

Supplementary Material

Facile N9-alkylation of xanthine derivatives and their use as precursors for N-heterocyclic carbene complexes.

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Table S1. Crystallographic and refinement details.

| | [Ag(NHC)(NH ₃)]PF ₆ (5) | [Ag(NHC) ₂]PF ₆ (7) | [AgCl(NHC)]·(9) | [AgCl(NHC)]·(10) | [AuCl(NHC)]·(12) | [AuCl(NHC)]·(13) |
|---|--|--|---|--|--|--|
| CCDC code | 2073071 | 2073072 | 2073073 | 2075635 | 2073074 | 2073075 |
| Empirical formula | C ₁₆ H ₂₀ ClF ₆ N ₅ O ₂ PAg | C ₃₂ H ₃₆ F ₆ N ₈ O ₄ PAg | C ₃₂ H ₃₆ Cl ₂ N ₈ O ₄ Ag ₂ | C ₄₈ H ₅₁ Cl ₆ N ₁₂ O ₆ Ag ₃ | C ₁₆ H ₁₈ ClN ₄ O ₂ Au | C ₁₆ H ₁₇ Cl ₂ N ₄ O ₂ Au |
| Formula weight | 602.66 | 849.53 | 883.33 | 1428.32 | 530.76 | 565.20 |
| Crystal system | Orthorhombic | Orthorhombic | Triclinic | Triclinic | Monoclinic | Monoclinic |
| Space group | Pna2 ₁ | Pca2 ₁ | P-1 | P-1 | P2 ₁ /n | P2 ₁ /n |
| a/Å | 18.2489(4) | 20.7353(5) | 8.7313(5) | 12.7960(4) | 11.3106(2) | 11.5439(4) |
| b/Å | 13.0368(3) | 10.7229(2) | 10.1183(6) | 14.2460(6) | 9.1372(2) | 9.3535(4) |
| c/Å | 9.0580(3) | 15.4374(4) | 11.1408(6) | 17.7630(8) | 16.0606(4) | 16.3214(6) |
| α/° | 90 | 90 | 107.453(5) | 112.002(2) | 90 | 90 |
| β/° | 90 | 90 | 103.485(5) | 97.983(5) | 91.485(2) | 92.204(4) |
| γ/° | 90 | 90 | 104.032(5) | 100.642(6) | 90 | 90 |
| Volume/Å ³ | 2154.97(9) | 3432.37(15) | 859.72(10) | 2872.6(2) | 1659.26(6) | 1761.01(12) |
| Z | 4 | 4 | 1 | 2 | 4 | 4 |
| ρ _{calc} mg/mm ³ | 1.858 | 1.644 | 1.706 | 1.651 | 2.125 | 2.132 |
| μ/mm ⁻¹ | 1.210 | 0.717 | 1.344 | 0.932 | 9.044 | 8.675 |
| F(000) | 1200.0 | 1728.0 | 444.0 | 1428 | 1016.0 | 1080.0 |
| Crystal size/mm ³ | 0.02 × 0.05 × 0.10 | 0.04 × 0.08 × 0.13 | 0.03 × 0.06 × 0.12 | 0.04 × 0.08 × 0.09 | 0.03 × 0.09 × 0.10 | 0.04 × 0.04 × 0.06 |
| 2θ range | 5.476 to 59.024° | 5.026 to 59.06° | 4.778 to 59.056° | 1.108 to 26.902° | 5.13 to 58.766° | 4.996 to 58.462° |
| Reflections collected | 7489 | 11608 | 7649 | 60327 | 8241 | 9461 |
| Independent reflections | 3933 | 6284 | 4014 | 17428 | 3825 | 4061 |
| Data/restraints/parameters | 3933/235/348 | 6284/1/494 | 4014/0/220 | 17428/0/686 | 3825/0/220 | 4061/0/229 |
| Goodness-of-fit on F ² | 1.028 | 1.052 | 1.066 | 1.031 | 1.064 | 1.029 |
| Final R indices [I>2σ(I)] | R ₁ = 0.0348 wR ₂ = 0.0786 | R ₁ = 0.0347 wR ₂ = 0.0705 | R ₁ = 0.0294 wR ₂ = 0.0634 | R ₁ = 0.0558 wR ₂ = 0.1522 | R ₁ = 0.0246 wR ₂ = 0.0493 | R ₁ = 0.0243 wR ₂ = 0.0403 |
| Largest difference peak/hole/eÅ ⁻³ | 0.67/-0.53 | 0.65/-0.82 | 0.48/-0.33 | 2.2/-2.5 | 1.29/-0.91 | 0.69/-1.10 |

Table S1 continued. Crystallographic and refinement details.

| | [AuCl(NHC)]·(14) | [RuCl ₂ (NHC)(p-cym)] (15) | [Cp*RhCl ₂ (NHC)] (18) | [Cp*RhCl ₂ (NHC)] (19) | [RhCl(NHC)(cod)]·(22) |
|---|--|---|--|--|--|
| CCDC code | 2073076 | 2075634 | 2073077 | 2073078 | 2073079 |
| Empirical formula | C ₁₀ H ₁₄ ClN ₄ O ₂ Au | C ₅₃ H ₆₅ Cl ₇ N ₈ O ₄ Ru ₂ | C ₂₆ H ₃₃ Cl ₂ N ₄ O ₂ Rh | C ₂₇ H ₃₄ Cl ₅ N ₄ O ₂ Rh | C ₂₄ H ₂₉ Cl ₂ N ₄ O ₂ Rh |
| Formula weight | 454.67 | 1328.42 | 607.37 | 726.74 | 579.32 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | I2/a | P2 ₁ /c | P2 ₁ /c | P2 ₁ /c | P2 ₁ /c |
| a/Å | 13.8722(4) | 13.3442(5) | 9.5291(4) | 9.4877(3) | 9.4637(7) |
| b/Å | 13.3255(3) | 20.1961(7) | 21.4169(12) | 21.5981(8) | 17.8884(17) |
| c/Å | 14.5932(4) | 20.7032(7) | 14.7086(7) | 14.6634(5) | 15.0763(16) |
| α/° | 90 | 90 | 90 | 90 | 90 |
| β/° | 107.474(3) | 95.414(2) | 102.977(4) | 101.454(3) | 99.401(9) |
| γ/° | 90 | 90 | 90 | 90 | 90 |
| Volume/Å ³ | 2573.12(12) | 5554.6(3) | 2025.1(3) | 2944.93(18) | 2518.0(4) |
| Z | 8 | 4 | 4 | 4 | 4 |
| ρ _{calc} mg/mm ³ | 2.347 | 1.589 | 1.379 | 1.639 | 1.528 |
| μ/mm ⁻¹ | 11.642 | 0.933 | 0.794 | 1.067 | 0.919 |
| F(000) | 1712.0 | 2712 | 1248.0 | 1480.0 | 1184.0 |
| Crystal size/mm ³ | 0.03 × 0.04 × 0.16 | 0.012 × 0.031 × 0.081 | 0.02 × 0.04 × 0.05 | 0.02 × 0.05 × 0.07 | 0.02 × 0.04 × 0.12 |
| 2θ range | 6.114 to 58.754° | 1.412 to 30.780° | 4.748 to 58.656° | 4.718 to 58.962° | 4.922 to 58.876° |
| Reflections collected | 6494 | 175605 | 15933 | 17628 | 14472 |
| Independent reflections | 2964 | 17268 | 6884 | 6803 | 5791 |
| Data/restraints/parameters | 2964/0/167 | 17268/0/691 | 6884/0/324 | 6803/0/360 | 5791/0/301 |
| Goodness-of-fit on F ² | 1.086 | 1.017 | 1.020 | 1.020 | 1.141 |
| Final R indices [I>2σ(I)] | R ₁ = 0.0216 wR ₂ = 0.0494 | R ₁ = 0.0515 wR ₂ = 0.1287 | R ₁ = 0.0385 wR ₂ = 0.0779 | R ₁ = 0.0305 wR ₂ = 0.0617 | R ₁ = 0.0653 wR ₂ = 0.1215 |
| Largest difference peak/hole/eÅ ⁻³ | 0.89/-1.16 | 2.6/-1.8 | 0.58/-0.51 | 0.45/-0.43 | 1.25/-0.78 |

