



Supporting Information

for

Bismuth(III) triflate: an economical and environmentally friendly catalyst for the Nazarov reaction

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Experimental section and copies of ^1H and ^{13}C NMR spectra of all new compounds

SUPPORTING INFORMATION

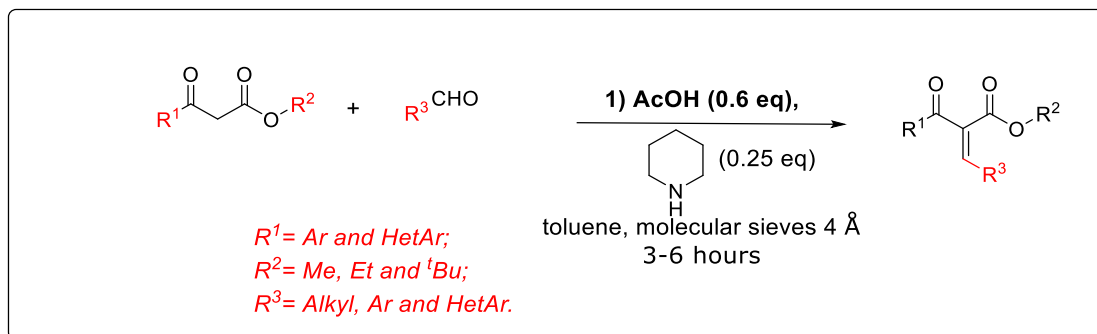
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General information

All chemicals and solvents were of analytical grade, purchased from commercial sources, and used without further purification unless otherwise stipulated. Unless otherwise noted, all reactions were performed under ambient atmosphere in oven-dried open-flask glassware with magnetic stirring. Reaction progress was monitored by analytical thin-layer chromatography (TLC) performed on Merck precoated silica gel 60 F254 (5–40 μm thickness) plates. The TLC plates were visualized with UV light (254 nm) and/or phosphomolybdic acid or sulfuric vanillin, followed by heating. The reaction products were purified by flash column chromatography using silica gel (230–400 mesh).

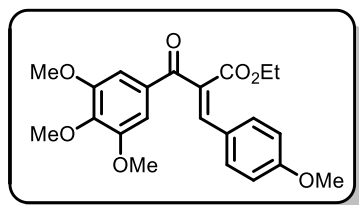
Nuclear magnetic resonance (NMR) spectra were recorded in CDCl₃ solution at room temperature, unless noted otherwise. ¹H NMR and proton-decoupled ¹³C NMR spectra were acquired on a Bruker DPX250 (250 MHz for ¹H NMR and 63 MHz for ¹³C NMR), Bruker Avance 400 (400 MHz for ¹H NMR and 101 MHz for ¹³C NMR), Bruker Avance 500 (500 MHz for ¹H and 126 MHz for ¹³C NMR), or Bruker Avance 600 (600 MHz for ¹H and 150 MHz for ¹³C NMR). Chemical shifts (δ) are reported in ppm and the coupling constant (*J*) in Hz. Signal multiplicity was assigned as singlet (s), doublet (d), double doublet (dd), double double doublet (ddd), triplet (t), quartet (qt), double quartet (dq), multiplet (m), and broad singlet (bs). High-resolution mass spectrometry (HRMS) was performed using electrospray ionization (ESI) on a Thermo Scientific Q Exactive mass spectrometer. Melting points were obtained using a Gehaka equipment model PF 1500 FARMA and were corrected. The compounds were named according to IUPAC rules using the program MarvinSketch 15.9.21.0.

General procedures and characterization data for compounds 9aa–gc, 10aa–dm, and 11aa–af



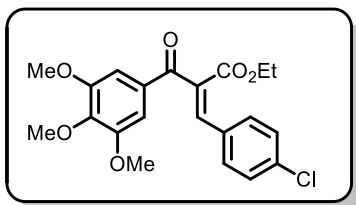
A solution of β -ketoester (1 mmol), aldehyde (1.5 mmol), acetic acid (0.6 mmol), piperidine (0.25 mmol), and molecular sieve (100 mg) in anhydrous toluene was refluxed. The reaction was monitored by TLC. After this period, the solvent was removed under reduced pressure. The crude reaction mixture was purified by column chromatography using a mobile phase of hexane/ethyl acetate 9:1–7:3, v/v.

Ethyl (2Z)-3-(4-methoxyphenyl)-2-[(Z)-3,4,5-trimethoxybenzoyl]prop-2-enoate (9aa**)**



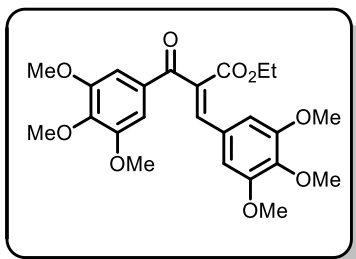
Purified by column chromatography (hexane/EtOAc 95:5–9:1) to give **9aa** (392 mg, 0.98 mmol, 98%) as a yellow solid. mp 103–104 °C. ¹H NMR (250 MHz, CDCl₃) δ 7.88 (s, 1H), 7.29 (d, *J* = 8.8 Hz, 2H), 7.20 (s, 2H), 6.75 (d, *J* = 8.9 Hz, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 3.81 (s, 6H), 3.74 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (63 MHz, CDCl₃) δ 194.98, 165.50, 161.54, 153.40, 143.42, 142.40, 132.35, 131.50, 128.55, 125.63, 114.47, 106.65, 61.52, 61.04, 56.38, 55.43, 14.30. IR (ATR, ν_{max}) 3403, 2918, 1589, 1455, 1321, 835, 747, 728 cm^{−1}. HRMS (ESI) *m/z* calcd for C₂₂H₂₅O₇⁺ [M + H]⁺ 401.1595, found 401.1601.

Ethyl (2Z)-3-(4-chlorophenyl)-2-[(Z)-3,4,5-trimethoxybenzoyl]prop-2-enoate (**9ab**)



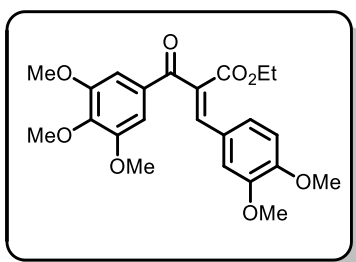
Purified by column chromatography (hexane/EtOAc 95:5–9:1) to give **9ab** (396 mg, 0,98 mmol, 98%) as a yellow solid. mp 87-89 °C (lit. 97-98 °C). ¹H NMR (400 MHz, Acetone) δ 8.00 (s, 1H), 7.92 (s, 1H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.38 – 7.30 (m, 2H), 7.24 (s, 2H), 4.24 (p, *J* = 7.0 Hz, 2H), 3.82 (s, 6H), 3.79 (s, 3H), 1.20 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, Acetone) 193.25, 164.40, 153.62, 143.67, 140.25, 135.68, 132.57, 132.16, 131.48, 131.29, 128.94, 106.52, 61.19, 59.88, 55.75, 13.59. IR (ATR, *ν*_{max}) 3403, 2918, 1589, 1455, 1321, 835, 747, 728 cm⁻¹. HRMS (ESI) *m/z* calcd for C₂₁H₂₂ClO₆⁺ [*M* + *H*]⁺ 405.1099, found 405.1105.

Ethyl 2-[(Z)-3,4,5-trimethoxybenzoyl]-3-(3,4,5-trimethoxyphenyl)prop-2-enoate (**9ac**)



Purified by column chromatography (hexane/EtOAc 95:5–9:1) to give **9ac** (391 mg, 0,85 mmol, 85%) as a white solid. mp 77-78 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.82 (s, 1H), 7.19 (s, 2H), 6.55 (s, 2H), 4.35 – 4.09 (m, 2H), 3.86 (s, 3H), 3.79 (s, 6H), 3.76 (s, 3H), 3.62 (s, 6H), 1.19 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 194.46, 165.04, 153.35, 153.06, 143.44, 142.41, 140.02, 131.39, 130.23, 128.14, 107.70, 106.41, 61.58, 60.95, 60.85, 56.31, 55.89, 14.18. HRMS (ESI) *m/z* calcd for C₂₄H₂₉O₉⁺ [*M* + *H*]⁺ 461.1806, found 461.1823.

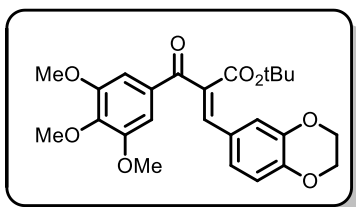
Ethyl (2Z)-3-(3,4-dimethoxyphenyl)-2-[(Z)-3,4,5-trimethoxybenzoyl]prop-2-enoate (**9ad**)



Purified by column chromatography (hexane/EtOAc 95:5–9:1) to give **9ad** (322 mg, 0,75 mmol, 75%) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.85 (s, 1H), 7.19 (s, 2H), 6.96 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.80 (d, *J* = 2.0 Hz, 1H), 6.75 – 6.69 (m, 1H), 4.27 – 4.13 (m, 2H), 3.87 (s, 3H), 3.80 (s, 3H), 3.78 (s, 6H), 3.59 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 195.01, 165.46, 153.46, 151.24,

148.92, 143.51, 142.62, 131.56, 128.73, 125.84, 125.12, 112.58, 111.12, 106.60, 61.60, 61.10, 56.43, 56.02, 55.73, 14.34. HRMS (ESI) m/z calcd for $C_{23}H_{27}O_8^+$ $[M + H]^+$ 431.1700, found 431.1708.

Tert-butyl (2*Z*)-3-(2,3-dihydro-1,4-benzodioxin-6-yl)-2-[(*Z*)-3,4,5-trimethoxybenzoyl]prop-2-enoate (**9ae**)

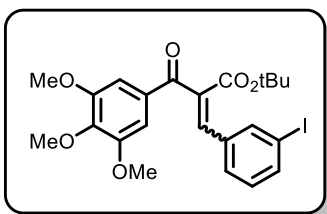


Purified by column chromatography (hexane/EtOAc 95:5–9:1) to give **9ae** (327 mg, 0,72 mmol, 72%) as a yellow oil. 1H NMR (500 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.21 (s, 2H), 6.93 – 6.86 (m, 2H), 6.75 (d, J = 8.3 Hz, 1H), 4.29 – 4.16 (m, 4H), 3.93 (s, 3H), 3.86 (s, 6H), 1.39 (s,

9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 194.99, 164.56, 153.37, 145.84, 143.61, 143.14, 141.58, 132.09, 130.95, 126.66, 124.51, 119.32, 117.82, 106.41, 82.19, 64.69, 64.24, 61.13, 56.43, 28.10. HRMS (ESI) m/z calcd for $C_{25}H_{29}O_8^+$ $[M + H]^+$ 457.1857, found 457.1862.

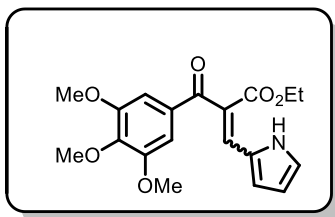
Tert-butyl (2)-3-(3-iodophenyl)-2-[-3,4,5-trimethoxybenzoyl]prop-2-enoate (**9af**)



Purified by column chromatography (hexane/EtOAc 95:5–8:2) to give **9af** (330 mg, 0,63 mmol, 63%) as a brown oil. $E/Z \approx 1:3$. 1H NMR (500 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.71 (t, J = 1.5 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.32 (s, 1H), 7.30 (s, 1H), 7.28 (s, 1H), 7.17 (s, 2H), 6.99 (t, J = 7.9 Hz,

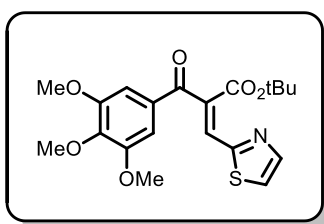
1H), 3.92 (s, 3H), 3.87 (s, 6H), 1.43 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.07, 163.94, 153.44, 153.13, 143.43, 139.89, 139.14, 139.05, 135.39, 134.62, 131.71, 130.55, 128.72, 125.34, 106.99, 106.46, 94.57, 82.79, 61.17, 61.11, 56.49, 56.42, 52.42, 28.09. HRMS (ESI) m/z calcd for $C_{23}H_{25}IO_6^+$ $[M + Na]^+$ 547.0594, found 547.0602.

Ethyl (2Z)-3-(1*H*-pyrrol-2-yl)-2-[(*Z*)-3,4,5-trimethoxybenzoyl]prop-2-enoate (**9ag**)



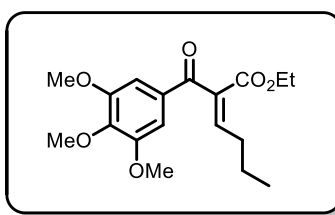
Purified by column chromatography (hexane/EtOAc 95:5–8:2) to give **9ag** (316 mg, 0,88 mmol, 88%) as a brown solid. *E/Z* $\approx$ 1:10. mp 105-108 °C. ^1H NMR (500 MHz, CDCl_3) δ 11.90 (s, 1H), 7.34 (s, 1H), 7.28 (s, 1H), 7.09 (d, J = 7.6 Hz, 2H), 6.80 – 6.74 (m, 1H), 6.39 (d, J = 3.7 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.94 (s, 3H), 3.90 (s, 6H), 1.07 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 193.92, 167.5, 152.98, 141.98, 136.92, 134.09, 127.54, 125.95, 123.30, 120.42, 111.58, 106.30, 61.20, 61.01, 56.33, 13.76. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{22}\text{NO}_6^+$ [$\text{M} + \text{H}$] $^+$ 360.1442, found 360.1449.

Tert-butyl (2Z)-3-(1,3-thiazol-2-yl)-2-[(*Z*)-3,4,5-trimethoxybenzoyl]prop-2-enoate (**9ah**)



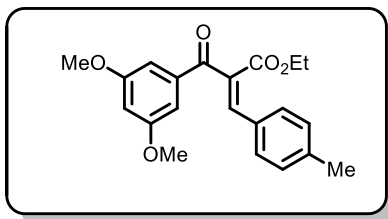
Purified by column chromatography (hexane/EtOAc 95:5–8:2) to give **9ah** (310 mg, 0,77 mmol, 77%) as a brown oil. ^1H NMR (400 MHz, CDCl_3) δ 7.94 (s, 1H), 7.83 (d, J = 3.2 Hz, 1H), 7.40 (d, J = 3.1 Hz, 1H), 7.20 (s, 2H), 3.91 (s, 3H), 3.85 (s, 6H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 193.11, 163.44, 160.37, 153.32, 145.08, 143.29, 135.64, 132.00, 131.47, 123.13, 106.32, 61.06, 56.37, 27.99. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{24}\text{NO}_6\text{S}^+$ [$\text{M} + \text{H}$] $^+$ 406.1319, found 406.1326.

Ethyl (2Z)-2-[(*Z*)-3,4,5-trimethoxybenzoyl]hex-2-enoate (**9ai**)



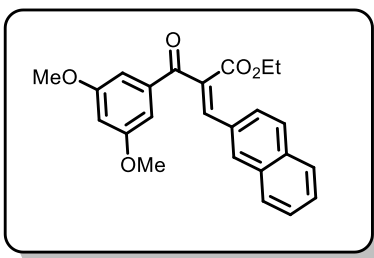
Purified by column chromatography (hexane/EtOAc 95:5–9:1) to give **9ai** (210 mg, 0,63 mmol, 63%) as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.28 (s, 1H), 7.18 (s, 2H), 4.25 – 4.18 (m, 2H), 3.96 (s, 3H), 3.91 (s, 6H), 2.12 (dd, J = 15.0, 7.6 Hz, 2H), 1.51 (dq, J = 14.6, 7.4 Hz, 2H), 1.21 (t, J = 7.1 Hz, 3H), 0.92 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 193.33, 164.62, 153.21, 148.04, 143.19, 133.65, 131.93, 106.49, 61.20, 60.97, 56.29, 31.59, 29.70, 21.79, 14.11, 13.81. HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{25}\text{O}_6^+$ [$\text{M} + \text{H}$] $^+$ 337,1646, found 337,1640.

Ethyl (2Z)-2-[(Z)-3,5-dimethoxybenzoyl]-3-(4-methylphenyl)prop-2-enoate (**9bj**)



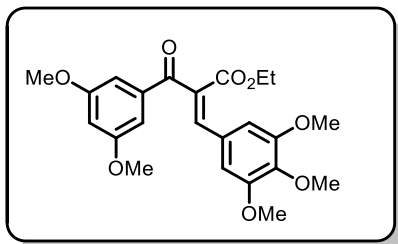
Purified by column chromatography (hexane/EtOAc 95:5–9:1) to give **9bj** (322 mg, 0,91 mmol, 91%) as a yellow solid. mp 80-83 °C ^1H NMR (400 MHz, CDCl_3) δ 7.90 (s, 1H), 7.60 (d, J = 1.9 Hz, 1H), 7.48 (dd, J = 8.4, 1.9 Hz, 1H), 7.25 (d, J = 8.2 Hz, 2H), 7.03 (d, J = 8.1 Hz, 2H), 6.79 (d, J = 8.4 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.91 (s, 3H), 3.89 (s, 3H), 2.26 (s, 3H), 1.20 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 194.52, 165.43, 154.11, 149.41, 142.29, 140.93, 130.38, 130.32, 130.29, 129.63, 129.59, 125.00, 110.35, 110.30, 61.51, 56.13, 56.07, 21.48, 14.22. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{23}\text{O}_5^+$ [$\text{M} + \text{H}$] $^+$ 355.1540, found 355.1541.

Ethyl (2Z)-2-[(Z)-3,5-dimethoxybenzoyl]-3-(naphthalen-2-yl)prop-2-enoate (**9bk**)



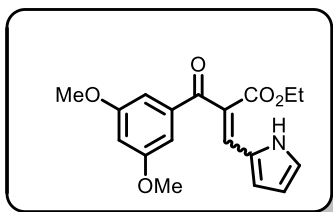
Purified by column chromatography (hexane/EtOAc 95:5–8:2) to give **9bk** (312 mg, 0,80 mmol, 80%) as a yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 8.13 (s, 1H), 7.92 (s, 1H), 7.81 – 7.72 (m, 2H), 7.68 (d, J = 8.7 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.41 (dd, J = 8.6, 1.6 Hz, 1H), 7.18 (d, J = 2.3 Hz, 2H), 6.65 (t, J = 2.3 Hz, 1H), 4.29 (q, J = 7.1 Hz, 2H), 3.79 (s, 6H), 1.25 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 195.57, 142.74, 138.35, 134.02, 133.12, 131.95, 131.36, 130.58, 128.87, 128.72, 127.76, 126.80, 126.02, 106.98, 106.53, 61.74, 55.69, 14.27. HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{23}\text{O}_5^+$ [$\text{M} + \text{H}$] $^+$ 391.1540, found 391.1547.

Ethyl (2Z)-2-[(Z)-3,5-dimethoxybenzoyl]-3-(3,4,5-trimethoxyphenyl)prop-2-enoate (**9bc**)



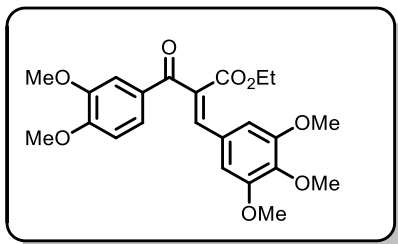
Purified by column chromatography (hexane/EtOAc 95:5–9:1) to give **9bc** (383 mg, 0.89 mmol, 89%) as a yellow solid. mp 126–128 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (s, 1H), 7.11 (d, *J* = 2.3 Hz, 2H), 6.64 (s, 1H), 6.57 (s, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 3.78 (s, 6H), 3.65 (s, 6H), 1.21 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 195.54, 165.03, 161.25, 153.13, 142.53, 140.08, 138.28, 130.46, 128.22, 107.82, 106.85, 106.39, 61.65, 60.94, 55.99, 55.70, 14.21. HRMS (ESI) *m/z* calcd for C₂₃H₂₇O₈⁺ [*M* + H]⁺ 431.1700, found 431.1707.

(*E/Z*)-Ethyl -2-[3,5-dimethoxybenzoyl]-3-(1*H*-pyrrol-2-yl)prop-2-enoate (**9bg**)



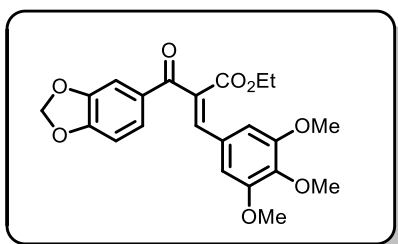
Purified by column chromatography (hexane/EtOAc 95:5–8:2) to give **9bg** (389 mg, 0.88 mmol, 88%) as a yellow oil. *E/Z* ≈ 1:1. ¹H NMR (500 MHz, CDCl₃) δ 11.84 (s, 1H), 10.39 (s, 1H), 9.47 (d, *J* = 1.2 Hz, 0H), 7.13 – 7.02 (m, 1H), 7.00 – 6.92 (m, 1H), 6.90 (dd, *J* = 3.9, 2.3 Hz, 2H), 6.70 (dq, *J* = 3.8, 1.7 Hz, 1H), 6.59 (td, *J* = 2.3, 1.1 Hz, 1H), 6.38 – 6.24 (m, 1H), 4.19 – 3.99 (m, 2H), 3.76 (d, *J* = 6.2 Hz, 6H), 0.98 (dt, *J* = 14.4, 7.2 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 196.83, 179.45, 167.52, 160.81, 160.77, 141.42, 141.19, 137.31, 136.33, 127.70, 127.65, 126.71, 126.25, 125.92, 123.65, 122.52, 120.93, 111.91, 111.70, 111.39, 106.53, 106.11, 105.58, 104.97, 61.26, 61.09, 55.70, 55.66, 14.02, 13.76. HRMS (ESI) *m/z* calcd for C₁₈H₂₀NO₅⁺ [*M* + H]⁺ 330.1336, found 330.1340.

Ethyl (2Z)-2-[(Z)-3,4-dimethoxybenzoyl]-3-(3,4,5-trimethoxyphenyl)prop-2-enoate (**9cc**) [1]



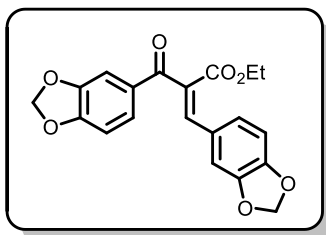
Purified by column chromatography (hexane/EtOAc 95:5–8:2) to give **9cc** (426 mg, 0,99 mmol, 99%) as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.82 (s, 1H), 7.60 (d, J = 1.8 Hz, 1H), 7.50 (dd, J = 8.4, 1.8 Hz, 1H), 6.82 (d, J = 8.4 Hz, 1H), 6.59 (s, 2H), 4.23 (q, J = 7.1 Hz, 2H), 3.90 (d, J = 1.7 Hz, 6H), 3.78 (s, 3H), 3.64 (s, 6H), 1.20 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 194.43, 165.29, 154.24, 153.10, 149.52, 142.18, 139.99, 130.57, 129.68, 128.32, 125.05, 110.49, 110.03, 107.81, 61.61, 60.94, 56.20, 56.16, 55.98, 14.24. HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{27}\text{O}_8^+$ [$\text{M} + \text{H}$] $^+$ 431.1700, found 431.1708.

Ethyl (2Z)-2-[(Z)-2H-1,3-benzodioxole-5-carbonyl]-3-(3,4,5-trimethoxyphenyl)prop-2-enoate (**9dc**) [2]



Purified by column chromatography (hexane/EtOAc 95:5–9:1) to give **9dc** (327 mg, 0,79 mmol, 79%) as a brown solid. mp 70–72 °C (lit. 97–98 °C). ^1H NMR (400 MHz, CDCl_3) δ 7.82 (s, 1H), 7.54 (dd, J = 8.2, 1.7 Hz, 1H), 7.48 (d, J = 1.6 Hz, 1H), 6.81 (d, J = 8.2 Hz, 1H), 6.61 (s, 2H), 6.06 (s, 2H), 4.25 (q, J = 7.1 Hz, 2H), 3.82 (s, 3H), 3.69 (s, 6H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 194.04, 165.23, 153.20, 152.83, 148.71, 108.48, 108.23, 107.83, 102.25, 61.70, 61.03, 56.09, 14.30. HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{23}\text{O}_8^+$ [$\text{M} + \text{H}$] $^+$ 415.1387, found 415.1405.

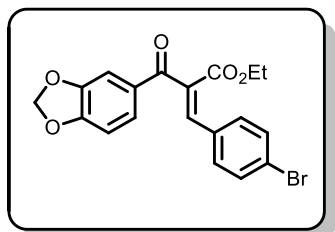
Ethyl (2Z)-3-(2H-1,3-benzodioxol-5-yl)-2-[(Z)-2H-1,3-benzodioxole-5-carbonyl]prop-2-enoate (**9dl**)



Purified by column chromatography (hexane/EtOAc 95:5–9:1) to give **9dl** (305 mg, 0,83 mmol, 83%) as a brown solid. mp 103–105 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.80 (s, 1H), 7.57 – 7.47 (m, 2H), 6.94 (dd, J = 8.2, 1.7 Hz, 1H), 6.80 (t, J = 4.9 Hz, 2H), 6.72 (d, J = 8.1 Hz, 1H), 6.05 (s, 2H), 5.93 (s, 2H), 4.22 (q, J = 7.1 Hz, 2H), 1.21 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 194.12, 165.40, 152.80, 149.77, 148.67, 148.24, 142.04, 131.41, 129.32, 127.26, 126.90,

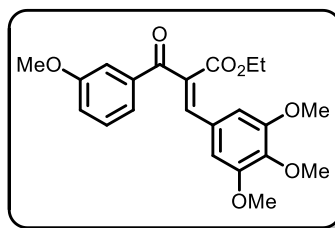
126.56, 109.32, 108.73, 108.41, 108.37, 102.20, 101.75, 61.59, 14.27. HRMS (ESI) m/z calcd for $C_{20}H_{17}O_7^+$ $[M + H]^+$ 369.0969, found 369.0972.

Ethyl (2Z)-2-[(Z)-2H-1,3-benzodioxole-5-carbonyl]-3-(4-bromophenyl)prop-2-enoate (**9dm**)



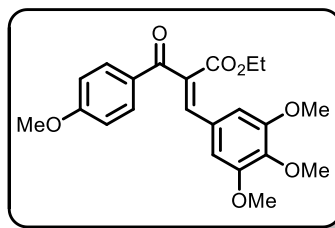
Purified by column chromatography (hexane/EtOAc 95:5–9:1) to give **9dm** (462 mg, 0,90 mmol, 90%) as a brown oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.50 – 7.44 (m, 2H), 7.40 – 7.35 (m, 2H), 7.26 – 7.20 (m, 2H), 6.78 (d, J = 8.1 Hz, 1H), 6.04 (s, 2H), 4.24 (q, J = 7.1 Hz, 2H), 1.21 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.41, 164.95, 152.94, 148.71, 140.77, 132.24, 132.19, 131.95, 131.61, 131.03, 126.56, 124.97, 108.37, 108.25, 102.24, 61.82, 14.21. HRMS (ESI) m/z calcd for $C_{19}H_{16}BrO_5^+$ $[M + H]^+$ 403.0176, found 403.0185.

Ethyl (2Z)-2-[(Z)-3-methoxybenzoyl]-3-(3,4,5-trimethoxyphenyl)prop-2-enoate (**9ec**)



Purified by column chromatography (hexane/EtOAc 95:5–9:1) to give **9ec** (393 mg, 0,98 mmol, 98%) as a yellow oil. mp 95.5–96.6 °C (lit. 97–98 °C). 1H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.50 (d, J = 7.4 Hz, 2H), 7.35 – 7.25 (m, 1H), 7.08 (d, J = 8.0 Hz, 1H), 6.56 (s, 2H), 4.21 (q, J = 7.0 Hz, 2H), 3.79 (s, 3H), 3.77 (s, 3H), 3.61 (s, 6H), 1.17 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.58, 164.97, 160.12, 153.06, 142.40, 140.01, 137.66, 130.53, 130.05, 128.15, 122.08, 120.51, 112.84, 107.75, 61.53, 60.83, 55.88, 55.47, 14.11. . HRMS (ESI) m/z calcd for $C_{22}H_{25}O_7^+$ $[M + H]^+$ 401.1595, found 401.1602.

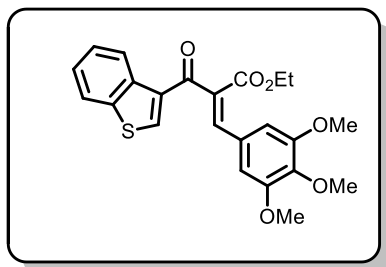
Ethyl (2Z)-2-[(Z)-4-methoxybenzoyl]-3-(3,4,5-trimethoxyphenyl)prop-2-enoate (**9fc**)



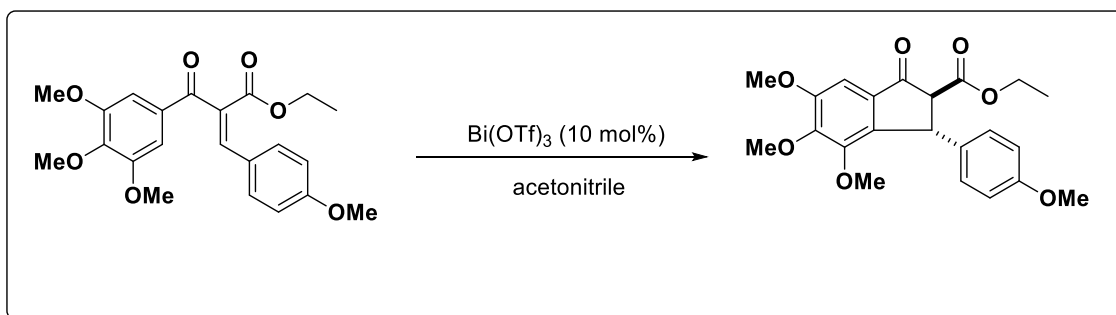
Purified by column chromatography (hexane/EtOAc 95:5–9:1) to give **9fc** (395 mg, 0,99 mmol, 99%) as a yellow oil. 1H NMR (250 MHz, $CDCl_3$) δ 7.92 (d, J = 8.8 Hz, 2H), 7.79 (s, 1H), 6.88 (d, J = 8.8 Hz, 2H), 6.58 (s, 2H), 4.21 (q, J = 7.1 Hz, 2H), 3.82 (s, 3H), 3.77 (s, 3H), 3.62 (s, 6H), 1.18 (t, J = 7.1 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 194.36, 165.28, 164.38, 153.12,

142.01, 139.98, 131.58, 130.77, 129.61, 128.34, 114.29, 107.83, 61.57, 60.93, 55.99, 55.62, 14.22. HRMS (ESI) m/z calcd for $C_{22}H_{25}O_7^+$ $[M + H]^+$ 401.1595, found 401.1600.

Ethyl (2Z)-2-[(Z)-1-benzothiophene-3-carbonyl]-3-(3,4,5-trimethoxyphenyl)prop-2-enoate (**9gc**)

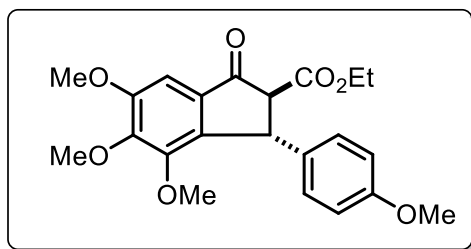


Purified by column chromatography (hexane/EtOAc 95:5–8:2) to give **9gc** (414 mg, 0.97 mmol, 97%) as a brown solid. mp 119–122 °C. 1H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, J = 8.1 Hz, 1H), 8.21 (s, 1H), 7.85 (d, J = 8.8 Hz, 2H), 7.54 (dd, J = 11.2, 3.9 Hz, 1H), 7.45 (dd, J = 11.2, 3.8 Hz, 1H), 6.65 (s, 2H), 4.33 – 4.23 (m, 2H), 3.77 (s, 3H), 3.54 (s, 6H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.95, 165.13, 153.03, 142.04, 140.89, 140.22, 139.96, 136.12, 134.88, 131.21, 128.11, 126.19, 125.89, 125.28, 122.47, 107.65, 61.61, 60.79, 55.80, 14.17. HRMS (ESI) m/z calcd for $C_{23}H_{23}O_6S^+$ $[M + H]^+$ 427.1210, found 427.1215.



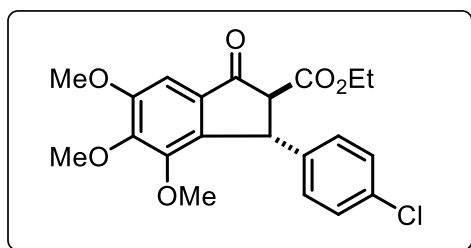
To a sealed tube were added the Knoevenagel product **9** (0.5 mmol), dry acetonitrile (2 mL), and $Bi(OTf)_3$ (0.05 mmol). The reaction mixture was stirred at 60 °C using magnetic stirring. The reaction was monitored by TLC. After confirming the completion of the reaction, the reaction mixture was concentrated under reduced pressure. The resulting crude reaction mixture was purified by column chromatography using a mobile phase of hexane/ethyl acetate 9:1–8:2, v/v.

Ethyl 4,5,6-trimethoxy-3-(4-methoxyphenyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (**10aa**)



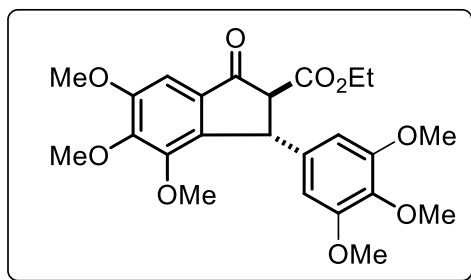
Purified by column chromatography (hexane/EtOAc 95:5–9:1) to give **10aa** (112 mg, 0,28 mmol, 93%) as a yellow oil. ^1H NMR (250 MHz, CDCl_3) δ 7.09 – 7.00 (m, 3H), 6.82 (d, J = 8.6 Hz, 2H), 4.89 (d, J = 3.1 Hz, 1H), 4.23 (q, J = 7.1 Hz, 2H), 3.90 (s, 6H), 3.76 (s, 3H), 3.56 (d, J = 3.1 Hz, 1H), 3.38 (s, 3H), 1.28 (t, J = 7.2 Hz, 3H). ^{13}C NMR (63 MHz, CDCl_3) δ 198.25, 168.65, 158.81, 155.33, 150.49, 149.62, 143.82, 134.97, 130.66, 128.57, 114.28, 101.14, 64.12, 61.94, 61.08, 60.28, 56.44, 55.41, 45.70, 14.36. HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{25}\text{O}_7^+$ [$\text{M} + \text{H}$] $^+$ 401.1595, found 401.1565.

Ethyl 4,5,6-trimethoxy-3-(4-chlorophenyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (**10ab**)



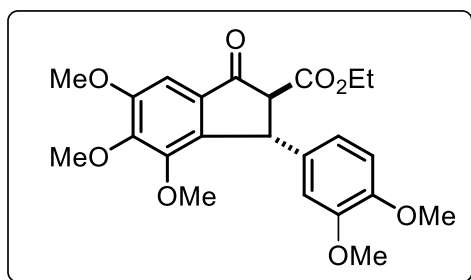
Purified by column chromatography (hexane/EtOAc 95:5–9:1) to give **10ab** (104 mg, 0,26 mmol, 86%) as a brown oil. ^1H NMR (400 MHz, CDCl_3) δ 7.29 (d, J = 8.2 Hz, 2H), 7.10 (s, 1H), 7.08 (d, J = 8.3 Hz, 2H), 4.93 (d, J = 3.2 Hz, 1H), 4.26 (q, J = 7.0 Hz, 2H), 3.93 (d, J = 2.3 Hz, 6H), 3.56 (d, J = 3.3 Hz, 1H), 3.45 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 197.47, 168.19, 155.42, 150.19, 149.37, 142.67, 141.31, 132.88, 130.51, 128.92, 128.76, 101.03, 63.61, 61.96, 60.96, 60.13, 56.31, 45.51, 14.20. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{22}\text{ClO}_6^+$ [$\text{M} + \text{H}$] $^+$ 405.1099, found 405.1107.

Ethyl 4,5,6-trimethoxy-1-oxo-3-(3,4,5-trimethoxyphenyl)-2,3-dihydro-1*H*-indene-2-carboxylate (**10ac**)



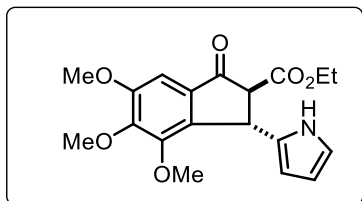
Purified by column chromatography (hexane/EtOAc 95:5–8:2) to give **10ac** (127 mg, 0,28 mmol, 93%) as a brown oil. ¹H NMR (500 MHz, CDCl₃) δ 7.09 (s, 1H), 6.32 (s, 2H), 4.88 (d, *J* = 3.3 Hz, 1H), 4.26 (qd, *J* = 7.1, 2.2 Hz, 2H), 3.92 (d, *J* = 1.3 Hz, 6H), 3.82 (s, 3H), 3.78 (s, 6H), 3.62 (d, *J* = 3.2 Hz, 1H), 3.45 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 197.97, 168.51, 155.43, 153.59, 150.50, 149.57, 143.19, 138.61, 137.23, 130.64, 104.56, 101.18, 63.83, 62.06, 61.10, 61.04, 60.35, 56.43, 56.33, 46.57, 14.37. HRMS (ESI) *m/z* calcd for C₂₄H₂₉O₉⁺ [*M* + *H*]⁺ 461.1806, found 461.1817.

Ethyl 3-(3,4-dimethoxyphenyl)-4,5,6-trimethoxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (**10ad**)



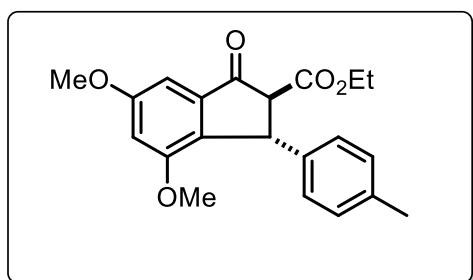
Purified by column chromatography (hexane/EtOAc 95:5–8:2) to give **10ad** (120 mg, 0,28 mmol, 94%) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.05 (s, 1H), 6.75 (d, *J* = 8.1 Hz, 1H), 6.64 – 6.59 (m, 2H), 4.86 (d, *J* = 3.1 Hz, 1H), 4.21 (q, *J* = 6.9 Hz, 2H), 3.88 (s, 6H), 3.82 (s, 3H), 3.78 (s, 3H), 3.57 (d, *J* = 3.1 Hz, 1H), 3.38 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 198.21, 168.63, 155.37, 150.52, 149.63, 149.31, 148.27, 143.61, 135.48, 130.65, 119.62, 111.51, 110.83, 101.17, 64.08, 62.02, 61.11, 60.36, 56.45, 56.13, 56.07, 46.06, 14.39. HRMS (ESI) *m/z* calcd for C₂₃H₂₇O₈⁺ [*M* + *H*]⁺ 431.1700, found 431.1708.

Ethyl 4,5,6-trimethoxy-1-oxo-3-(1*H*-pyrrol-2-yl)-2,3-dihydro-1*H*-indene-2-carboxylate (**10ag**)



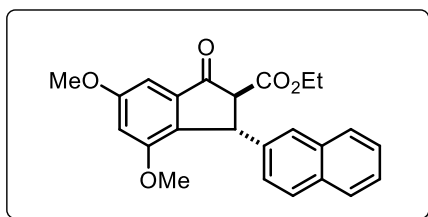
Purified by column chromatography (hexane/EtOAc 95:5–8:2) to give **10ag** (87 mg, 0,24 mmol, 81%) as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 8.83 (s, 1H), 7.28 (s, 1H), 7.07 (s, 1H), 6.73 (d, $J = 1.4$ Hz, 1H), 6.13 (d, $J = 3.0$ Hz, 1H), 5.96 (s, 1H), 5.06 (d, $J = 2.9$ Hz, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 3.98 (s, 3H), 3.93 – 3.89 (m, 1H), 3.91 (s, 3H), 3.76 (s, 3H), 1.33 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 197.23, 168.41, 155.13, 149.90, 149.24, 141.85, 131.50, 129.95, 117.45, 108.43, 105.18, 101.78, 62.01, 61.26, 61.07, 60.94, 56.32, 39.14, 14.19. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{22}\text{NO}_6^+$ [$\text{M} + \text{H}$] $^+$ 360.1442, found 360.1433.

Ethyl 4,6-dimethoxy-3-(4-methylphenyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (**10bj**)



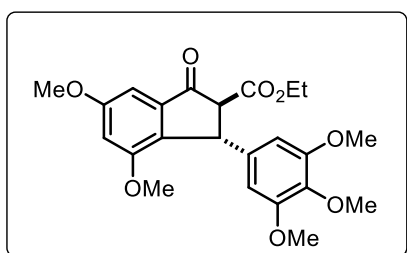
Purified by column chromatography (hexane/EtOAc 95:5–9:1) to give **10bj** (88 mg, 0,25 mmol, 83%) as a yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 7.23 (s, 1H), 7.18 (d, $J = 3.7$ Hz, 1H), 7.10 (d, $J = 8.0$ Hz, 2H), 6.99 (dd, $J = 11.5$, 8.0 Hz, 2H), 6.61 (d, $J = 2.5$ Hz, 1H), 4.82 (d, $J = 4.0$ Hz, 1H), 4.22 (dd, $J = 7.1$, 5.2 Hz, 2H), 3.90 (s, 3H), 3.81 (s, 3H), 3.56 (d, $J = 4.1$ Hz, 1H), 2.31 (s, 3H), 1.27 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 197.46, 168.99, 156.49, 152.24, 150.29, 139.20, 137.32, 129.90, 129.76, 128.20, 127.91, 127.61, 107.46, 104.42, 64.11, 61.91, 56.56, 56.38, 48.25, 21.26, 14.42. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{23}\text{O}_5^+$ [$\text{M} + \text{H}$] $^+$ 355.1540, found 355.1545.

Ethyl 4,6-dimethoxy-3-(naphthalen-2-yl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (**10bk**)



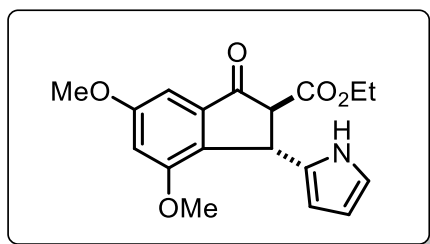
Purified by column chromatography (hexane/EtOAc 95:5–8:2) to give **10bk** (94 mg, 0,24 mmol, 80%) as an orange solid. mp 130-131 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.91 – 7.72 (m, 3H), 7.58 (d, *J* = 1.8 Hz, 1H), 7.54 – 7.41 (m, 3H), 7.18 (dd, *J* = 8.5, 1.9 Hz, 1H), 6.93 (d, *J* = 2.1 Hz, 1H), 6.70 (d, *J* = 2.2 Hz, 1H), 5.13 (d, *J* = 3.1 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.90 (s, 3H), 3.70 (d, *J* = 3,0 Hz, 2H), 3.61 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 199.05, 168.37, 162.14, 157.88, 139.80, 138.13, 137.76, 133.47, 132.49, 128.49, 127.75, 127.66, 126.17, 125.88, 125.70, 125.31, 106.92, 96.61, 64.19, 61.90, 55.86, 55.62, 46.09, 14.23. HRMS (ESI) *m/z* calcd for C₂₄H₂₃O₅⁺ [*M* + *H*]⁺ 391.1540, found 391.1544.

Ethyl 4,6-dimethoxy-1-oxo-3-(3,4,5-trimethoxyphenyl)-2,3-dihydro-1*H*-indene-2-carboxylate (**10bc**)



Purified by column chromatography (hexane/EtOAc 95:5–9:1) to give **10bc** (110 mg, 0,26 mmol, 85%) as a yellow solid. mp 144-145 °C. ¹H NMR (400 MHz, CDCl₃) δ 6.87 (d, *J* = 2.1 Hz, 1H), 6.69 (d, *J* = 2.1 Hz, 1H), 6.27 (s, 2H), 4.86 (d, *J* = 2.9 Hz, 2H), 4.31 – 4.23 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 3.85 – 3.82 (m, 3H), 3.77 (s, 6H), 3.70 (s, 3H), 3.62 (d, *J* = 3.0 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 199.11, 168.49, 162.24, 158.01, 153.46, 138.28, 138.05, 137.77, 137.01, 107.05, 104.34, 96.76, 64.29, 62.04, 61.00, 56.29, 55.98, 55.85, 46.29, 14.40. HRMS (ESI) *m/z* calcd for C₂₃H₂₇O₈⁺ [*M* + *H*]⁺ 431.1700, found 431.1708.

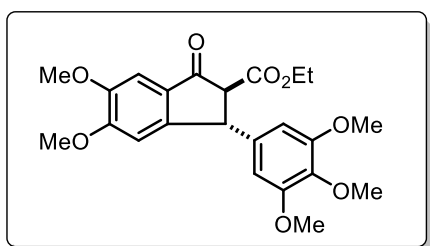
Ethyl 4,6-dimethoxy-1-oxo-3-(1*H*-pyrrol-2-yl)-2,3-dihydro-1*H*-indene-2-carboxylate (**10bg**)



Purified by column chromatography (hexane/EtOAc 95:5–8:2) to give **10bg** (76 mg, 0,23 mmol, 77%) as a yellow solid. mp 100-102 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.57 (s, 1H), 6.72 (d, *J* = 2.1 Hz, 1H), 6.62 (d, *J* = 2.1 Hz, 1H),

6.60 (m, 1H), 5.99 (q, *J* = 2.9 Hz, 1H), 5.79 (m, 1H), 4.91 (d, *J* = 2.7 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 0H), 3.77 (s, 3H), 3.73 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 198.52, 168.50, 162.11, 157.50, 137.26, 137.22, 131.77, 117.51, 108.44, 107.29, 104.96, 97.58, 62.21, 61.62, 56.24, 56.06, 39.14, 14.40. HRMS (ESI) *m/z* calcd for C₁₈H₁₉NNaO₅⁺ [*M* + Na]⁺ 352.1155, found 352.1165.

