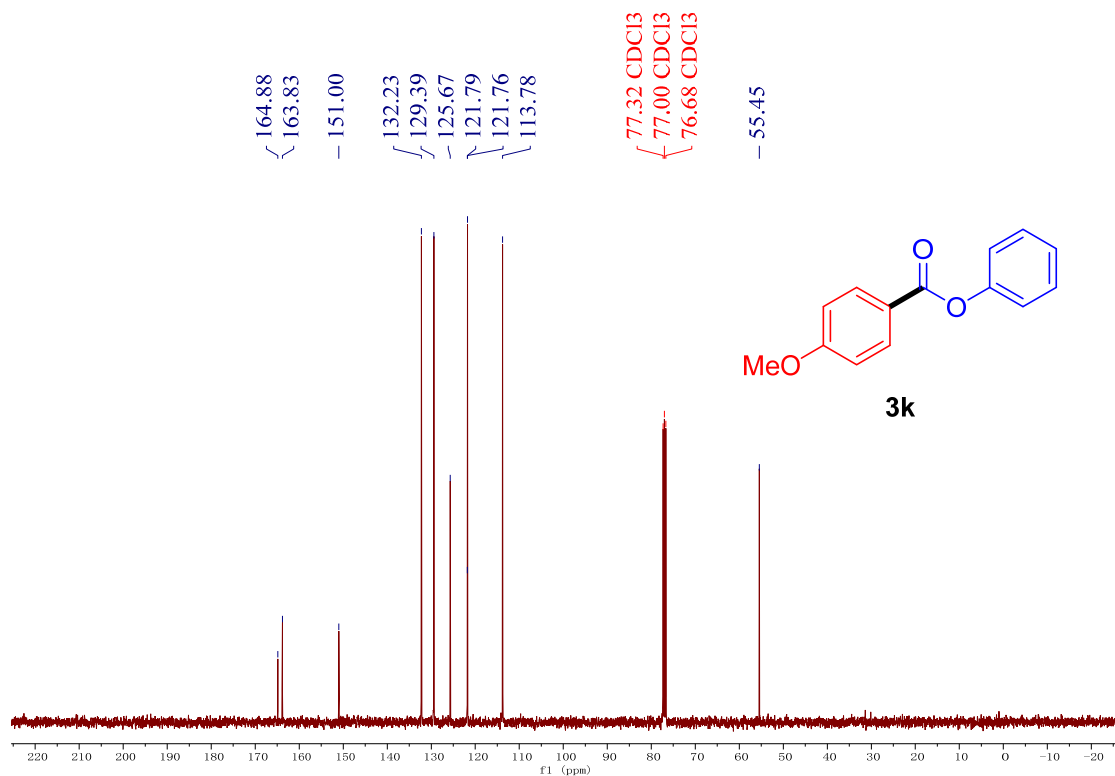


Figure S27. ^1H NMR spectrum of **3I** (400 MHz, CDCl_3)

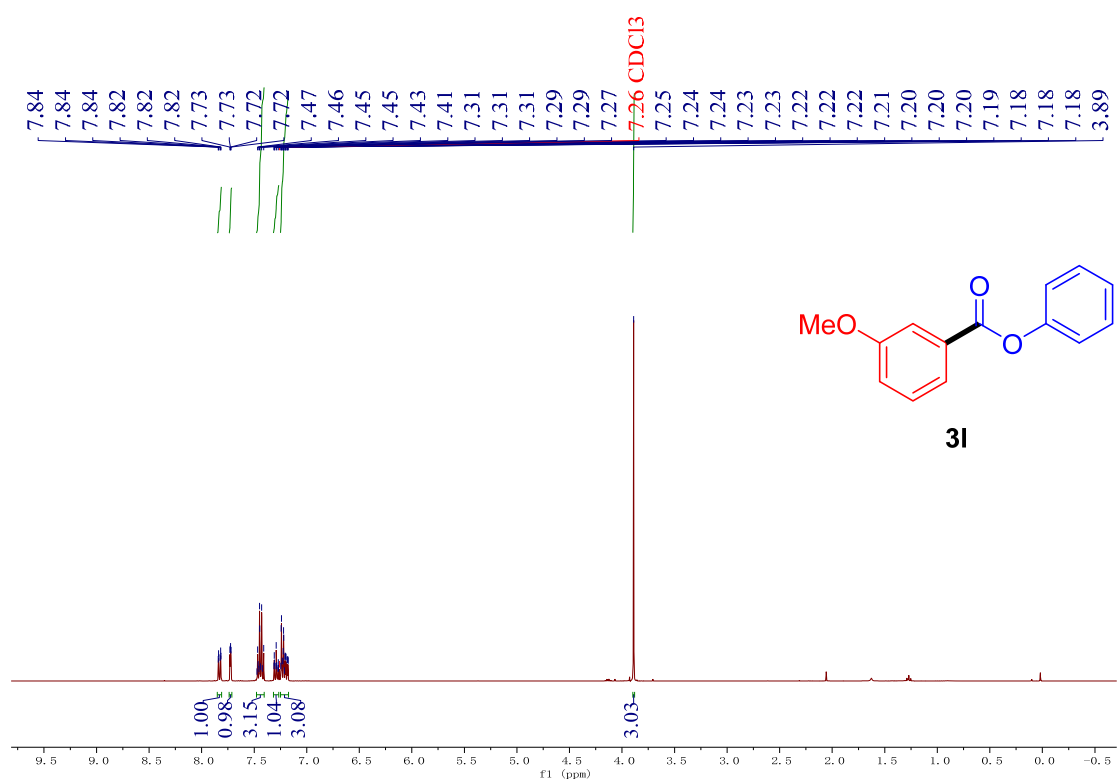


Figure S28. ^{13}C NMR spectrum of **3I** (100 MHz, CDCl_3)

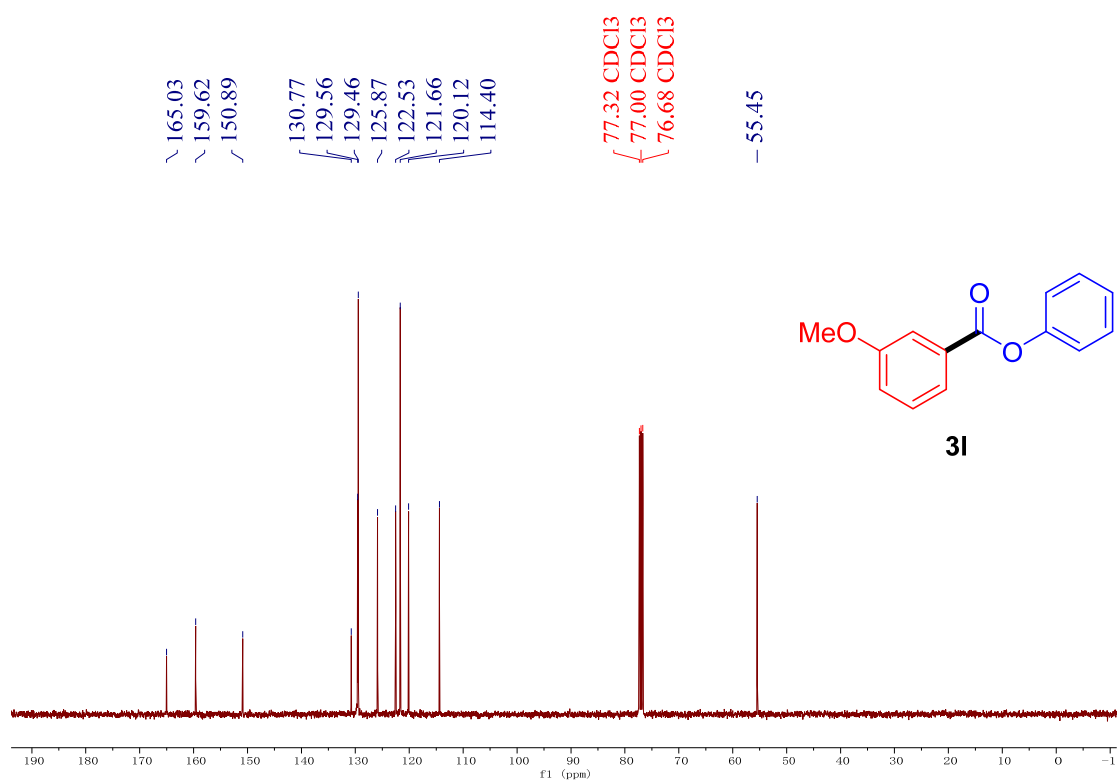


Figure S29. ^1H NMR spectrum of **3m** (400 MHz, CDCl_3)

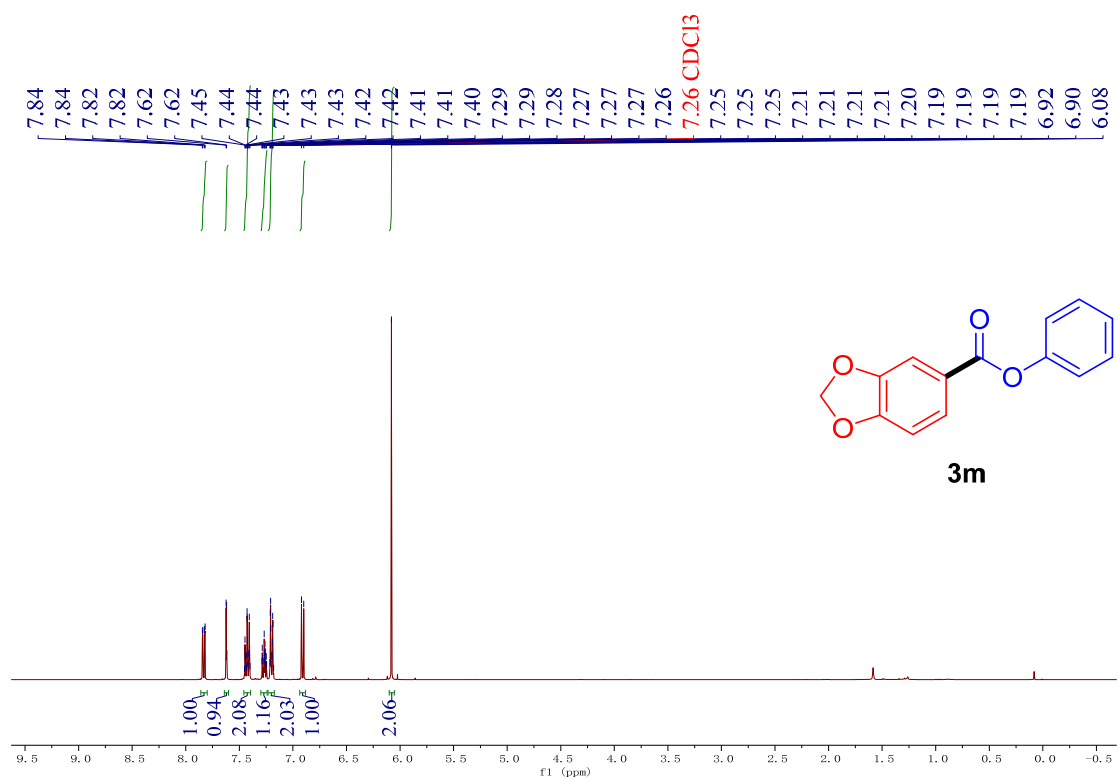


Figure S30. ^{13}C NMR spectrum of **3m** (100 MHz, CDCl_3)

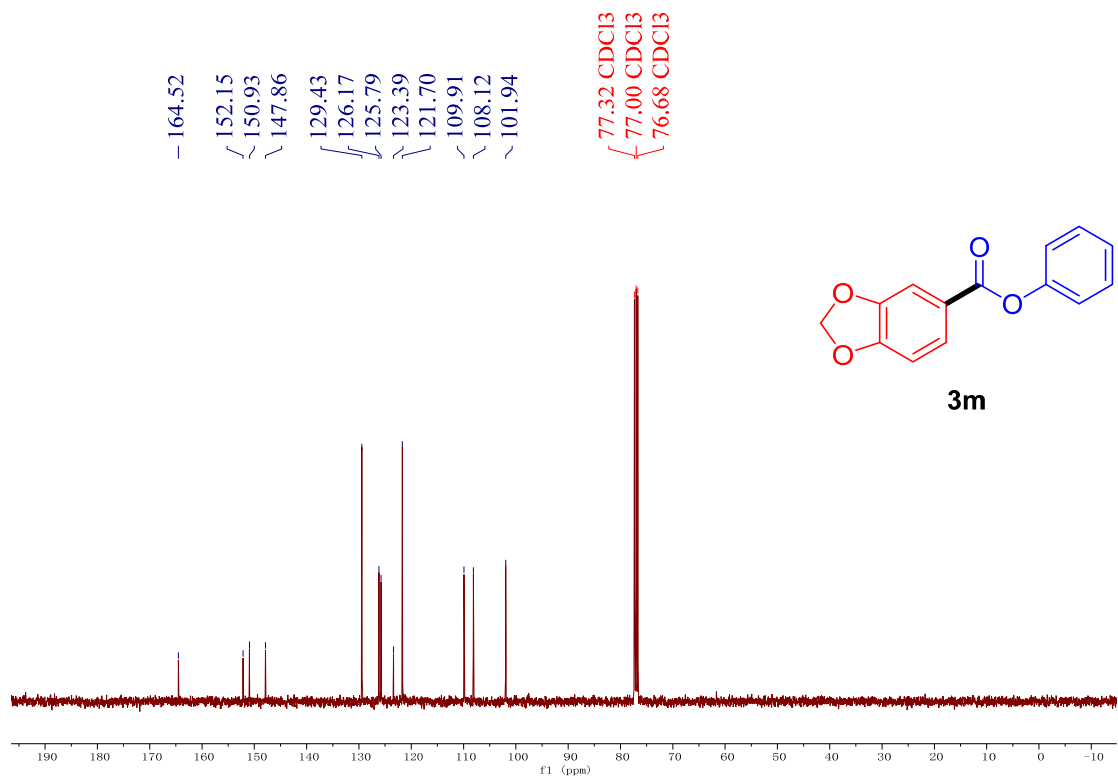


Figure S31. ^1H NMR spectrum of **3n** (400 MHz, CDCl_3)

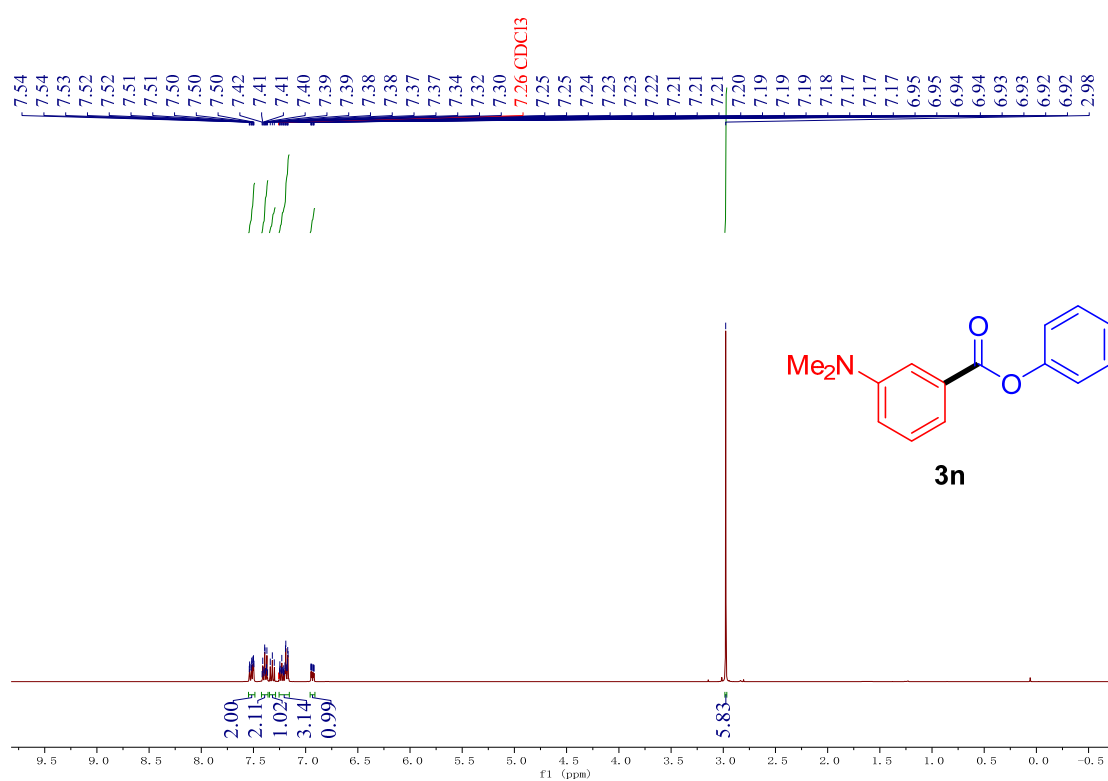


Figure S32. ^{13}C NMR spectrum of **3n** (100 MHz, CDCl_3)

