Supporting Information

Highly efficient and ambient-temperature synthesis of benzimidazoles via Co(III)/Co(II)-mediated redox catalysis

Ren-Yuan Zhong, Wu-Lin Xiong, Hao-Yuan Zhang, Tong-Tong Zeng, Shan-Shan Gong* and Qi Sun*

Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science and Technology Normal University, 605 Fenglin Avenue, Nanchang, Jiangxi 330013, PR China

E-mail: gongshanshan@jxstnu.edu.cn; sunqi@jxstnu.edu.cn

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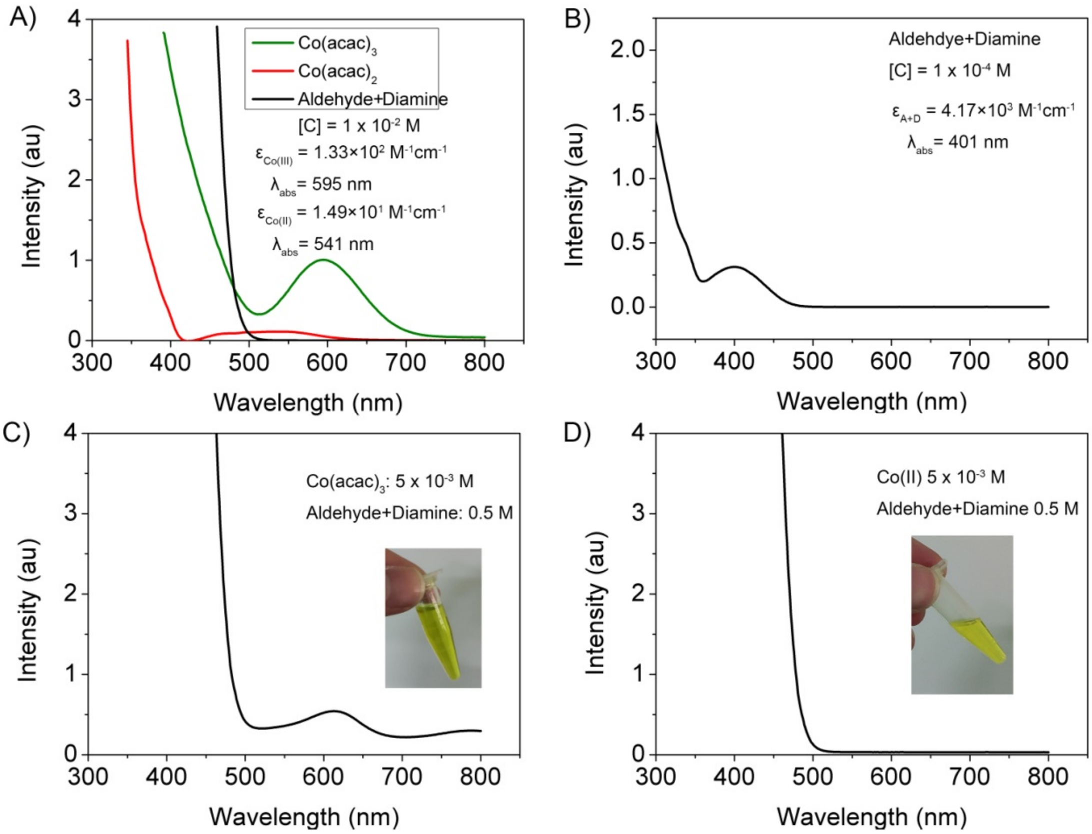

Note: The UV-Vis absorptions of $Co(acac)_2$, $Co(acac)_3$, and the mixture of 1.05 mmol of benzaldehyde and 1.0 mmol of *N*-phenyl-*o*-phenylenediamine (15 min after mixing) in CH_2Cl_2 (obtained at 10^{-2} M) indicated that the molar extinction coefficient of $Co(acac)_3$ is low ($\varepsilon = 1.33\times10^2\ M^{-1}cm^{-1}$, $\lambda_{abs,max} = 595$ nm), while that of $Co(acac)_2$ is even lower ($\varepsilon = 1.49\times10^1\ M^{-1}cm^{-1}$, $\lambda_{abs,max} = 541$ nm) (Figure S1A). These results is in agreement with their faint colors in Figure 1C (4×10^{-3} M in CH_2Cl_2). Meanwhile, the absorption of the mixture of benzaldehyde and *N*-phenyl-*o*-phenylenediamine (obtained at 10^{-4} M) is much higher ($\varepsilon = 4.17\times10^3\ M^{-1}cm^{-1}$, $\lambda_{abs,max} = 401$ nm) (Figure S1B).

[$Co(acac)_3$] (0.01 eq.) for UV-Vis absorption monitoring was set at 5×10^{-3} M ([Aldehdyde+Diamine] = 0.5 M). The absorption data clearly showed the peak of Co(III) at ~600 nm when $Co(acac)_3$ was initially added to the mixture (Figure S1C). After the green color faded quickly, the signal at ~600 nm disappeared completely (Figure S1D). This result is in agreement with the color change observed in both glass vial and TLC plate (Figure 1). But the very small molar extinction coefficient made the observation of Co(II) very hard.

Figure S1. UV-Vis absorption change of $Co(acac)_3$ upon addition to benzaldehyde and *N*-phenyl-*o*-phenylenediamine: The UV-Vis absorptions of $Co(acac)_2$, $Co(acac)_3$, and Aldehyde+Diamine mixture at 10^{-2} M (A), Aldehyde+Diamine mixture at 10^{-4} M (B), Aldehyde+Diamine mixture upon addition of 0.01 eq. of $Co(acac)_3$ (C), and after the green color of Aldehyde+Diamine mixture with $Co(acac)_3$ faded (D).