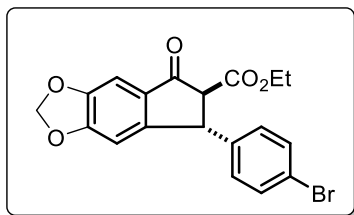
Ethyl 5,6-dimethoxy-1-oxo-3-(3,4,5-trimethoxyphenyl)-2,3-dihydro-1*H*-indene-2-carboxylate (**10cc**)



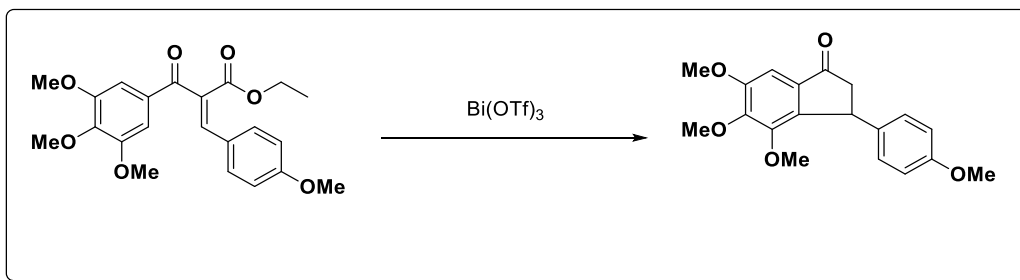
Purified by column chromatography (hexane/EtOAc 95:5–8:2) to give **10cc** (104 mg, 0,24 mmol, 81%) as a brown oil. ¹H NMR (400 MHz, CDCl₃) δ 7.23 (s, 1H), 6.69 (s, 1H), 6.34 (s, 2H), 4.84 (d, *J* = 4.1 Hz, 1H), 4.29 (dd, *J* = 7.1, 4.3 Hz, 2H), 3.95 (s, 3H), 3.90

(s, 3H), 3.85 (s, 3H), 3.80 (s, 6H), 3.63 (d, *J* = 4.1 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 197.15, 168.91, 156.57, 153.84, 151.69, 150.44, 137.85, 137.46, 128.17, 107.47, 104.94, 104.48, 63.95, 61.99, 61.01, 56.65, 56.35, 48.82, 14.43. HRMS (ESI) *m/z* calcd for C₂₃H₂₇O₈⁺ [*M* + H]⁺ 431.1700, found 431.1706.

Ethyl 5-(4-bromophenyl)-7-oxo-2*H*,5*H*,6*H*,7*H*-indeno[5,6-*d*][1,3]dioxole-6-carboxylate (**10dm**)

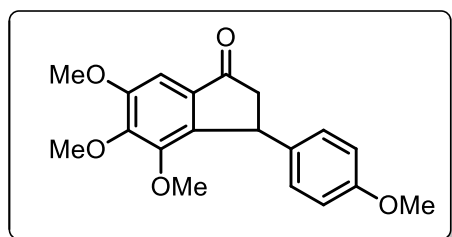


Purified by column chromatography (hexane/EtOAc 95:5–9:1) to give **10dm** (99 mg, 0,25 mmol, 82%) as a yellow oil. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.84 (s, 1H), 7.50 – 7.45 (m, 2H), 7.39 (d, J = 8.6 Hz, 2H), 7.26 – 7.19 (m, 2H), 6.79 (d, J = 8.1 Hz, 1H), 6.05 (s, 2H), 4.25 (q, J = 7.1 Hz, 2H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 193.39, 164.91, 152.90, 148.66, 140.74, 132.30, 132.15, 131.89, 131.57, 130.97, 129.66, 126.53, 124.94, 108.34, 108.21, 102.20, 61.79, 14.18. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{16}\text{BrO}_5^+$ [$\text{M} + \text{H}$] $^+$ 403.0176, found 403.0183.



To a sealed tube were added the Knoevenagel product **9** (0.5 mmol), dry acetonitrile (2 mL), and $\text{Bi}(\text{OTf})_3$ (0.05 mmol). The reaction mixture was stirred at 100 °C using magnetic stirring. The reaction was monitored by TLC. After confirming the completion of the reaction, the reaction mixture was concentrated under reduced pressure. The resulting crude reaction mixture was purified by column chromatography using a mobile phase of hexane/ethyl acetate 9:1–8:2, v/v.

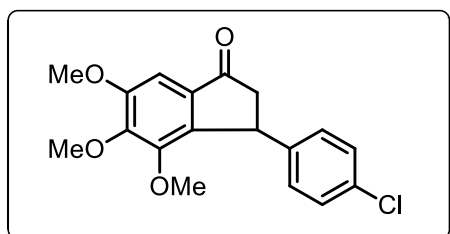
4,5,6-Trimethoxy-3-(4-methoxyphenyl)-2,3-dihydro-1*H*-inden-1-one (**11aa**) [3]



Purified by column chromatography (hexane/EtOAc 95:5–9:1) to give **11aa** (91 mg, 0,28 mmol, 93%) as a yellow solid. mp 60–62 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.10 (s, 1H), 7.06 – 7.02 (m, 2H), 6.86 – 6.80 (m, 2H), 4.56 (dd, J = 8.0, 2.5 Hz, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 3.79 (s, 3H), 3.38 (s, 3H), 3.19 (dd, J = 19.3,

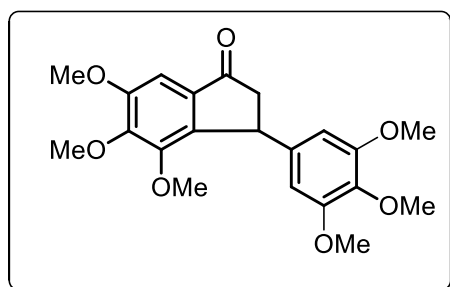
8.0 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.69, 158.47, 155.04, 150.59, 149.01, 145.05, 136.61, 132.33, 128.40, 114.16, 100.45, 61.06, 60.28, 56.42, 55.43, 47.52, 41.03. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{21}\text{O}_5^+$ $[\text{M} + \text{H}]^+$ 329.1384, found 190.1391.

4,5,6-Trimethoxy-3-(4-chlorophenyl)-2,3-dihydro-1H-inden-1-one (**11ab**) [4]



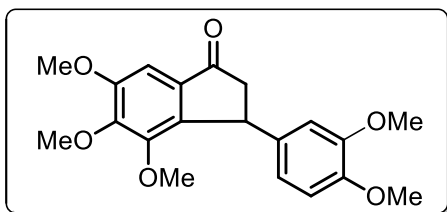
Purified by column chromatography (hexane/EtOAc 95:5–9:1) to give **11ab** (87 mg, 0,26 mmol, 87%) as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.32 – 7.22 (m, 2H), 7.09 (s, 1H), 7.05 (d, J = 8.4 Hz, 2H), 4.56 (dd, J = 8.0, 2.5 Hz, 1H), 3.93 (s, 3H), 3.91 (s, 3H), 3.42 (s, 3H), 3.19 (dd, J = 19.2, 8.0 Hz, 1H), 2.56 (dd, J = 19.2, 2.6 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 204.94, 155.29, 150.45, 148.89, 144.09, 143.12, 132.49, 132.35, 128.91, 128.78, 100.49, 61.06, 60.25, 56.42, 47.16, 41.14. HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{18}\text{ClO}_4^+$ $[\text{M} + \text{H}]^+$ 333.0888, found 333.0894.

4,5,6-Trimethoxy-3-(3,4,5-trimethoxyphenyl)-2,3-dihydro-1H-inden-1-one (**11ac**) [4]



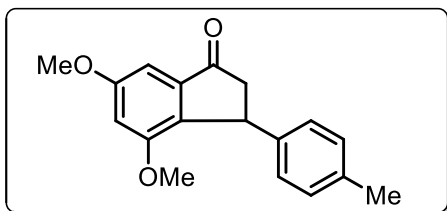
Purified by column chromatography (hexane/EtOAc 95:5–8:2) to give **11ac** (105 mg, 0,27 mmol, 90%) as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.06 (s, 1H), 6.28 (s, 2H), 4.49 (dd, J = 8.0, 2.5 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.78 (s, 3H), 3.75 (s, 6H), 3.40 (s, 3H), 3.14 (dd, J = 19.3, 8.0 Hz, 1H), 2.59 (dd, J = 19.3, 2.5 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.34, 155.11, 153.47, 150.56, 148.91, 144.35, 140.27, 136.85, 132.34, 104.38, 100.46, 61.02, 60.30, 56.36, 56.28, 47.23, 42.07. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{25}\text{O}_7^+$ $[\text{M} + \text{H}]^+$ 389.1595, found 389.1596.

4,5,6-Trimethoxy-3-(3,4-dimethoxyphenyl)-2,3-dihydro-1*H*-inden-1-one (**11ad**)



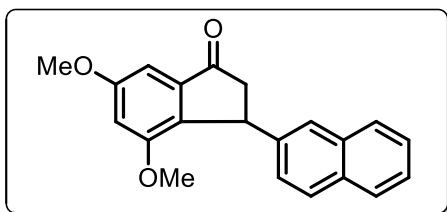
Purified by column chromatography (hexane/EtOAc 95:5–9:1) to give **11ad** (87 mg, 0,24 mmol, 81%) as a yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.10 (s, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 6.68 – 6.57 (m, 2H), 4.55 (dd, *J* = 7.9, 2.5 Hz, 1H), 3.94 (s, 3H), 3.92 (s, 3H), 3.86 (s, 3H), 3.82 (s, 3H), 3.40 (s, 3H), 3.19 (dd, *J* = 19.2, 8.0 Hz, 1H), 2.61 (dd, *J* = 19.3, 2.5 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 205.47, 154.89, 150.43, 149.04, 148.83, 147.73, 144.65, 136.96, 132.17, 119.25, 111.25, 110.50, 100.30, 60.89, 60.17, 56.24, 55.93, 55.89, 47.30, 41.29. HRMS (ESI) *m/z* calcd for C₂₀H₂₃O₆⁺ [*M* + *H*]⁺ 359.1489, found 359.1493.

4,6-Dimethoxy-3-(4-methylphenyl)-2,3-dihydro-1*H*-inden-1-one (**11bj**) [5]



Purified by column chromatography (hexane/EtOAc 95:5–9:1) to give **11bj** (60 mg, 0,21 mmol, 71%) as a brown oil ¹H NMR (400 MHz, CDCl₃) δ 7.24 (s, 1H), 7.14 (d, *J* = 7.9 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.66 (s, 1H), 4.47 (dd, *J* = 7.7, 3.3 Hz, 1H), 3.95 (s, 3H), 3.86 (s, 3H), 3.21 (dd, *J* = 19.0, 7.7 Hz, 1H), 2.62 (dd, *J* = 19.0, 3.4 Hz, 1H), 2.35 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 204.91, 155.96, 153.52, 150.01, 141.03, 136.77, 129.78, 127.62, 107.65, 103.86, 56.46, 56.34, 47.52, 44.04, 21.22. HRMS (ESI) *m/z* calcd for C₁₈H₁₉O₃⁺ [*M* + *H*]⁺ 283.1329, found 283.1337.

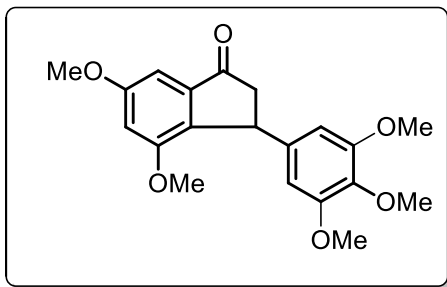
4,6-Dimethoxy-3-(naphthalen-2-yl)-2,3-dihydro-1*H*-inden-1-one (**11bk**)



Purified by column chromatography (hexane/EtOAc 95:5–8:2) to give **11bk** (72 mg, 0,23 mmol, 76%) as a yellow solid. mp 138-139 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.90 – 7.70 (m, 3H), 7.55 (d, *J* = 1.8 Hz, 1H), 7.52 – 7.36 (m, 2H), 7.18 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.93 (d, *J* = 2.1 Hz, 1H), 6.67 (d, *J* = 2.1 Hz, 1H), 4.76 (dd, *J* = 8.0, 2.3 Hz, 1H), 3.91 (s, 3H), 3.62 (s, 3H), 3.30 (dd, *J* = 19.3, 7.9 Hz, 1H), 2.70 (dd, *J* = 19.3, 2.3 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 206.50, 162.02, 158.15, 141.56,

139.54, 139.44, 133.69, 132.48, 128.44, 127.84, 127.81, 126.21, 125.71, 125.66, 125.63, 106.33, 96.12, 55.99, 55.76, 47.77, 41.63. HRMS (ESI) m/z calcd for $C_{21}H_{19}O_3^+$ [$M + H$] $^+$ 319.1329, found 319.1335.

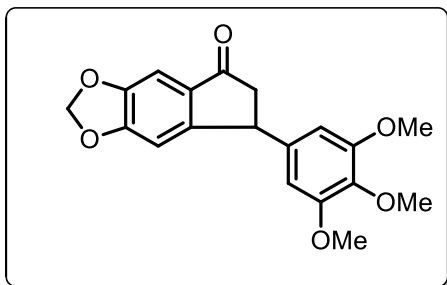
4,6-Dimethoxy-3-(3,4,5-trimethoxyphenyl)-2,3-dihydro-1*H*-inden-1-one (**11bc**)



Purified by column chromatography (hexane/EtOAc 95:5–8:2) to give **11bc** (92 mg, 0,26 mmol, 86%) as a yellow solid. mp 142–143 °C. 1H NMR (400 MHz, $CDCl_3$) δ 6.87 (d, $J = 1.9$ Hz, 1H), 6.67 (d, $J = 1.9$ Hz, 1H), 6.27 (s, 2H), 4.52 (dd, $J = 7.9, 2.0$ Hz, 1H), 3.88 (s, 3H), 3.83 (s, 3H),

3.78 (s, 6H), 3.71 (s, 3H), 3.21 (dd, $J = 19.2, 7.9$ Hz, 1H), 2.63 (dd, $J = 19.2, 2.1$ Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.43, 161.97, 158.11, 153.36, 139.89, 139.30, 139.26, 136.69, 106.31, 104.27, 96.12, 61.01, 56.28, 55.96, 55.82, 47.73, 41.76. HRMS (ESI) m/z calcd for $C_{20}H_{23}O_6^+$ [$M + H$] $^+$ 359.1489, found 359.1492.

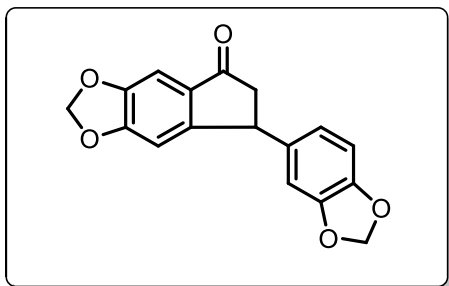
7-(3,4,5-Trimethoxyphenyl)-2*H*,5*H*,6*H*,7*H*-indeno[5,6-*d*][1,3]dioxol-5-one (**11dc**)



Purified by column chromatography (hexane/EtOAc 95:5–9:1) to give **11dc** (85 mg, 0,25 mmol, 83%) as a yellow solid. mp 176–178 °C. 1H NMR (500 MHz, $CDCl_3$) δ 7.15 (s, 1H), 6.66 (s, 1H), 6.32 (s, 2H), 6.09 (d, $J = 1.1$ Hz, 2H), 4.37 (dd, $J = 7.7, 3.4$ Hz, 1H), 3.84 (s, 3H), 3.82 (s,

6H), 3.21 (dd, $J = 19.0, 7.8$ Hz, 1H), 2.68 (dd, $J = 19.1, 3.5$ Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.74, 155.35, 154.56, 153.58, 148.80, 139.22, 136.99, 131.50, 105.81, 104.47, 102.40, 101.78, 60.86, 56.19, 47.14, 44.66. HRMS (ESI) m/z calcd for $C_{19}H_{19}O_6^+$ [$M + H$] $^+$ 343.1176, found 343.1183.

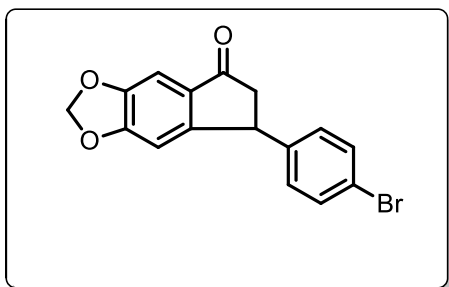
7-(2*H*-1,3-Benzodioxol-5-yl)-2*H*,5*H*,6*H*,7*H*-indeno[5,6-*d*][1,3]dioxol-5-one (**11dl**)



Purified by column chromatography (hexane/EtOAc 95:5–9:1) to give **11dl** (76 mg, 0,26 mmol, 86%) as a brown solid. mp 193-195 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.14 (s, 1H), 6.76 (d, *J* = 7.9 Hz, 1H), 6.69 – 6.61 (m, 2H), 6.53 (d, *J* = 1.8 Hz, 1H), 6.10 – 6.04 (m, 2H), 5.95 (d, *J* = 1.7

Hz, 1H), 4.38 (dd, *J* = 7.7, 3.4 Hz, 1H), 3.19 (dd, *J* = 19.1, 7.8 Hz, 1H), 2.62 (dd, *J* = 19.0, 3.5 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 203.70, 155.54, 154.52, 148.73, 148.19, 146.60, 137.46, 131.51, 120.82, 108.38, 107.58, 105.81, 102.35, 101.75, 101.11, 47.30, 44.01. HRMS (ESI) *m/z* calcd for C₁₇H₁₃O₅⁺ [*M* + *H*]⁺ 297.0757, found 297.0762.

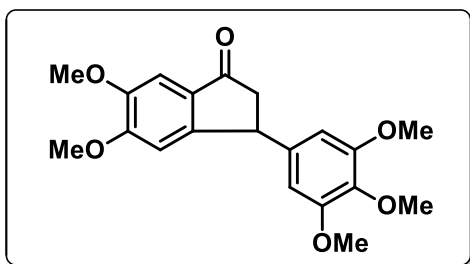
7-(4-Bromophenyl)-2*H*,5*H*,6*H*,7*H*-indeno[5,6-*d*][1,3]dioxol-5-one (**11dm**)



Purified by column chromatography (hexane/EtOAc 95:5–9:1) to give **11dm** (80 mg, 0,24 mmol, 81%) as a brown solid. mp 167-169 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.15 (s, 1H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.58 (s, 1H), 6.08 (d, *J* = 3.0 Hz, 2H), 4.42 (dd, *J* = 7.8, 3.3

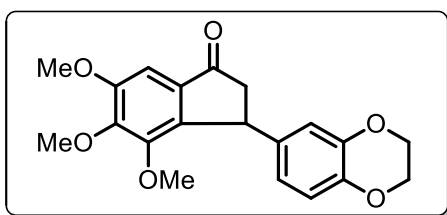
Hz, 1H), 3.22 (dd, *J* = 19.0, 7.8 Hz, 1H), 2.61 (dd, *J* = 19.0, 3.4 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 203.42, 154.99, 154.80, 149.06, 142.85, 132.23, 131.79, 129.44, 121.07, 105.92, 102.62, 102.08, 47.22, 43.90. HRMS (ESI) *m/z* calcd for C₁₆H₁₂BrO₃⁺ [*M* + *H*]⁺ 330.9964, found 330.9973.

5,6-Dimethoxy-3-(3,4,5-trimethoxyphenyl)-2,3-dihydro-1*H*-inden-1-one (**11cc**)



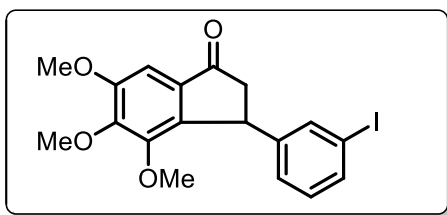
Purified by column chromatography (hexane/EtOAc 95:5–8:2) to give **11cc** (101 mg, 0,28 mmol, 94%) as a yellow solid. mp 137-139 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.25 (s, 1H), 6.69 (s, 1H), 6.32 (s, 2H), 4.43 (dd, *J* = 7.6, 3.3 Hz, 1H), 3.96 (s, 3H), 3.89 (s, 3H), 3.85 (s, 3H), 3.81 (s, 6H), 3.21 (dd, *J* = 19.0, 7.7 Hz, 1H), 2.64 (dd, *J* = 19.0, 3.4 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 204.73, 156.02, 153.76, 153.03, 150.13, 144.79, 139.71, 137.13, 130.08, 107.64, 104.73, 103.90, 61.04, 56.55, 56.35, 47.40, 44.77, 29.77. HRMS (ESI) *m/z* calcd for C₂₀H₂₃O₆⁺ [*M* + *H*]⁺ 359.1489, found 359.1494.

3-(2,3-Dihydro-1,4-benzodioxin-6-yl)-4-ethyl-5,6-dimethoxy-2,3-dihydro-1*H*-inden-1-one (**11ae**)



Purified by column chromatography (hexane/EtOAc 95:5–9:1) to give **11ae** (83 mg, 0,23 mmol, 78%) as a brown oil. ¹H NMR (500 MHz, CDCl₃) δ 7.09 (s, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 6.60 (d, *J* = 7.3 Hz, 2H), 4.50 (d, *J* = 6.8 Hz, 1H), 4.24 (s, 3H), 3.93 (s, 6H), 3.47 (s, 3H), 3.16 (dd, *J* = 19.2, 7.9 Hz, 1H), 2.58 (d, *J* = 19.3 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 205.40, 154.89, 150.40, 148.79, 144.53, 143.51, 142.19, 137.72, 132.18, 120.17, 117.26, 115.87, 100.29, 64.38, 64.31, 60.92, 60.17, 56.26, 47.29, 40.95. HRMS (ESI) *m/z* calcd for C₂₀H₂₁O₆⁺ [*M* + *H*]⁺ 357.1333, found 357.1335.

3-(3-Iodophenyl)-4,5,6-trimethoxy-2,3-dihydro-1*H*-inden-1-one (**11af**)



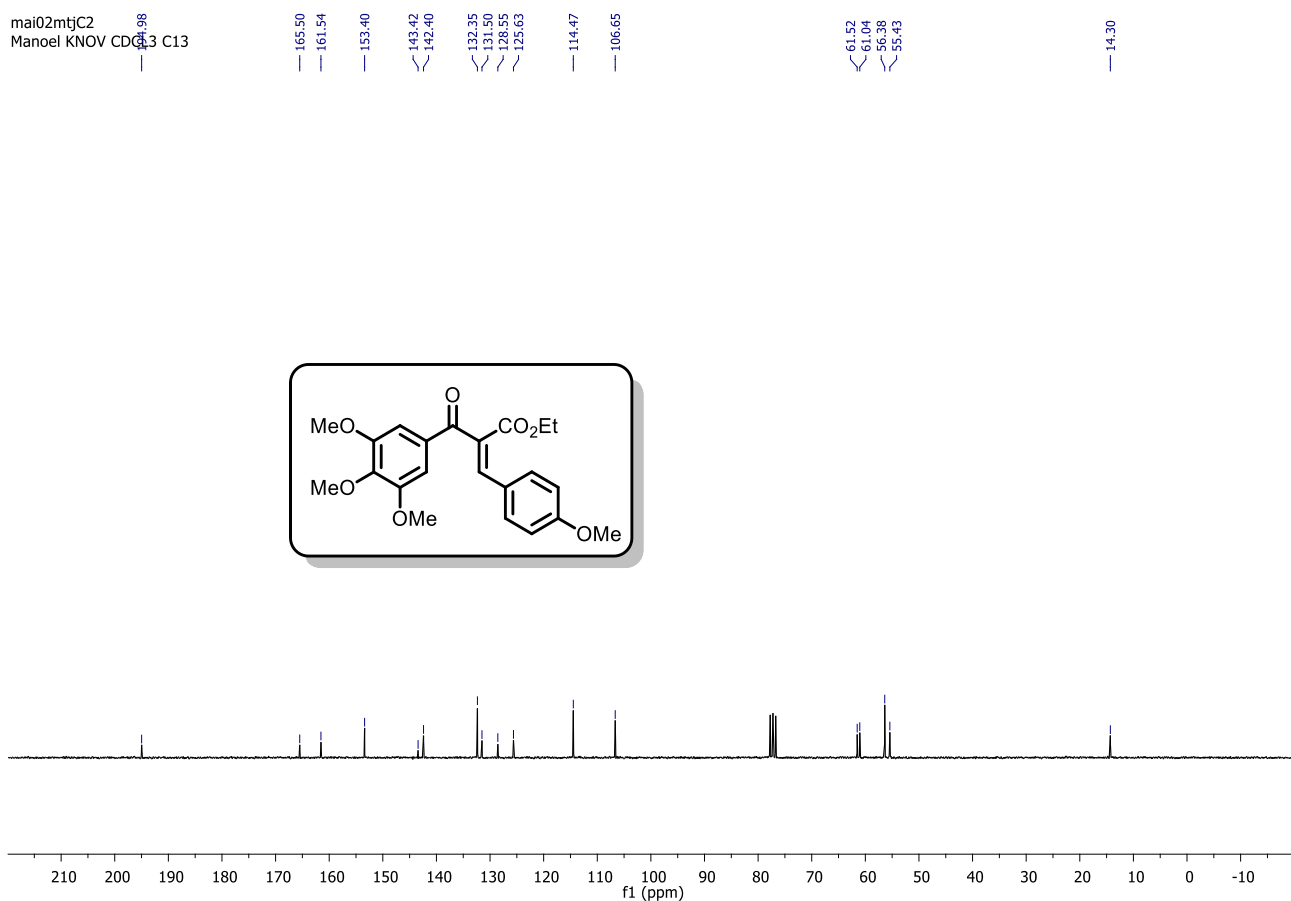
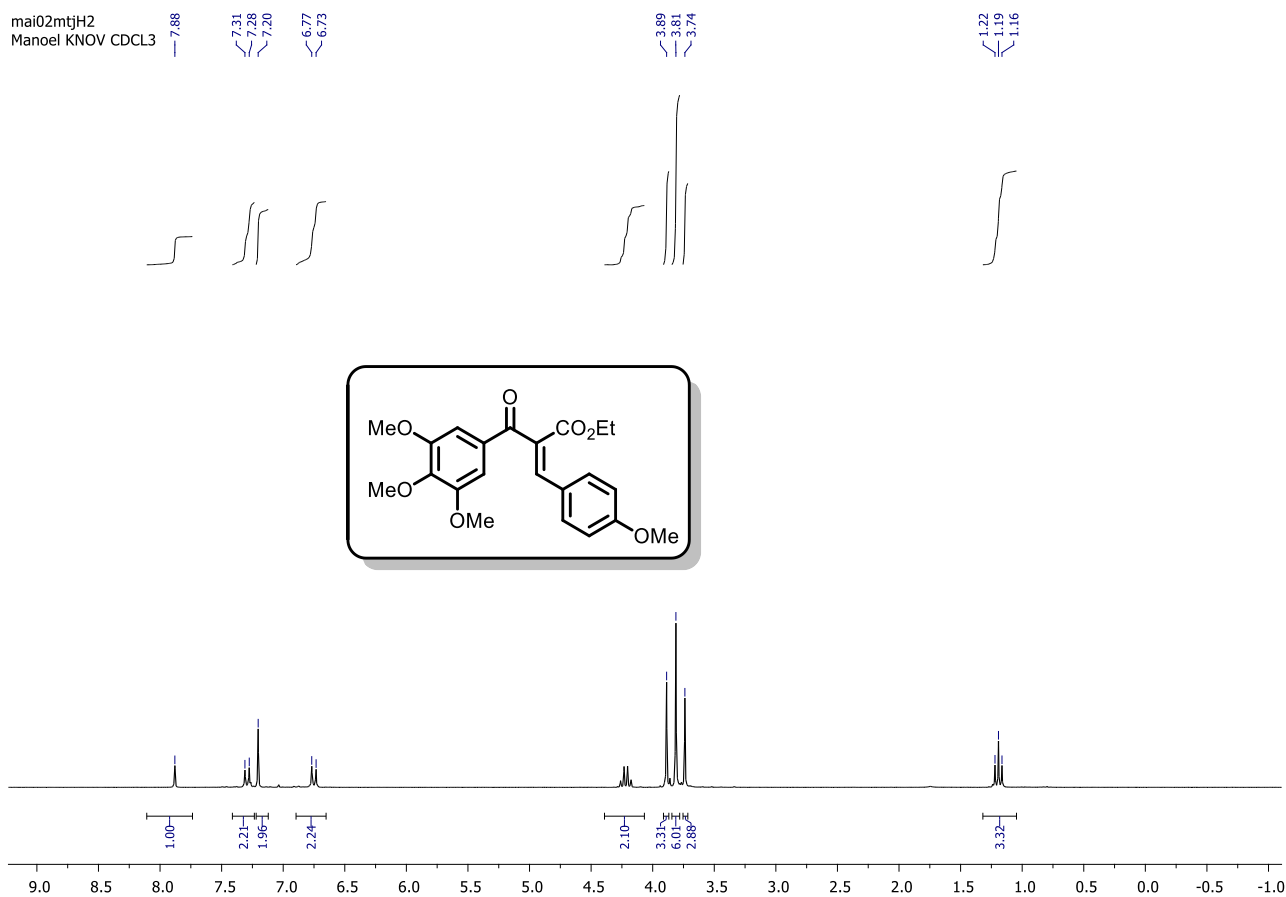
Purified by column chromatography (hexane/EtOAc 95:5–9:1) to give **11af** (93 mg, 0,22 mmol, 73%) as a yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.57 (d, *J* = 7.5 Hz, 1H), 7.50 (s, 1H), 7.15 – 6.99 (m, 3H), 4.52 (d, *J* = 6.2 Hz, 1H), 3.95 (s, 3H), 3.93 (s, 3H), 3.43 (s, 3H), 3.19 (dd, *J* = 19.2, 8.0 Hz, 1H), 2.60 (d, *J* = 19.3

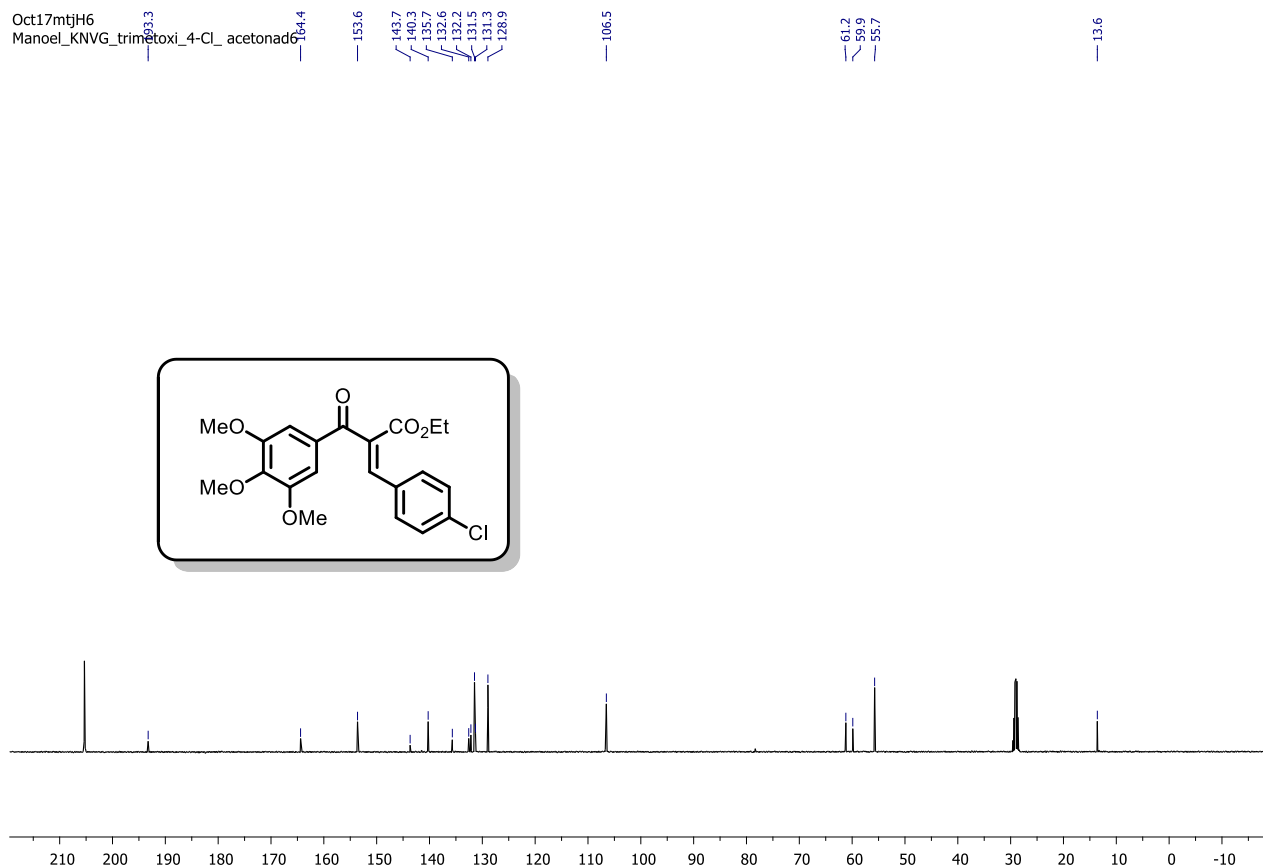
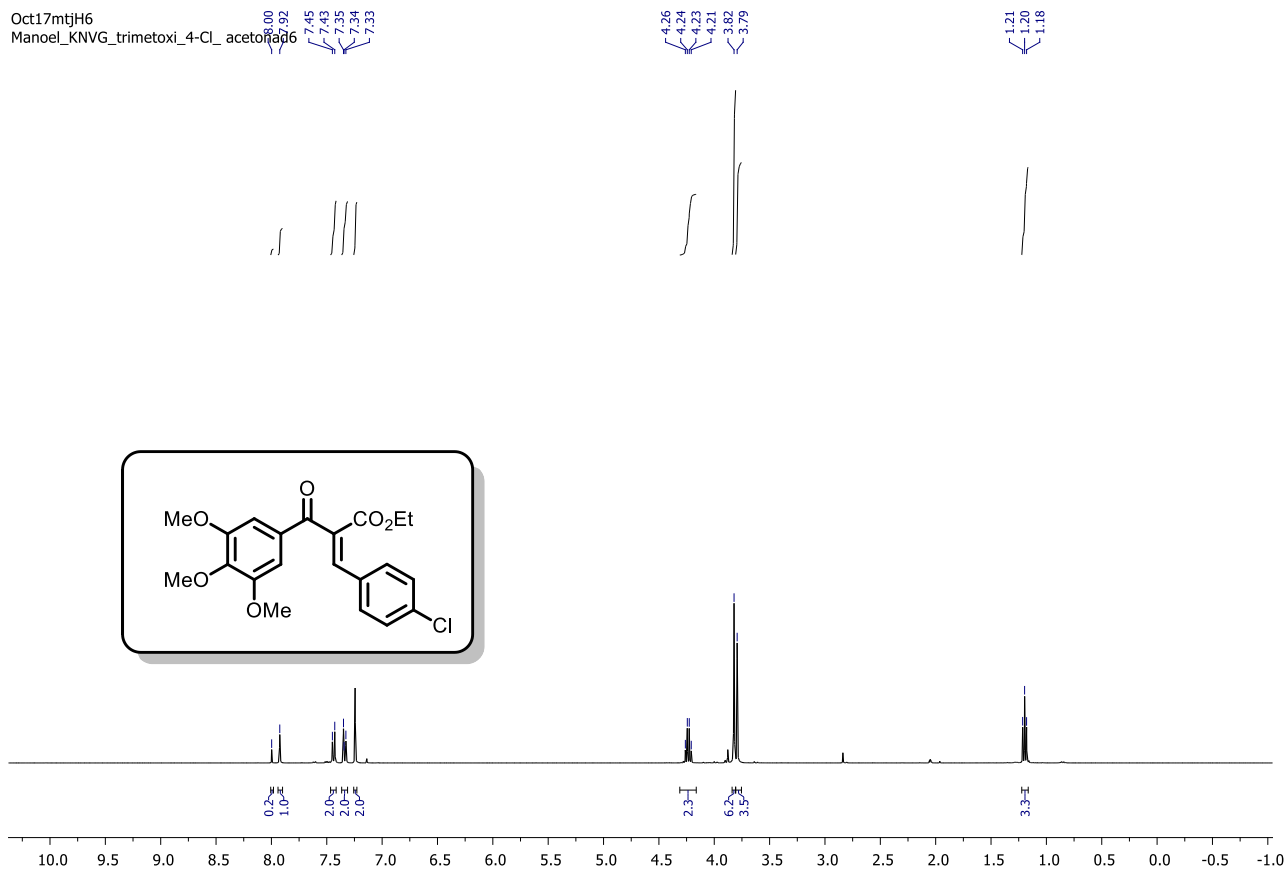
Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 155.37, 150.48, 148.94, 146.98, 143.89, 136.57, 135.97, 132.39, 130.57, 126.73, 100.58, 94.67, 61.10, 60.30, 56.47, 47.02, 41.31. HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{18}\text{IO}_4^+$ $[\text{M} + \text{H}]^+$ 425.0244, found 425.0253.

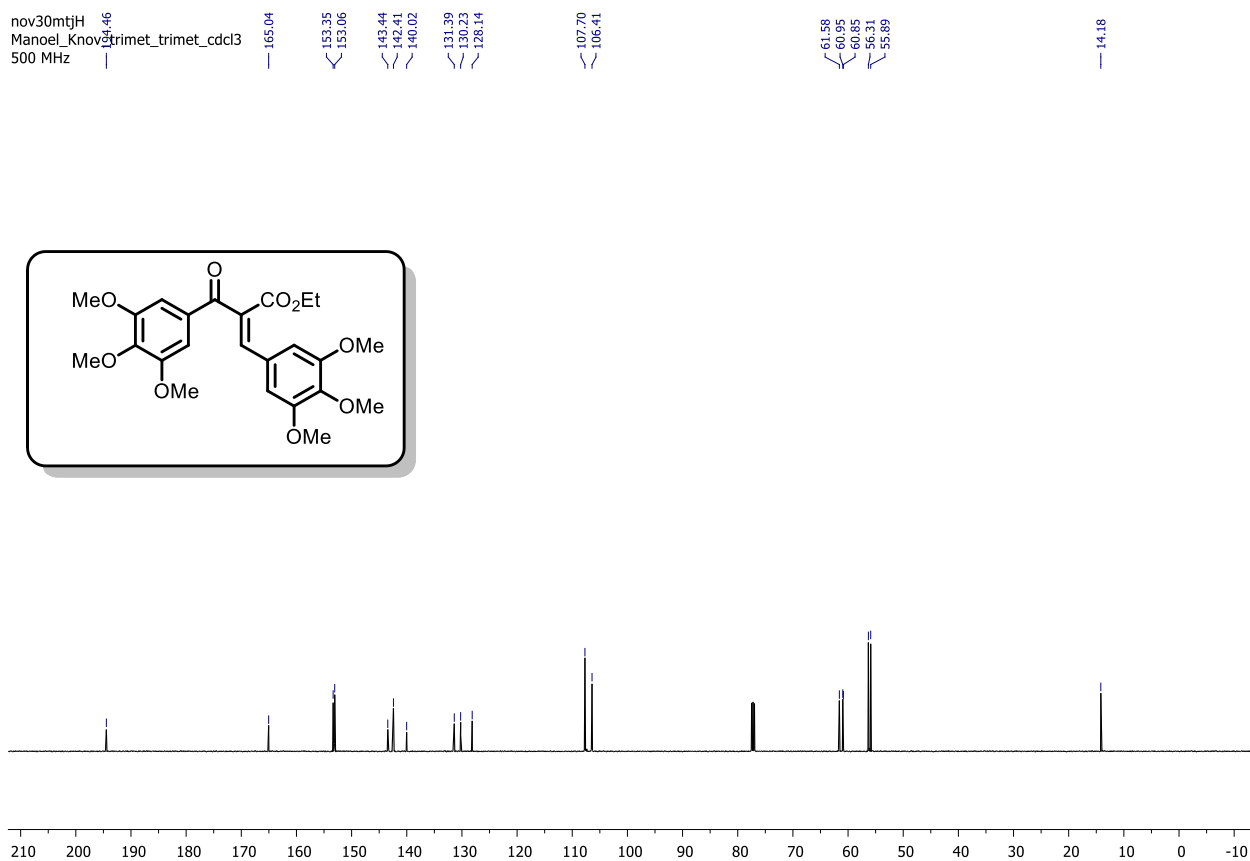
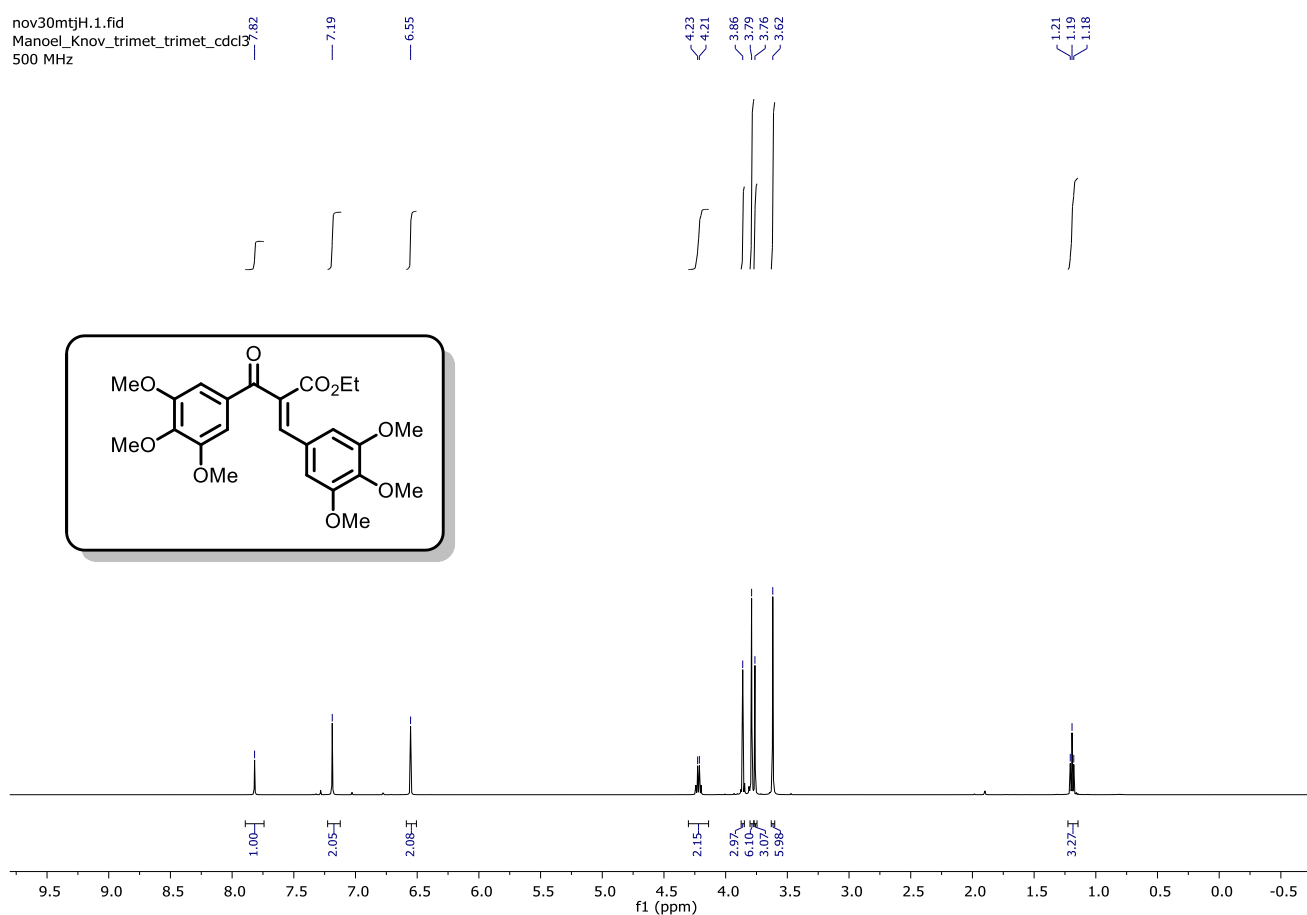
References

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¹H NMR and ¹³C NMR spectra







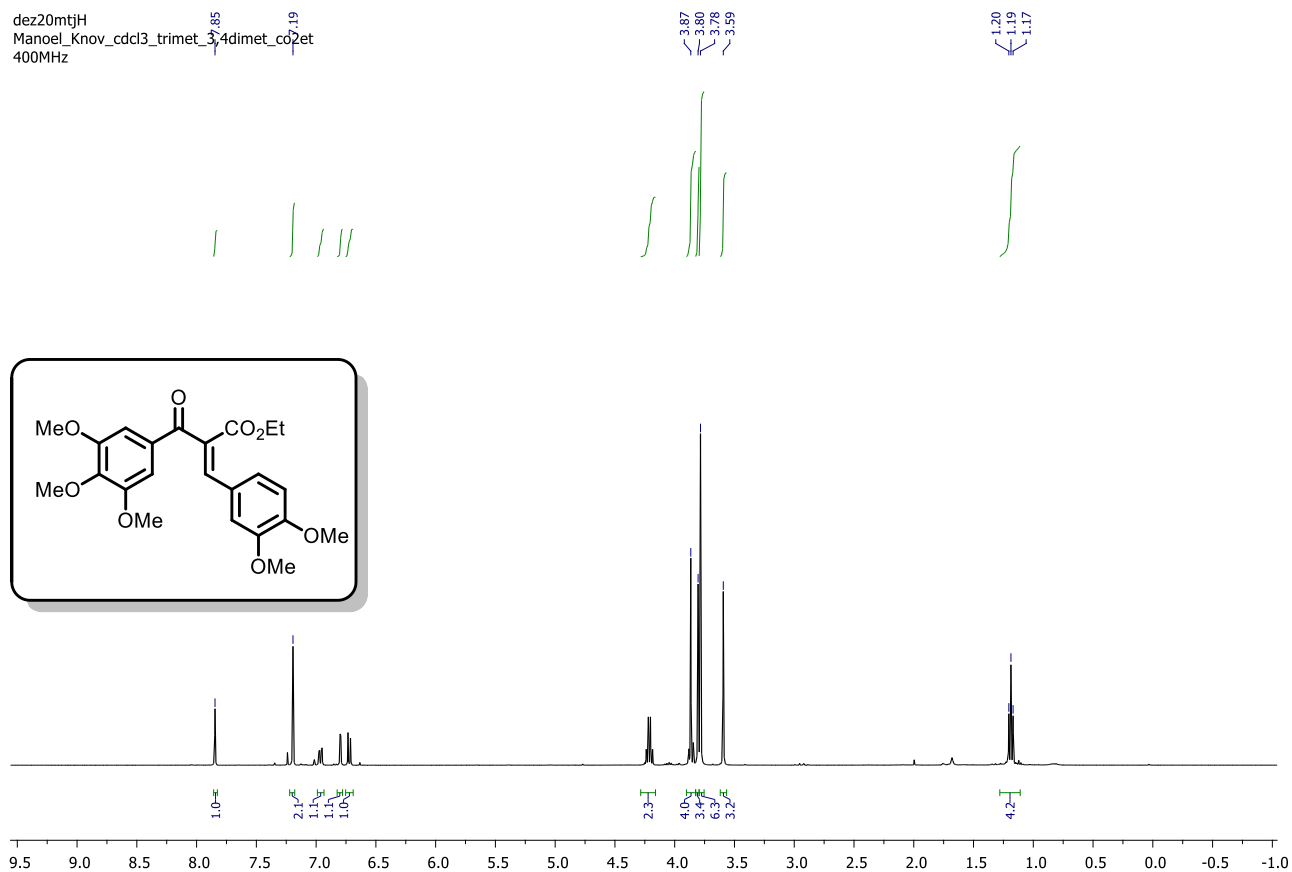


Figure S7. ^1H NMR spectrum (400 MHz, CDCl_3) of compound **9ad**.