NMR spectra

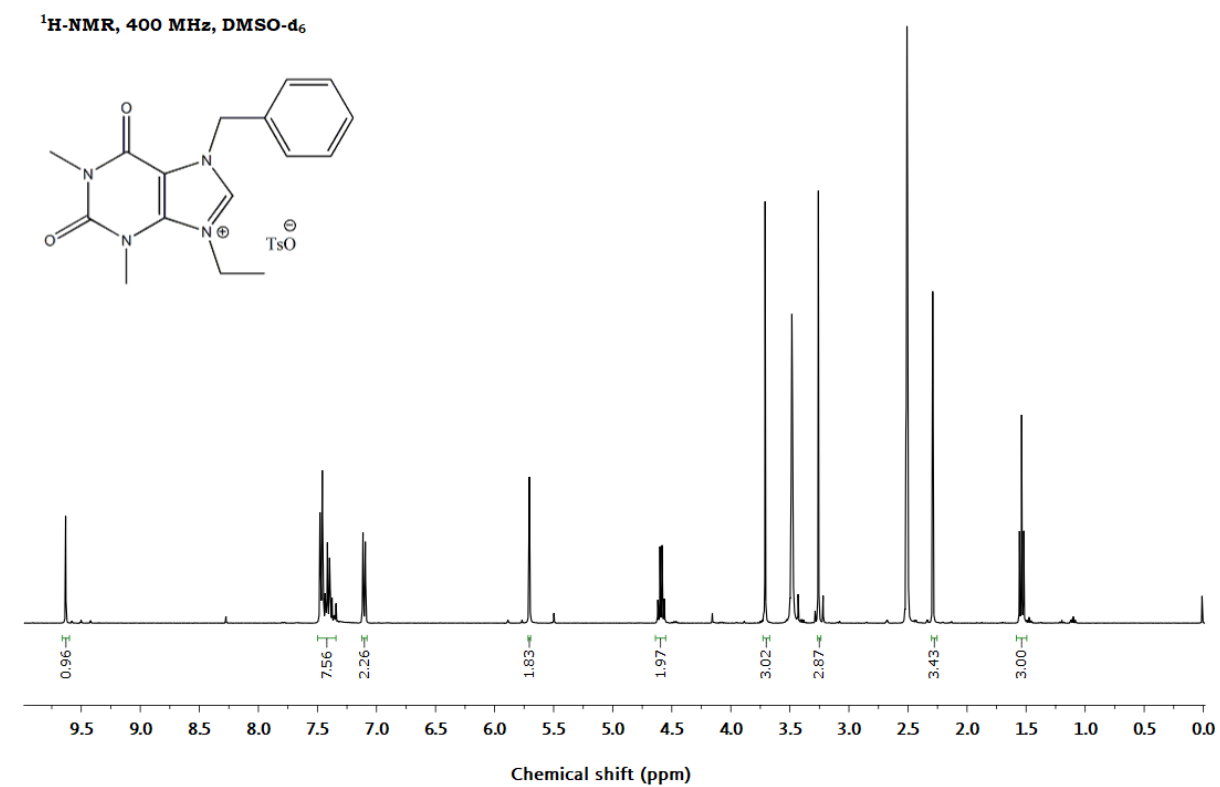


Figure S1

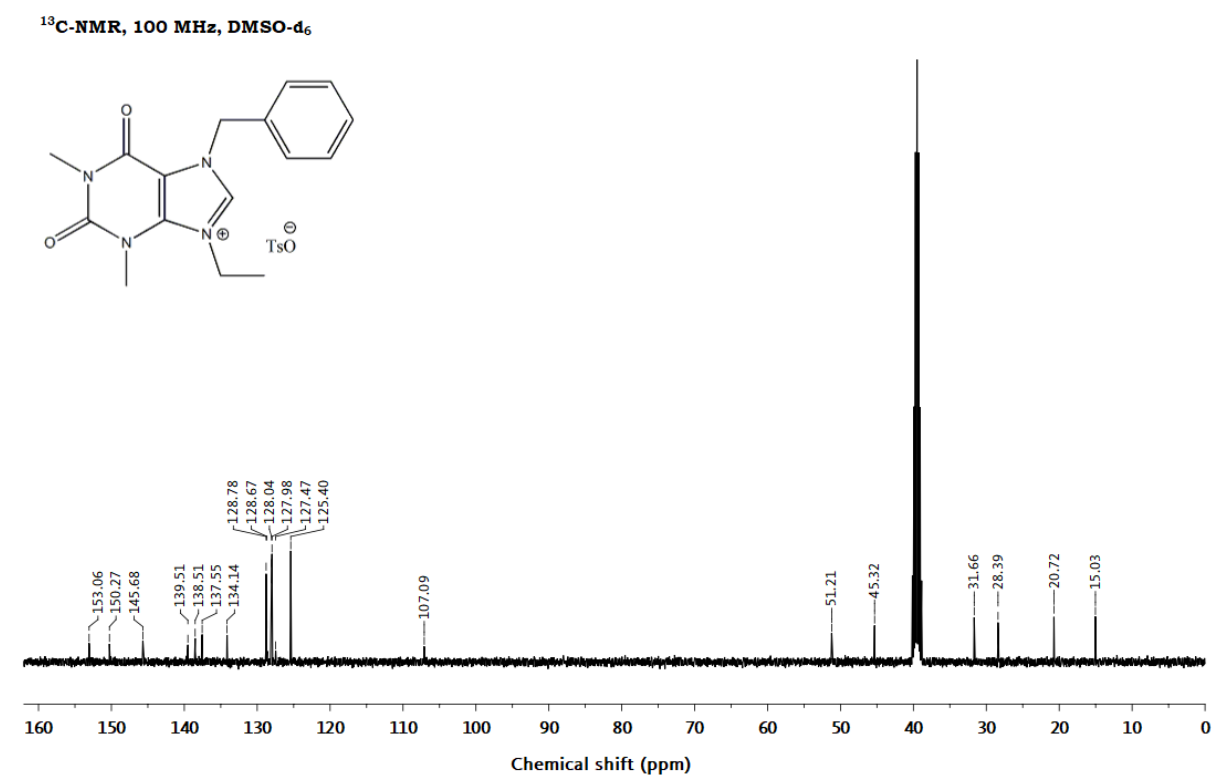


Figure S2

¹H-NMR, 400 MHz, DMSO-d₆

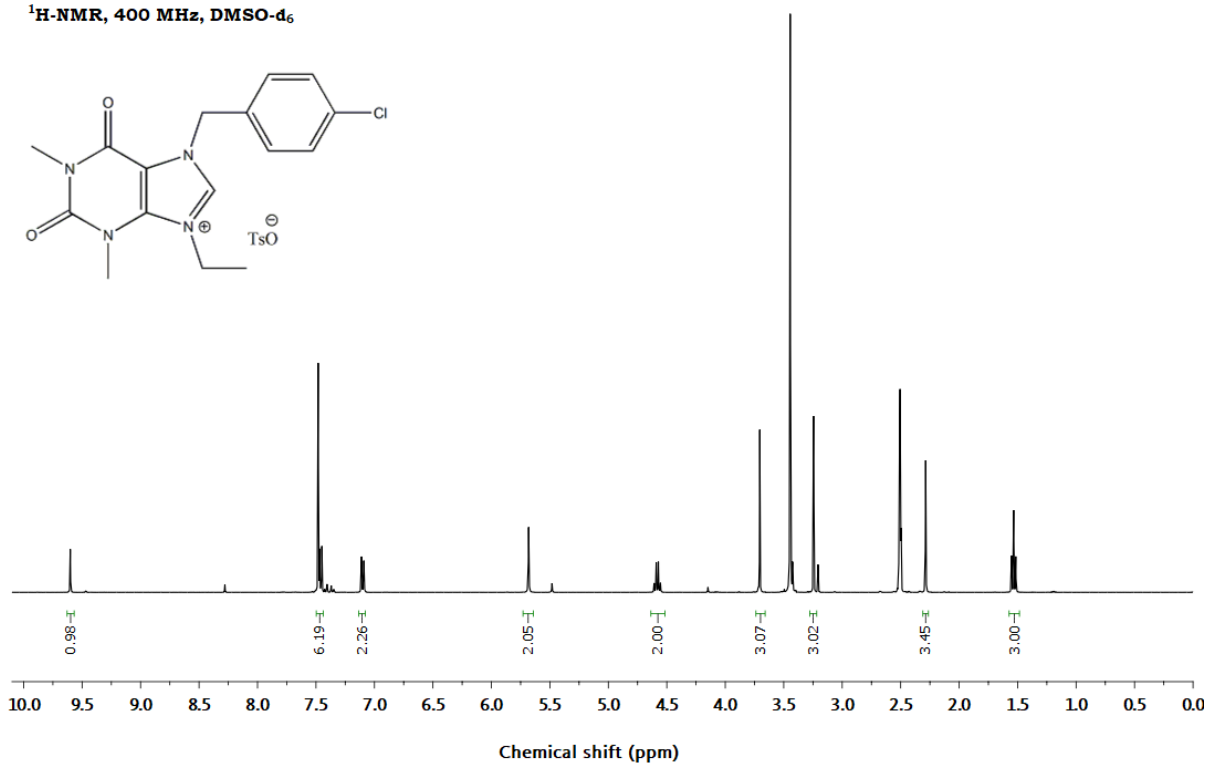


Figure S3

¹³C-NMR, 100 MHz, DMSO-d₆

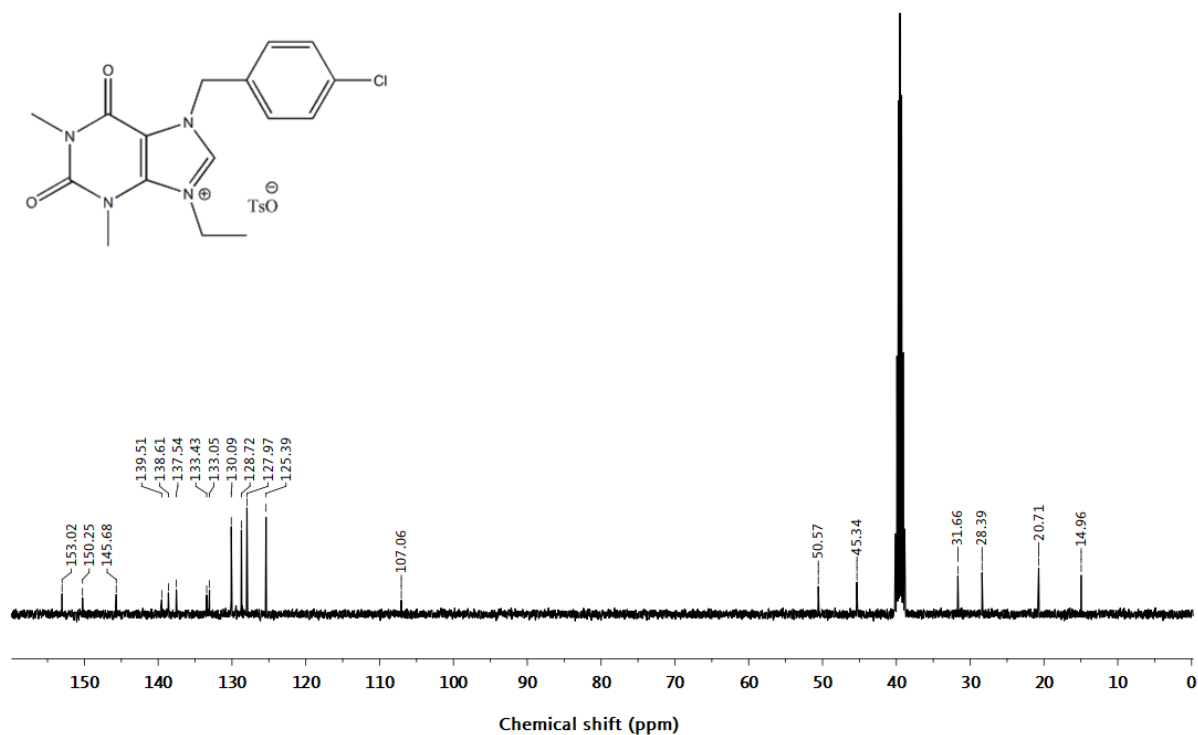


Figure S4

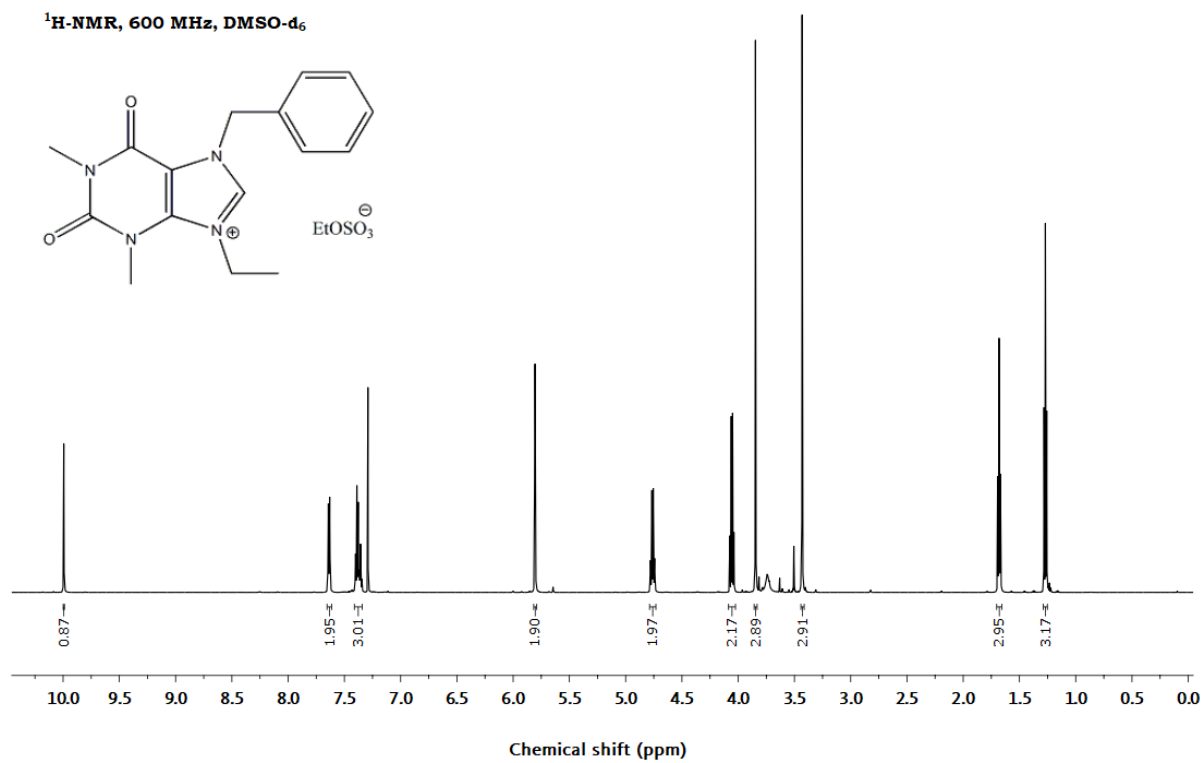


Figure S5

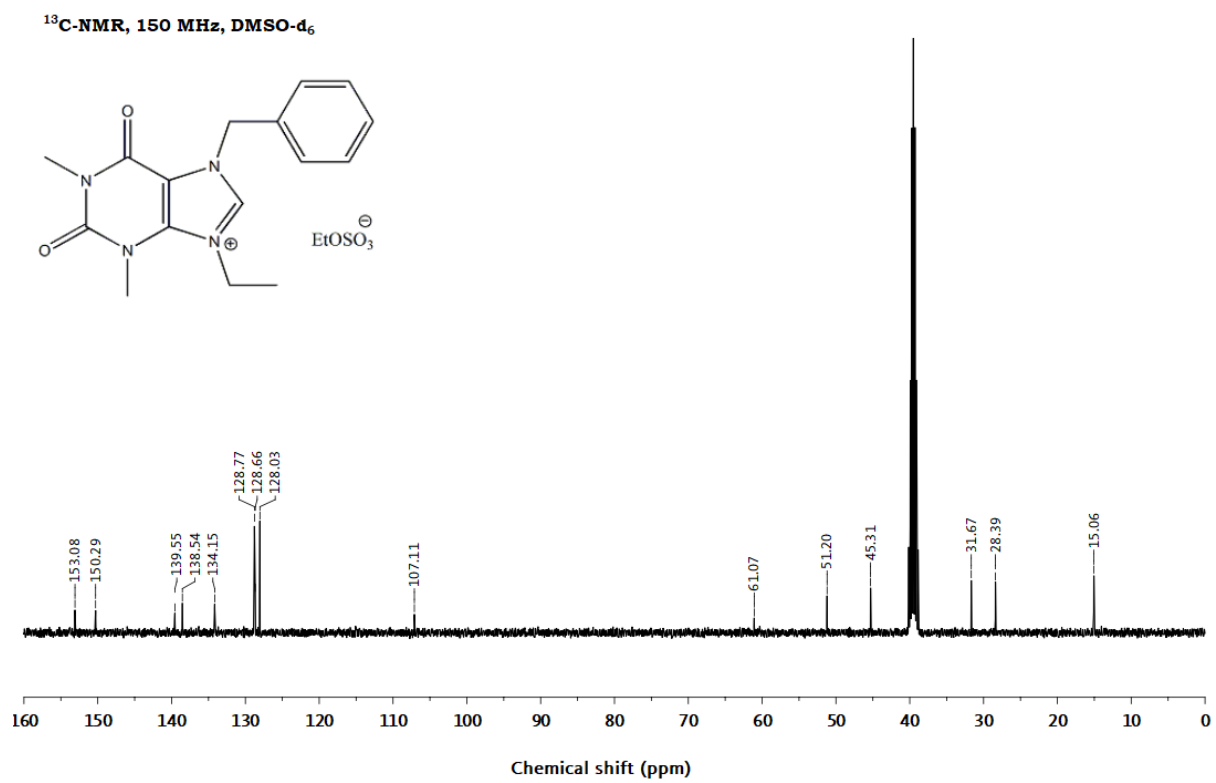


Figure S6

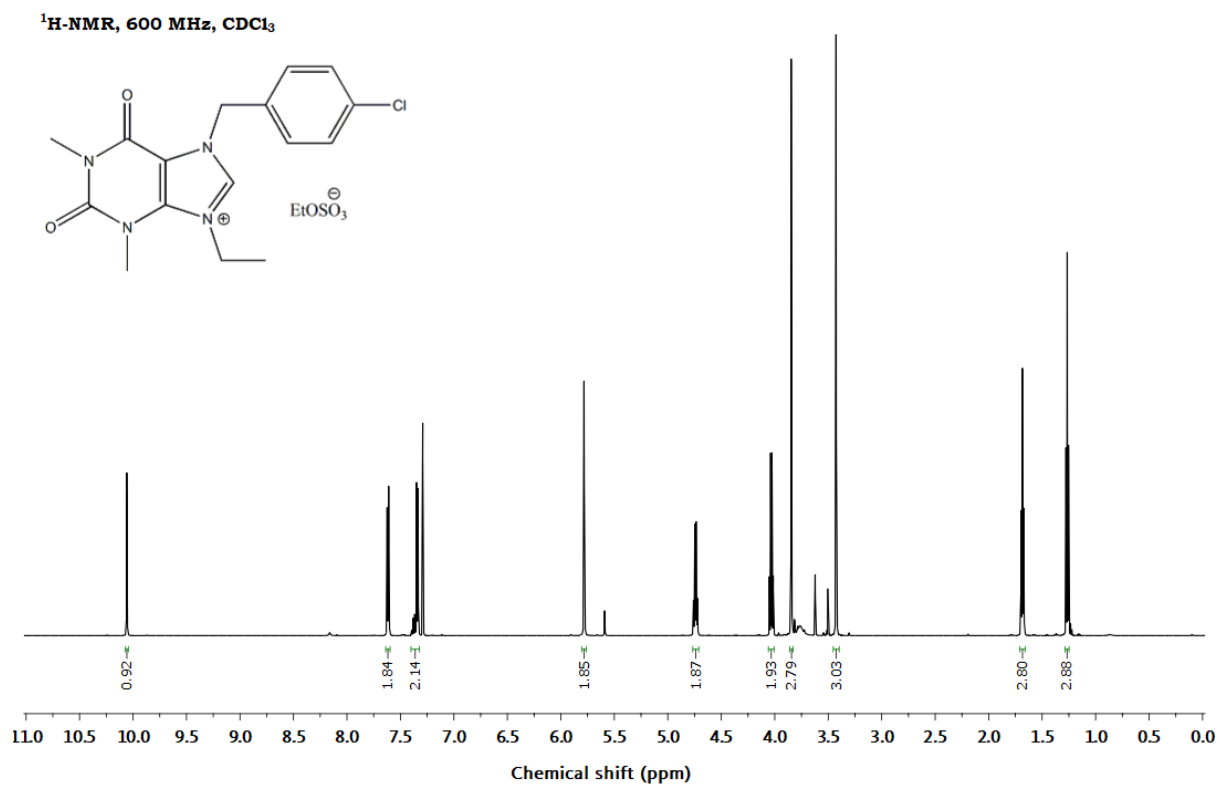


Figure S7

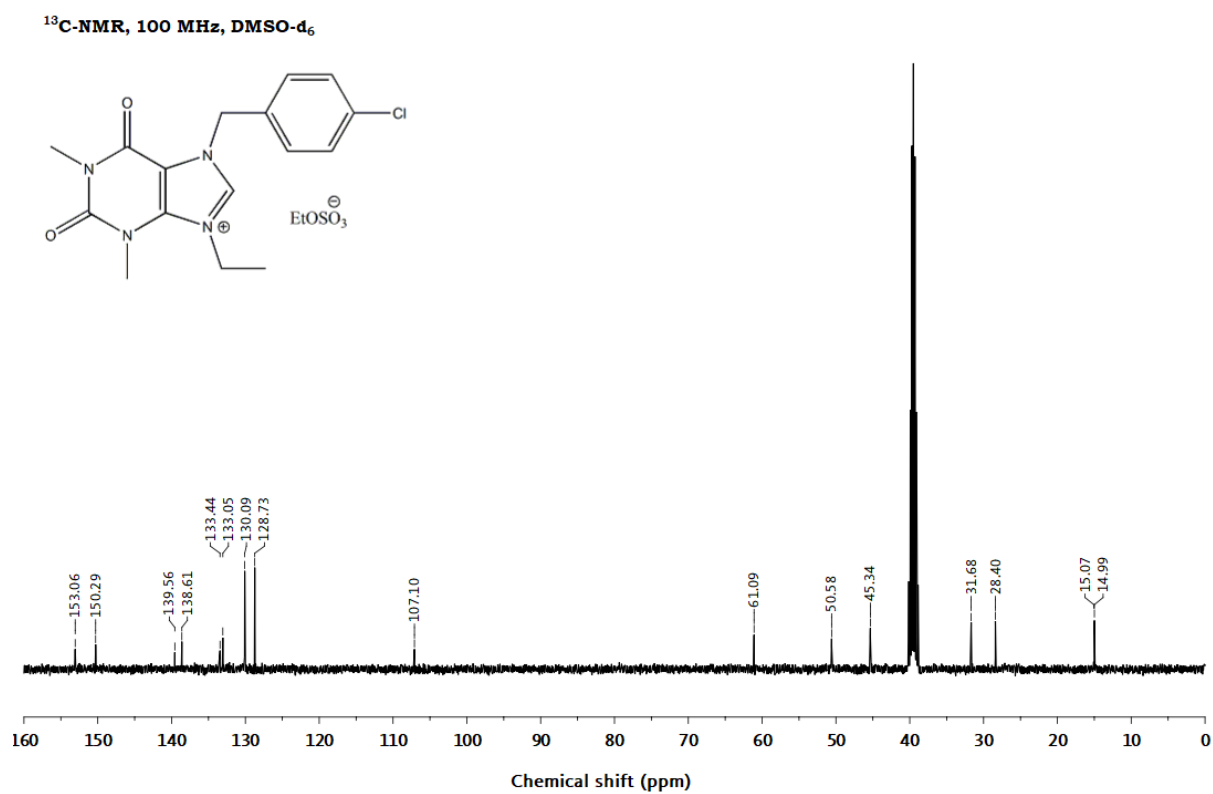


Figure S8

¹H-NMR, 600 MHz, DMSO-d₆

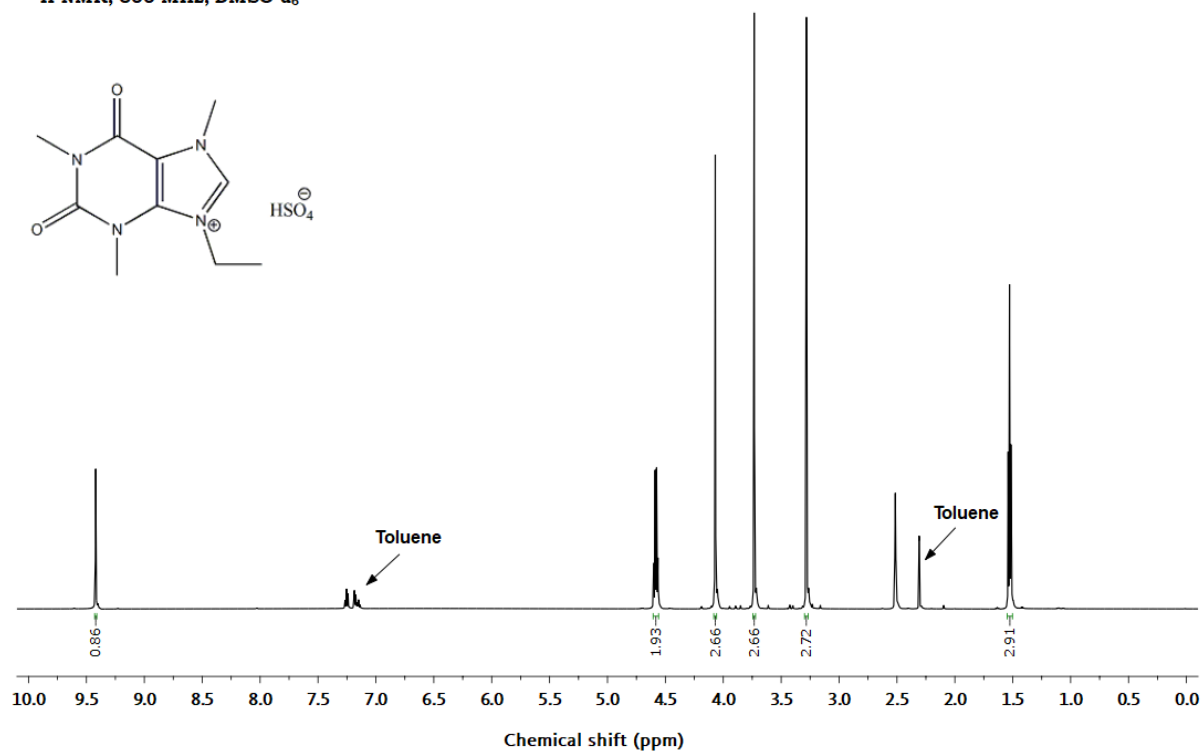


Figure S9

¹³C-NMR, 100 MHz, DMSO-d₆

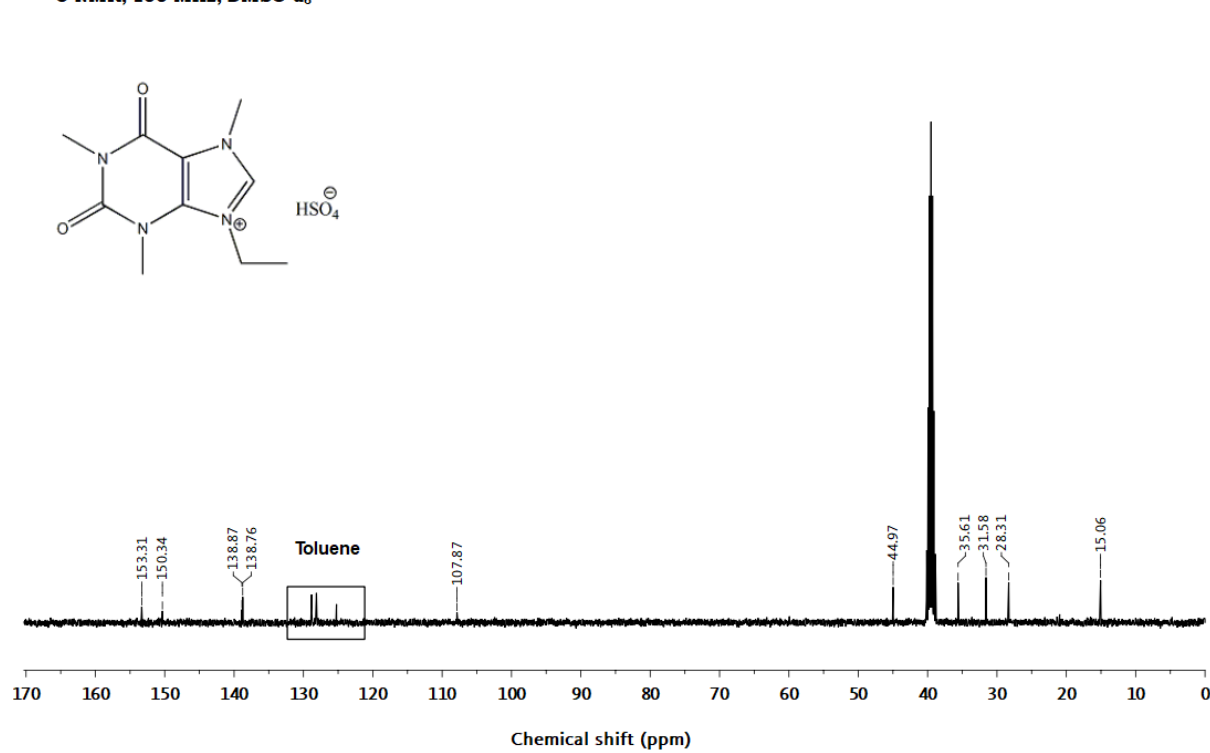


Figure S10

¹H-NMR, 400 MHz, DMSO-d₆

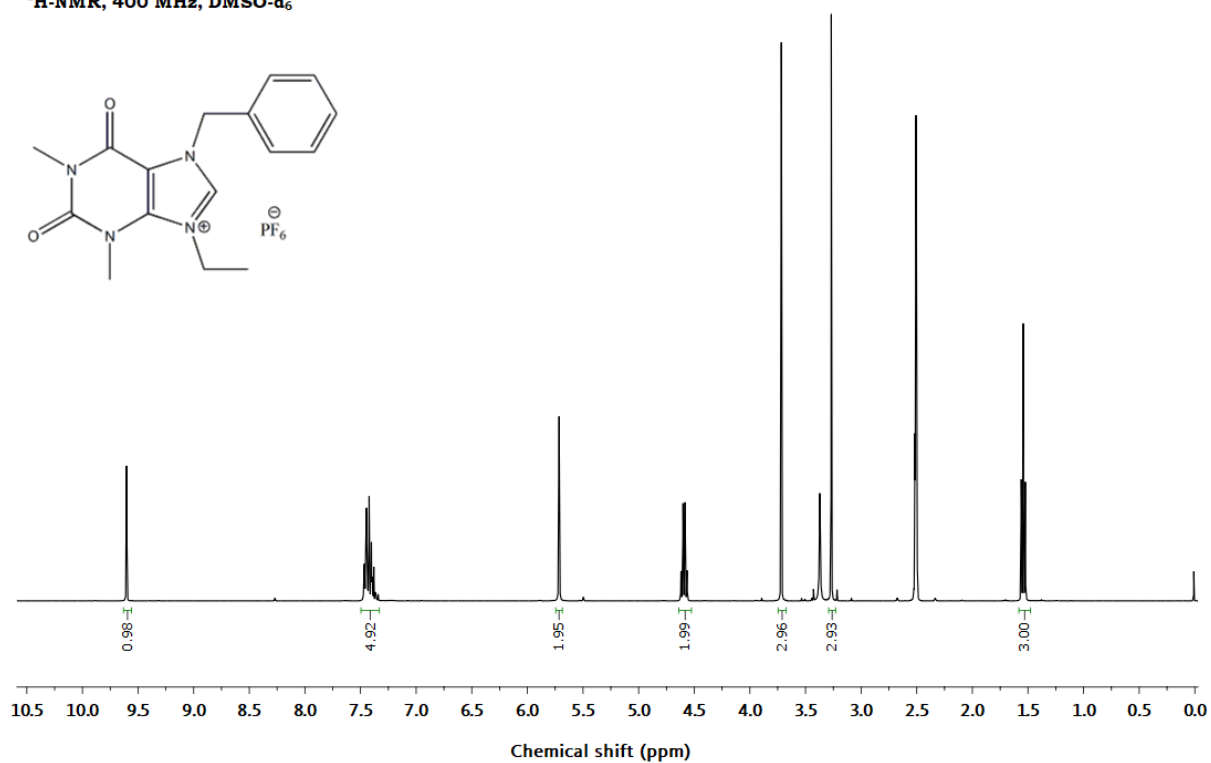