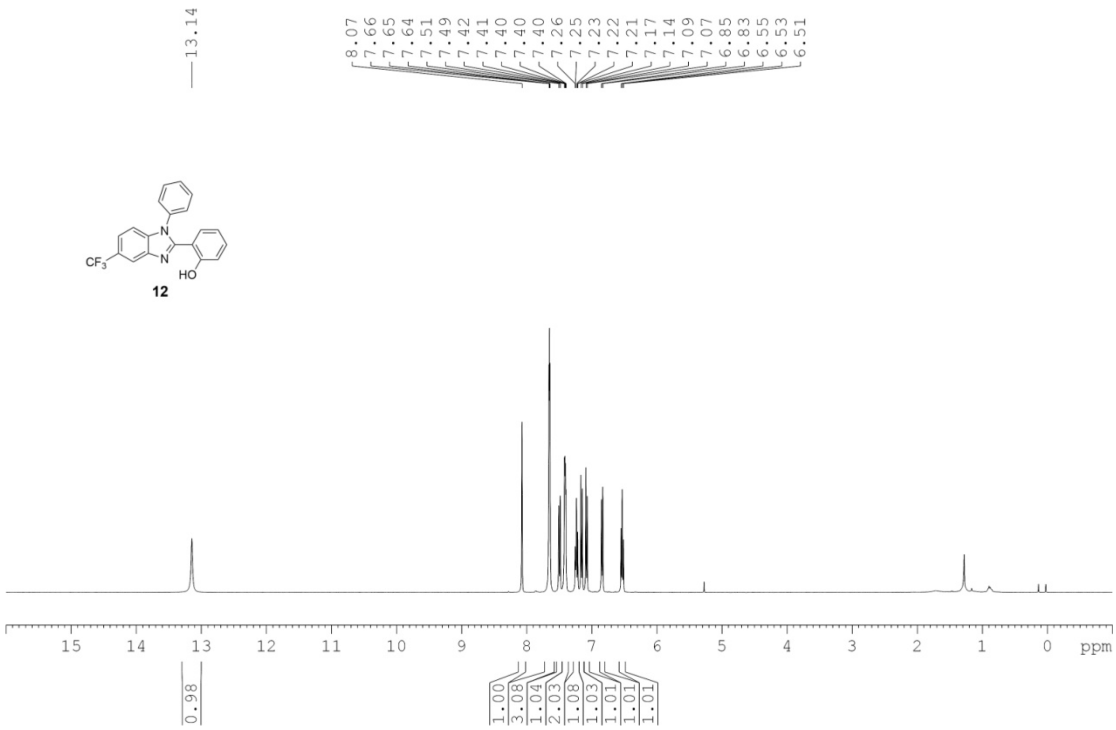

Figure S2. ^{1}H NMR spectrum of **12**

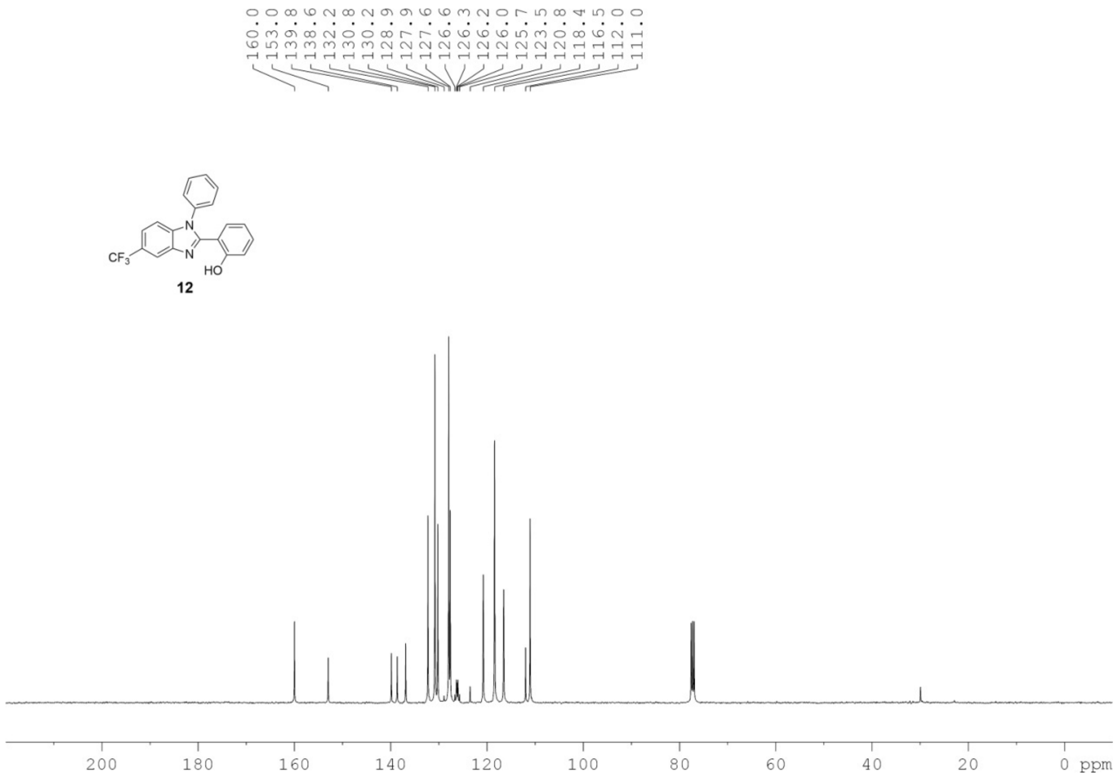

Figure S3. ^{13}C NMR spectrum of **12**

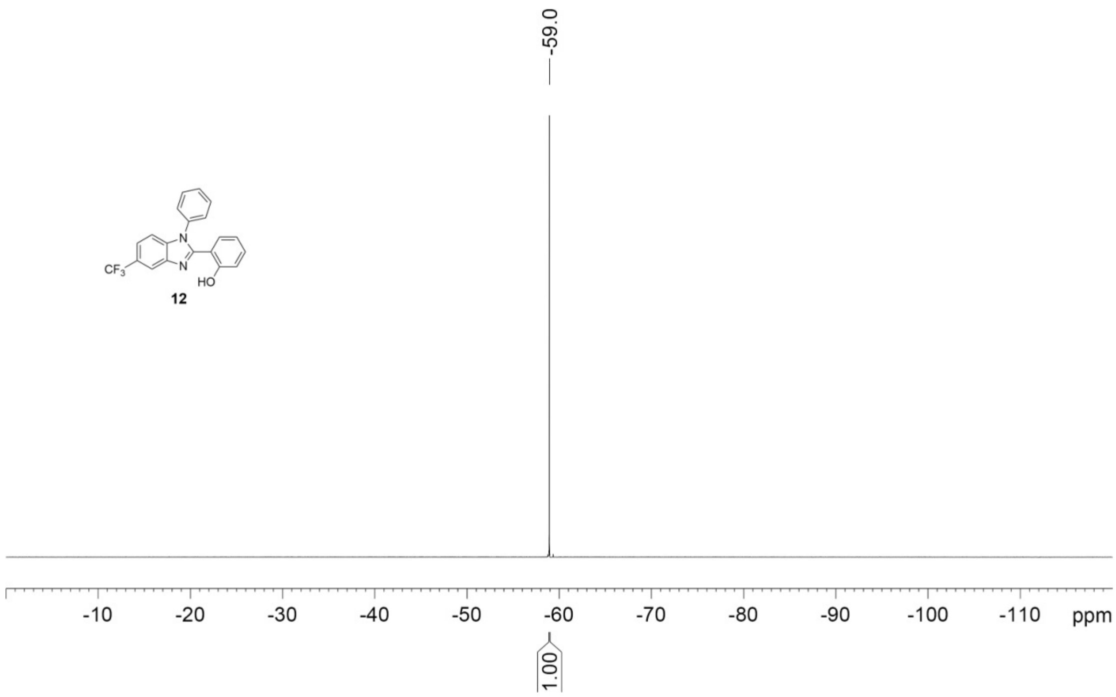