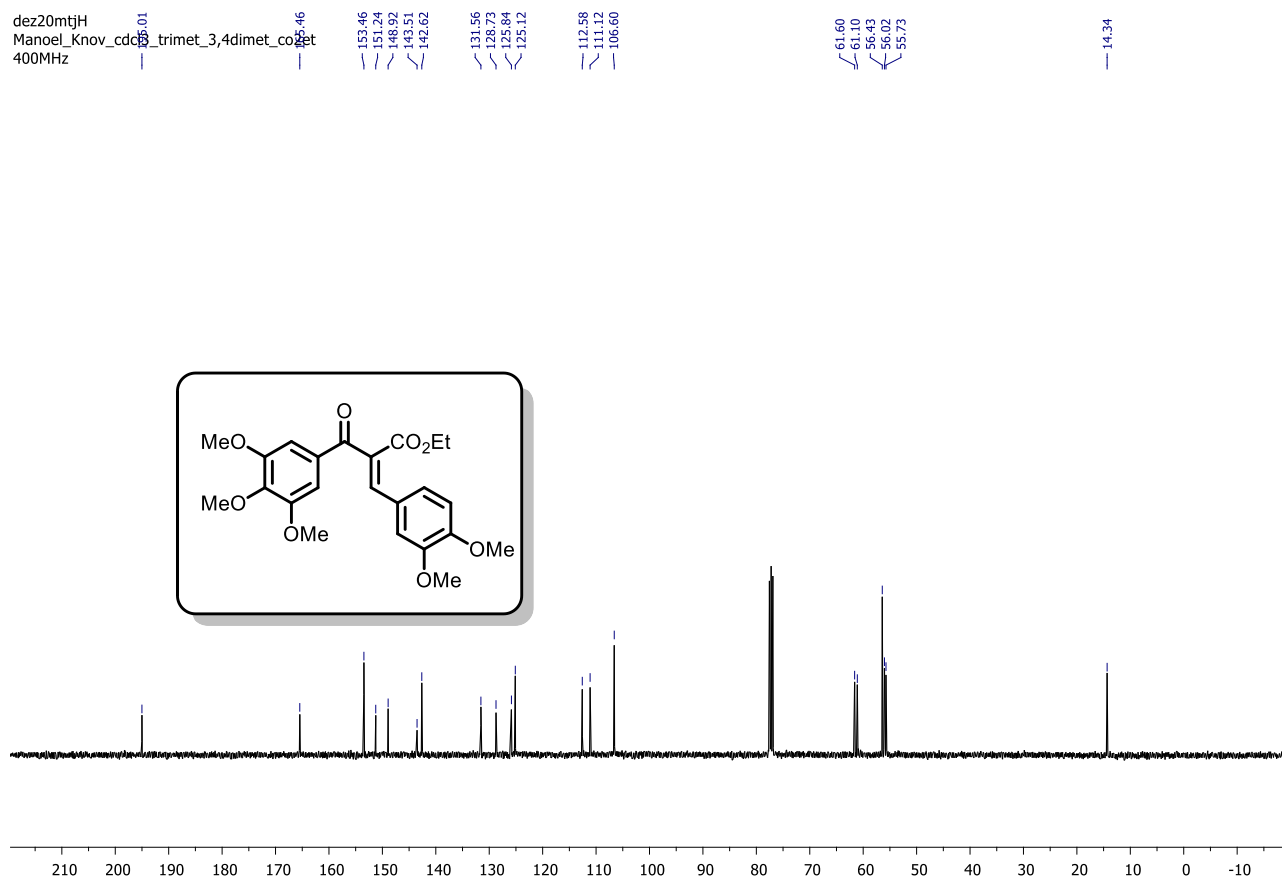


Figure S8. ^{13}C NMR spectrum (101 MHz, CDCl_3) of compound **9ad**.

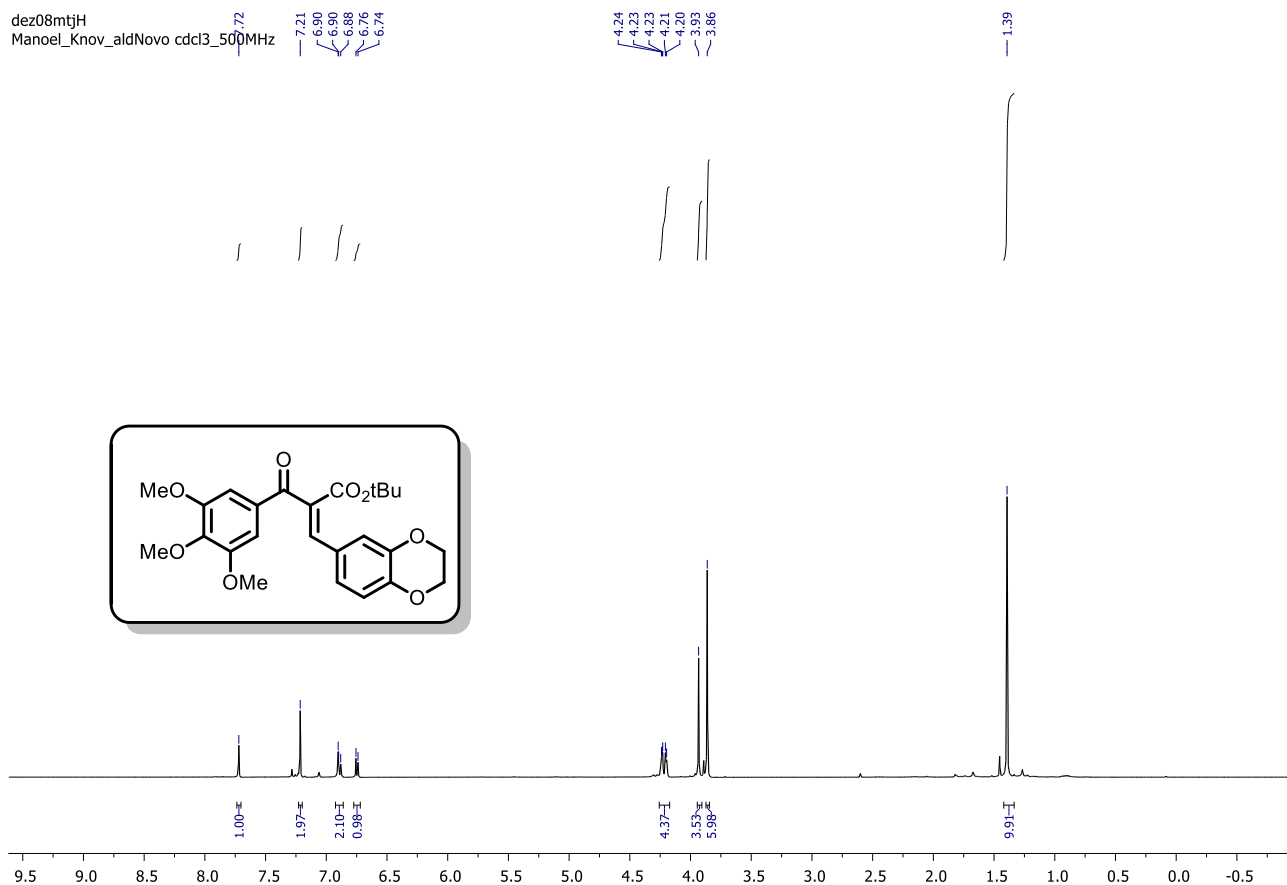


Figure S9. ^1H NMR spectrum (500 MHz, CDCl_3) of compound **9ae**.

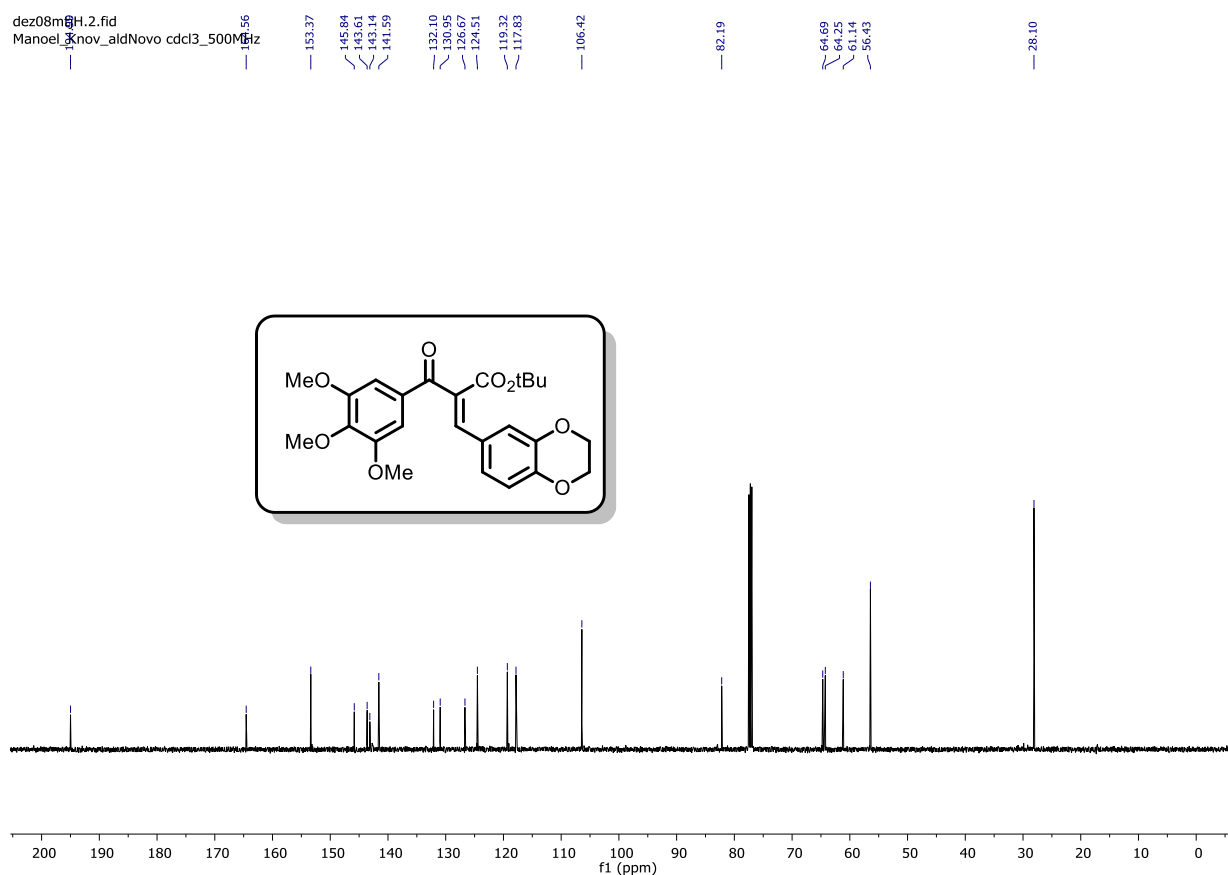


Figure S10. ^{13}C NMR spectrum (126 MHz, CDCl_3) of compound **9ae**.

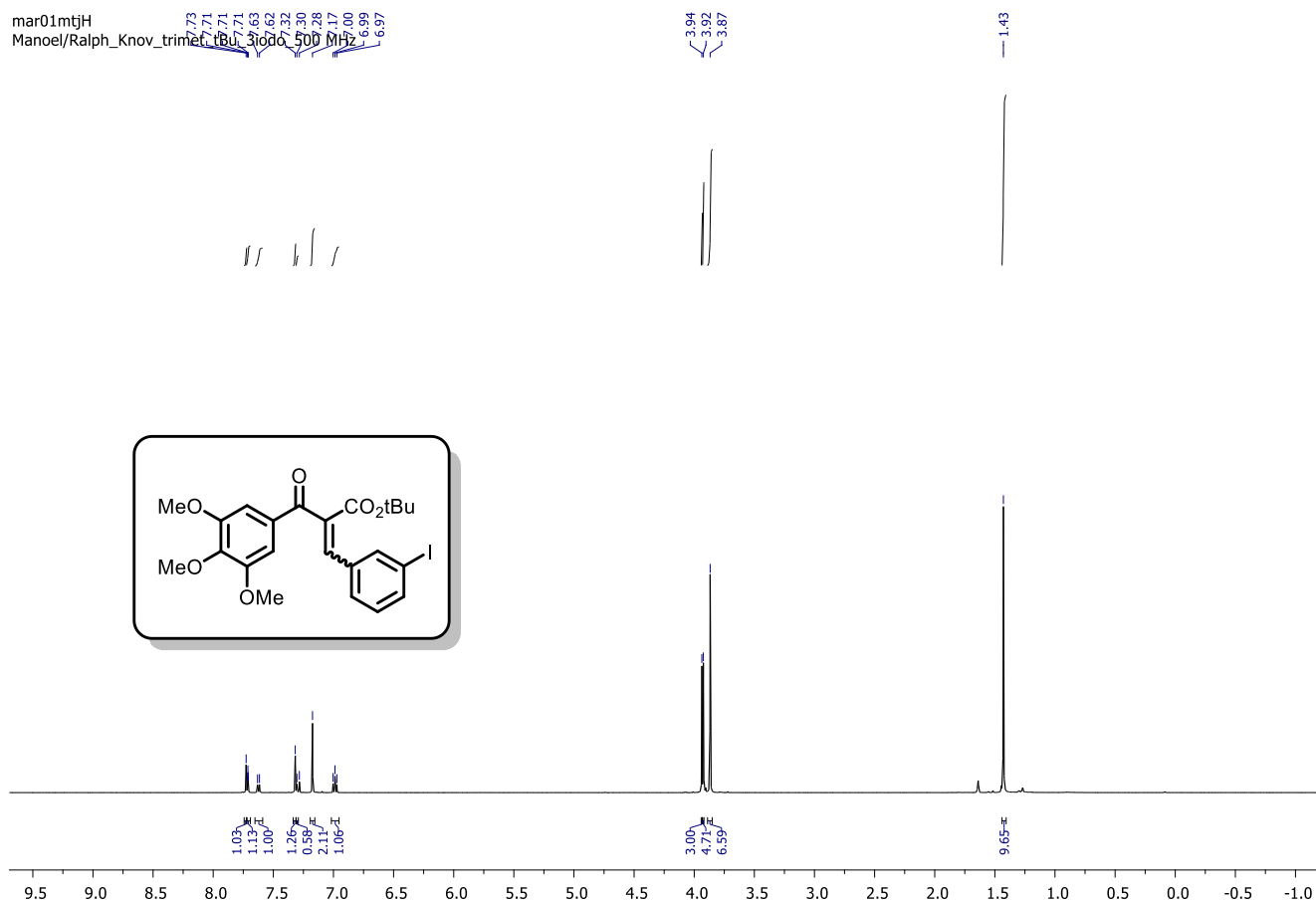


Figure S11. ¹H NMR spectrum (500 MHz, CDCl₃) of compound **9af**.

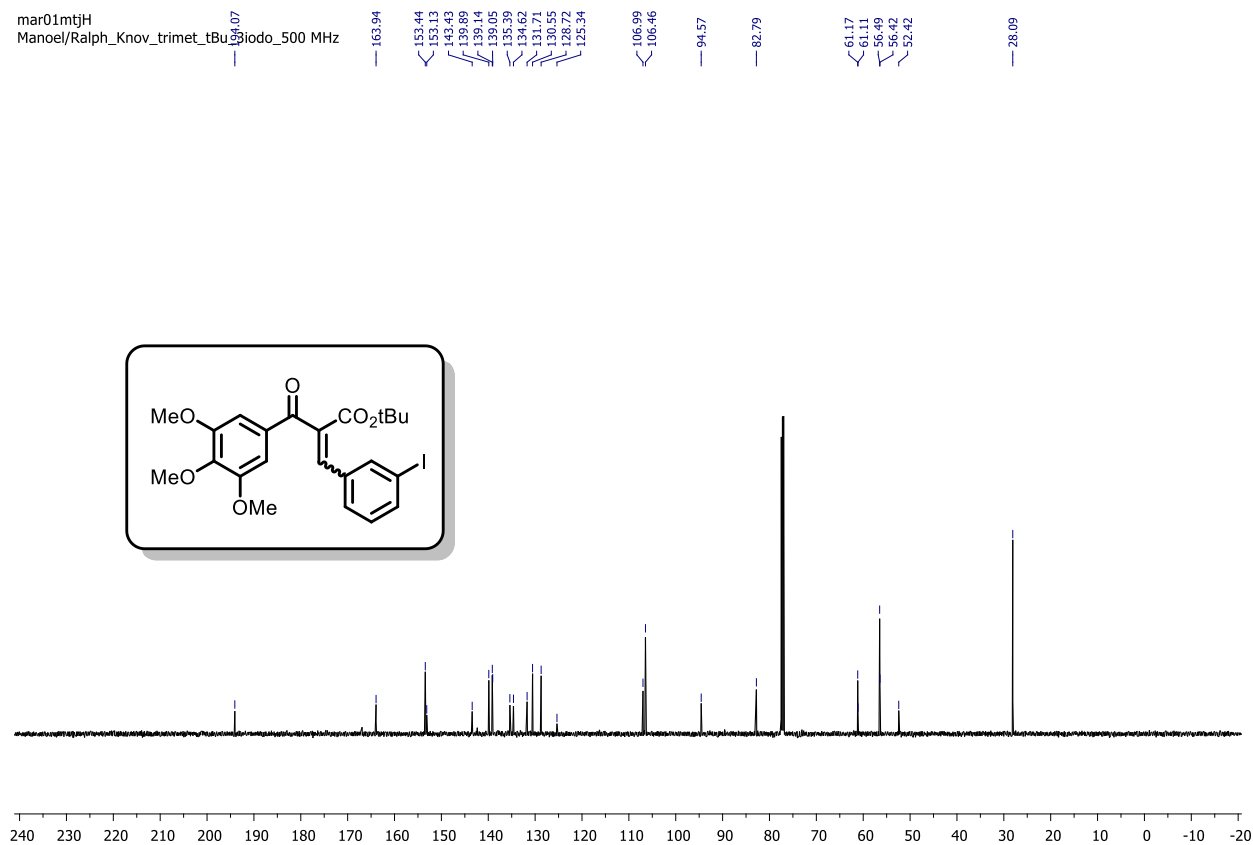
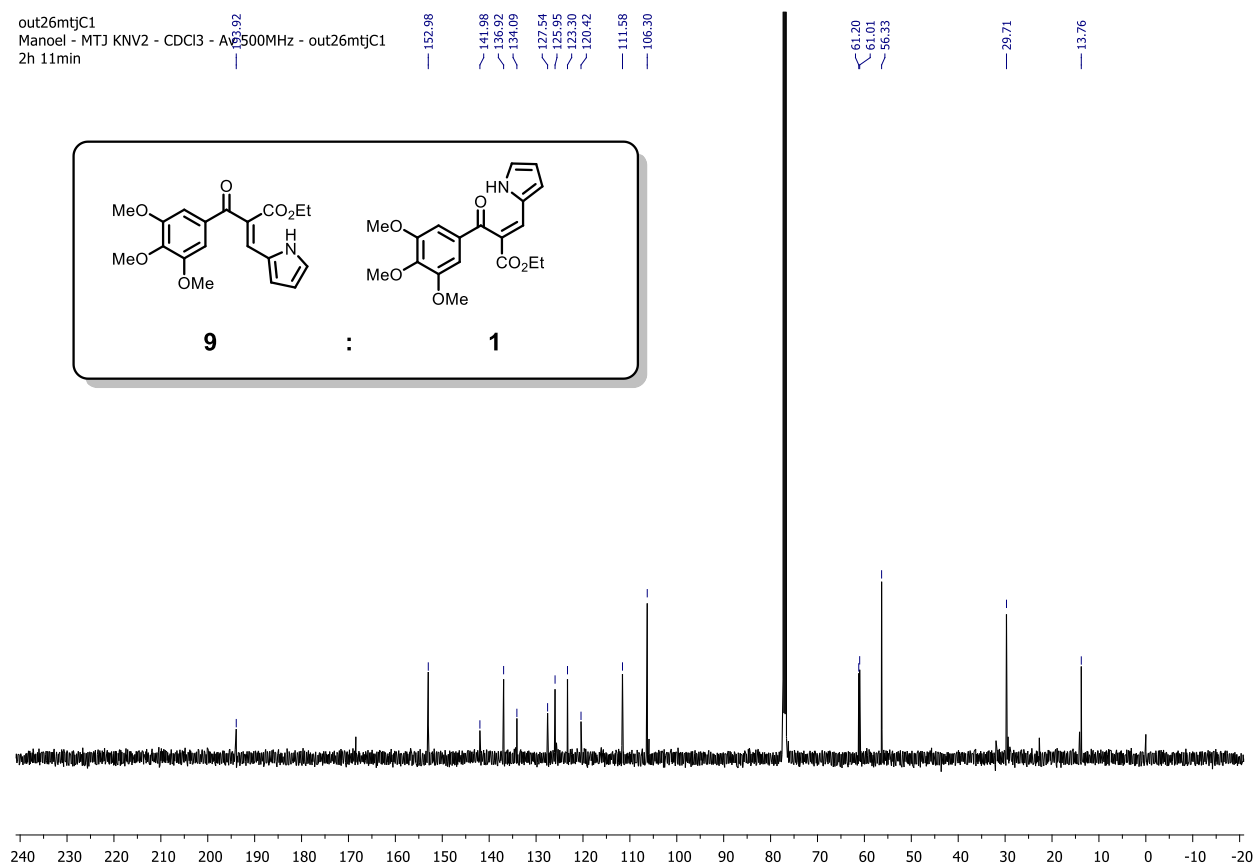
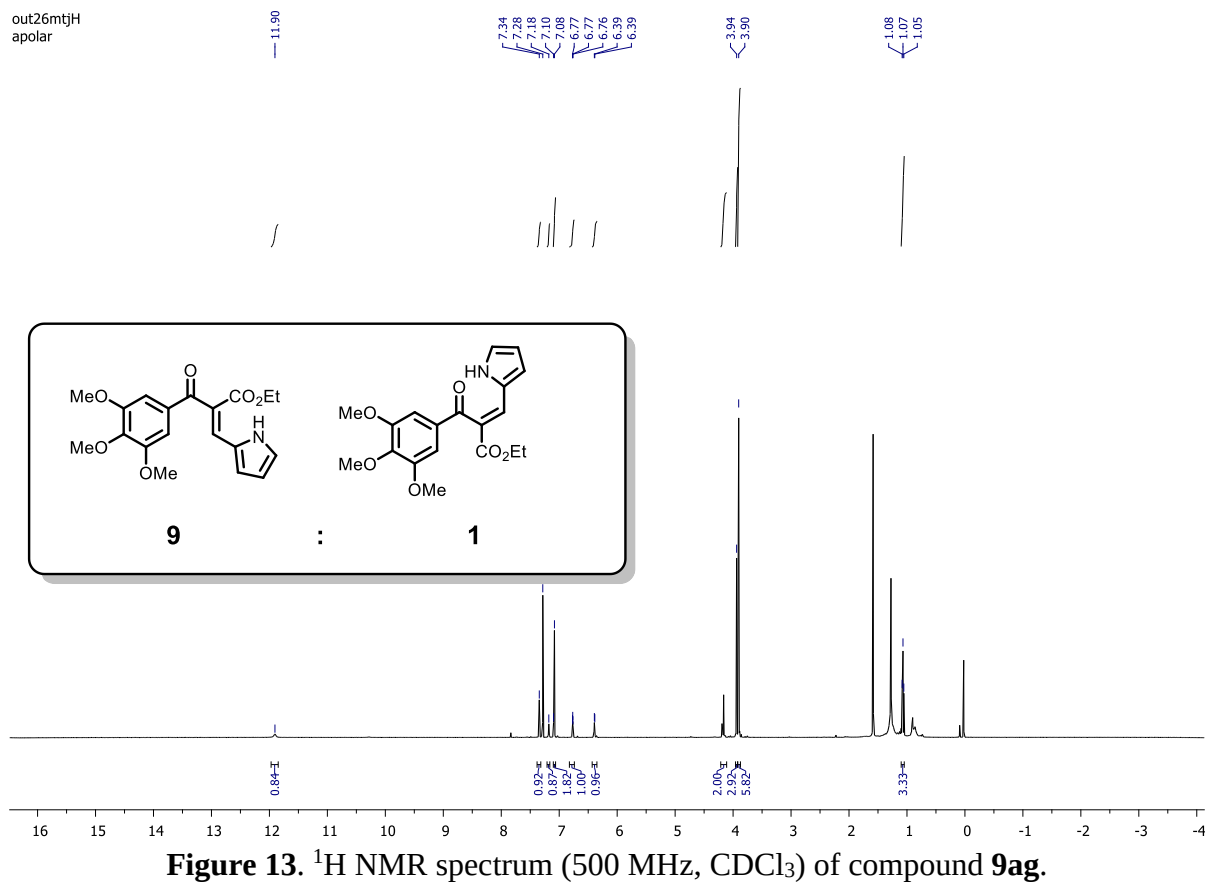
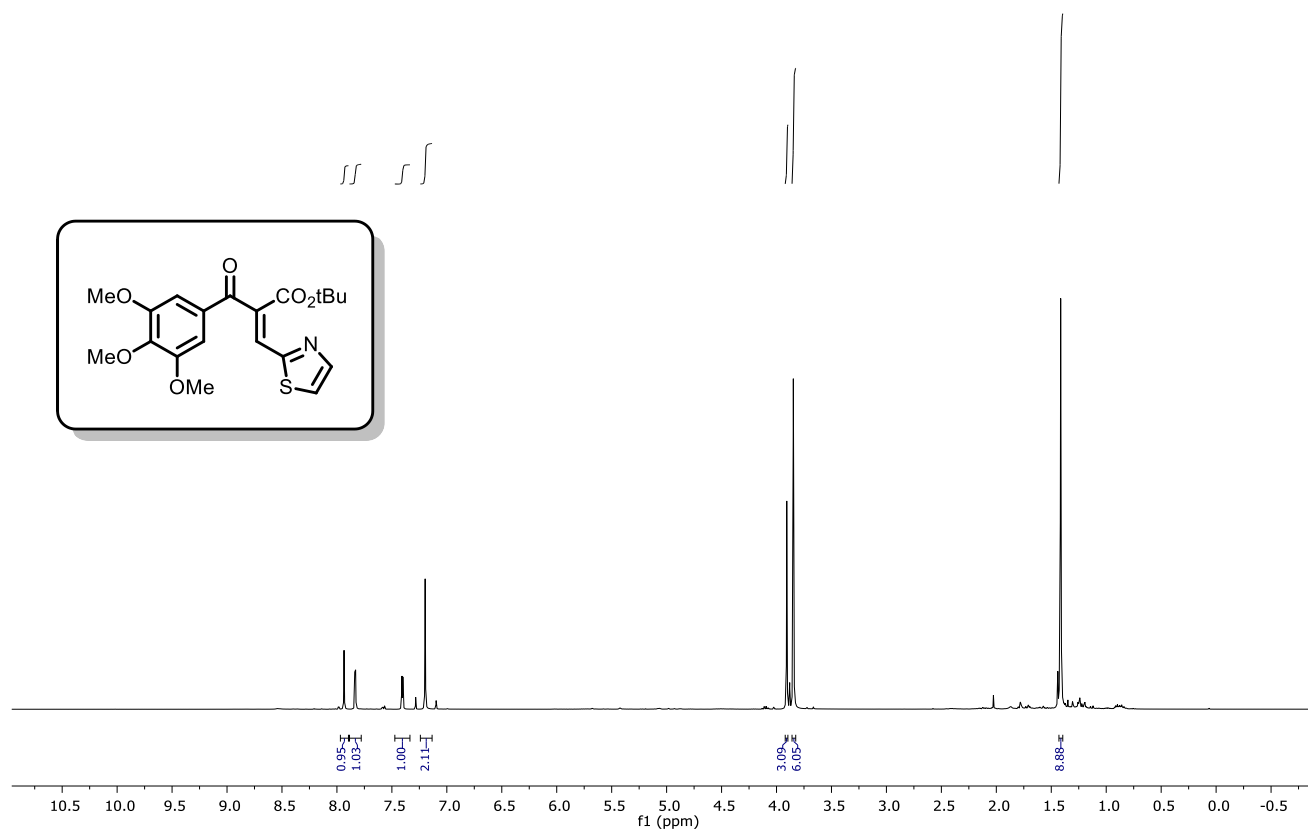
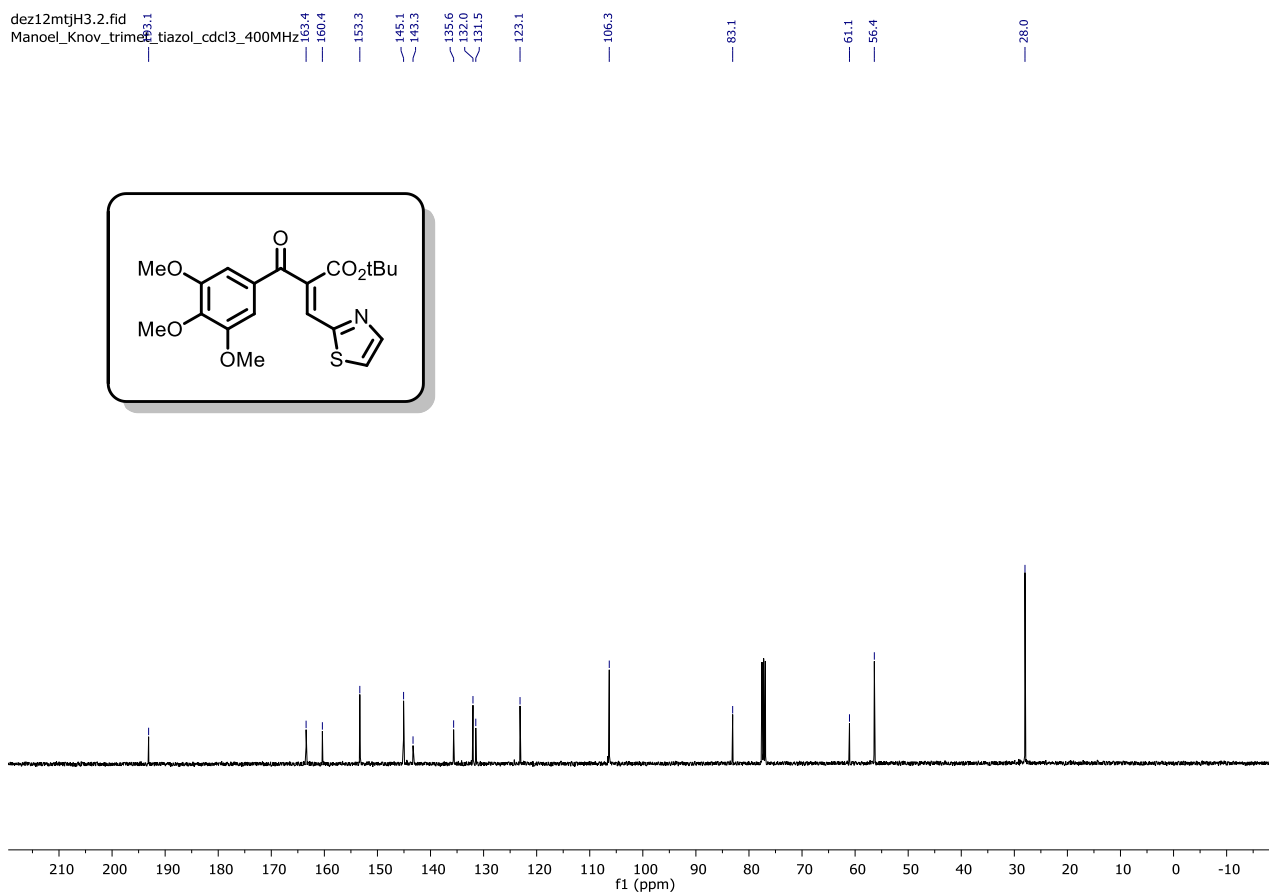


Figure S12. ¹³C NMR spectrum (126 MHz, CDCl₃) of compound **9af**.





dez12mtjH3.2.fid
Manoel_Knov_trimet_tiazol_cdcl3_400MHz



out23mtjH2.1.fid

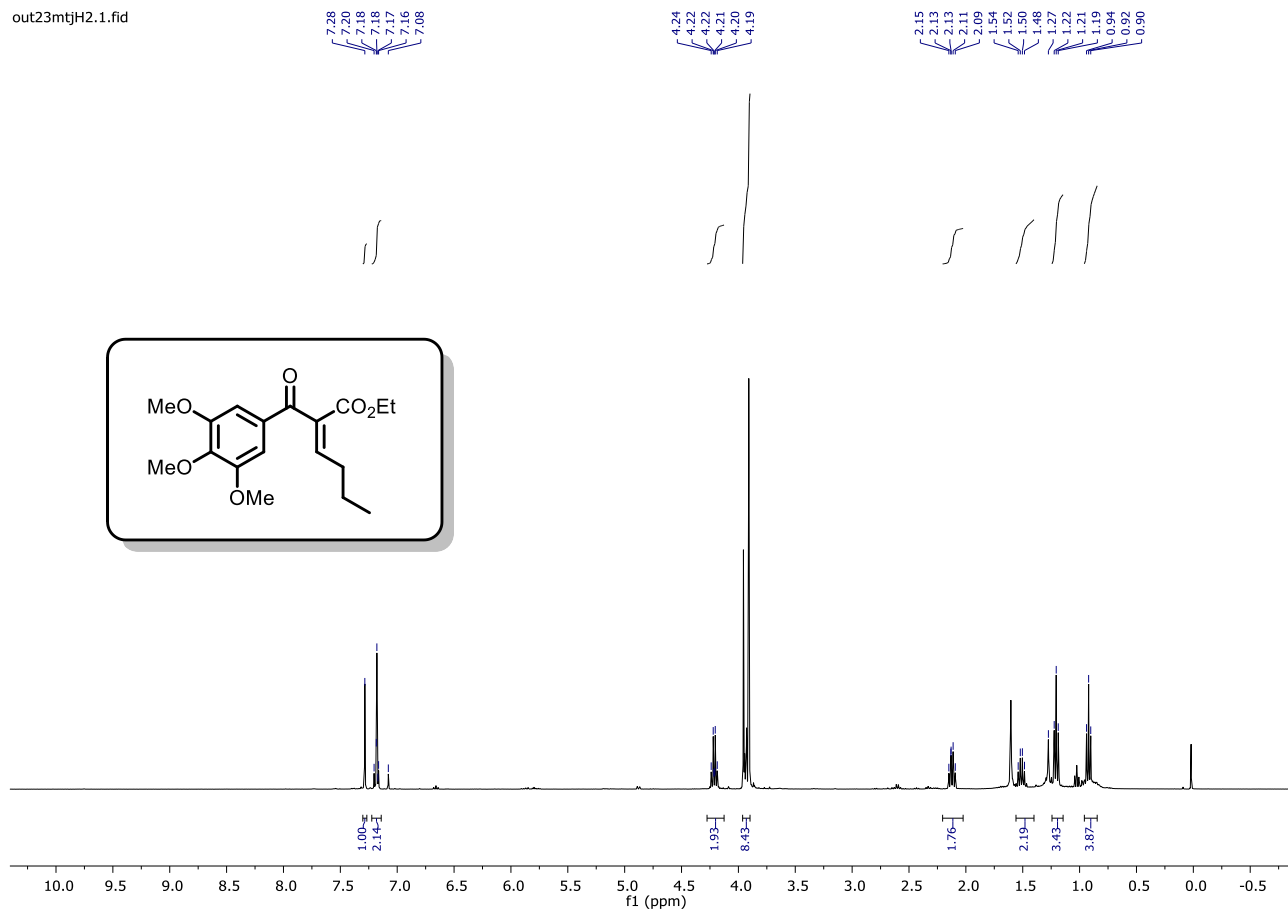


Figure S17. ¹H NMR spectrum (400 MHz, CDCl₃) of compound **9ai**.

out24mtjC1.1.fid
Manoel - MTJ KNV
5 horas

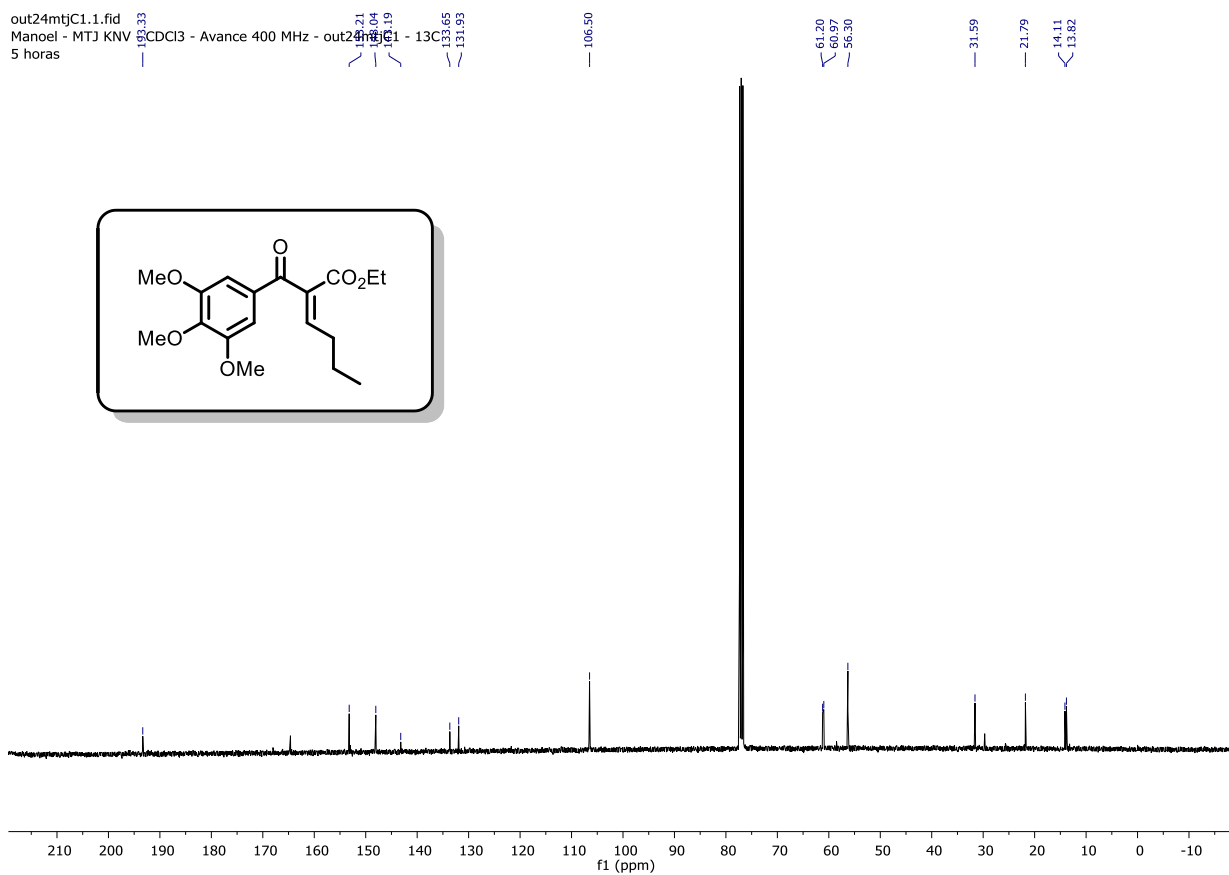


Figure S18. ¹³C NMR spectrum (101 MHz, CDCl₃) of compound **9ai**.

fev05mtjH
Manoel_Knov_3,5-dimet_trimet_Co2et
CDCl3

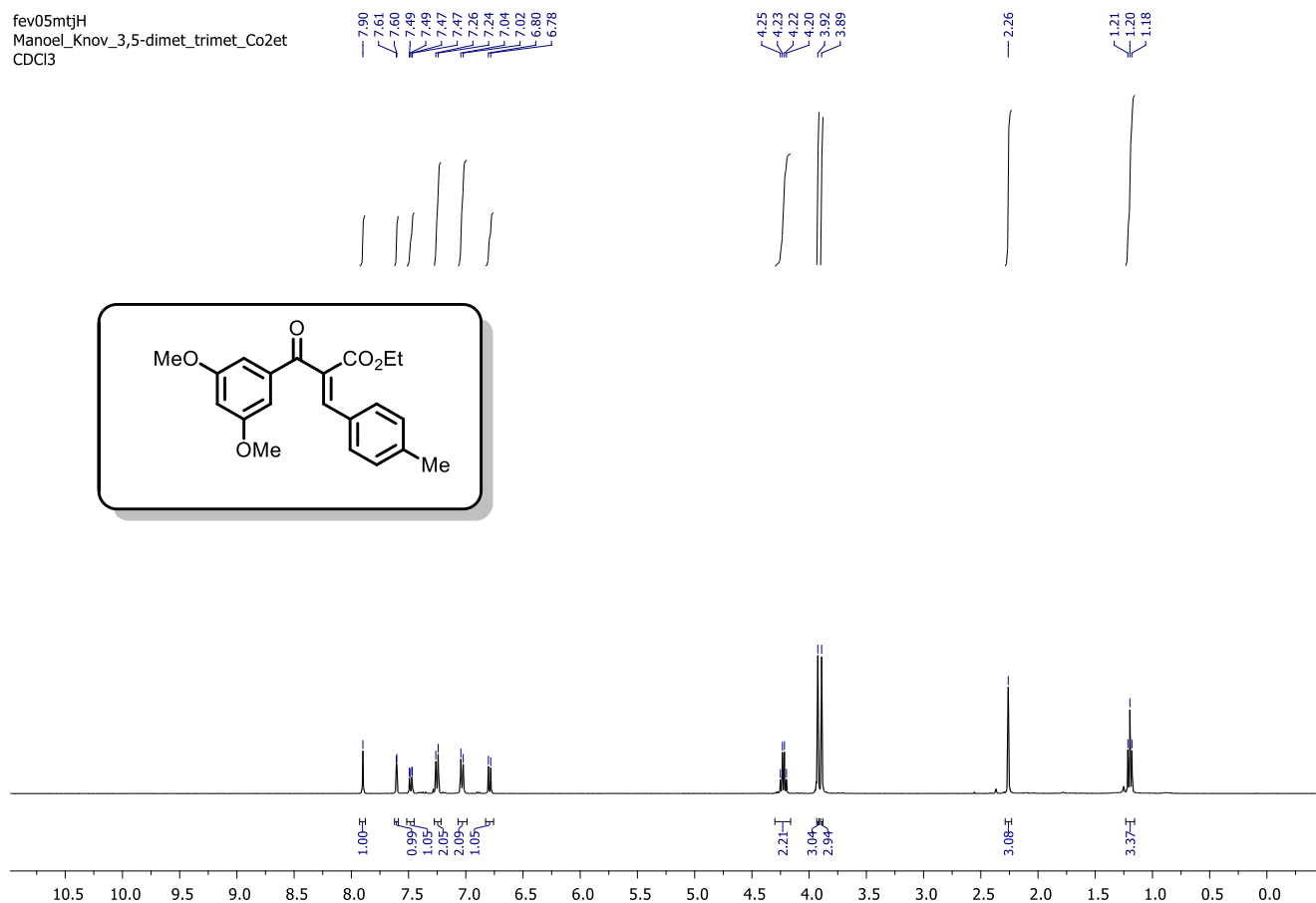


Figure S19. ¹H NMR spectrum (400 MHz, CDCl₃) of compound **9bj**.

fev05mtjH
Manoel_Knov_3,5-dimet_trimet_Co2et
CDCl3

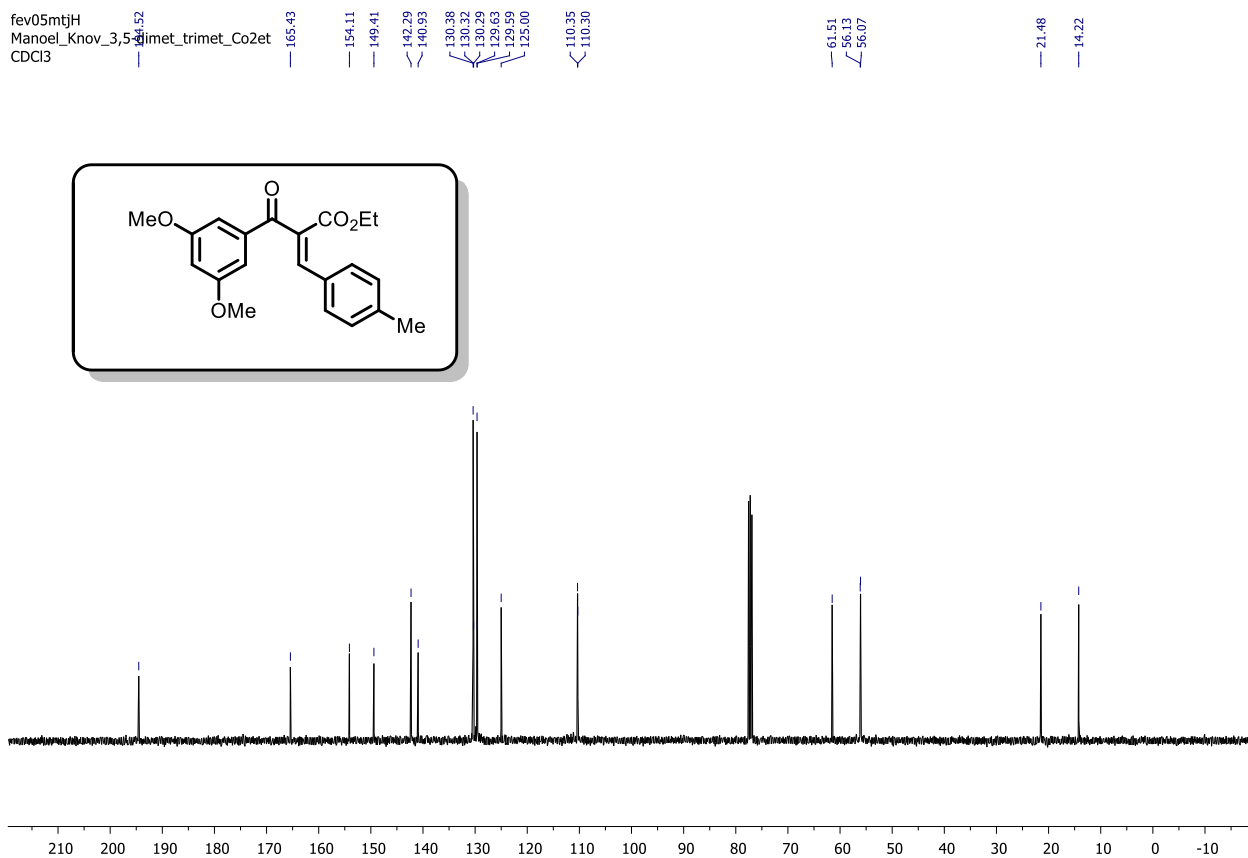


Figure S20. ¹³C NMR spectrum (101 MHz, CDCl₃) of compound **9bj**.