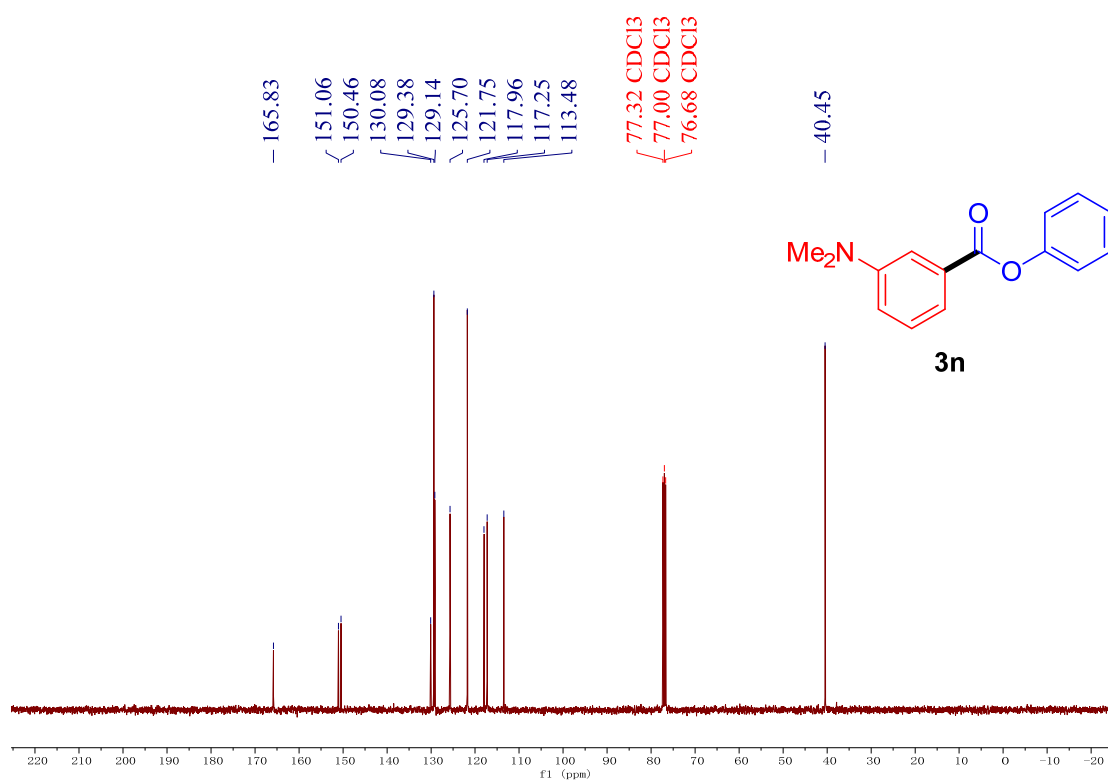


Figure S33. ^1H NMR spectrum of **3o** (400 MHz, CDCl_3)

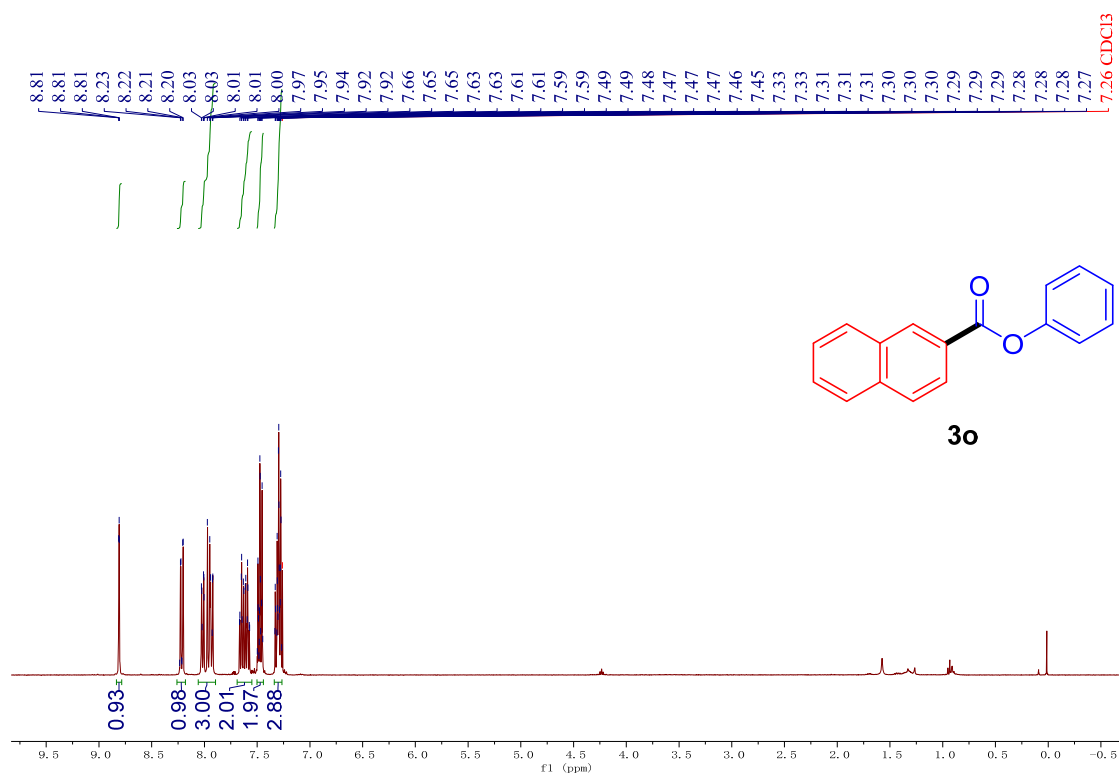


Figure S34. ^{13}C NMR spectrum of **3o** (100 MHz, CDCl_3)

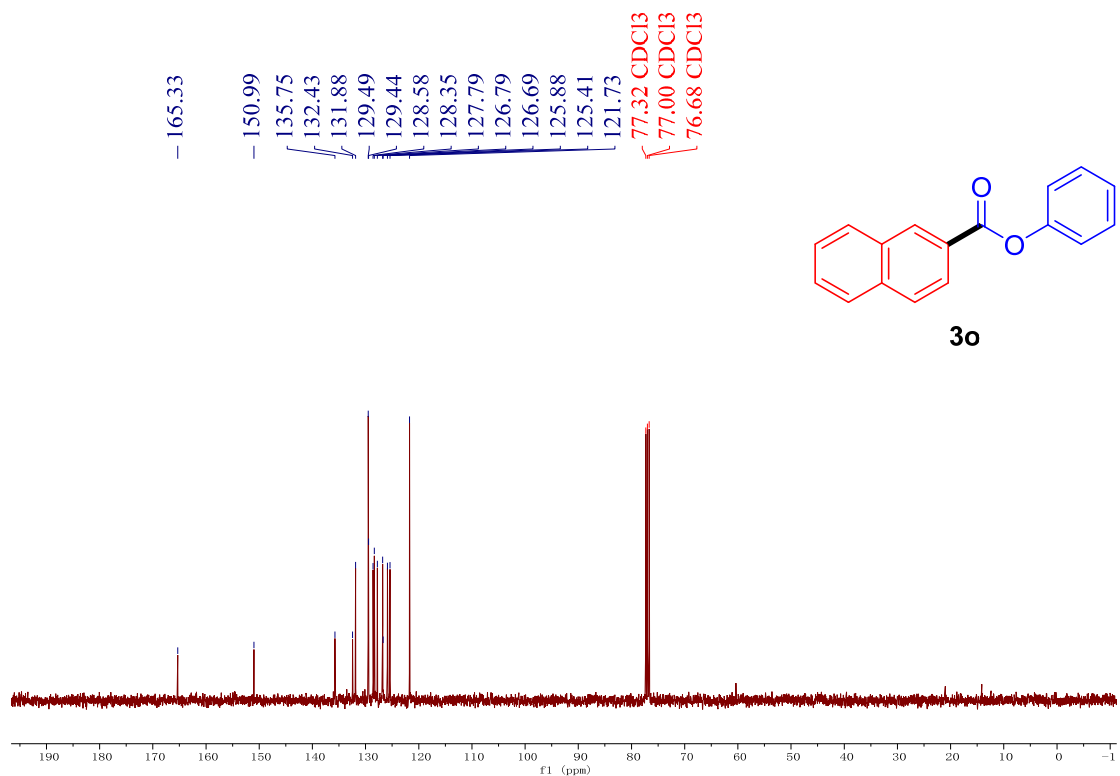


Figure S35. ^1H NMR spectrum of **3p** (400 MHz, CDCl_3)

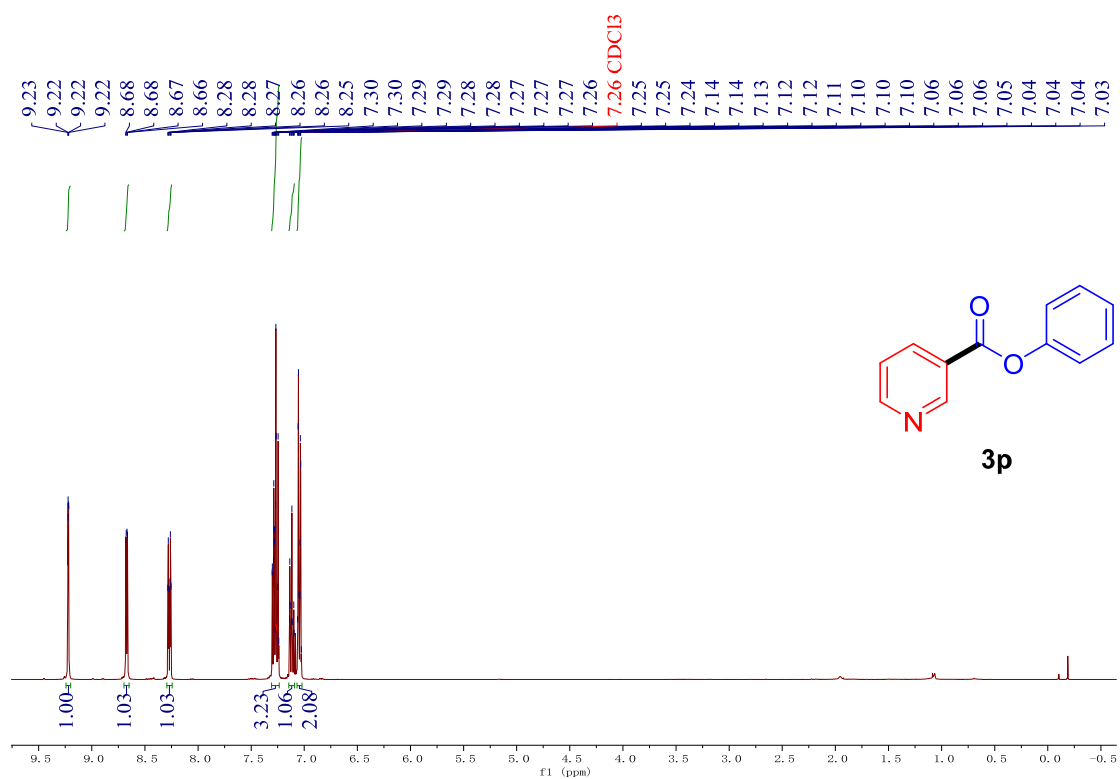


Figure S36. ^{13}C NMR spectrum of **3p** (100 MHz, CDCl_3)

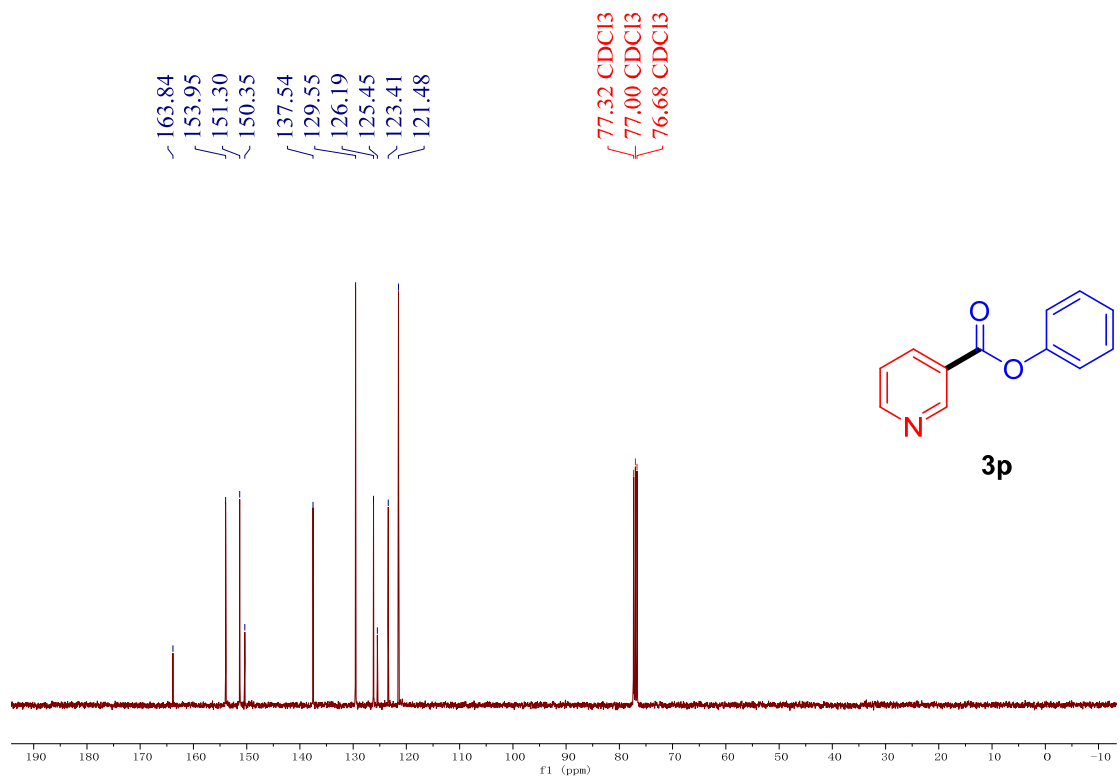


Figure S37. ^1H NMR spectrum of **3q** (400 MHz, CDCl_3)

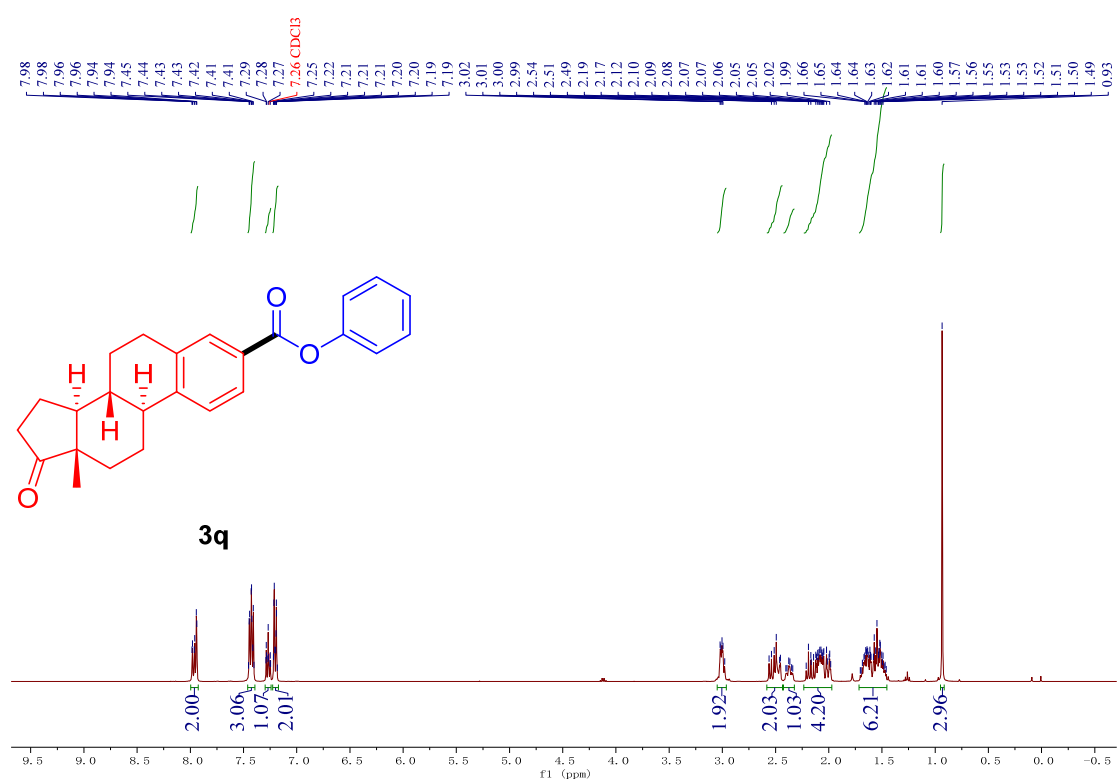


Figure S38. ^{13}C NMR spectrum of **3q** (100 MHz, CDCl_3)

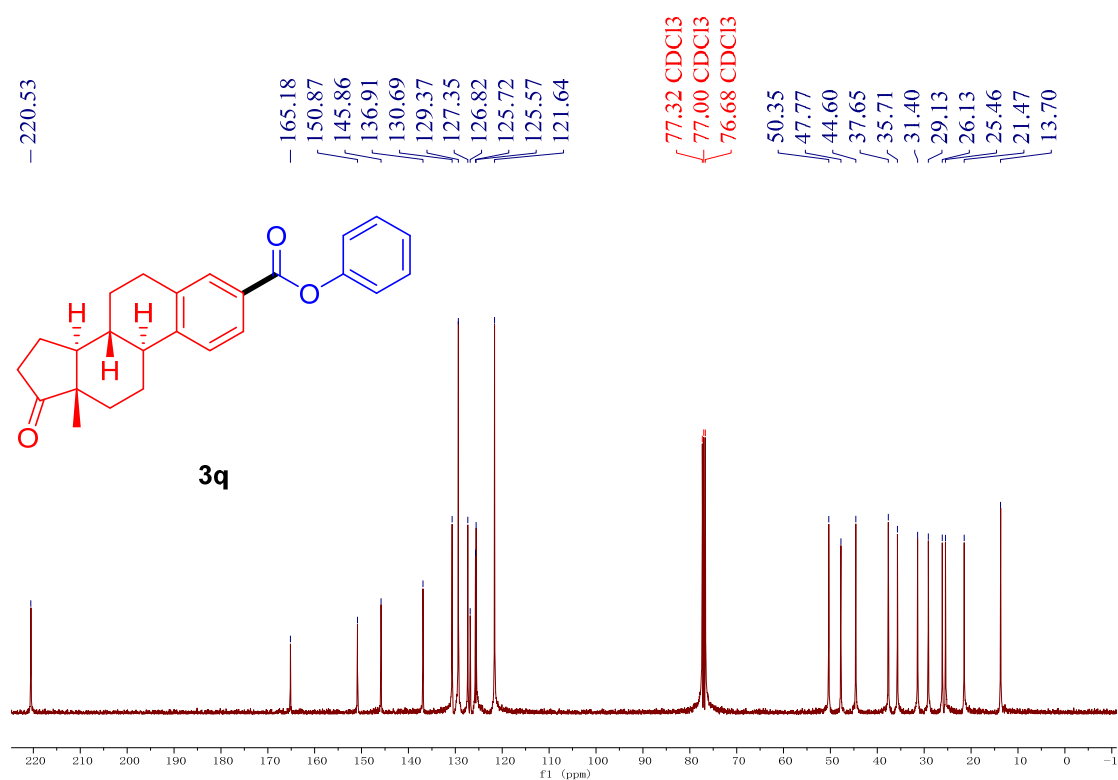


Figure S39. ^1H NMR spectrum of **3r** (400 MHz, CDCl_3)