Figure S11

¹³C-NMR, 100 MHz, DMSO-d₆

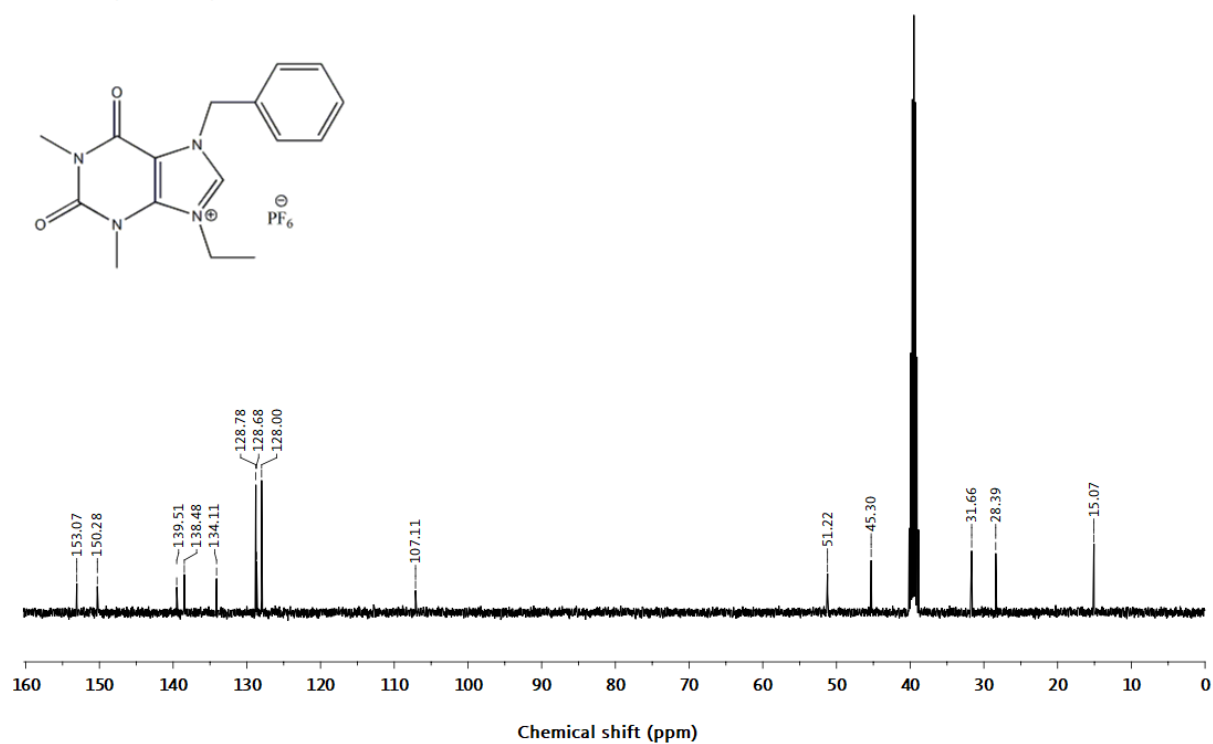


Figure S12

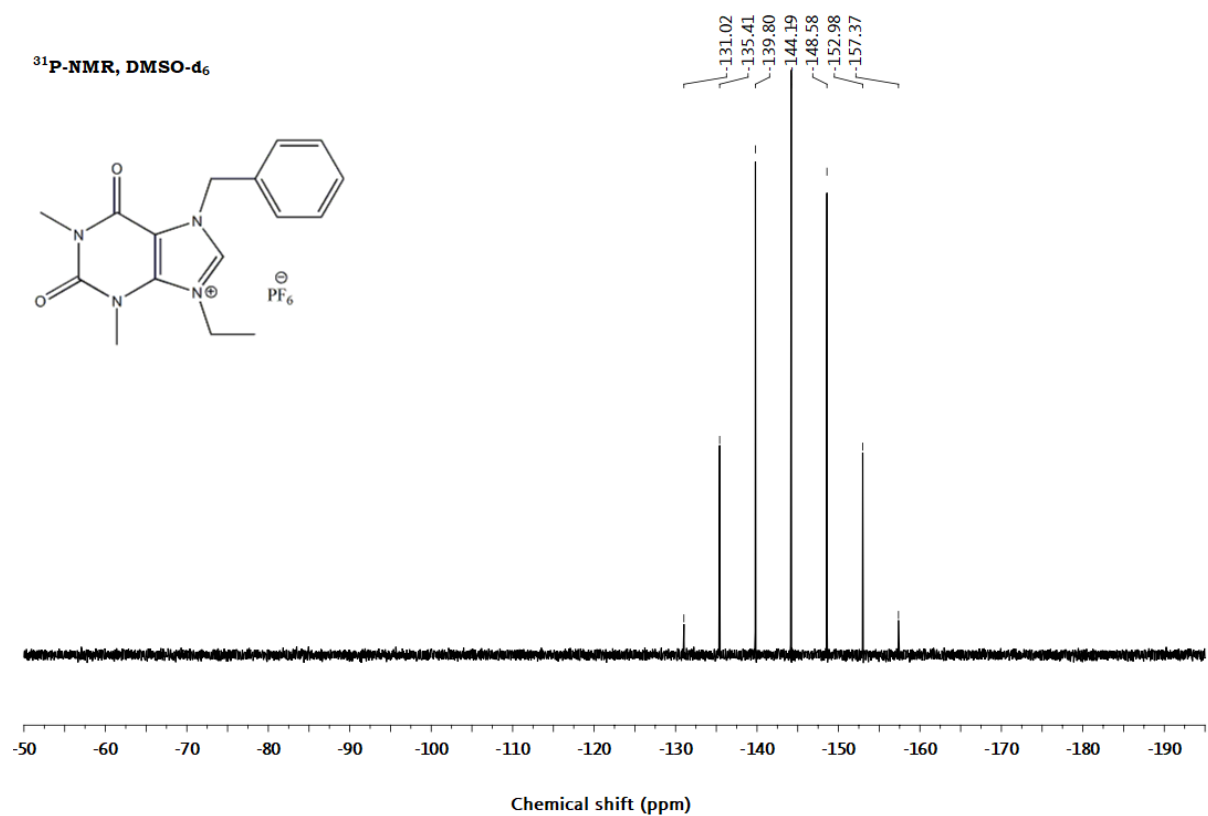


Figure S13

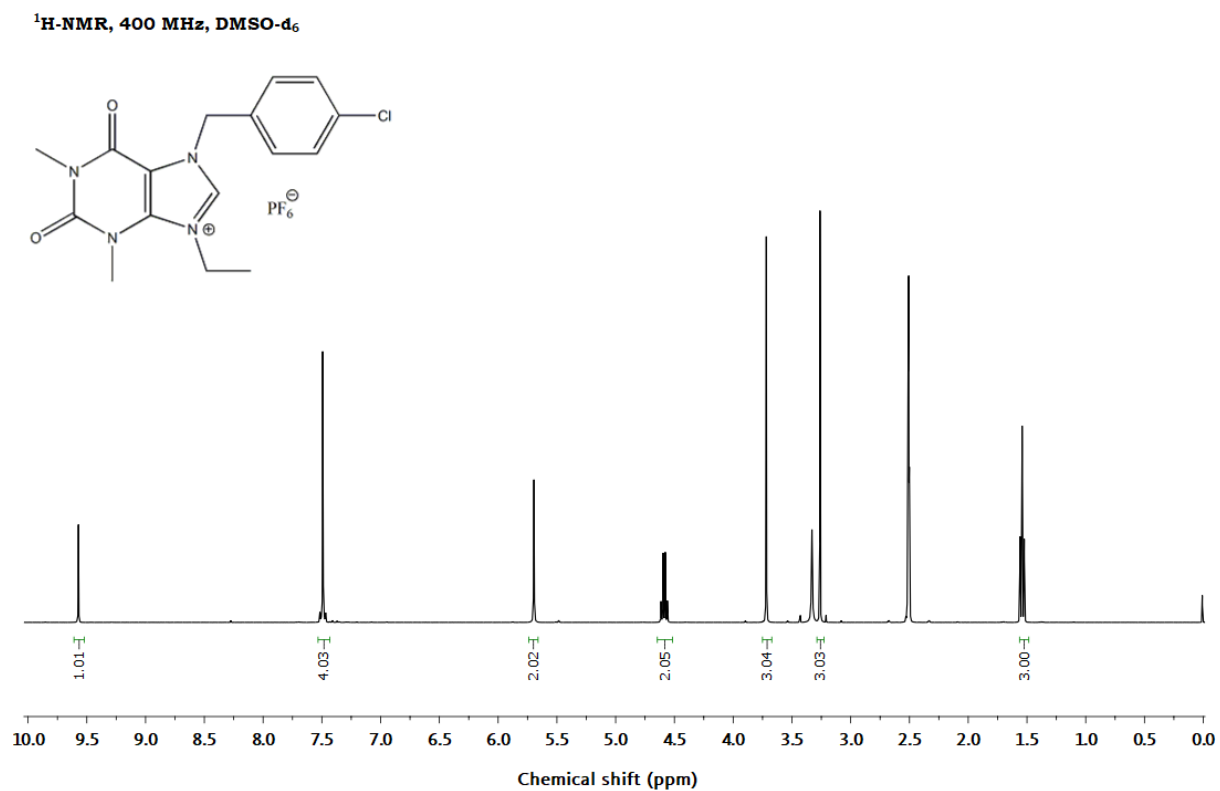


Figure S14

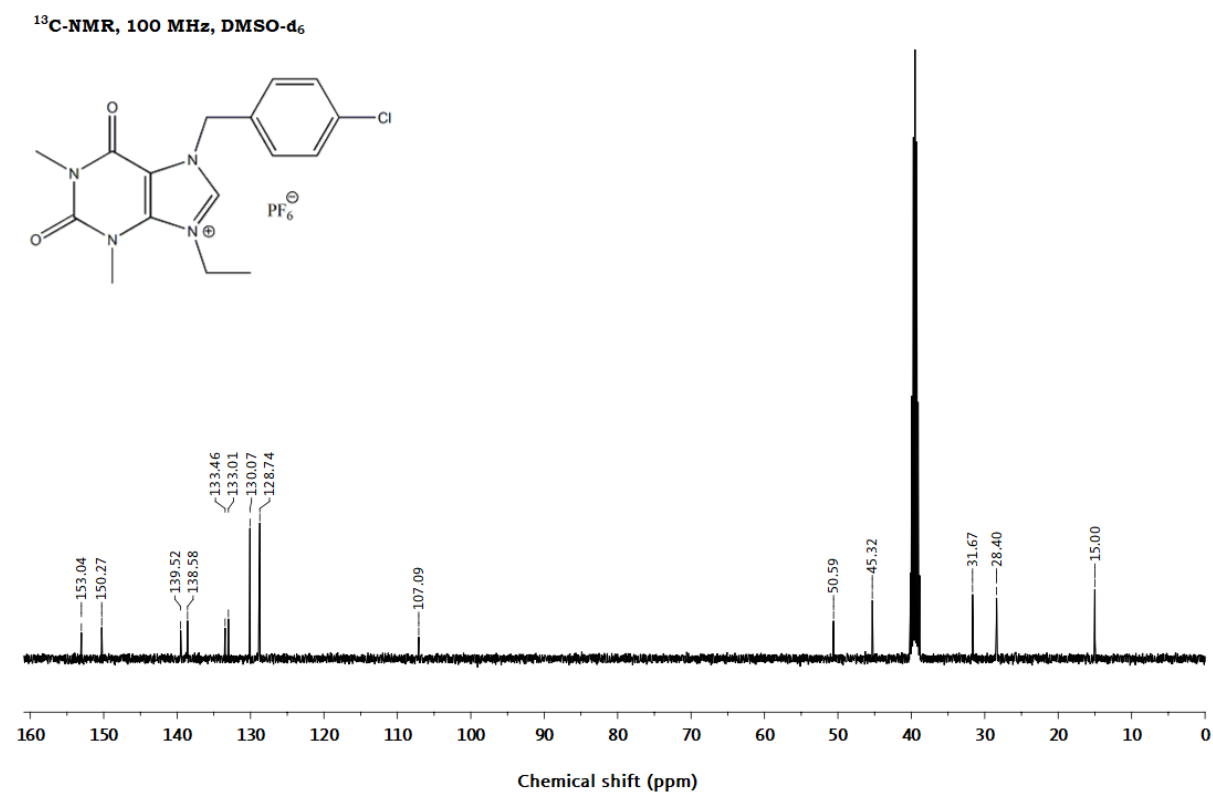


Figure S15

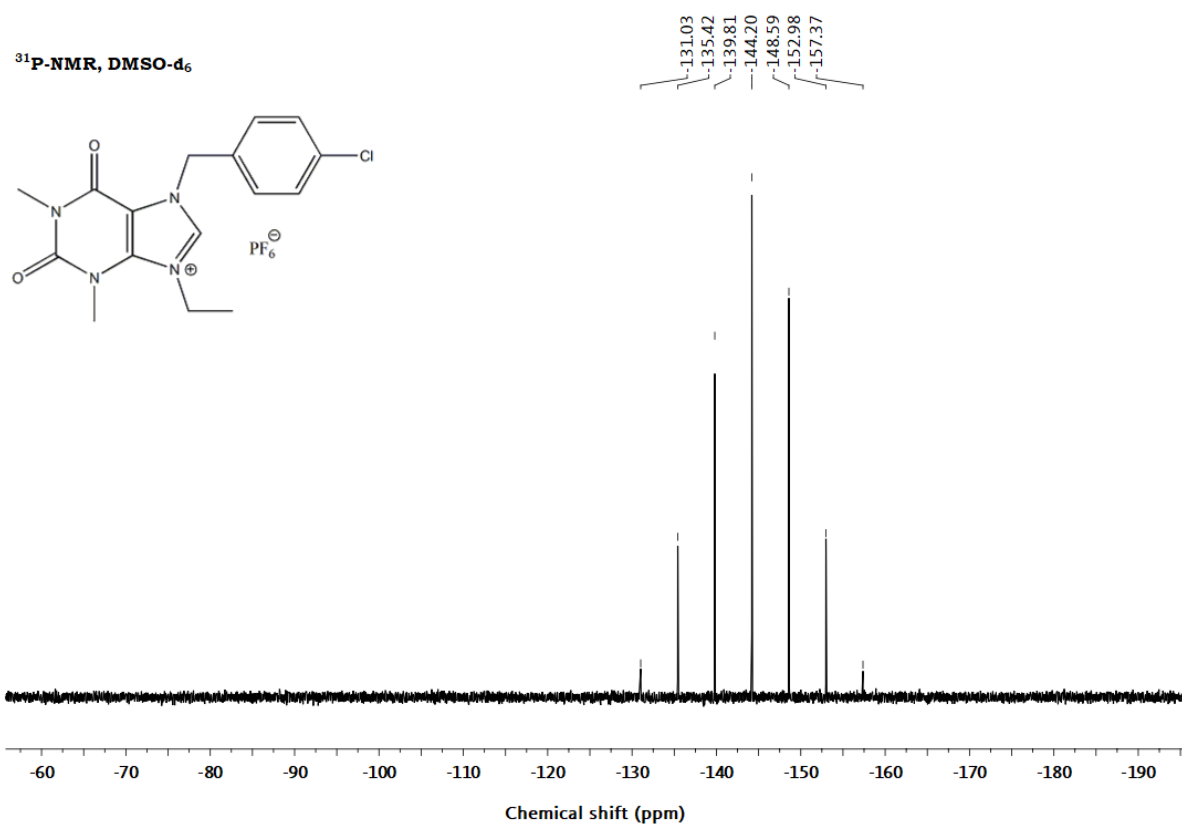


Figure S16

¹H-NMR, 400 MHz, DMSO-d₆

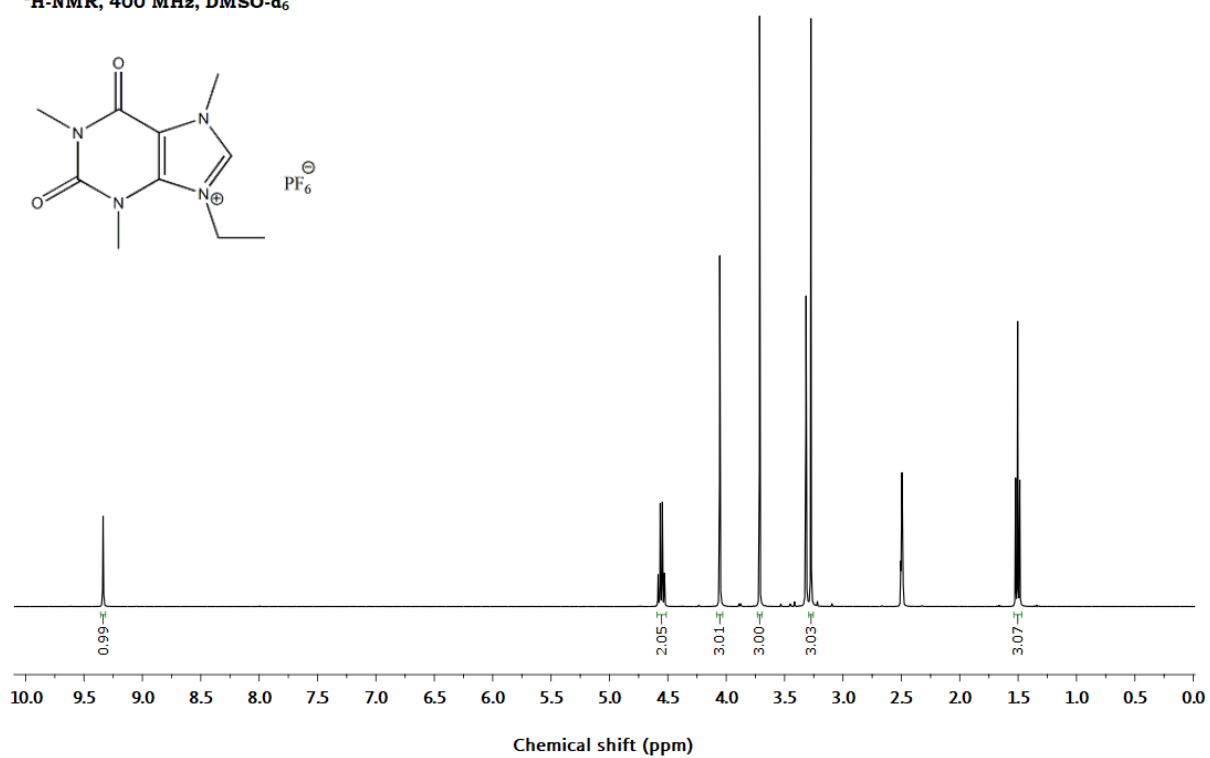


Figure S17

¹³C-NMR, 100 MHz, DMSO-d₆

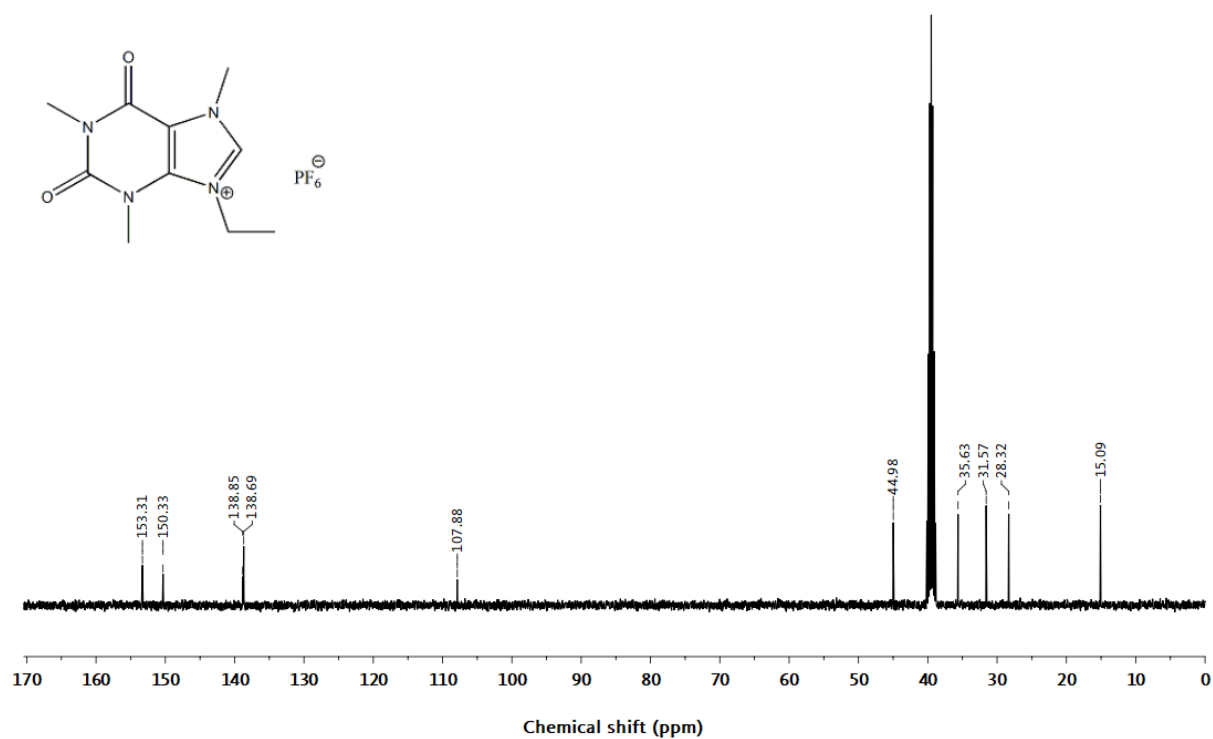


Figure S18

³¹P-NMR, DMSO-d₆

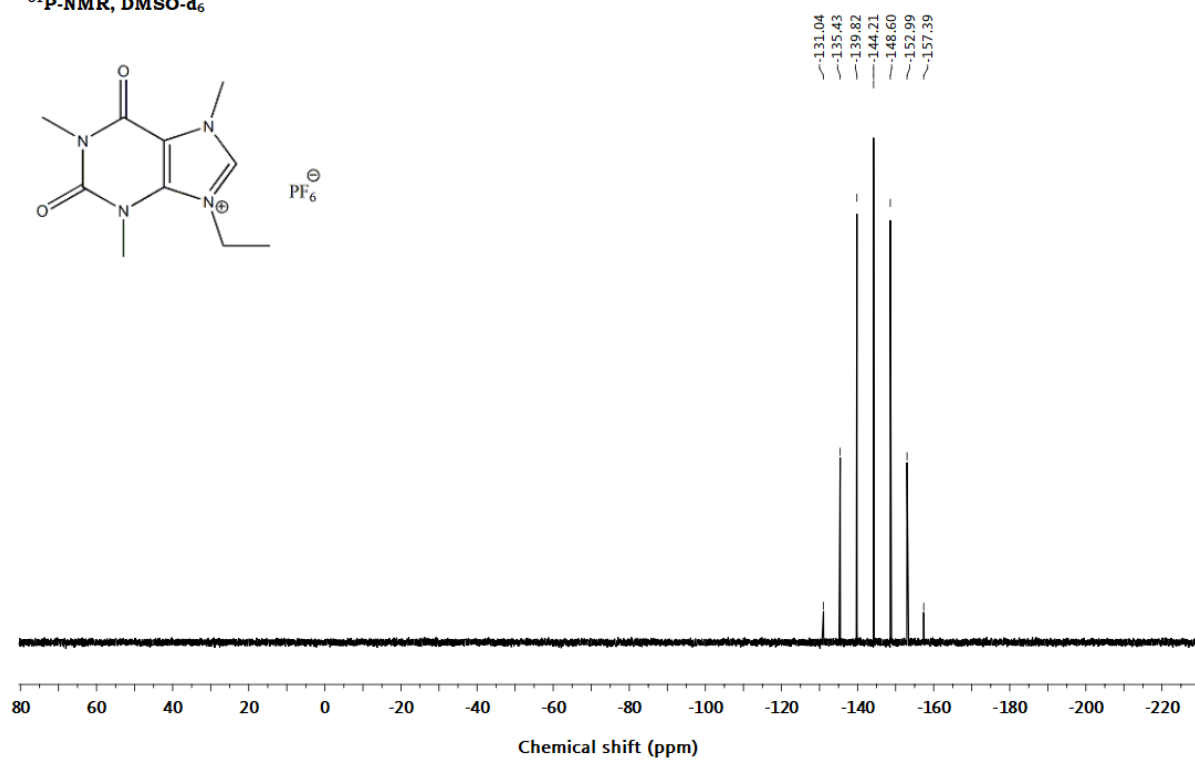


Figure S19

¹H-NMR, 400 MHz, DMSO-d₆

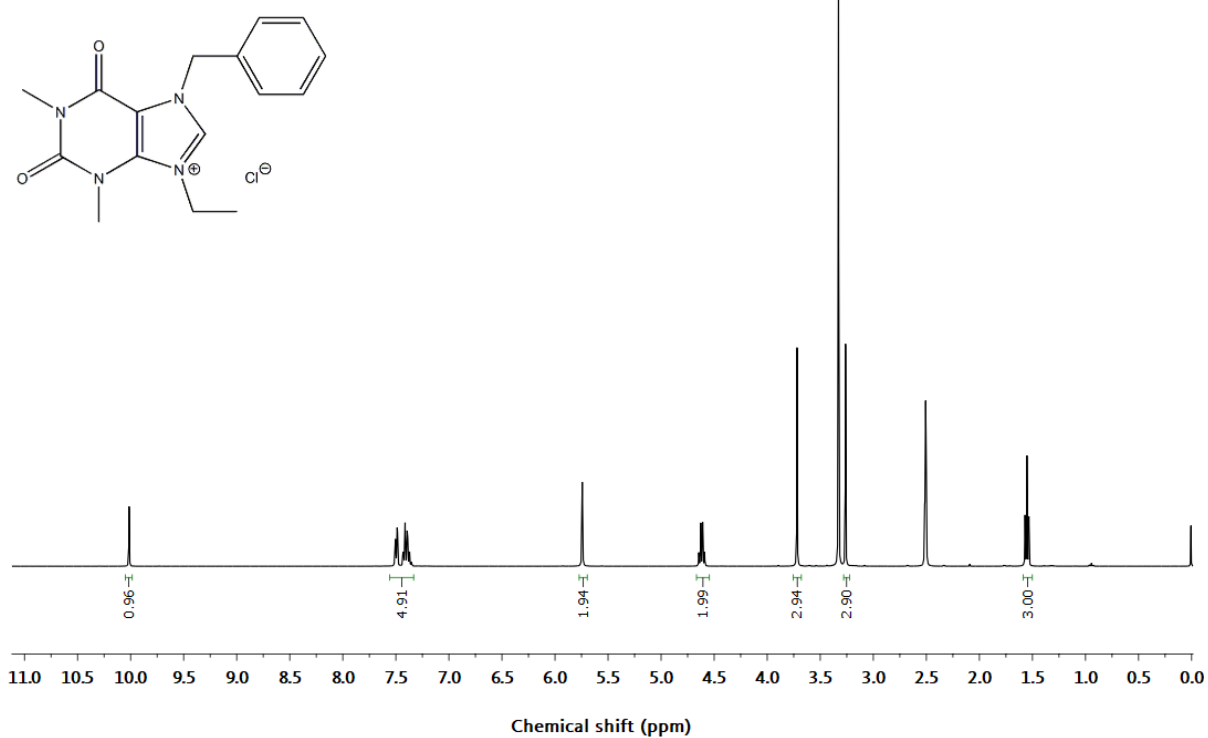


Figure S20

¹³C-NMR, 100 MHz, DMSO-d₆

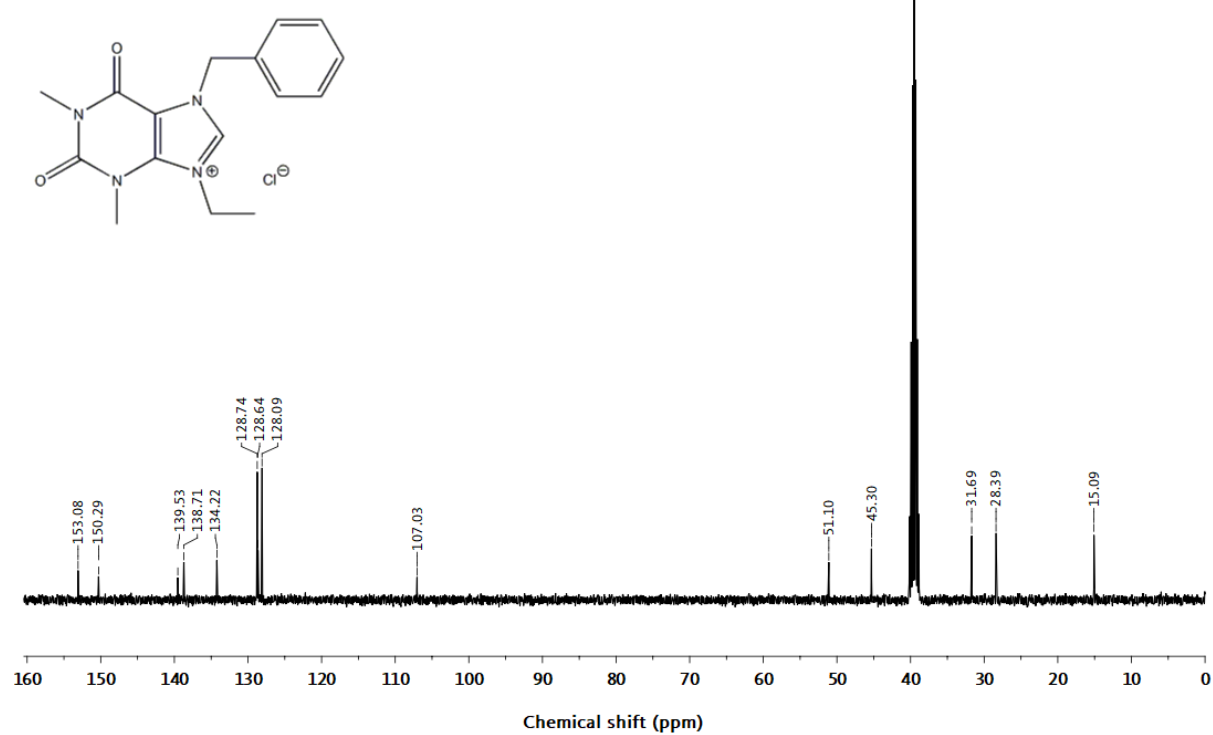