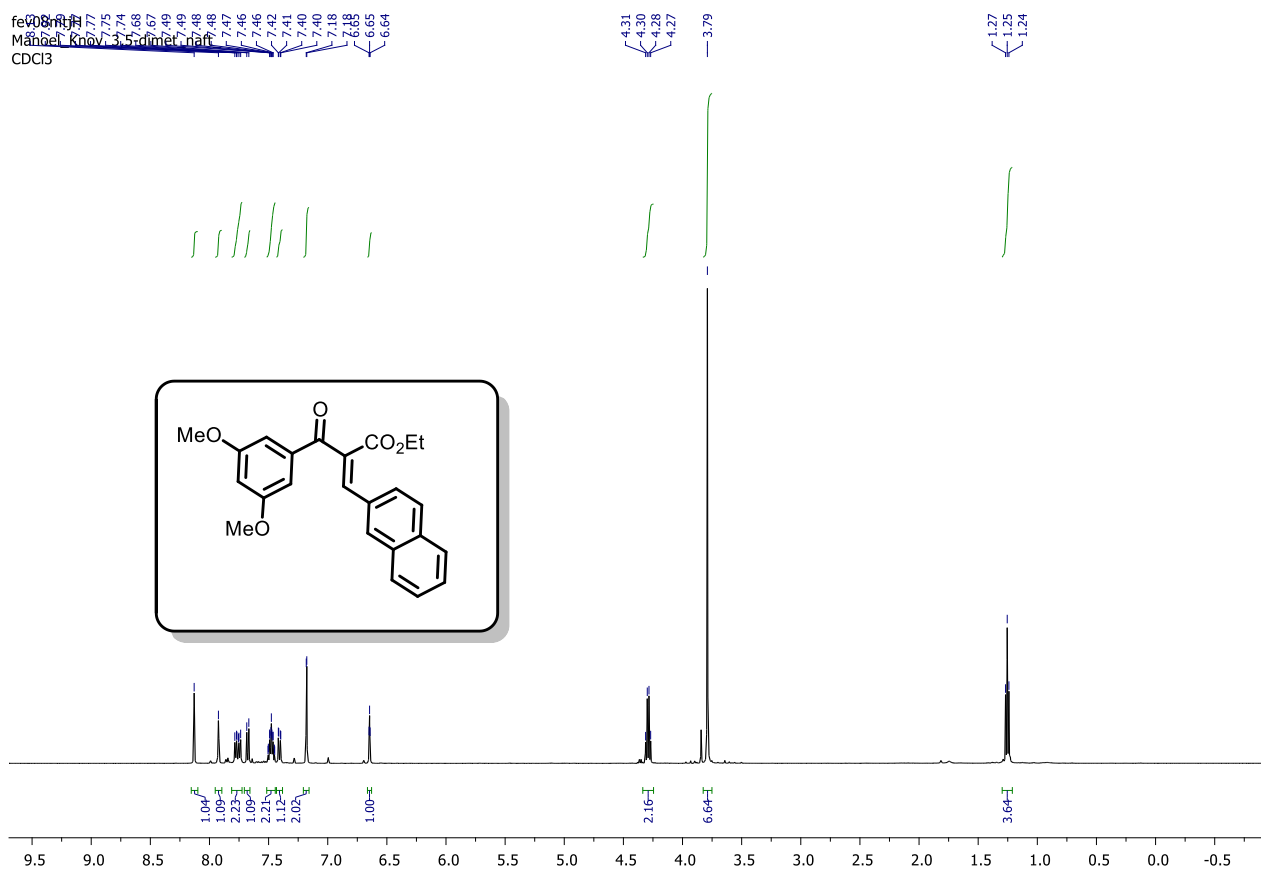


Figure S21. ¹H NMR spectrum (500 MHz, CDCl₃) of compound **9bk**.

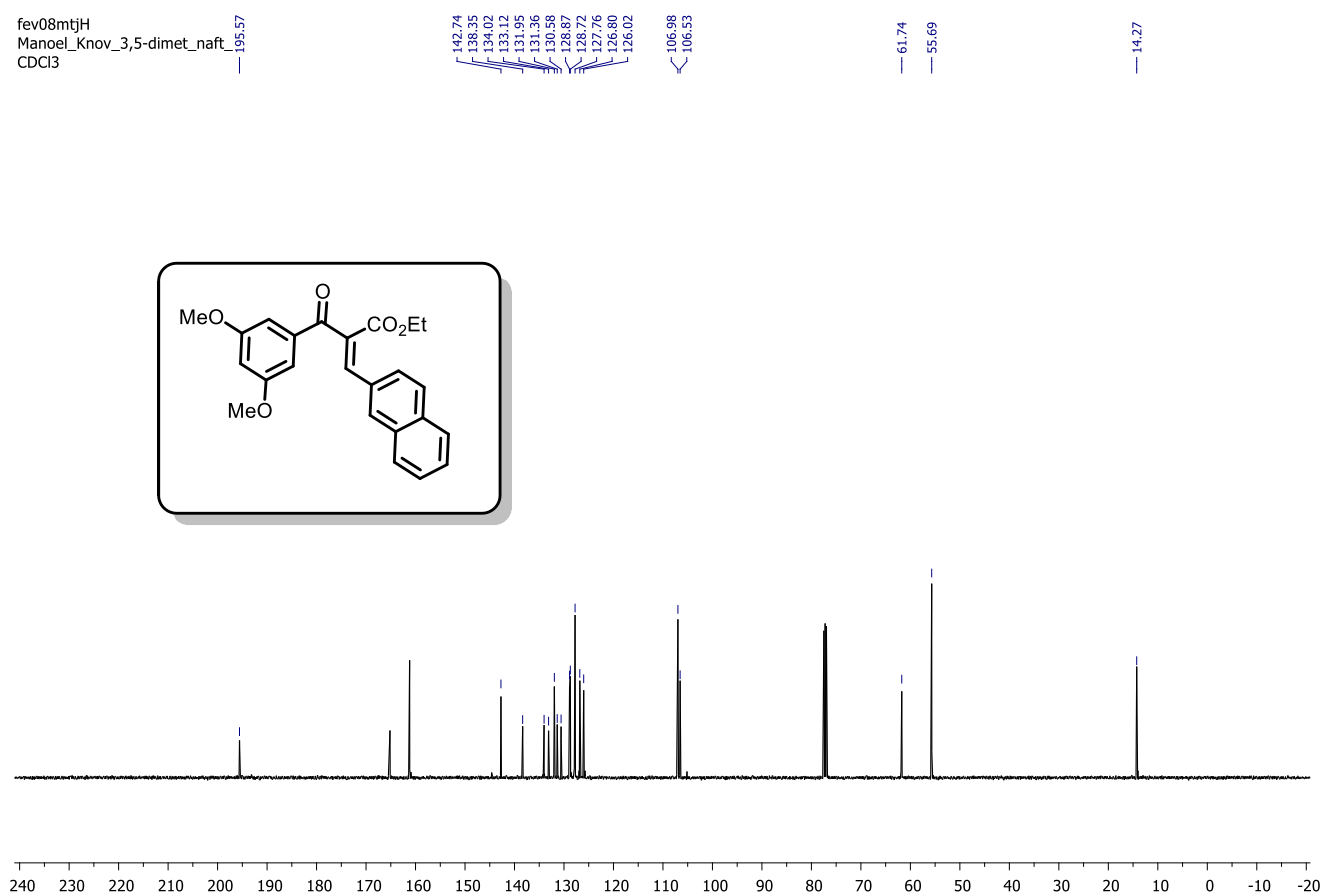


Figure S22. ¹³C NMR spectrum (126 MHz, CDCl₃) of compound **9bk**.

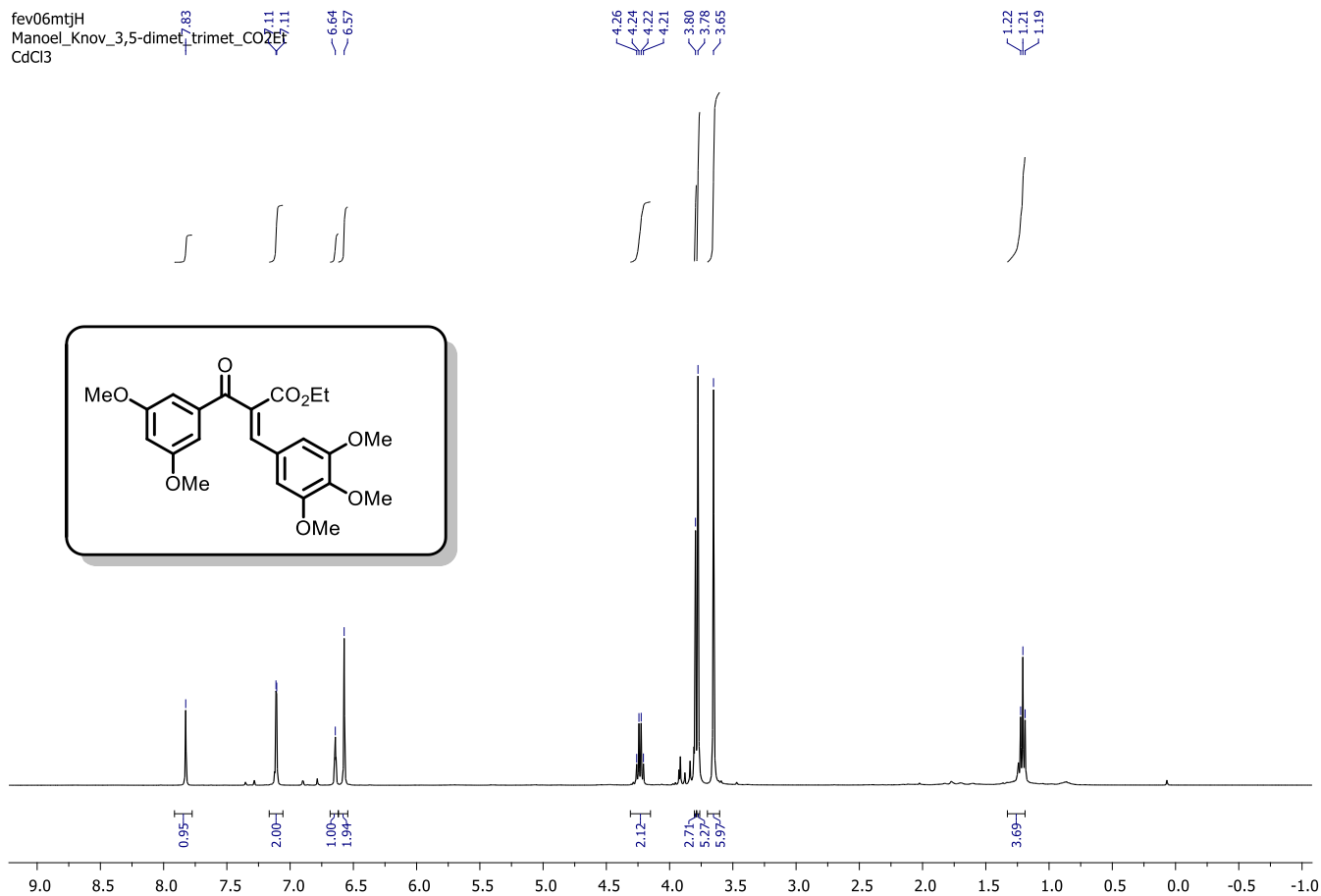


Figure S23. ¹H NMR spectrum (400 MHz, CDCl₃) of compound **9bc**.

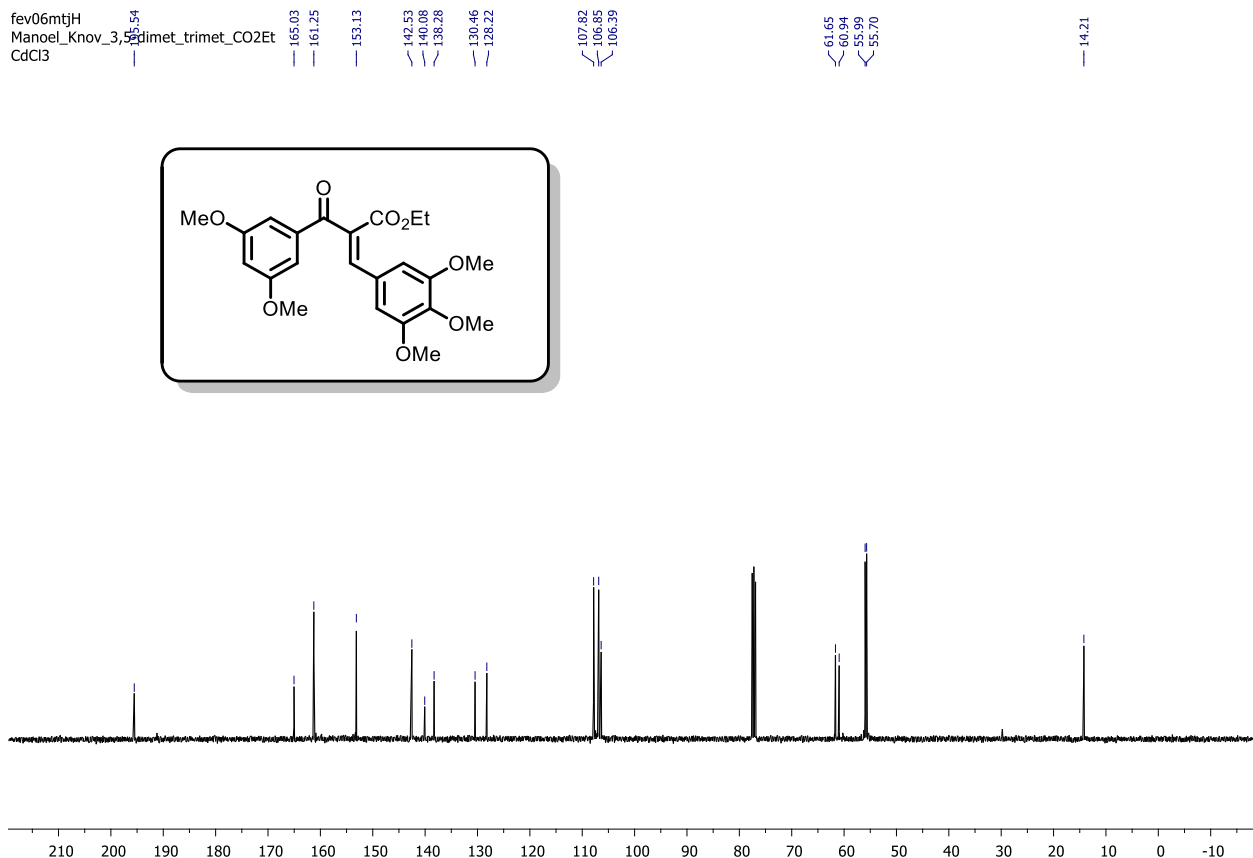
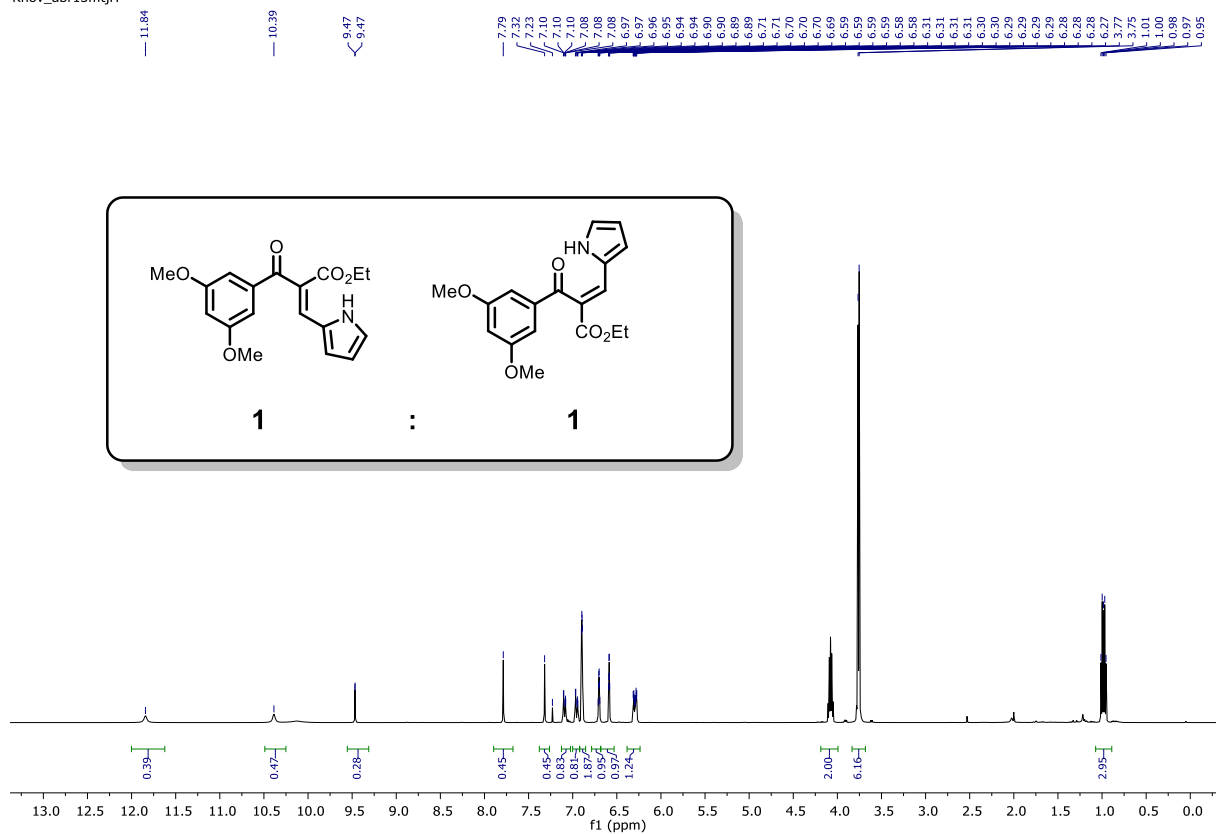
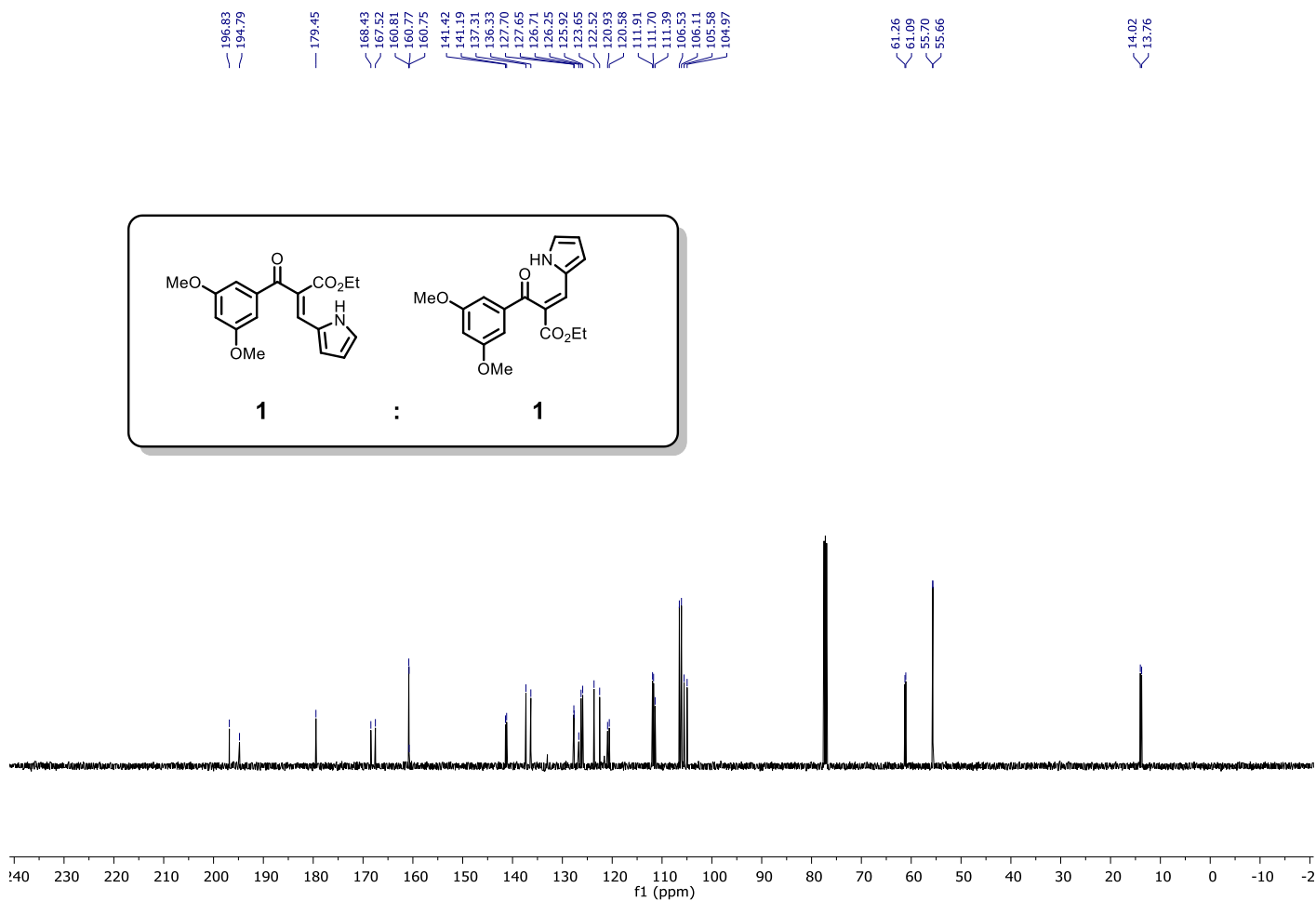


Figure S24. ¹³C NMR spectrum (101 MHz, CDCl₃) of compound **9bc**.

Figure S25. ¹H NMR spectrum (500 MHz, CDCl₃) of compound 9bg.Figure S26. ¹³C NMR spectrum (126 MHz, CDCl₃) of compound 9bg.

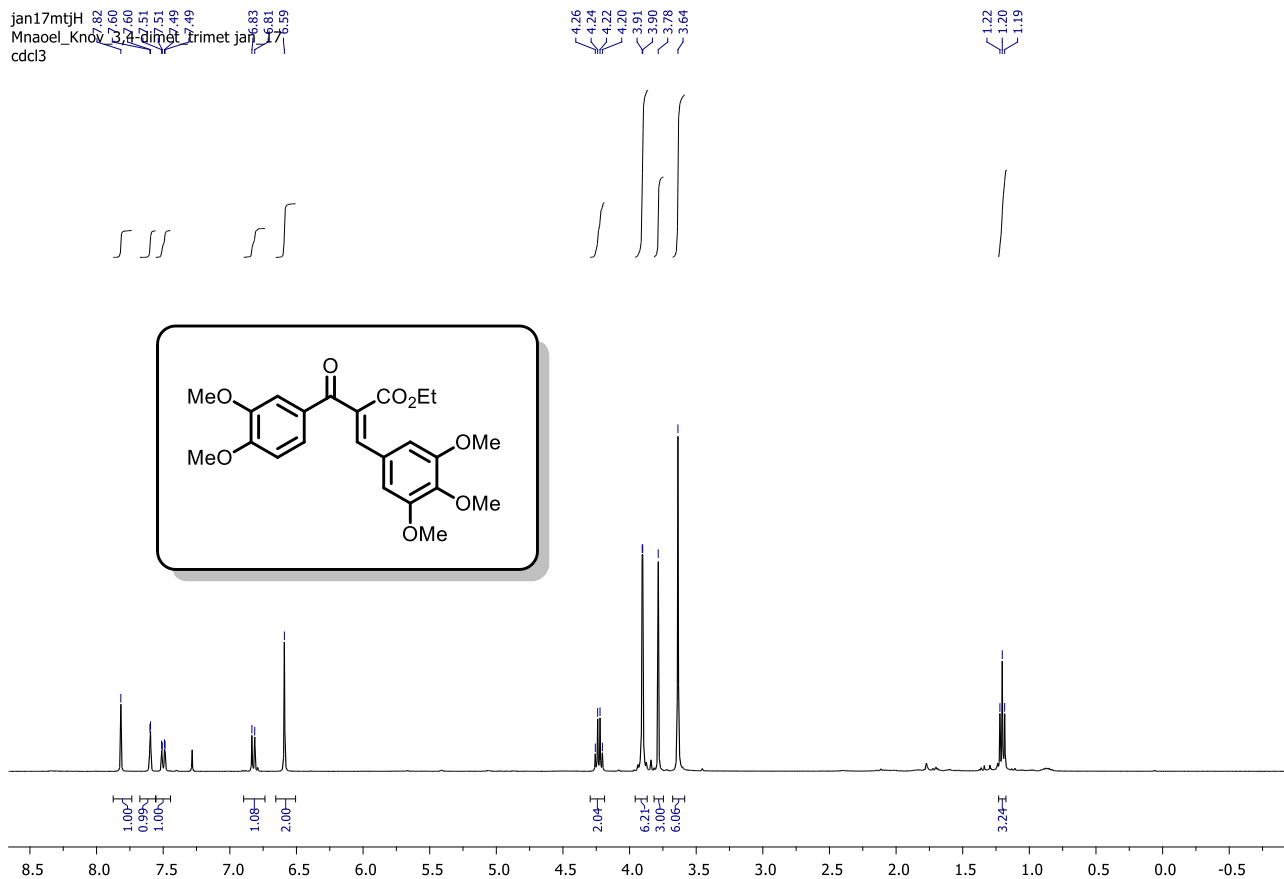


Figure S27. ¹H NMR spectrum (400 MHz, CDCl₃) of compound 9cc.

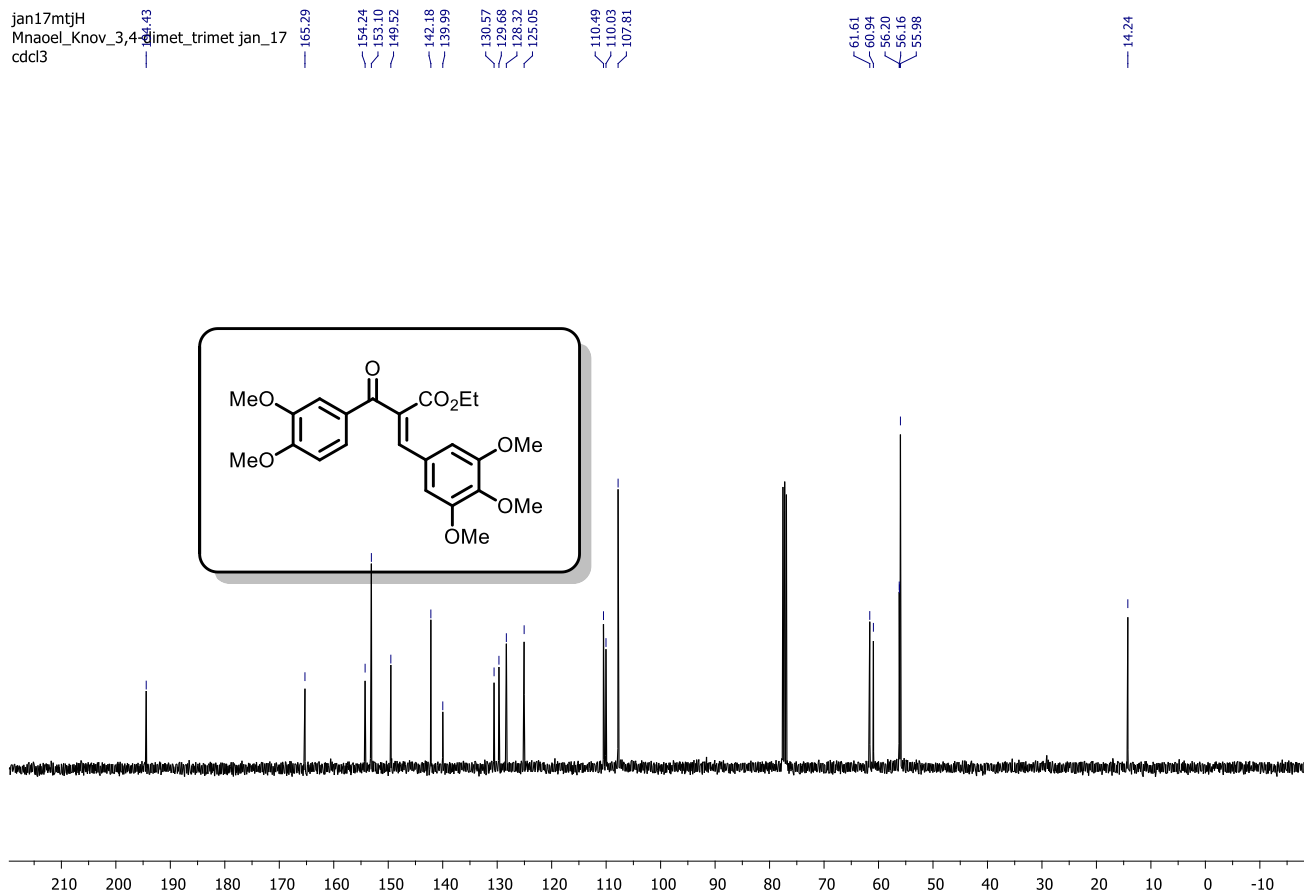
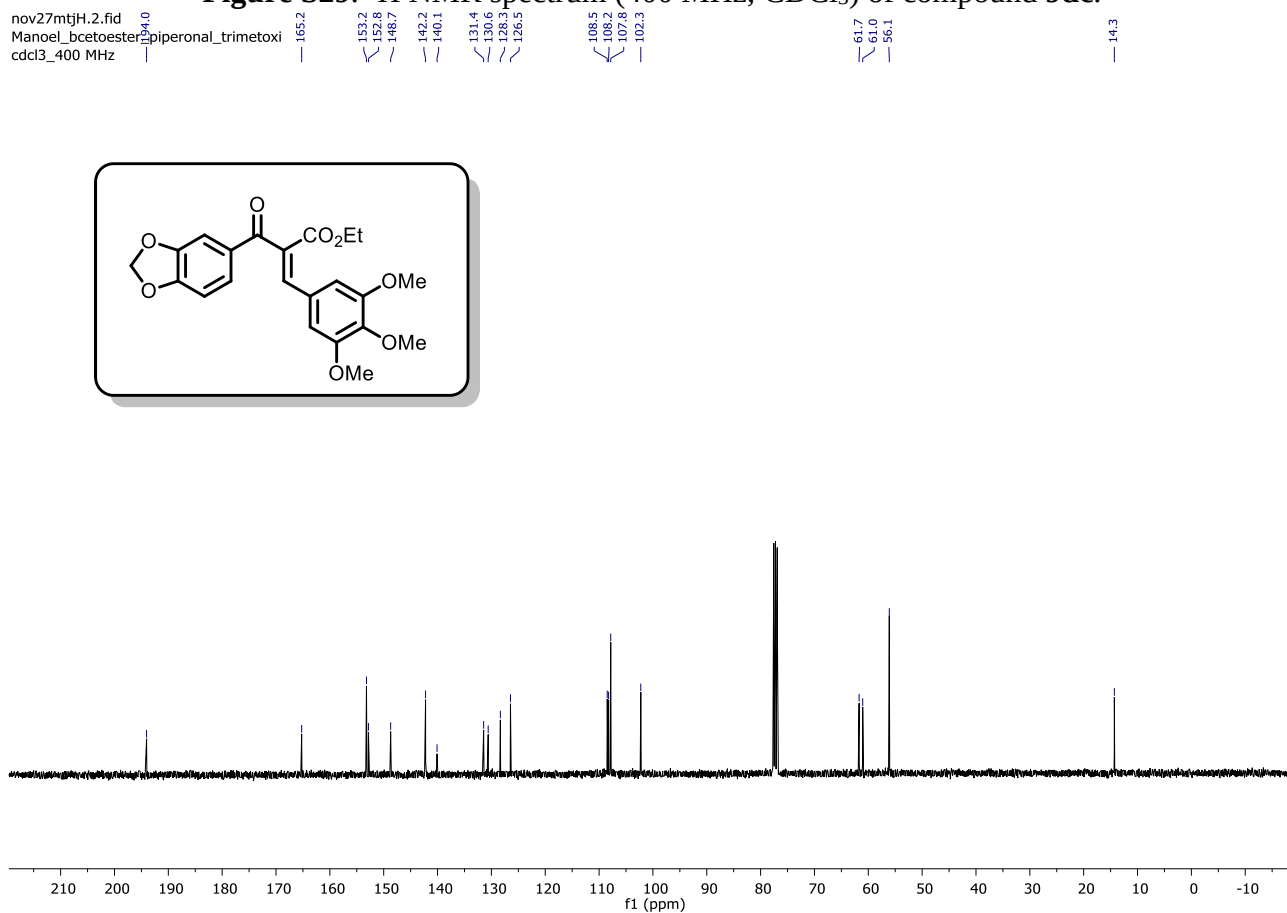
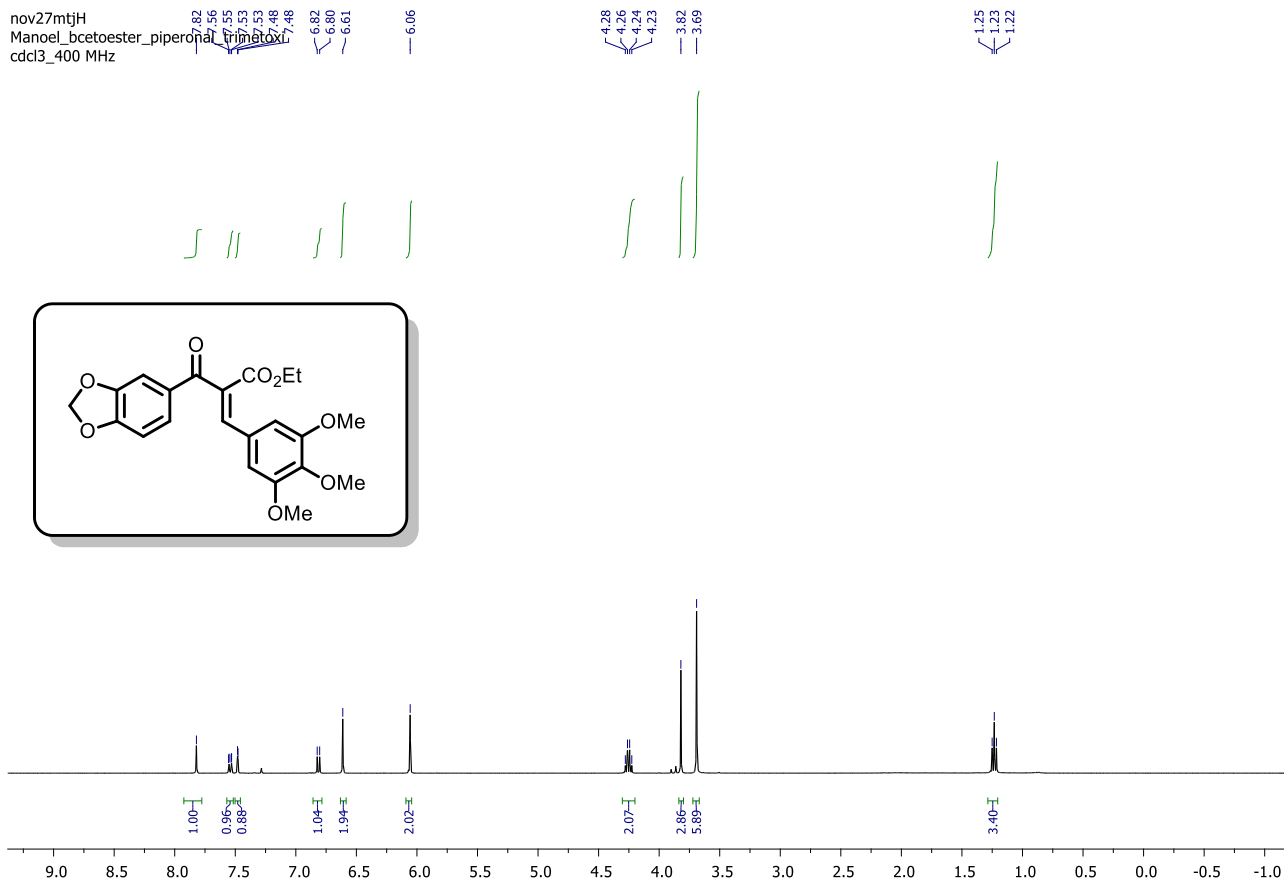


Figure S28. ¹³C NMR spectrum (101 MHz, CDCl₃) of compound 9cc.



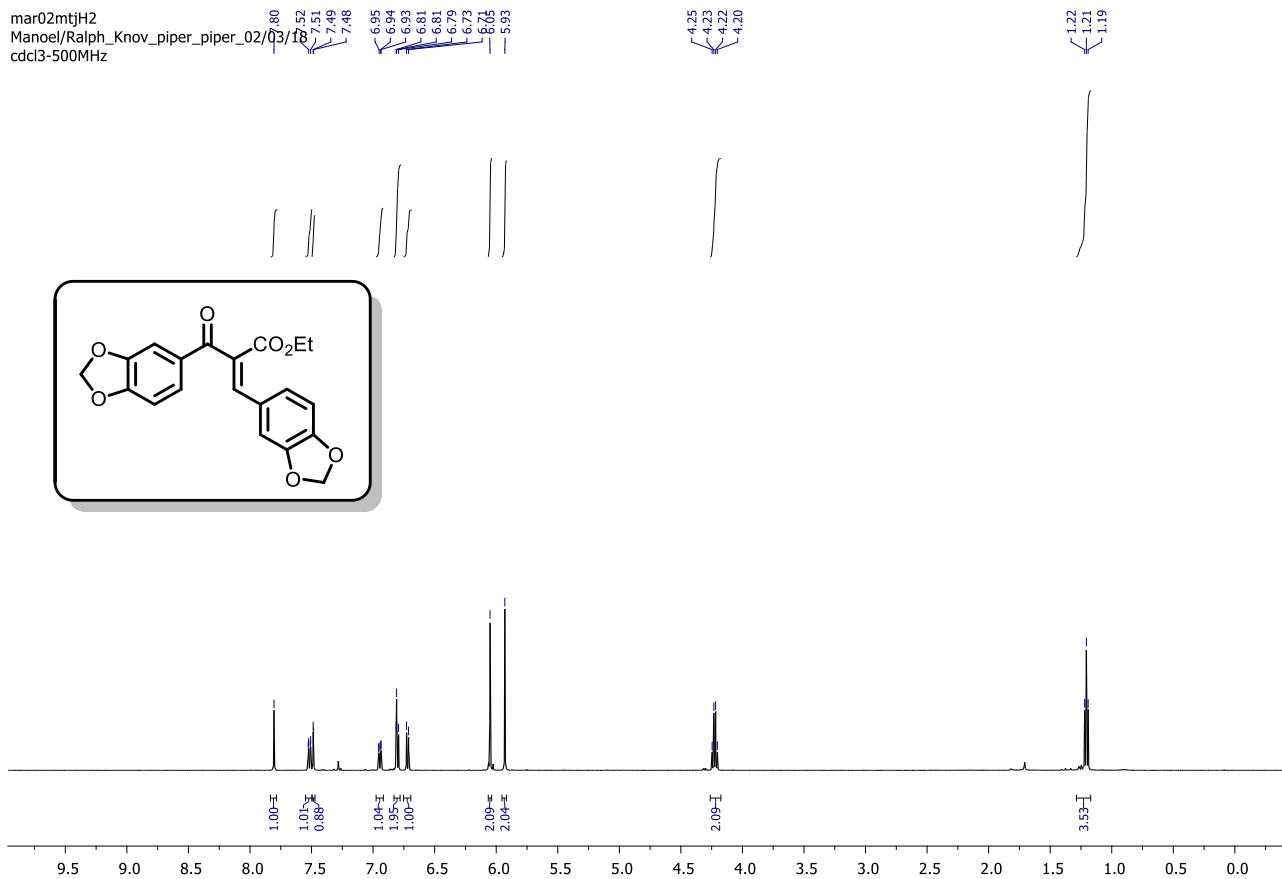


Figure S31. ¹H NMR spectrum (500 MHz, CDCl₃) of compound 9dl.

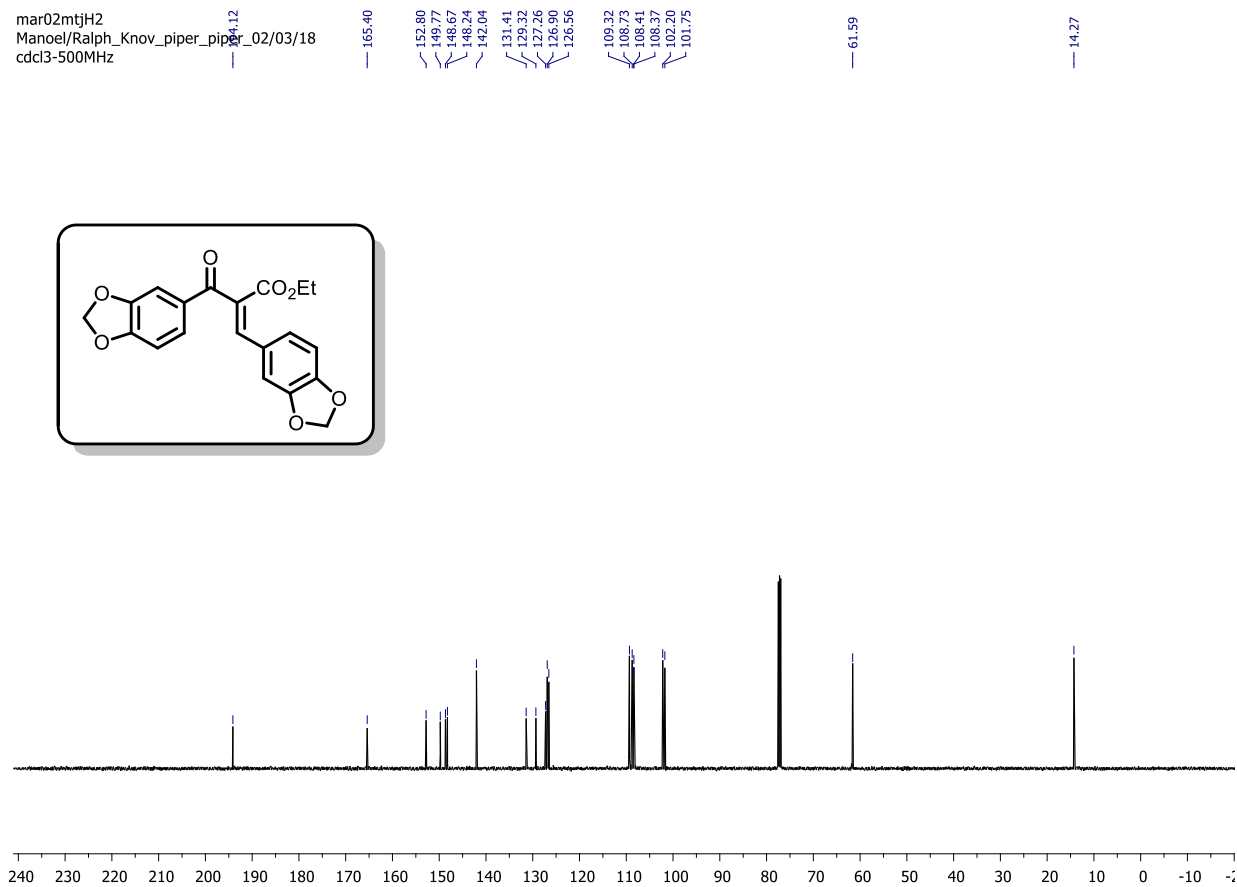


Figure S32. ¹³C NMR spectrum (126 MHz, CDCl₃) of compound 9dl.

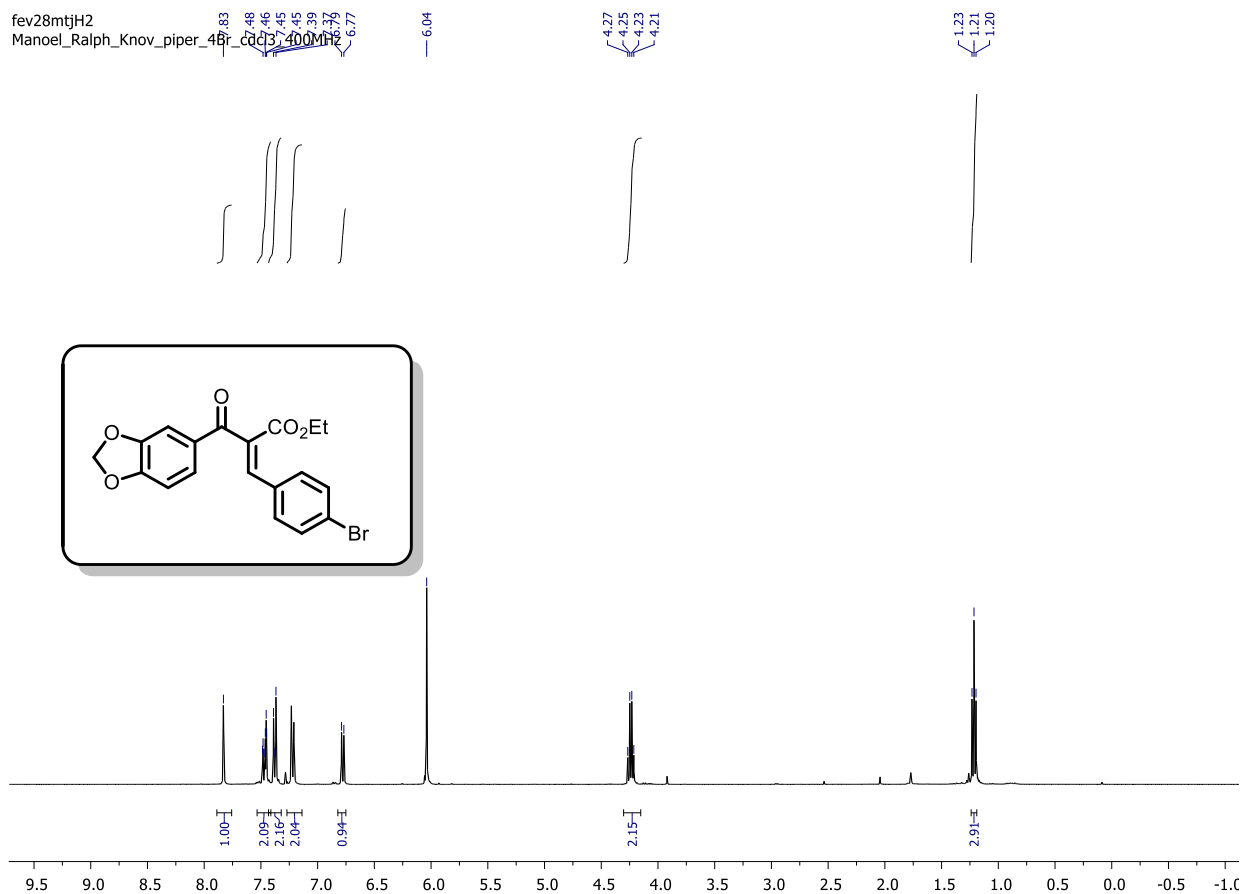


Figure S33. ^1H NMR spectrum (400 MHz, CDCl_3) of compound **9dm**.