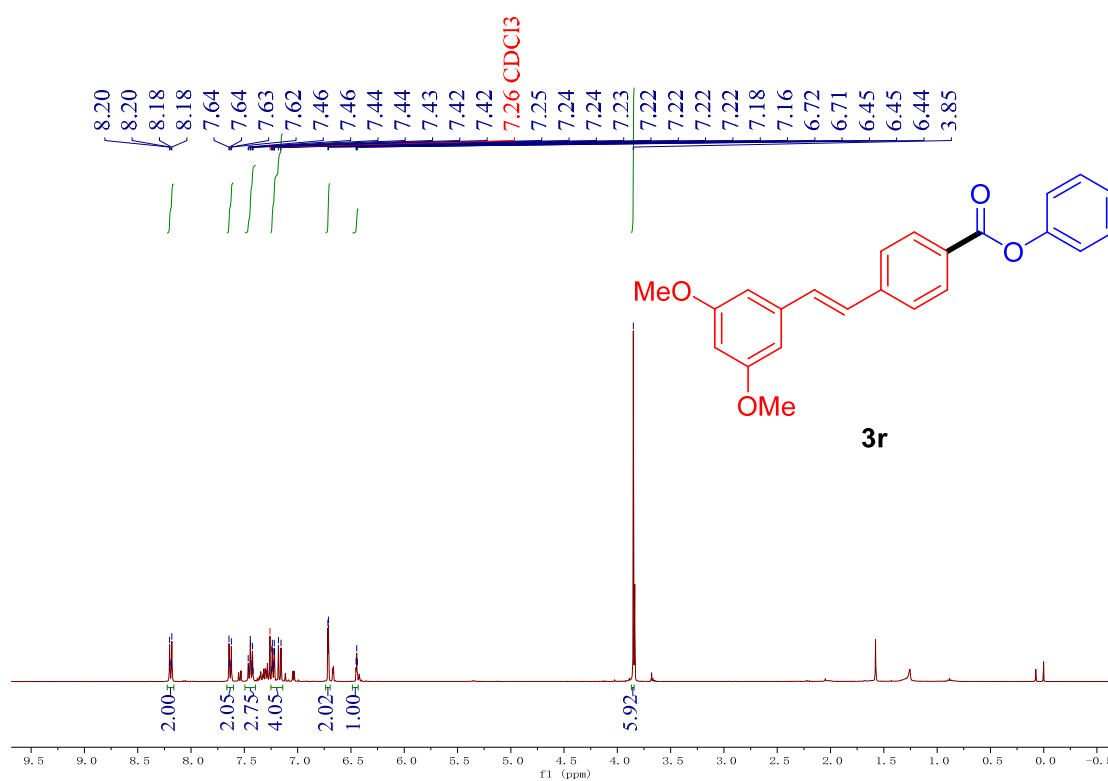


Figure S40. ^{13}C NMR spectrum of **3r** (100 MHz, CDCl_3)

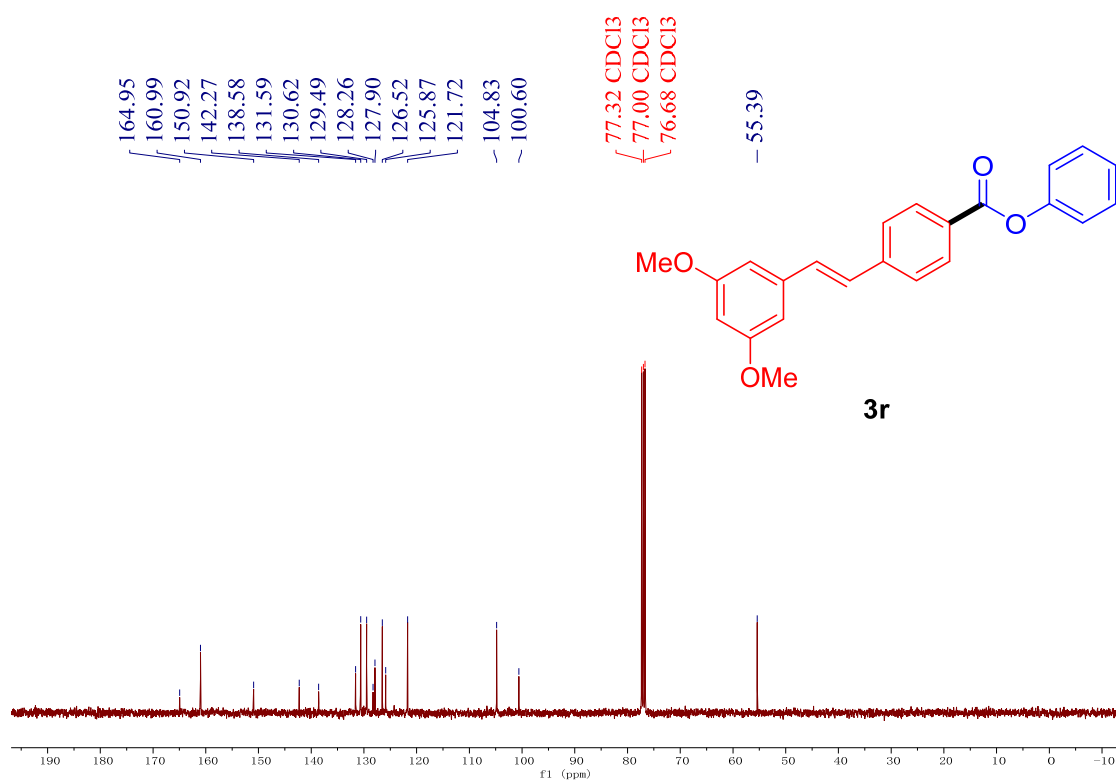


Figure S41. ^1H NMR spectrum of **4b** (400 MHz, CDCl_3)

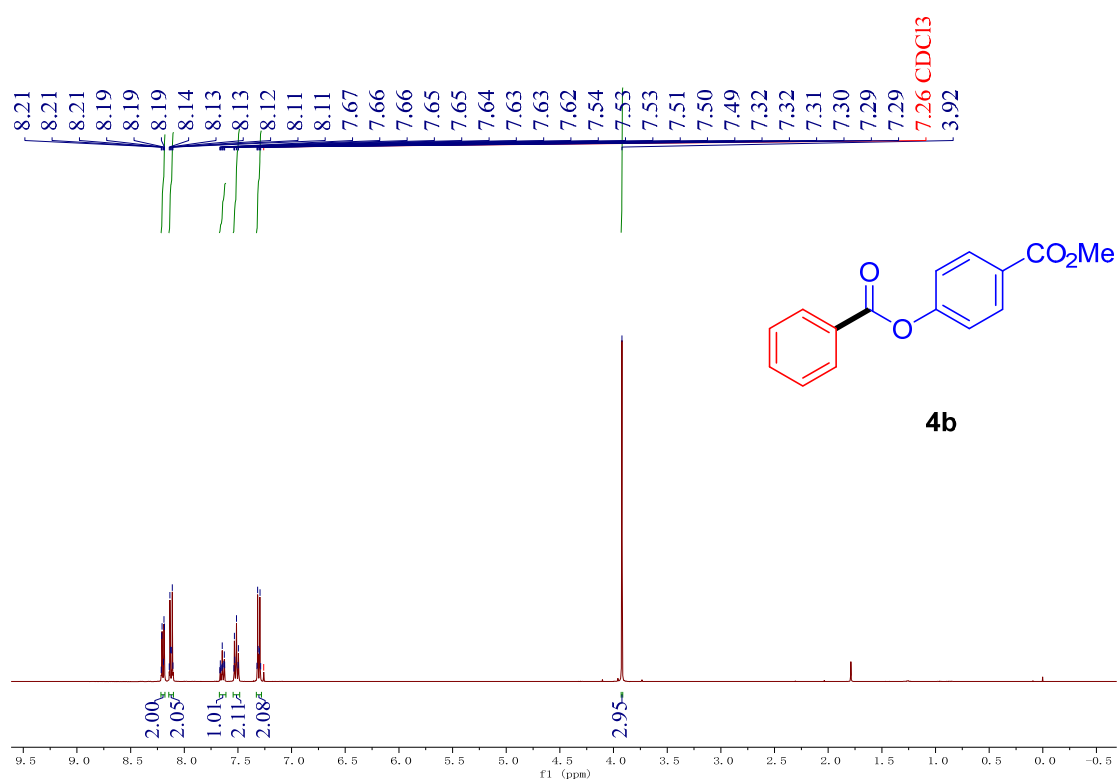


Figure S42. ^{13}C NMR spectrum of **4b** (100 MHz, CDCl_3)

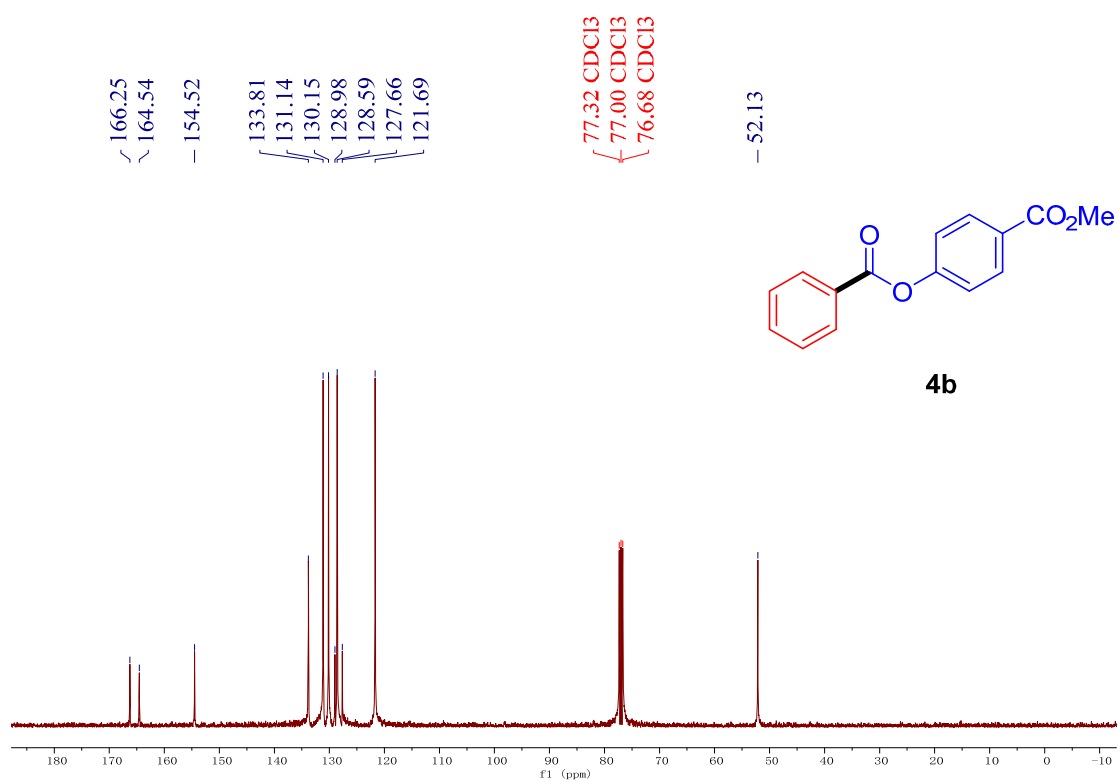


Figure S43. ^1H NMR spectrum of **4c** (400 MHz, CDCl_3)

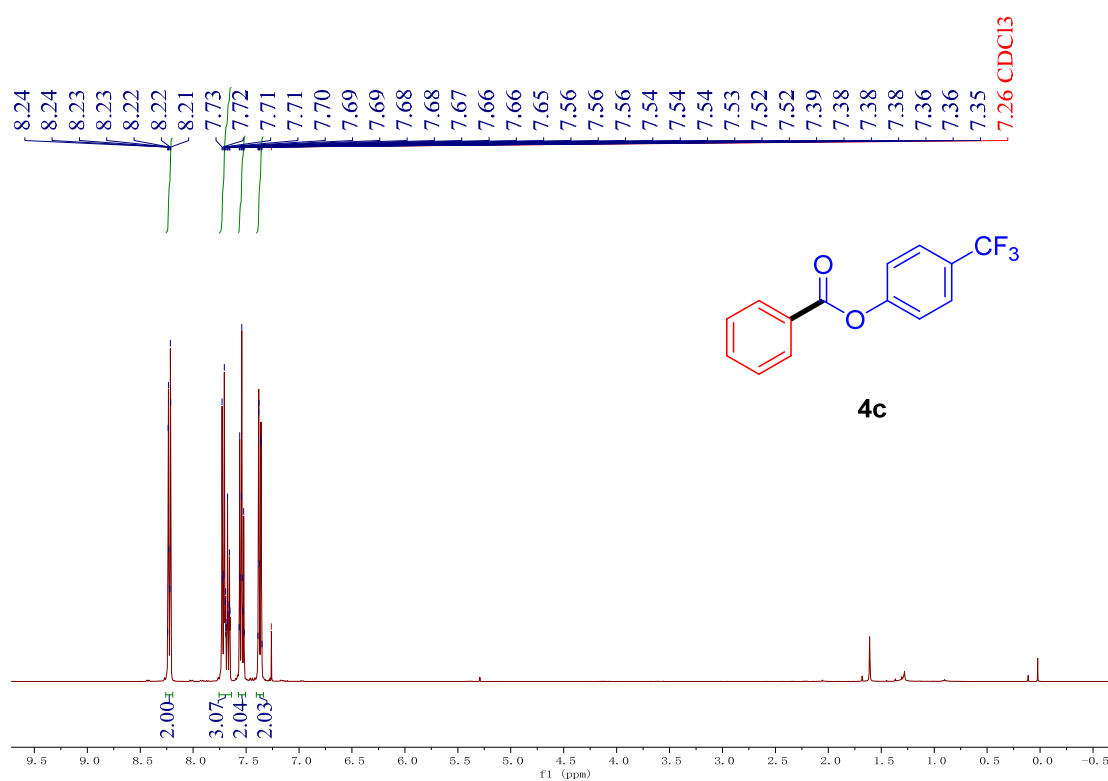


Figure S44. ^{13}C NMR spectrum of **4c** (100 MHz, CDCl_3)

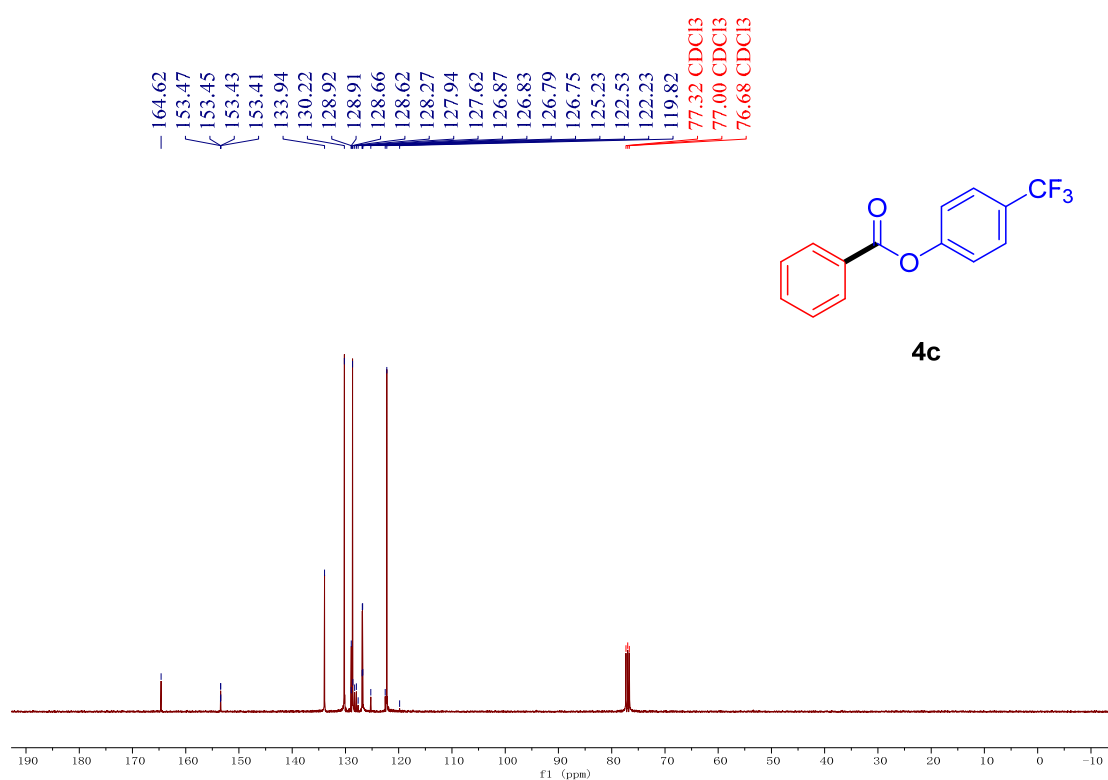


Figure S45. ^{19}F NMR spectrum of **4c** (376 MHz, CDCl_3)