Figure S4. ^{19}F NMR spectrum of **12**

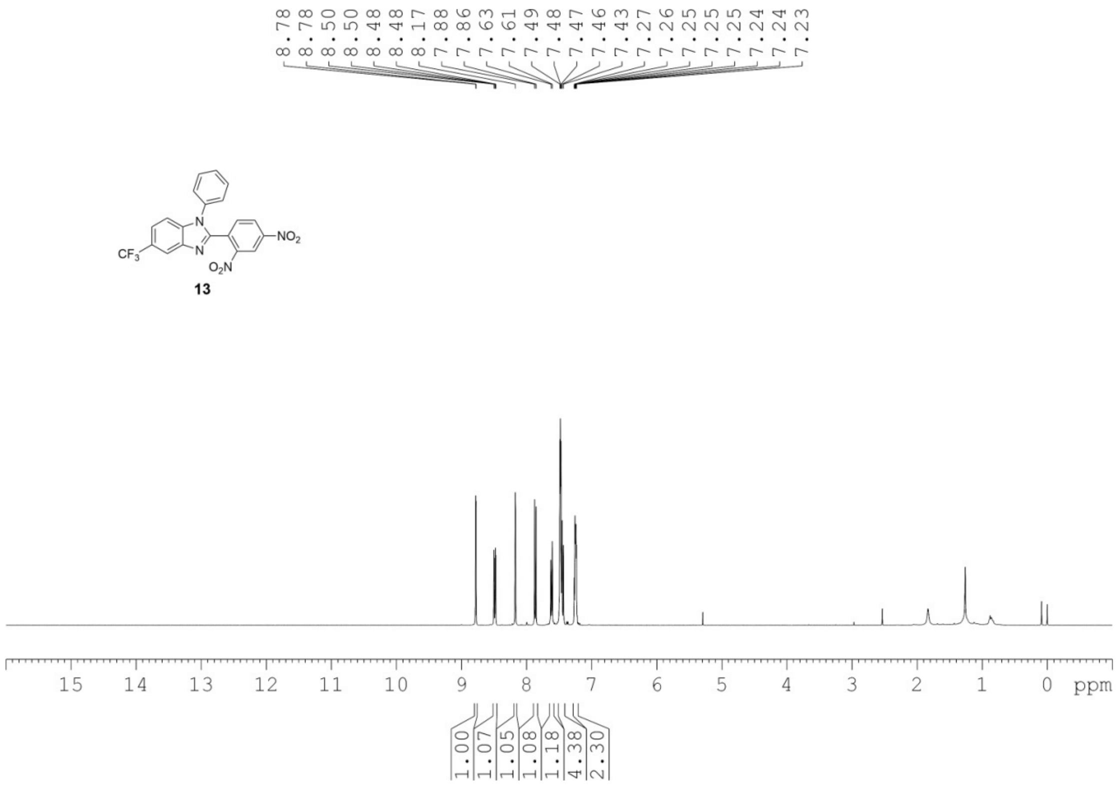

Figure S5. ^{1}H NMR spectrum of **13**

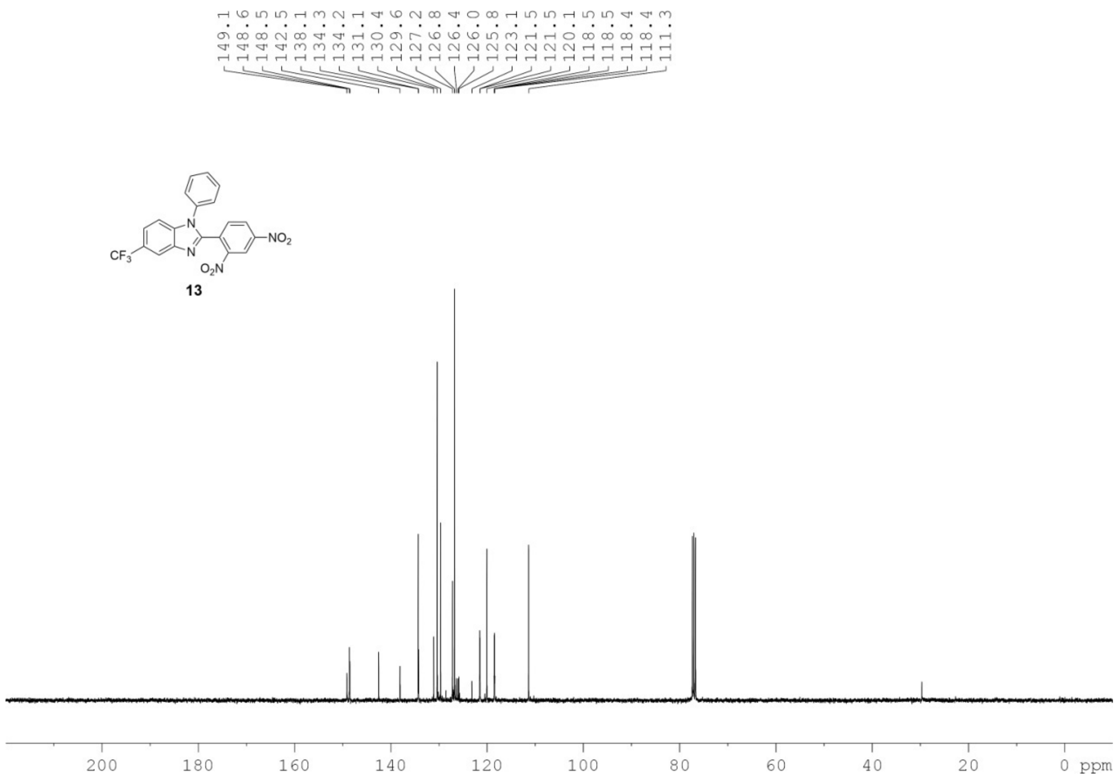

Figure S6. ^{13}C NMR spectrum of **13**