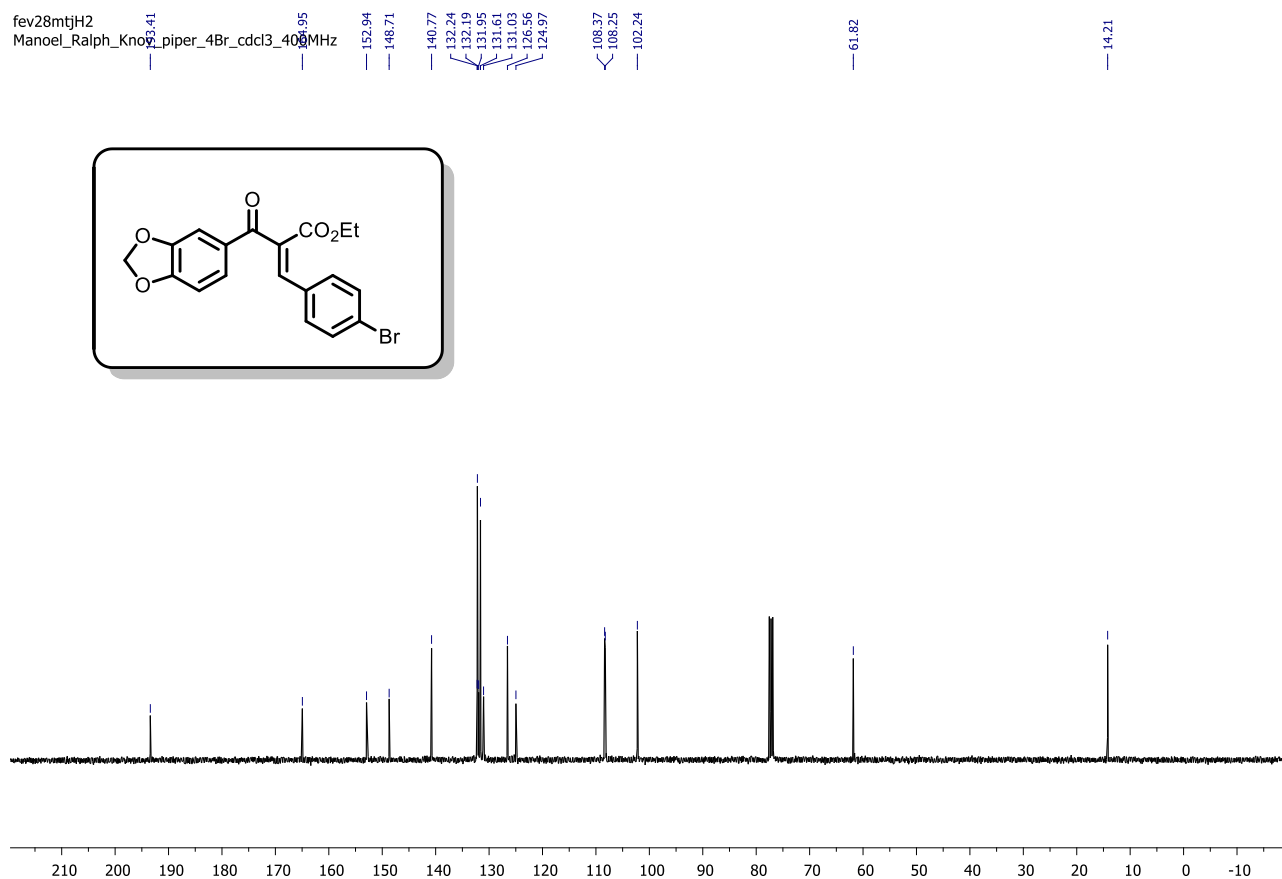
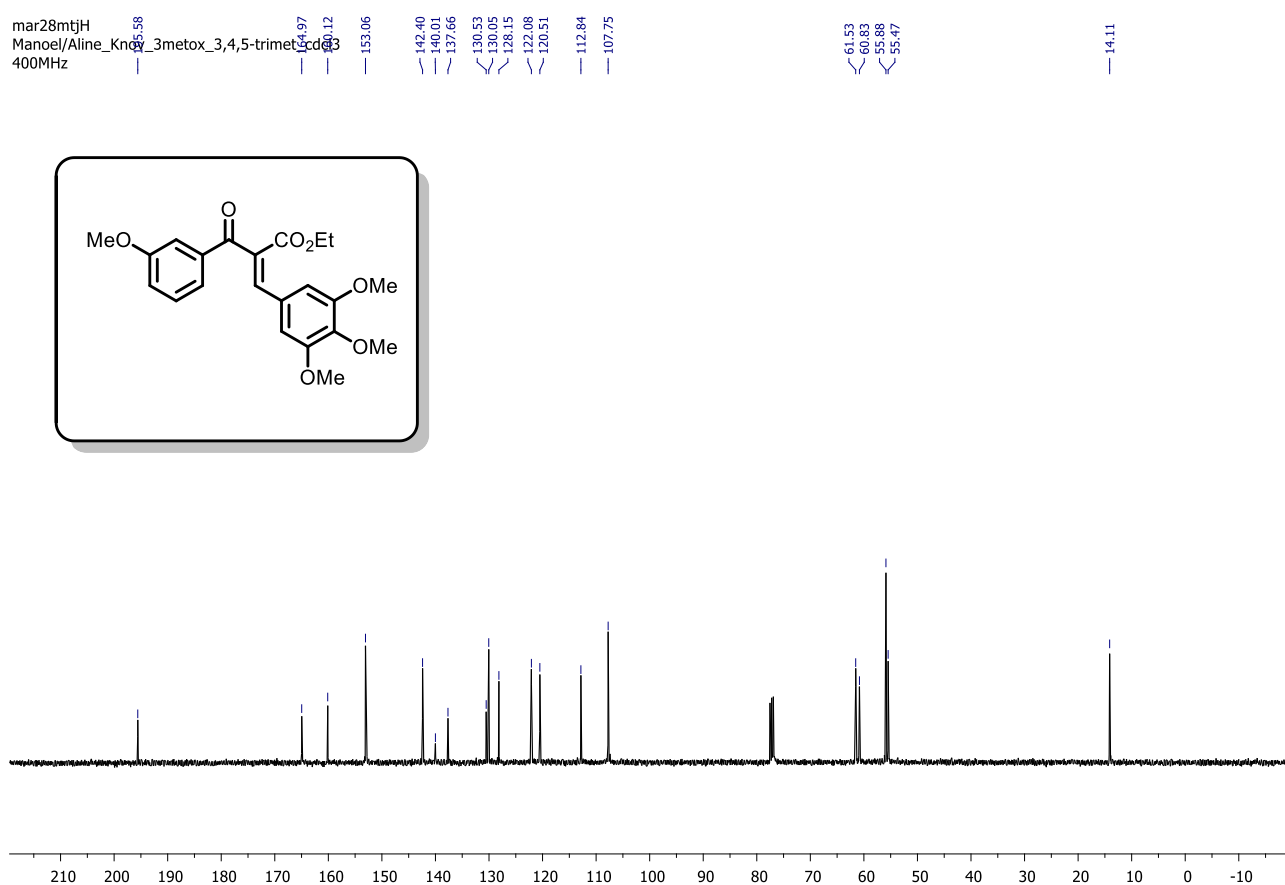
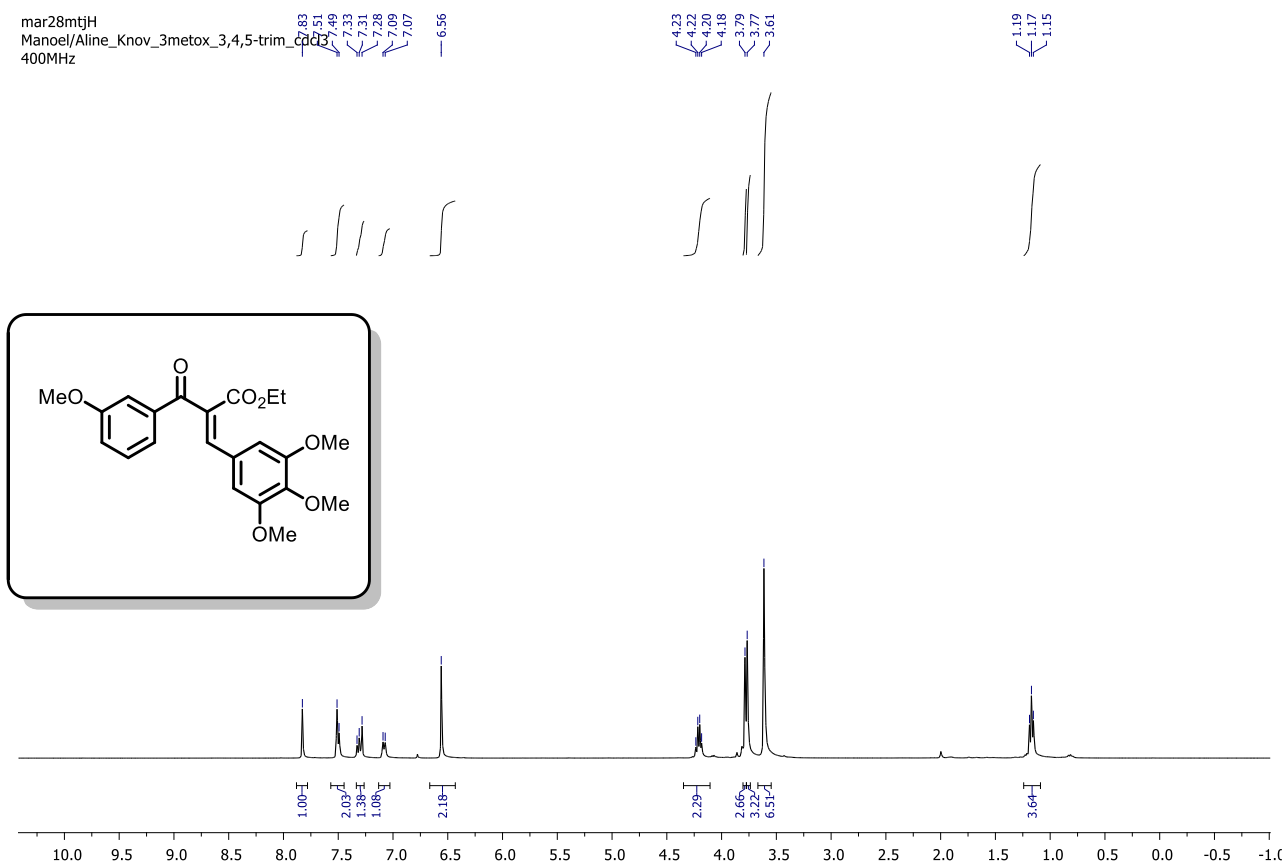
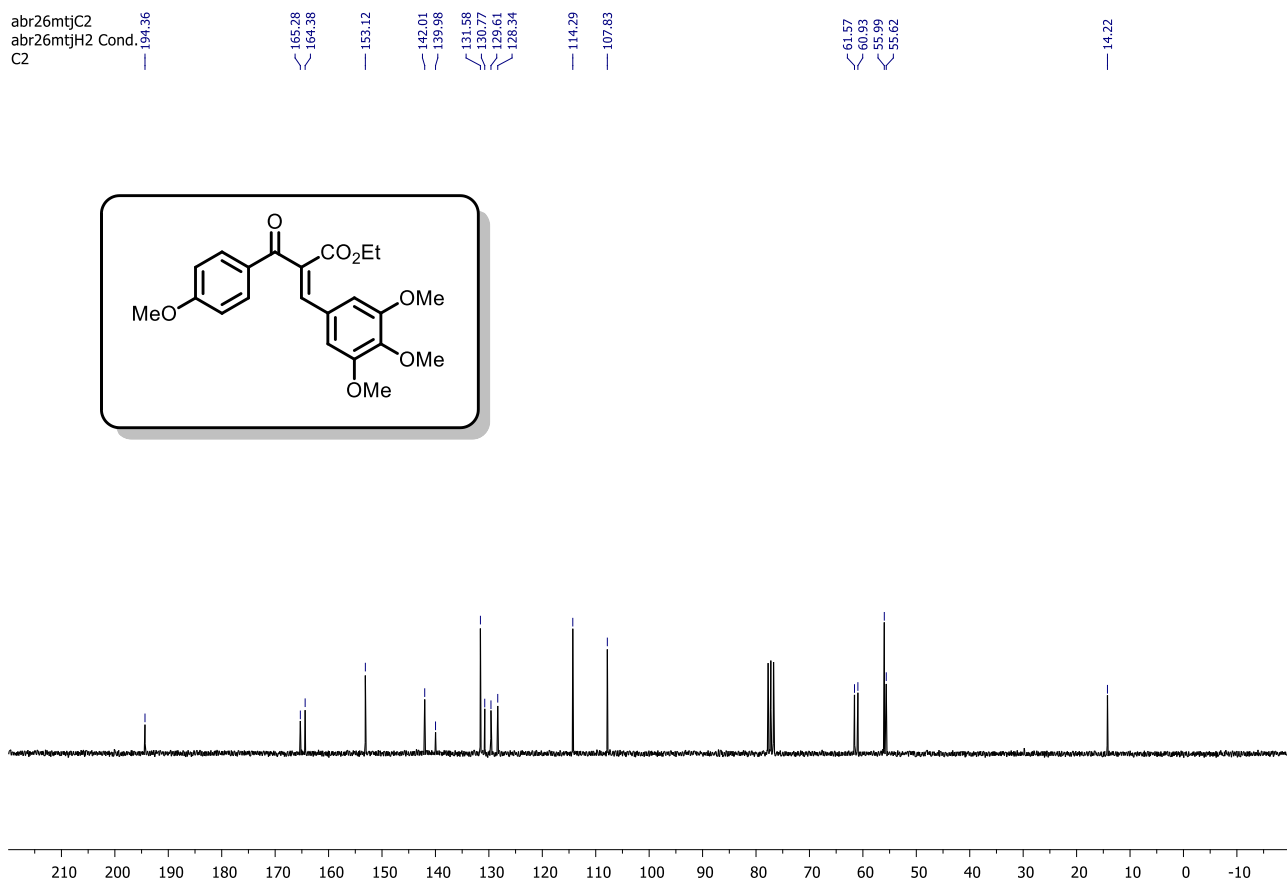
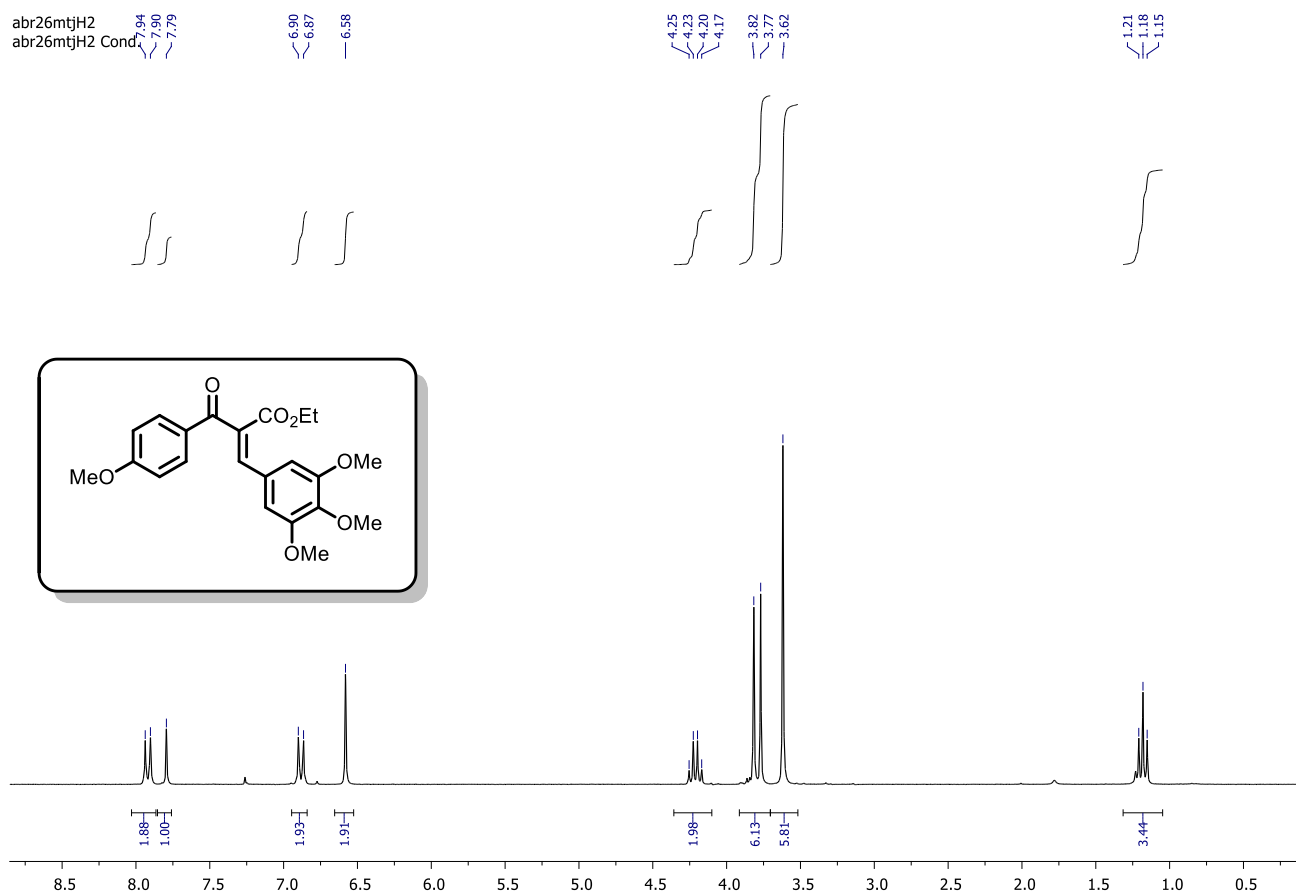


Figure S34. ^{13}C NMR spectrum (101 MHz, CDCl_3) of compound **9dm**.





out23mtjH
Manoel_KNOVG2_CDCL3_BenzTio_trimet

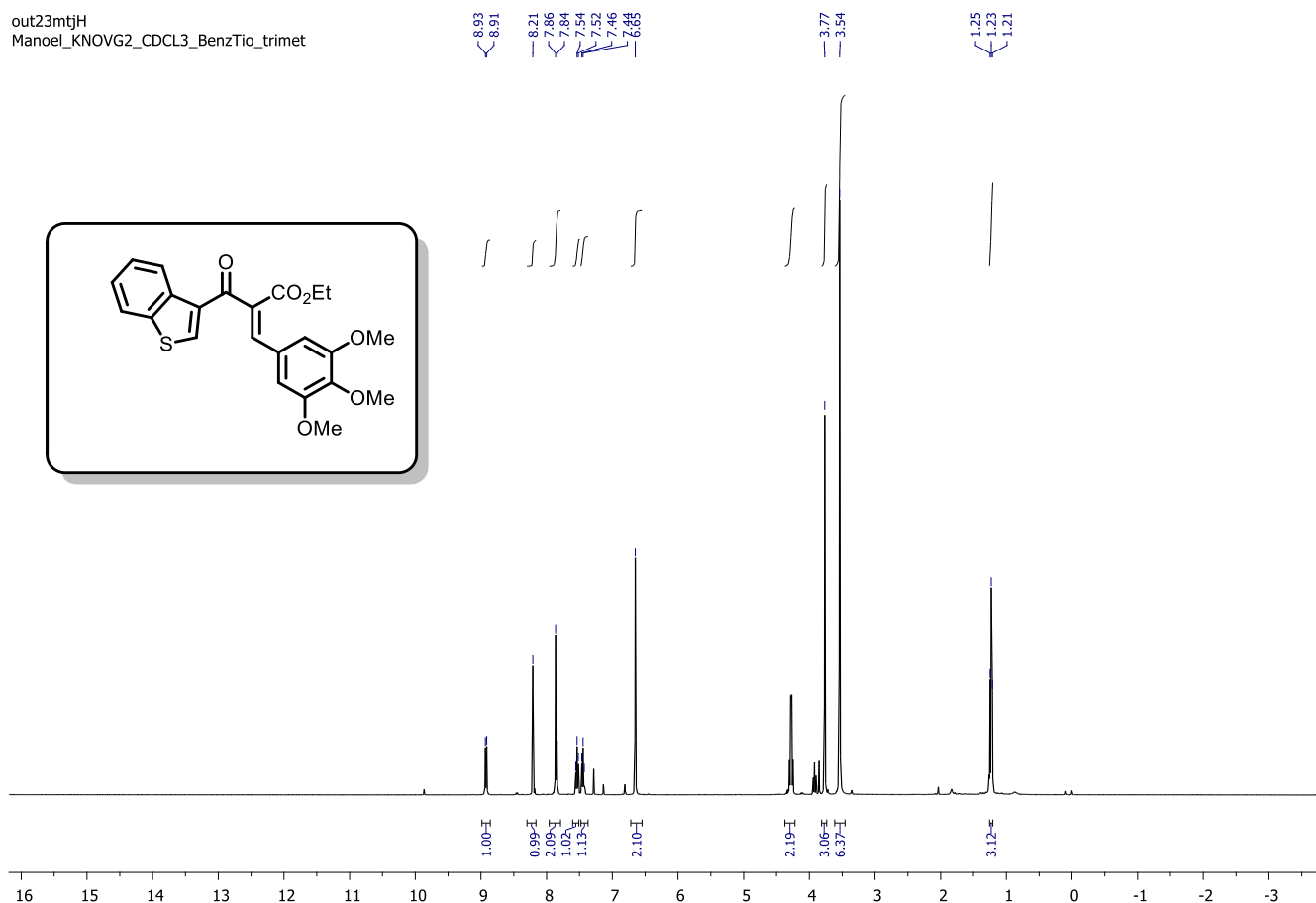


Figure S39. ^1H NMR spectrum (400 MHz, CDCl_3) of compound **9gc**.

out23mtjH
Manoel_KNOVG2_CDCL3_BenzTio_trimet

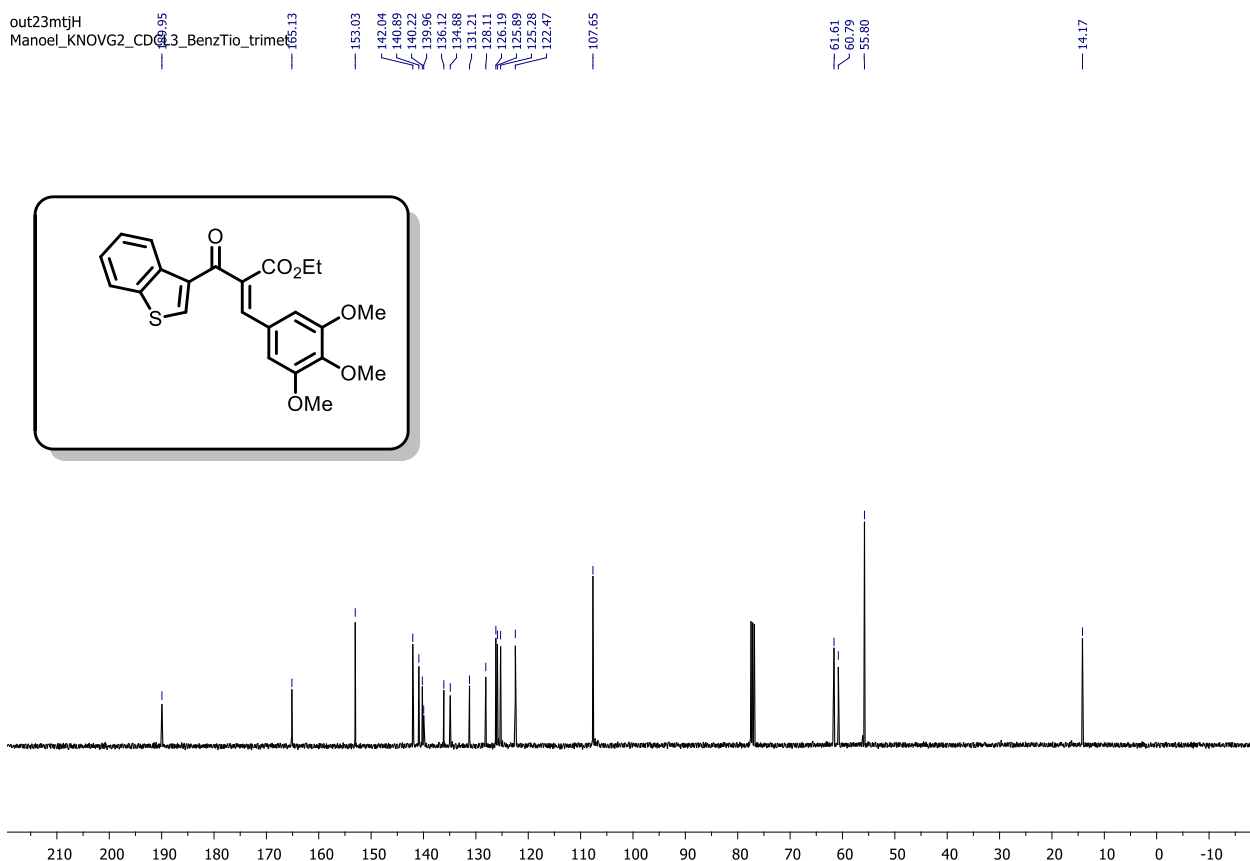


Figure S40. ^{13}C NMR spectrum (101 MHz, CDCl_3) of compound **9gc**.

mai04mtjH
Manoel Nazarov_trimet_pOme mai04mtjH

7.07
7.04
7.01
6.83
6.80

4.89
4.88
4.27
4.24
4.21
4.18
3.90
3.76
3.74
3.57
3.56
3.38

1.31
1.28
1.25

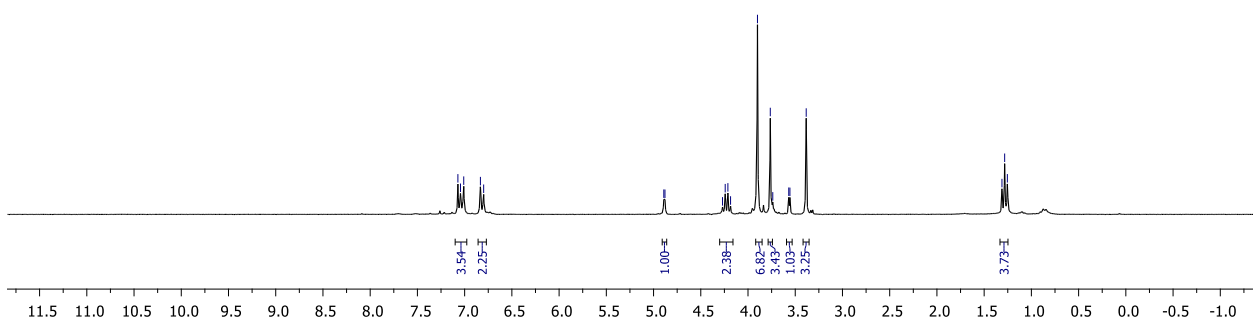
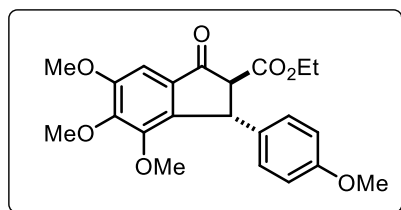


Figure S41. ^1H NMR spectrum (250 MHz, CDCl_3) of compound **10aa**.

mai04mtjC
Manoel Nazarov_trimet_pOme mai04mtjC

158.25
158.65
158.81
155.33
150.49
149.62
143.82
134.97
133.66
128.57
114.28
101.14
64.12
61.94
61.08
60.28
56.44
55.41
45.70
14.36

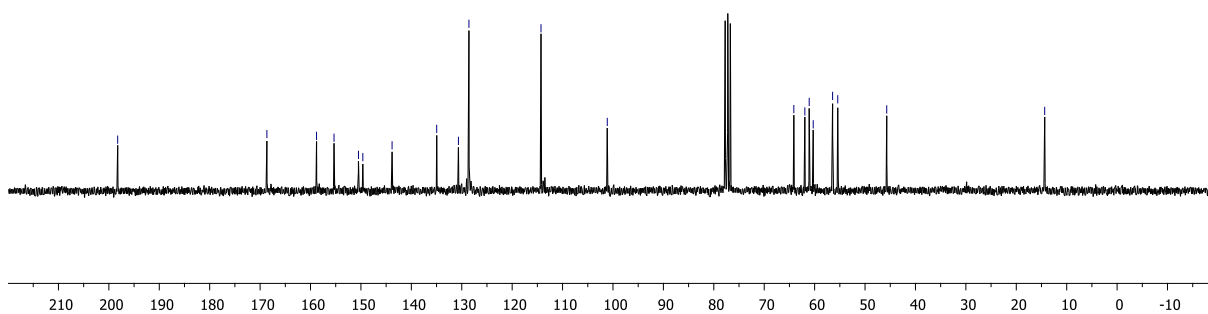
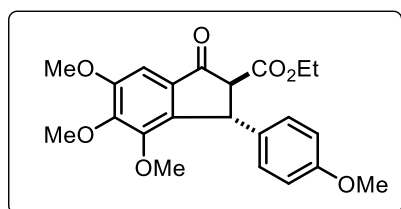


Figure S42. ^{13}C NMR spectrum (63 MHz, CDCl_3) of compound **10aa**.

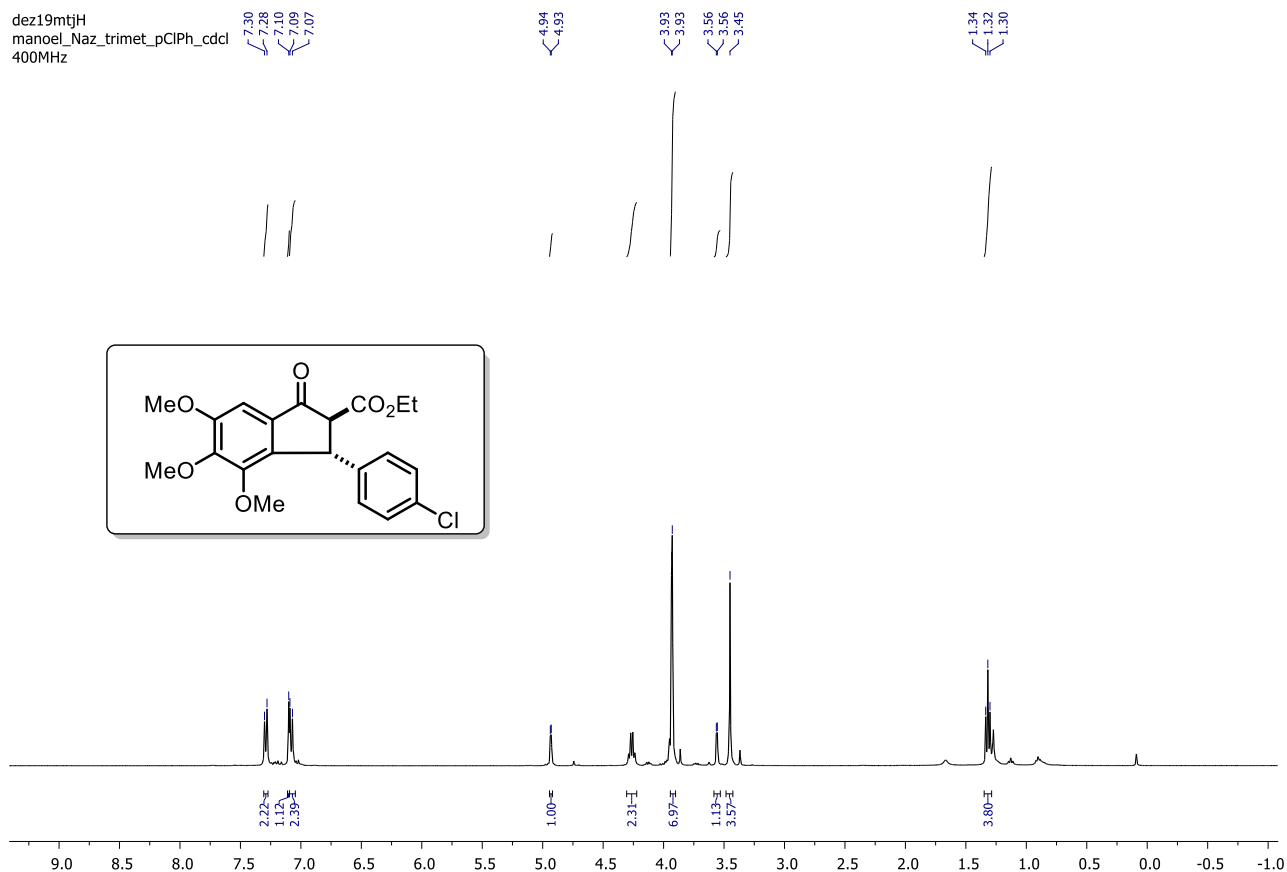


Figure S43. ^1H NMR spectrum (400 MHz, CDCl_3) of compound **10ab**.

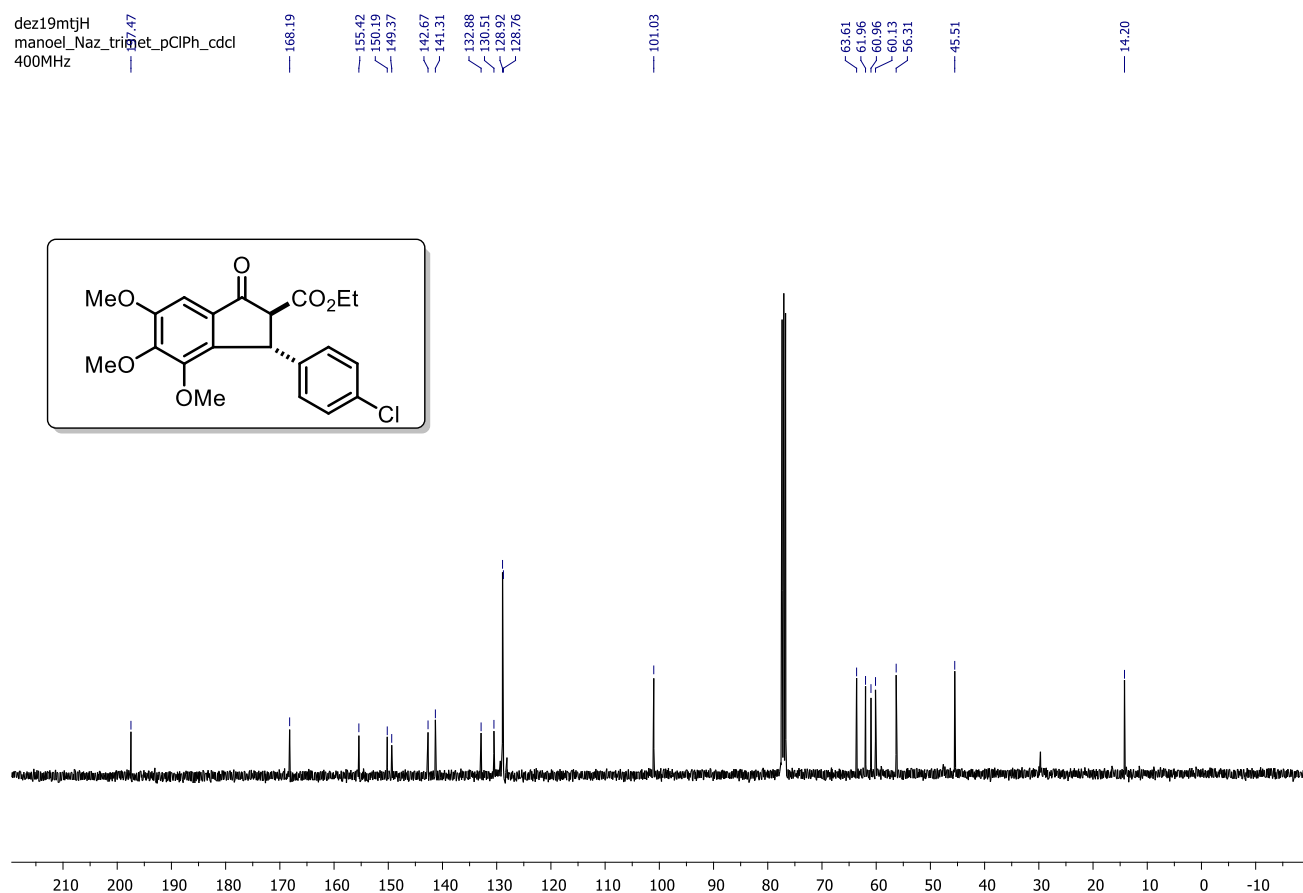
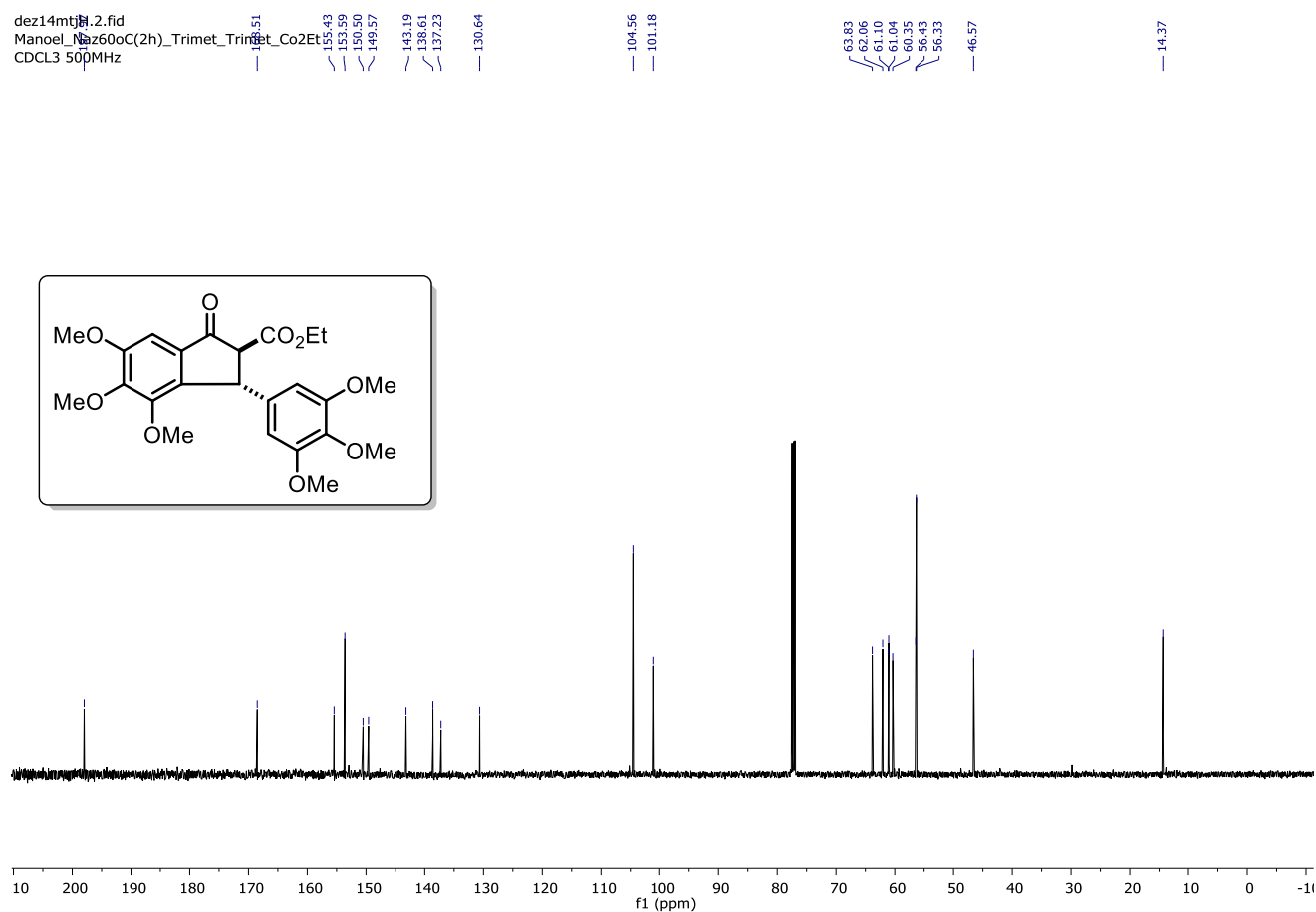
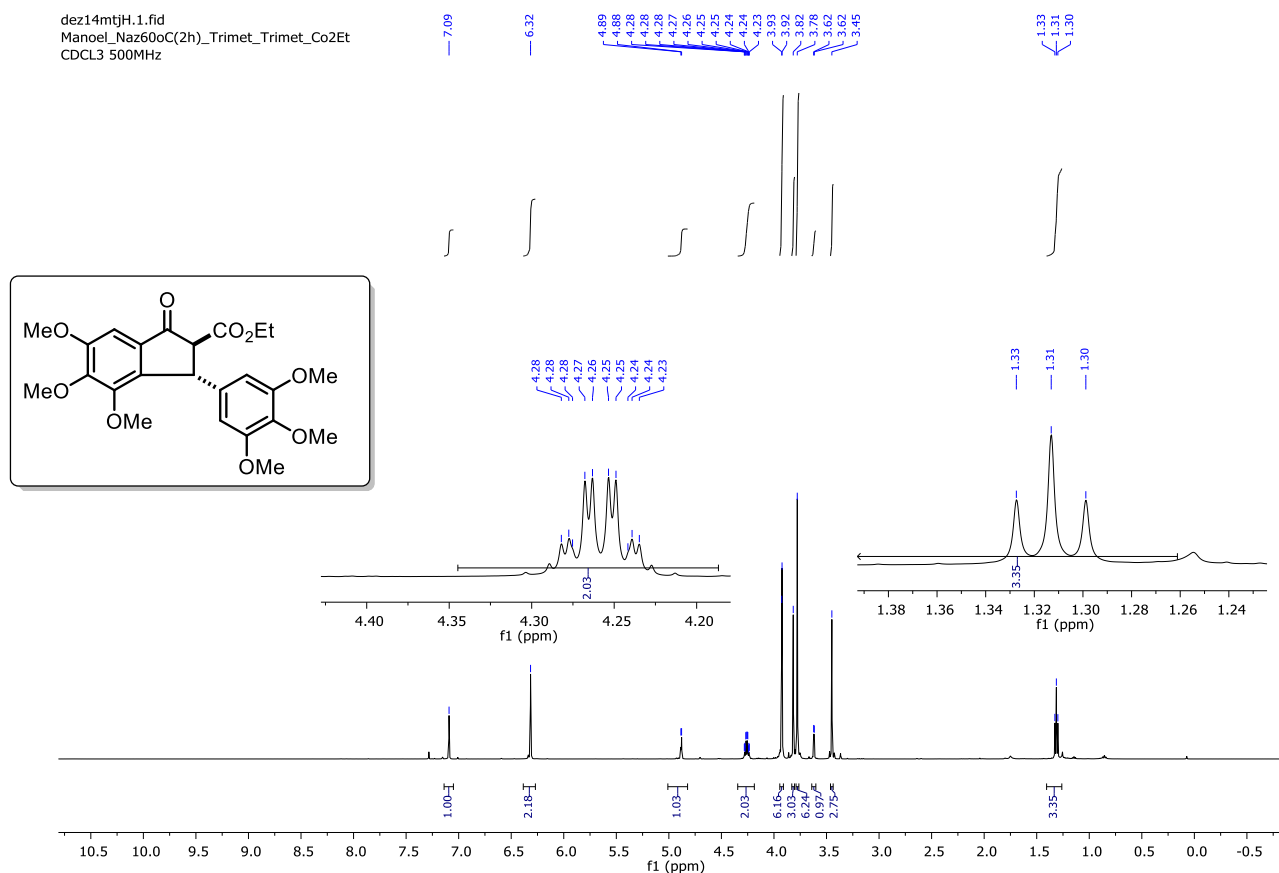


Figure S44. ^{13}C NMR spectrum (101 MHz, CDCl_3) of compound **10ab**.