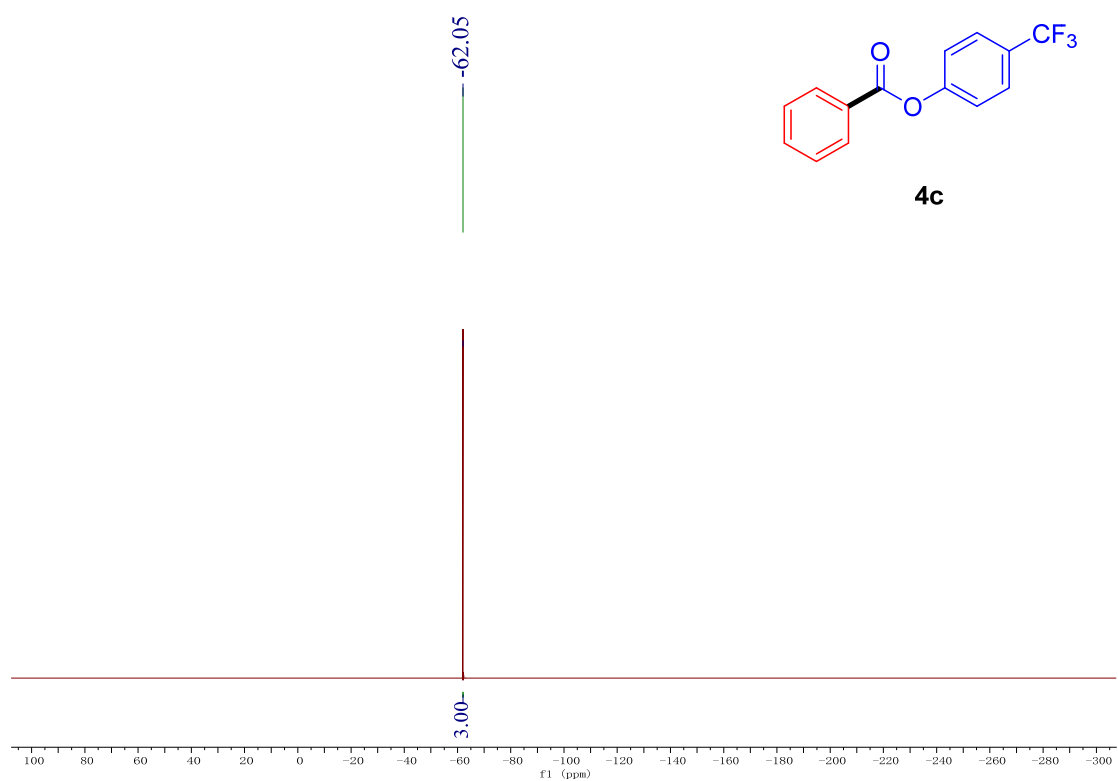


Figure S46. ^1H NMR spectrum of **4d** (400 MHz, CDCl_3)

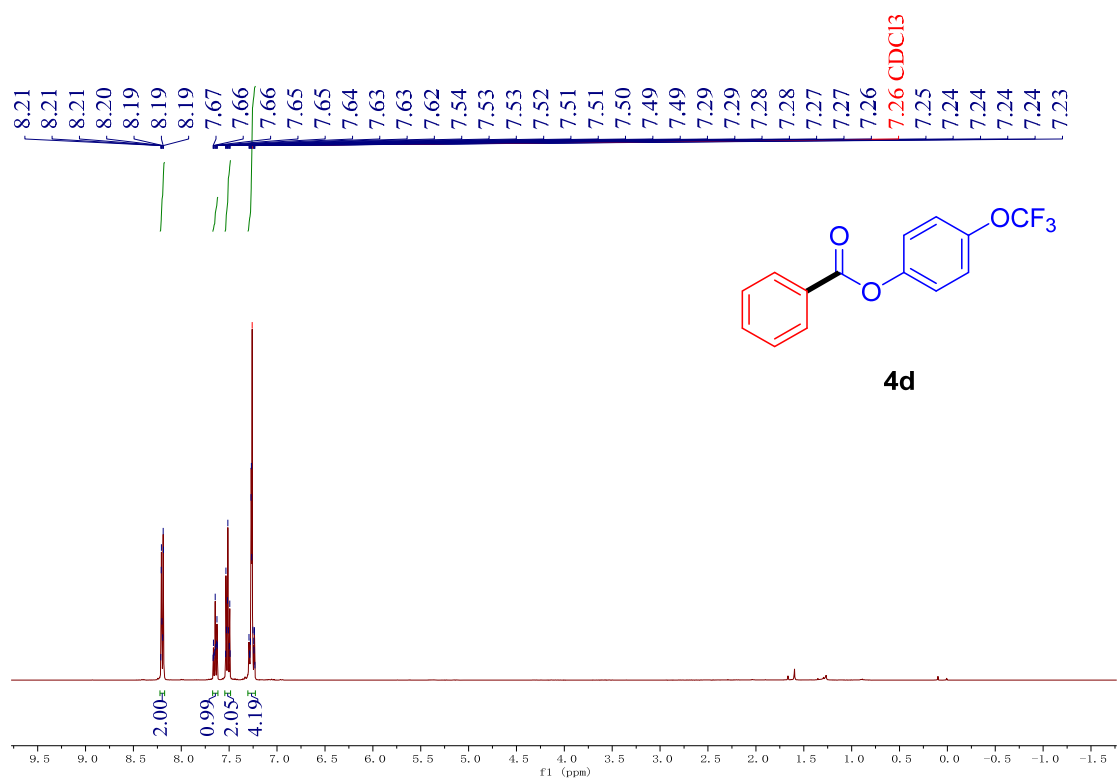


Figure S47. ^{13}C NMR spectrum of **4d** (100 MHz, CDCl_3)

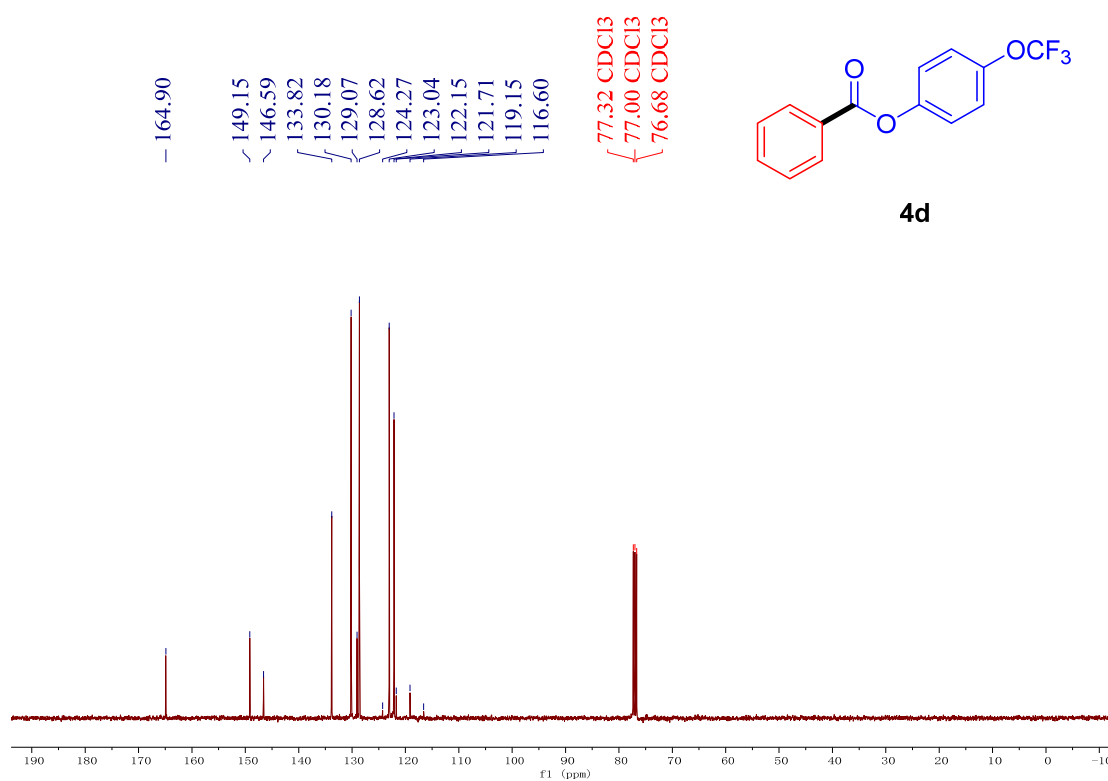


Figure S48. ^{19}F NMR spectrum of **4d** (376 MHz, CDCl_3)

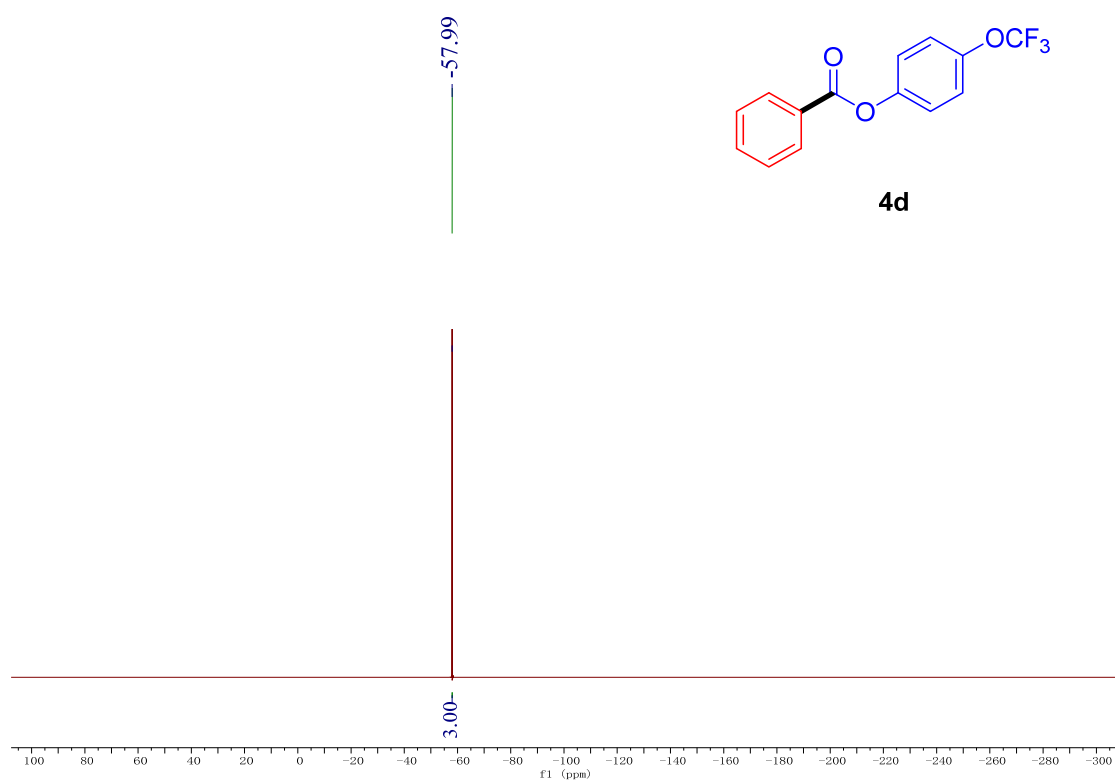


Figure S49. ^1H NMR spectrum of **4e** (400 MHz, CDCl_3)

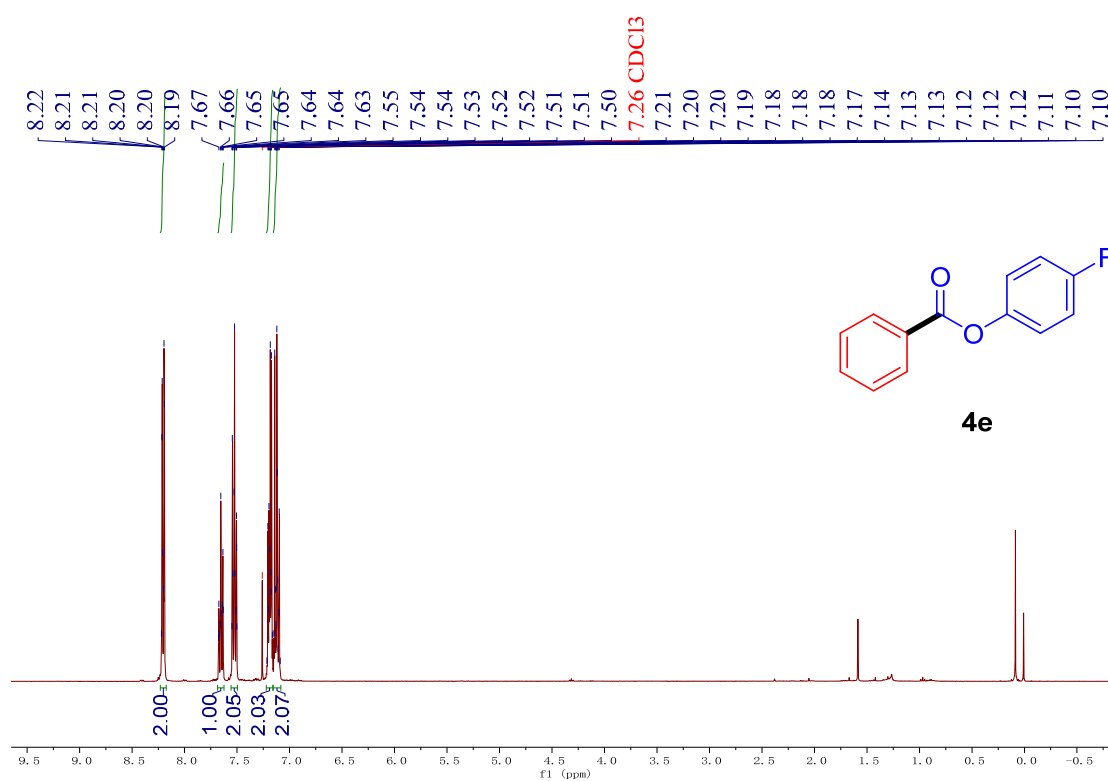


Figure S50. ^{13}C NMR spectrum of **4e** (100 MHz, CDCl_3)

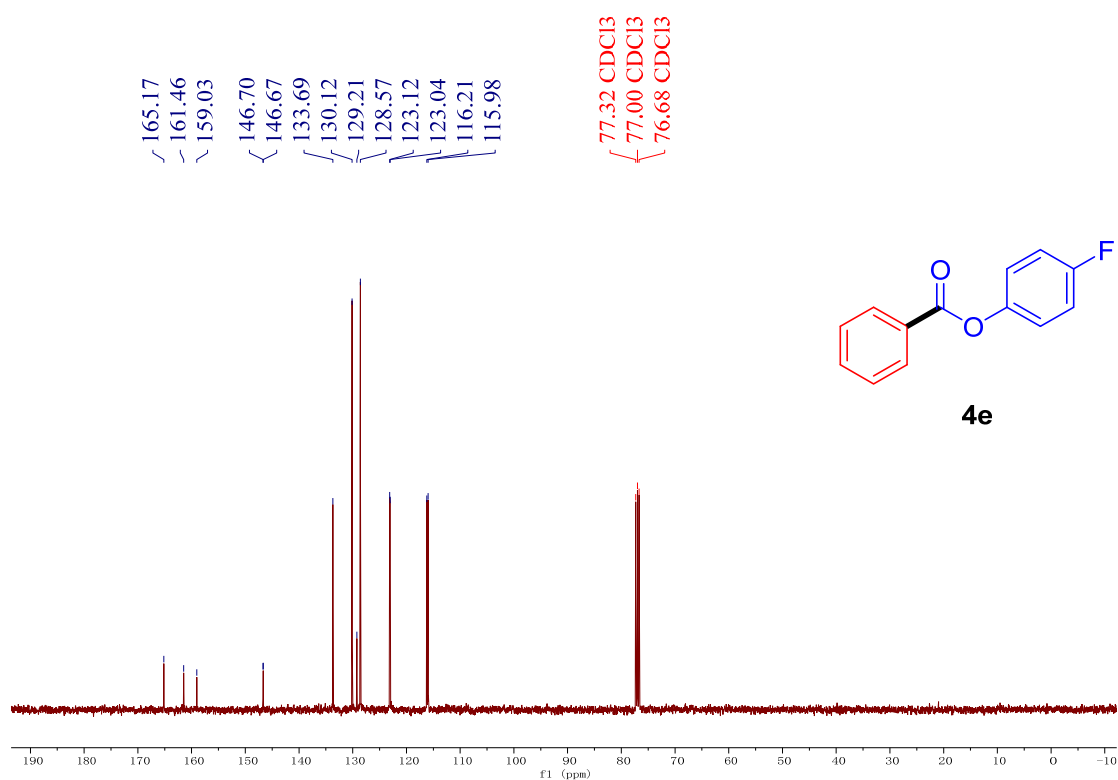


Figure S51. ^{19}F NMR spectrum of **4e** (376 MHz, CDCl_3)

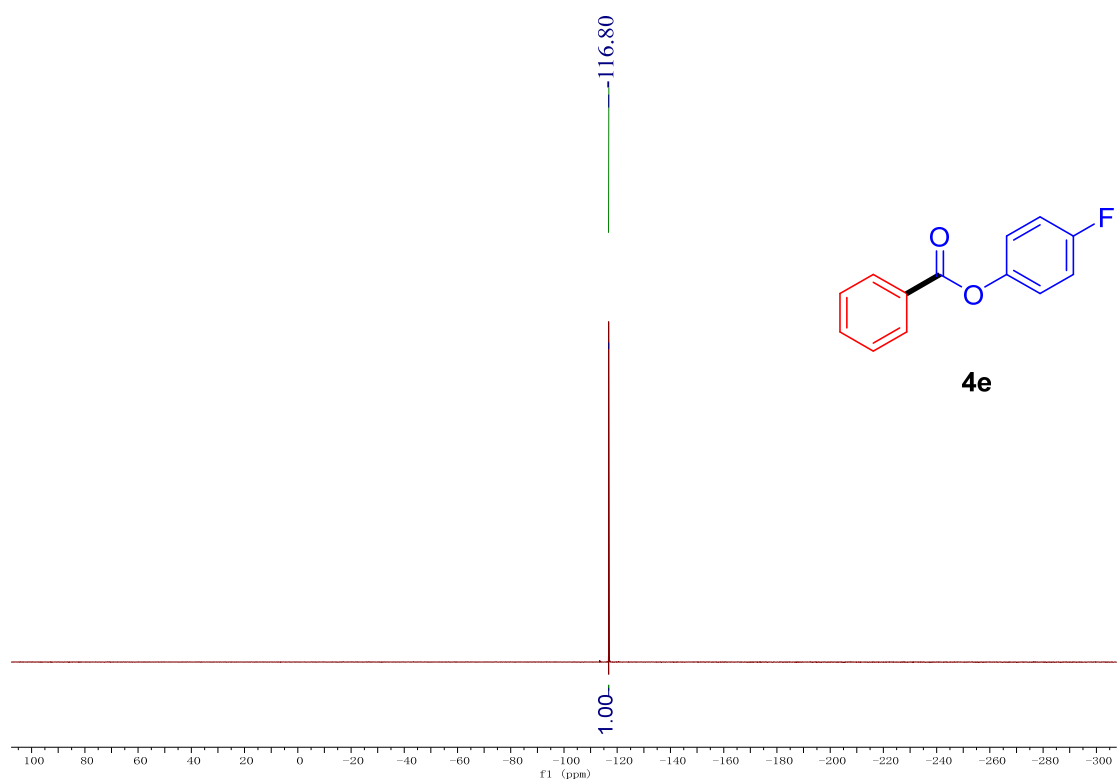


Figure S52. ^1H NMR spectrum of **4f** (400 MHz, CDCl_3)