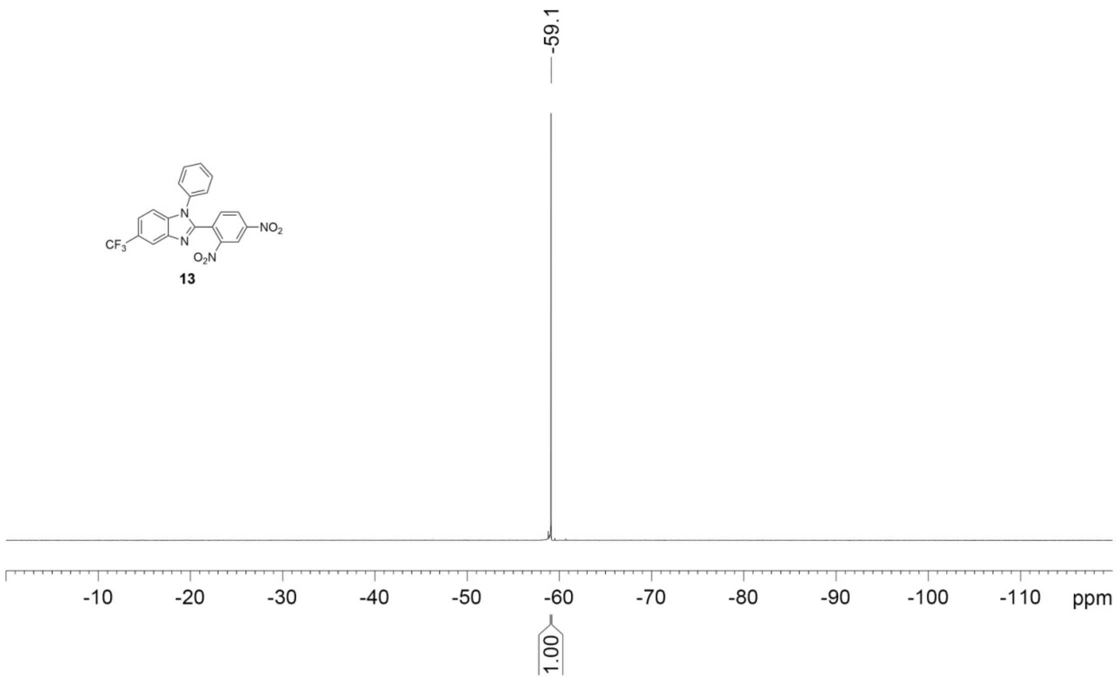

Figure S7. ^{19}F NMR spectrum of **13**

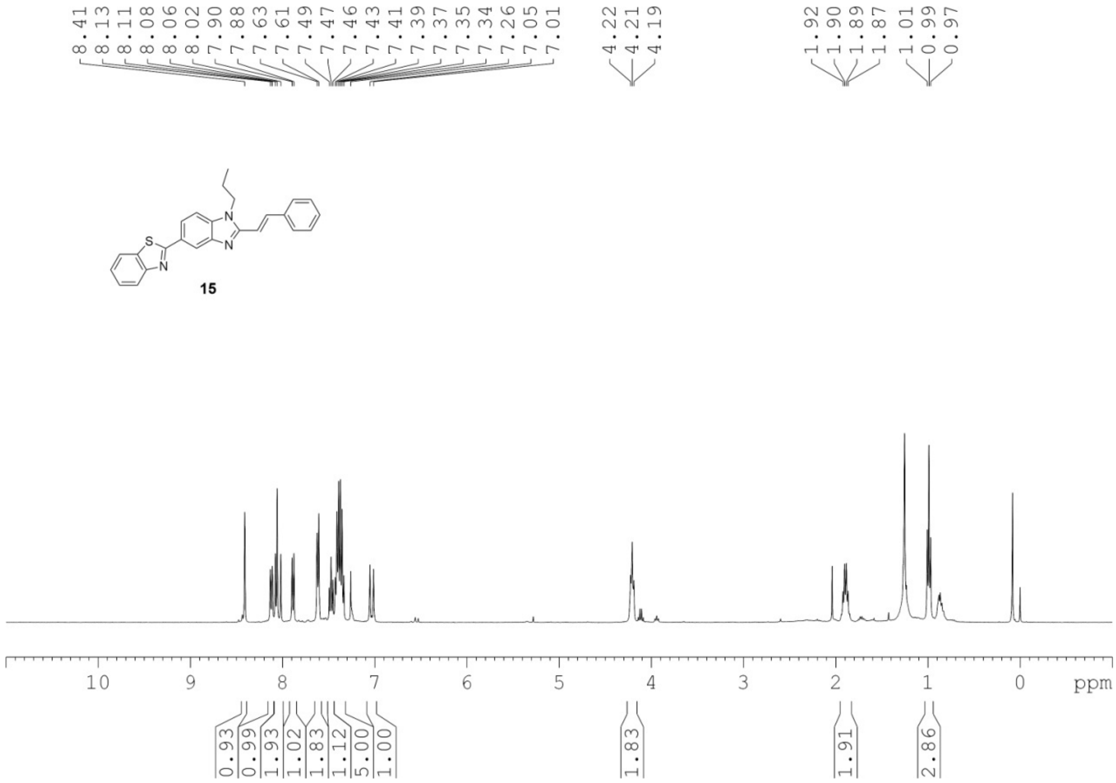

Figure S8. ^{1}H NMR spectrum of **15**

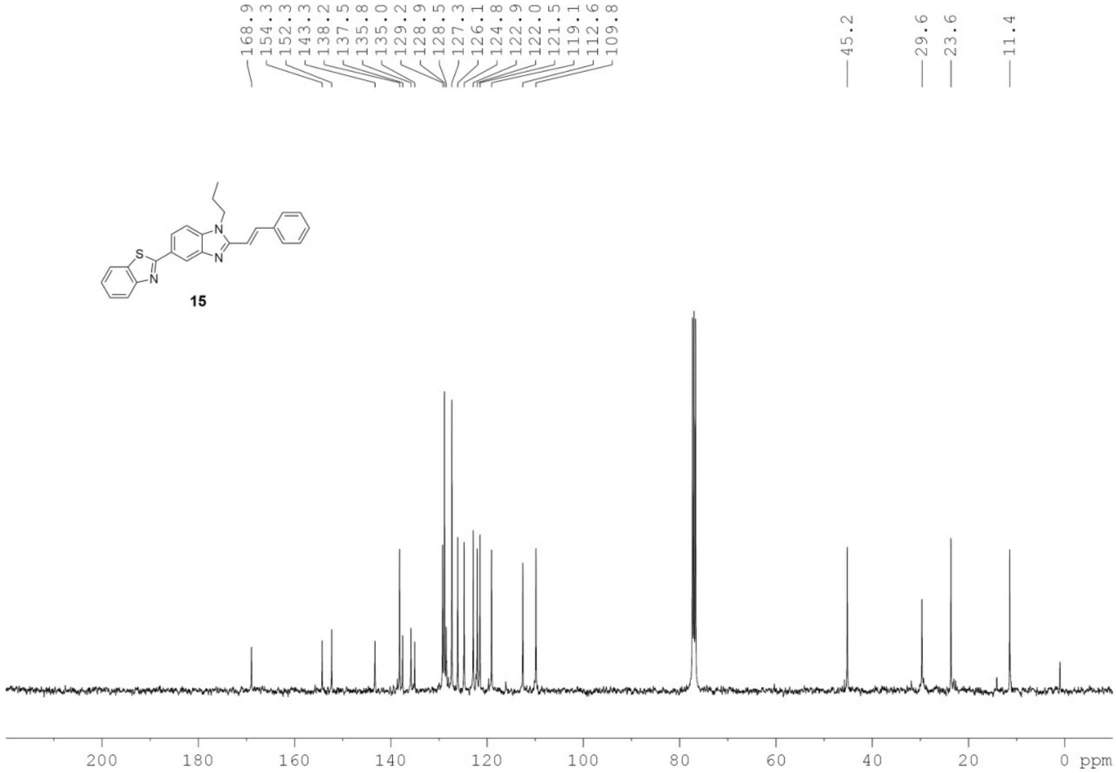

Figure S9. ^{13}C NMR spectrum of **15**