dez22mtjH
Manoel_Naz_trimet_3,4-dimetox_Et
CDCL3_400MHz

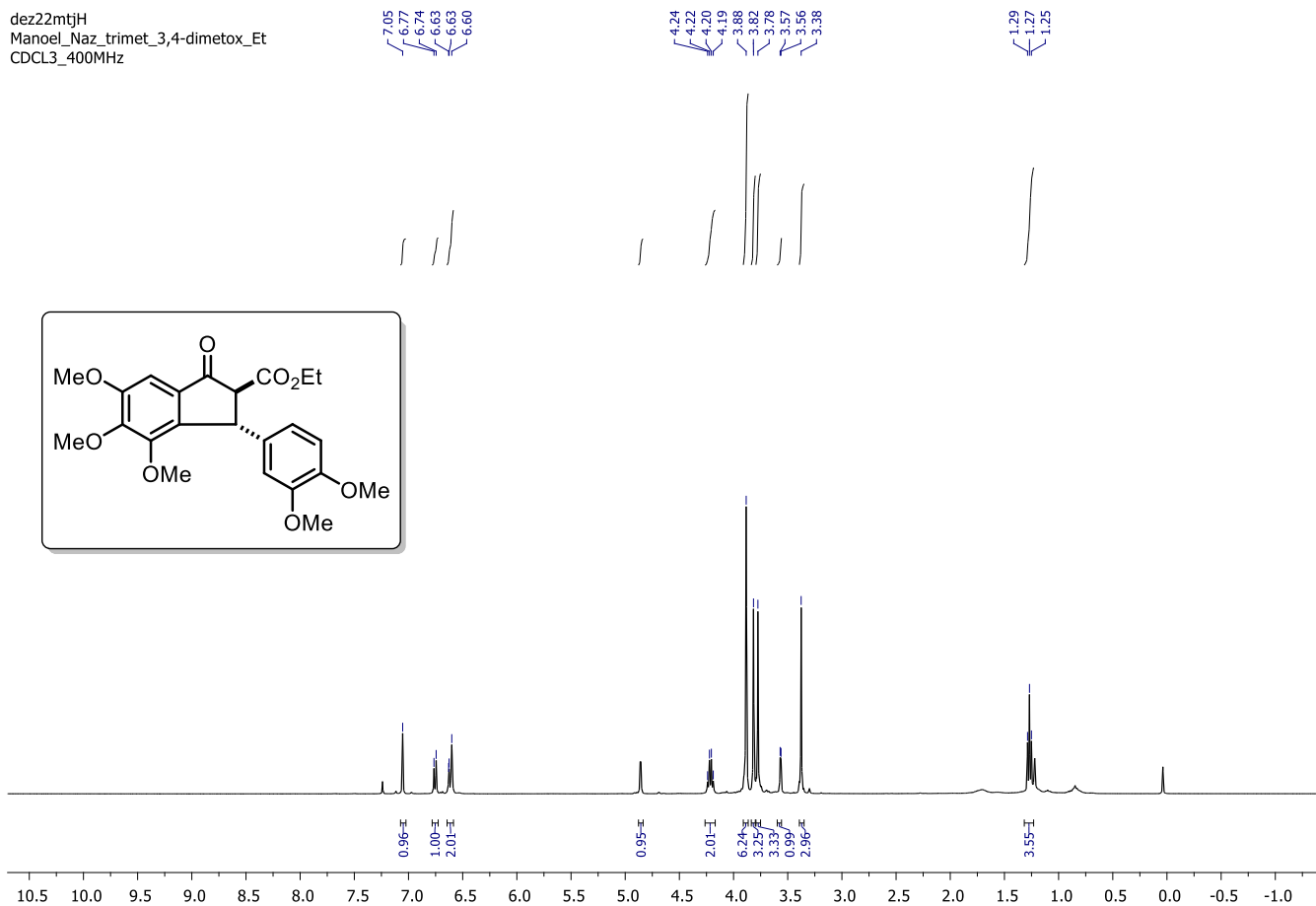


Figure S47. ¹H NMR spectrum (400 MHz, CDCl₃) of compound 10ad.

dez22mtjH
Manoel_Naz_trimet_3,4-dimetox_Et
CDCL3_400MHz

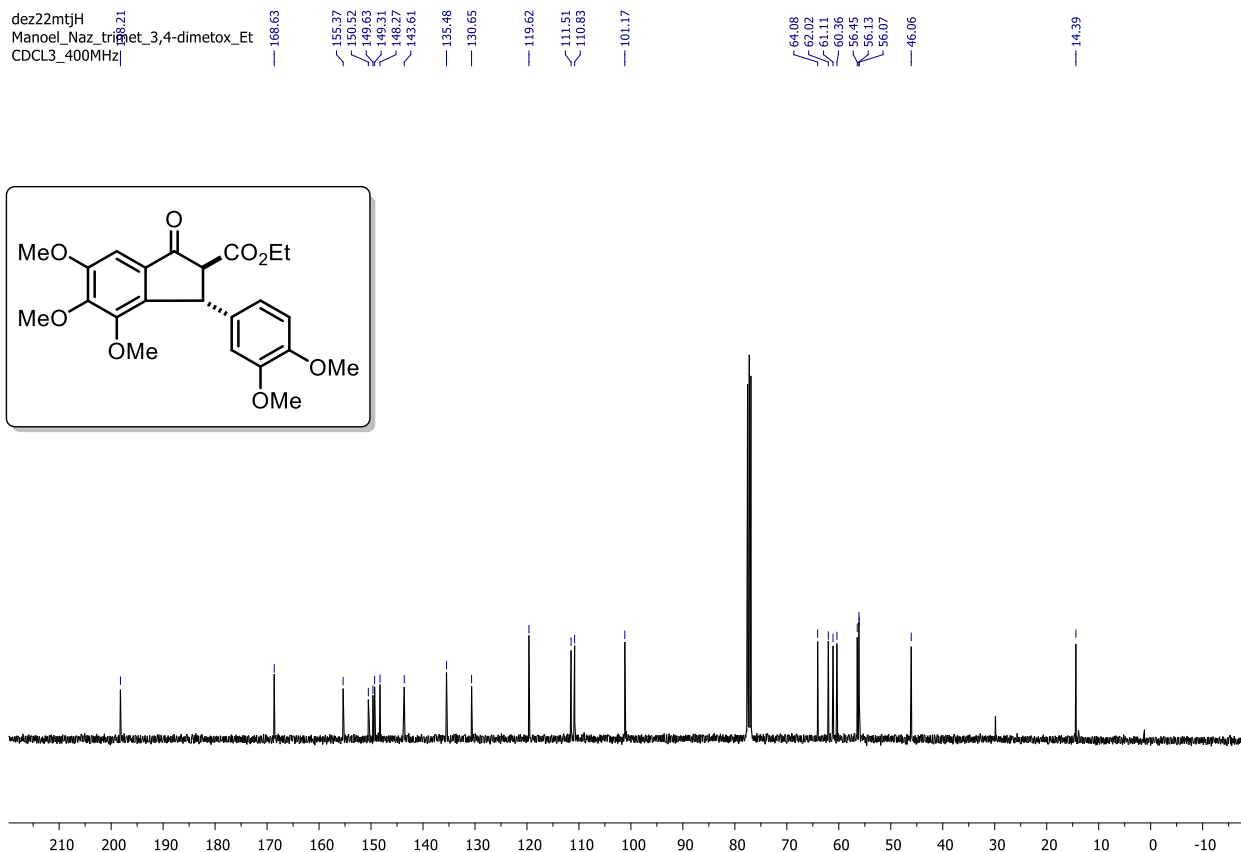


Figure S48. ¹³C NMR spectrum (101 MHz, CDCl₃) of compound 10ad.

mar26mtjH2
Manoel_Naz_pirrol_cdc13_400MHz

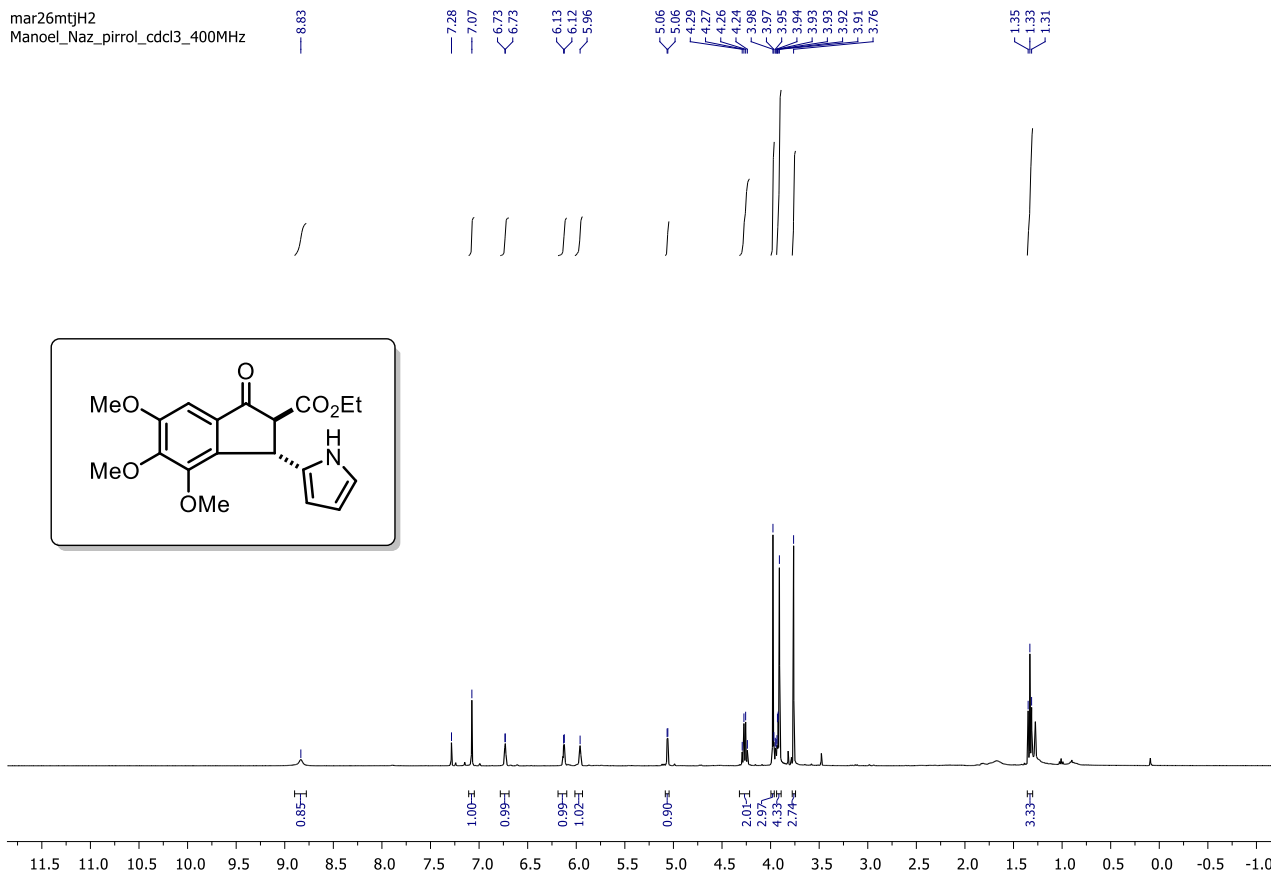


Figure S49. ¹H NMR spectrum (400 MHz, CDCl₃) of compound **10ag**.

mar27mtjC1
Manoel - PIR-TRM-NAZ - CDCl3 - Avance 400 MHz
5 horas

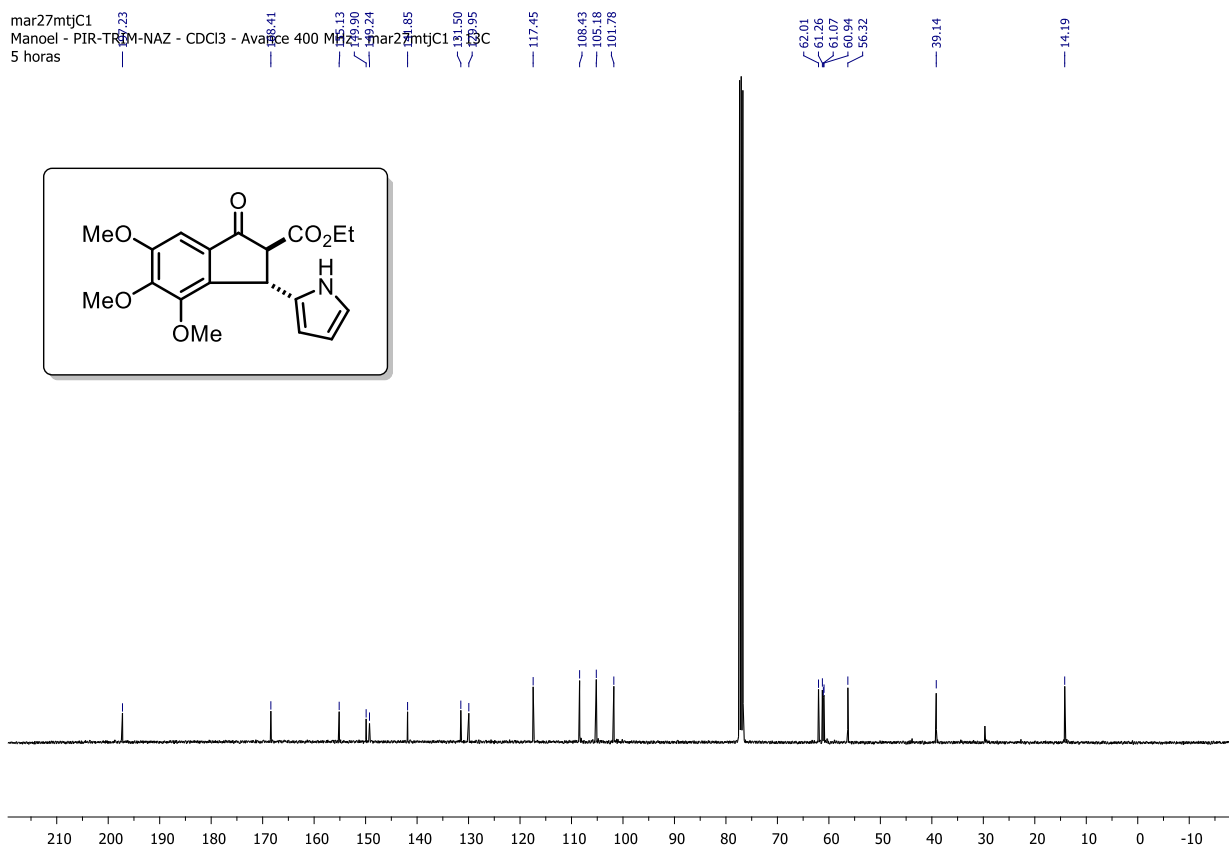


Figure S50. ¹³C NMR spectrum (101 MHz, CDCl₃) of compound **10ag**.

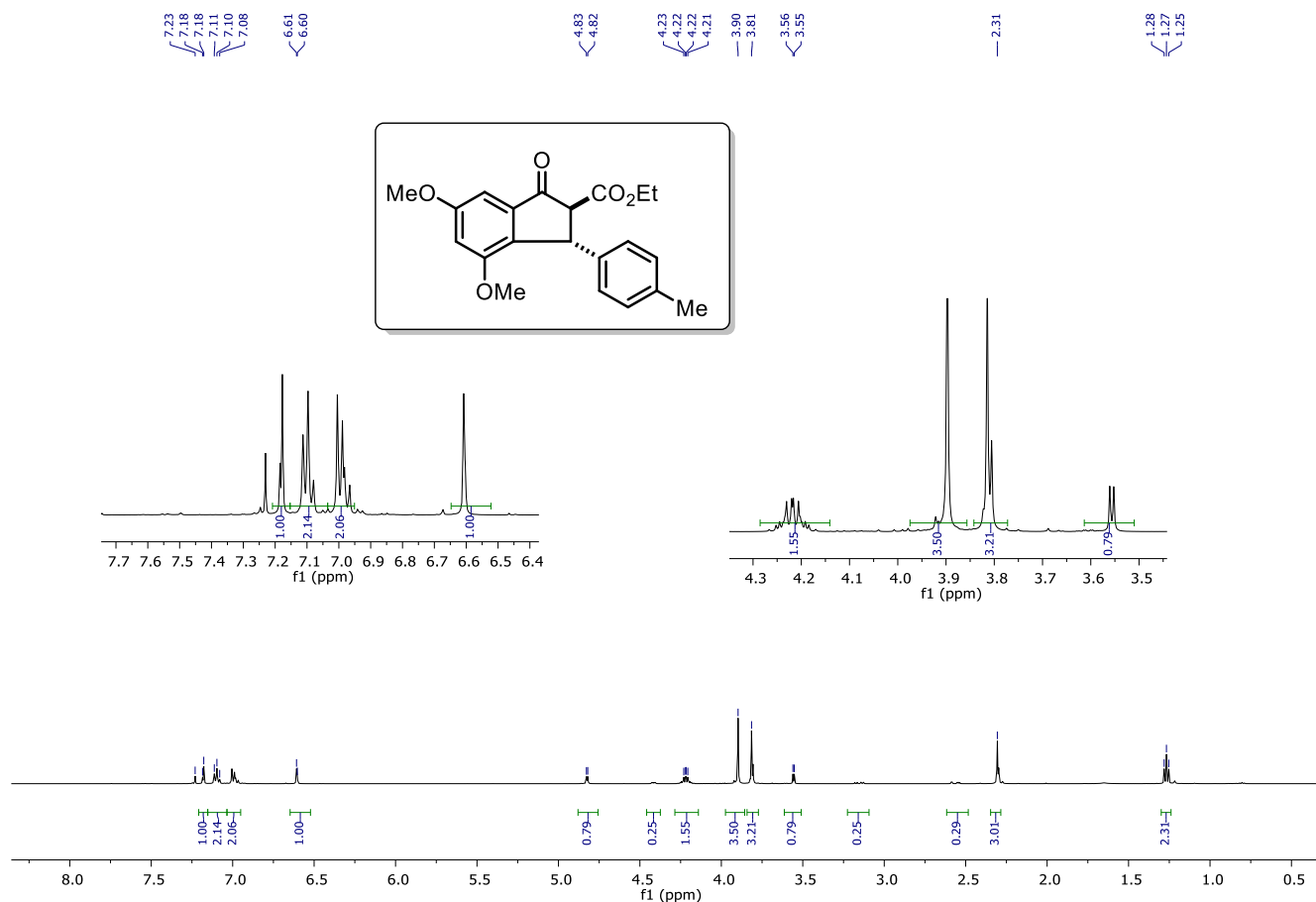


Figure S51. ¹H NMR spectrum (500 MHz, CDCl₃) of compound **10bj**.

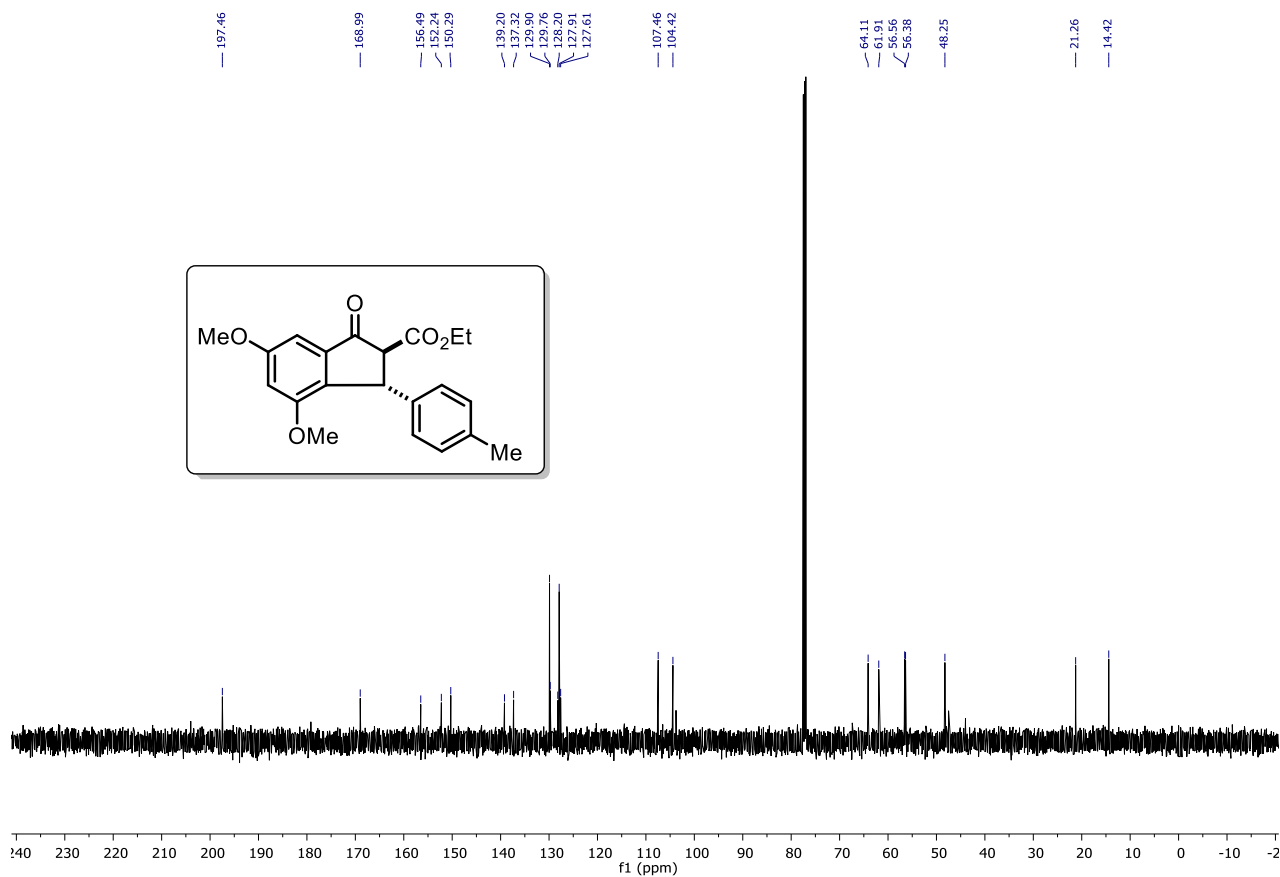


Figure S52. ¹³C NMR spectrum (126 MHz, CDCl₃) of compound **10bj**.

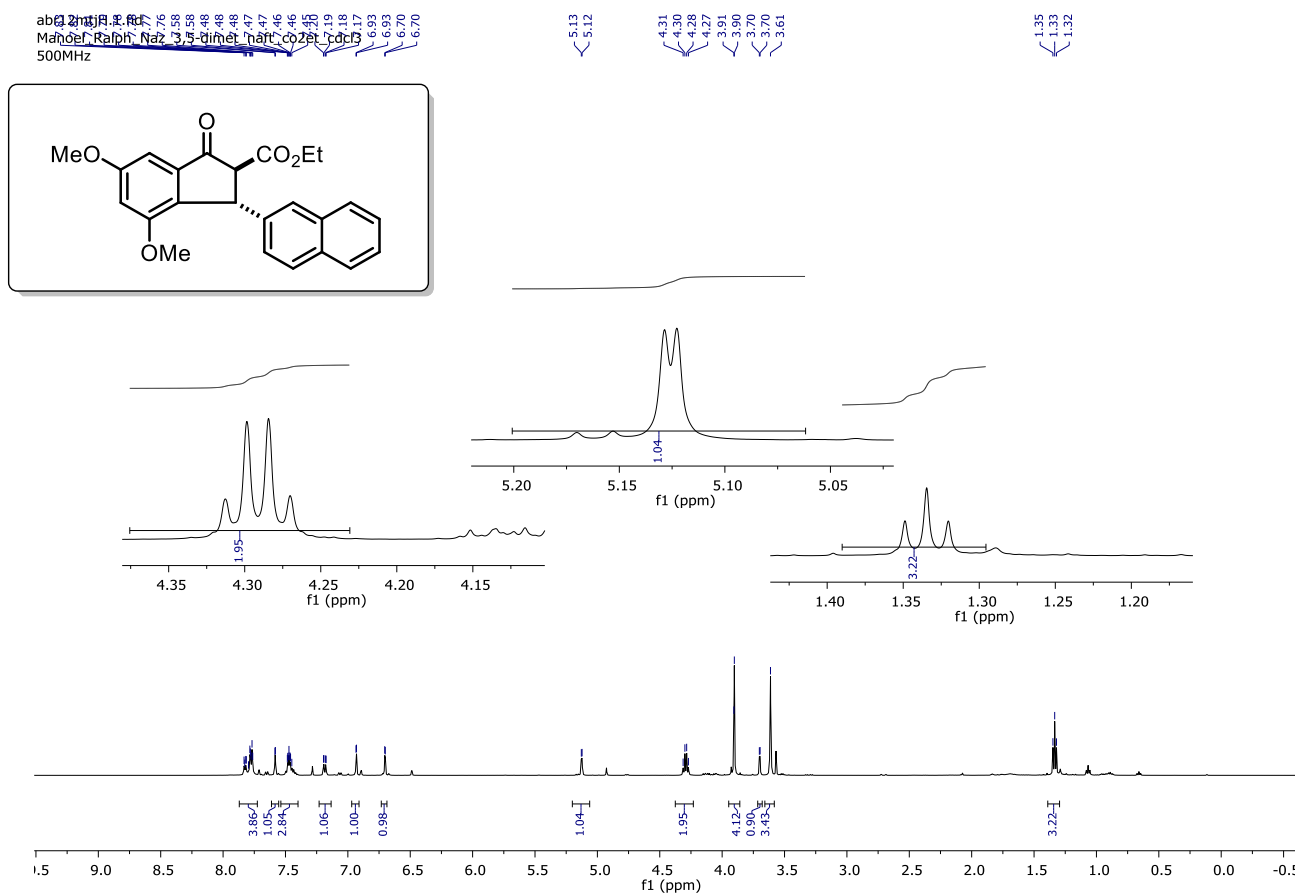


Figure S53. ^1H NMR spectrum (500 MHz, CDCl_3) of compound **10bk**.

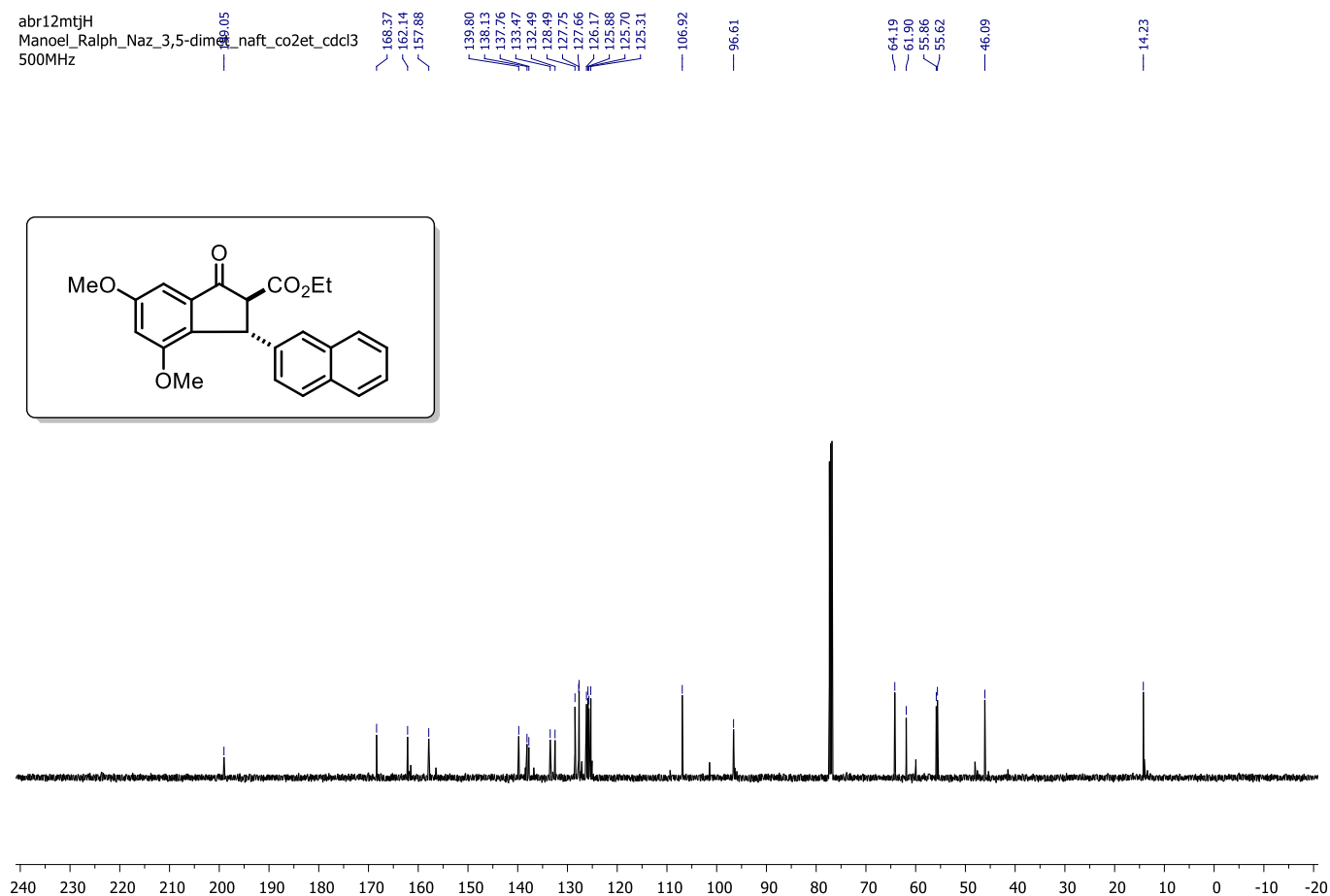
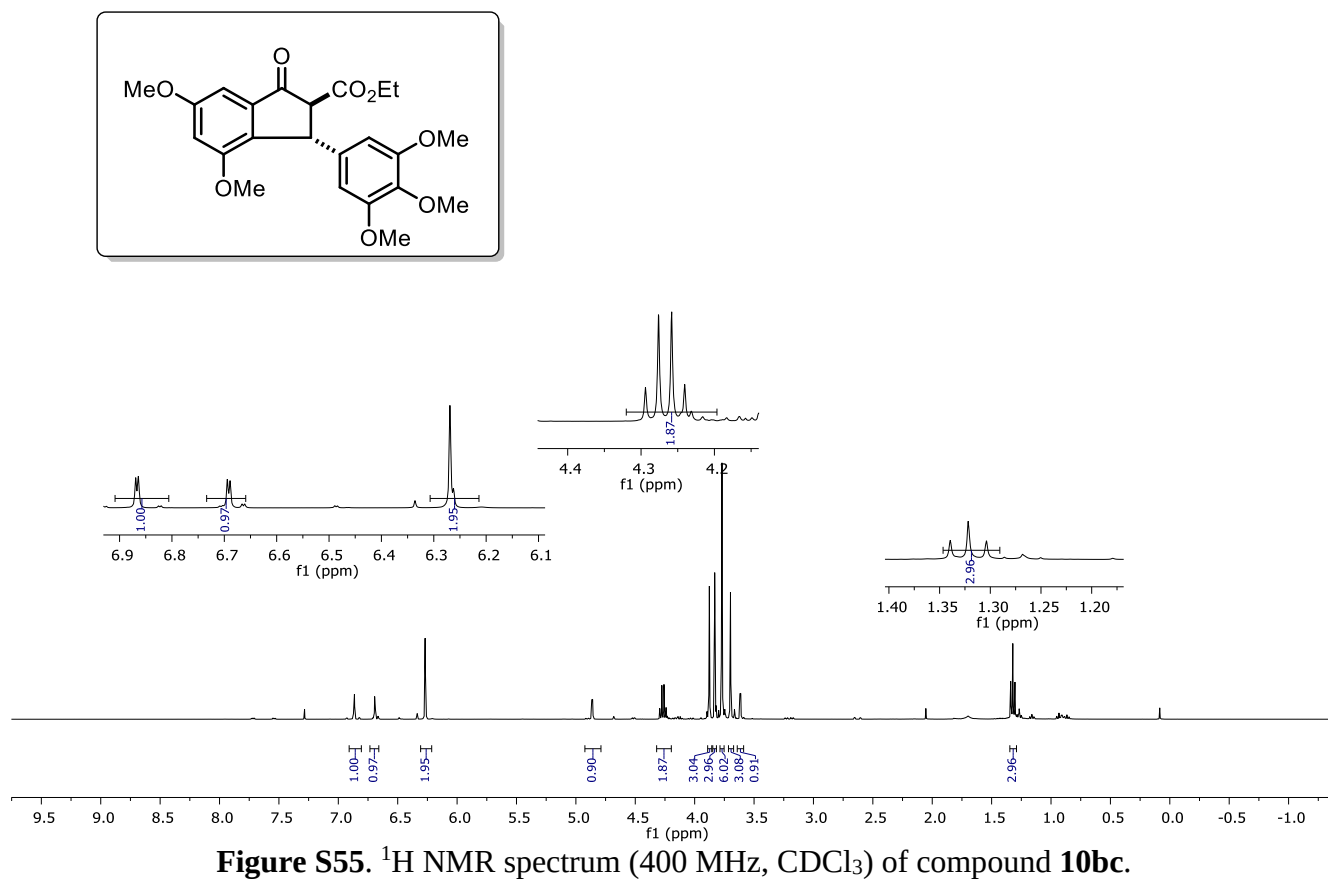


Figure S54. ^{13}C NMR spectrum (126 MHz, CDCl_3) of compound **10bk**.



mar05mtjH
Manoel/Aline2_indadona_3,5-dimet_trimet_400MHz



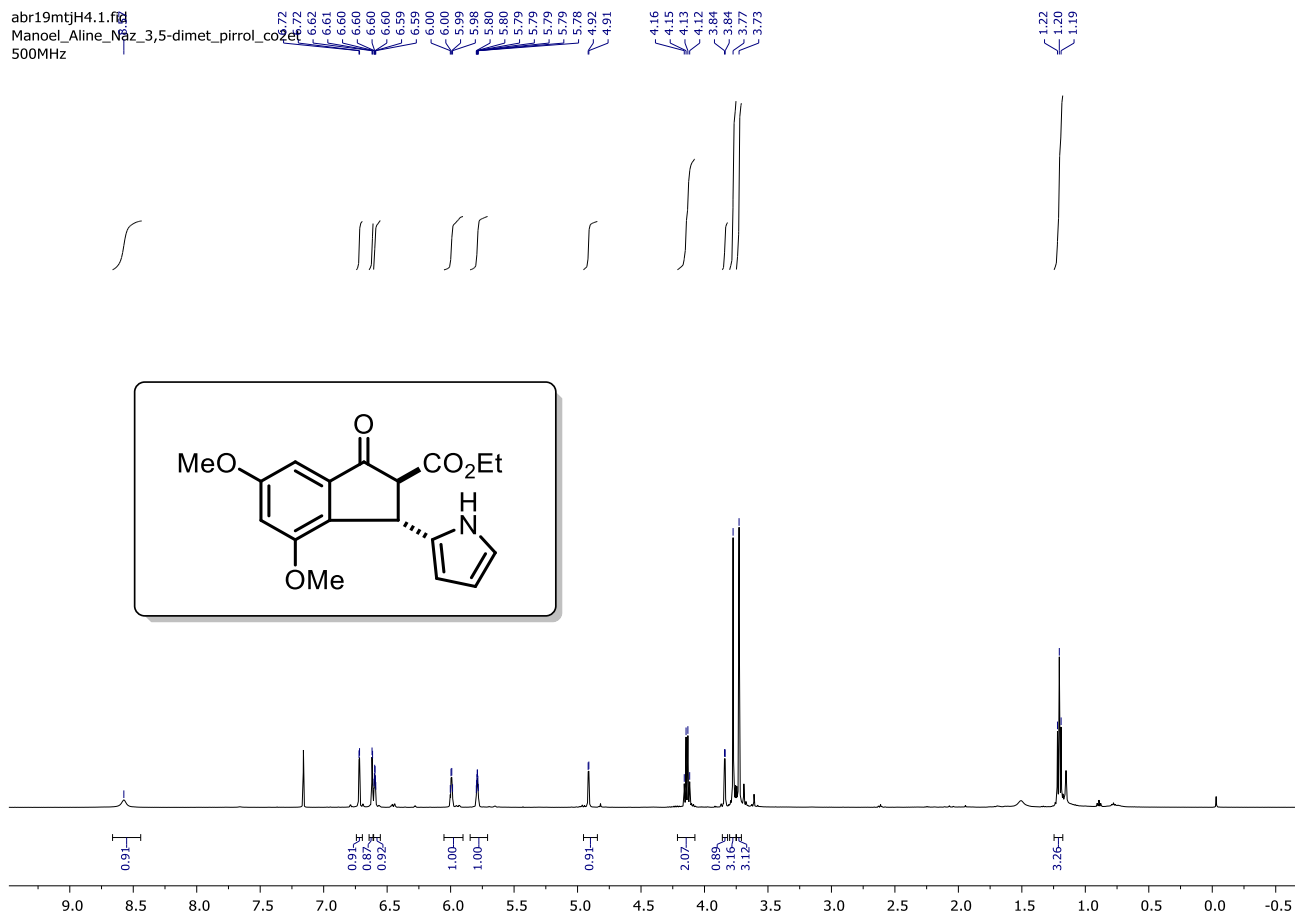


Figure S57. ¹H NMR spectrum (500 MHz, CDCl₃) of compound **10bg**.

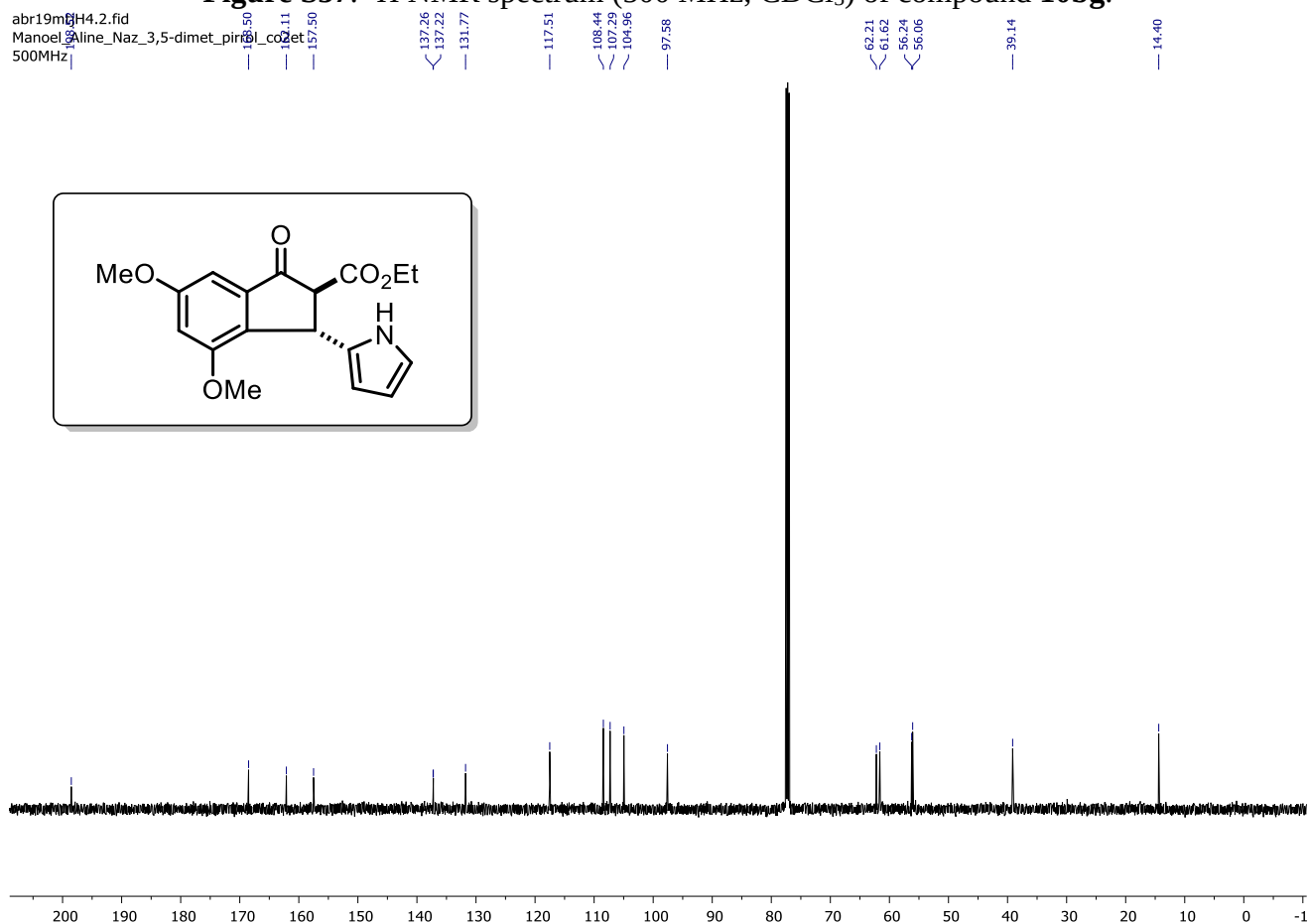


Figure S58. ¹³C NMR spectrum (125 MHz, CDCl₃) of compound **10bg**.

mar06mtjH2
Manoel/Aline_Nazar_3,4-dimet_trimet_cdc13_400MHz



Figure S59. ¹H NMR spectrum (400 MHz, CDCl₃) of compound 10cc.

mar06mtjH2
Manoel/Aline_Nazar_3,4-dimet_trimet_cdc13_400MHz

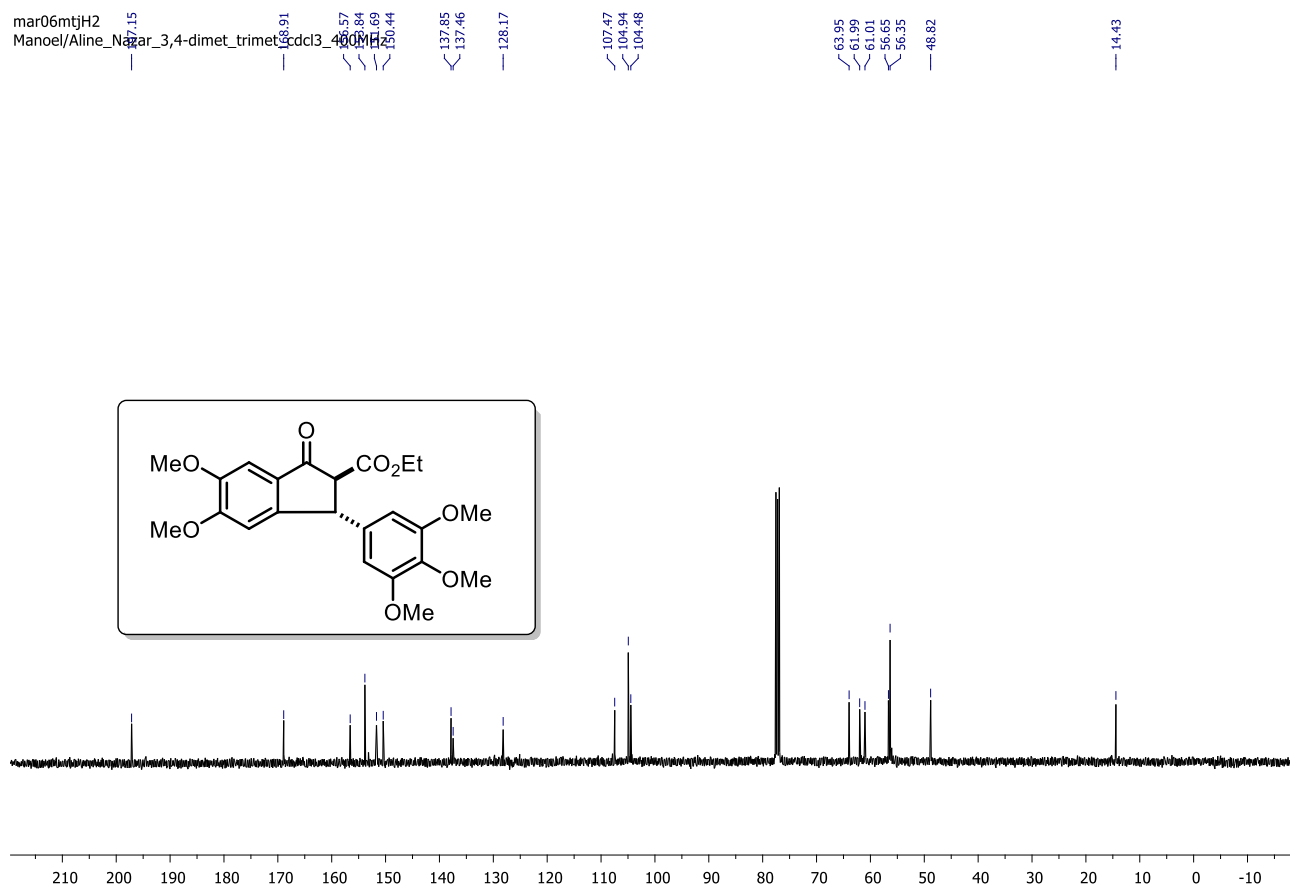
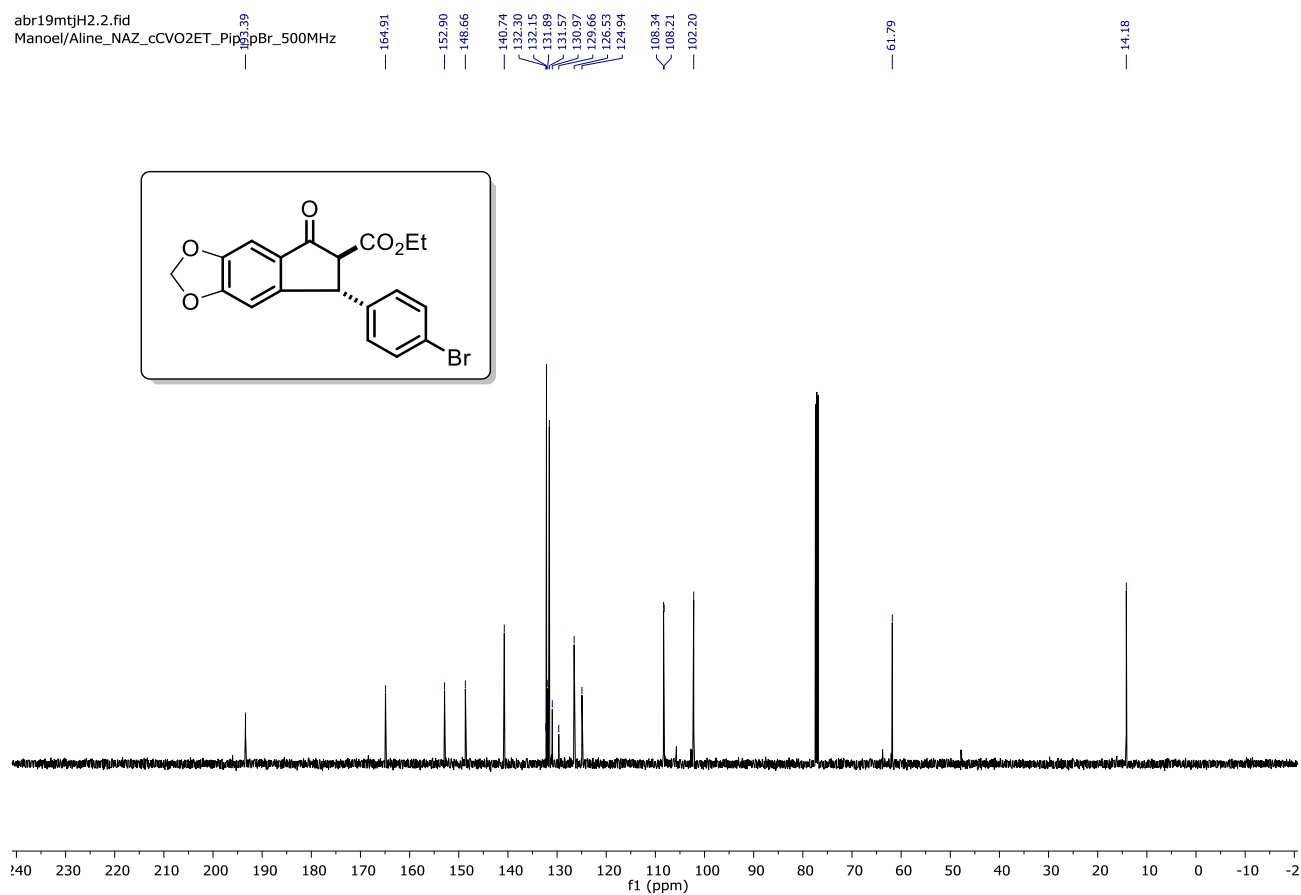
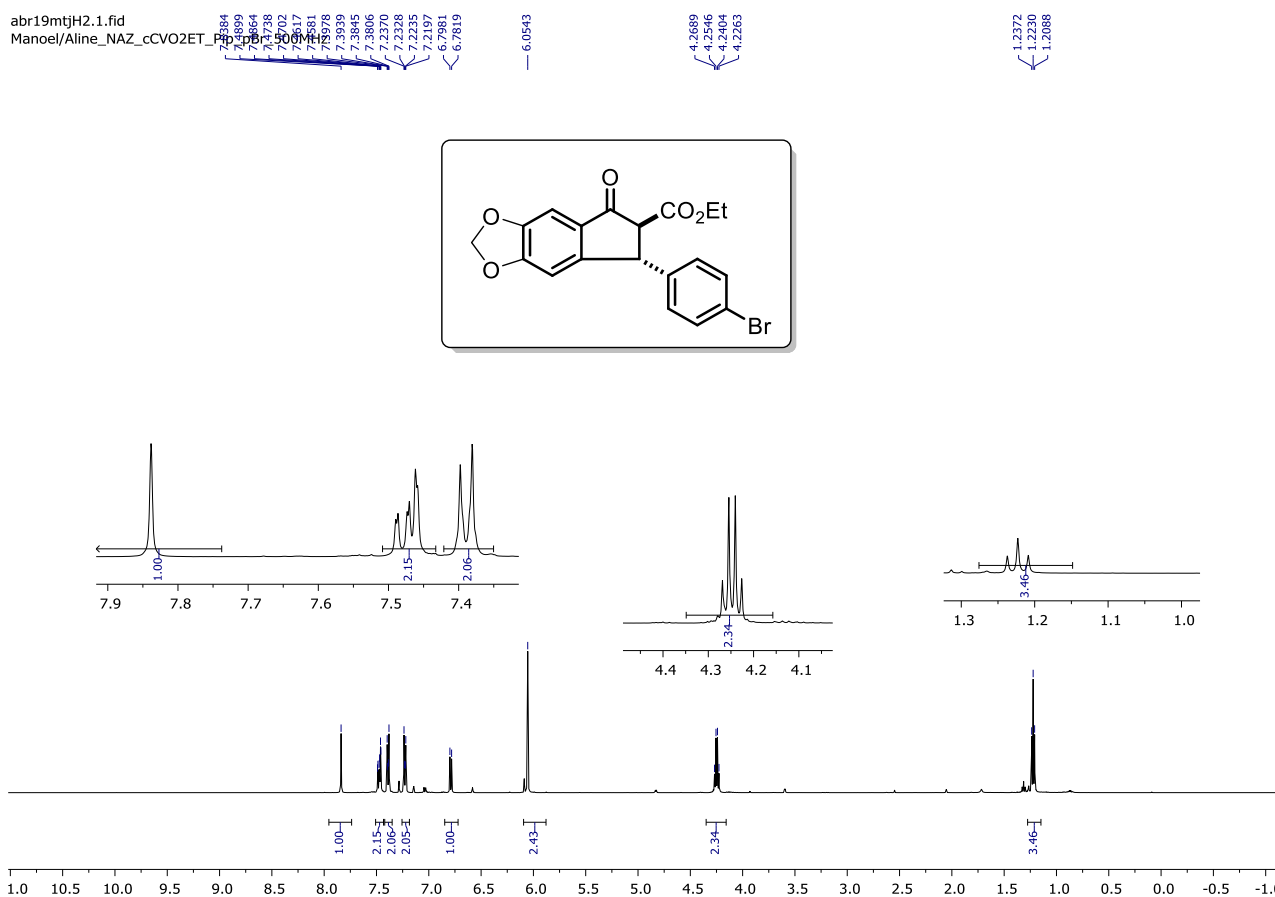