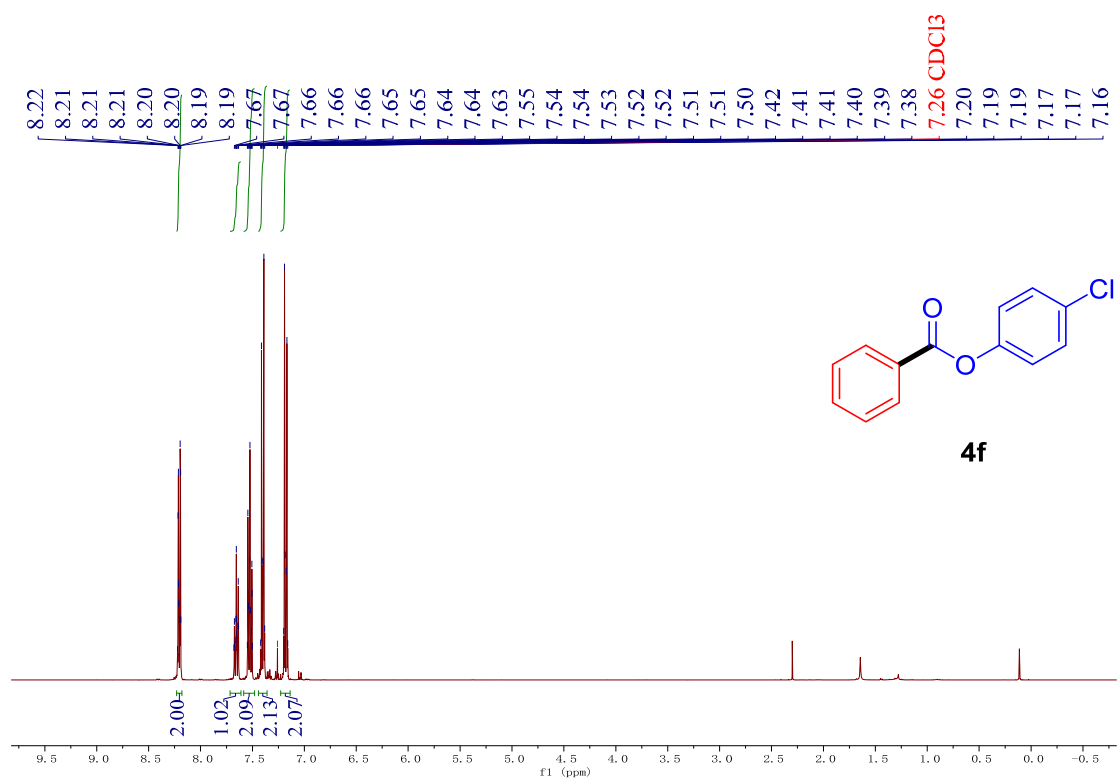


Figure S53. ^{13}C NMR spectrum of **4f** (100 MHz, CDCl_3)

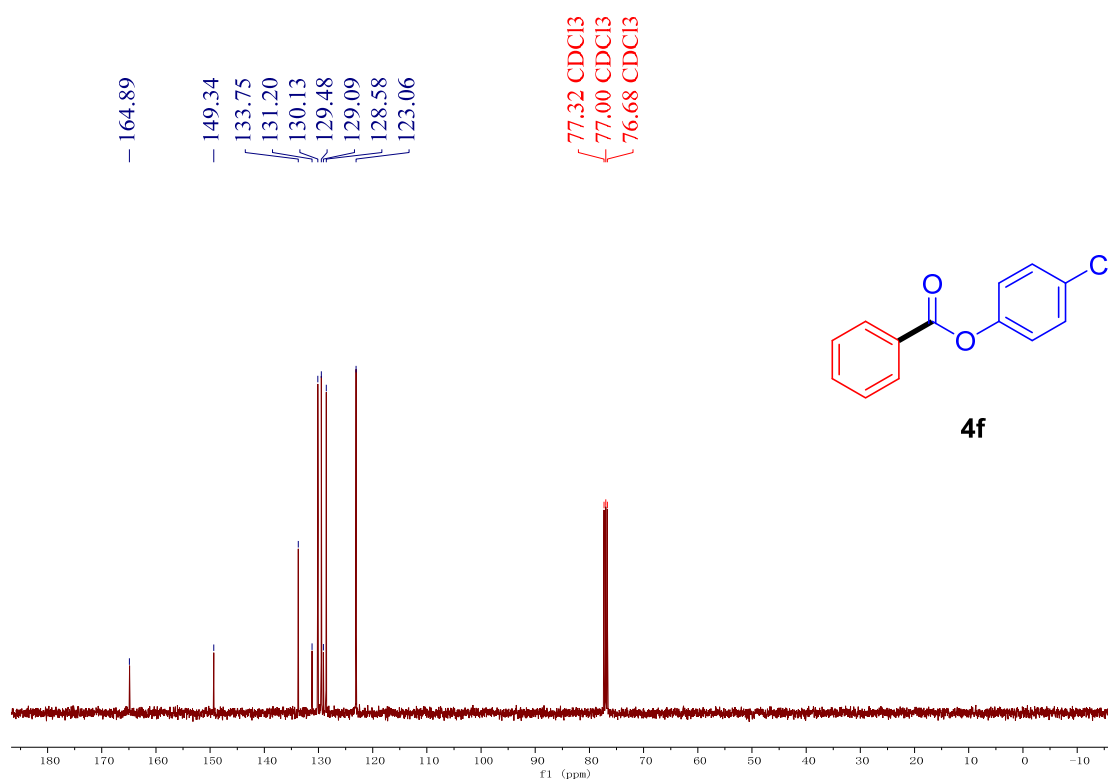


Figure S54. ^1H NMR spectrum of **4g** (400 MHz, CDCl_3)

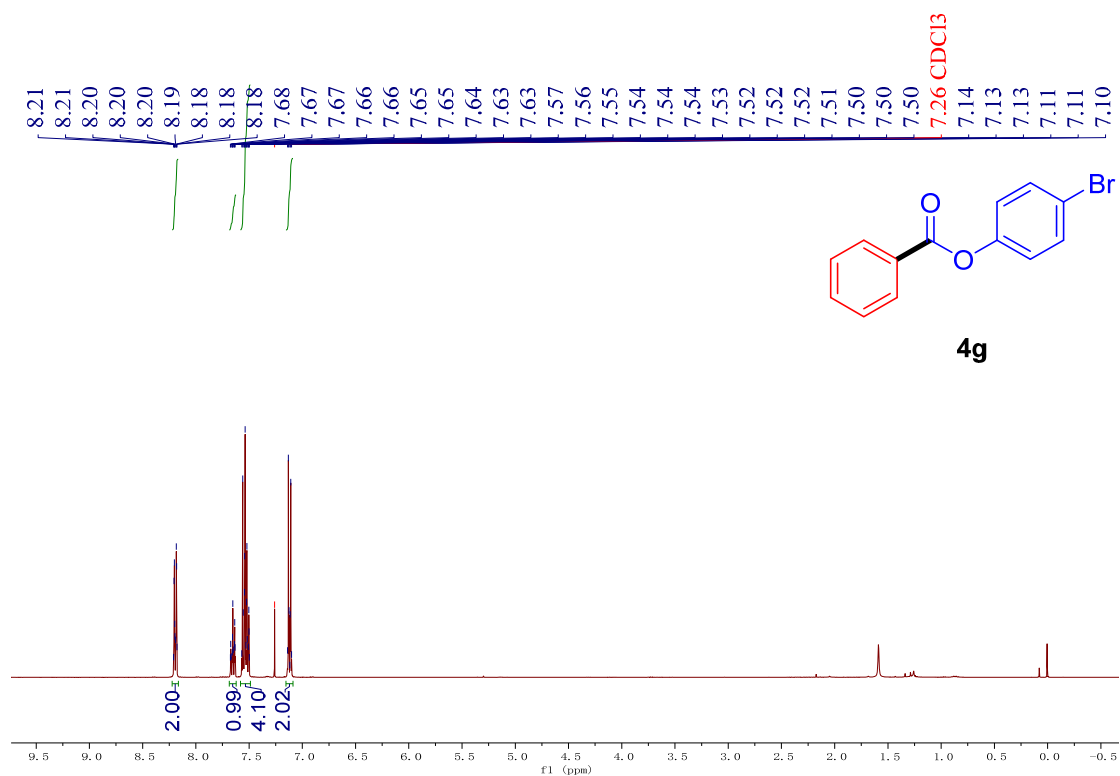


Figure S55. ^{13}C NMR spectrum of **4g** (100 MHz, CDCl_3)

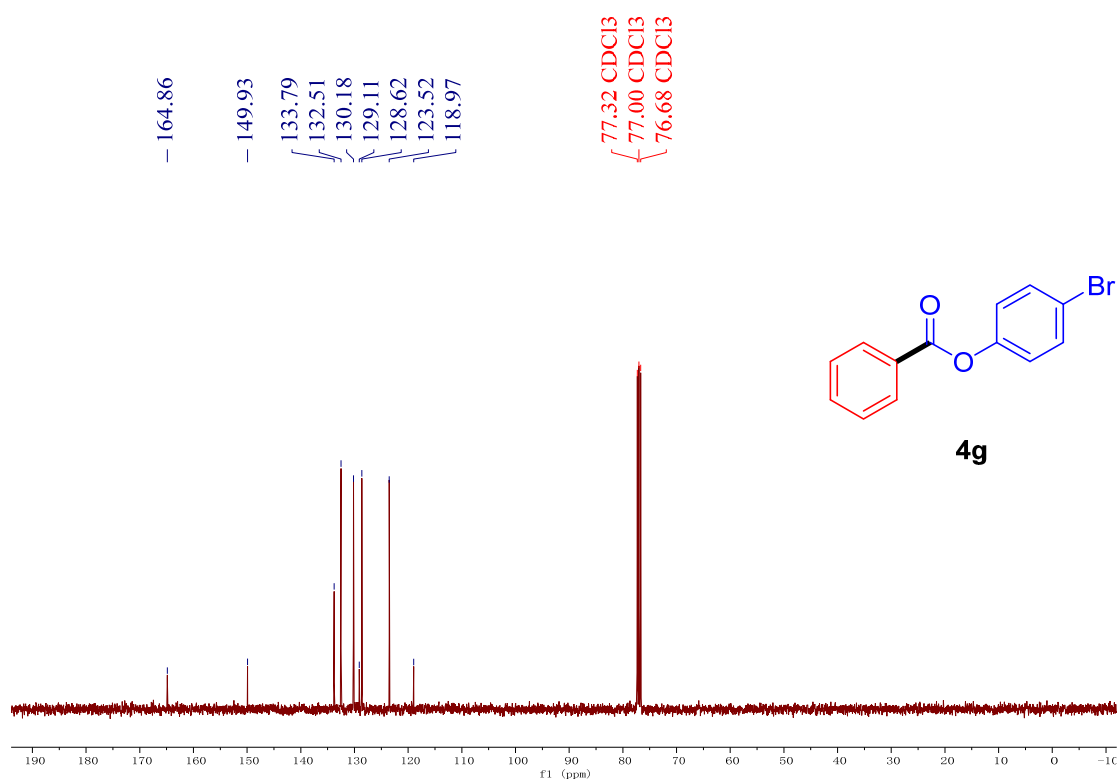


Figure S56. ^1H NMR spectrum of **4h** (400 MHz, CDCl_3)

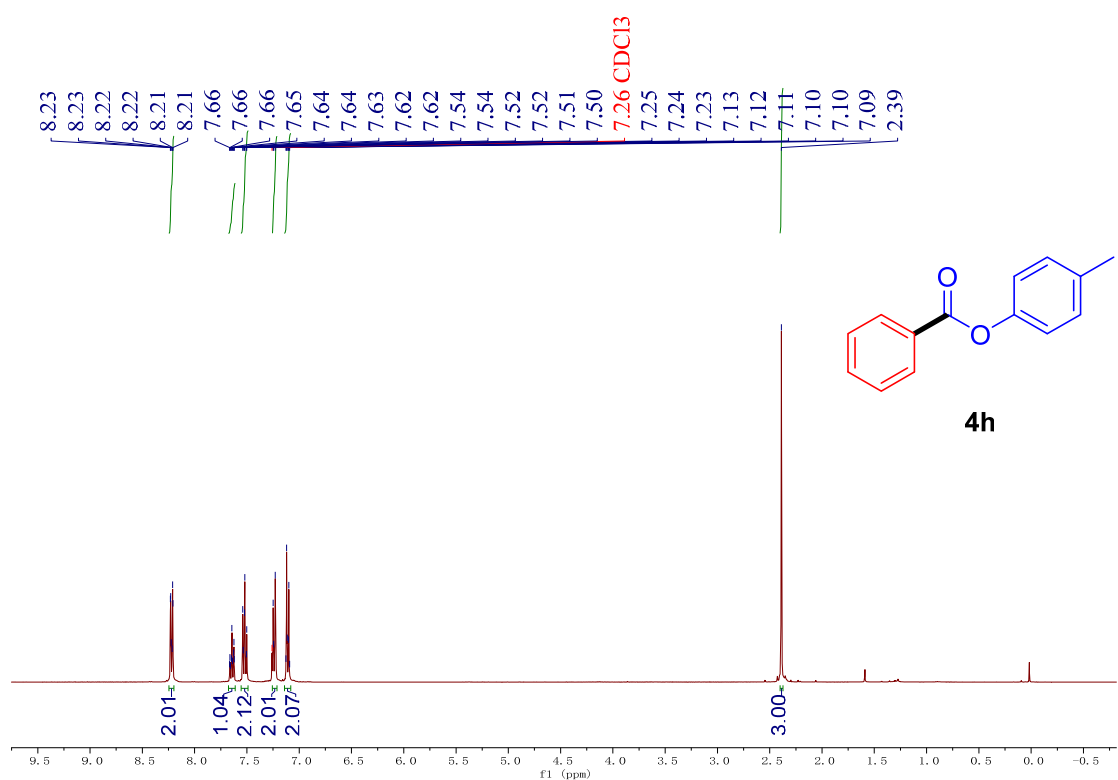


Figure S57. ^{13}C NMR spectrum of **4h** (100 MHz, CDCl_3)

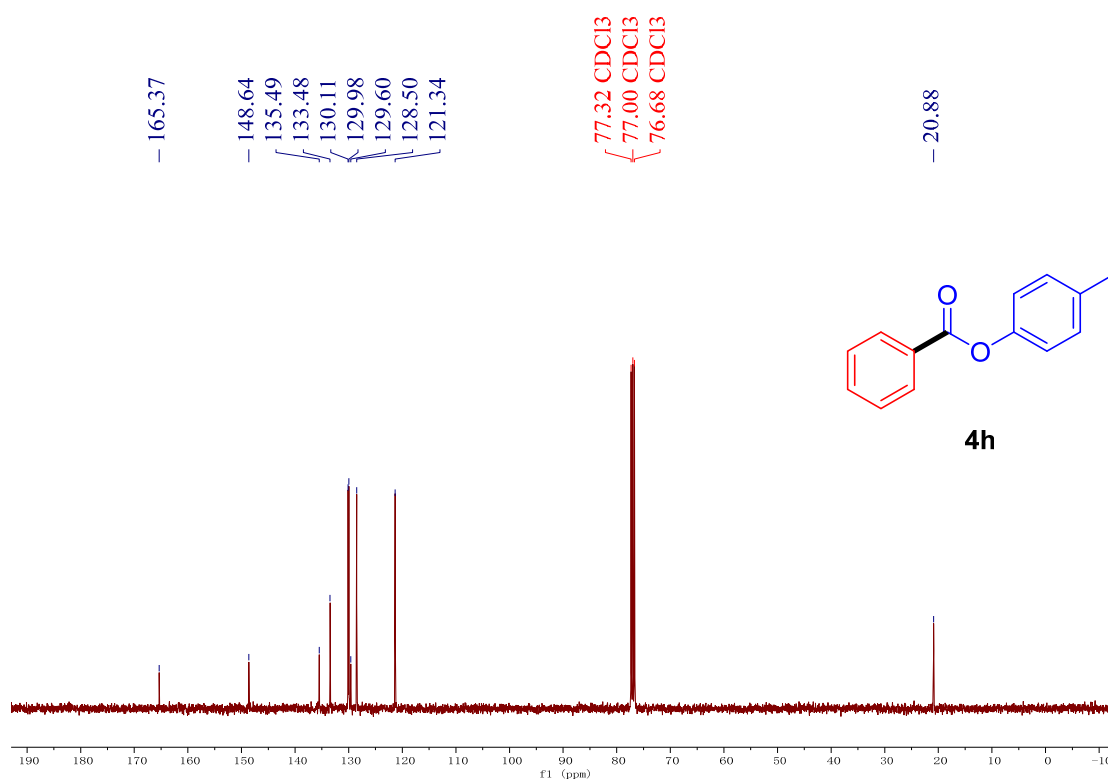


Figure S58. ^1H NMR spectrum of **4i** (400 MHz, CDCl_3)