Figure S21

³⁵Cl-NMR, 54 MHz, DMSO-d₆

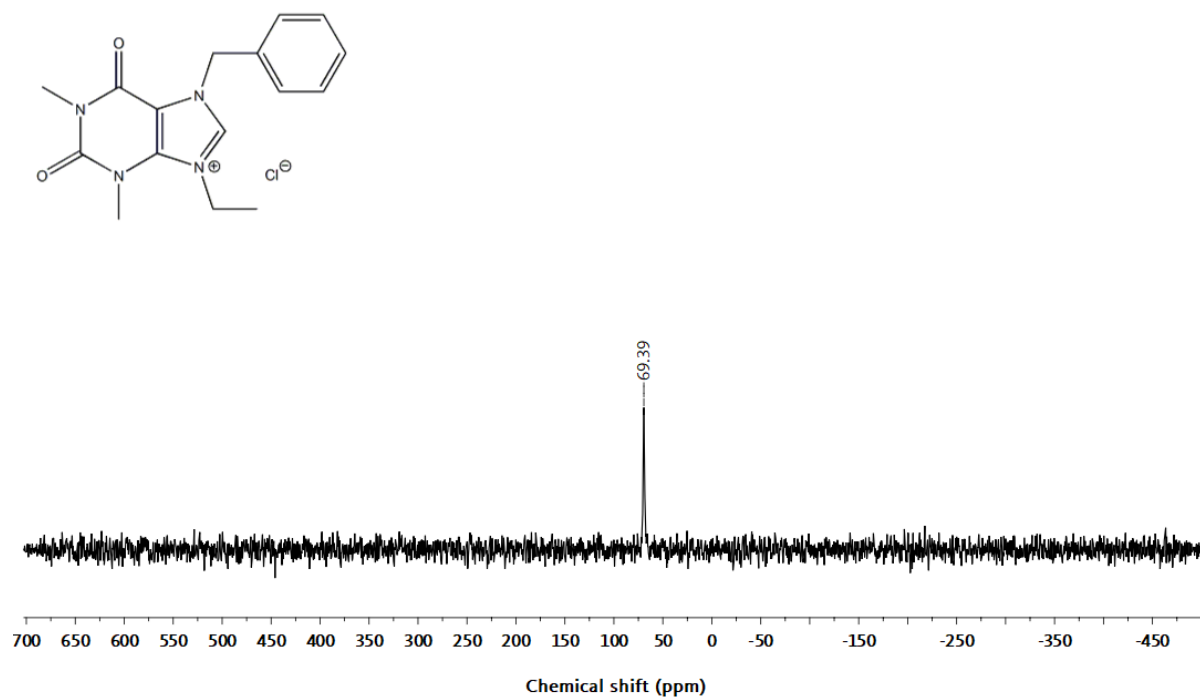


Figure S22

¹H-NMR, 400 MHz, DMSO-d₆

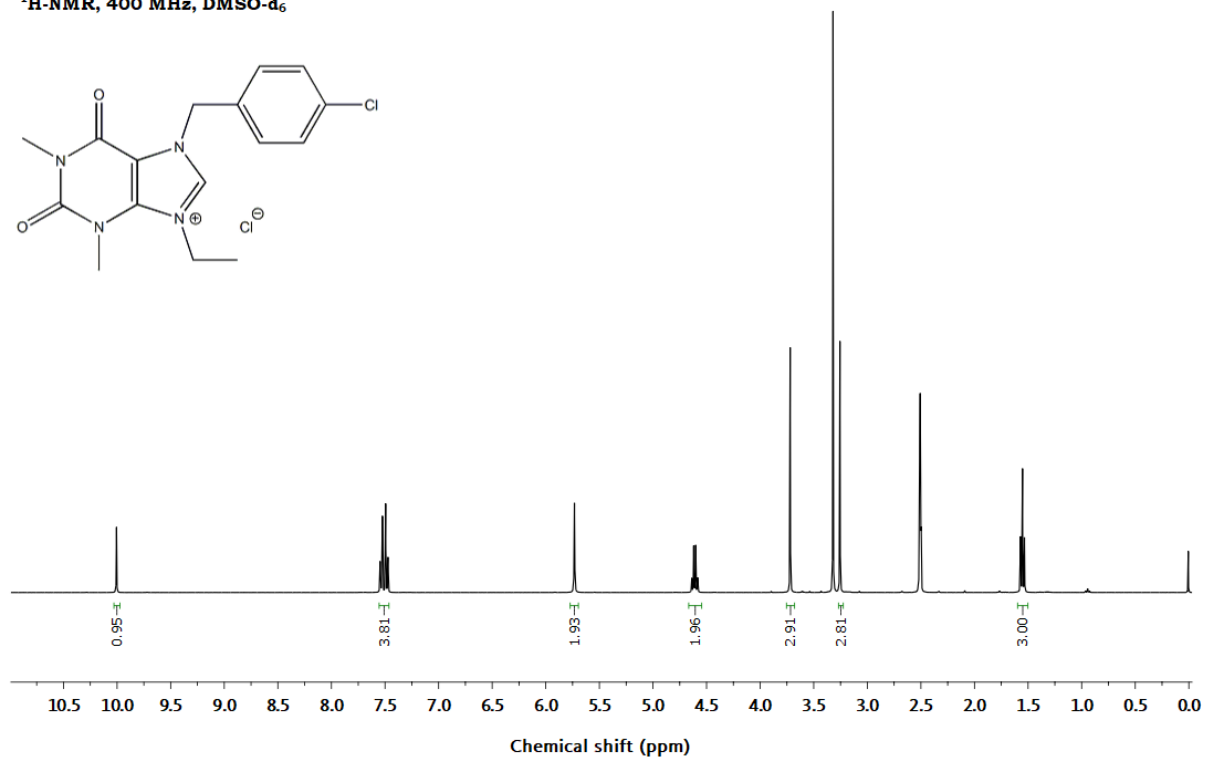


Figure S23

¹³C-NMR, 100 MHz, DMSO-d₆

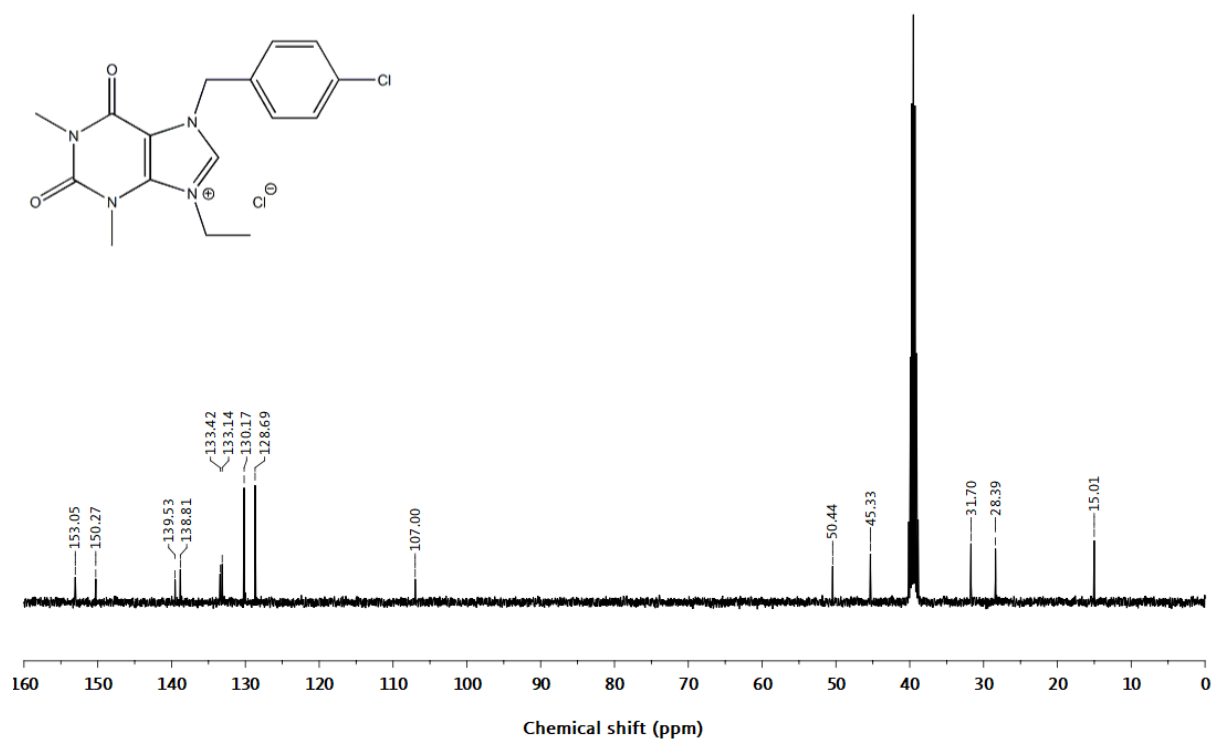


Figure S24

³⁵Cl-NMR, 54 MHz, DMSO-d₆

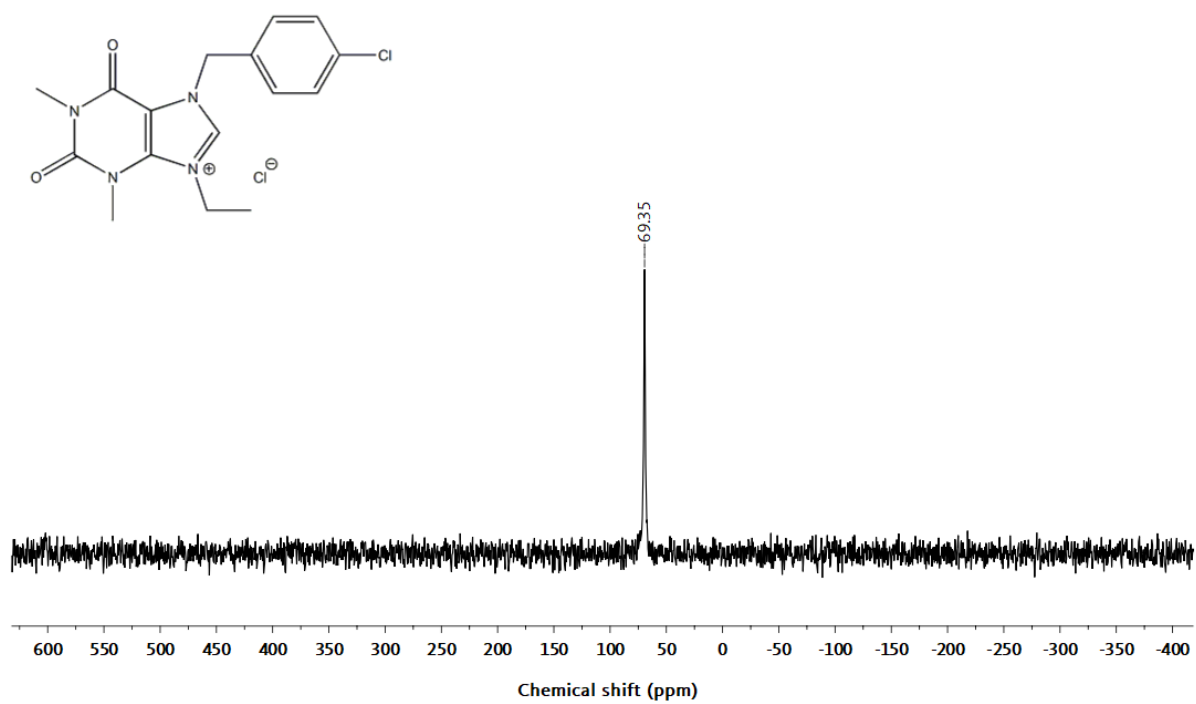


Figure S25

¹H-NMR, 400 MHz, DMSO-d₆

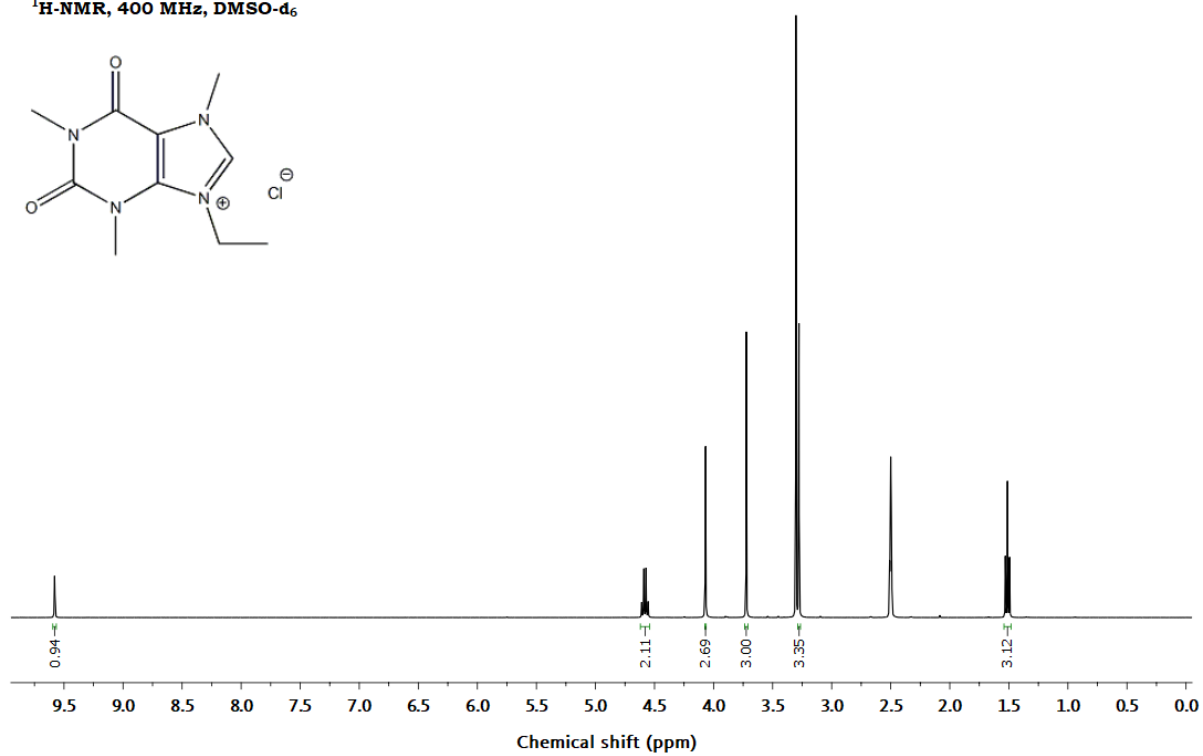


Figure S26

¹³C-NMR, 150 MHz, DMSO-d₆

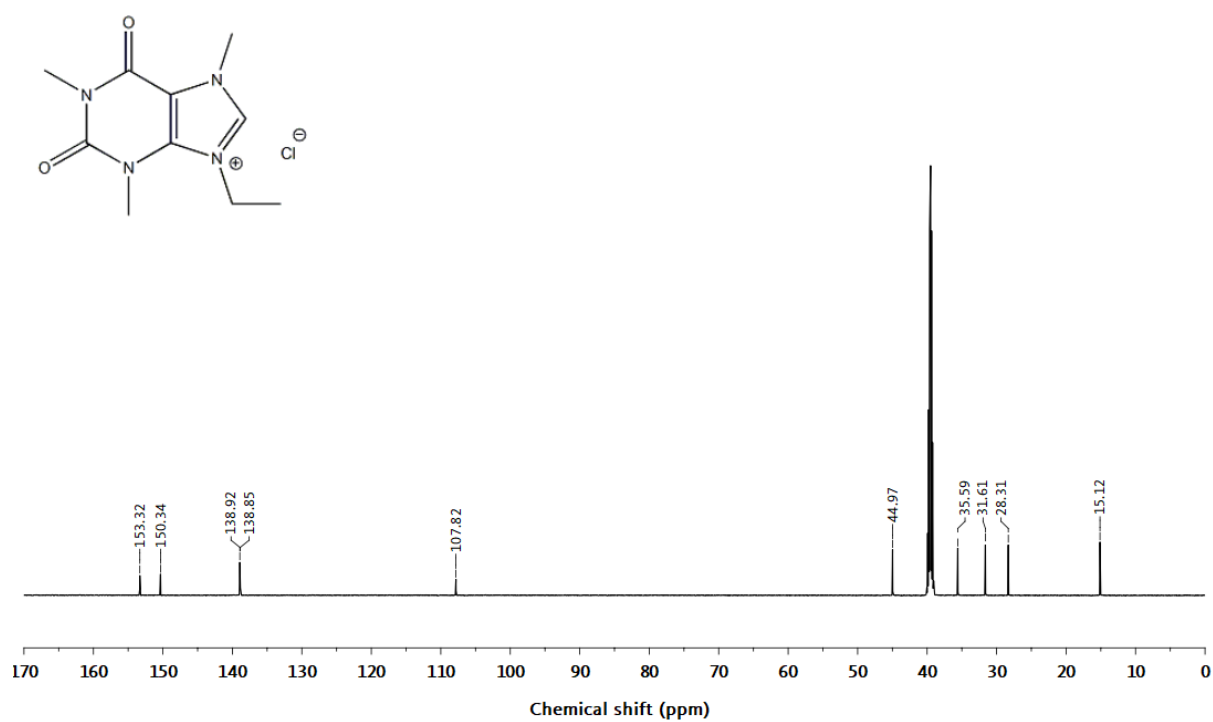


Figure S27

³⁵Cl-NMR, 39 MHz, DMSO-d₆

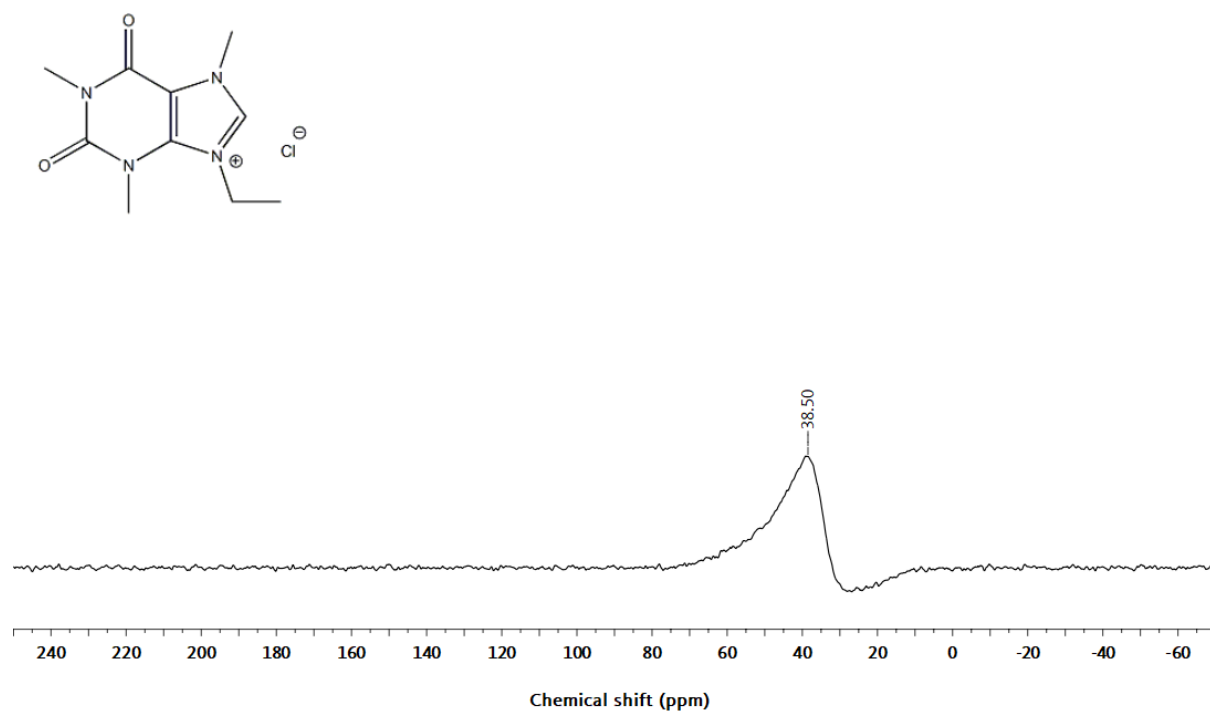


Figure S 28

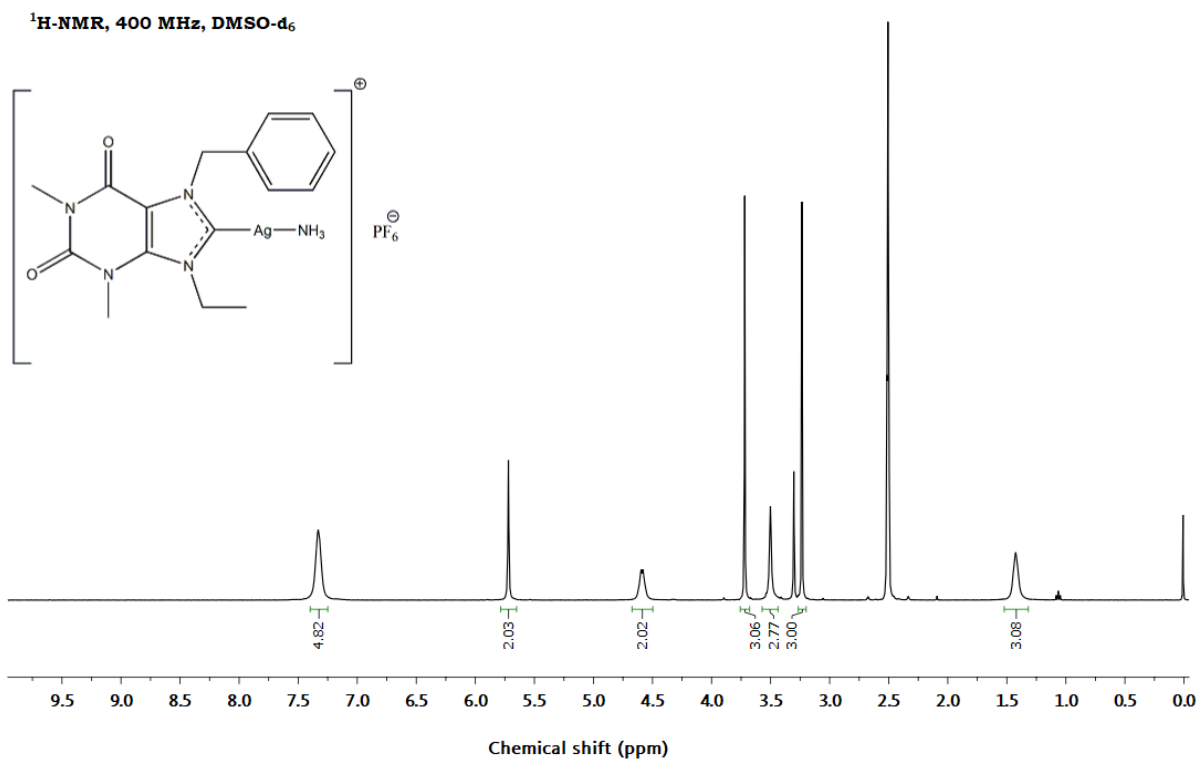


Figure S29

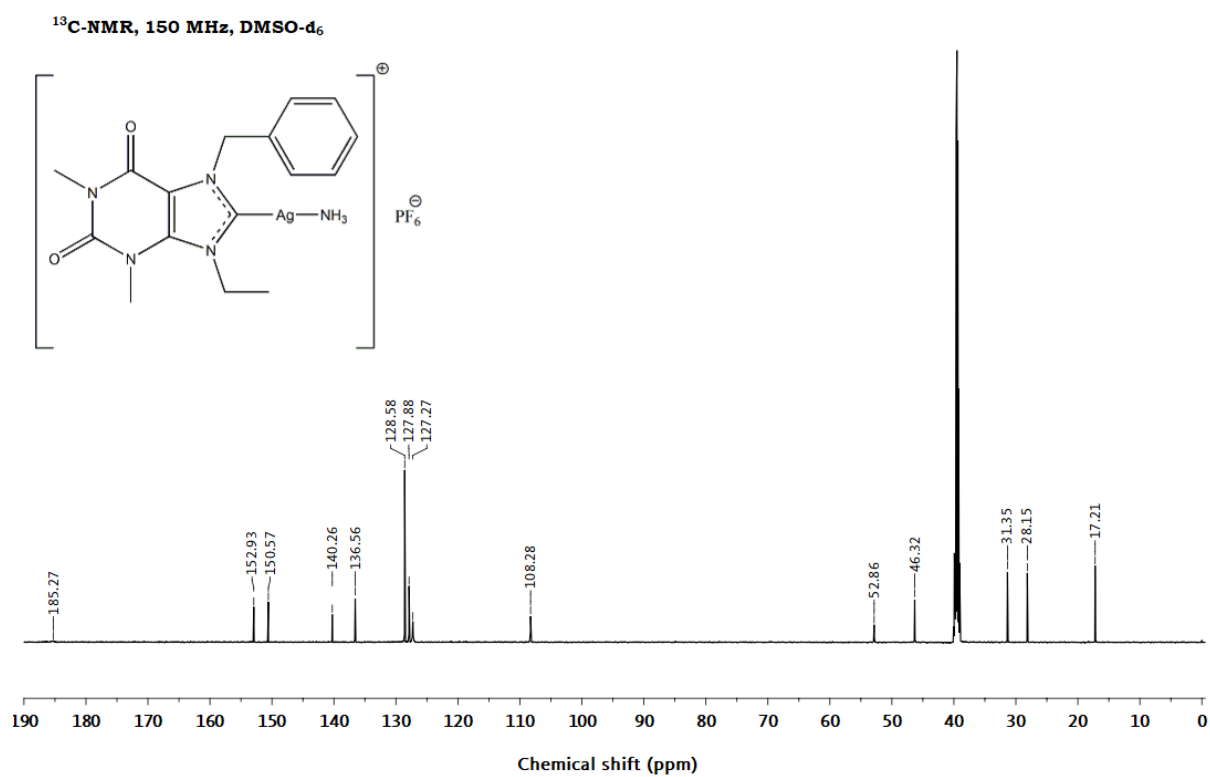


Figure S30