Figure S60. ¹³C NMR spectrum (101 MHz, CDCl₃) of compound 10cc.



nov14mtjH
Manoel_Naz2_descarb_trimet_4OMe-CDCL3
400MHz

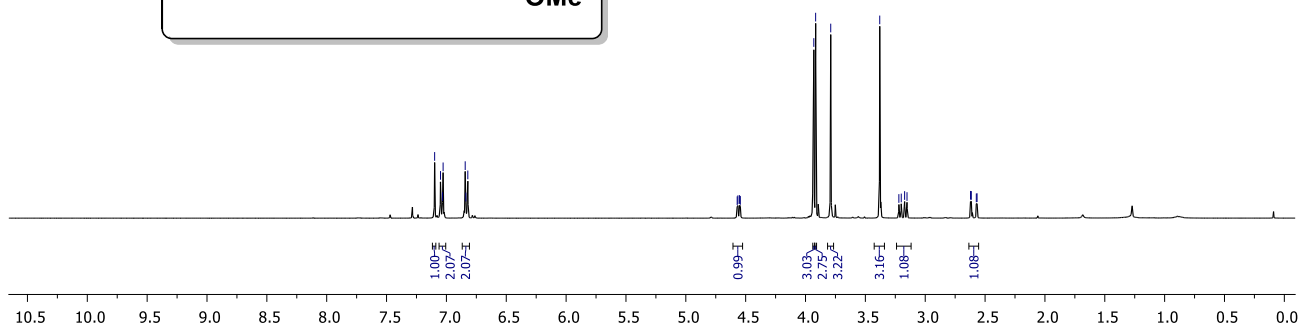
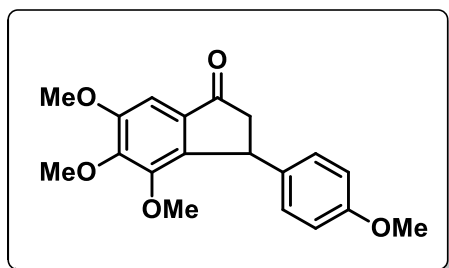
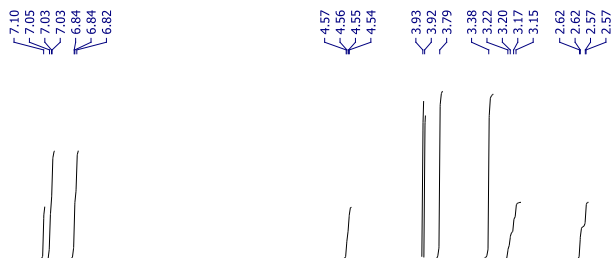


Figure S63. ¹H NMR spectrum (400 MHz, CDCl₃) of compound 11aa.

nov14mtjH
Manoel_Naz2_descarb_trimet_4OMe-CDCL3
400MHz

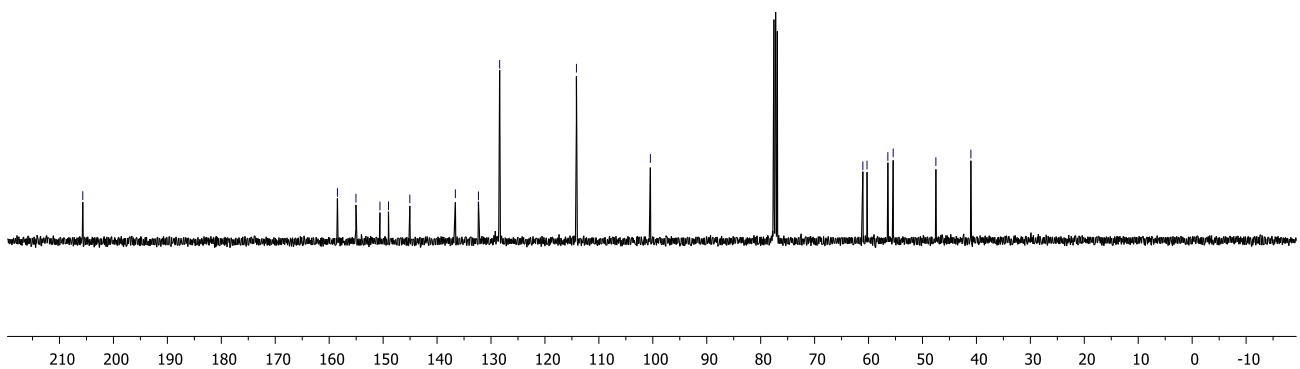
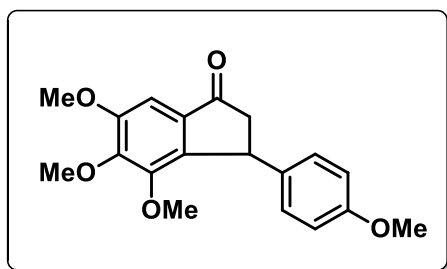


Figure S64. ¹³C NMR spectrum (101 MHz, CDCl₃) of compound 11aa.

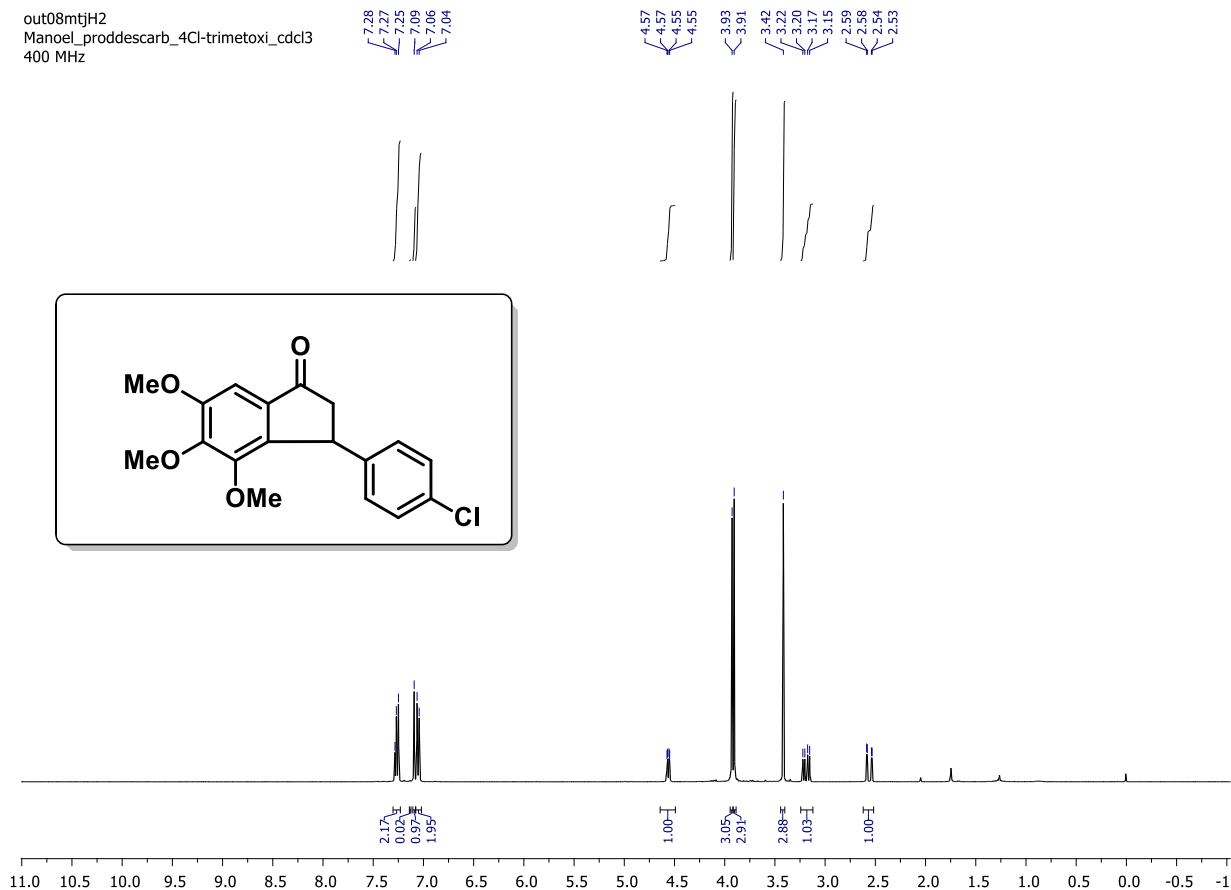


Figure S65. ^1H NMR spectrum (400 MHz, CDCl_3) of compound **11ab**.

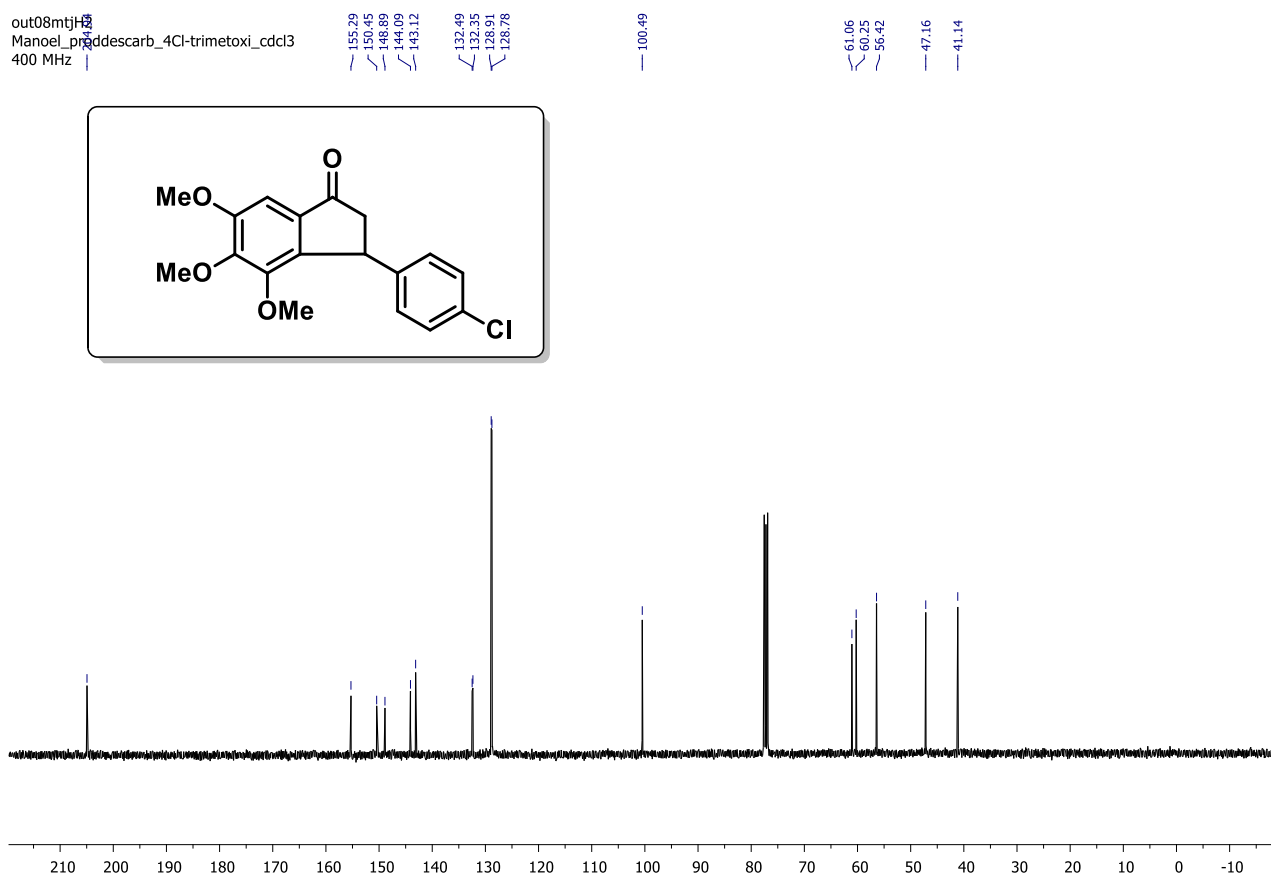


Figure S66. ^{13}C NMR spectrum (101 MHz, CDCl_3) of compound **11ab**.

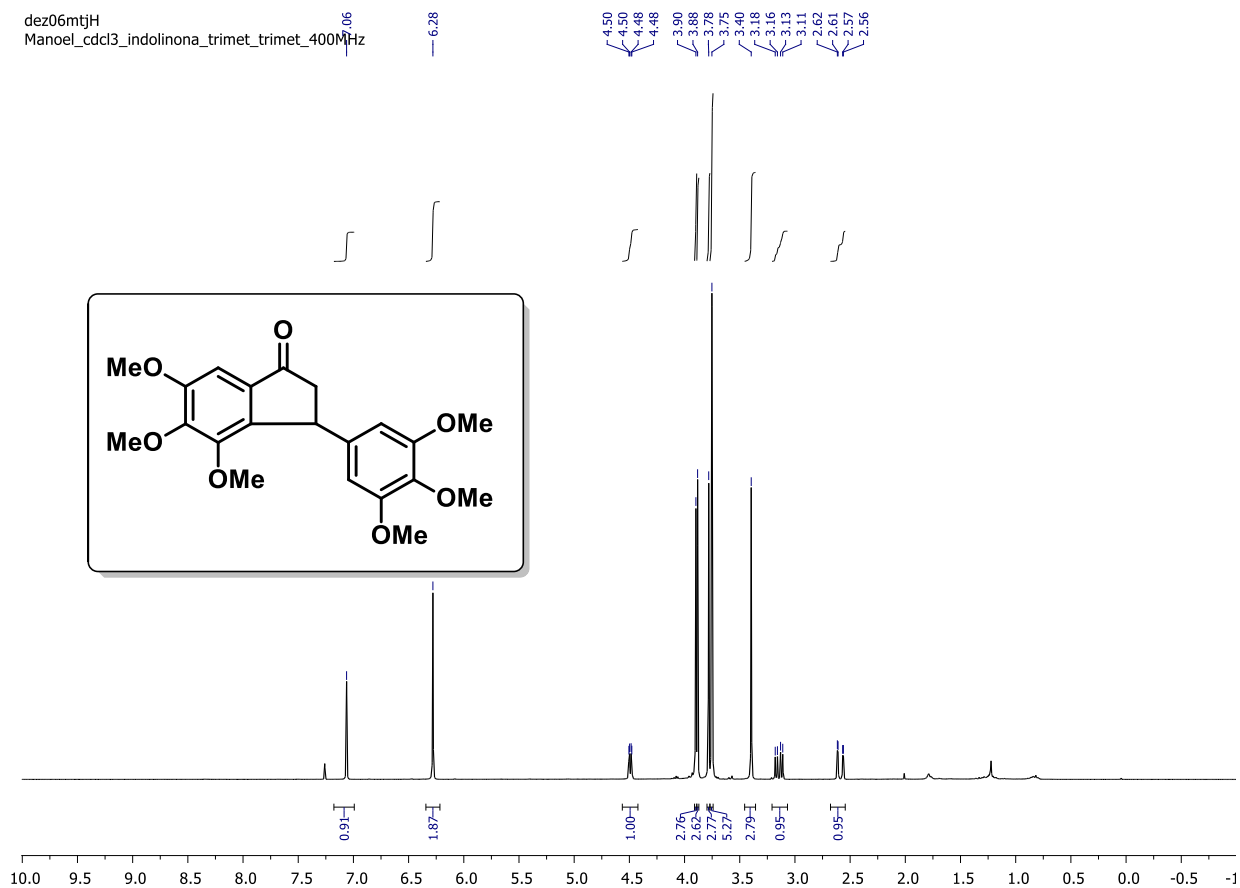


Figure S67. ^1H NMR spectrum (400 MHz, CDCl_3) of compound **11ac**.

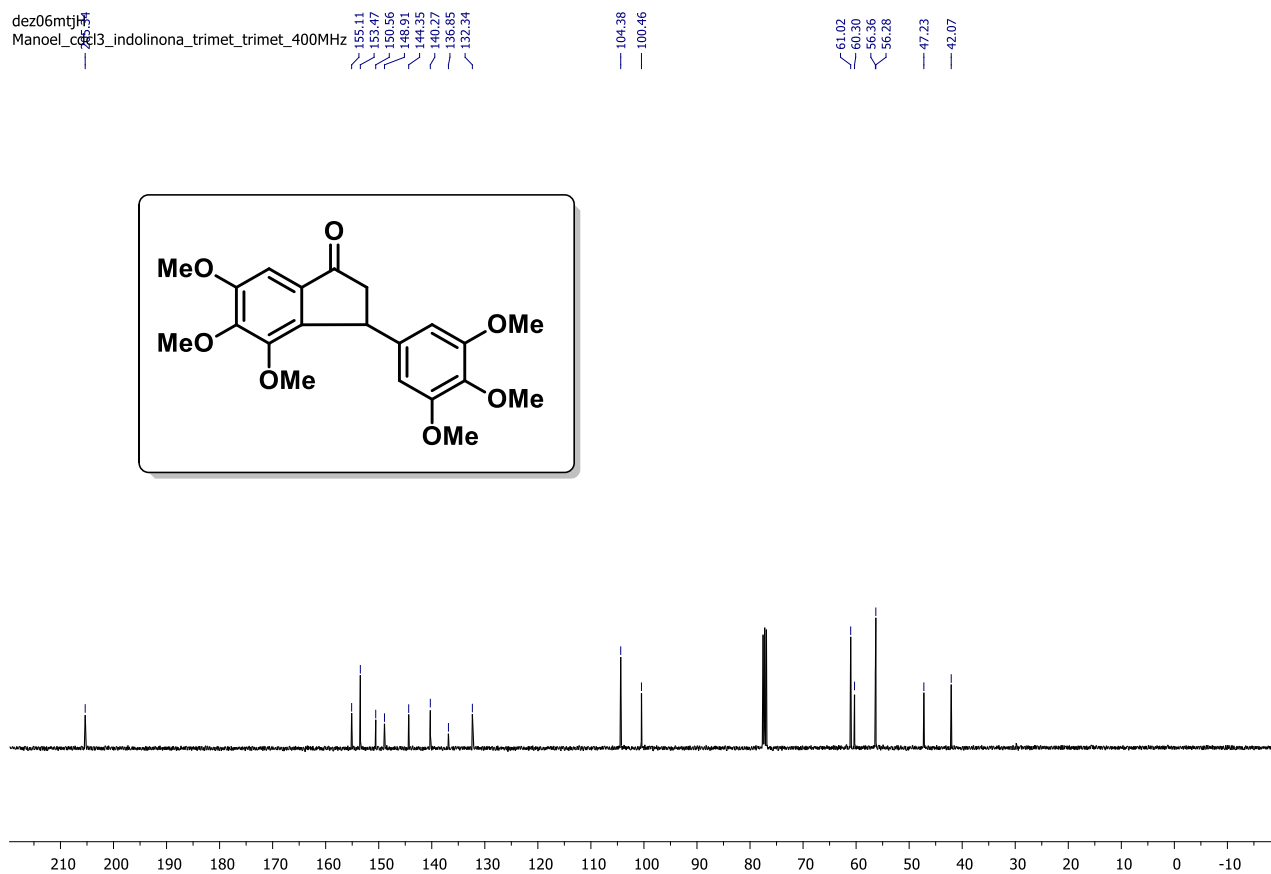


Figure S68. ^{13}C NMR spectrum (101 MHz, CDCl_3) of compound **11ac**.

mar02mtjH
Manoel/Aline_Nazav_trimet_3,4dimet_cdc13_500MHz

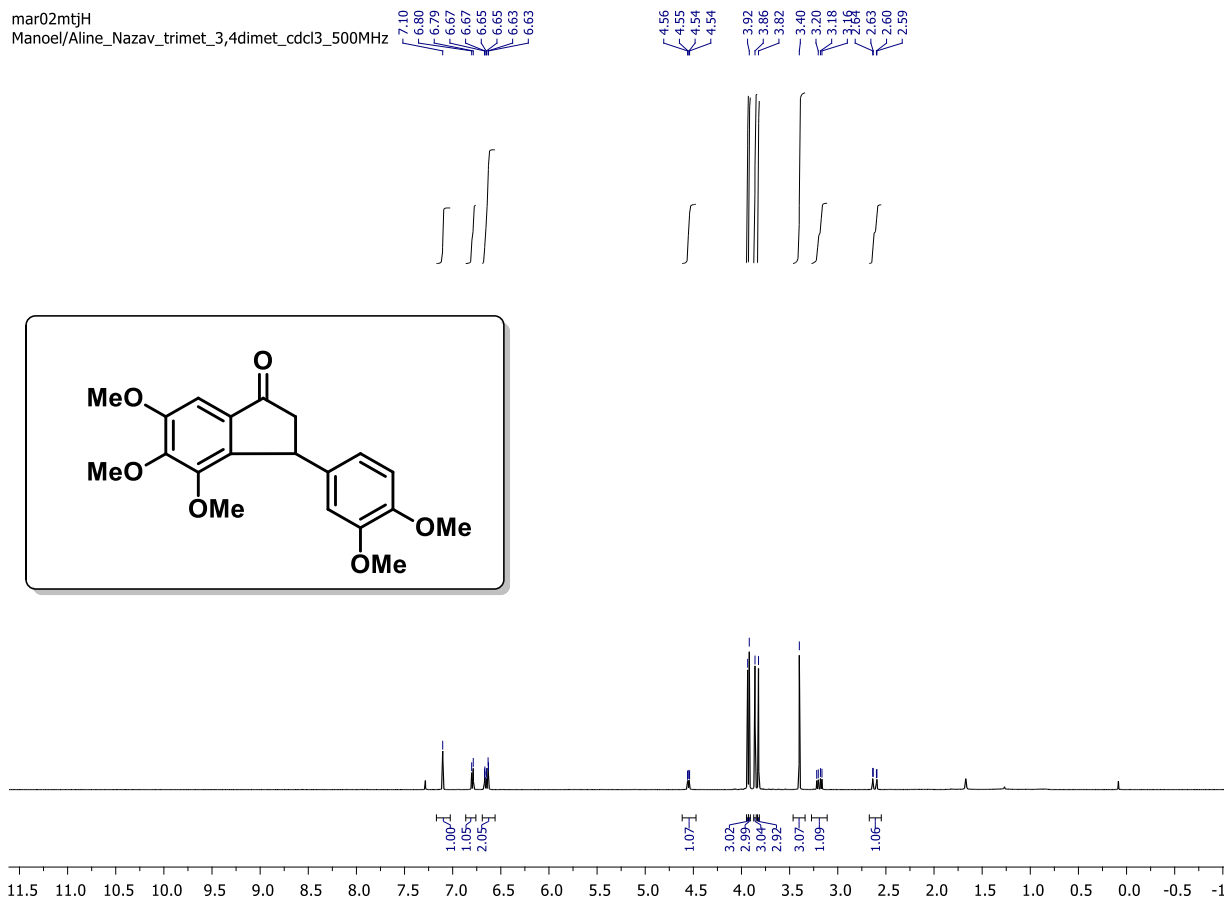


Figure S69. ¹H NMR spectrum (500 MHz, CDCl₃) of compound **11ad**.

mar02mtjC
Manoel/Aline

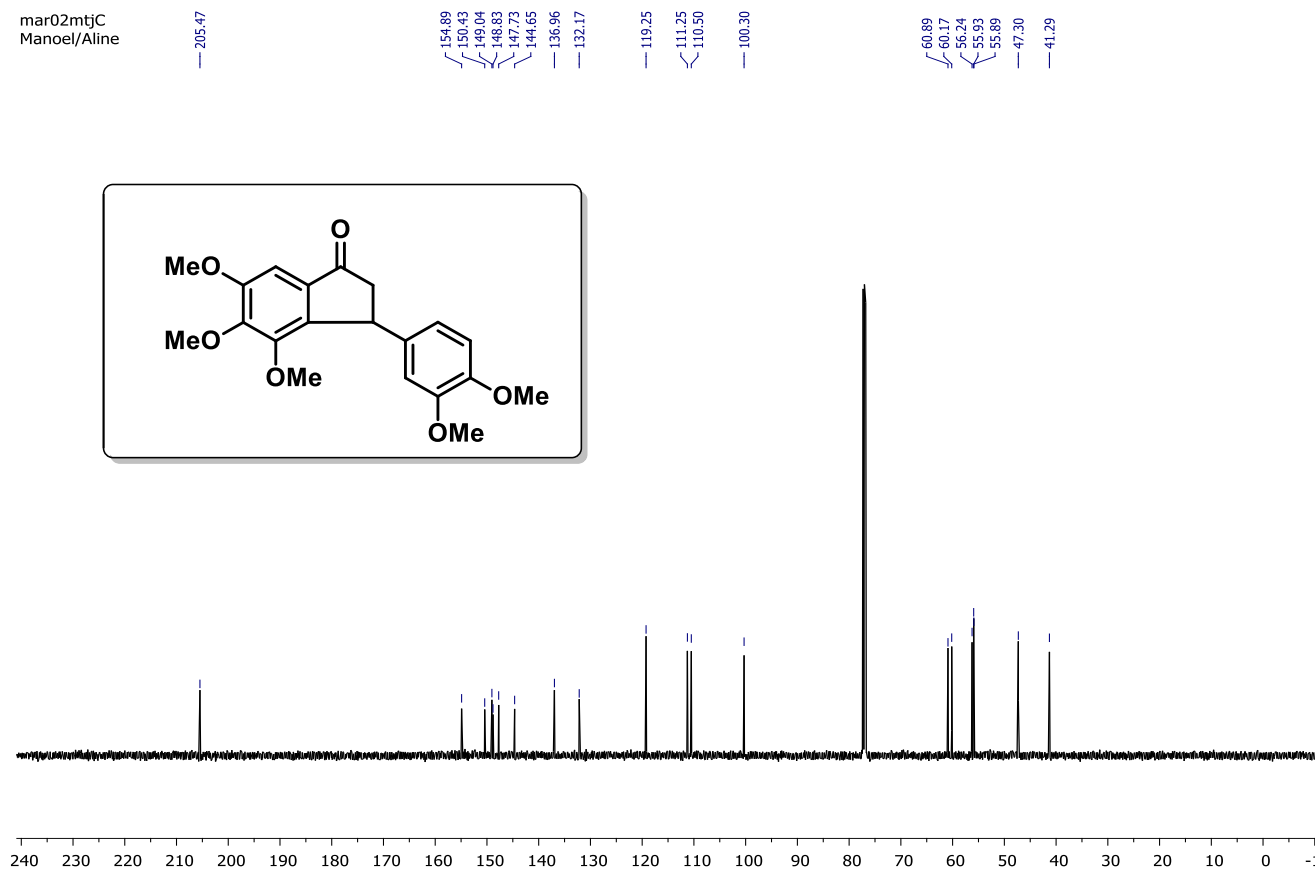


Figure S70. ¹³C NMR spectrum (126 MHz, CDCl₃) of compound **11ad**.

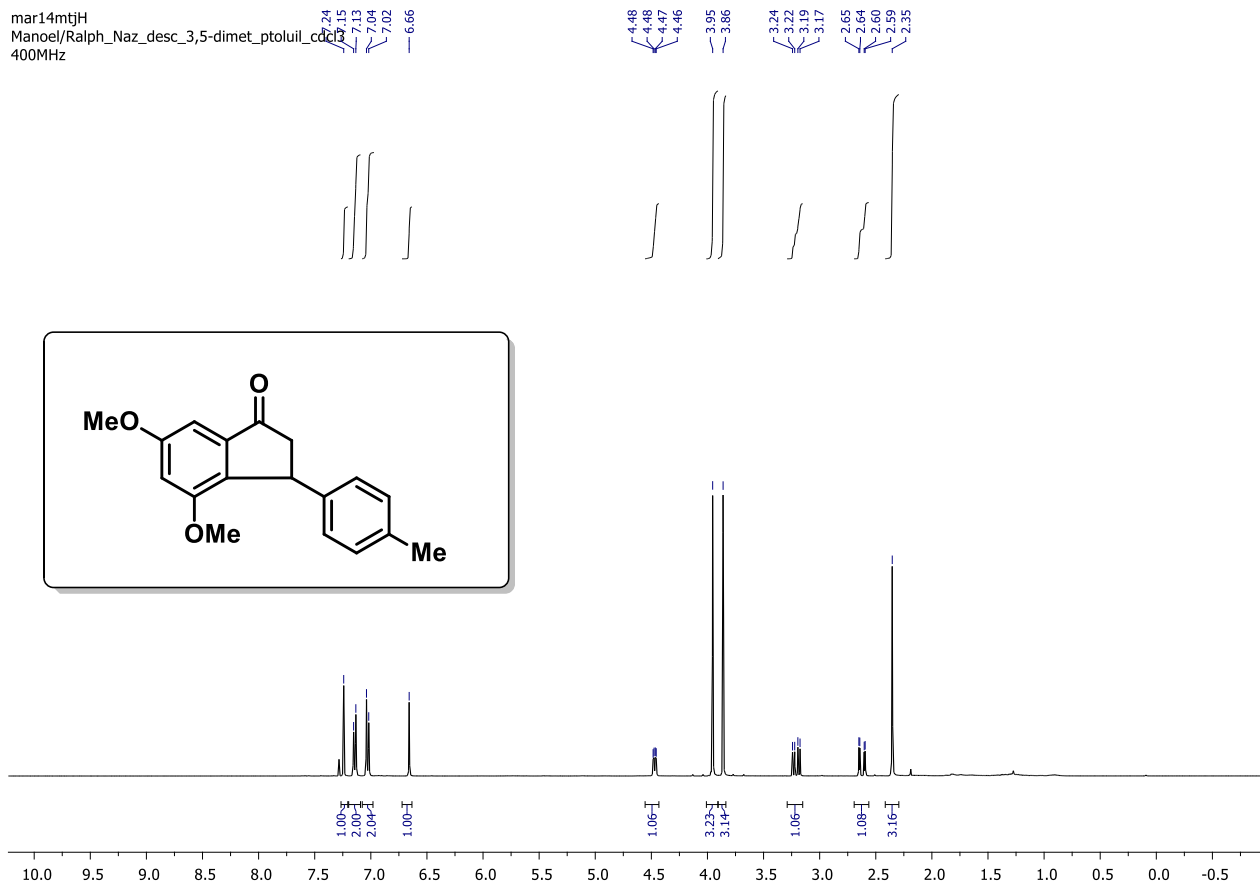


Figure S71. ¹H NMR spectrum (400 MHz, CDCl₃) of compound **11bj**.

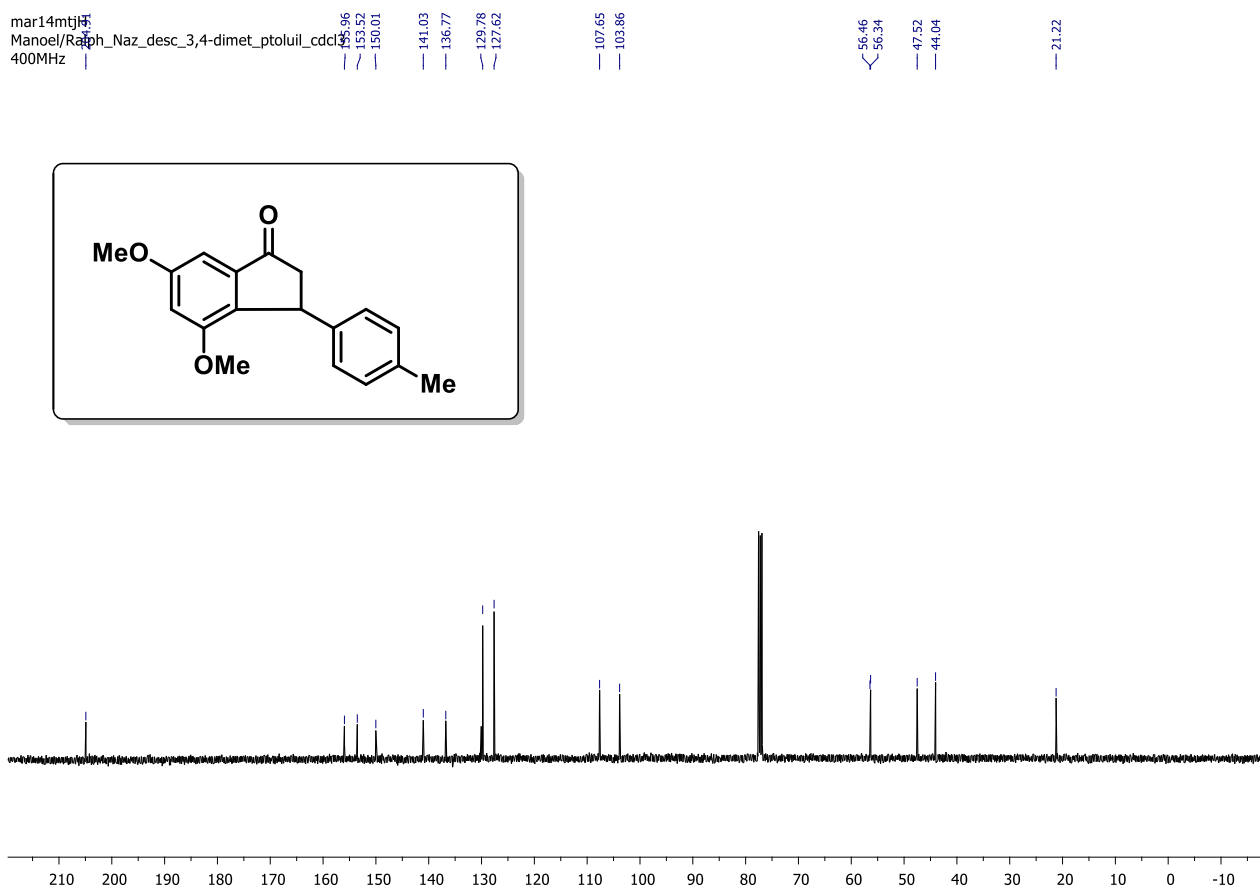


Figure S72. ¹³C NMR spectrum (101 MHz, CDCl₃) of compound **11bj**.

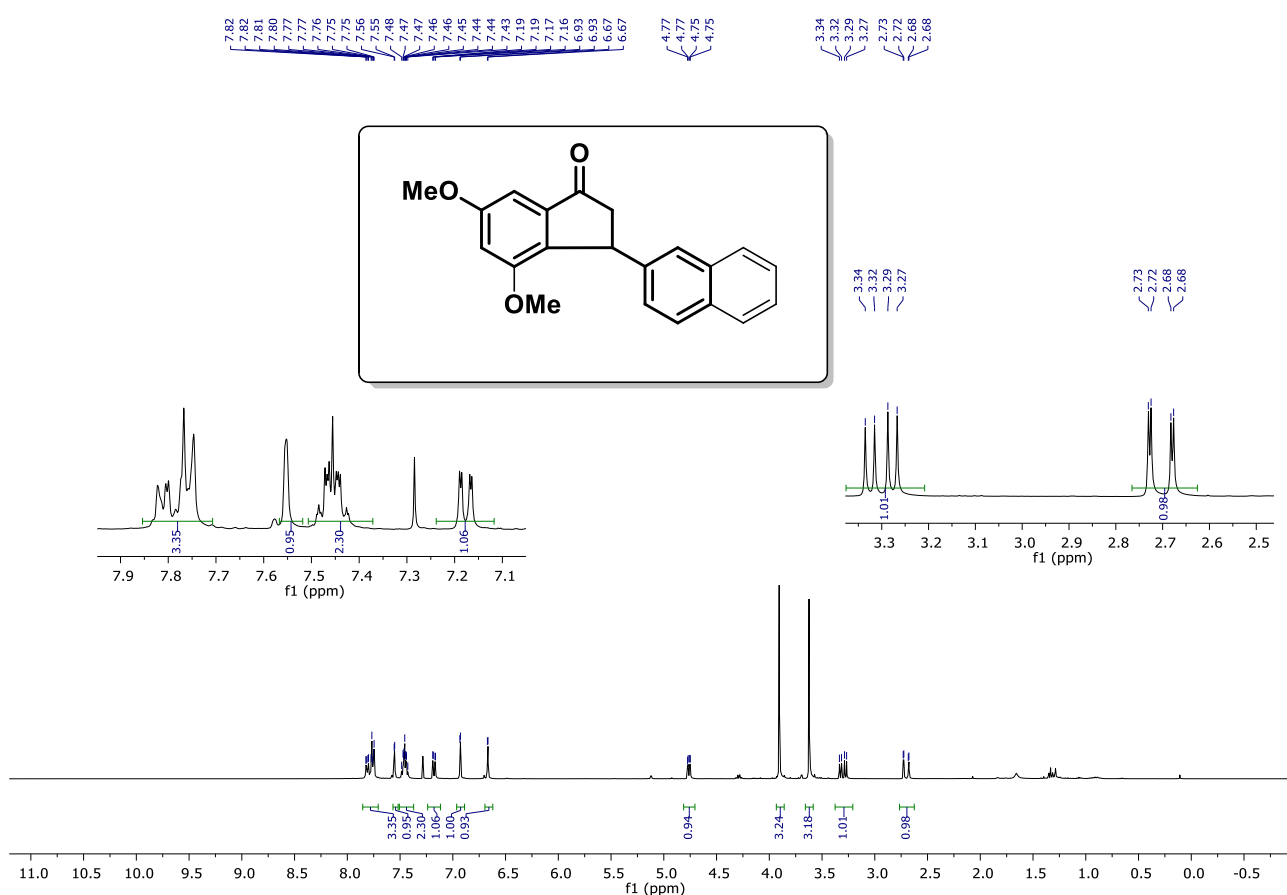


Figure S73. ¹H NMR spectrum (400 MHz, CDCl₃) of compound **11bk**.