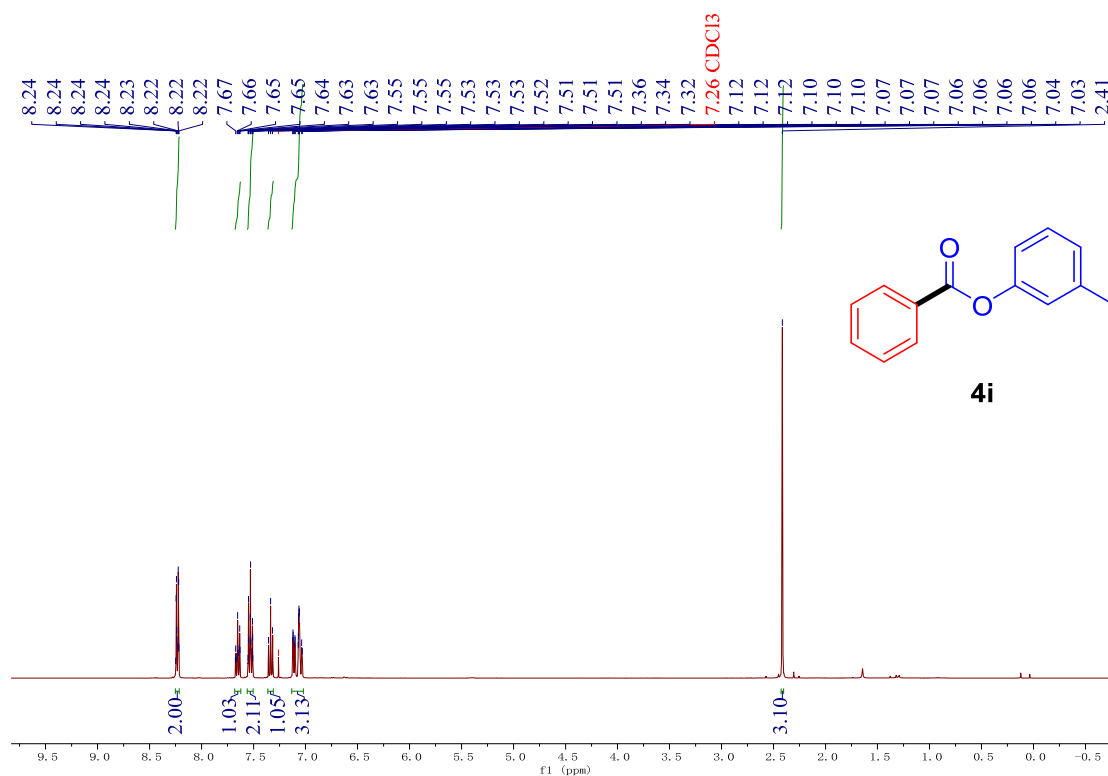


Figure S59. ^{13}C NMR spectrum of **4i** (100 MHz, CDCl_3)

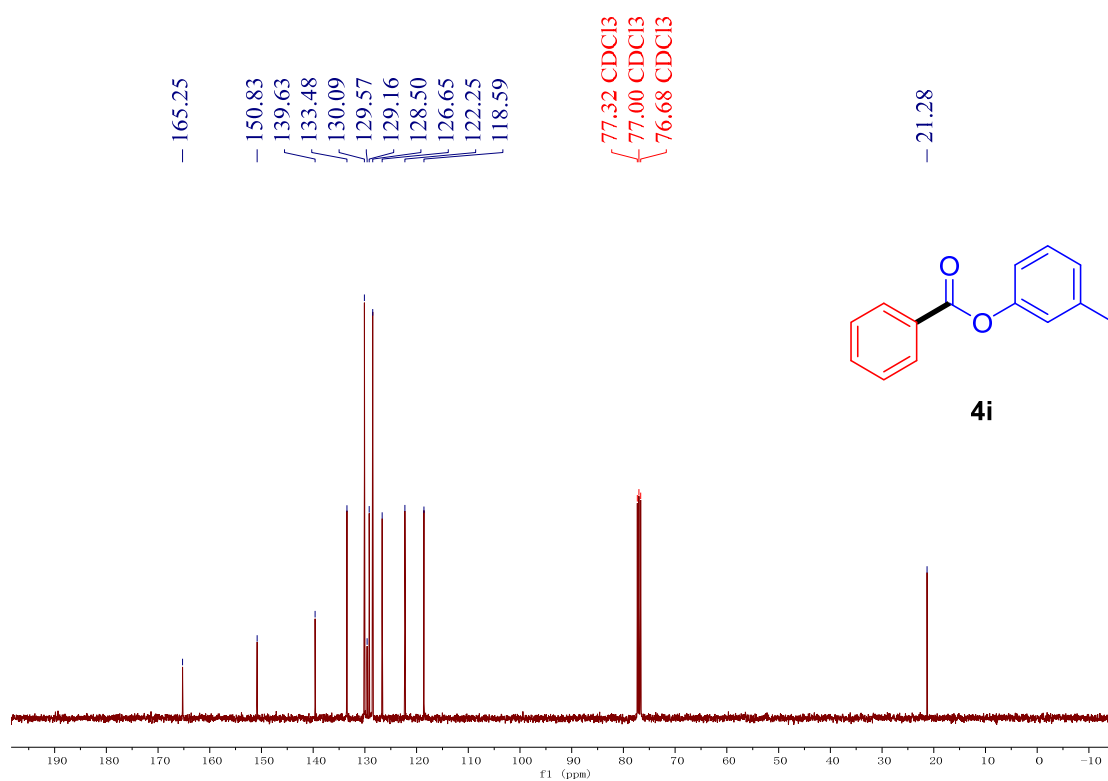


Figure S60. ^1H NMR spectrum of **4j** (400 MHz, CDCl_3)

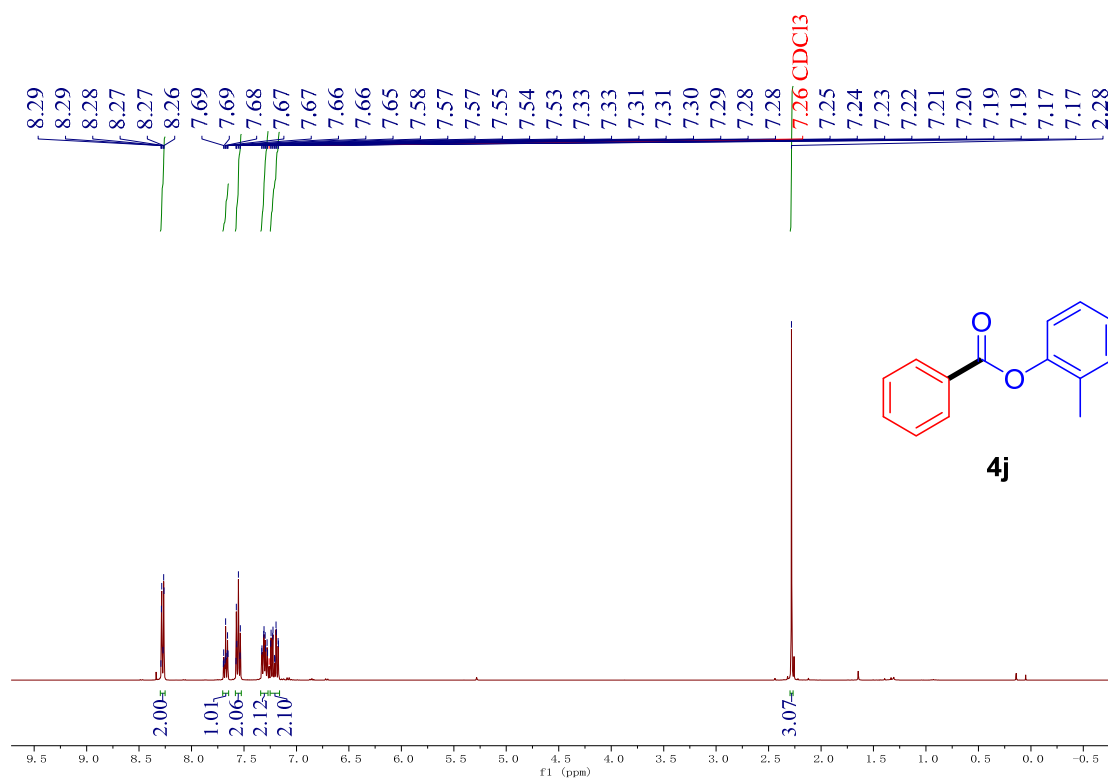


Figure S61. ^{13}C NMR spectrum of **4j** (100 MHz, CDCl_3)

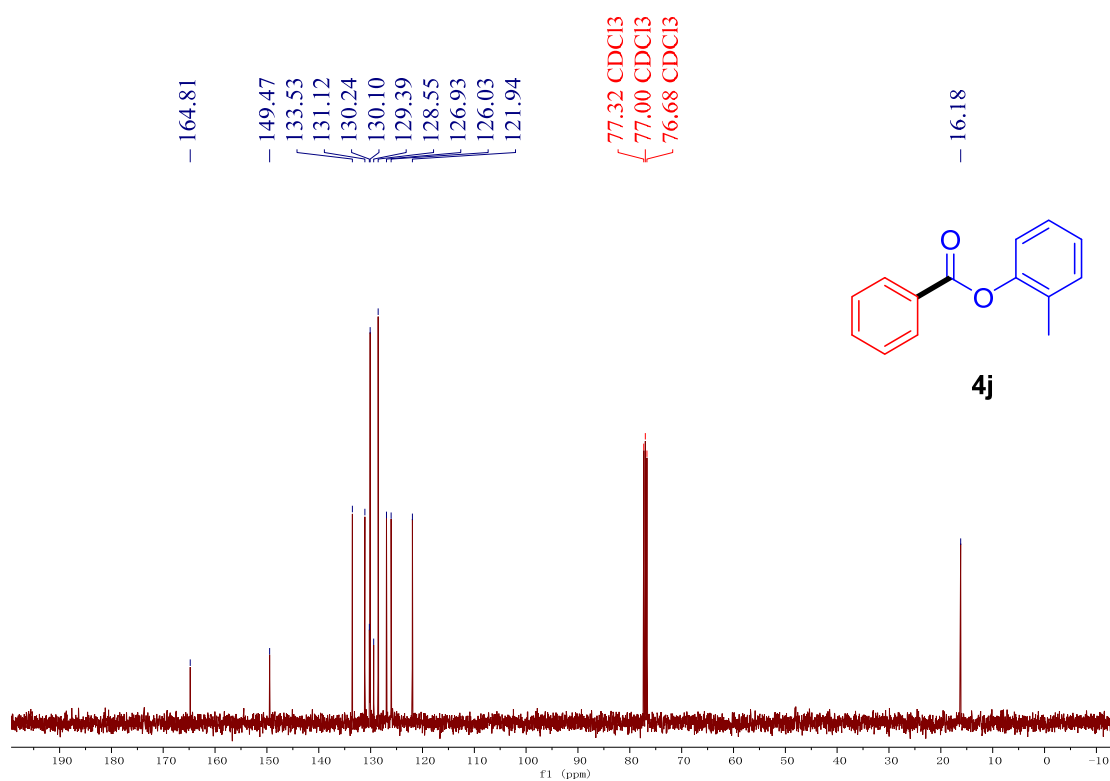


Figure S62. ^1H NMR spectrum of **4k** (400 MHz, CDCl_3)

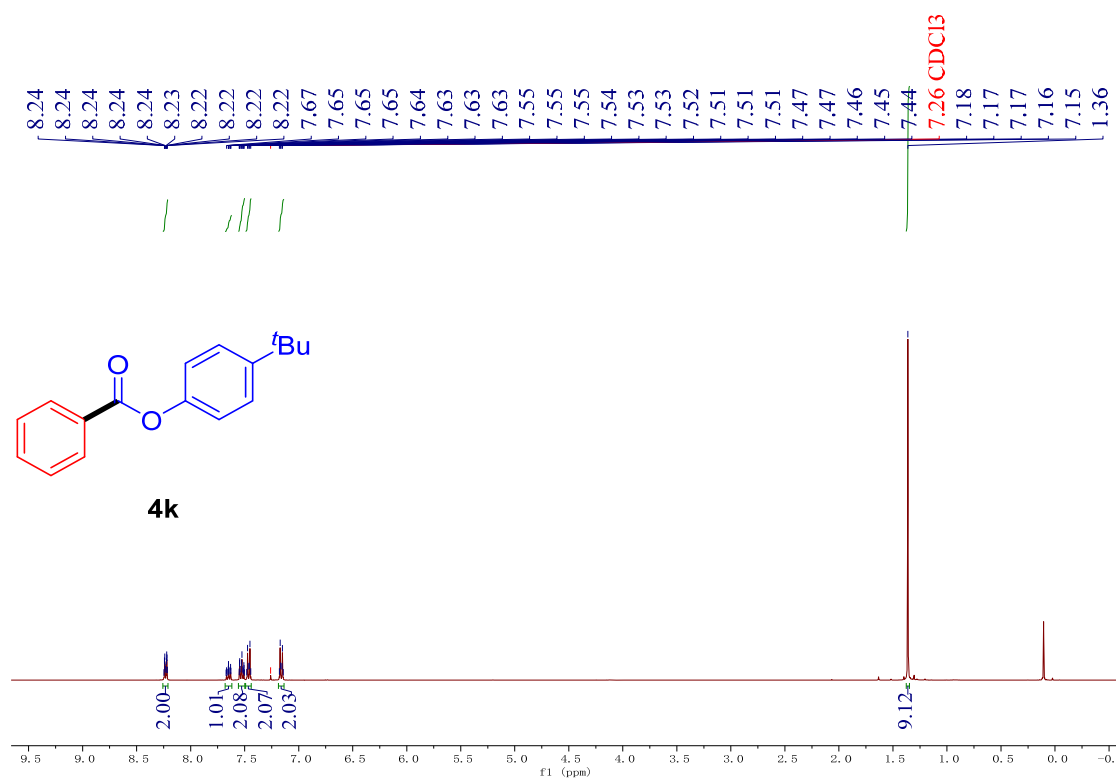


Figure S63. ^{13}C NMR spectrum of **4k** (100 MHz, CDCl_3)

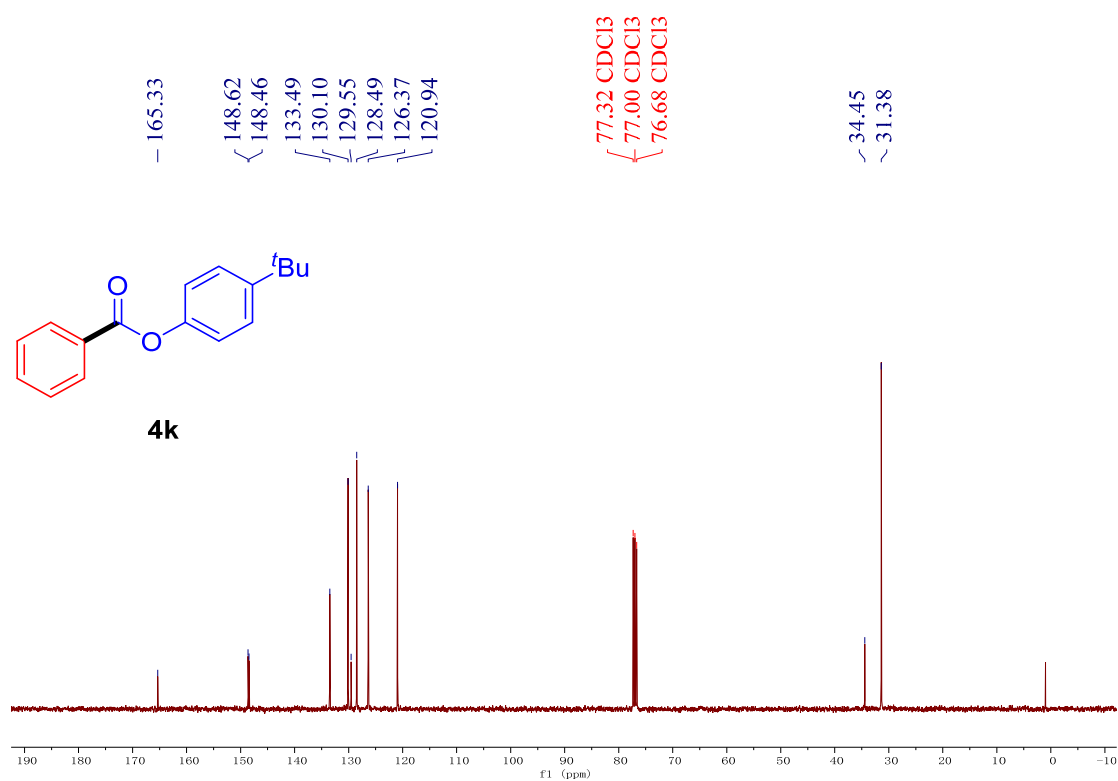


Figure S64. ^1H NMR spectrum of **4l** (400 MHz, CDCl_3)