³¹P-NMR, DMSO-d₆

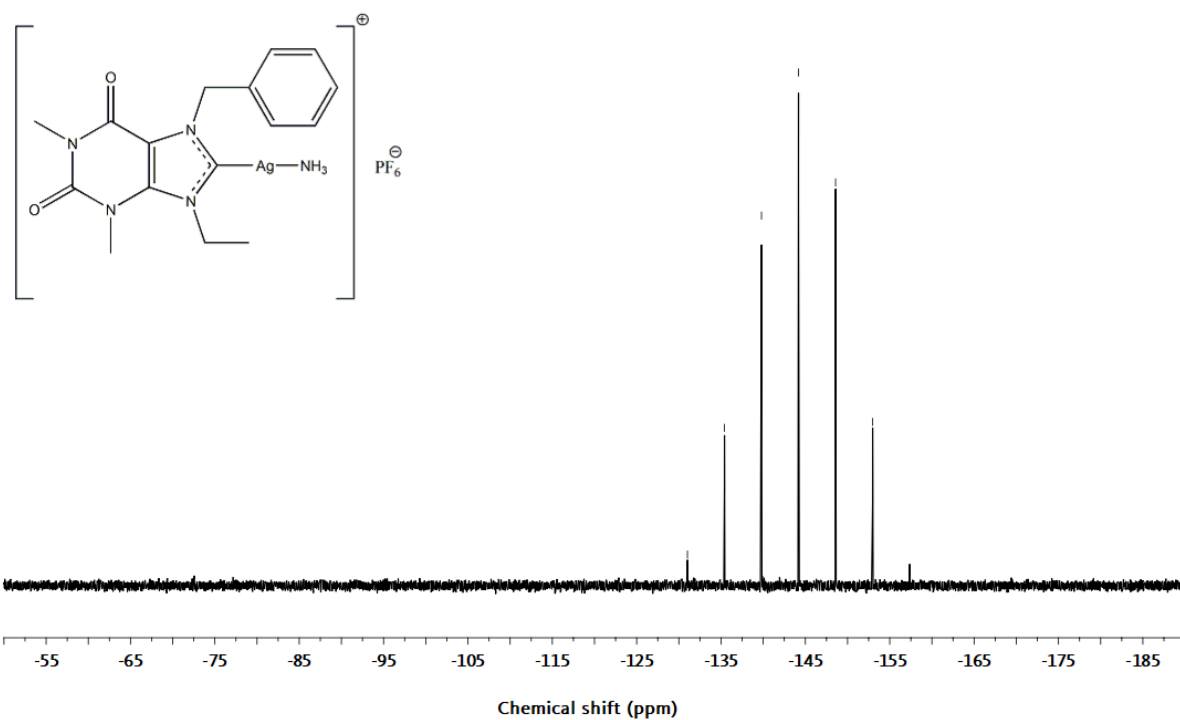


Figure S31

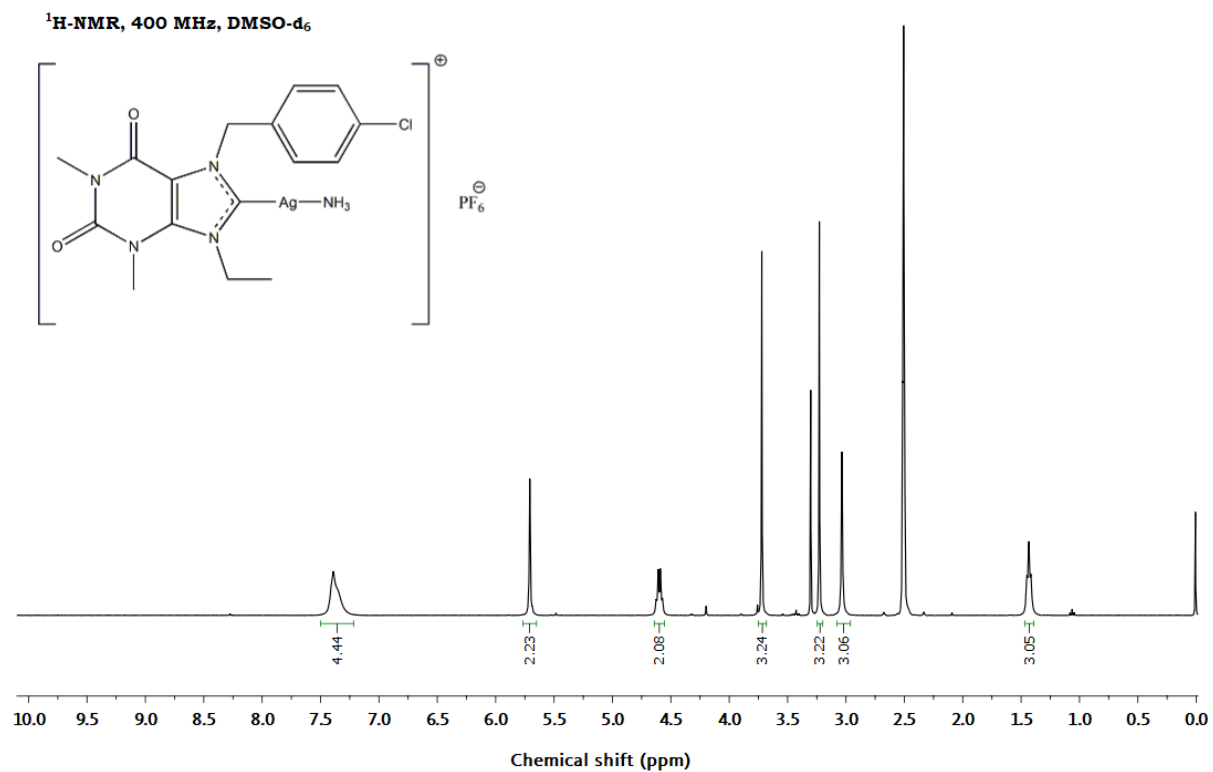


Figure S32

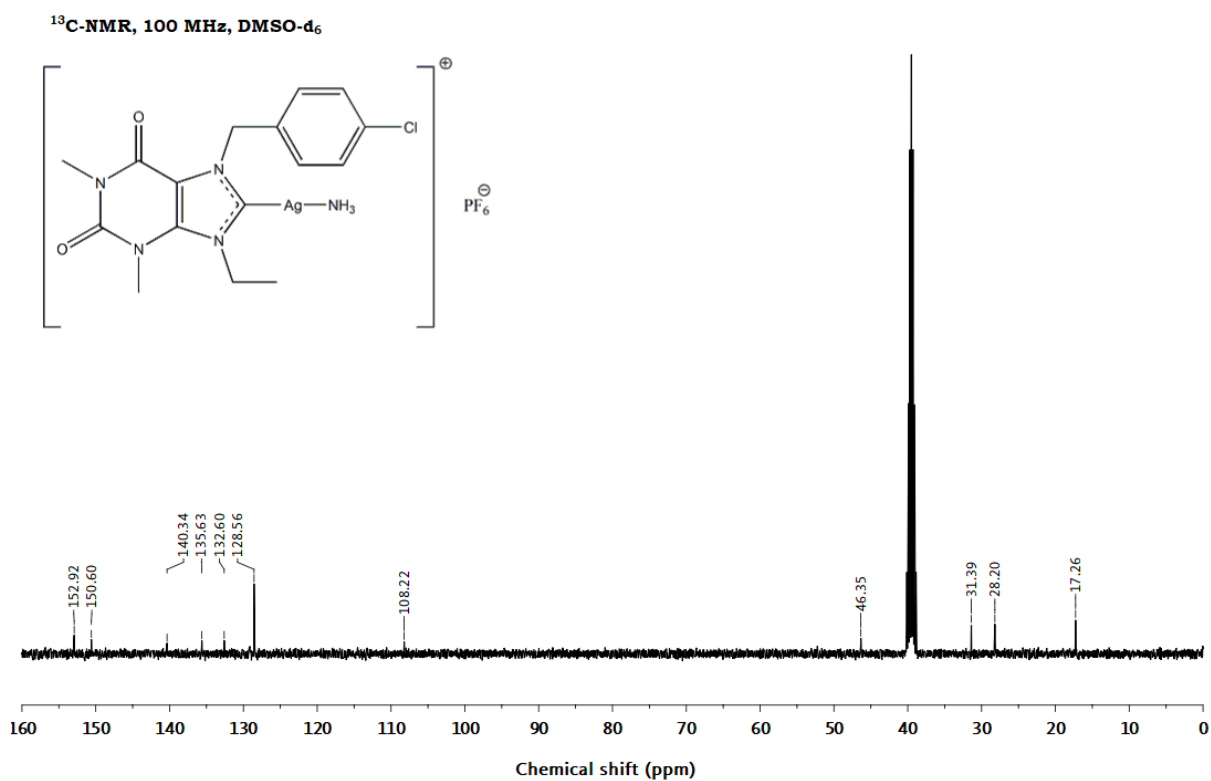


Figure S33

³¹P-NMR, DMSO-d₆

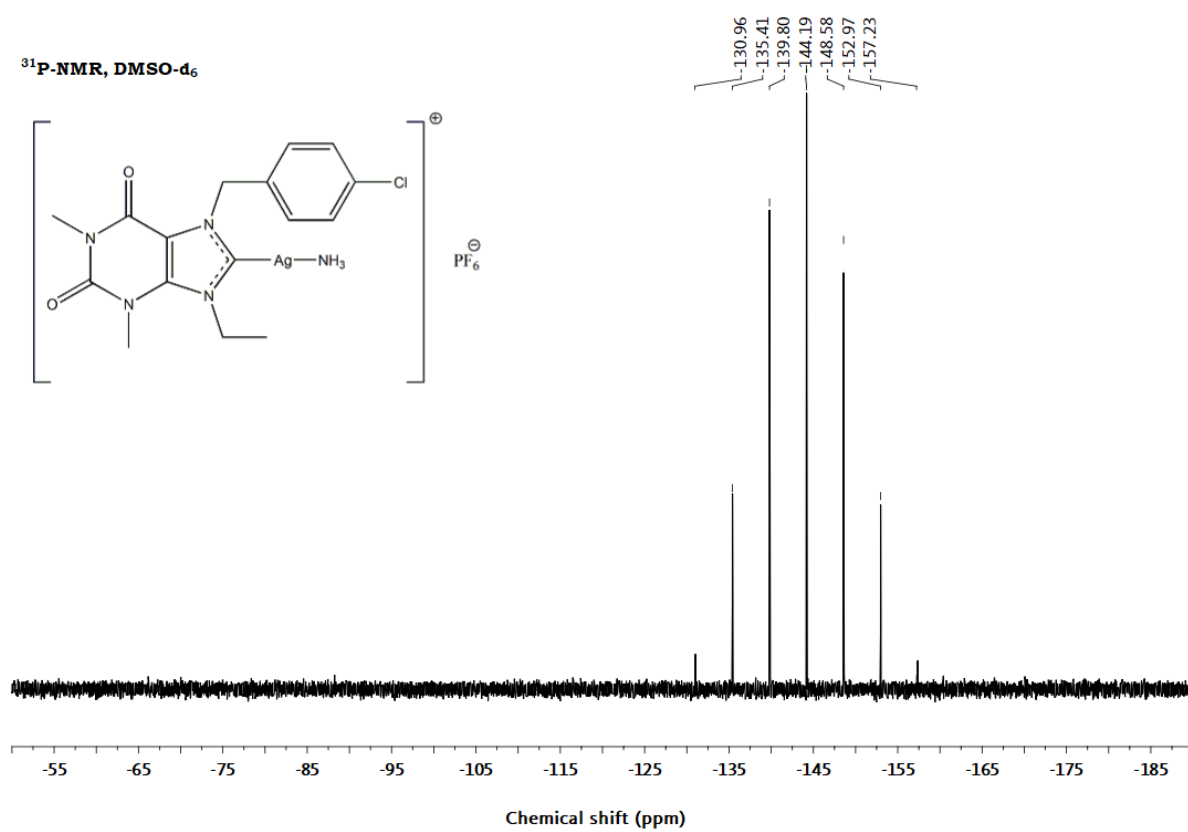


Figure S34

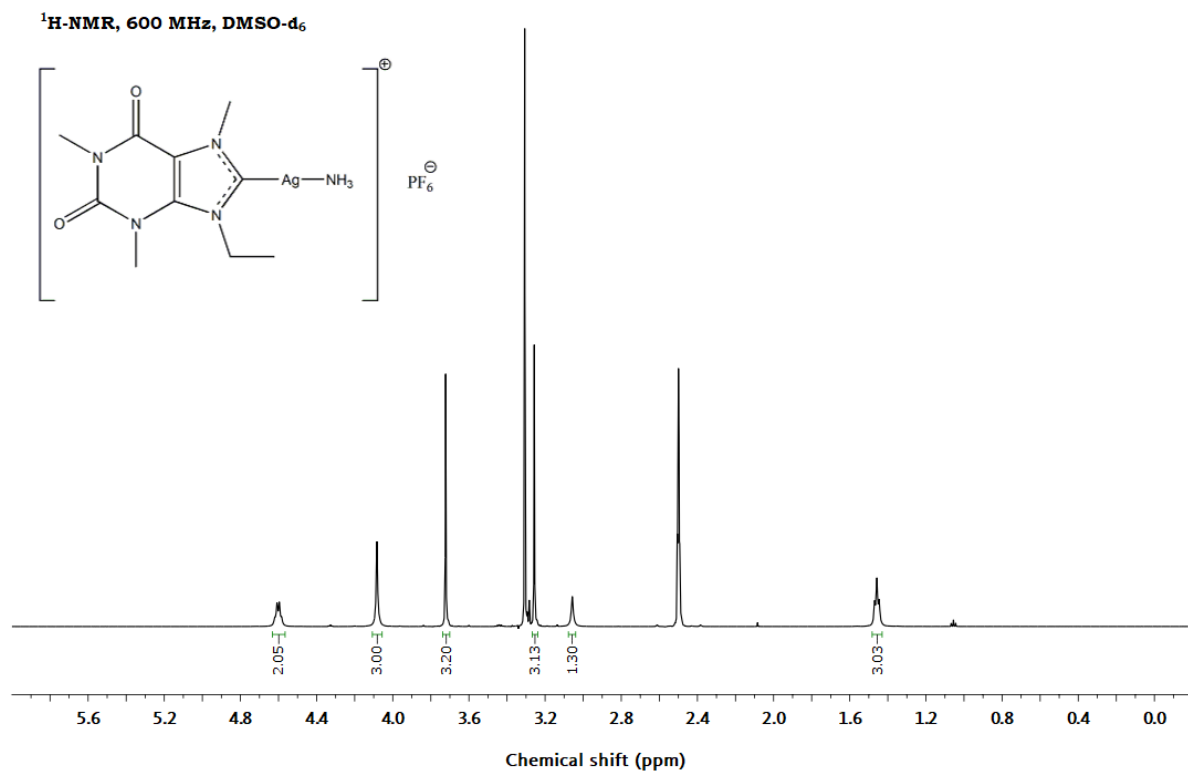


Figure S35

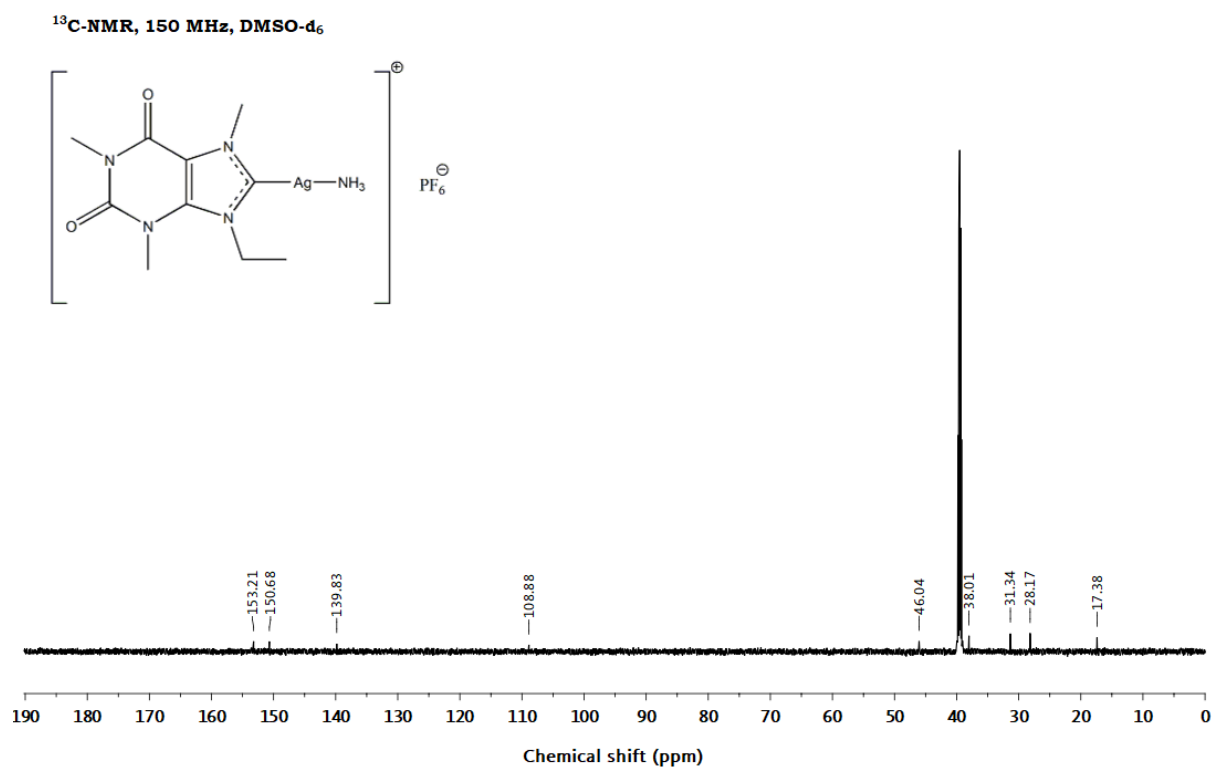


Figure S36

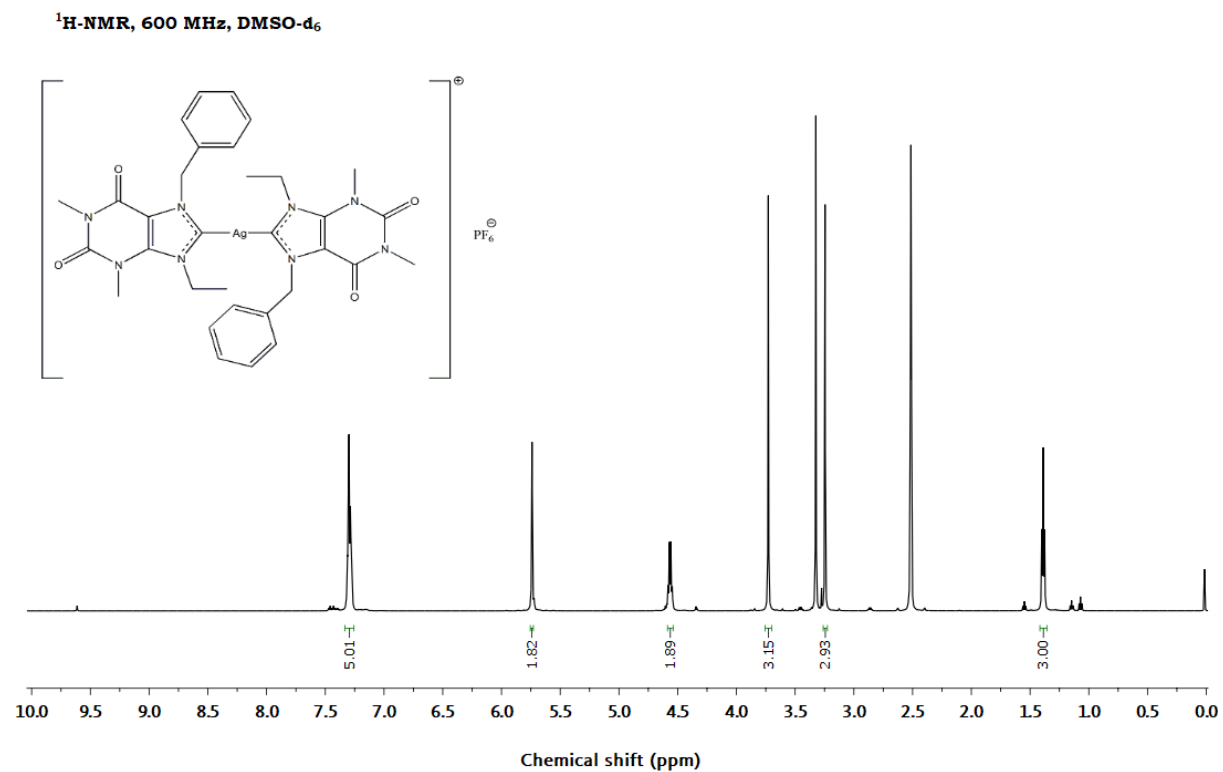


Figure S37

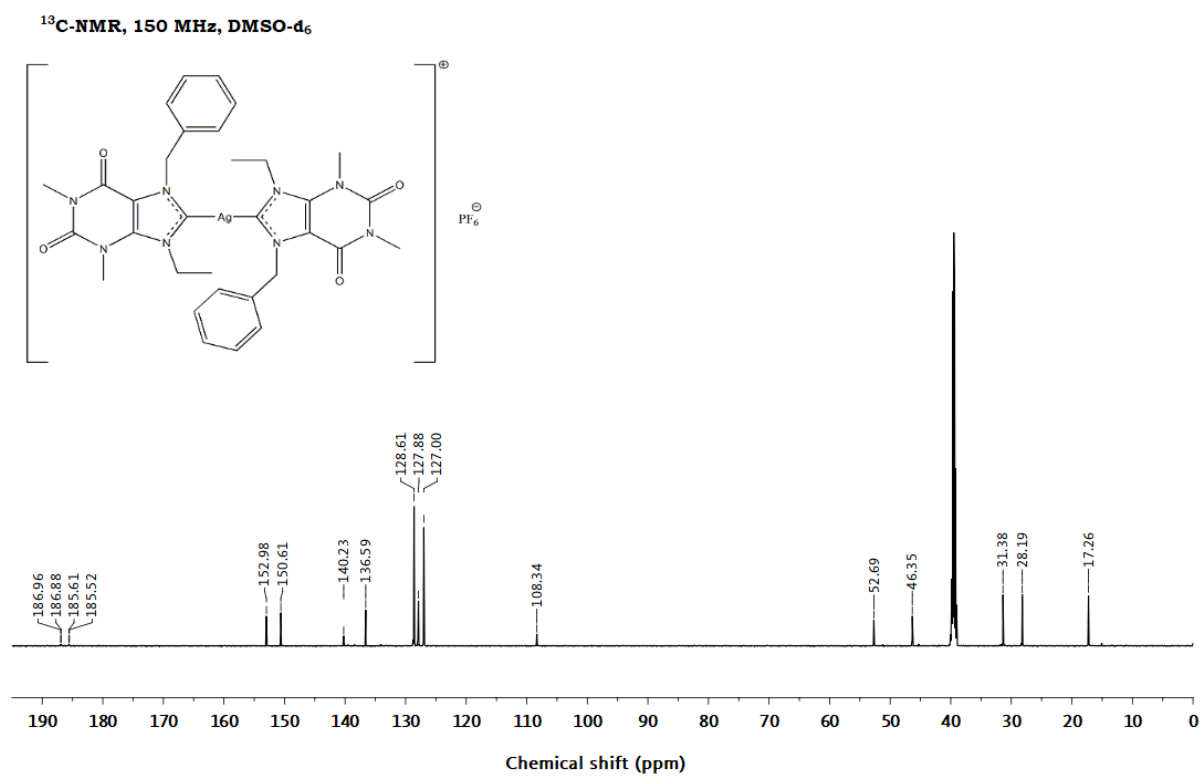


Figure S 38

³¹P-NMR, Acetone-d₆

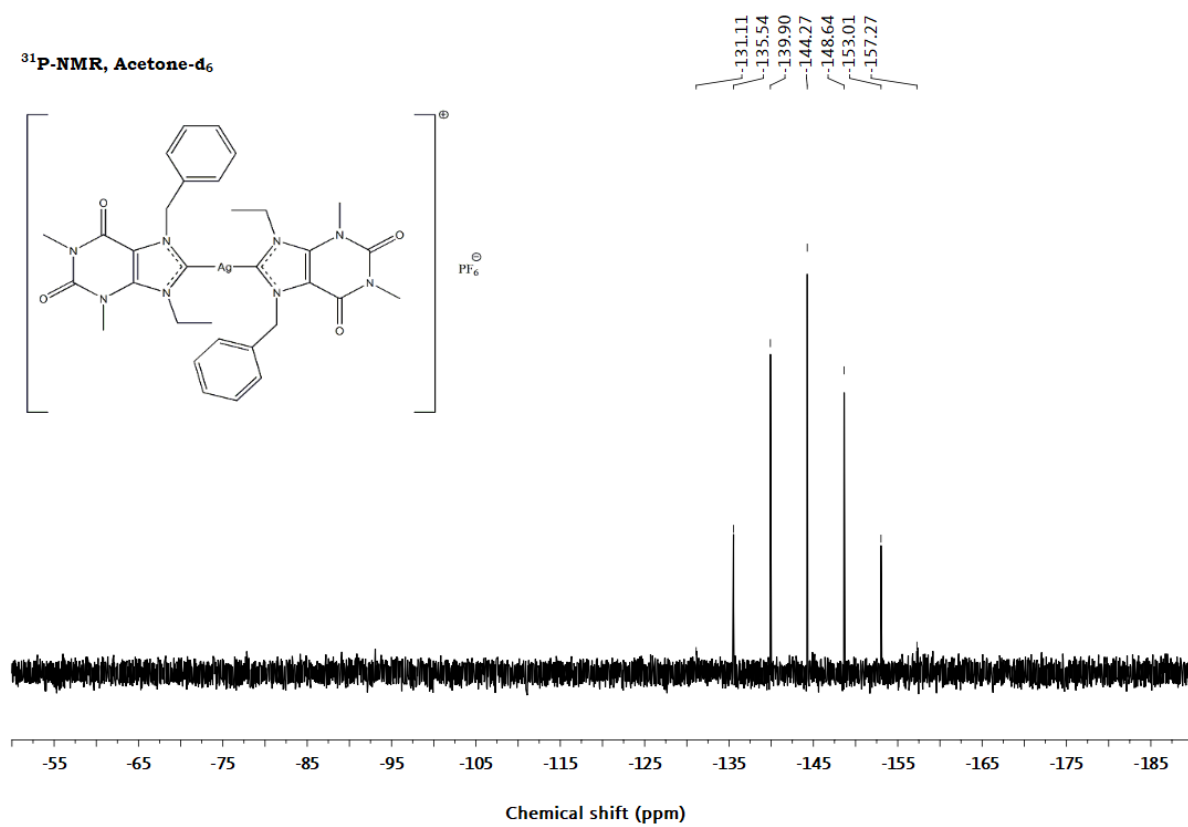


Figure S39

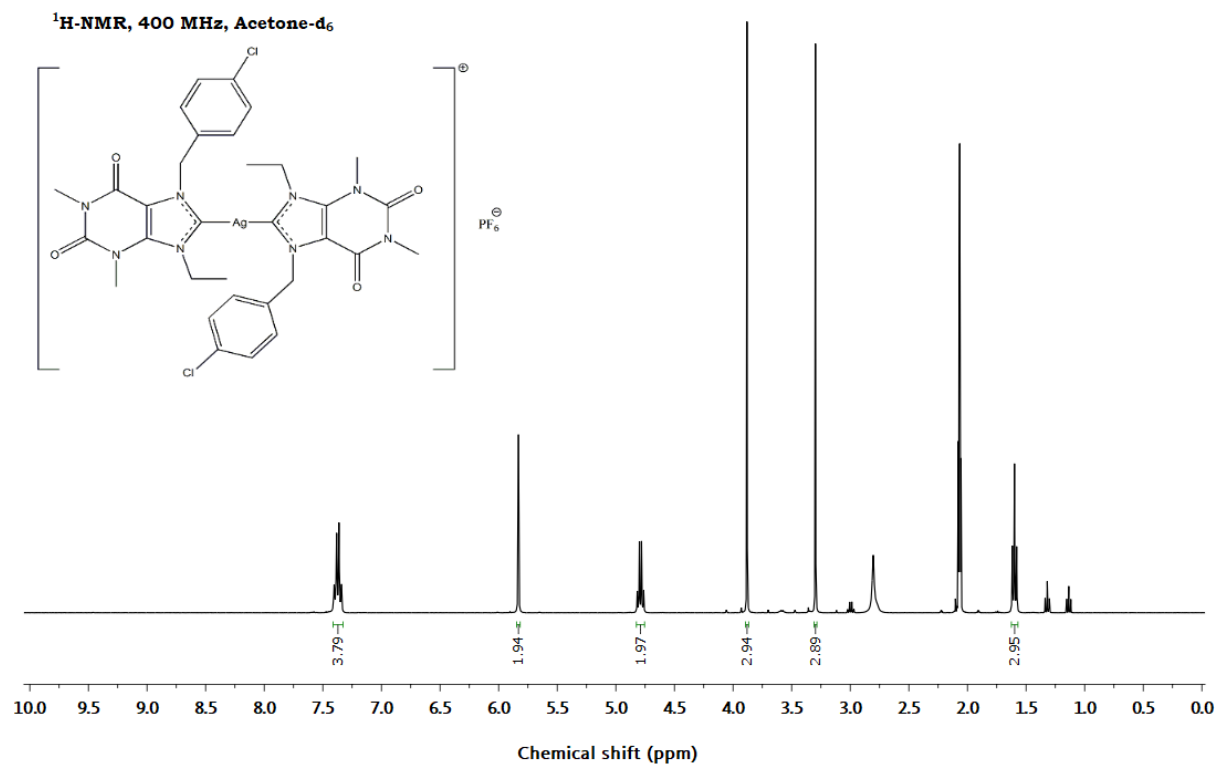


Figure S40

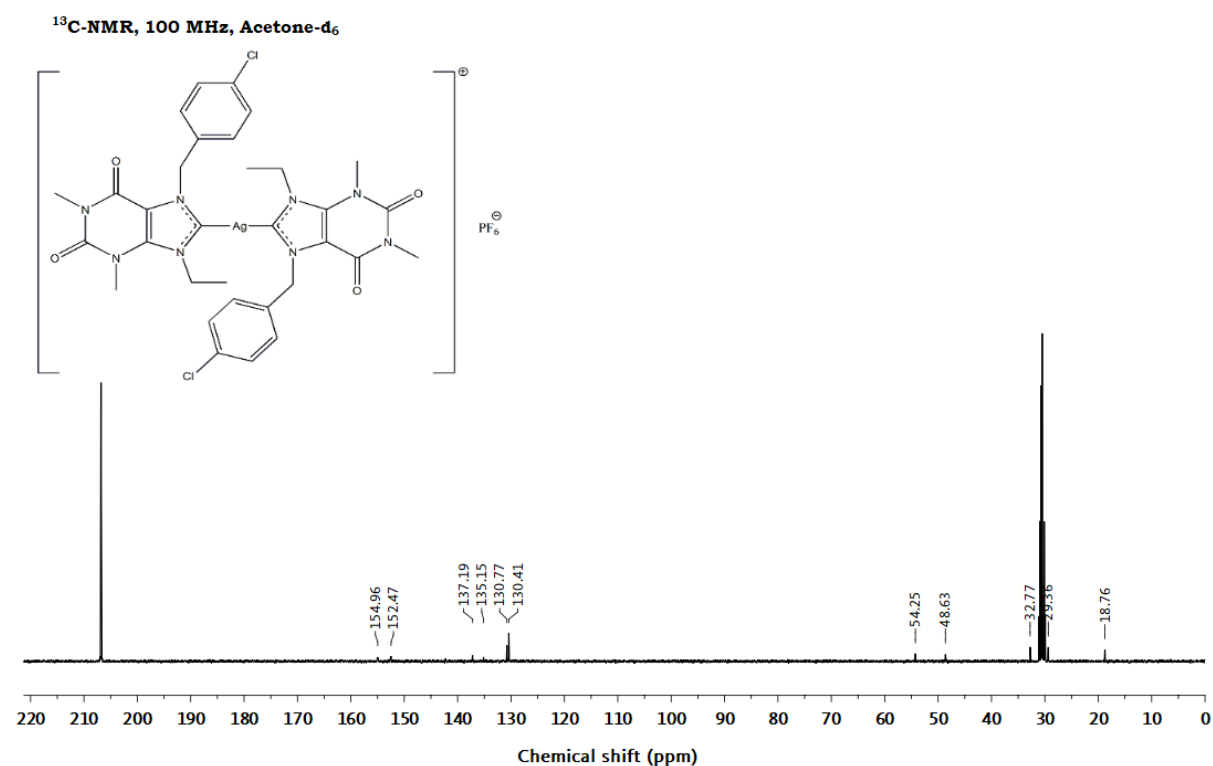


Figure S41

³¹P-NMR, Acetone-d₆

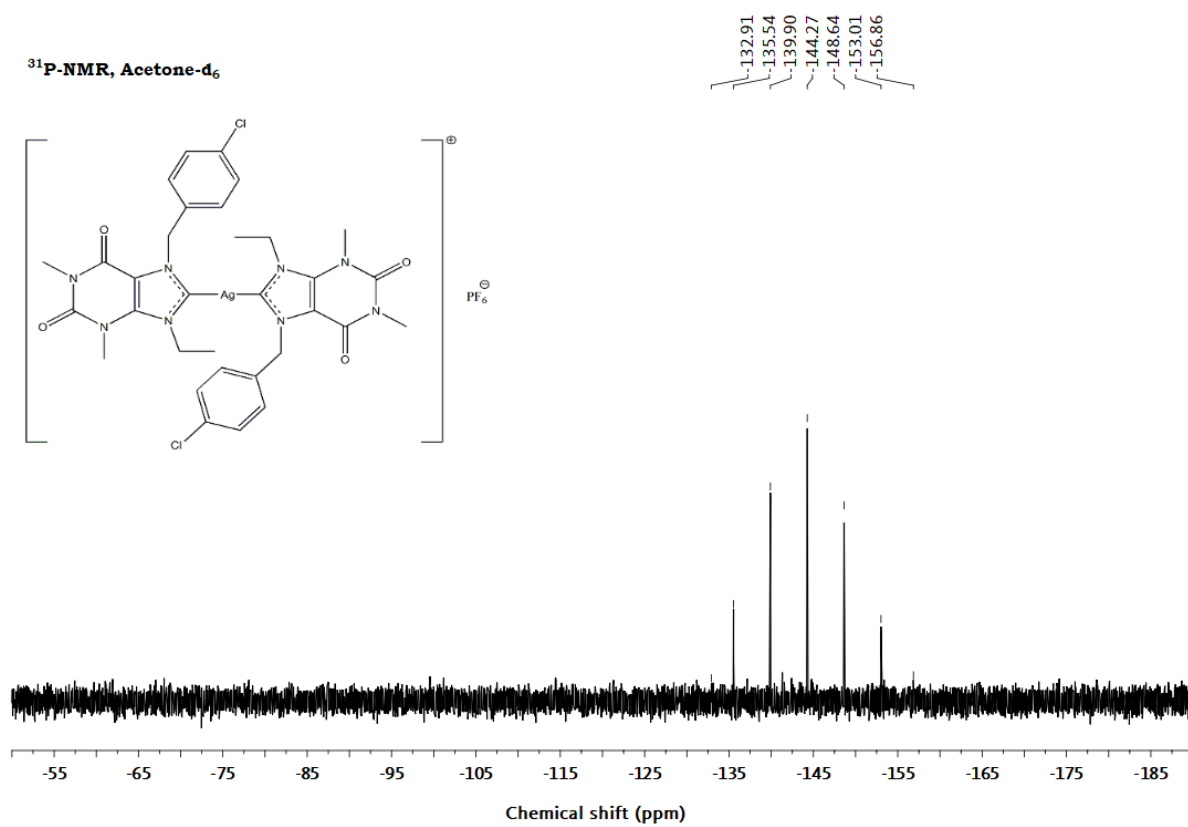