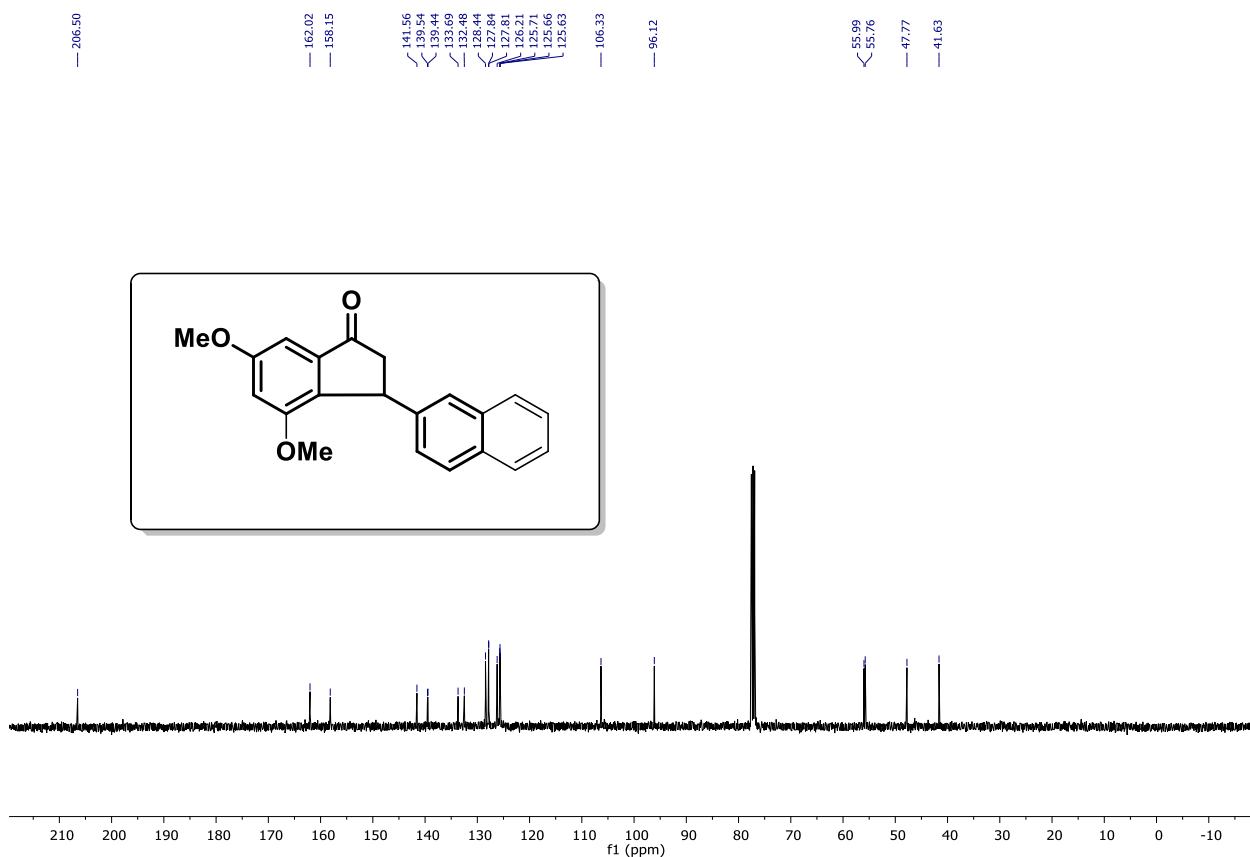
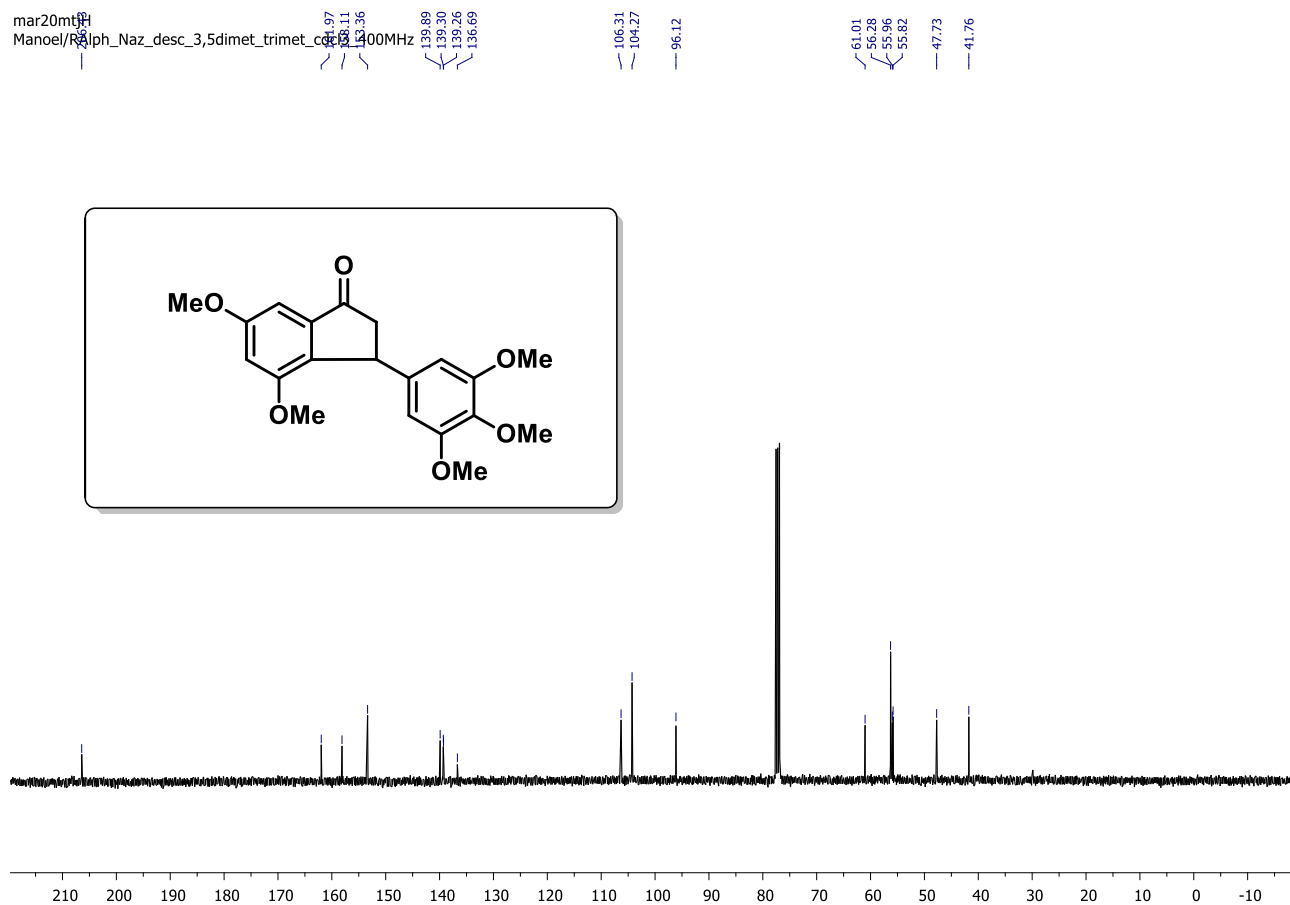
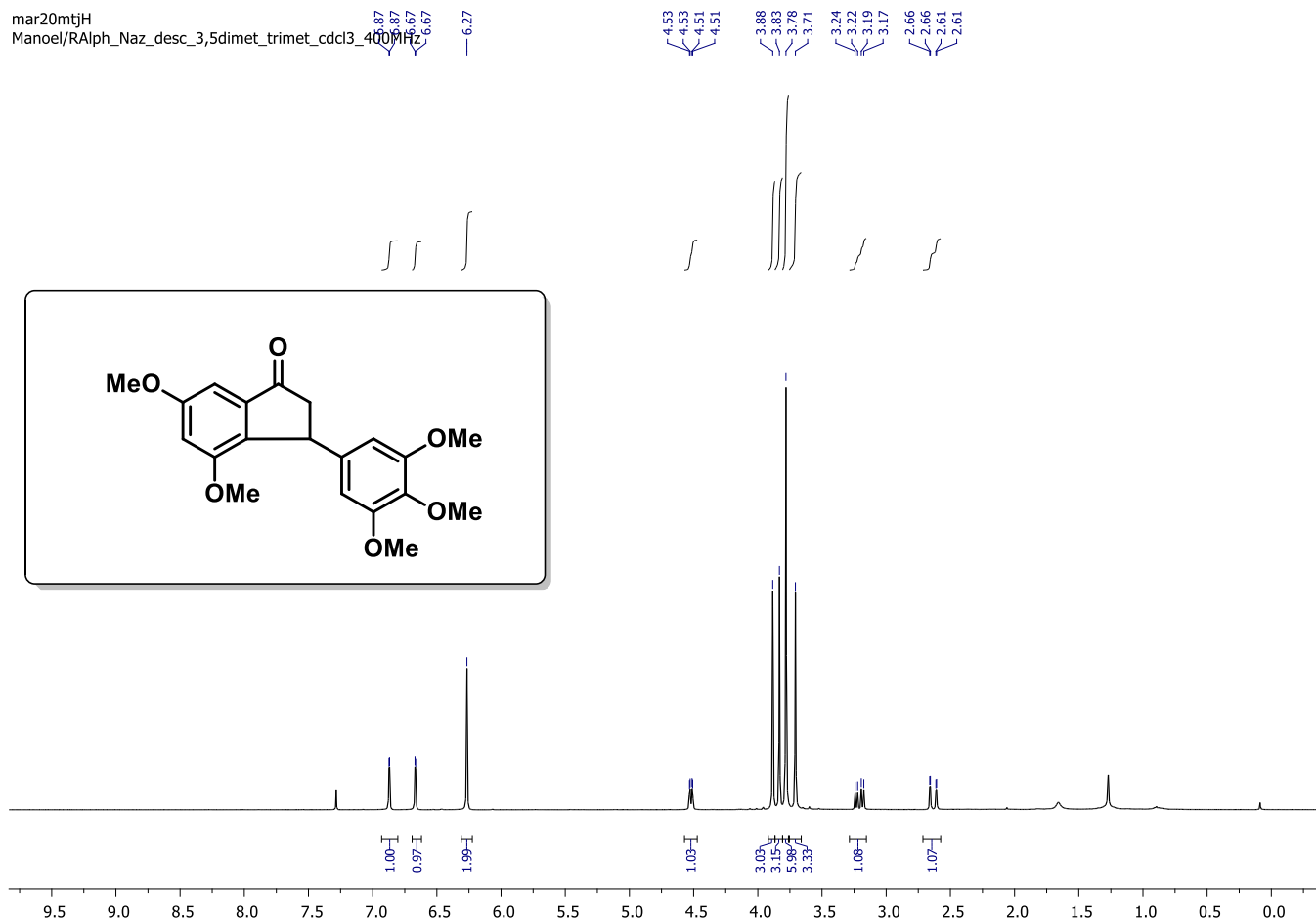


Figure S74. ¹³C NMR spectrum (101 MHz, CDCl₃) of compound **11bk**.



nov30mtjH2
Manoel_indolinona_piper_trimet_cdcl3
500 MHz

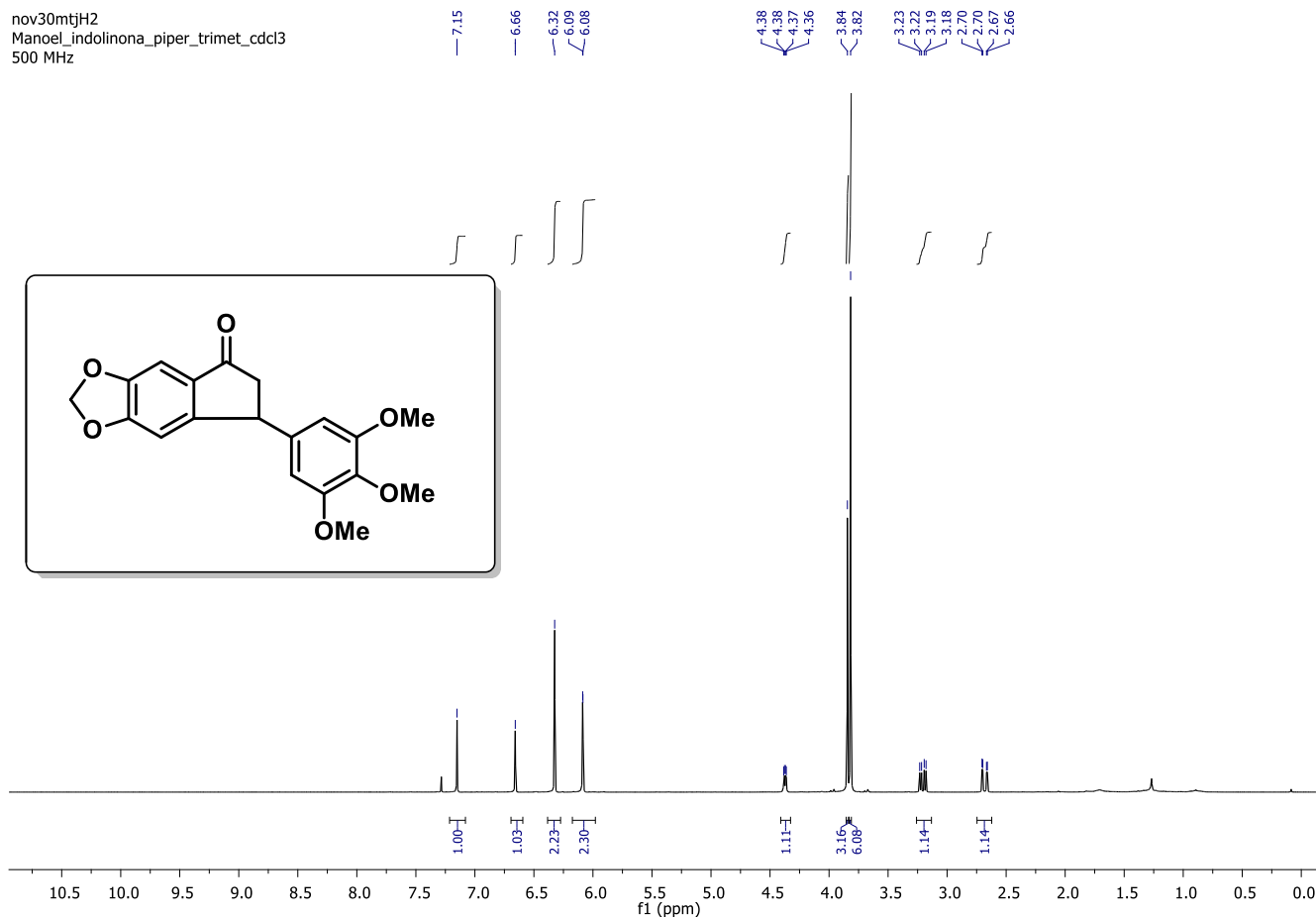


Figure S77. ¹H NMR spectrum (500 MHz, CDCl₃) of compound 11dc.

nov30mtjH2
Manoel_indolinona_piper_trimet_cdcl3
500 MHz

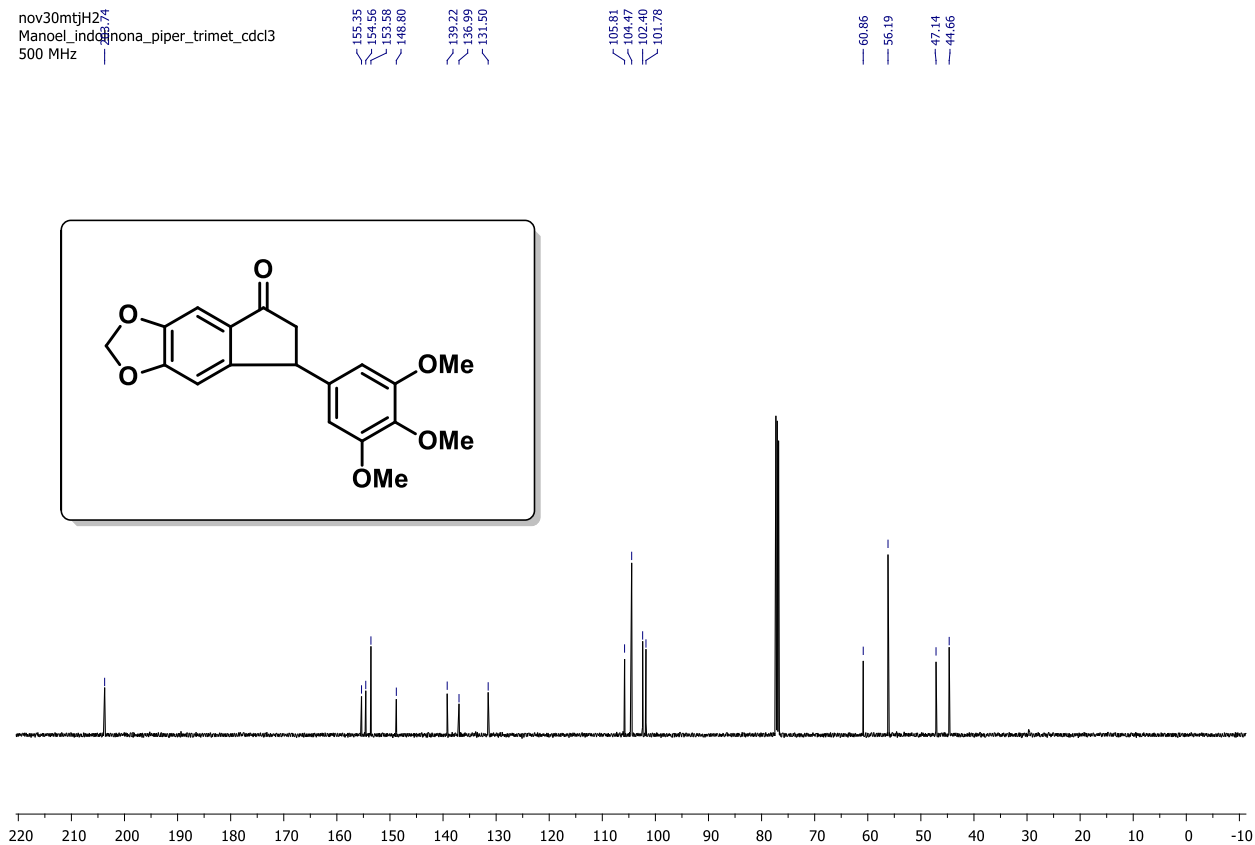


Figure S78. ¹³C NMR spectrum (126 MHz, CDCl₃) of compound 11dc.

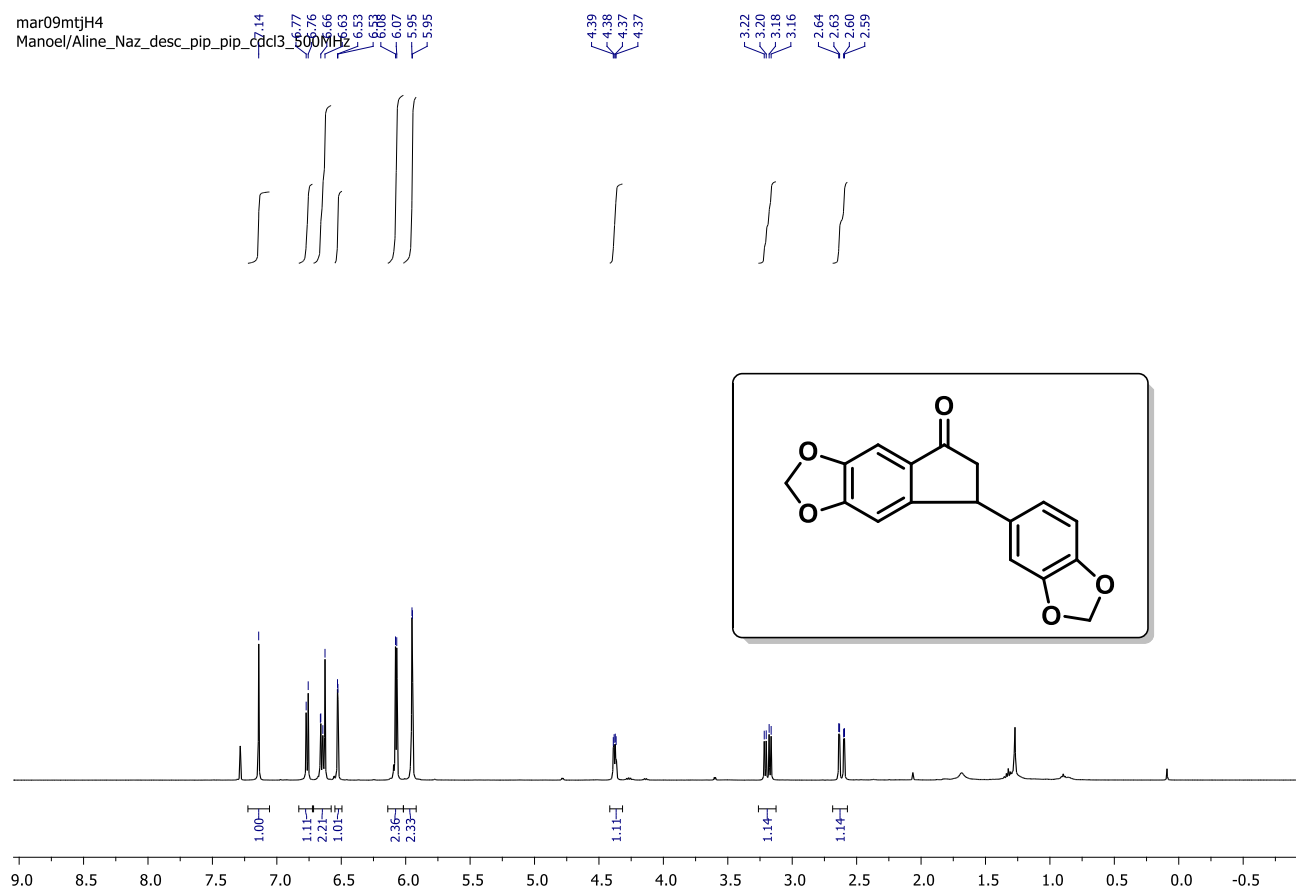


Figure S79. ^1H NMR spectrum (500 MHz, CDCl_3) of compound **11dl**.

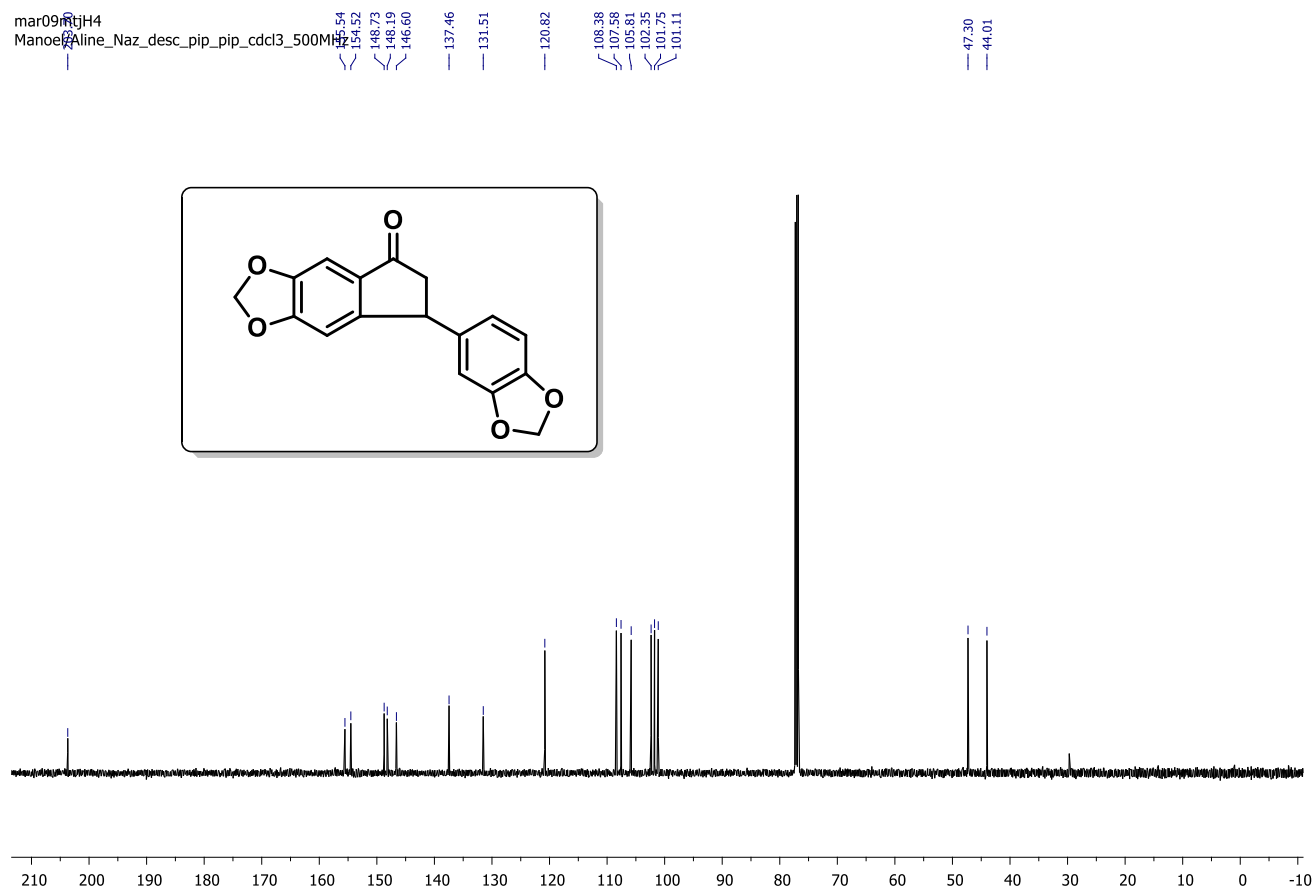


Figure S80. ^{13}C NMR spectrum (126 MHz, CDCl_3) of compound **11dl**.

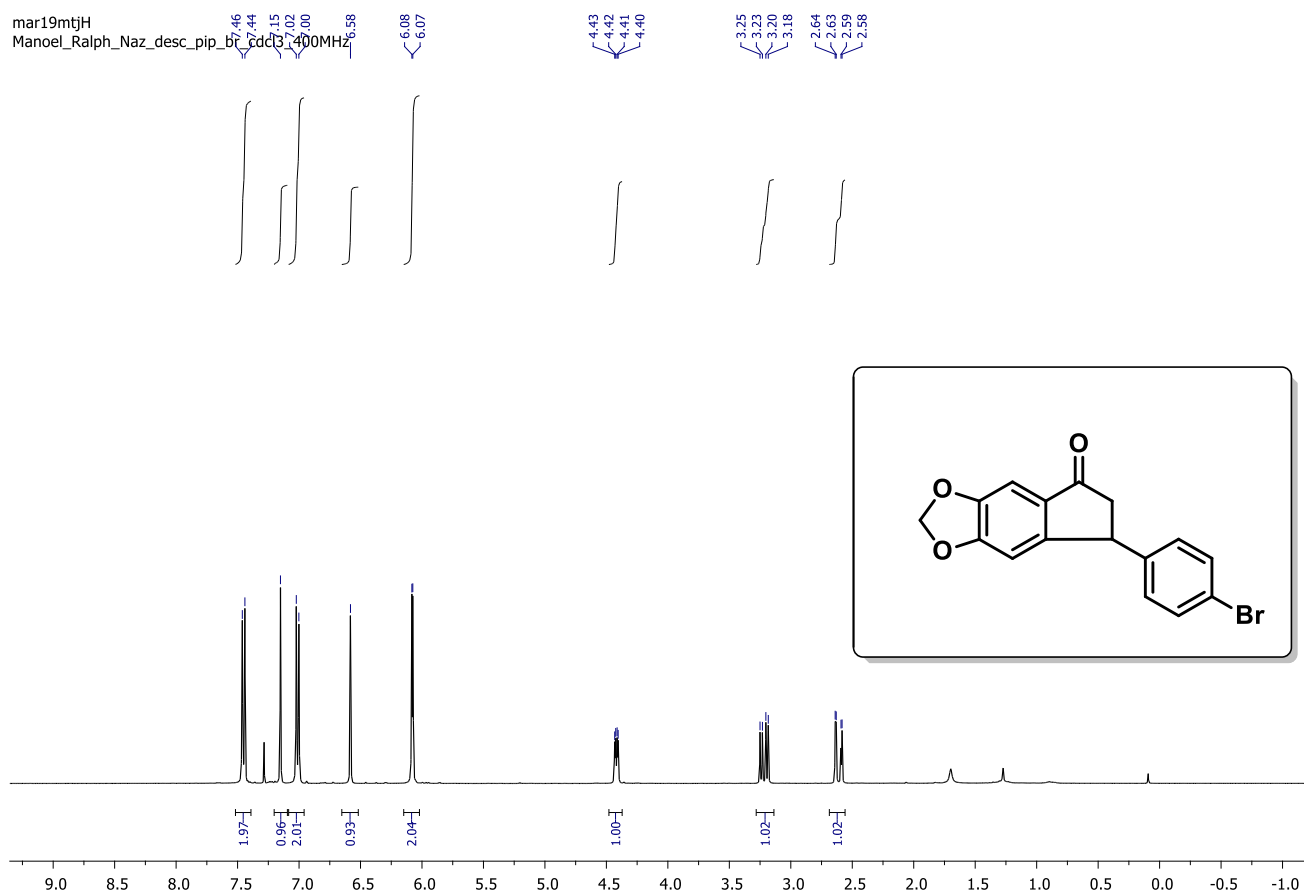


Figure S81. ¹H NMR spectrum (500 MHz, CDCl₃) of compound **11dm**.

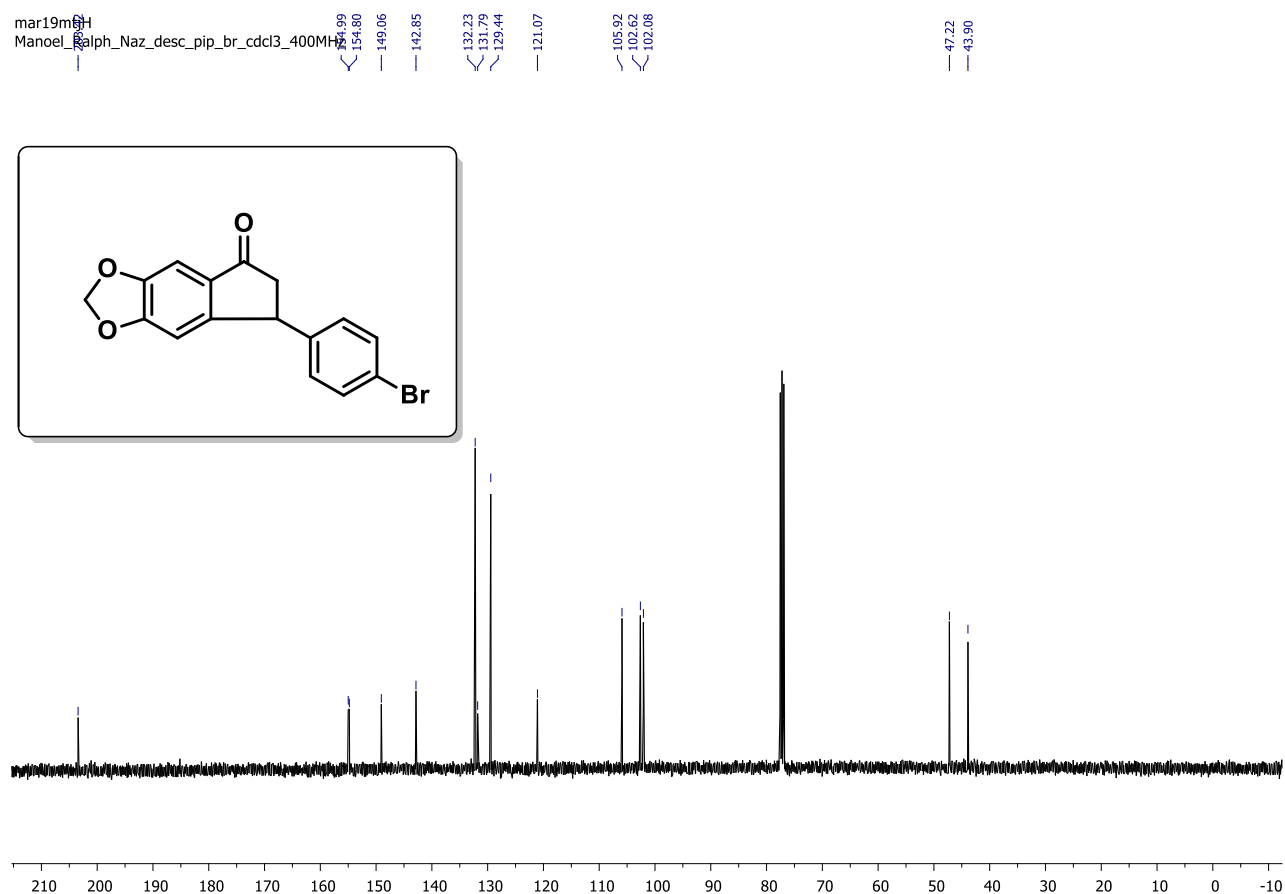


Figure S82. ¹³C NMR spectrum (126 MHz, CDCl₃) of compound **11dm**.

mar13mtjH2
Manoel/Aline_Ralph_ind_desc_3,4-dimet_trimet_cdc13_400MHz

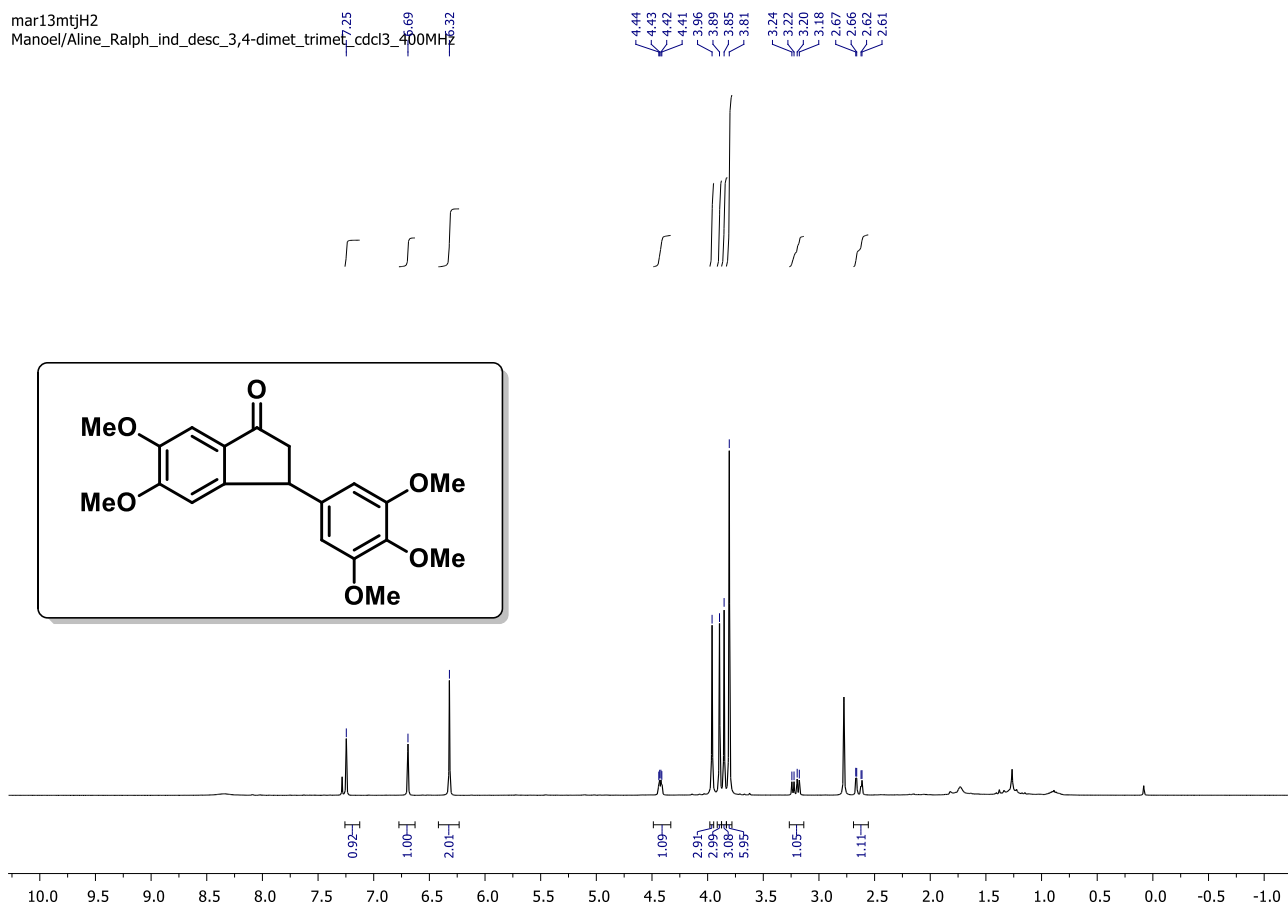


Figure S83. ¹H NMR spectrum (400 MHz, CDCl₃) of compound 11cc.

mar13mtjH2
Manoel/Aline_Ralph_ind_desc_3,4-dimet_trimet_cdc13_100MHz

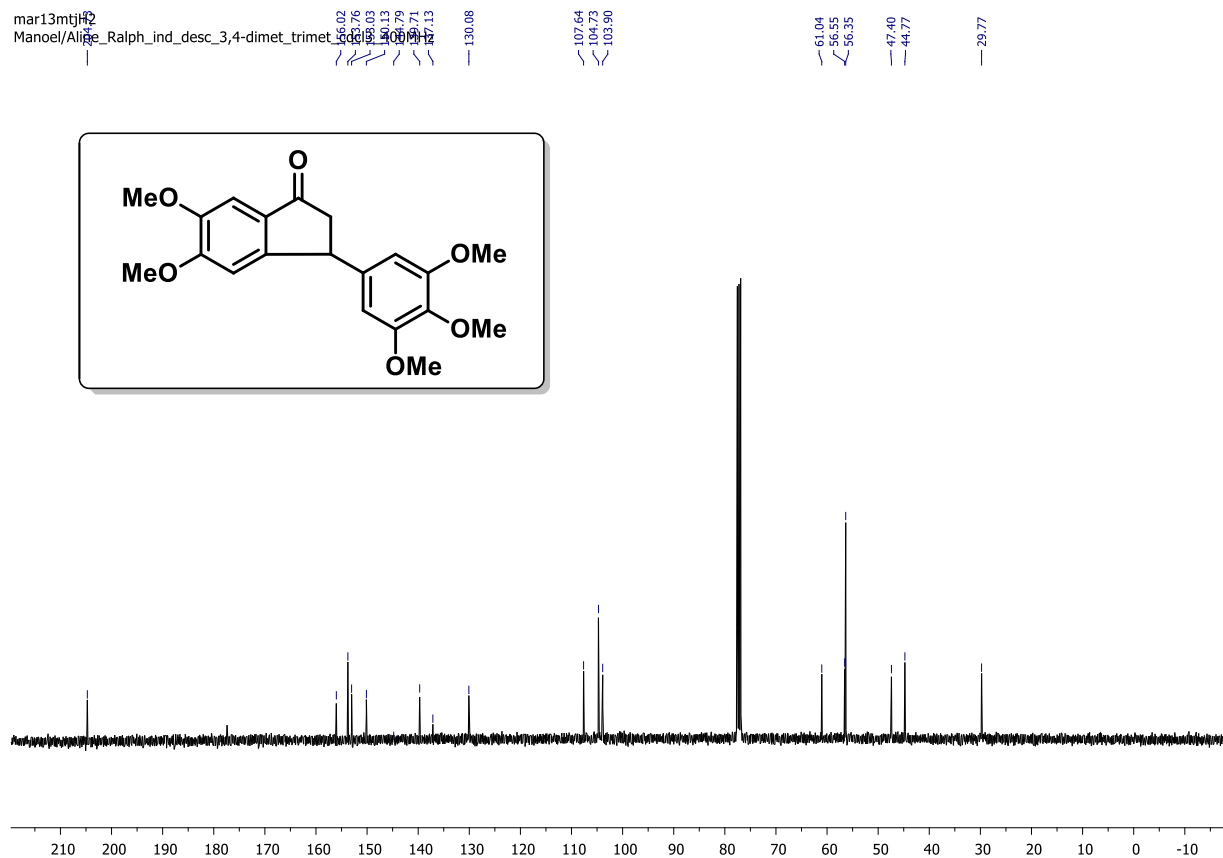


Figure S84. ¹³C NMR spectrum (101 MHz, CDCl₃) of compound 11cc.

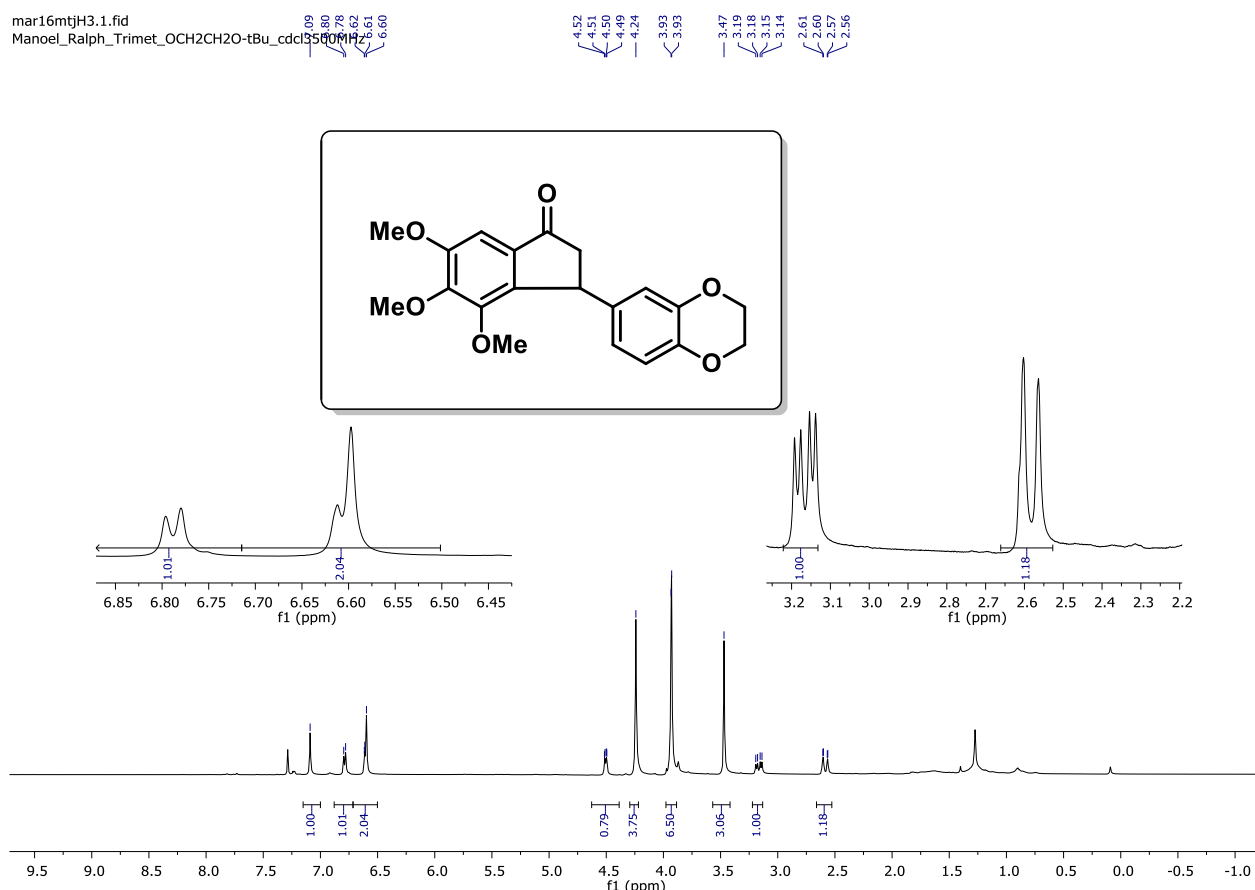


Figure S85. ¹H NMR spectrum (500 MHz, CDCl₃) of compound **11ae**.



Figure S86. ¹³C NMR spectrum (126 MHz, CDCl₃) of compound **11ae**.

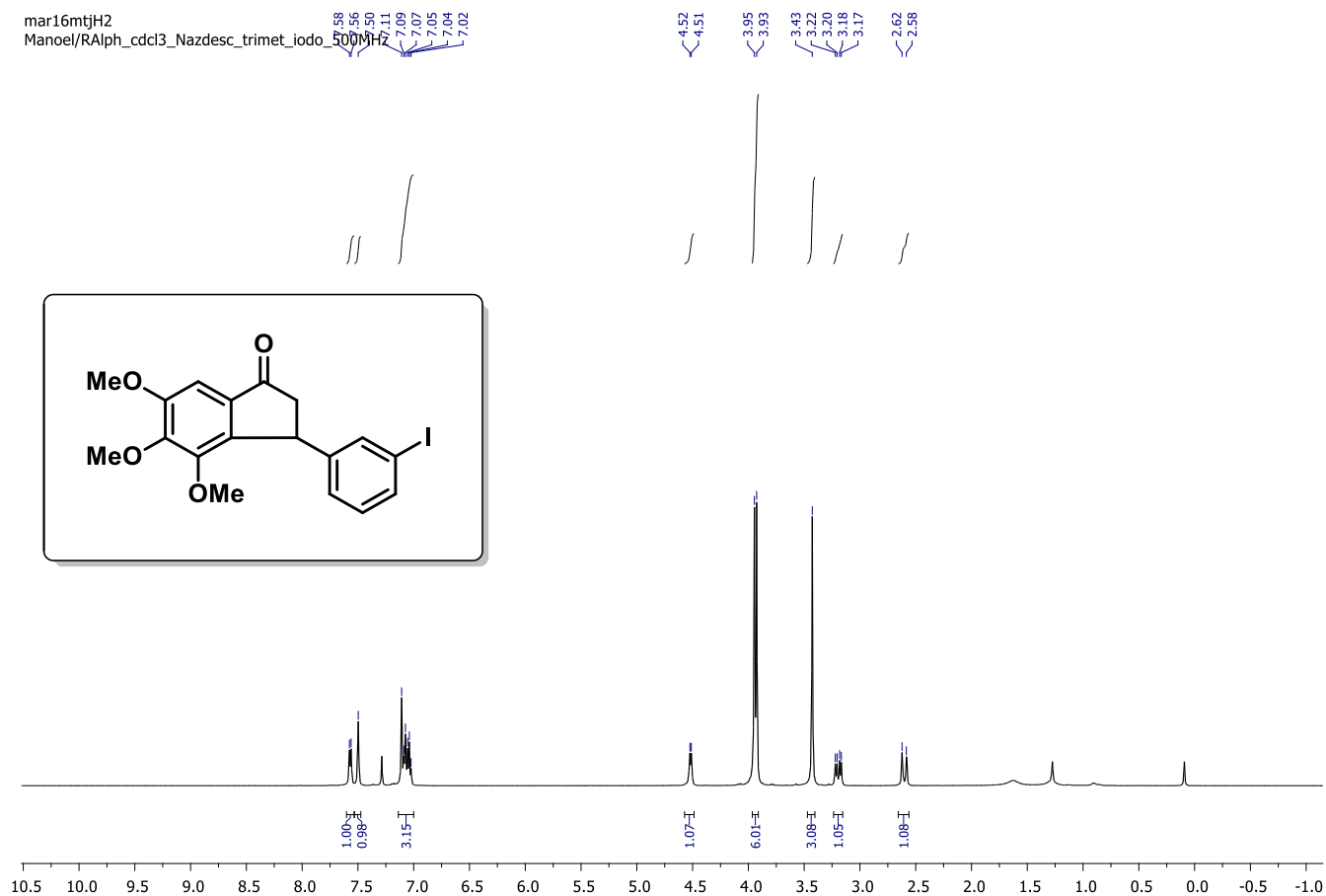


Figure S87. ¹H NMR spectrum (500 MHz, CDCl₃) of compound **11af**.

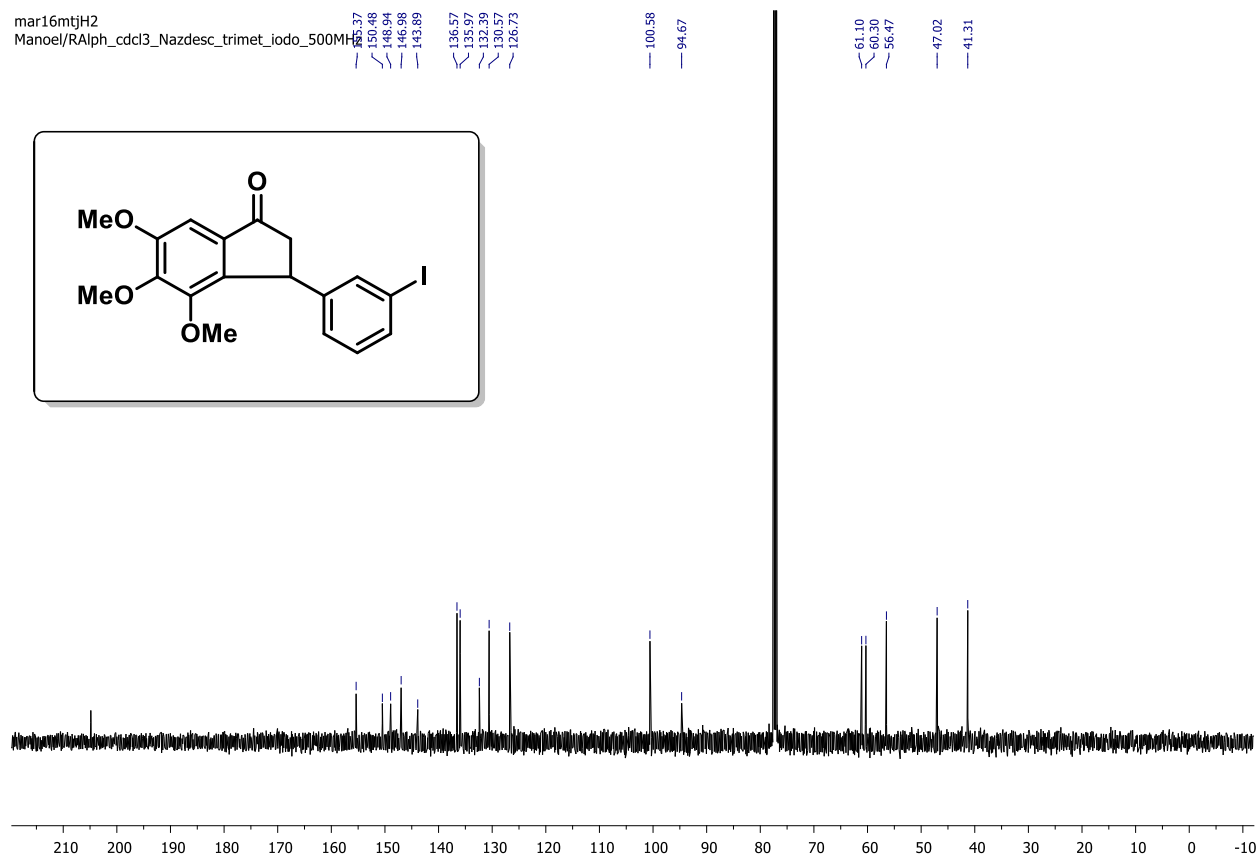


Figure S88. ¹³C NMR spectrum (126 MHz, CDCl₃) of compound **11af**.