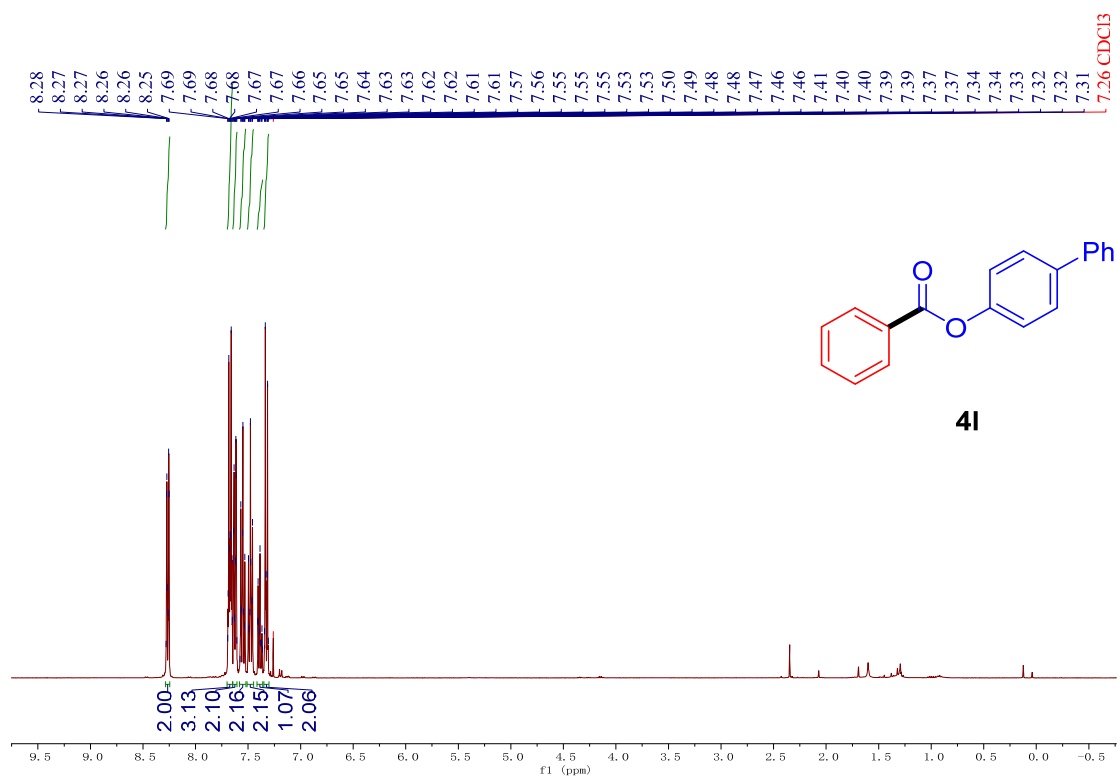


Figure S65. ^{13}C NMR spectrum of **4l** (100 MHz, CDCl_3)

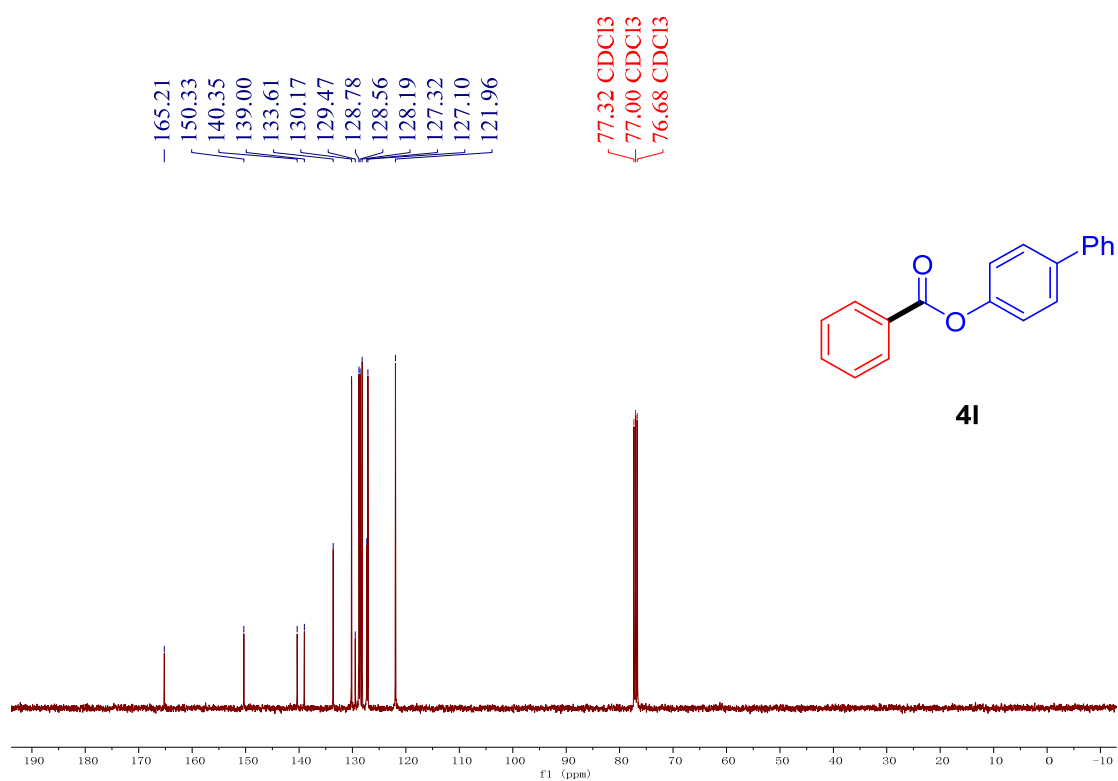


Figure S66. ^1H NMR spectrum of **4m** (400 MHz, CDCl_3)

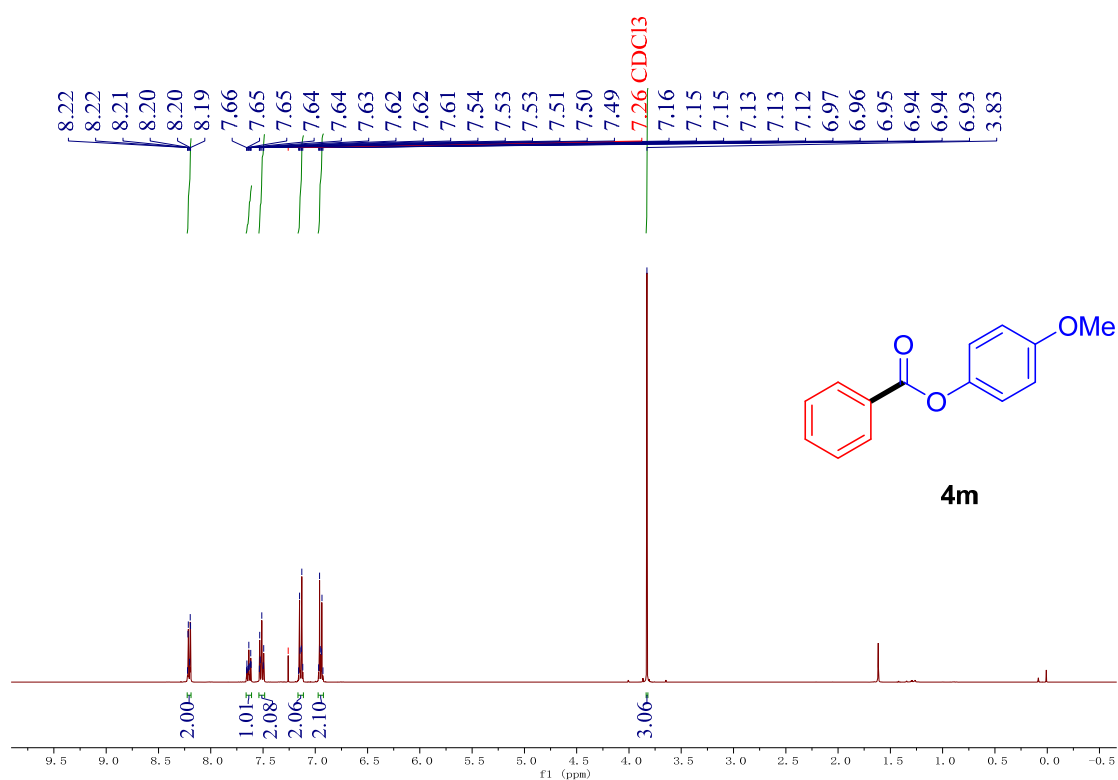


Figure S67. ^{13}C NMR spectrum of **4m** (100 MHz, CDCl_3)

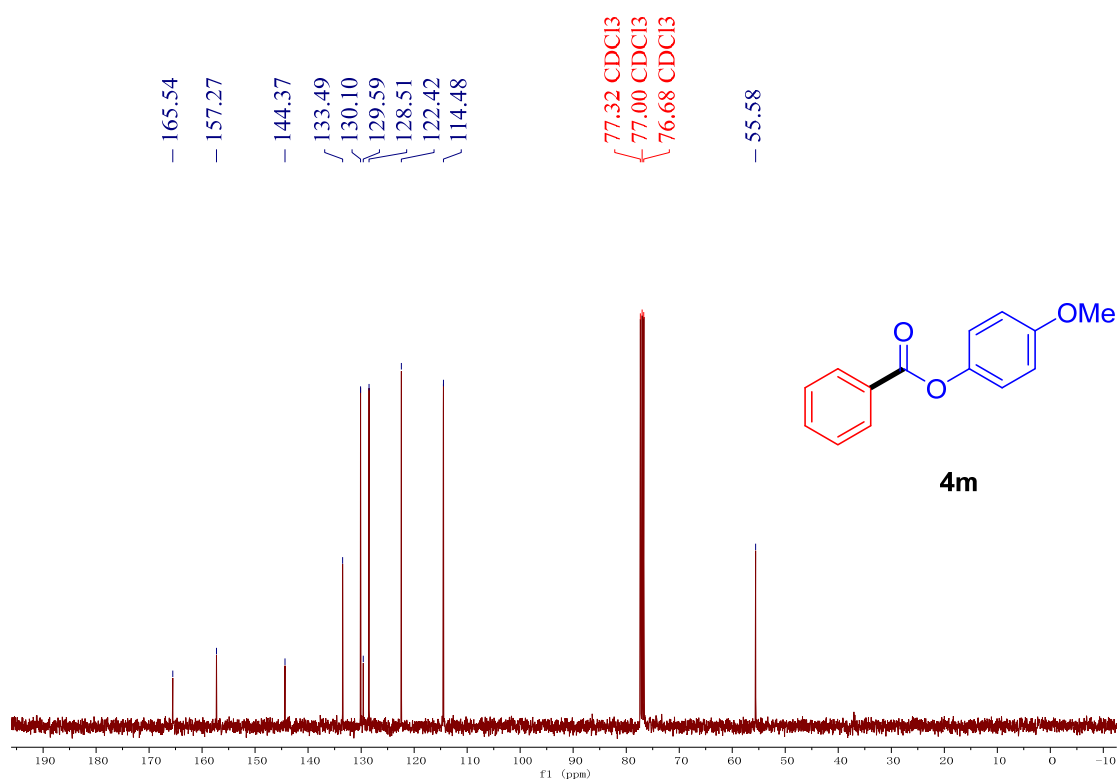


Figure S68. ^1H NMR spectrum of **4n** (400 MHz, CDCl_3)

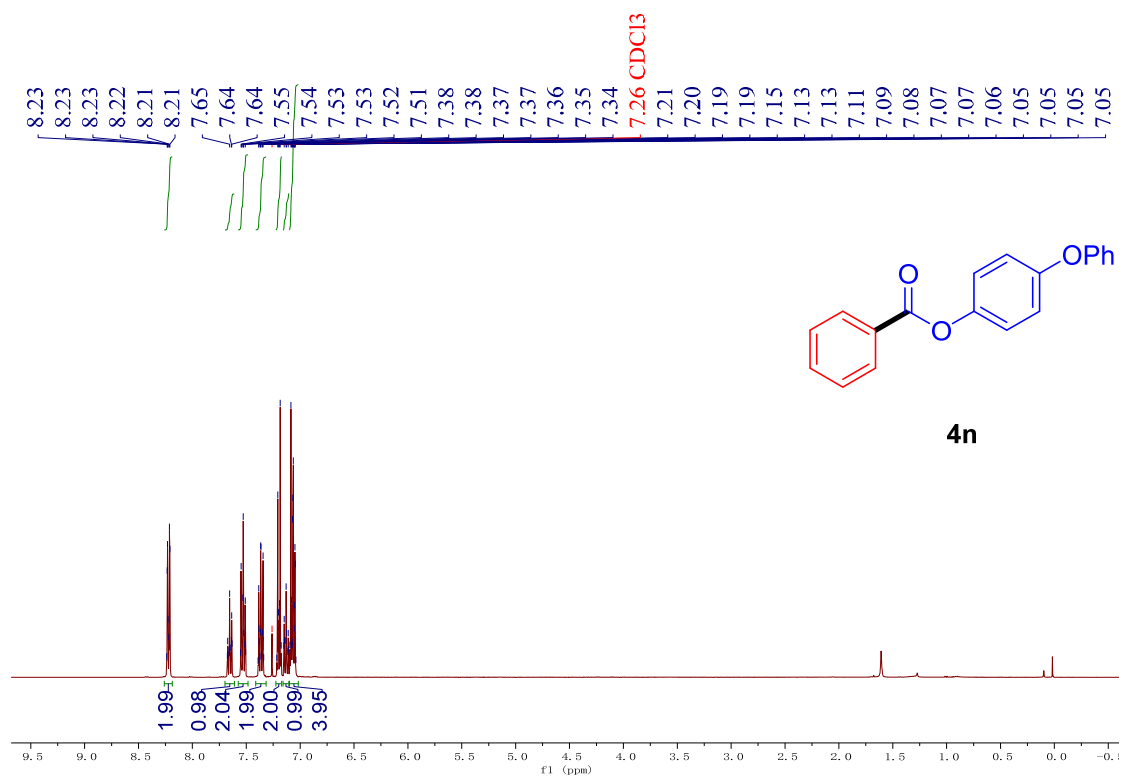


Figure S69. ^{13}C NMR spectrum of **4n** (100 MHz, CDCl_3)

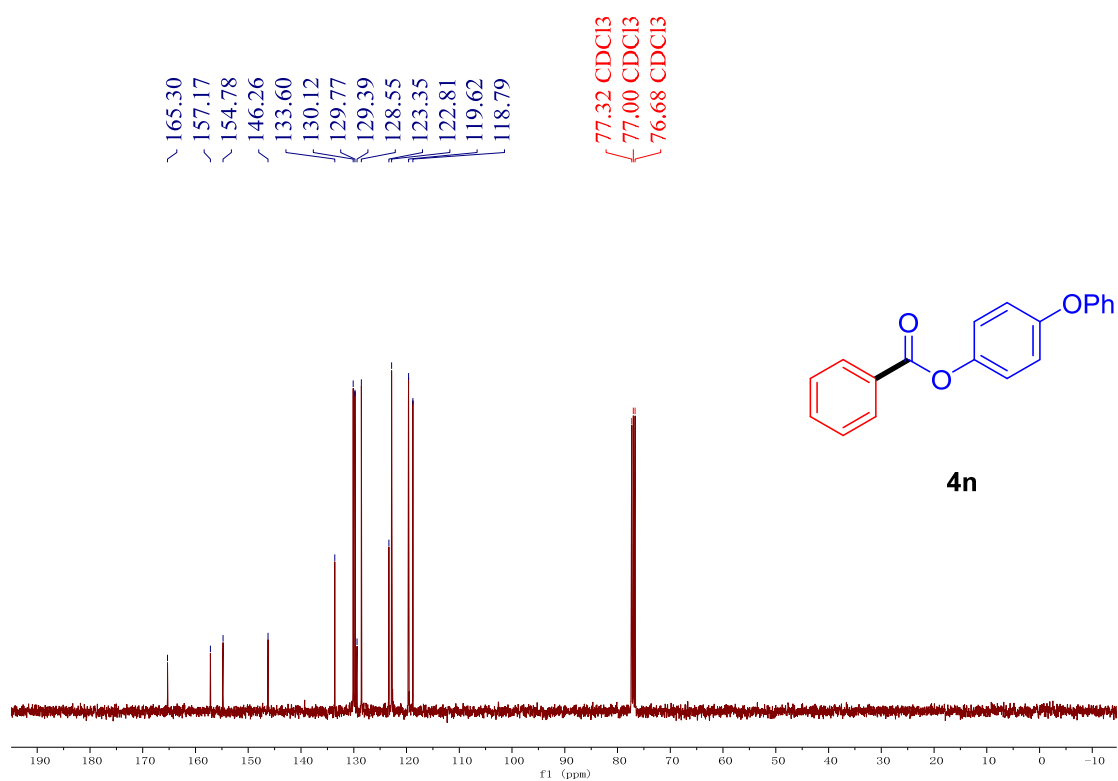


Figure S70. ^1H NMR spectrum of **4o** (400 MHz, CDCl_3)

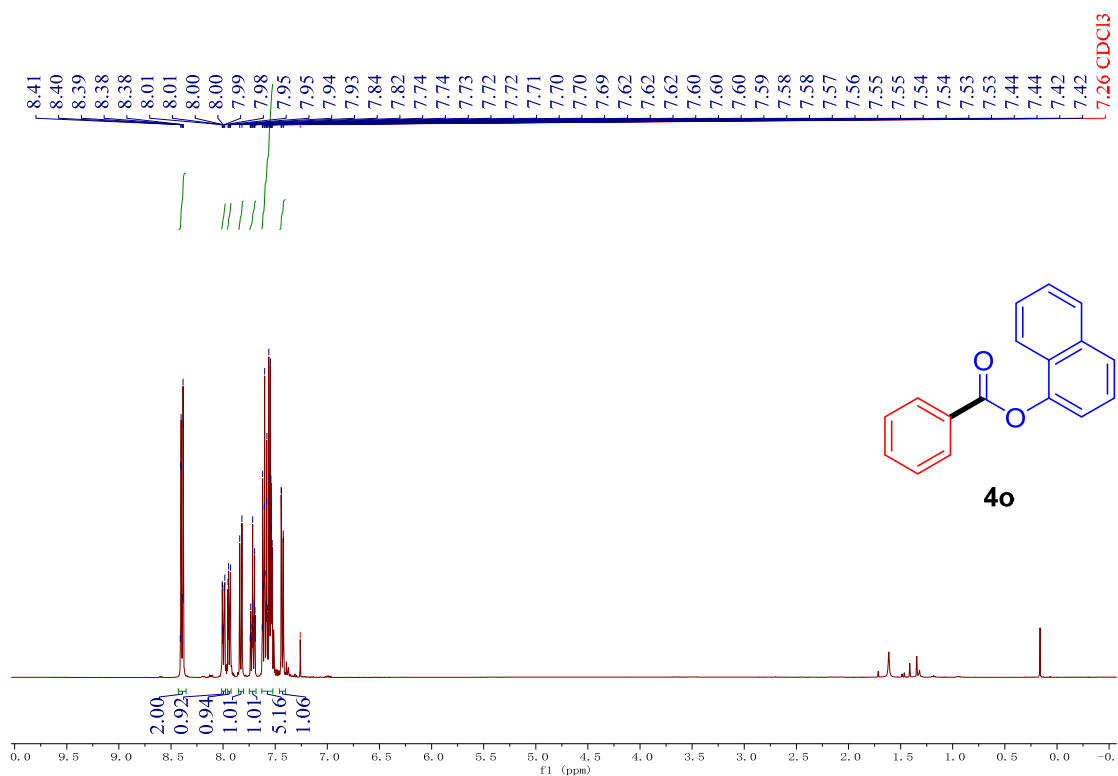


Figure S71. ^{13}C NMR spectrum of **4o** (100 MHz, CDCl_3)