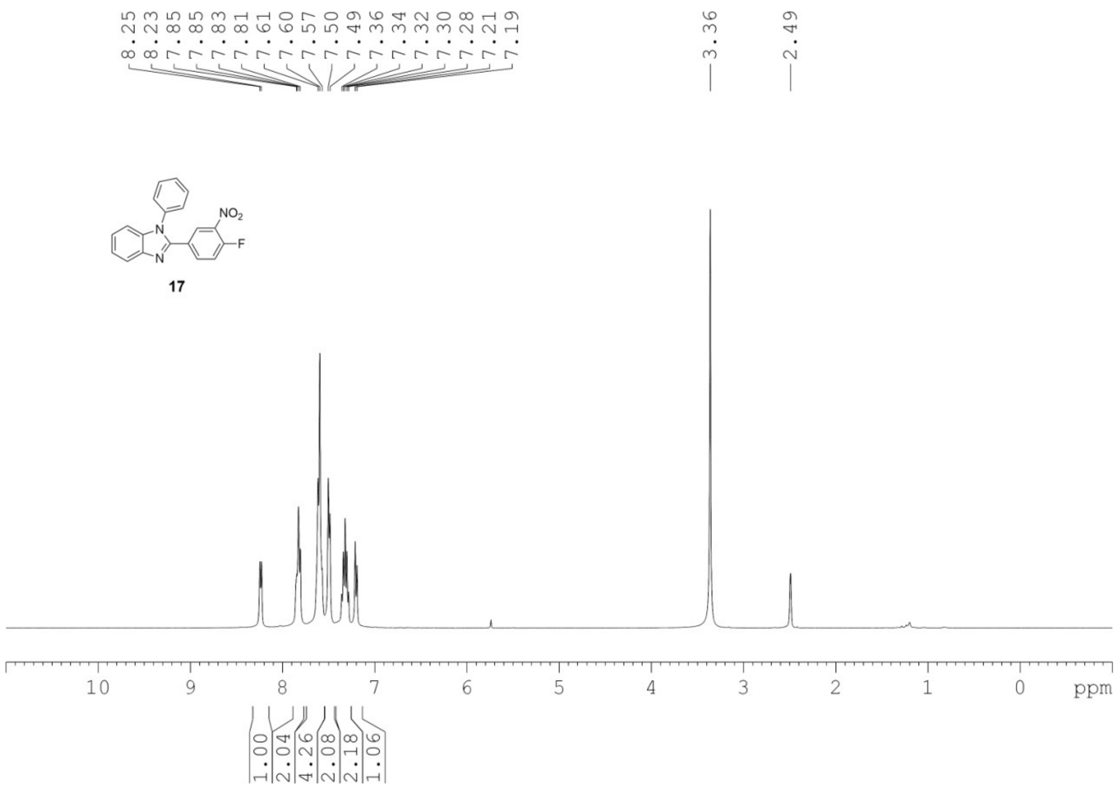

Figure S10. ^{1}H NMR spectrum of **17**

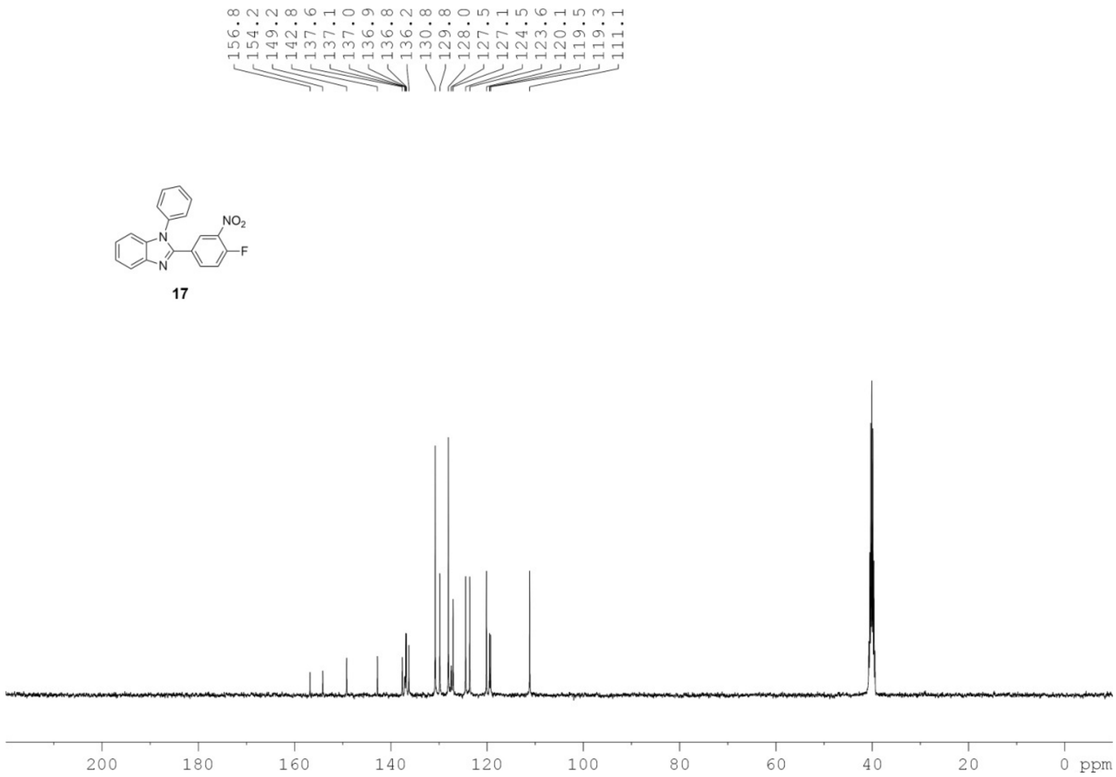

Figure S11. ^{13}C NMR spectrum of **17**

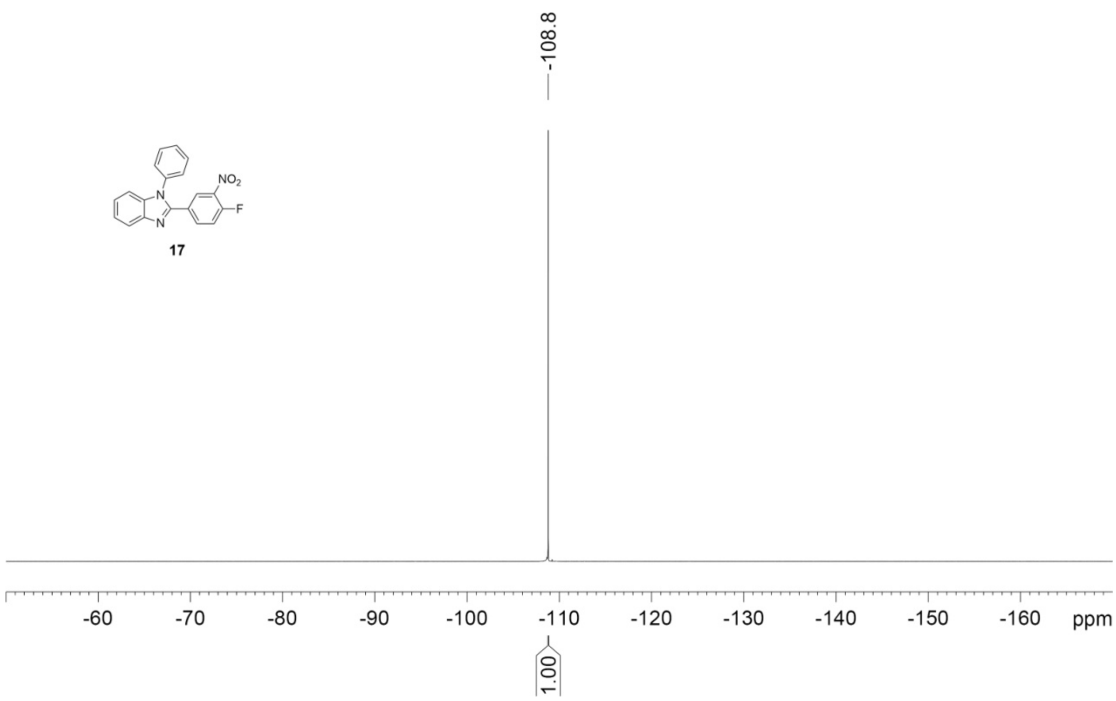