Figure S42

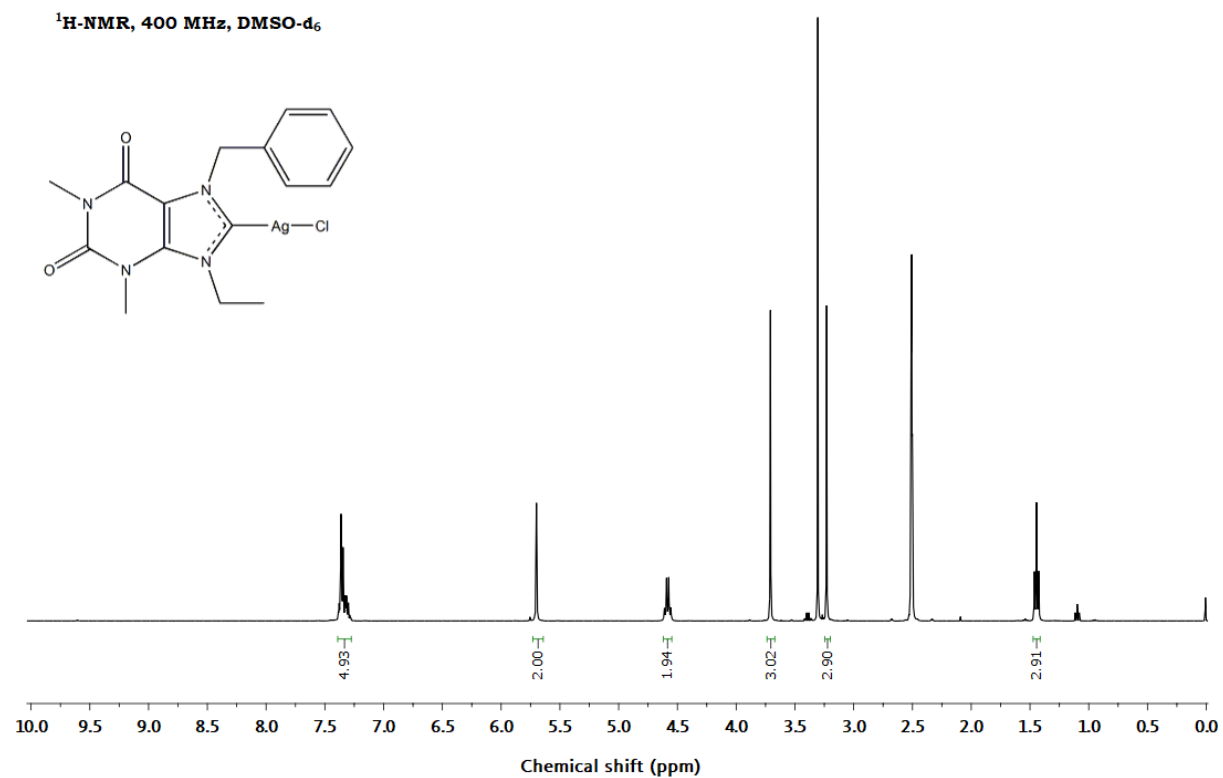


Figure S43

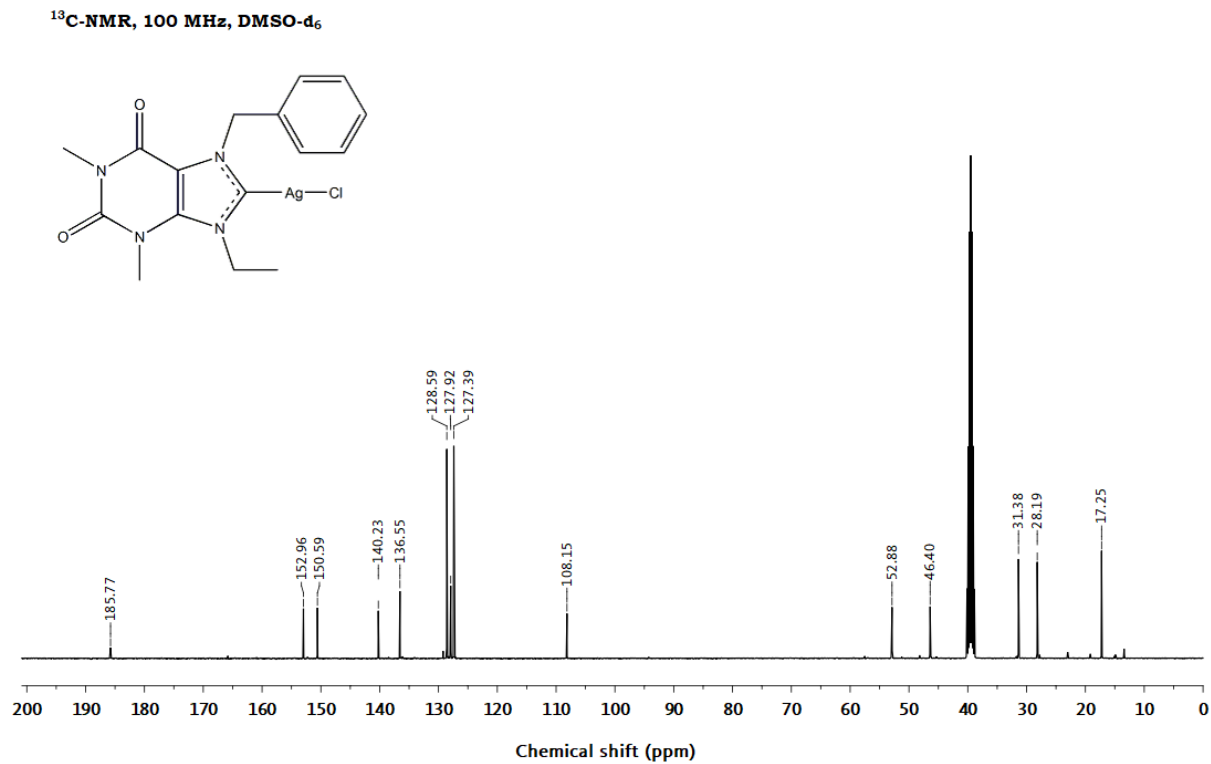


Figure S44

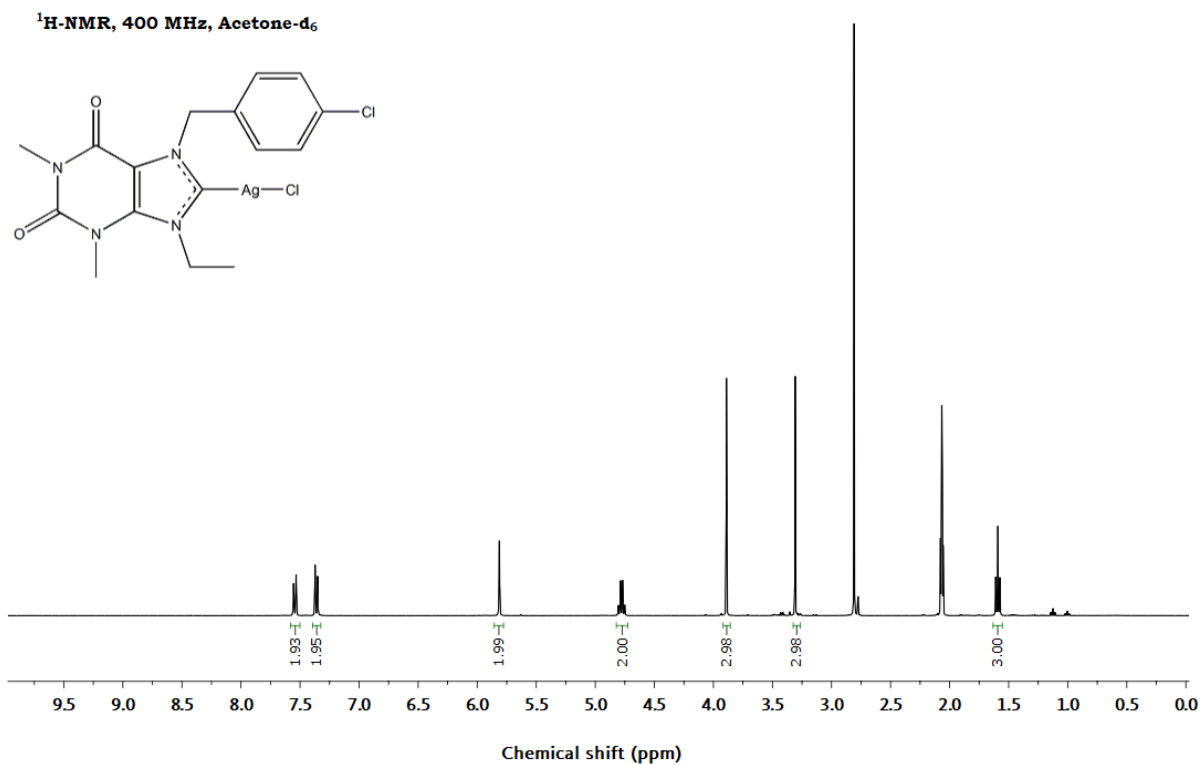


Figure S45

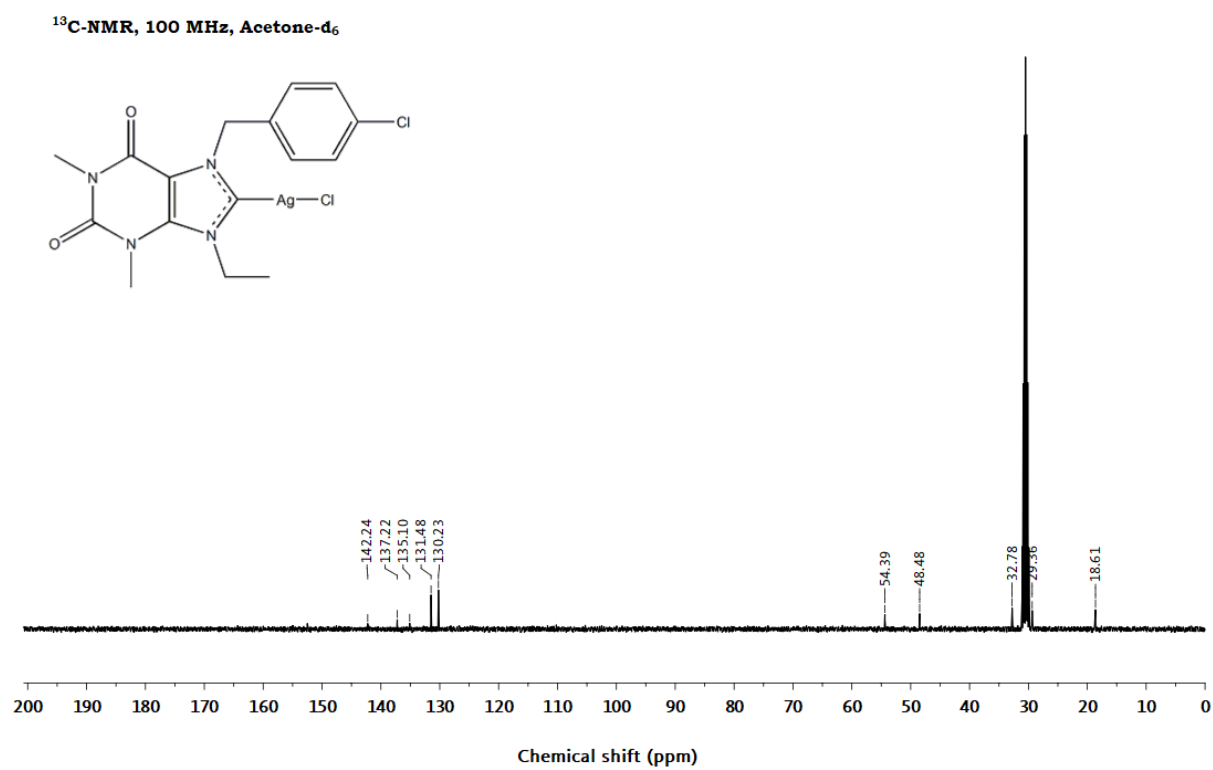


Figure S46

¹H-NMR, 400 MHz, CDCl₃, 223 K

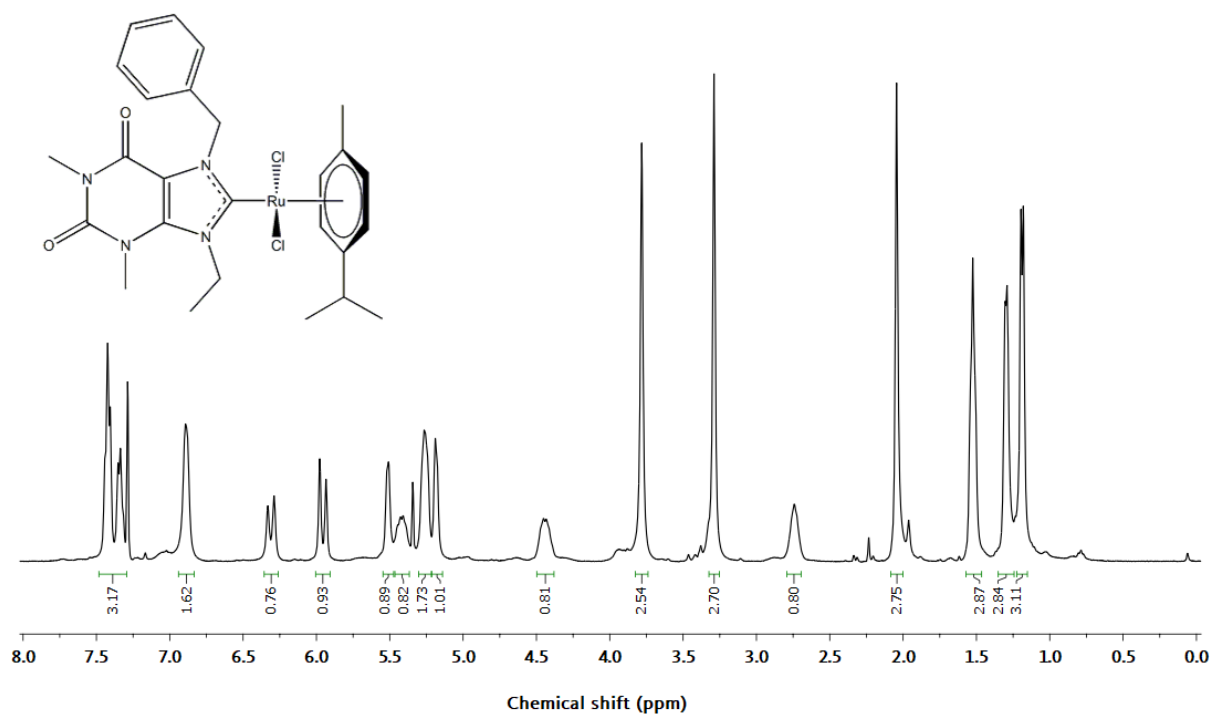


Figure S47

¹³C-NMR, 100 MHz, CDCl₃, 223 K

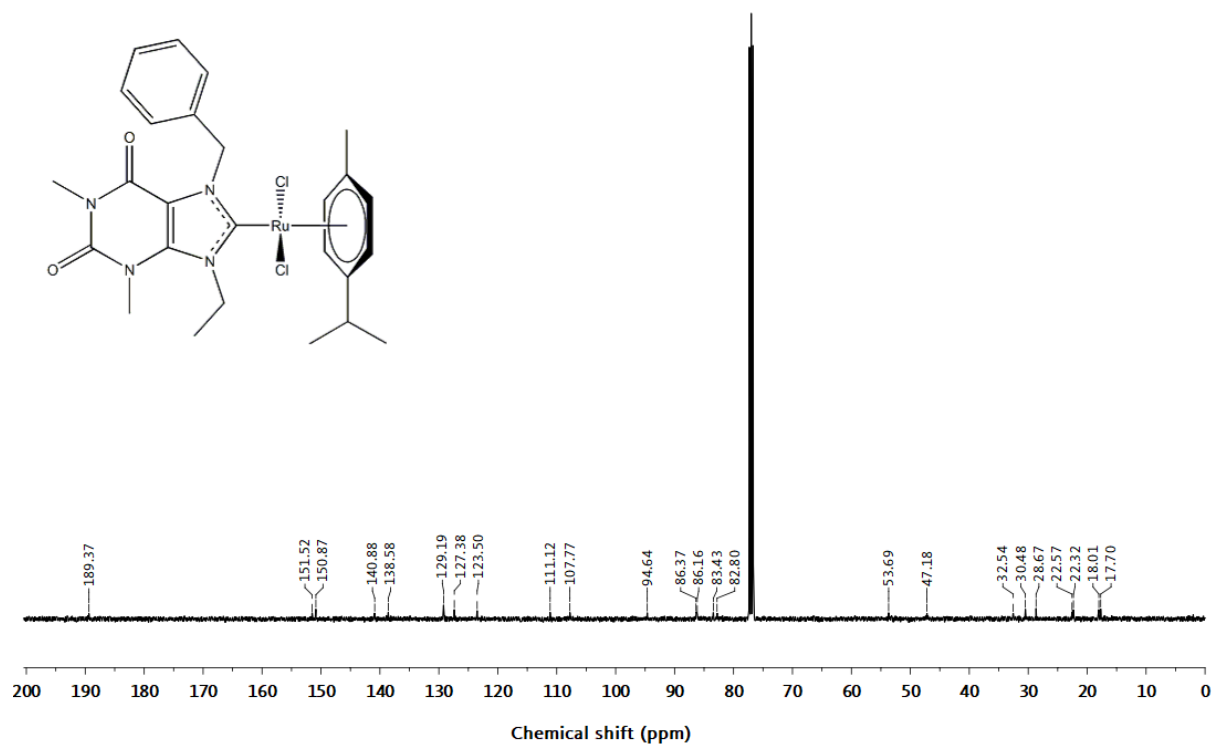


Figure S48

¹H-NMR, 400 MHz, CDCl₃, 223 K

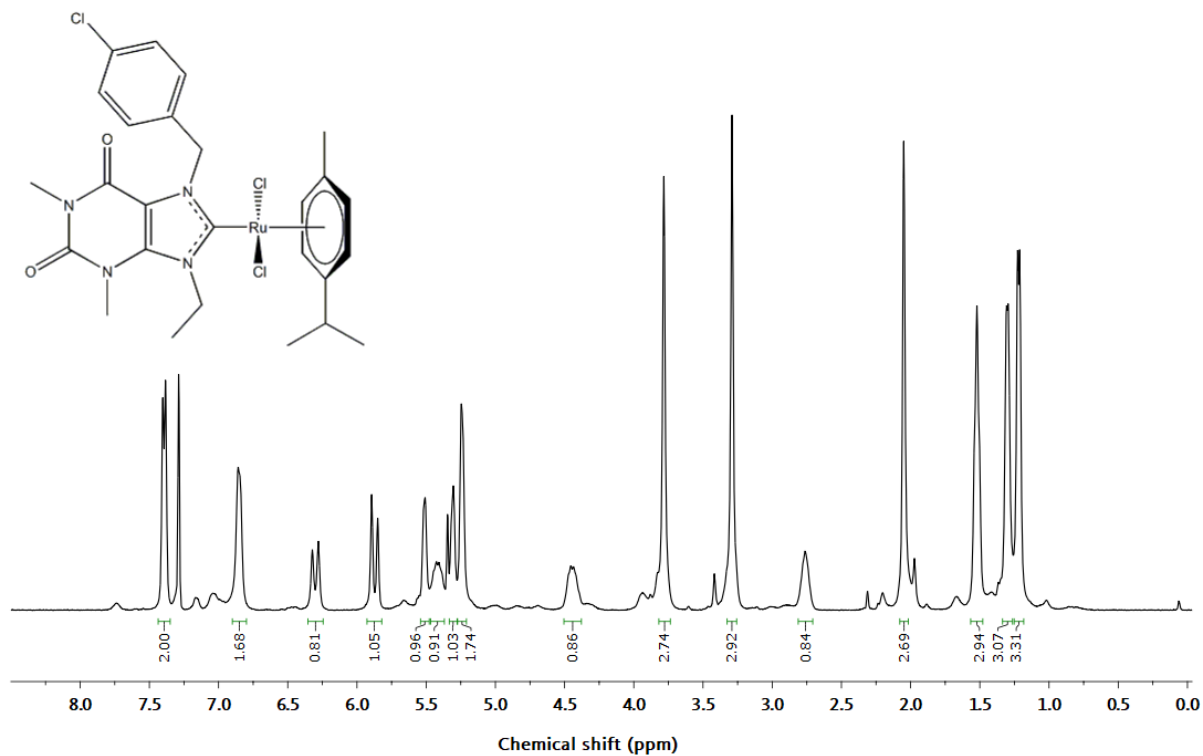


Figure S49

¹³C-NMR, 100 MHz, CDCl₃, 223 K

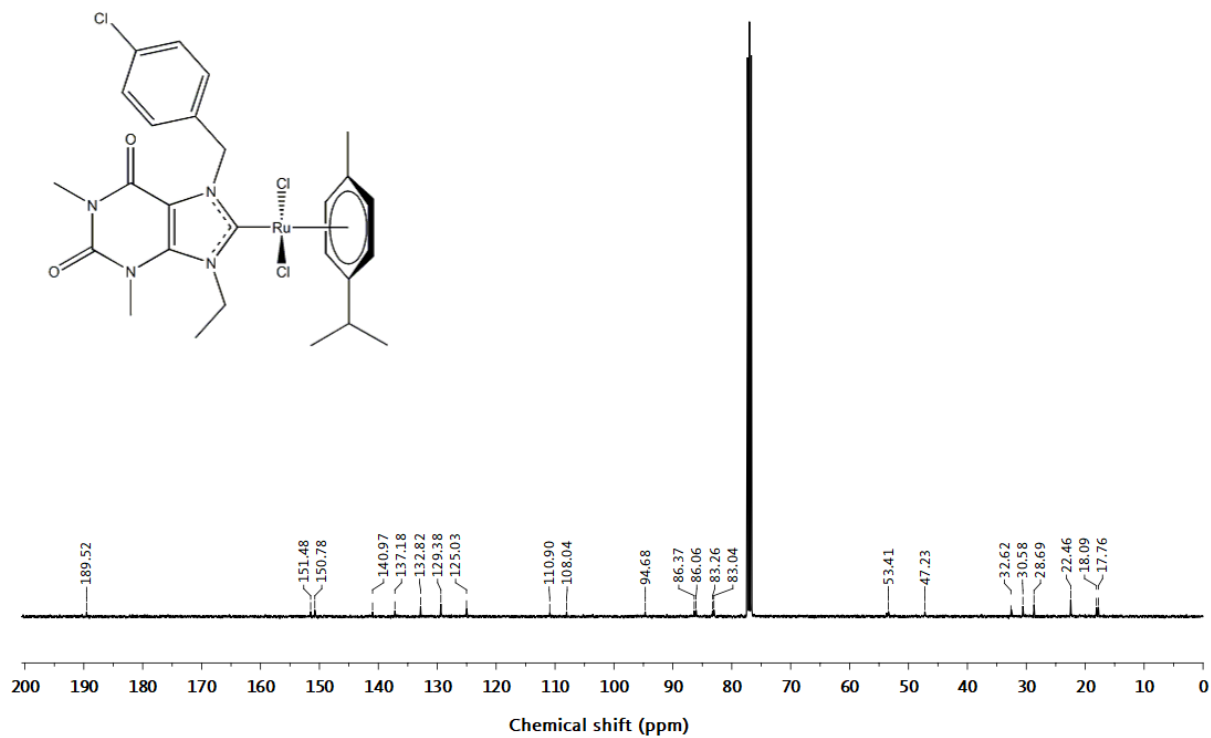


Figure S50

¹H-NMR, 600 MHz, CDCl₃

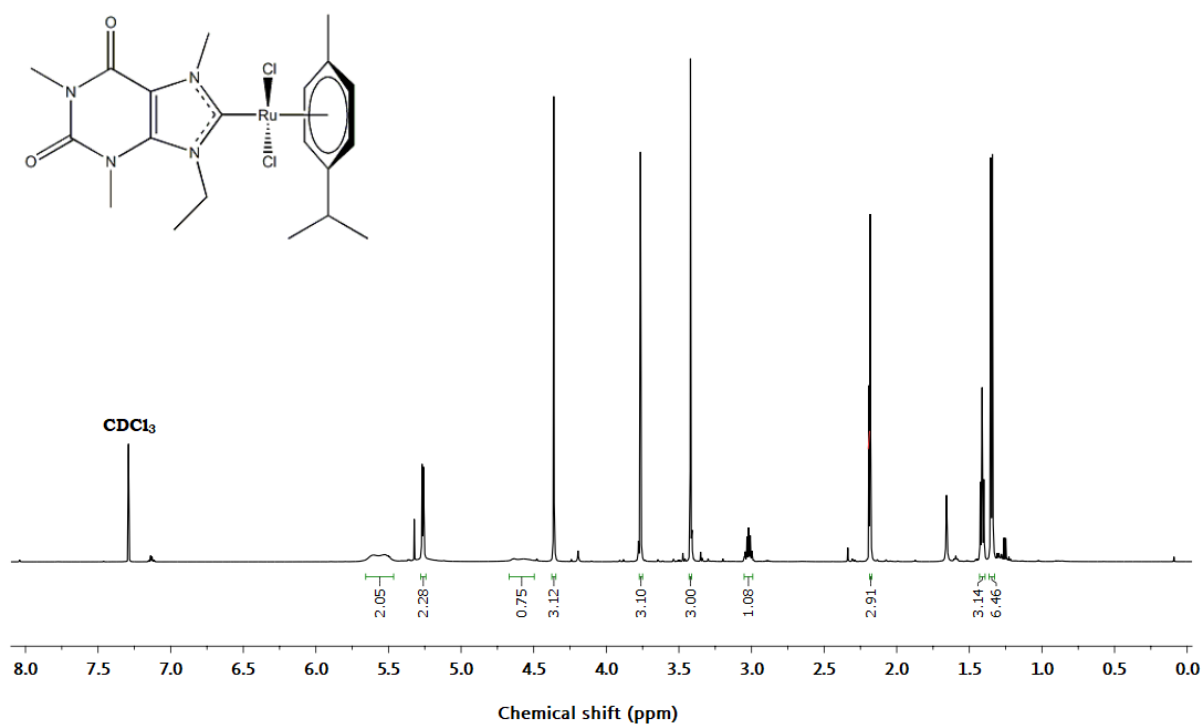


Figure S51

¹³C-NMR, 150 MHz, CDCl₃