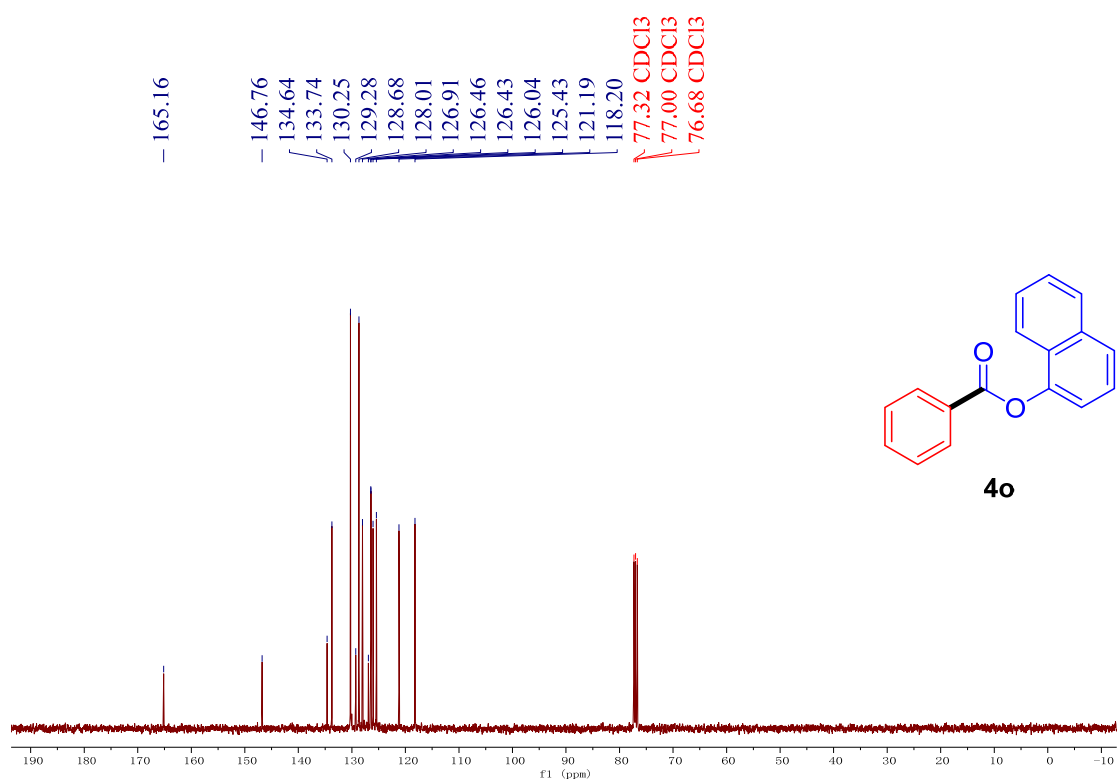


Figure S72. ^1H NMR spectrum of **4p** (400 MHz, CDCl_3)

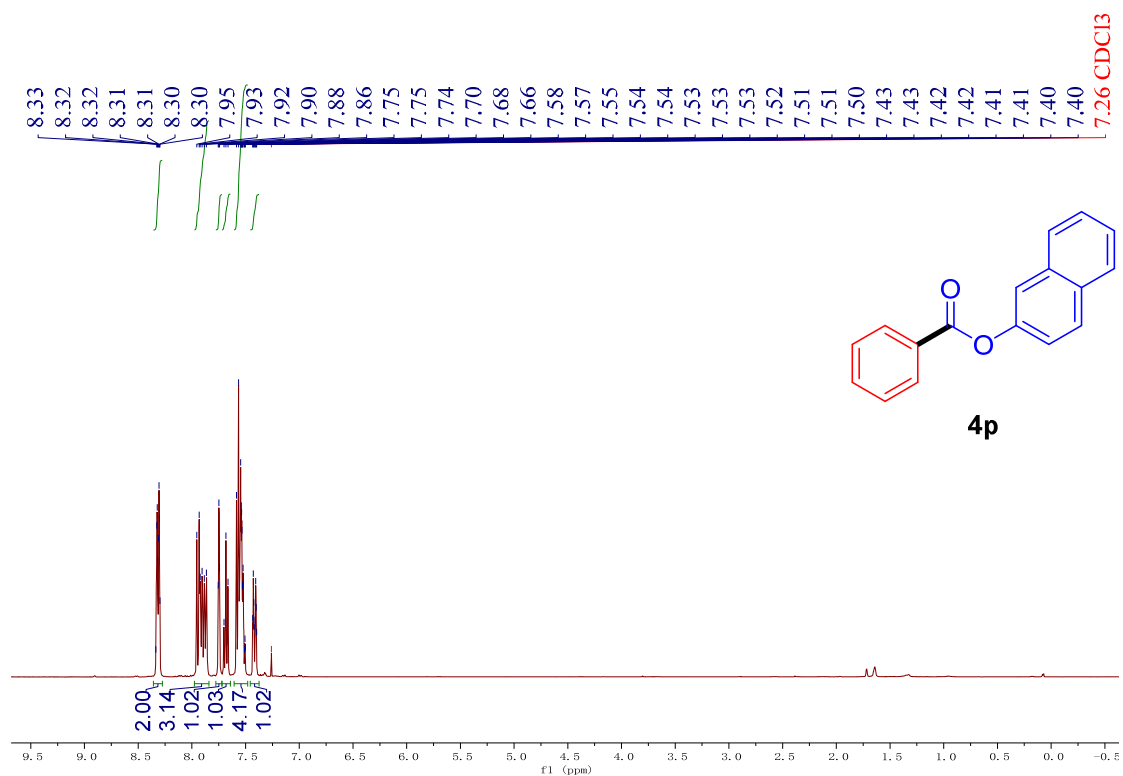


Figure S73. ^{13}C NMR spectrum of **4p** (100 MHz, CDCl_3)

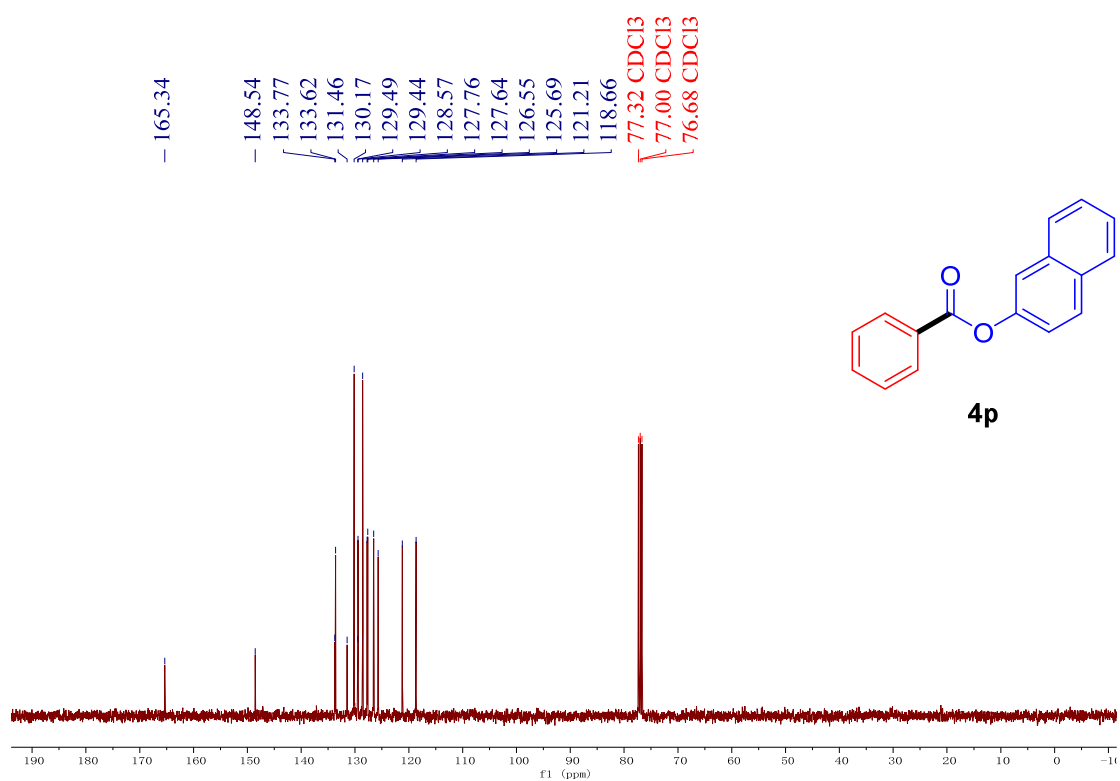


Figure S74. ^1H NMR spectrum of **4q** (400 MHz, CDCl_3)

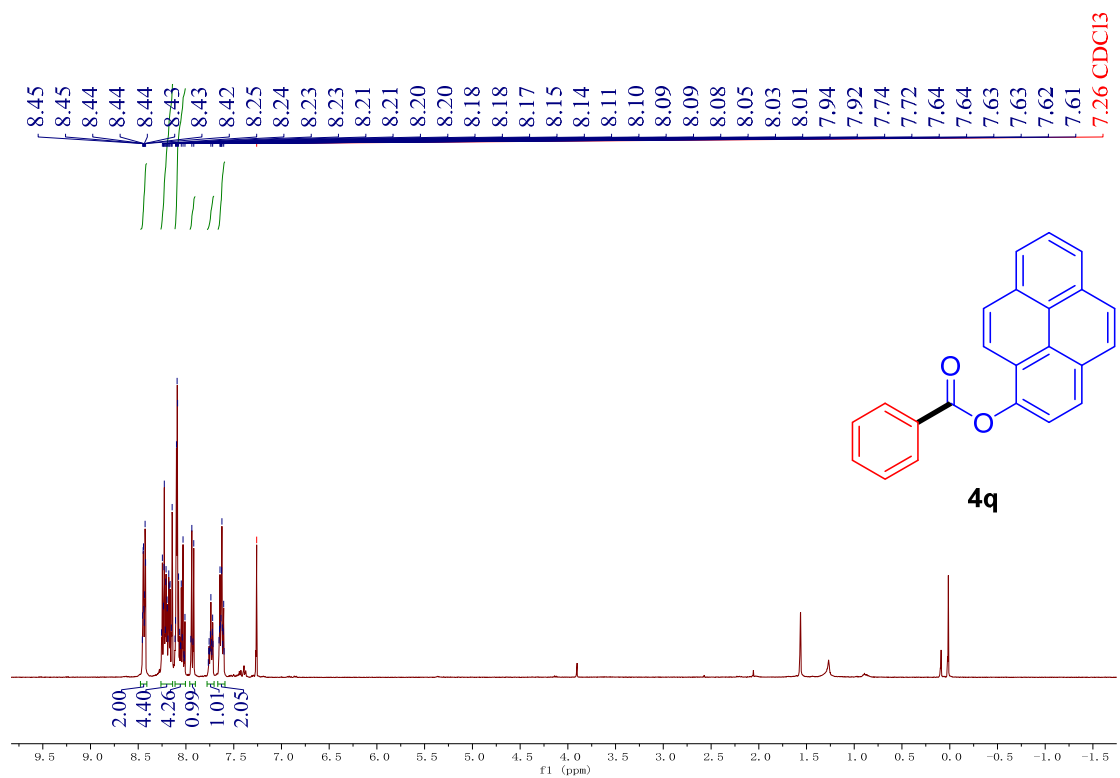


Figure S75. ^{13}C NMR spectrum of **4q** (100 MHz, CDCl_3)

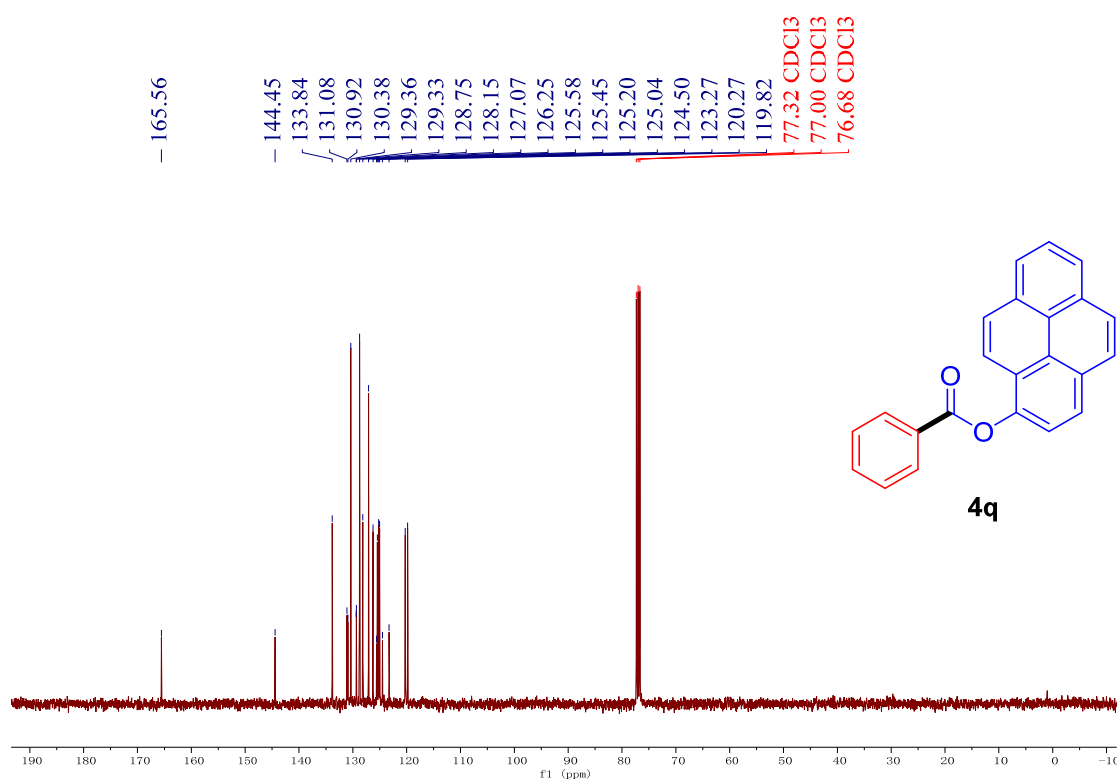


Figure S76. ^1H NMR spectrum of **4s** (400 MHz, CDCl_3)

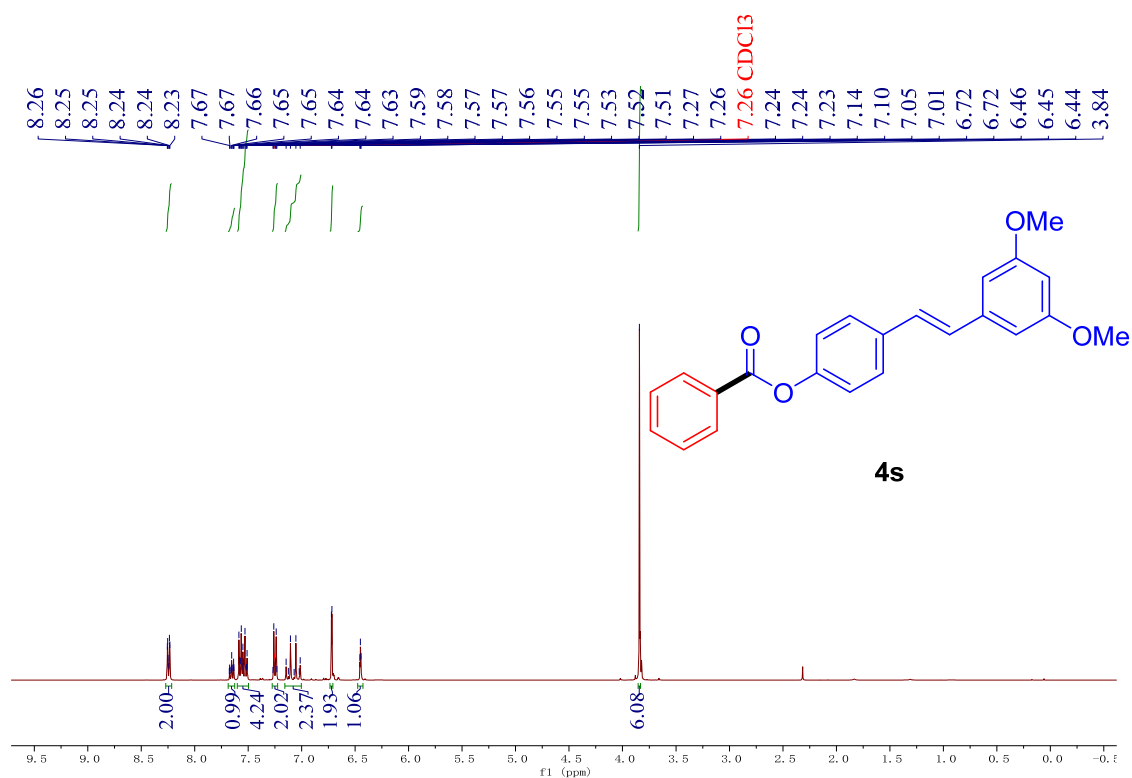


Figure S77. ^{13}C NMR spectrum of **4s** (100 MHz, CDCl_3)