Figure S12. ^{19}F NMR spectrum of **17**

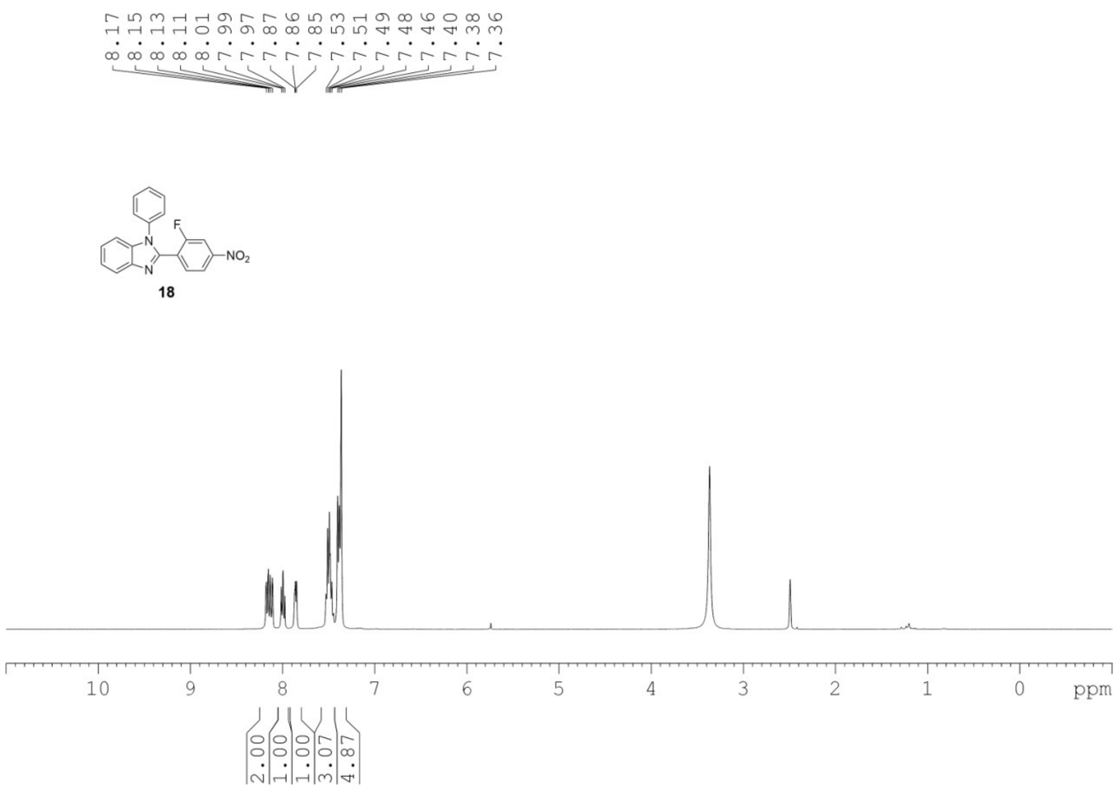

Figure S13. ^{1}H NMR spectrum of **18**

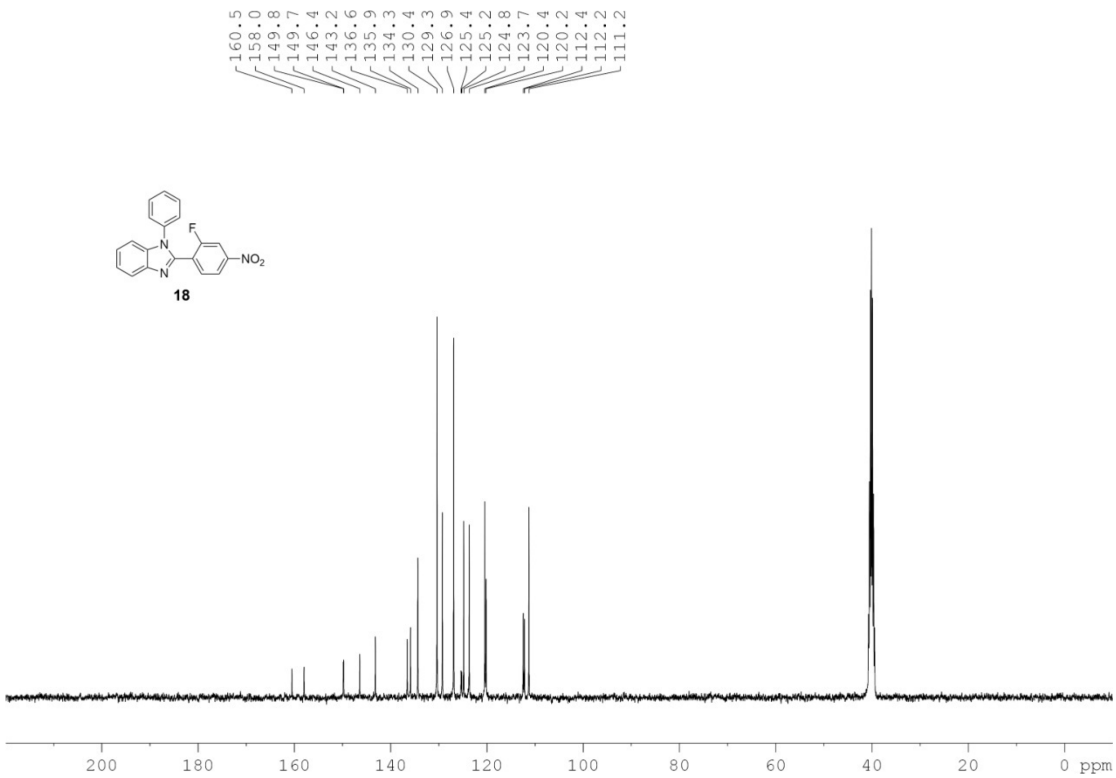

Figure S14. ^{13}C NMR spectrum of **18**