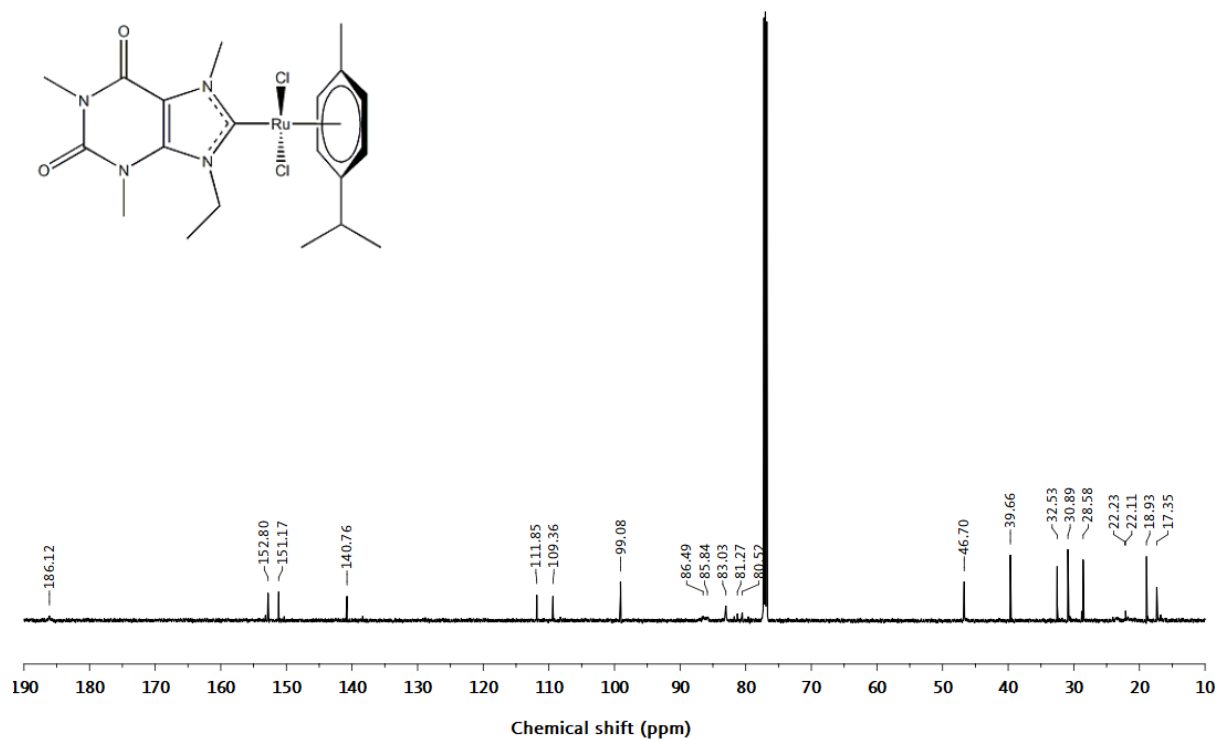


Figure S52

¹H-NMR, 400 MHz, CDCl₃

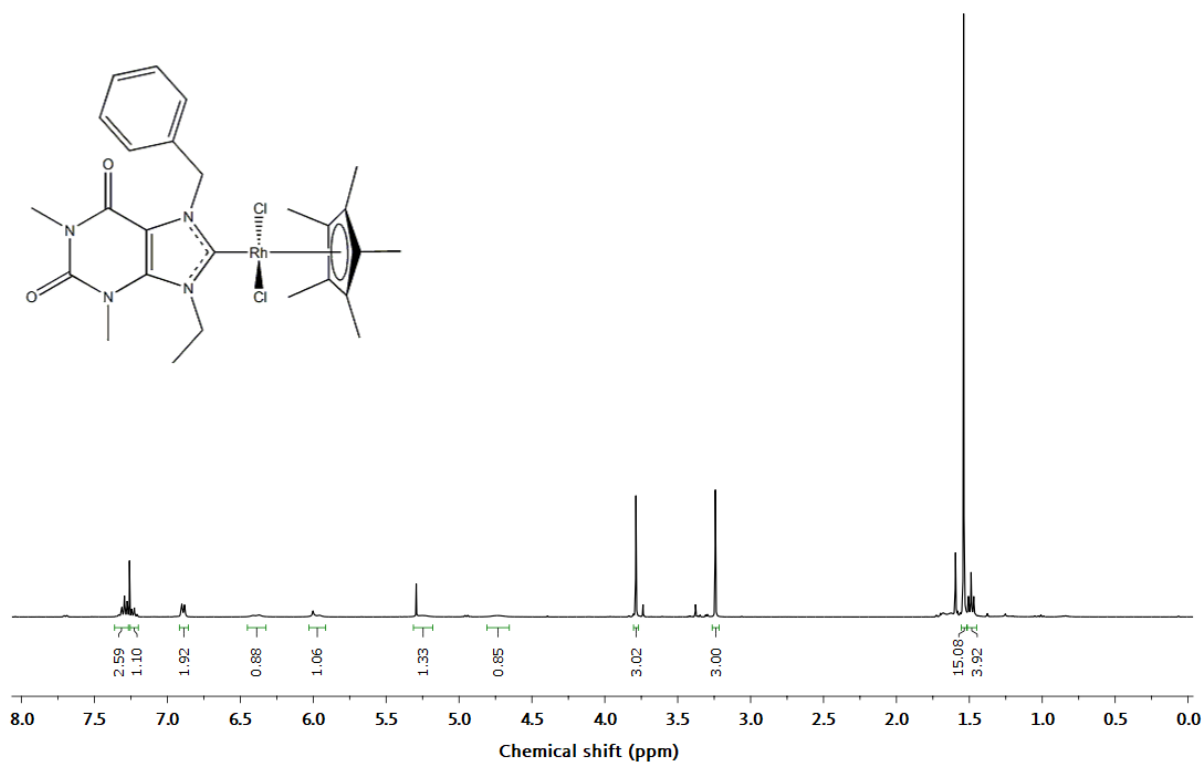


Figure S53

¹³C-NMR, 150 MHz, CDCl₃

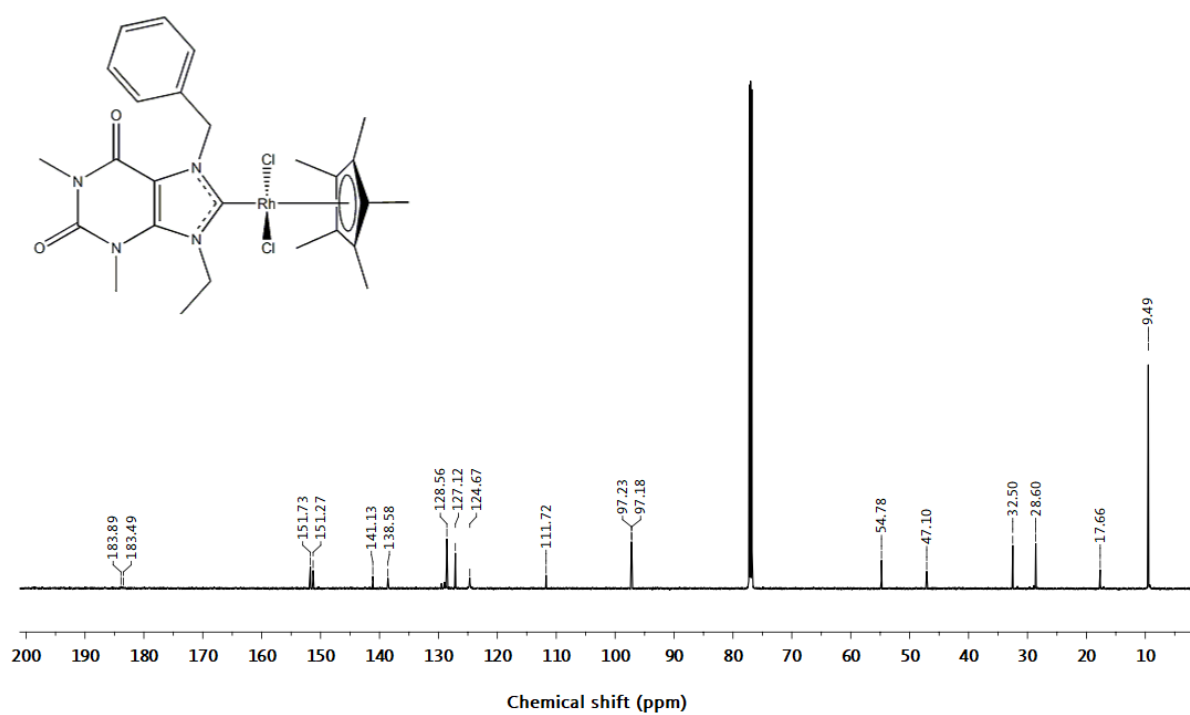


Figure S54

¹H-NMR, 400 MHz, CDCl₃

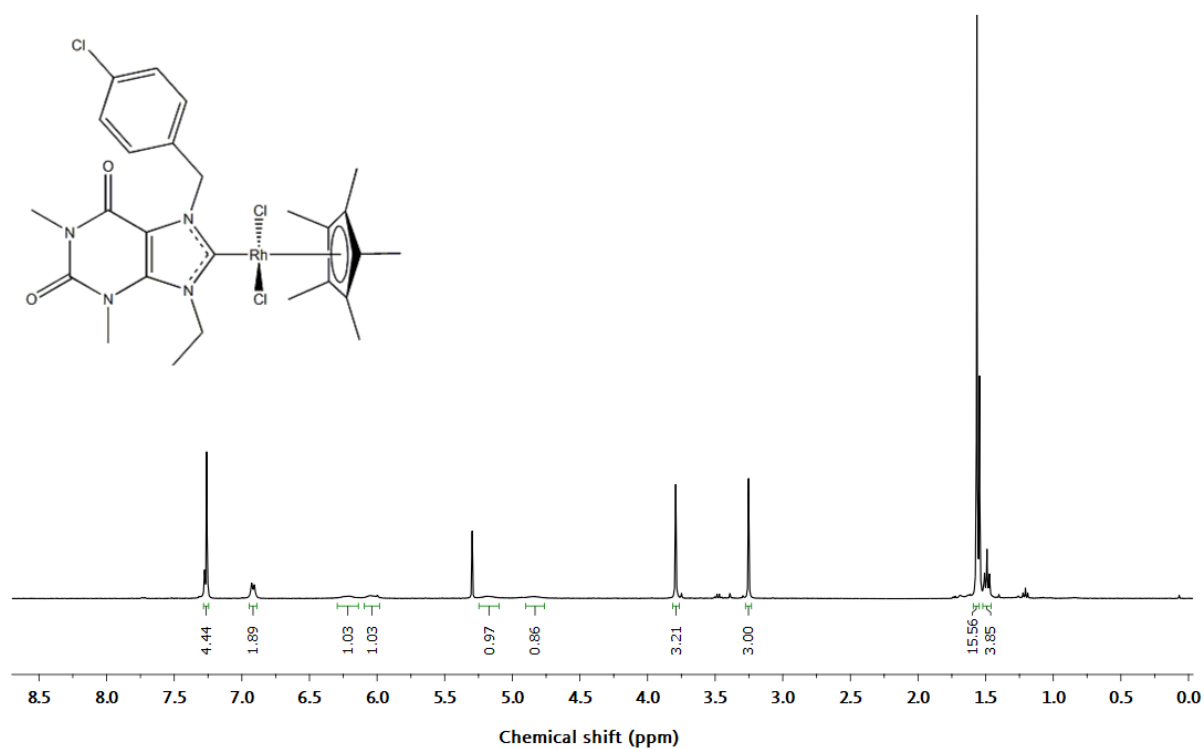


Figure S55

¹³C-NMR, 150 MHz, CDCl₃

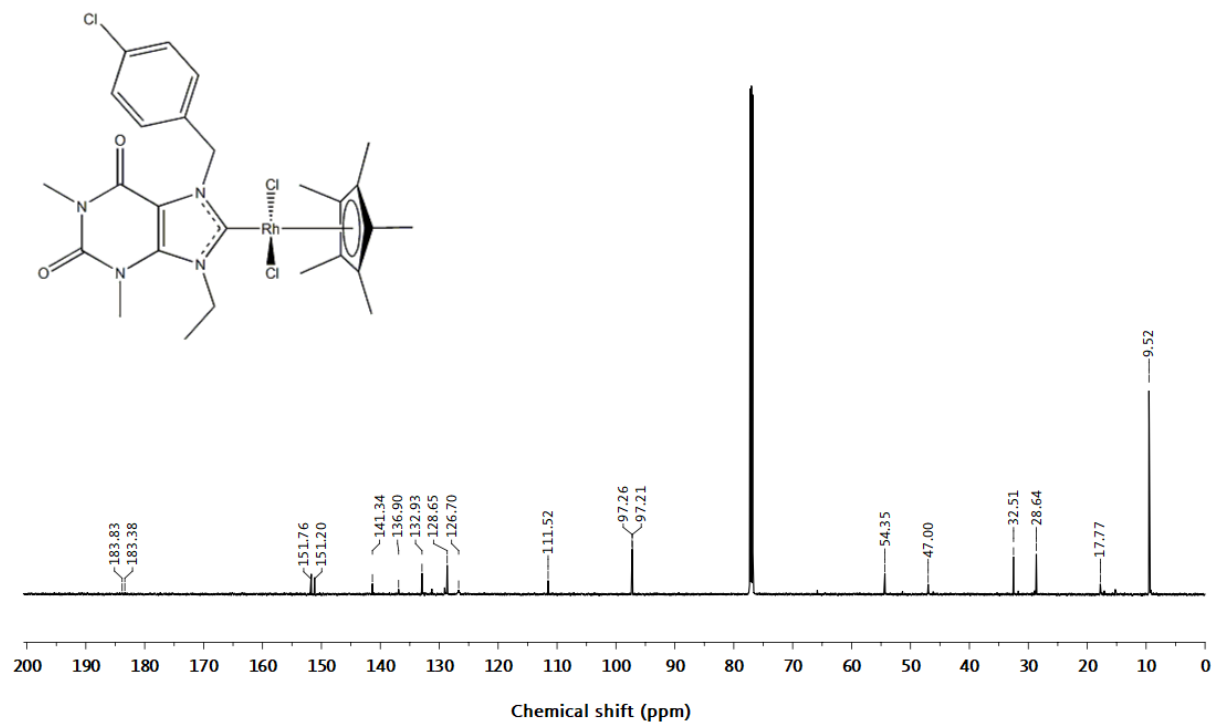


Figure S56

¹H-NMR, 600 MHz, CDCl₃

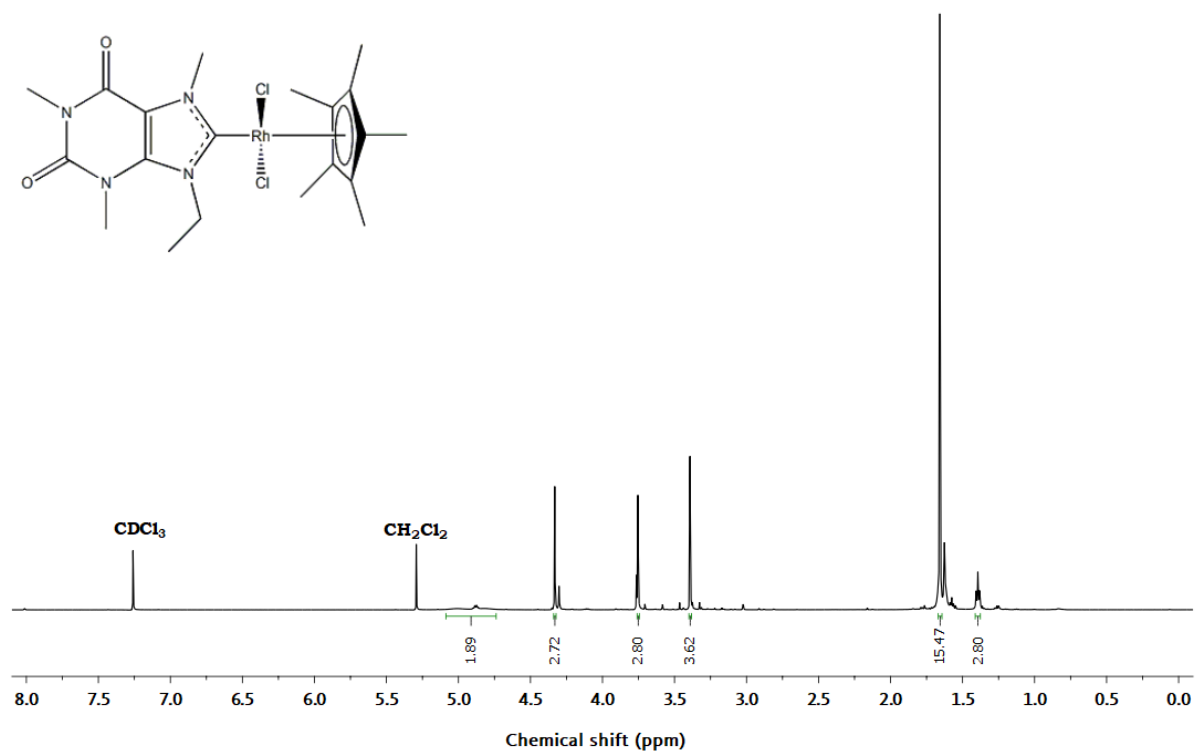


Figure S57

¹³C-NMR, 150 MHz, CDCl₃

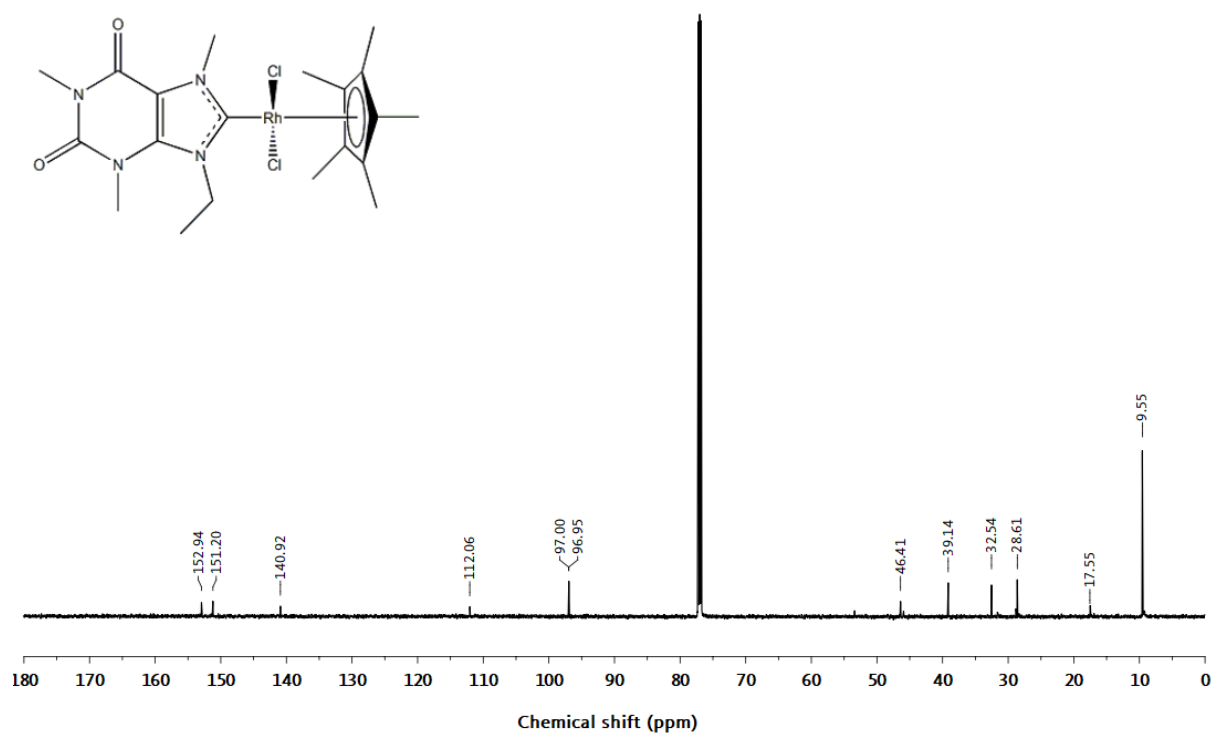


Figure S58

¹H-NMR, 400 MHz, CDCl₃

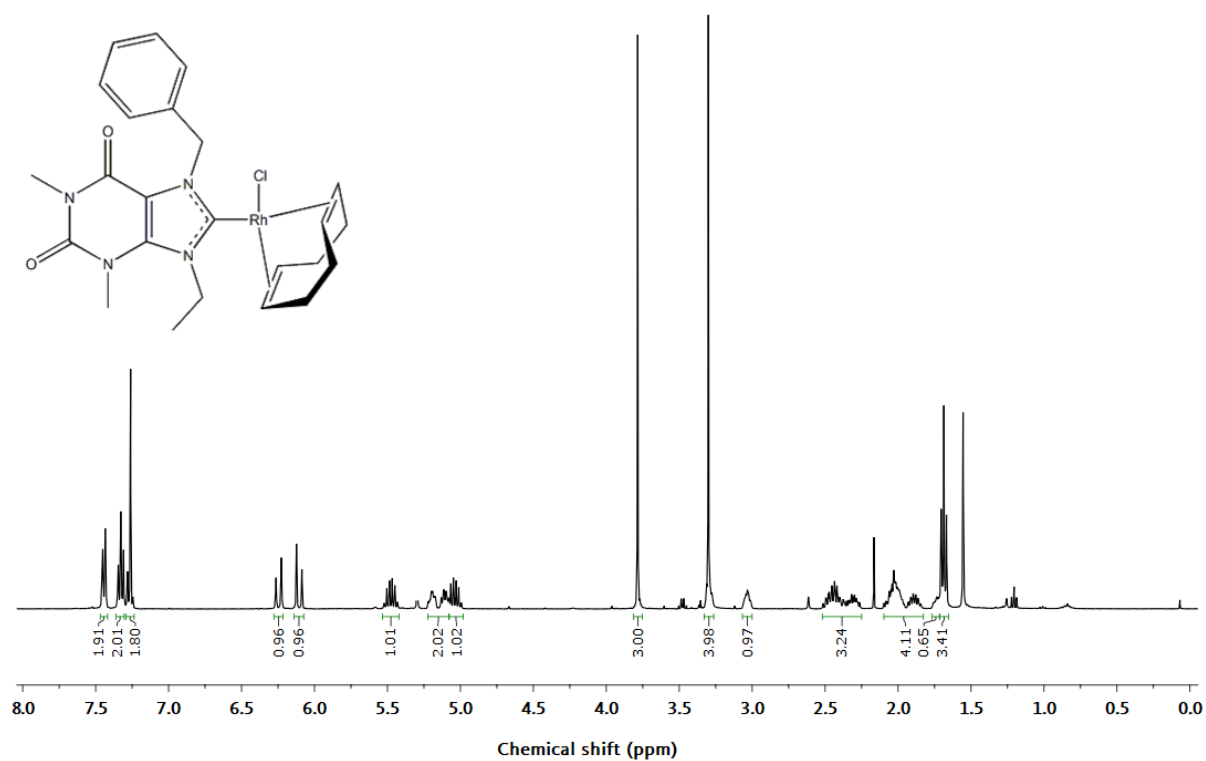


Figure S59

¹³C-NMR, 100 MHz, CDCl₃

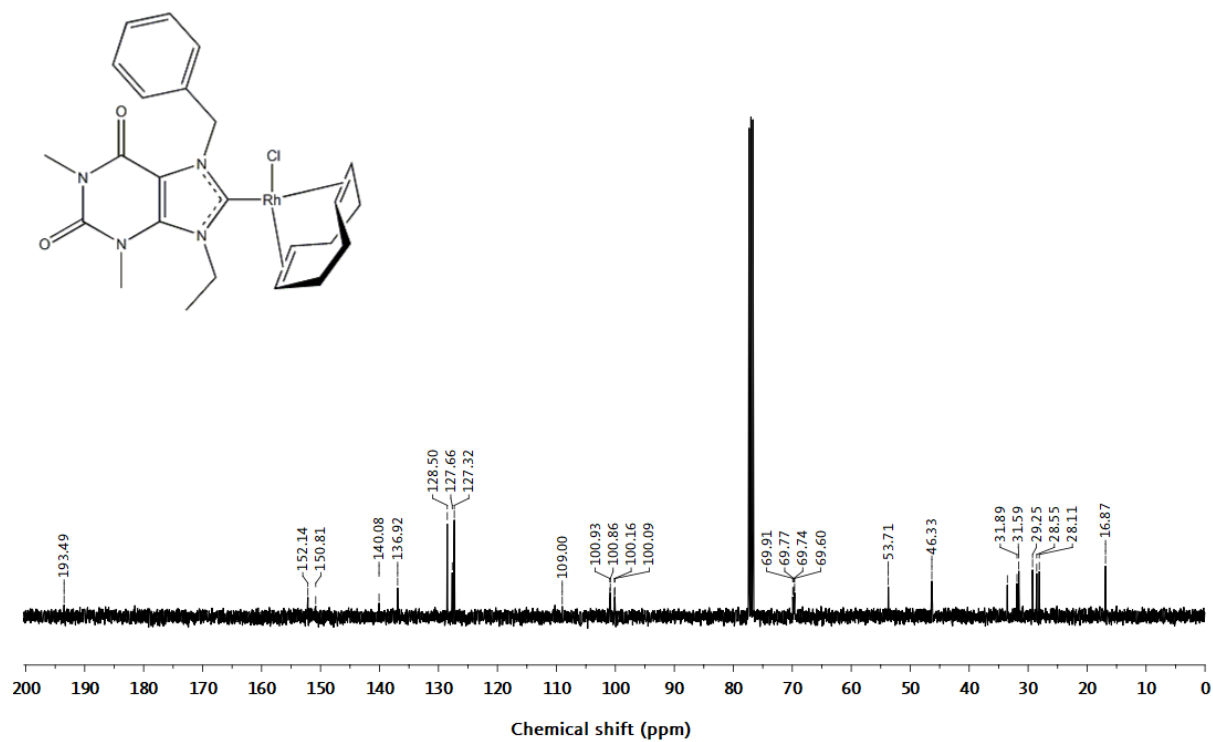


Figure S60

¹H-NMR, 400 MHz, CDCl₃

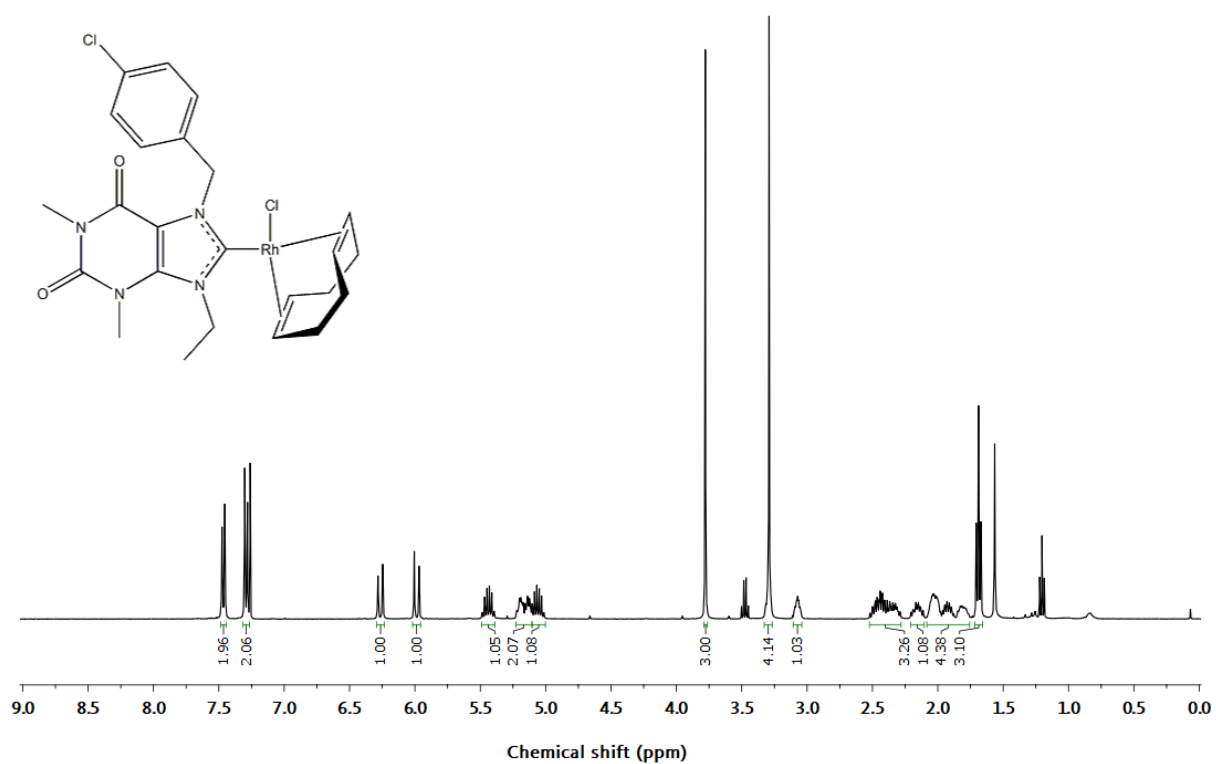


Figure S61

¹³C-NMR, 100 MHz, CDCl₃

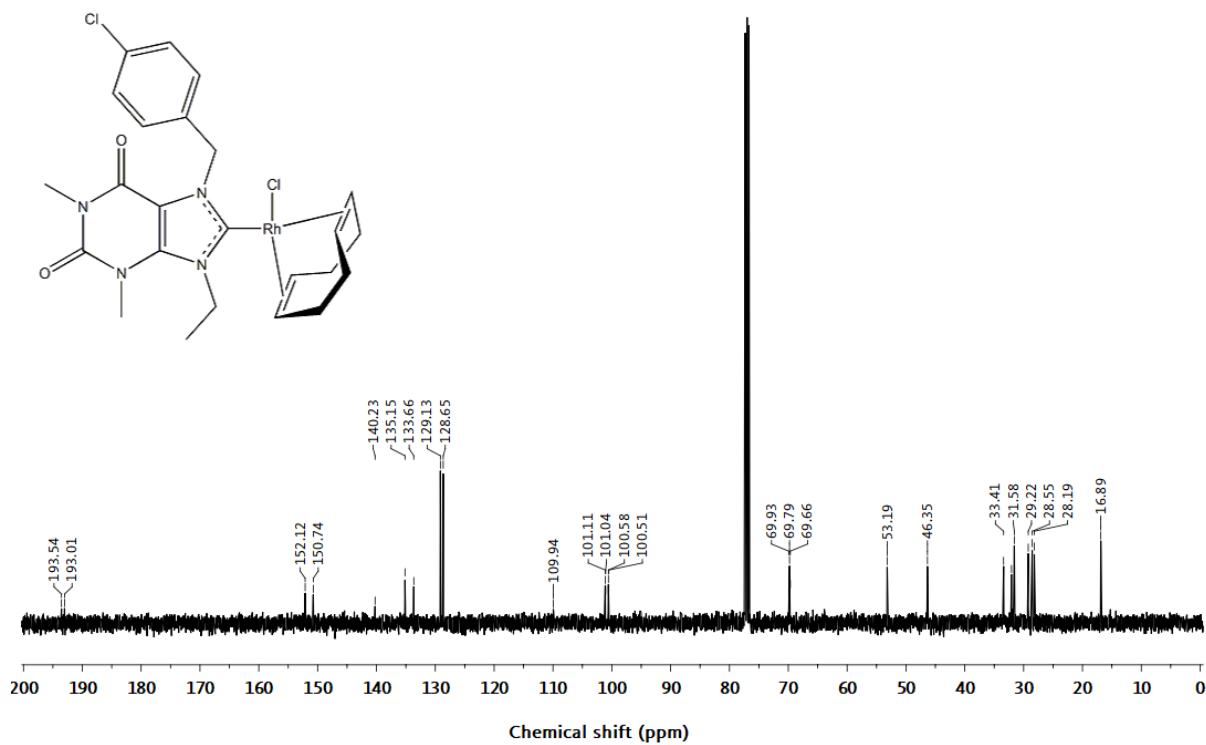


Figure S62

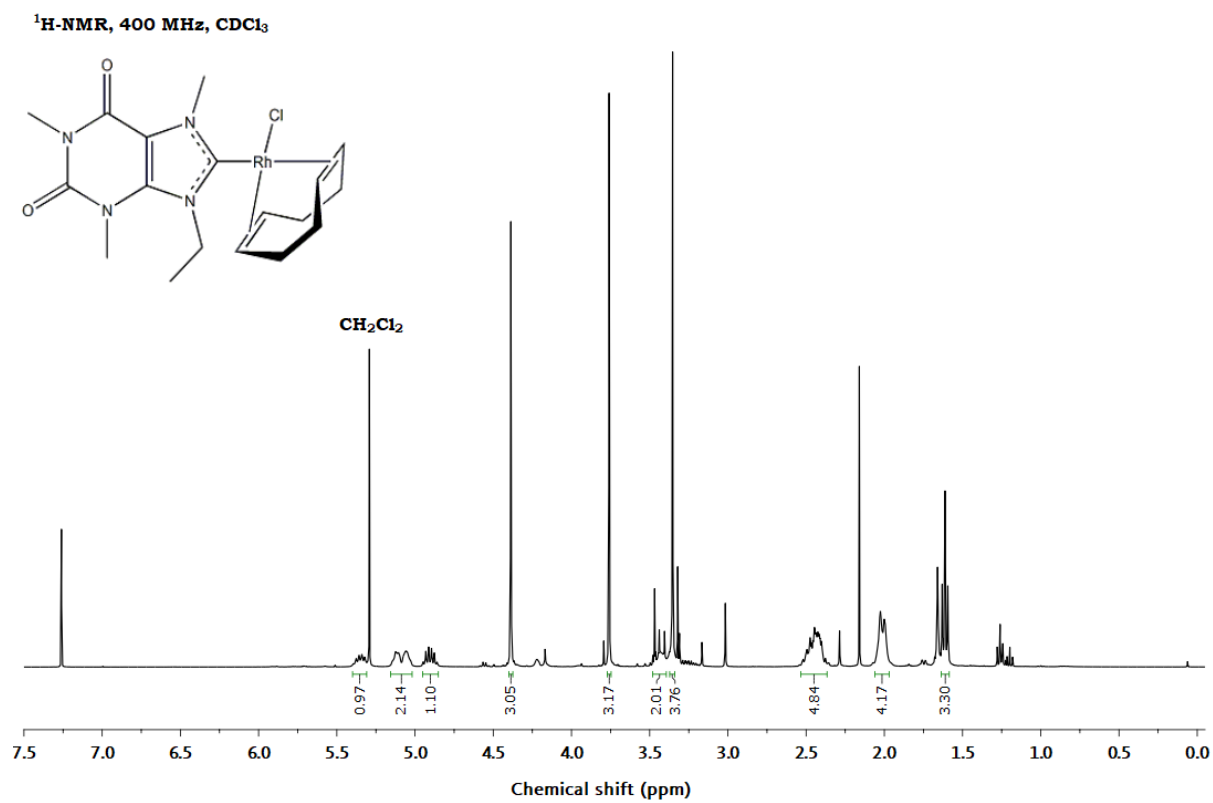


Figure S63

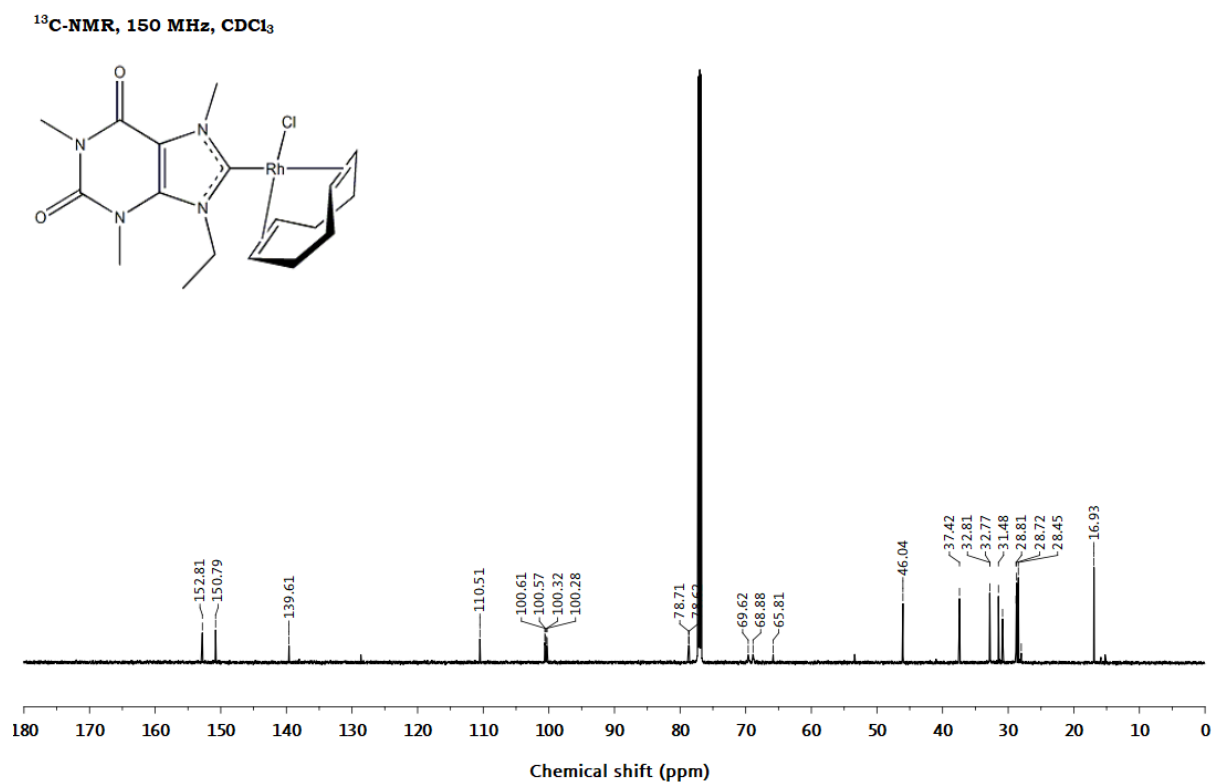


Figure S64

¹H-NMR, 600 MHz, CDCl₃

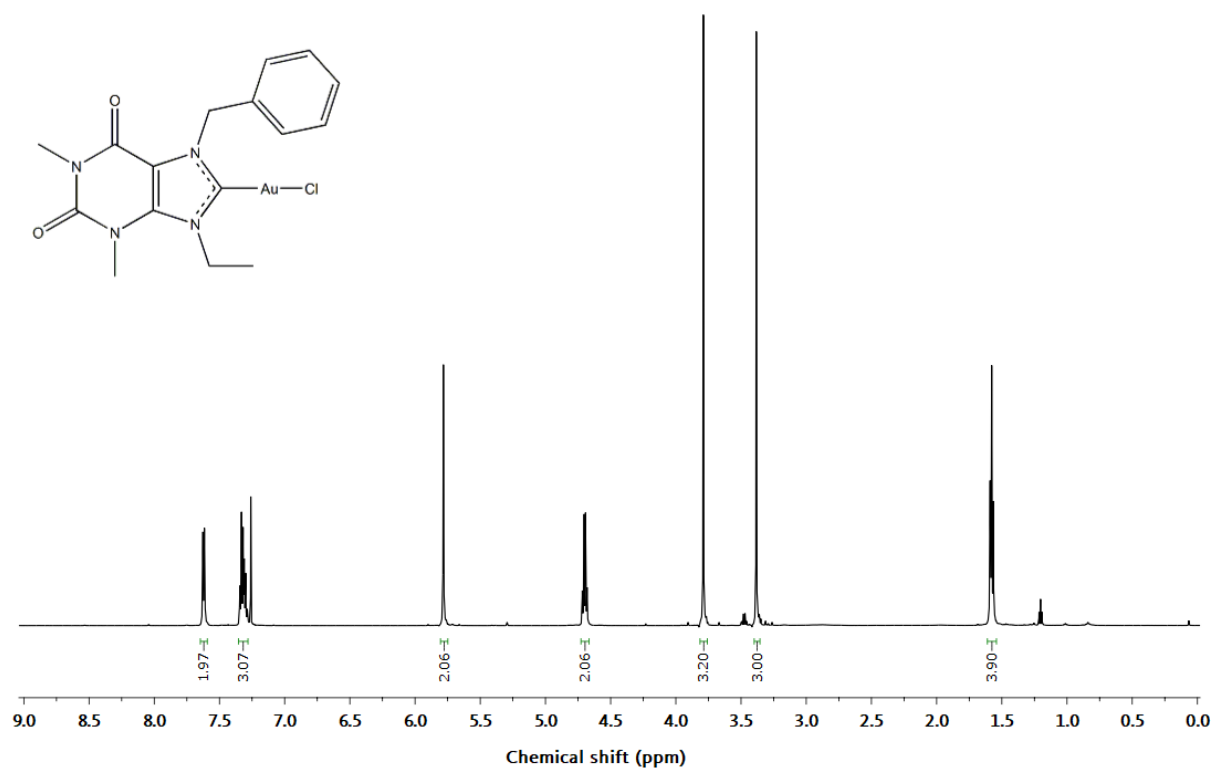


Figure S65

¹³C-NMR, 150 MHz, CDCl₃

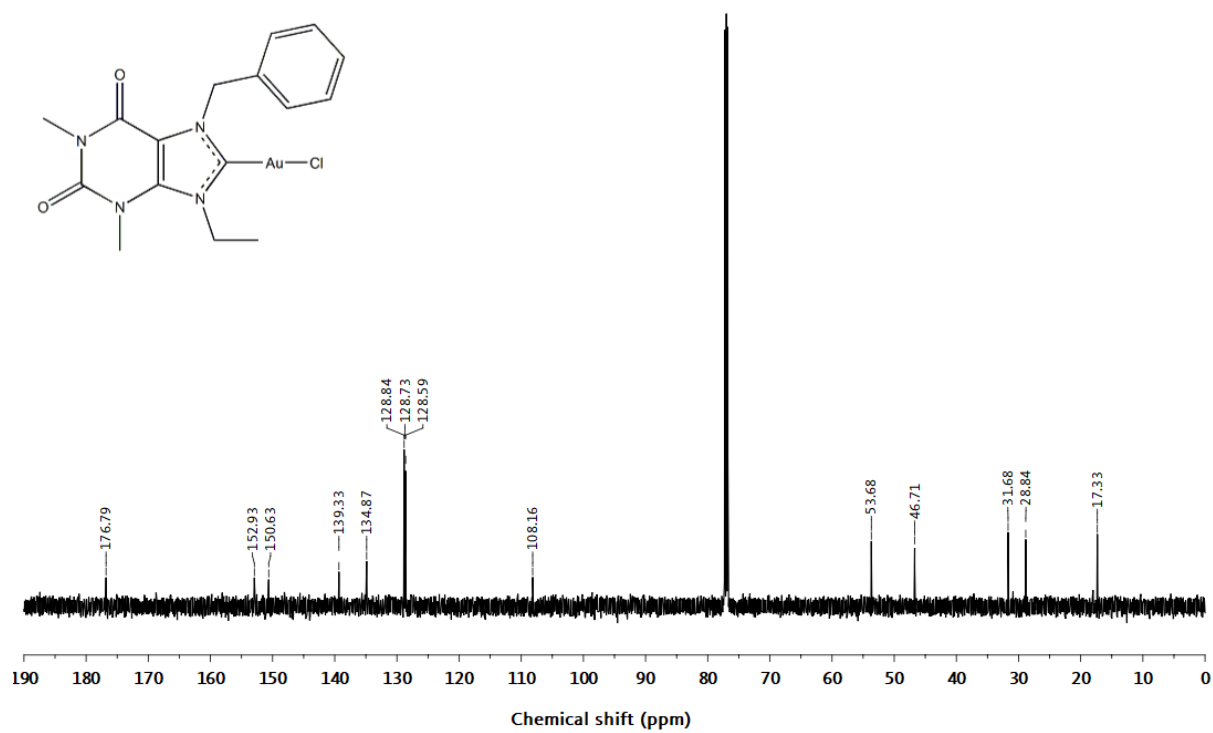


Figure S66

¹H-NMR, 600 MHz, CDCl₃

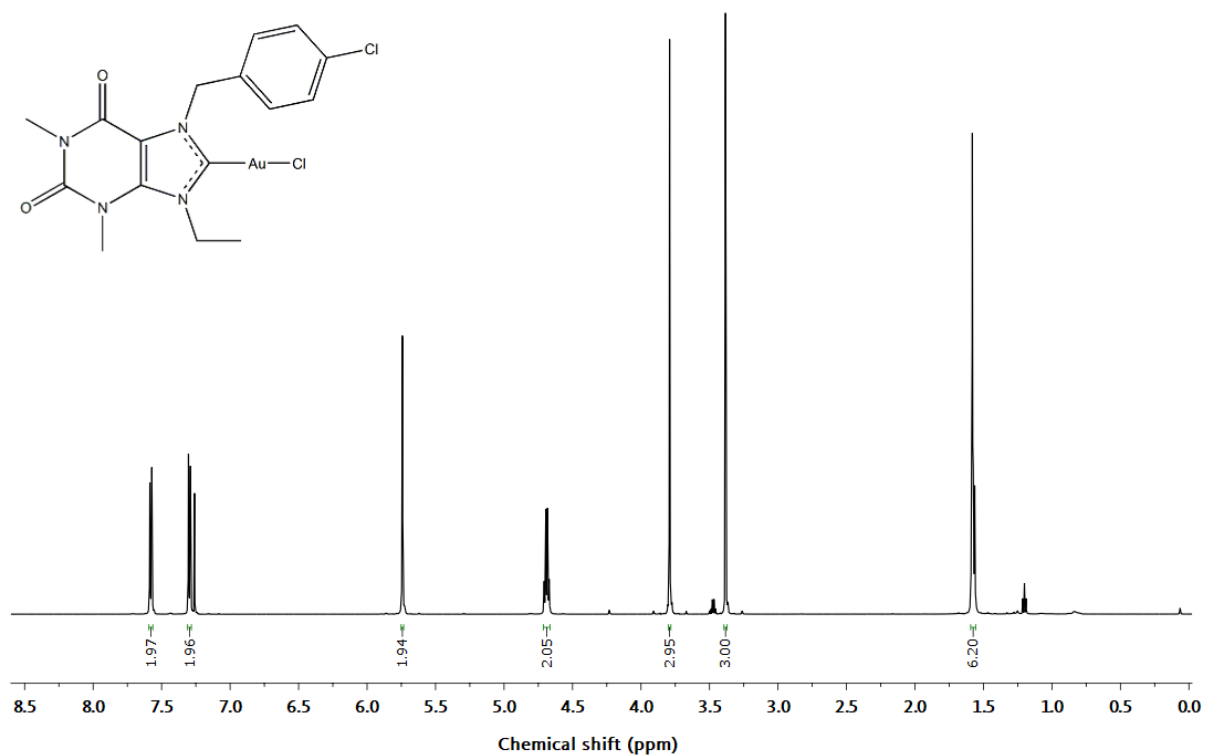


Figure S67

¹³C-NMR, 150 MHz, CDCl₃

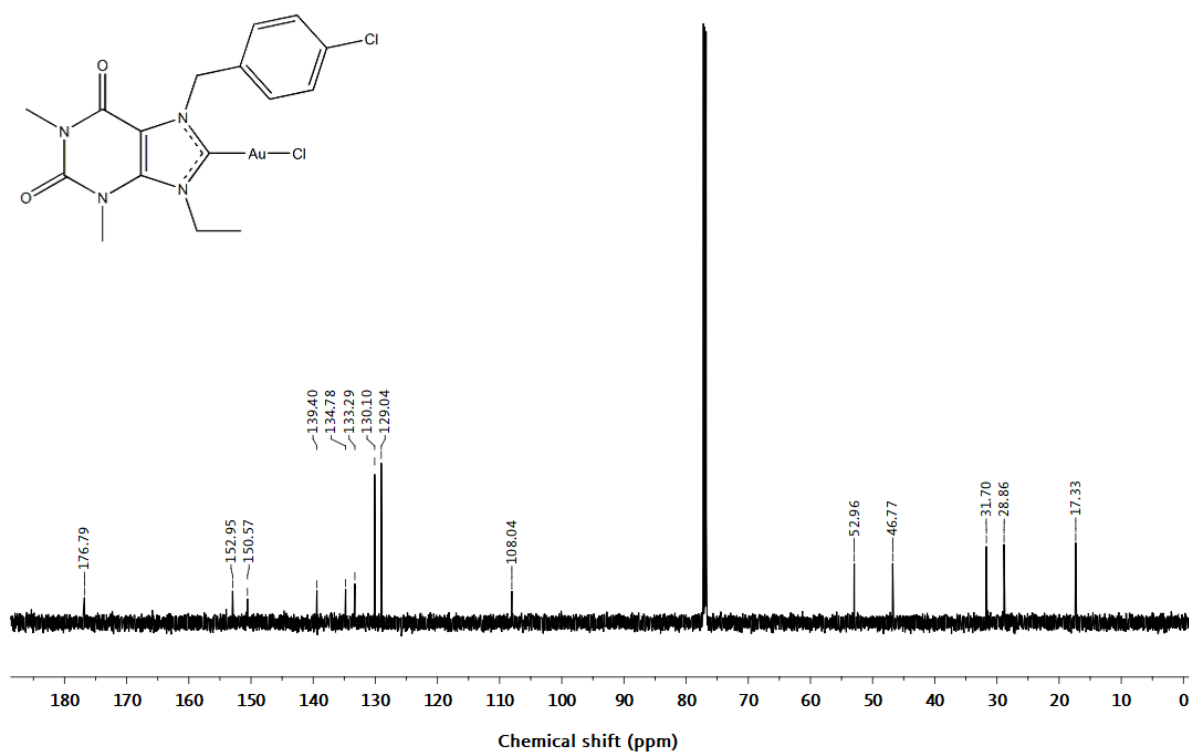


Figure S68

¹H-NMR, 400 MHz, CDCl₃

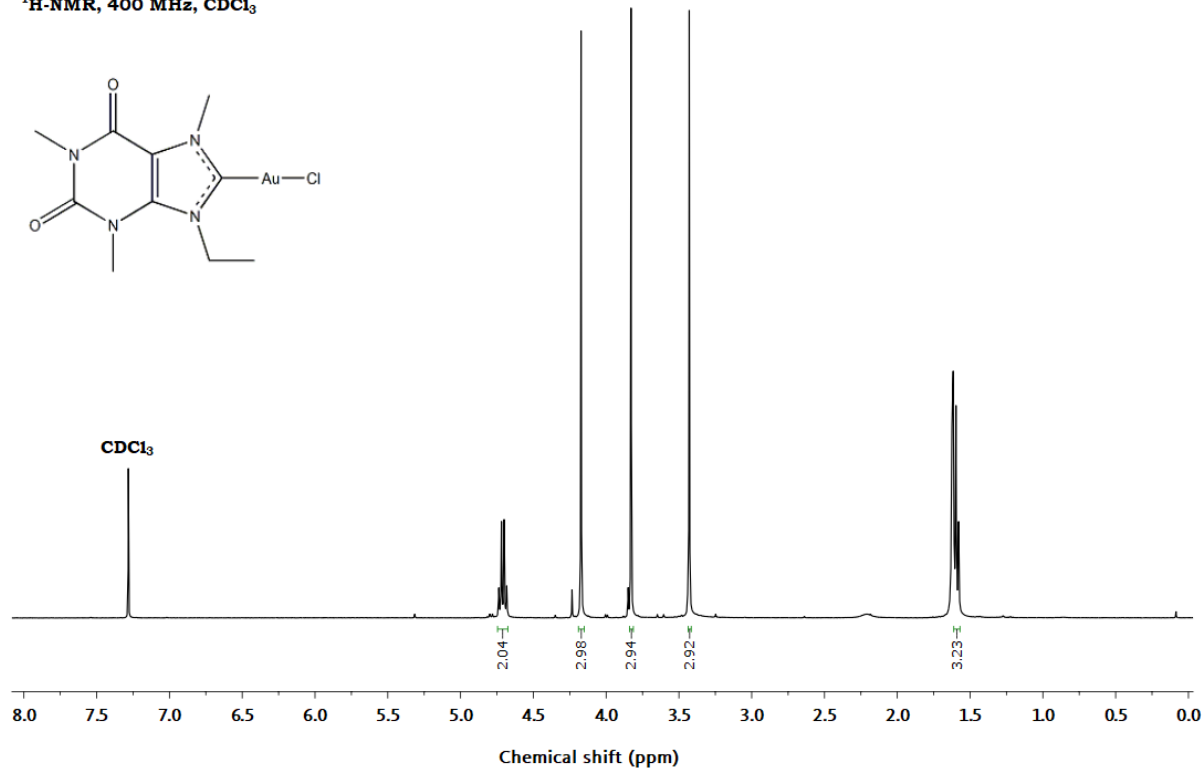


Figure S69

¹³C-NMR, 100 MHz, CDCl₃

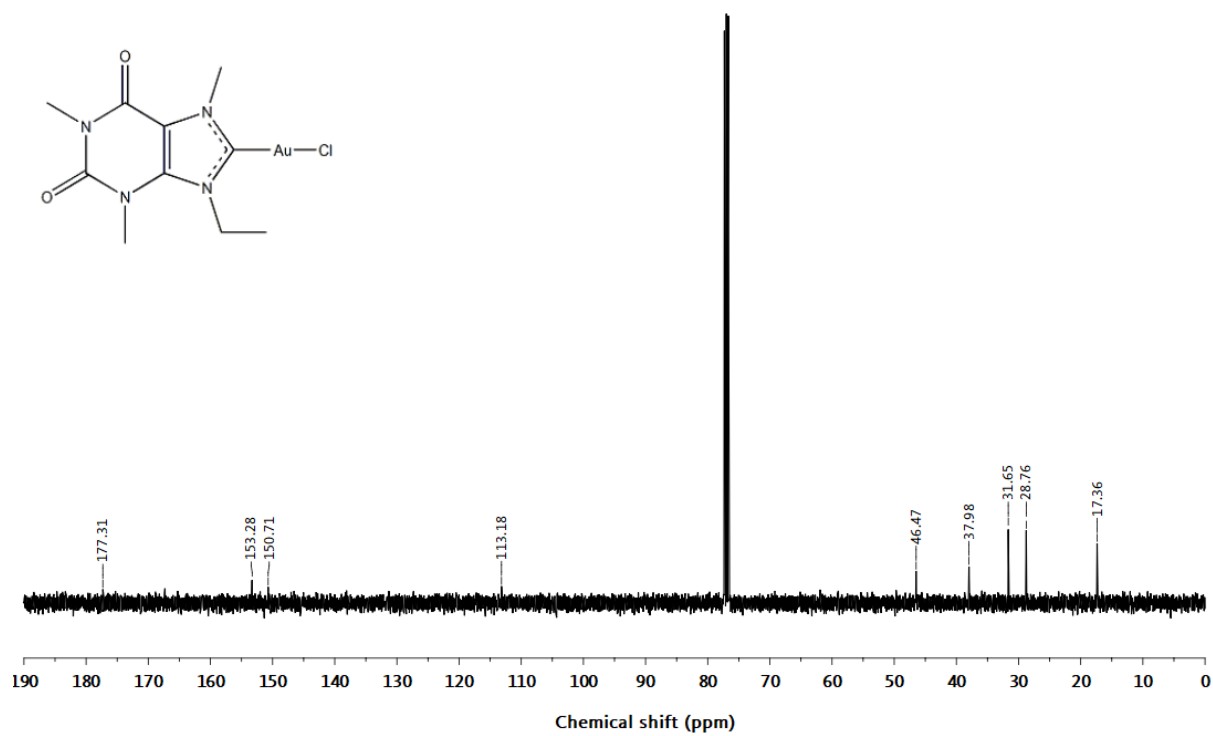


Figure S70