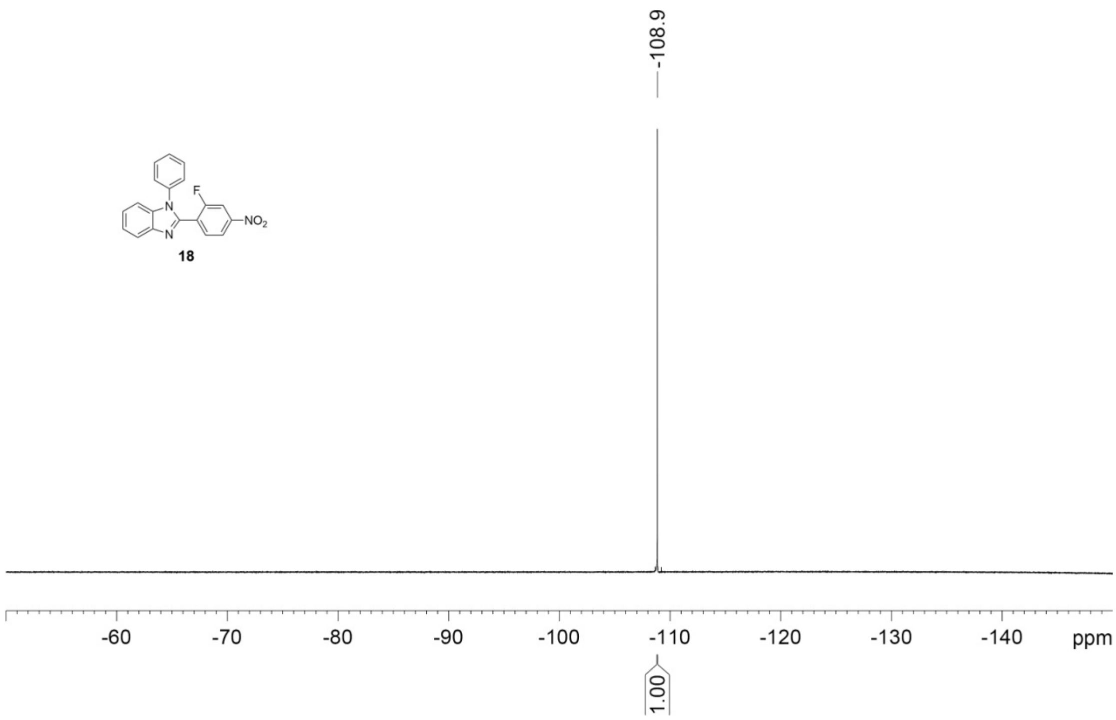

Figure S15. ^{19}F NMR spectrum of **18**

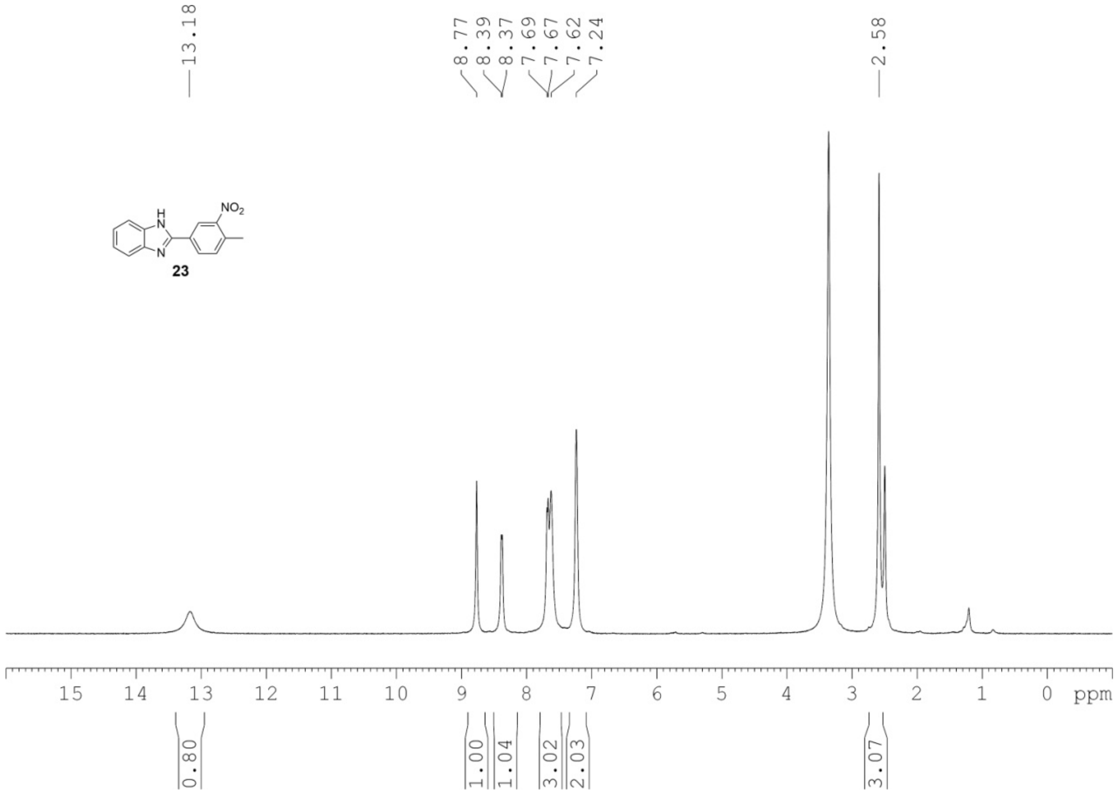

Figure S16. ^{1}H NMR spectrum of **23**

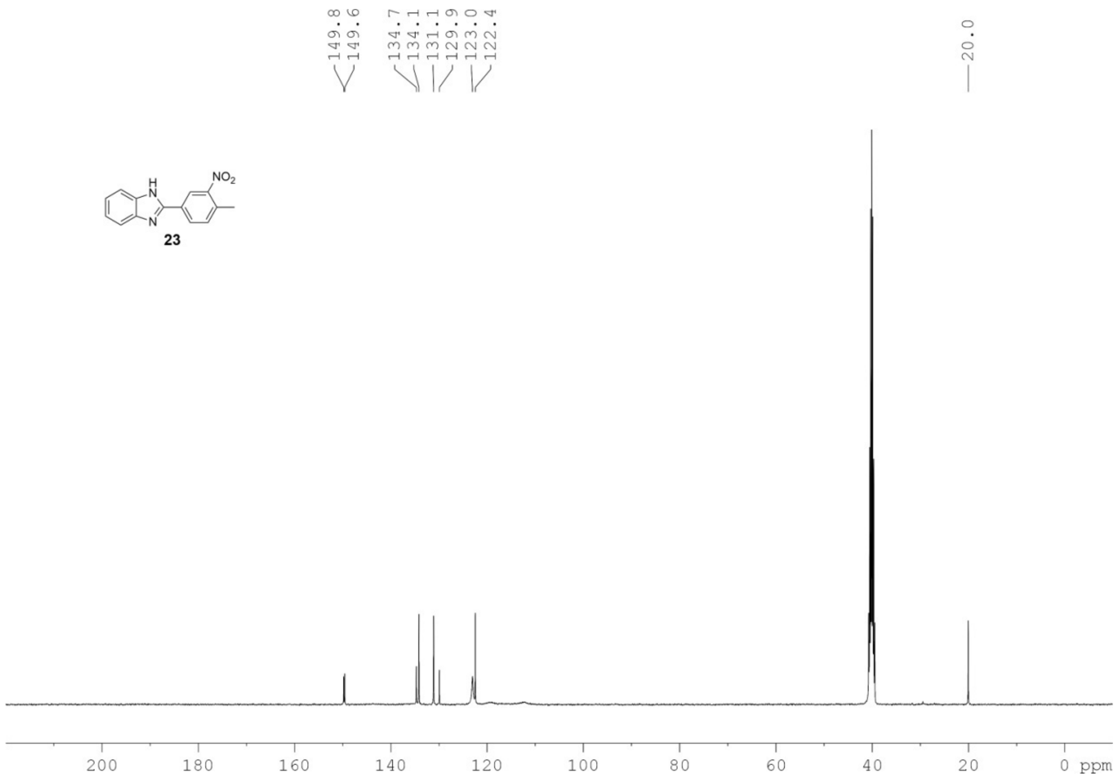

Figure S17. ^{13}C NMR spectrum of **23**

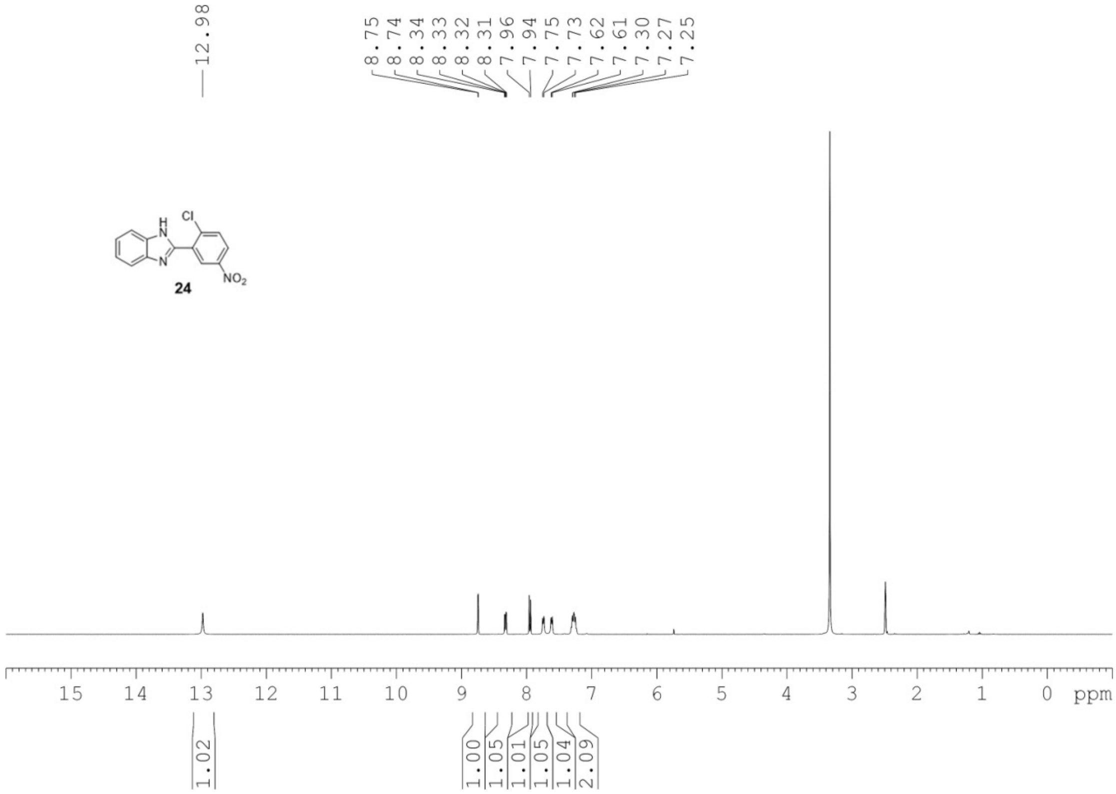

Figure S18. ^{1}H NMR spectrum of **24**

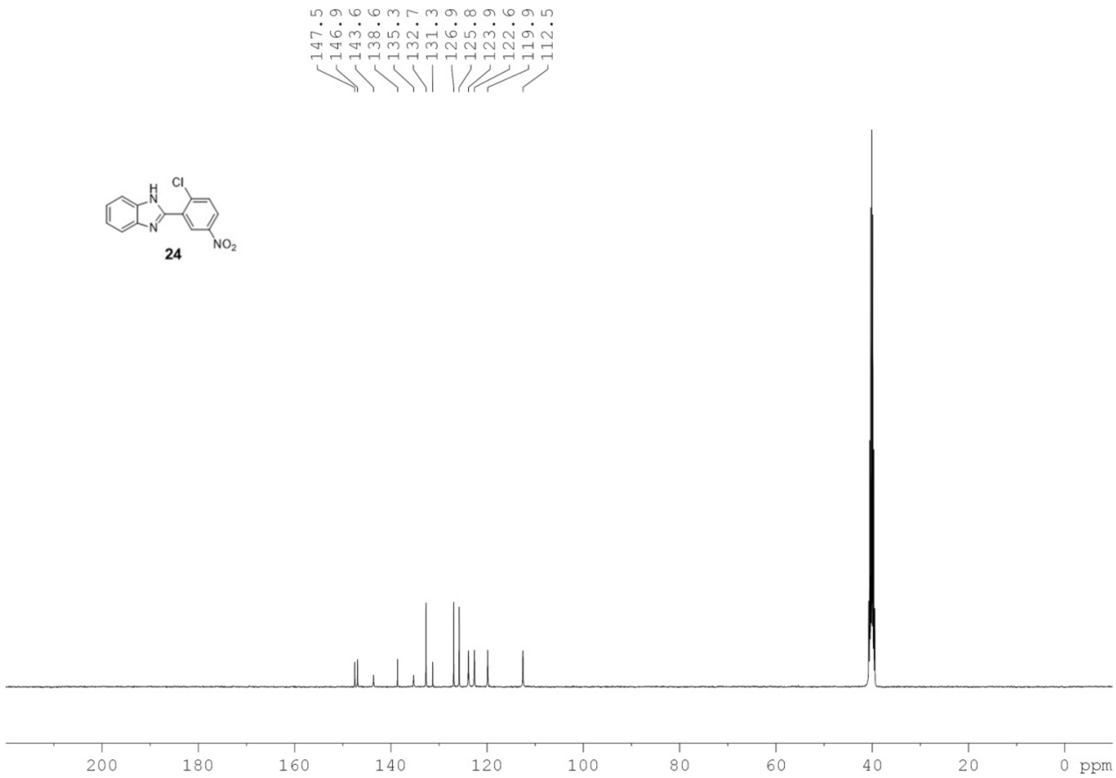

Figure S19. ^{13}C NMR spectrum of **24**